

From Studies of the Electronic Structures of Molecules to Molecular Electronics

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Abstract

This Thesis presents work that advances our understanding of the ground and excited state electronic structures, charge transfer properties and electrical conductivity of linearly and cross-conjugated conjugated organic compounds and organometallic complexes containing these species as ligands. The themes, concepts and methods have been further applied to aspects of cyanocarbon chemistry, organometallic cluster chemistry, the chemistry of metal acetylide complexes, and further aspects of molecular materials chemistry. Across these studies, main themes involving the chemistry of mixed-valence complexes and molecular electronics are readily identified.

The model compound 1,4-bis(phenylethynyl)benzene (BPEB) has been demonstrated to exhibit conventional fluorescence properties in fluid solution, with slower rates of relaxation of the singlet excited state in viscous media leading to heterogeneous emission. Such conformational distributions in solution have also been identified in other molecular systems, and add considerably to the understanding of the charge transfer processes in hole-transport materials as well as the descriptions of the electronic structures of mixed valence complexes. Synthetic work has given functionalised BPEB derivatives, allowing the development of liquid-crystalline materials from this prototypical rigid molecular rod, including identification of an unusual optical texture arising from a SmB_{hex} phase.

Studies of metal acetylide complexes have shown how both the symmetry properties of the ancillary ligands and the radial distribution of the metal valence d-orbitals can be used to tune the electronic structure of both the parent complex and the radical cations derived from one-electron oxidation. Consequently, the redox character of the representative complexes $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]^+$, $[\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}'^+]^+$ and $[\text{Ru}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}'^+]^+$ ($\text{Cp}' = \text{Cp}, \text{Cp}^*$) vary from the strongly metal-localised processes of the Mo examples to substantially ligand based processes in the case of the Ru systems. In the case of Fe, the good symmetry match but poor spatial overlap of the 3d and $\text{C}\equiv\text{C}$ π systems gives more metal-based redox character, with greater alkynyl character than in the analogous Mo complexes but appreciably less than in the case of Ru systems. These characteristics have been used to design bimetallic mixed-valence complexes with electronic structures that test and explore the limits of the assumptions of Marcus-Hush theory and the two-state model, and more complex cases where the degree of ligand vs. metal character and localised vs. delocalised character is strongly conformationally dependent. The work carried out here has shown how the concerted application of UV-vis-NIR and IR data and computational sampling of the potential energy hypersurface at an appropriate level of theory can assist in deriving more accurate descriptions of the electronic structures of the resulting conformational ensembles. Particular effort has been directed towards the electronic structures of complexes $[\{\text{Cp}'(\text{PP})\text{M}\}(\mu\text{-C}\equiv\text{CXC}\equiv\text{C})\{\text{M}(\text{PP})\text{Cp}'\}]^+$ ($\text{X} = \text{bond, arylene}$; $\text{M} = \text{Fe, Ru}$), resulting in a re-classification of the well-known iron complex $[\{\text{Cp}^*(\text{dppe})\text{Fe}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Fe}(\text{dppe})\text{Cp}'\}]^+$ as a localised, Class II mixed-valence system. This work has further demonstrated the utility of spectroelectrochemical methods in such studies. The extension of these studies to metal complexes bearing cyanoacetylide, cyanocarbon, cumulated and cross-conjugated carbon ligands has opened new avenues for the exploration of electron transfer through 'extended' cyanides and branched (cross-conjugated) ligands. These works have added

considerable insight to the understanding of chemical bonding with metal acetylide, polyynyl, polyynediyl and related species as a function of redox state, and the chemical reactivity of novel quinoidal cumulenes.

The enabling work with BPEB systems, metal acetylide complexes and polyynes has allowed extensive explorations of the electrical properties of such systems within single molecule and monolayer film molecular junctions. Metal complexes of general form *trans*-[M(C≡CR)_n] and [M(terpy)₂] have been studied in single molecule junctions, allowing development of structure-property relationships including HOMO and LUMO conductance channels, and identifying adventitious contacts (short circuits) to aryl-rich ancillary ligands. Solvent and electrolytic gating effects in single-molecule junctions have been explored, leading to the development of ideal gate coupling in ionic-liquids and consequently an exceptionally efficient single-molecule transistor.

Monolayer molecular junctions formed from BPEB-based scaffolds have been used in conjunction with single-molecule measurements demonstrate that near-neighbour effects do not significantly effect molecular conductance in the tunnelling regime. By combining strongly coupled mixed-valence dimer-of-dimer Rh₂-paddlewheel fragments and efficient hopping mechanisms with layer-by-layer methods of synthesis, highly efficient metal-complex molecular wires capable of long-range transmission of electric currents have been designed. A number of strategies that introduce a 'top contact' electrode directly onto the exposed top surfaces of molecular monolayers have been developed. The electrical characterisation of the resulting nascent monolayer-film molecular electronic devices provides new directions for future hybrid molecular electronic devices.

Taken as a whole, this body of work expands and advances our understanding of the chemistry, electronic structures, electron transfer and electrical properties of linearly conjugated and cross-conjugated compounds and complexes. The critical role that distributions of molecular conformations play in the observable spectroscopic properties and charge transfer characteristics of such systems, especially mixed-valence derivatives, has been identified, and proposals for the description of the electronic structures of such complex ensembles have been made. Molecular junctions have been used to explore the electrical characteristics of these systems, novel surface contacting groups introduced and methods for device fabrication established.

Statement

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint award of this degree.

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Paul J. Low
March 2019

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LIBRARY NOTE:

Curriculum Vitae, pages 6-14 are unavailable.

List of Publications

Publication summary, full lists and metrics

My career publication history of over 200 papers is readily available from major research directories, as well as being indexed in general search platforms such as Web of Science and Scopus.

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Book Chapters

Molecular Wires: An Overview of the Building Blocks of Molecular Electronics, **P.J. Low** and S. Marqués-González, in *Single-Molecule Electronics*, **2016**, Springer (Singapore), M. Kiguchi (Ed), pp 87-116.

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Biographies and In Memoriam Texts

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An overview of the nature and significance of the research conducted, by topic.

The preceding pages contain a chronological listing of original journal articles and reviews arising from independent research conducted at the University of Western Australia (2013 – present) and the University of Durham (1999 - 2013), and postdoctoral work at the Steacie Institute for Molecular Sciences (1997 – 1999). Lists of publications arising from studies contributing to the award of the degrees of Doctor of Philosophy (Ph.D.) and Bachelor of Science (Honours) (B.Sc.(Hons)) from the University of Adelaide are included for completeness.

The independent contributions can be broadly, if not comprehensively, summarised as

The study of the syntheses, electronic structure, redox, spectroscopic and electrical behaviour of linearly and cross-conjugated compounds, and metal complexes featuring these species as ligands.

In addition to the development of synthetic methodologies, much of the work is characterised and distinguished by the combined use of spectroelectrochemical techniques and computational methods to explore the electronic structure of redox-active molecular compounds and metal complexes. This has permitted considerable insight to be gained to the nature of the chemical bonding with metal acetylide, polyynyl, polyynidyl and related species as a function of redox state and conformation.

Within the body of independent research, one can identify a significant contribution concerning the study of intramolecular electron transfer processes between organic, main group or organometallic electrophores through linearly and cross-conjugated π -conjugated organic systems. In turn, these studies have led to questions concerning the electronic character and spectroscopic signatures of ‘mixed-valence’ (MV) compounds, especially those in which dynamic changes in molecular conformation result in a distribution of localised to delocalised electronic structures. Such dynamic ensembles do not conform to the traditional categorisation within a single Robin-Day class or at a borderline. In collaboration with Professor Martin Kaupp (Technische Universität Berlin), methods of analysis and descriptions of the electronic structures of these ensemble systems that combine spectroscopic data with calculations performed with new global and local-hybrid DFT functionals have been developed.

A second major area of activity concerns exploration and explanation of the electrical behaviour of molecules within single-molecule and ‘large-area’ monolayer film molecular junctions. Contributions to these areas include protagonism for metal complexes in molecular electronics and studies of metal complexes within molecular junctions. A significant body of work has explored the role of various anchoring groups to contact both organic and organometallic compounds to metallic and carbon electrode surfaces. In addition, medium and environmental effects have been studied, leading to identification of solvent gating in polyyn- and viologen-based molecular wires, whilst the demonstration of highly efficient gate-coupling in ionic liquids has led to the development of an electrochemically gated single-molecule transistor. A variety of strategies and ‘soft’ deposition techniques have been introduced that allow for the construction of ‘top contact’ electrodes directly on molecular monolayers, providing routes to the construction and subsequent electrical characterisation of

nascent monolayer-film molecular electronic devices. These multidisciplinary endeavours have been carried out in collaboration with the groups of Professors Richard Nichols and Simon Higgins (University of Liverpool), who have carried out the single molecule junction studies, Dr Pilar Cea and Dr Santiago Martín (University of Zaragoza), who have contributed the surface studies and thin-film measurements, and Professor Colin Lambert (University of Lancaster), who has provided theoretical and computational support to these investigations.

These main themes are underpinned by studies concerning essential, fundamental advances in:

- the synthesis and excited state electronic properties of phenylene(ethynylene) compounds;
- the redox chemistry of poly(triarylamine) compounds;
- the coordination chemistry of polyynes on both mono-metallic and cluster frameworks;
- explorations of the synthesis, redox properties and electronic transfer capabilities of carborane clusters with ‘three-dimensional’ aromatic character;
- advances in the synthesis, redox properties and electronic structures of metal carbene, vinylidene, alkynyl, polyynyl complexes and related compounds, including cyanoacetylides, cyanovinylidenes and quinoidal cumulenes;
- the synthetic chemistry and electron-transfer properties of cross-conjugated carbon-rich compounds and derived metal complexes;

An outline of contributions and the significance of research conducted in the course of independent investigations, and the publications arising, are collated and summarised in the sections that follow.

Oligo(phenylene(ethynylene)) (OPE) compounds

The oligo(phenylene(ethynylene)) (OPE) structural motif (**Figure 1**) is widely found in molecular materials chemistry, offering a highly anisotropic, rigid molecular shape, an extensively delocalised electronic structure, exceptional thermal stability and high quantum yield of fluorescence.

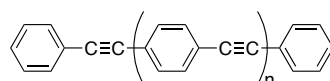
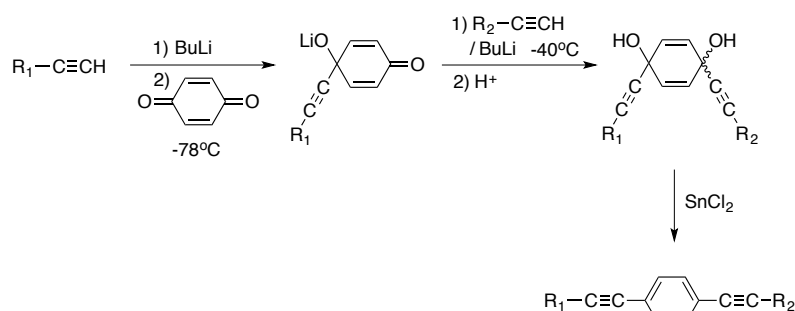


Figure 1 A sketch of an oligo(phenylene(ethynylene)) (OPE).

The OPE motif has figured prominently in our work, both as an example of a conjugated, carbon-rich ligand structure, and also as a prototypical ‘wire-like’ backbone in many molecules studied within single-molecule and thin-film / large area molecular junctions. A number of background and enabling studies of the synthesis, liquid-crystalline properties and excited state characteristics of molecules featuring this structure have underpinned these activities, and are summarised here.

The Sonogashira cross-coupling reaction is an extremely convenient tool for the preparation of OPE-based compounds, provided the appropriate (di)bromo or iodo arylene is available. The preparation of asymmetrically substituted derivatives using this approach requires protecting group strategies, iodo-bromo arylene reagents, or excess dihaloarylene. There was therefore some interest in the use of alternative preparative strategies, and we turned attention to the sequential addition of lithiated acetylenes to benzoquinones, naphthaquinones and anthraquinones as the key C-C bond-forming process (**Scheme 1**) [19]. At temperatures below $-40\text{ }^{\circ}\text{C}$ the quinones react with only one equivalent of lithium acetylides to cleanly give the mono-substituted products, even in the presence of excess lithium acetylide; this selectivity for carbonyl addition contrasts the competition from Michael addition observed with Grignard and sodium acetylides. The addition of a second equivalent of the same or a different acetylide could be readily achieved at modestly higher temperatures to give the (differentially) di-substituted ene-diols. Ready reduction on treatment with SnCl_2 gave the diethynylarylene compounds in good overall yields (ca. 60%).



Scheme 1. A ‘palladium free’ preparation of arylene(ethynylene) based molecular compounds [19].

Using both this quinone-based chemistry and conventional Sonogashira cross-couplings a variety of 1-[(4'-alkoxy)phenylethynyl]-4-(phenylethynyl)benzenes and methyl 4-[(4''-alkoxy)phenylethynyl-4'-(phenylethynyl)] benzoates could be prepared. Both series displayed chemical stability up to $210\text{ }^{\circ}\text{C}$, the derivatives featuring the

methyl ester head-group offering rather higher melting points and generally stabilising a more diverse range of mesophases at higher temperatures than found for the simpler phenyl-terminated compounds. The nematic phases observed with shorter and intermediate chain length alkyloxy tails gave way to smectic phases in derivatives with longer alkoxy substituents. X-ray diffraction analysis has been used to identify a SmB_{hex} phase in three members of the simple alkoxy-substituted 1,4-bis(phenylethynyl)benzene series, which is stable over a relatively small thermal range (ca. 120–140°C) and give rise to unusual moss-like textures when observed by optical hot-stage microscopy (**Figure 2**) [45].

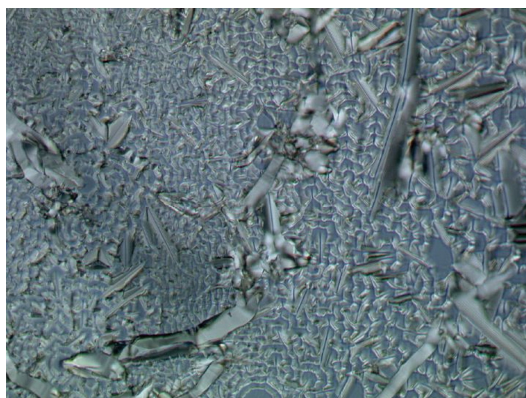


Figure 2 The unusual, characteristic moss-like optical texture associated with the SmB_{hex} phase of 1-[(4'-hexadecyloxy)phenylethynyl]-4-(phenylethynyl)benzene at 124°C [45].

The optical properties of OPE-based compounds attract attention, with donor-acceptor substituted derivatives often exhibiting low-lying excited states with significant charge transfer character and, in well-designed cases, fluorescent quantum yields approaching unity [23]. Despite claims to the contrary, the parent 1,4-bis(phenylethynyl)benzene (BPEB) undergoes emission from the lowest vibrational level of the first excited singlet state (i.e. obeys Kasha's Rule) rather than from a population of excited state rotamers (**Figure 3**). However, in highly viscous, low-temperature glasses, the material does exhibit inhomogeneous fluorescence behaviour, and wavelength-dependent excitation and emission spectra, indicative of a slow rate of relaxation of conformers of the excited states compared to the rate of fluorescence [8].

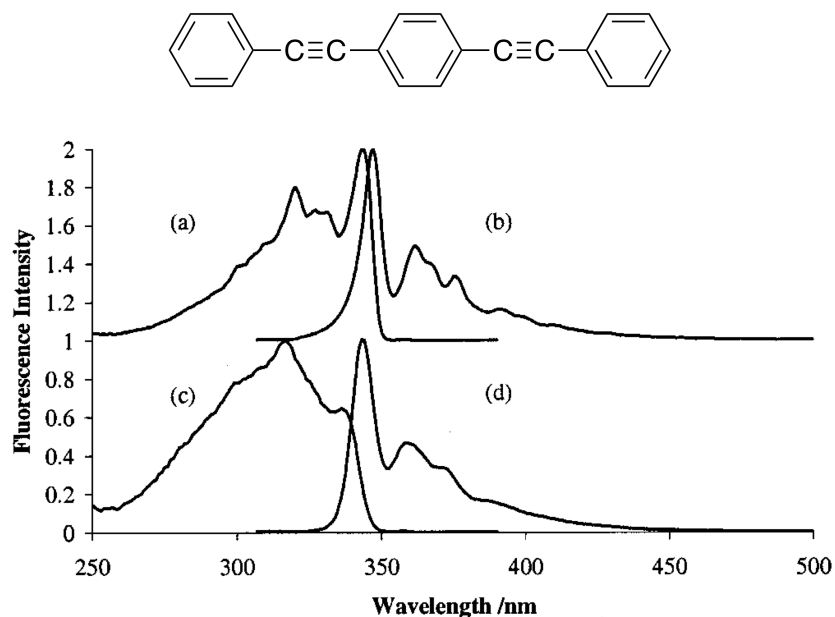


Figure 3 Normalised, corrected fluorescence excitation and emission spectra of 1,4-bis(phenylethynyl)benzene (BPEB) in EPA at (a, b) 77 K and (c, d) 298 K determined with excitation at 320 nm and emission at 360 nm [8].

Using ps-time-resolved resonance Raman (TR^3) spectroscopic methods it has been shown that the S_1 state offers an intense $\nu(C\equiv C)$ band at 2128 cm^{-1} , demonstrating that there is no significant evolution of cumulenyl or quinoidal character in the S_1 state (**Figure 4**) [11]; the lack of structural reorganisation is consistent with the small Stokes shift observed in emission spectra of BPEB and the rather extensively delocalised electronic structure of this prototypical conjugated organic oligomer.

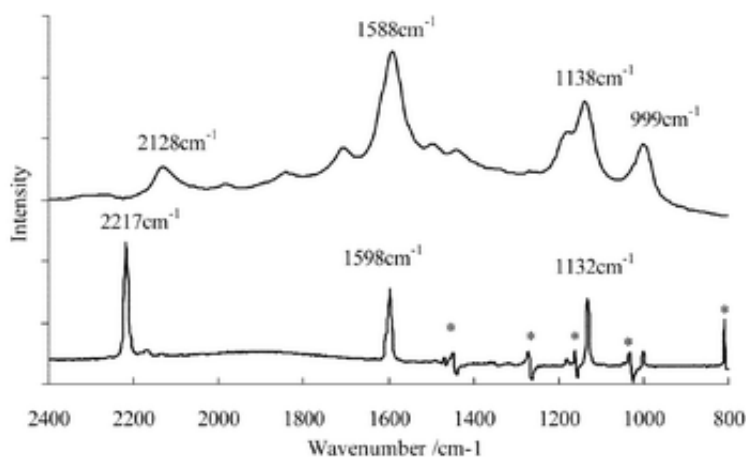


Figure 4 The TR^3 spectrum of the S_1 state of BPEB in cyclohexane recorded 50 ps after pump (267 nm) using a 588 nm probe (upper trace) and the ground state, non-resonance Raman spectrum (probe 532 nm, lower trace). Asterisks mark miscancelled solvent bands [11].

Cavity ring-down spectroscopy was employed to complete the assessment of the physical and photophysical characteristics of BPEB, with the torsional motions of a jet-cooled molecular beam of BPEB and the tetra-deuterated derivative 1,4-bis(phenylethynyl)-2,3,5,6-tetradeuteriobenzene satisfactorily modelled with a simple cosine potential revealing a ground-state barrier to rotation of some 220 – 235 cm^{-1} i.e. ca. 3 kJ mol^{-1} [31]. When this figure is compared with the thermal room temperature background (kT ca. 207 cm^{-1}), it is apparent from a simple Boltzmann distribution that at ambient temperature in fluid solution approximately 30% of the sample will have sufficient thermal energy for the phenyl(ene) rings to be freely rotating. This finding highlights the difficulties in decoupling the role of electron hopping and tunnelling on the transport properties of molecular wires based on the OPE motif and the assumptions inherent in molecular models based only on the lowest energy ground state structure.

The low energy barrier to rotation of phenylene rings and, as will be shown later, metal fragments, around $\text{C}\equiv\text{C}$ ‘axels’ leading to conformer distributions in the ground state play an important role in the optoelectronic properties of many of the systems explored. The development of methods to allow these conformational distributions to be accounted within descriptions of the ground state electronic structures has emerged as something of a key theme in the more recent work from the group.

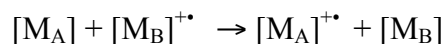
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Chemistry of OLED components

Our interests in the chemistry and electronic structures of conjugated compounds, molecular photophysics, redox-active molecules and inter- and intra-molecular charge transfer processes led to a series of investigations of the fundamental properties of triarylaminines, *N,N,N',N'*-tetraaryl-(1,2'-biphenyl)-4,4'-diamines, and related oligomers, which are widely used as hole-injecting and hole-transport materials in organic light-emitting diode devices. In turn, emissive heavy-metal complexes in which spin-orbit effects permit efficient singlet-triplet intersystem crossing and enhanced emission efficiencies relative to fluorescent organic emitters have attracted attention.

The hole transport efficiency of a molecular material is dependent on a number of physical and chemical parameters including oxidation potential, packing arrangements in the solid state and associated reorganisation energy barriers to charge transfer. In simplest terms, the migration of charge through a molecular solid can be represented in terms of a hopping model in which an electron is transferred between a neutral molecule, [M], and a neighbouring radical cation, [M]^{•+}



The net free energy change of the reaction is clearly zero, and from Marcus theory the activation barrier to intermolecular electron transfer, ΔG^{\ddagger} , will be $\lambda/4$, where λ is the reorganisation energy. The reorganisation energy contains contributions from the geometric rearrangement of [M_A] to [M_A]^{•+}, [M_B]^{•+} to [M_B], solvent reorganisation and ion-pairing interactions. Although *N,N,N',N'*-tetraaryl-(1,2'-biphenyl)-4,4'-diamines, such as *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), are well established hole transport materials, at the time of our investigations, given these materials are chosen in part because of their tendency to give amorphous solids free of crystal-grain boundaries, experimentally determined structural information concerning these compounds was exceptionally limited. Through a series of systematic studies, crystallographically determined structures of a number of *N,N,N',N'*-tetraaryl-(1,2'-biphenyl)-4,4'-diamines were obtained [16, 22], including the first crystallographically characterised example of a radical cation of this family (Figure 5) [14].

Through examination of the structures, the influence of structure and geometric constraints on electrochemical potentials [22], the spectroscopic characteristics of the one-electron oxidised mixed-valence products obtained from UV-vis-NIR [14, 16, 22] and Raman [17] spectroelectrochemistry the critical geometric changes accompanying oxidation were mapped, with the reorganisation of the biphenyl moiety towards a more planar conformation dominating the Marcus-type contributions to the overall reorganisation energy, accompanied by a rotation of the *N,N*-aryl moieties to positions more orthogonal to the biphenyl plane (**Figure 5**). As an extension to these studies, new Hartwig-Buchwald style catalysts for the selective preparation of di- and triarylaminines were also developed based on palladium complexes of sterically congested diisopropylphosphinoferecenes were developed in collaboration with Hierso's group [108].

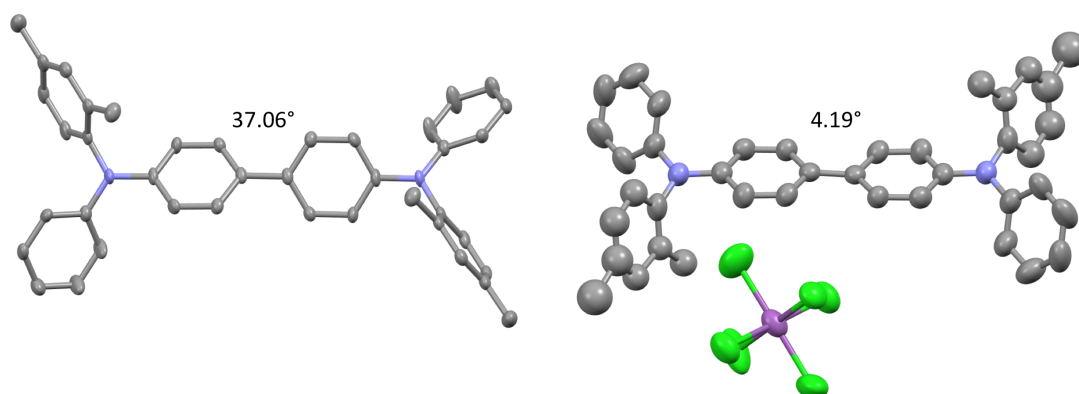


Figure 5 Plots of the crystallographically determined structures of *N,N'*-diphenyl-*N,N'*-bis(2,4-dimethylphenyl)-(1,1'-biphenyl)-4,4'-diamine (left) and its radical cation as the $[\text{SbCl}_6]^-$ salt (*N* atoms shown in blue; hydrogen atoms and a disordered component of the 2,4-dimethylphenyl ring omitted for clarity). The central torsion angle between the biphenyl rings is shown, indicating the planarisation of this moiety that accompanies oxidation [14].

In collaboration with Chi and his team, we have turned attention to the nature of the emissive states in Ir(III) and Os(II) phosphors and the incorporation of these species into OLED device structures. Our interests in NIR absorption spectroscopy drew us to consider near infrared (NIR) emitting materials. NIR emitting materials are highly prized for applications in biological imaging, sensing and optical telecommunication platforms, however the design of such compounds and the realisation of devices are compounded by difficulties arising from the rate of non-radiative decay, which tends to increase as the emission energy decreases (the energy gap law). A particular highlight of this work was therefore the development of a new series of Os(II) NIR-emitting phosphors (**Figure 6**) with electroluminescent maxima near 690 nm and external quantum efficiencies of 1 – 2% (c.f. solid state photoluminescence λ_{max} ca. 717 – 772 nm, ϕ 0.5 – 8.8%) and turn-on voltages < 3V [120].

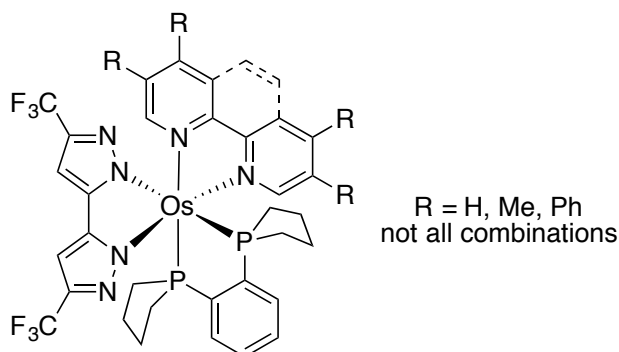


Figure 6 The charge neutral NIR emitting Os(II) complexes prepared and studied in collaboration with Chi and his group [120]

A further series of three charge-neutral Ir(III) complexes bearing neutral chelating ligands 4,4'-di-*t*-butyl-2,2'-bipyridine (dtbbpy) and monoanionic cyclometallated ligands derived from 2-phenylpyridine (ppyH), and either two monoanionic chloride or monodentate pyrazolate ligands or a single dianionic chelate derived from 5,5'-di(trifluoromethyl)-3,3'-bipyrazole (bipzH₂) or 5,5'-(1-methylethylidene)-bis-(3-trifluoromethyl-1H-pyrazole) (mepzH₂), was successfully synthesized from ligand substitution reactions of [Ir(dtbbpy)(ppy)Cl₂]. Hybrid density functional theory calculations reveal the LUMO to be π^* (dtbbpy) in character for all complexes, whilst the HOMO offers $d(\text{Ir})-\pi(\text{phenyl})$ or $\pi(\text{bipz})$ character (**Figure 7**). Our time-dependent DFT (TD DFT) calculations further show that the emissive processes are dominated by ligand(ppy)-to-ligand(dtbbpy) (phenyl group-to-bipyridine) charge transfer admixed with metal-to-ligand transition. Organic light emitting diodes with intense orange emission and peak external quantum efficiencies, luminance efficiencies, and power efficiencies of 18.1% (59.0 cd/A and 38.6 lm/W) and 16.6% (53.3 cd/A and 33.5 lm/W), respectively were obtained in best cases [132].

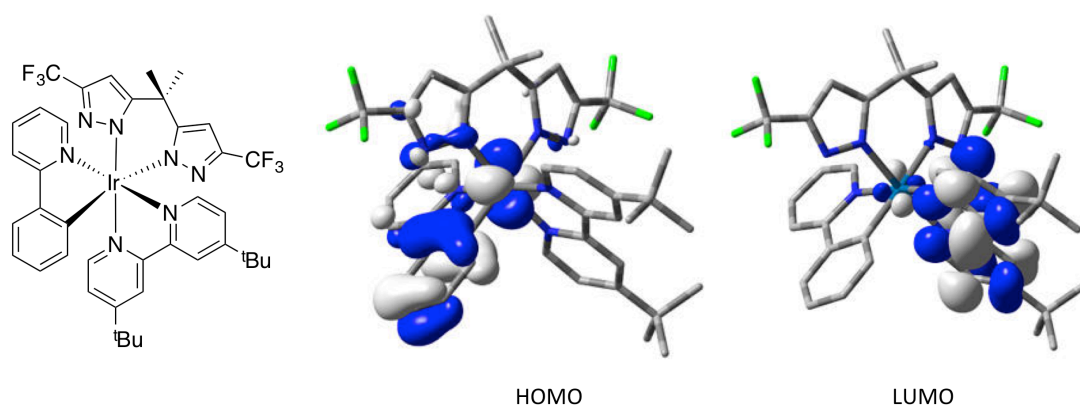


Figure 7 An example of an Ir(III) OLED emitter [Ir(dtbbpy)(ppy)(mepz)], and plots (± 0.04 (e/bohr^3)^{1/2}) of the calculated HOMO and LUMO [132].

Neutral Ir(III) based phosphors with bis(tridentate) ligand geometries offering CNN [(4-(*tert*-butyl)-2-(2,4-difluoro-phenyl)-6-(3-isopropylimidazol-2-ylidene)pyridine derivatives] and CNC (2-pyrazol-3-yl-6-phenyl-pyridine derivatives) coordination modes were also prepared and used to create tuneable colour emission from green to saturated red. Our TD DFT calculations were used to help establish that the emission in these species originates largely from ³ML_nCT processes, with the colour of emission strongly influenced by the substituents on the dianionic 2-pyrazol-3-yl-6-phenyl-pyridine tridentate chelate ligand [137].

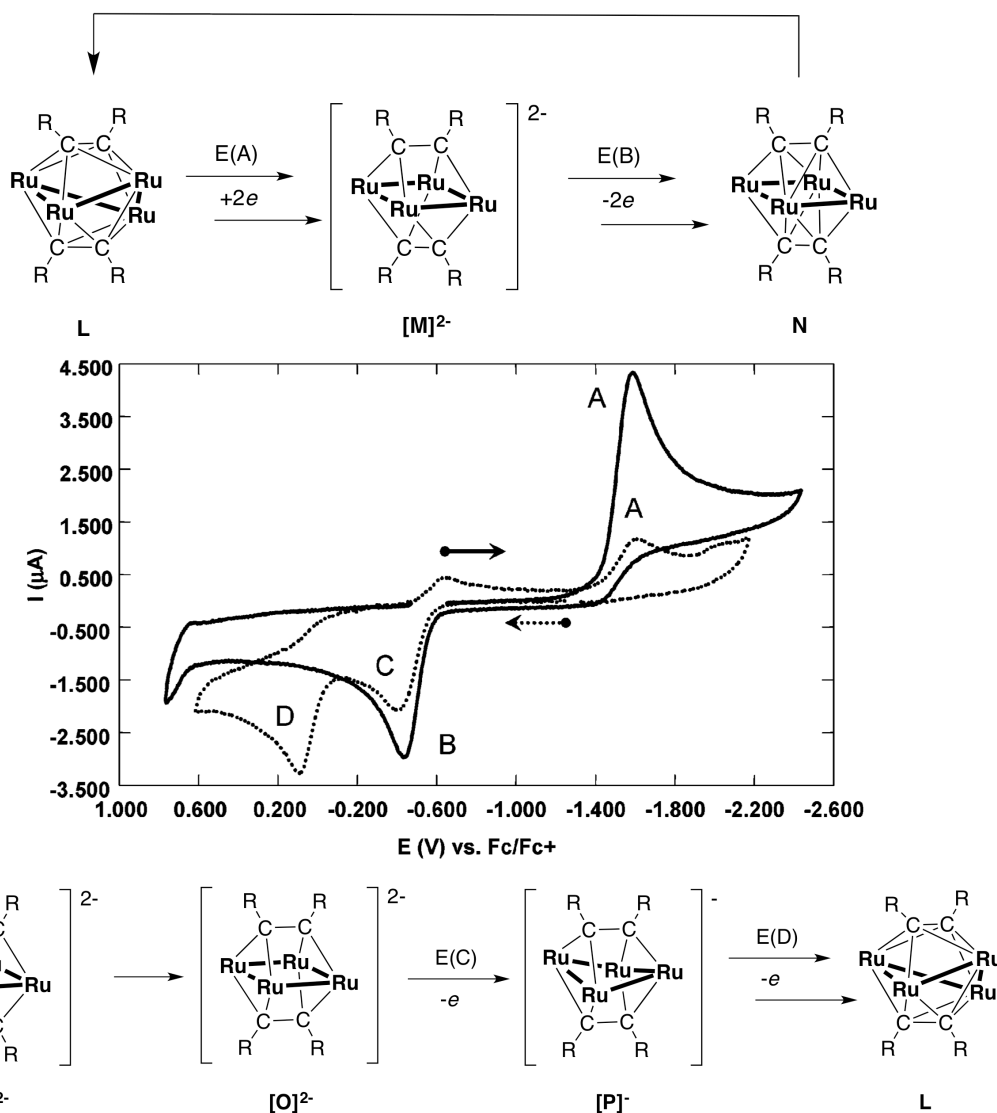
In summary, structure-property relationships in triarylamine based hole-transporting materials have been established with particular focus on the geometric factors influencing Marcus-style reorganisation energies. A variety of DFT and TD DFT calculations have been used to explore the emissive state in heavy metal phosphors, allowing tailored ligand designs to achieve good device characteristics and a rare example of a NIR emitting device.

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Bimetallic and Cluster Chemistry

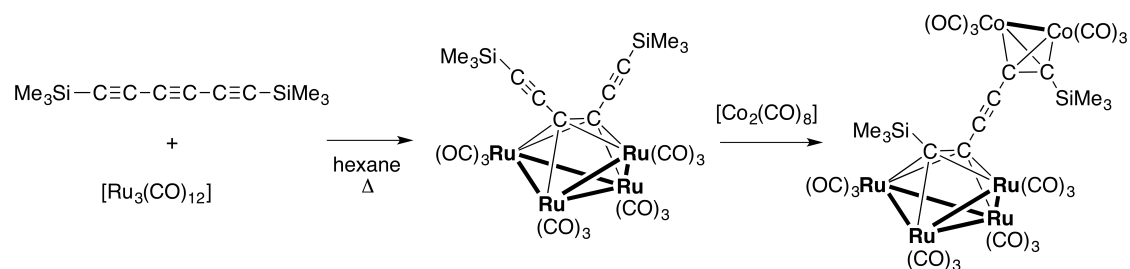
Molecular clusters can be (loosely) defined as those compounds comprised of a polyhedral array of atoms, including structures that can be conceptually derived from such arrays through the addition or removal of atoms at the vertices. Some philosophical and nuanced electronic arguments exist about the position of bimetallic species within or without the cluster family. Here, the chemistry developed from bimetallic species is described alongside the chemistry of the cluster complexes with which it is most closely aligned, and in order to distinguish clearly from the chemistry of ligand-bridged bis(metallic) complexes described in later sections.



Scheme 2 The remarkable redox-induced rearrangements of 62-CVE / 9-SEP closo- M_4C_4 clusters $[Ru(\mu-RC_2R)_2(CO)_{11}]$ (**L**) are defined by a sequence of 2e reduction (E(A)) to give a 64-CVE square cluster $[M]^{2-}$. On the CV timescale, $[M]^{2-}$ is reduced in a 2e step to **N**, which rearranges thermally to **L**. On the longer timescale of bulk electrolysis, $[M]^{2-}$ rearranges to $[O]^{2-}$, which reduces in two 1e steps via $[P]^-$ to **L**. Reorientation of the acetylide ligands (or carbon vertices) and flexing of the Ru_4 metal framework from butterfly to square geometries accommodate these electronic changes (CO ligands omitted for clarity) [20].

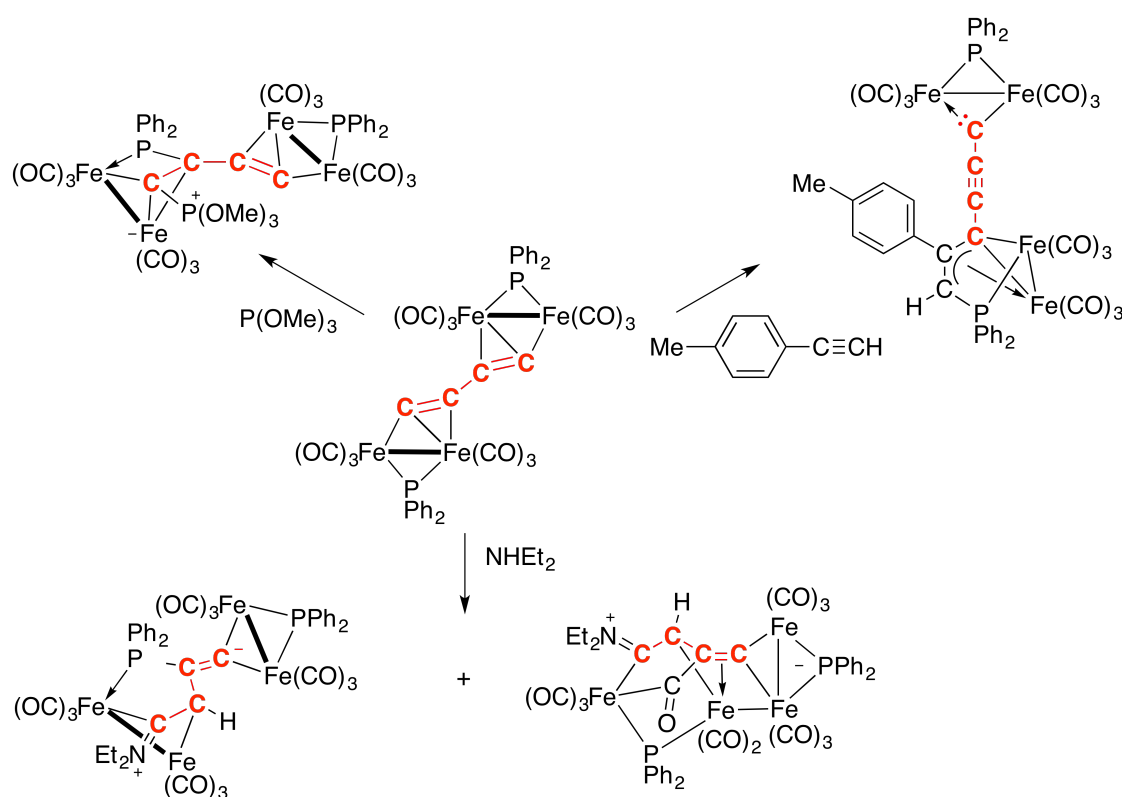
Clusters can be formed from one or more of the main group or metallic elements, and are often supported by a further array of peripheral ligands and interstitial atoms [RSC1 – RSC5]. Clusters that may be satisfactorily described in terms of localised two-electron bonds, or the effective atomic number rule, are known. However, more typically the bonding in clusters with structures derived from deltahedra is better described in terms of the delocalised bonding model summarised variously as Wade’s Rules, Wade-Mingos Rules or Polyhedral Skeletal Electron Pair theory. Given the composition of reactants and/or products, many synthetic strategies for the preparation of clusters can be designed and reactions rationalised through the application of Wade’s Rules [7]. The relationship between the number of cluster valence electrons and cluster geometry gives clusters an almost unmatched capacity to serve as ‘electron sinks’ with a rich redox response through the expansion or formal cleavage of bonds and structural rearrangement (**Scheme 2**) [20], as well as the ability to accommodate the addition or elimination of ligands and metal fragments through modifications of the cluster core structure and stabilise unusual organic fragments through coordination to, or incorporation in, the cluster framework.

With these concepts in mind, reactions of cluster compounds with acetylenes offers a wide-range of opportunities to explore the construction of metallocarbon clusters through the use of the alkyne π -system as a ligand around which to condense a metal cluster framework [24]. In early work conducted with A.J. Carty we explored some of the first reactions of the hexatriyne $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CSiMe}_3$ with Ru and Co clusters demonstrating the utility of the ‘carbon-string’ as a framework around which to assemble low to medium nuclearity clusters [C1 – C6, 15]. Despite the potential for a vast array of reaction products given the number of coordination sites offered by the hexatriyne and the propensity for metal clusters to undergo thermal fragmentation and condensation reactions, initial coordination was found to be strongly favoured at the most electron-rich, central alkyne moiety. Remarkably high yielding reactions allowing large-scale preparations of the cluster products could therefore be optimised. Curiously, further reaction of the pendant alkynes with metal cluster precursors was found to lead to a unusual cluster slippage reaction, with the original metal cluster core being displaced along the carbon string to give examples of bis(cluster) complexes featuring a bridging $\text{Me}_3\text{SiC}_2\text{C}\equiv\text{CC}_2\text{SiMe}_3$ ligand, providing an unexpected entry to carbon-bridged bis(cluster) systems (**Scheme 3**) [C4].



Scheme 3 The preparation of $[\text{Ru}_4(\mu\text{-Me}_3\text{SiC}\equiv\text{CC}_2\text{C}\equiv\text{CC}_2\text{SiMe}_3)(\text{CO})_{12}]$ and reaction with $[\text{Co}_2(\text{CO})_8]$ [C4].

Although the Si-C bond proved stable within the metal cluster coordination sphere, phosphinoalkynes are activated on metal clusters via facile P-C bond cleavage reactions [R5]. Thermal reactions (THF, reflux) of the readily obtained 1,4-bis(diphenylphosphino)buta-1,3-diyne, $\text{Ph}_2\text{PC}\equiv\text{CC}\equiv\text{CPh}_2$, with $\text{Fe}_3(\text{CO})_{12}$ proceeds via $[\{\text{Fe}_3(\text{CO})_{11}\}_2(\mu\text{-Ph}_2\text{PC}\equiv\text{CC}\equiv\text{CPh}_2)]$ to give $[\{\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)\}_2(\mu\text{-C}_2\text{C}_2)]$ [2, 38]. In turn, $[\{\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)\}_2(\mu\text{-C}_2\text{C}_2)]$ has been used as a scaffold to explore the reactions of the coordinated C_4 fragment with nucleophiles [2] and terminal alkynes [38], revealing the propensity for nucleophilic attack or insertion reactions involving the electron-deficient $\text{C}(\alpha)$ carbon. The structures of the products give an indication of the capacity of the C_4 moiety to propagate electronic effects, with addition of electron donors to $\text{C}(\alpha)$ leading to increased electron density at $\text{C}(\delta)$ and more carbene-like η^1 -coordination to the remote $\{\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)\}$ fragment (**Scheme 4**).



Scheme 4 Reactions of $[\{\text{Fe}_2(\text{CO})_6\}_2(\mu\text{-C}_2\text{C}_2)]$ illustrating the reactivity of the metal coordinated C_4 chain [2, 38].

Our interests in ligand-mediated electronic effects between remote metal centres [B16] evolved into the pursuit of similar studies concerning electronic interactions between cluster electrophores through carbon-rich and all-carbon ligands [R6]. At low temperatures (ca. -30°C , THF / 0.1 M $[\text{NBu}_4]\text{PF}_6$), the $\{\text{Co}_2\text{C}_2\}$ core in many $[\text{Co}_2(\mu\text{-RC}_2\text{R}')(\text{CO})_4(\text{dppm})]$ clusters gives rise to electrochemically reversible reduction and oxidation processes, and when combined with the π -character of the HOMO and LUMO that is readily able to mix with conjugated bridges [R6], makes them useful tools for such studies. A study of the nature of the bridging moiety interpolated

between two $\{\text{Co}_2\text{C}_2(\text{SiMe}_3)(\text{CO})_4(\text{dppm})\}$ electrophores provides some early examples of key features that have underpinned much of our latter work with mixed-valence complexes (*vide infra*). The energetic miss-match between the HOMO orbitals of the $\{\text{Co}_2\text{C}_2(\text{SiMe}_3)(\text{CO})_4(\text{dppm})\}$ fragments and a triarylamine bridge (consistent with both the ca. 0.5 V difference in cluster and amine oxidation potentials, and the NIR / IR spectroelectrochemical response using the $\nu(\text{CO})$ bands as a diagnostic marker) prevents any significant through-bond electronic interactions. In this case, the interactions between the cluster cores takes place largely via through-space mechanisms, as evinced by the significant increase in $\Delta E_{1/2}$ between the two cluster based electrochemical waves from measurements in $[\text{NBu}_4]\text{PF}_6$ to those in electrolyte featuring the weakly coordinating $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion [86]. Although offering ‘three dimensional aromatic’ character, the *para*-carbonanyl bridge $\text{C}_2\text{B}_{10}\text{H}_{10}$ serves as a σ -based bridge, propagating electrostatic interactions between the Co_2C_2 cluster cores [4, 21], a point further explored in mononuclear complexes described later in this Thesis. In contrast, the greater cluster π -bridge π mixing in 1,4-phenylene and butadiyndiyl ($-\text{C}\equiv\text{CC}\equiv\text{C}-$) bridged clusters leads to both a stronger electronic coupling between the cluster cores and also an increasingly important contribution from the bridge π -system to the redox process and the electronic structure of the one-electron (mixed-valence) redox product [21].

An examination of the electronic interactions between a mononuclear ruthenium fragment and a redox-active cobalt-carbon cluster core via polycarbon bridging ligands has also been undertaken [1]. Here electronic absorption and IR spectroscopies were combined with electrochemical information and an early demonstration of Electron Localisation Function (ELF) calculations on discrete molecular species, revealing a degree of charge transfer between the $\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ -based donor and $\{\text{Co}_2(\text{CO})_4(\text{dppm})\}$ -based acceptor through C_4 and C_6 -based bridges, but not any pronounced cumulated character in the carbon-based bridge (**Figure 8**) [C5].

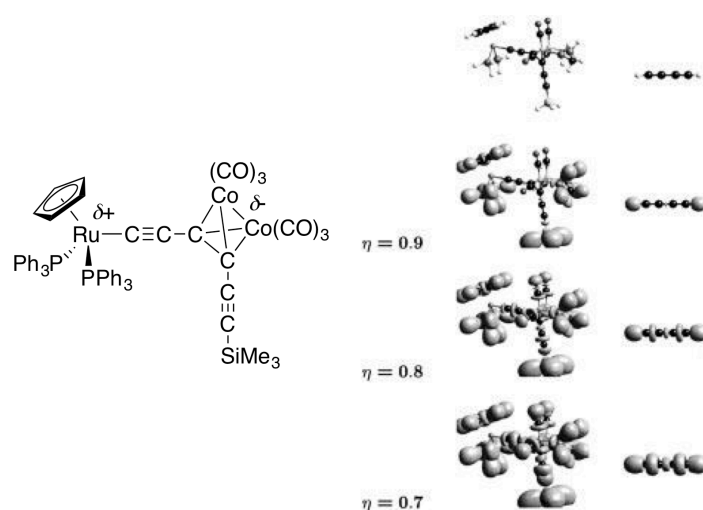
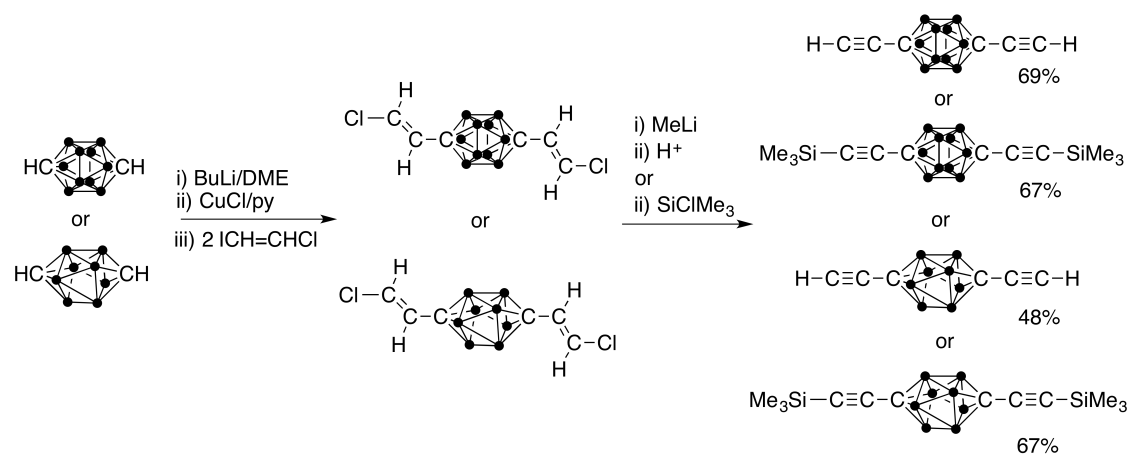


Figure 8 The complex $\text{Ru}(\text{C}\equiv\text{C}\{\text{C}_2\text{Co}_2(\text{CO})_3\}\text{C}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ and plots of the ELF isosurface from a simplified structural model, with $\text{HC}\equiv\text{CC}\equiv\text{CH}$ for reference. The disk-shaped attractors at the $\text{Ru}-\text{C}$ and $\equiv\text{C}-\text{C}_2\text{Co}_2$ bonds indicate that these bonds have negligible π -character

Main group clusters also offer a wealth of opportunities for the exploration of redox-induced structural changes and potential to serve as conduits for electronic effects. We were drawn to the chemistry of carborane clusters through the inspirational presence of Professor Ken Wade (FRS) at Durham, and aided in this work by the exceptionally talented Dr Mark Fox. The development of a convenient synthesis of the *bis*(ethynyl)-*para*-carboranes, 1,12-(RC≡C)₂-1,12-C₂B₁₀H₁₀ and 1,10-(RC≡C)₂-1,10-C₂B₈H₈ (R = H or Me₃Si) (**Scheme 5**) [36] was essential to the further use of the carborane moiety as a bridge in both the cluster based mixed-valence systems described above, and the C,C'-diethynylcarborane-bridged metal acetylide complexes described later in this Thesis.



Scheme 5 A revised and simplified synthetic approach to C,C'-diethynylcarboranes (unlabelled vertices = BH) showing overall yield [36].

Of particular interest to the present cluster-focussed discussion is the identification of the one-electron redox activity of 1,2-Ph₂-1,2-C₂B₁₀H₁₀. Wade's Rules identify a relationship between the geometry of a deltahedral cluster and the number of 'skeletal electron pairs' (i.e. the number of electron pairs available for bonding within the cluster core). In the simplest expression, a closed (*closo*) deltahedron is stabilised by 2n+2 electrons or n+1 electron pairs. Addition of an extra electron pair (i.e. n+2 electron pairs) results in opening of a bond or removal of a vertex to give a more open nest-like (*nido*) structure. Addition of a further electron pair (n+3 electron pairs) gives web- or net-like (*aracho*) structures with structures derived from removal of two vertices from the parent *closo* deltahedron. In discussion of the work that follows, it is important to recognise that Wade was keen to note that 'those' rules never prohibited odd-electron processes.

Drawn by our interests in the 'electron sink' properties of clusters and the use of electron counting rules to predict redox-driven structural change, we undertook some rare explorations of the electrochemical properties of carboranes. Given the well established 2e-relationships linking *closo*, *nido* and *arachno* structures, the discovery of a facile *one-electron* reduction of the *ortho*-carborane 1,2-Ph₂-1,2-C₂B₁₀H₁₀ to give the radical anion [1,2-Ph₂-1,2-C₂B₁₀H₁₀]^{•-} with an unusual 2n+3 electron count was most unexpected. The radical anion could be characterised by UV-vis-NIR and IR spectroelectrochemistry and further explored using DFT methods [40]. The addition of an extra electron to that expected from the electron counting rules for a *closo*-structure results in lengthening of the C–C bond from 1.763 Å to 2.389 Å (B3LYP/6-31G*),

generating a structure with a near-square face similar to those found in more open cluster geometries [40]. This one-electron redox chemistry has since proven to be quite a normal feature of *ortho*-carborane clusters [56, 92].

In addition to the identification of new redox chemistry and a structural family of ‘non-Wadian’ carboranes, the readily reducible *ortho*-carboranes have also been exploited as unusual electron acceptors in donor-acceptor dyads. The *C*-dimesitylboryl-*ortho*-carboranes 1-(BMes₂)-2-R-1,2-C₂B₁₀H₁₀ (R = H, Ph) were modestly emissive in the solid state ($\Phi = 2 - 7\%$), and much less so in solution ($\Phi < 1\%$), with a large Stokes shift (ca. 12,000 cm⁻¹) consistent with the substantial reorganisation of the cluster on charge transfer from the mesitylene donor [121]. The combination of both electron withdrawing BMes₂ and phenyl moieties was sufficient to stabilise the electrochemically generated dianion [1-(BMes₂)-2-Ph-1,2-C₂B₁₀H₁₀]²⁻ and allow its isolation as the sodium salt. A dynamic bowl-shaped *nido*-cage geometry was confirmed for both this dianion and the parent [1,2-Ph₂-1,2-C₂B₁₀H₁₀]²⁻ using a combination of spectroelectrochemistry, alkali metal reduction, experimental ¹¹B NMR spectroscopy and DFT calculations, neatly completing the redox-driven transformations of [2n+2]-*closo*, [2n+3]-*pseudo nido* and [2n+4]-*nido* cluster structures [121].

In summary, this body of work has developed the synthetic and redox chemistry of transition metal and main group clusters bearing alkyne and acetylide ligands. The reactivity of metal-supported carbon chains has been explored, revealing facile C-C, C-N and C-P bond forming reactions, whilst the use of clusters as electrophores or electron-accepting fragments has provided systems through which electronic interactions between cluster sites can be explored by electrochemical, spectroscopic and computational methods.

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Metal vinyl, acetylide and polyynyl chemistry

Our contributions to the synthetic chemistry, redox and spectroscopic properties, and electronic structures of the broad families of acetylide $[M(C\equiv CR)L_n]$, polyynyl $[M\{(C\equiv C)_xR\}L_n]$ and vinyl $[M(CH=CHR)L_n]$ complexes, relevant precursors and the reactions of these ligands are summarised in this section.

Facile and reliable routes to half-sandwich complexes $[MCl(dppe)Cp']$ ($M = Fe, Ru$; $Cp' = Cp, Cp^*$) [145] and the 5-coordinate species $[RuCl(dppe)_2]OTf$ [58] have been optimised. Simple procedures to ruthenium acetylide complexes *trans*- $[RuCl(C\equiv CR)(dppe)_2]$ that avoid the use of the thermodynamically unstable *cis*- $[RuCl_2(dppe)_2]$ precursor (the preparation of which has recently been described in detail by the Humphrey group [163]) have been developed [58], as have slow, but effective, routes to *trans*- $[Ru(C\equiv CR)_2\{P(OEt)_3\}_4]$ complexes [151]. Facile decarboxylation reactions of propiolic acids ($RC\equiv CCO_2H$; $R = H, Ph$) and salts ($RC\equiv CCO_2K$) occur in the presence of $[RuClL_2Cp]$ ($L_2 = (PPh_3)_2, dppe$) to give $[Ru(C\equiv CR)L_2Cp]$ via intermediate carboxylate complexes $[Ru(O_2CC\equiv CR)L_2Cp]$, that are calculated to rearrange via an η^2 -alkyne species and extrude CO_2 [88]. Transmetalation reactions of phosphine gold acetylide derivatives $[Au(C\equiv CR)(PPh_3)]$ also give convenient entry to a wide range of metal acetylide complexes [55]. An extension of this chemistry to include trans-metallation to copper(I) allowed entry to a mild Sonogashira protocol from gold-stabilised alkynes and diynes. For example, sequential cross-coupling of $Ph_3PAuC\equiv CC\equiv CAuPPh_3$, prepared in one step from $Me_3SiC\equiv CC\equiv CSiMe_3$, with different aryl iodides proved to be a useful route to asymmetric 1,3-diynes $ArC\equiv CC\equiv CAr'$ from a symmetrically substituted 1,3-diyne precursor [74]. A greatly improved route to the key C_4 building block 1,4-bis(trimethylsilyl)buta-1,3-diyne that alleviates the experimental difficulties inherent in a large scale Hay alkyne homo-coupling reaction of trimethylsilylacetylene has been disclosed; importantly this improved route avoids the conditions responsible for a significant explosion during the preparation of this compound in the hands of the extremely experienced Perepichka group at McGill University [160].

An early DFT (B3LYP, 3-21G*/6-31G**) study of the electronic structures of half-sandwich ruthenium (poly)ynyl complexes $[Ru\{(C\equiv C)_nR\}L_2Cp]$ and $[Ru\{(C\equiv C)_nR\}L_2Cp]^+$ ($n = 1 - 6$; $R = H, CH_3, C_6H_5, p-C_6H_4NH_2, p-C_6H_4NO_2, CN$; $L = CO, PH_3$) was conducted in collaboration with Rousseau, building on earlier work to establish of the electronic structures of similarly structured half-sandwich ruthenium acetylide complexes reported by Humphrey and McGrady, and iron diynyl complexes by Lichtenberger. The HOMOs of the polyynyl complexes are best described in terms of a strong metal-carbon σ -bond complimented by a series of filled orbital-filled orbital antibonding π interactions for all polyynyl chain lengths (**Figure 9**). The HOMO energy is sensitive to the degree of σ -donation from the polyynyl ligand, and hence the basicity and in turn chain length of this fragment. In contrast, at this level of theory, the LUMO composition shifts from metal (d_{xy}) to polyynyl (π^*) with increasing chain length. The distribution of charge along the carbon chain ligand is influenced by both the metal fragment $[Ru(PH_3)_2Cp]$ vs. $Ru(CO)_2Cp$ and the non-metallic end-cap, hinting at possibilities to tune charge-controlled reactions of the metal-supported carbon chain. On oxidation the odd electron is delocalized over the $\{M-(C\equiv C)_n-R\}$ fragment, becoming increasingly carbon-chain in character with increasing chain length, although the net bonding description retains polyynyl character [5].

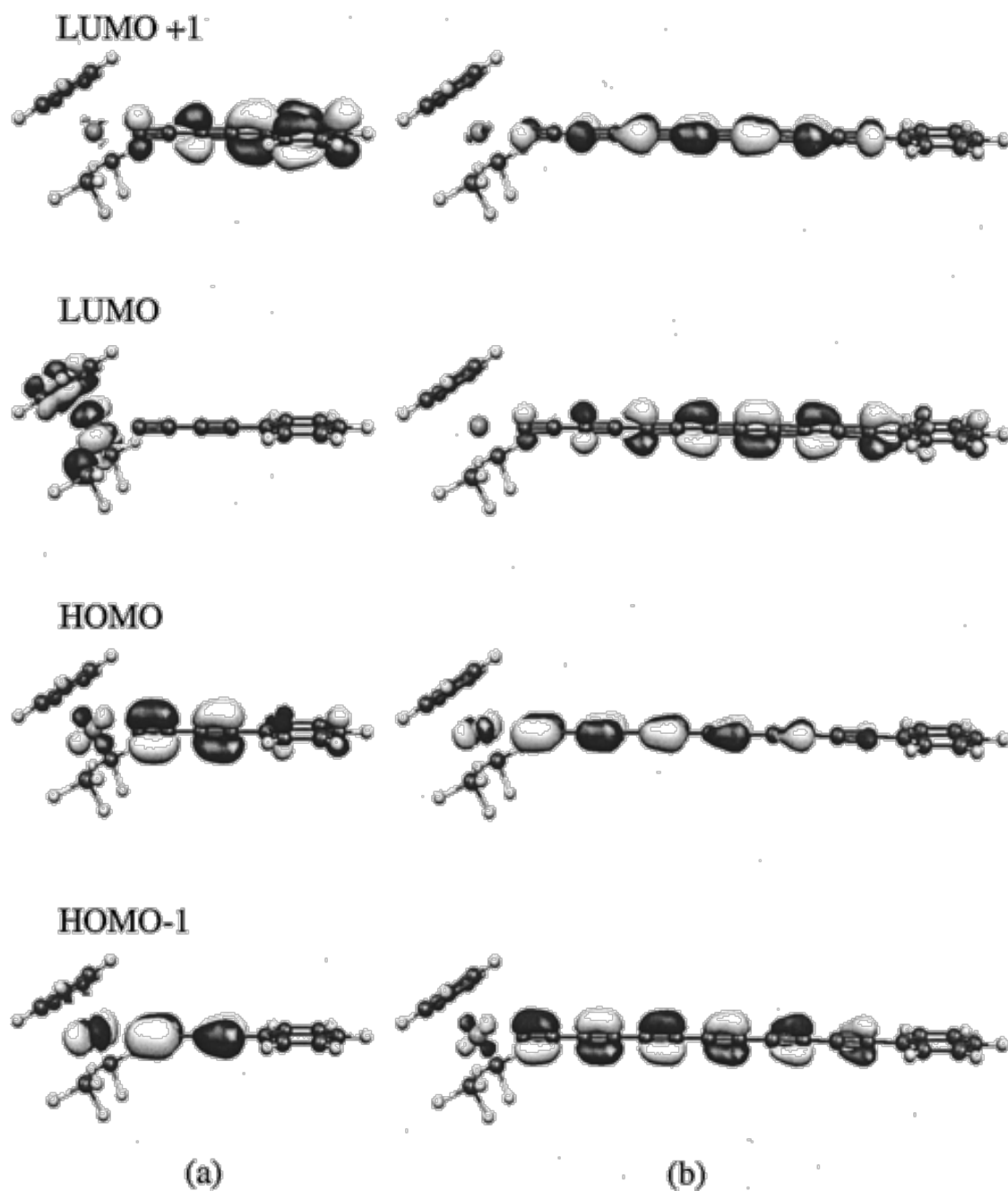


Figure 9 Isosurface (± 0.005 (e/bohr^3)^{1/2}) plots of the frontier orbitals of (a) $[\text{Ru}\{(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_5\}(\text{PH}_3)_2\text{Cp}]$ and (b) $[\text{Ru}\{(\text{C}\equiv\text{C})_6\text{C}_6\text{H}_5\}(\text{PH}_3)_2\text{Cp}]$ [5].

Subsequent studies have built on these general descriptions, including exploration of the synthesis and structures of cyanoacetylide and cyanobutadiynyl complexes (*vide infra*), and further detailed studies of the electronic structure of metal acetylide and polyynediyl complexes through combined application of spectroelectrochemical and higher-level DFT calculations. In the case of Group 8 complexes, detailed studies of the redox properties and spectroelectrochemical response of half-sandwich complexes $[\text{Ru}(\text{C}\equiv\text{CAr})(\text{L}_2)\text{Cp}']^{n+}$ ($n = 0, 1$; $\text{L}_2 = (\text{PPh}_3)_2$, $\text{Cp}' = \text{Cp}$; $\text{L}_2 = \text{dppe}$; $\text{Cp}' = \text{Cp}^*$; $\text{Ar} = \text{phenyl}$, $p\text{-tolyl}$, 1-naphthyl , 9-anthryl [41], $\text{C}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$, $\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{Y}$ { $\text{Y} = \text{OMe}$, Me , NO_2 , CO_2Me } [77]) and octahedral bis(acetylide) analogues $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^{1-4})_2(\text{dppe})_2]^{n+}$ and $[\text{trans-Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^{1-4})(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^{2-4})(\text{dppe})_2]^{n+}$

[111], supported by DFT calculations, confirm the redox non-innocence of the alkynyl ligand in these species (**Figure 10**).

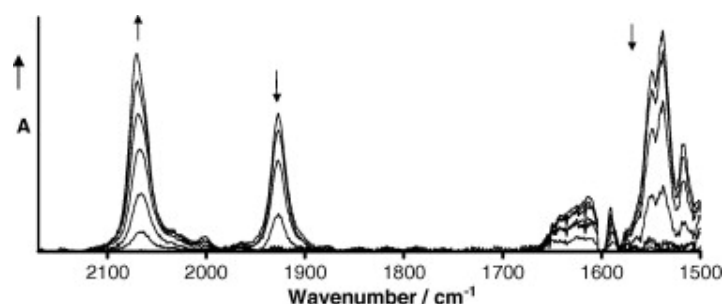
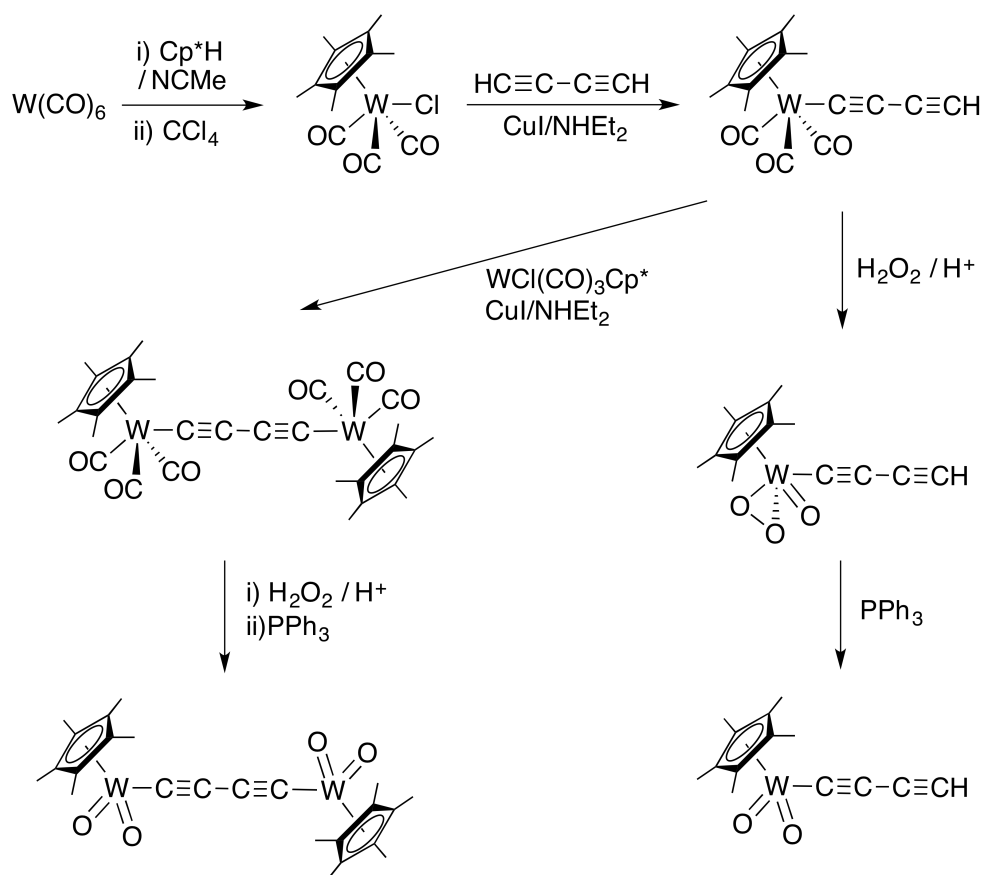


Figure 10 IR spectra recorded on back reduction of $[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*]^+$ to $[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*]$ in a spectroelectrochemical cell ($\text{CH}_2\text{Cl}_2/0.1 \text{ M NBu}_4\text{PF}_6$, ambient temperature). The large shift in the $\nu(\text{C}\equiv\text{C})$ bands and IR activity of the phenyl $\nu(\text{C}=\text{C})$ ring-breathing mode clearly indicate the redox activity of the $\text{C}\equiv\text{CPh}$ ligand [41].

A similar concerted application of experimental data, principally from UV-vis-NIR and IR spectroelectrochemical studies, and electronic structure calculations has shown that the vinyl ligands in related $[\text{Ru}(\text{CH}=\text{CHAr})(\text{CO})(\text{PPh}_3)\text{Tp}^*]$ complexes are also redox-active, with the small shift in $\nu(\text{CO})$ band as a function of molecular oxidation state ($\Delta\nu(\text{CO})$ ca. 50 cm^{-1}) proving diagnostic [90]. Furthermore, these data confirm the sensitivity of the electronic structure to molecular conformation and the important role played by the relative orientation of the plane of arylene ring with respect to the metal fragment, and hence the overlap of the aromatic π and π^* orbitals with the metal d_{xz} and d_{yz} orbitals through the alkyne (or alkene) π -system. Evidence for the ground state population of various such conformers is obtained from IR spectroscopy, where multiple conformers give rise to additional shoulders to the $\nu(\text{C}\equiv\text{C})$ (or $\nu(\text{CO})$) bands [109] [150]. The identification of a distribution of conformers in fluid solution at room temperature provides a conceptual framework through which to better understand the nature of bimetallic Group 8 complexes featuring acetylide and vinyl-based bridging ligands, as described in greater detail below (*vide infra*).

The organometallic ruthenium fragments $\{\text{Ru}(\text{PP})\text{Cp}'\}$, $\{\text{Ru}(\text{dppe})_2\text{X}\}$ and $\{\text{Ru}(\text{CO})(\text{PPh}_3)\text{Tp}^*\}$ are therefore better considered as strongly electron-donating substituents to the conjugated organic ligand than a readily accessible Ru(II/III) electrophore, although the extent of interaction is dependent on the molecular conformation as discussed further below. For example, during explorations of Pd^0/Cu^1 -catalysed cross-coupling reactions of the terminal buta-1,3-diynyl complex $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}]$ with aryl iodides, ArI , to give substituted complexes $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CAr})(\text{PPh}_3)_2\text{Cp}]$, a homocoupling reaction of the diynyl complex (cat. $\text{Pd}^0/\text{Cu}^1/\text{O}_2$) to give the bimetallic 1,3,5,7-octatetrayn-1,8-diyl complex $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]$ was also developed. Spectroelectrochemical studies in the UV-vis-NIR and IR regions revealed the formation of intermolecular carbon-chain coupling products following one-electron oxidation [118]. These intermolecular coupled products could be isolated and characterised following chemical oxidation of hexatriyndiyl-bridged $\{\text{Ru}(\text{dppe})\text{Cp}\}$ analogues (*vide infra*), clearly demonstrating the redox activity of the C_8 fragment.

The key precursor to W carbonyl and oxo-chemistry, $[\text{WCl}(\text{CO})_3\text{Cp}^*]$, is readily prepared in a one-pot, two-step reaction of $[\text{W}(\text{CO})_6]$ with Cp^*H in NCMe (to give the hydride complex $[\text{WH}(\text{CO})_3\text{Cp}^*]$) followed by treatment with CCl_4 [10]. A simple CuI -catalysed reaction of $[\text{WCl}(\text{CO})_3\text{Cp}^*]$ with $\text{HC}\equiv\text{CC}\equiv\text{CH}$ gave the diyndiyl complex $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*]$ which could be reacted in turn with a further equivalent of $[\text{WCl}(\text{CO})_3\text{Cp}^*]$ under the same condition to give the butadiyndiyl complex $[\{\text{Cp}^*(\text{CO})_3\text{W}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{W}(\text{CO})_3\text{Cp}^*\}]$. Quite remarkably, the butadiyndiyl and C_4 ligands were stable to forcing oxidative conditions (H_2O_2 / conc. H_2SO_4) to give the oxo-peroxo derivatives $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})(\text{O}_2)\text{Cp}^*]$ and $[\{\text{Cp}^*(\text{O}_2)(\text{O})\text{W}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{W}(\text{O})(\text{O}_2)\text{Cp}^*\}]$. Whilst the butadiyndiyl derivative smoothly converted directly to the bis(dioxo) complex $[\{\text{Cp}^*(\text{O})_2\text{W}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{W}(\text{O})_2\text{Cp}^*\}]$ in the course of the reaction, further reaction of $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})(\text{O}_2)\text{Cp}^*]$ with PPh_3 was necessary to access $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2\text{Cp}^*]$ (**Scheme 6**). On the basis of the crystallographically determined structural changes in the carbon chain along the sequence $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*]$ to $[\{\text{Cp}^*(\text{CO})_3\text{W}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{W}(\text{CO})_3\text{Cp}^*\}]$ to $[\{\text{Cp}^*(\text{O})_2\text{W}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{W}(\text{O})_2\text{Cp}^*\}]$ some delocalisation along the C_4 bridge between the $\text{W}(\text{II})$ (d^4) fragments could be evinced, but as might be reasonably expected, not between the $\text{W}(\text{VI})$ (d^0) centres, with these high-oxidation state species offering frontier orbitals dominated by the carbon chain [10].



Scheme 6 The synthesis of tungsten carbonyl, oxo-dioxo and dioxo, diyndyl and diydiyl complexes [10].

The electronic structures of Group 6 complexes $[\text{M}(\text{C}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ ($\text{M} = \text{Mo}, \text{W}$) are distinctly different from those of the ruthenium(II), tungsten(II) and

tungsten(VI) compounds described above. Complexes $[M(C\equiv CR)(dppe)(\eta-C_7H_7)]$ are conveniently prepared from $[MBr(dppe)(\eta-C_7H_7)]$ [115] and a terminal or trimethylsilyl-protected acetylene, via formation and deprotonation of the analogous vinylidene complex $[M\{C=C(H)R\}(dppe)(\eta-C_7H_7)]^+$ ($M = Mo$ [66], W [71]) or from the trimethylsilyl-protected acetylene and KF via an *in situ* desilylation-metallation protocol ($M = Mo$ [66]), based on methods developed earlier [B13]. In contrast to the $\eta^5-C_5R_5$ ligand, the e_1 and e_2 orbitals of the larger C_7H_7 ring are better able to enter into forward and back π - and δ -type bonding interactions with the metal d_{xy} , d_{yz} , d_{xz} and $d_{x^2-y^2}$, stabilising these orbitals and removing them from the frontier region. This leaves the d_{z^2} , which interacts only weakly with the a_1 orbital of the C_7H_7 fragment, to feature prominently in the molecular HOMO (**Figure 11**). The overlap of the d_{z^2} orbital and the alkynyl ligand π -orbitals is limited, a fact that accounts for many of the key observations concerning the spectroscopic and redox properties of these species [66, 115]. For example the range of oxidation potentials in complexes with electron donating and withdrawing R groups and the shift in $\nu(C\equiv C)$ bands on oxidation are much smaller in $[M(C\equiv CR)(dppe)(\eta-C_7H_7)]$ complexes ($M = Mo$ [66], W [71]; $\Delta E_{1/2}$ ca 160 mV; $\Delta\nu(C\equiv C)$ ca. -30 cm^{-1}) than those of analogous $[Ru(C\equiv CR)(dppe)Cp^*]$ derivatives ($\Delta E_{1/2} > 300\text{ mV}$, $\Delta\nu(C\equiv C)$ ca. -145 cm^{-1}), and reflect the differences in predominantly metal vs. ligand character in these redox processes.

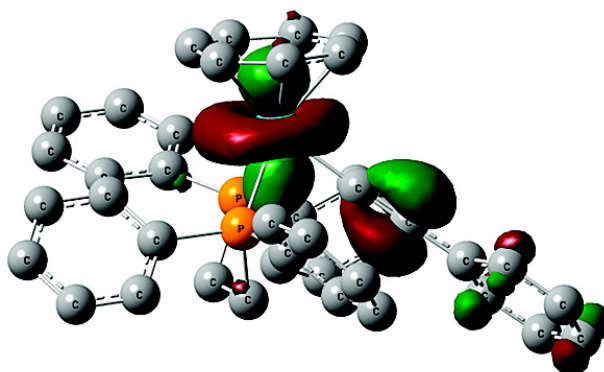
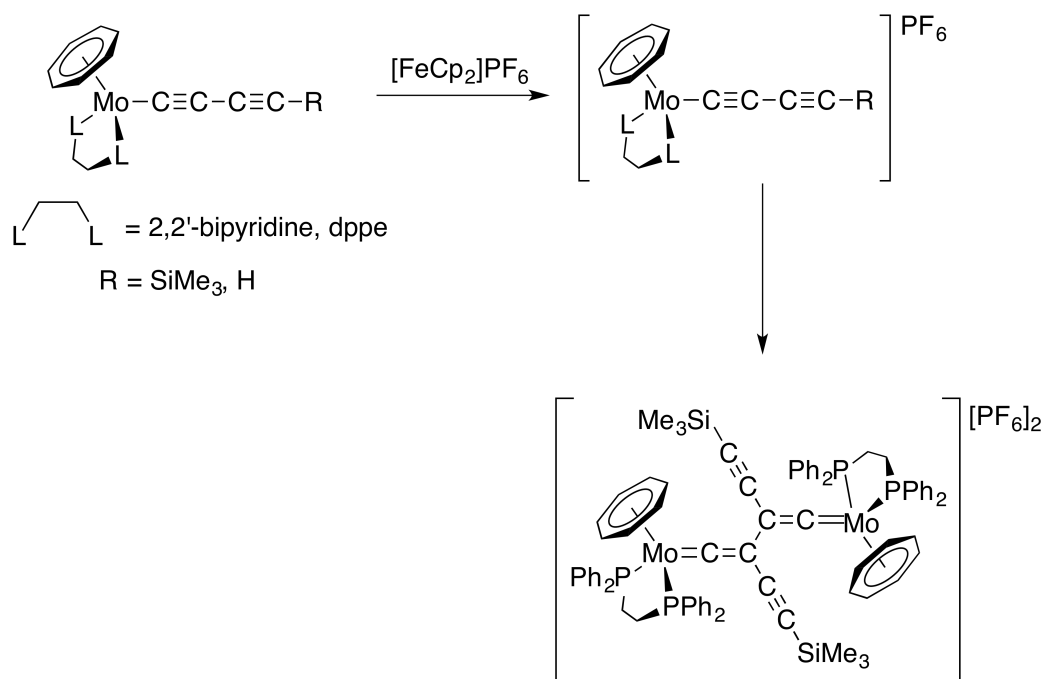


Figure 11 A plot ($0.04\text{ (e/bohr}^3)^{1/2}$) of the HOMO of $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]$ [66].

These electronic features have been exploited to design the first examples of spectroscopically observable metal diyne and triynyl radical cations, $[Mo\{(C\equiv C)_nSiMe_3\}(L_2)(\eta-C_7H_7)]^+$ ($n = 2$, $L_2 = dppe$, 2,2'-bipyridine (bpy), 4,4'- t Bu₂-2,2'-bipyridine (t Bu₂-bpy); $n = 3$, $L_2 = dppe$, bpy), the precursors to which are most conveniently obtained from $Li(C\equiv C)_nSiMe_3$ and $[MoBr(NN)(\eta-C_7H_7)]$ ($NN = bpy$, t Bu₂-bpy) and ligand exchange with $dppe$ ($NN = bpy$) [64, 89]. Small positive shifts (ca. $< +20\text{ cm}^{-1}$) in the position of the $\nu(C\equiv C)$ bands on oxidation in a spectroelectrochemical cell, together with the observation of well-resolved isotropic EPR spectra with clearly defined hyperfine coupling to $^{95,97}Mo$, ^{31}P and $^1H(C_7H_7)$ following chemical oxidation clearly indicate the metal-centred nature of the radical. Whilst the one-electron oxidation products derived from the $L_2 = dppe$ systems were less kinetically stable undergoing $C(\beta)-C(\beta')$ coupling ($n = 2$) [64] or slow decomposition ($n = 3$) [89], the $L_2 = bpy$ and t Bu₂-bpy derivatives proved stable

enough for spectroelectrochemical study *in situ*. Remarkably, the radical cation $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{bpy})(\eta\text{-C}_7\text{H}_7)]^+$ was stable enough to permit isolation and crystallographic characterisation as the PF_6 salt (**Scheme 7**). The increased back-bonding from the Mo centre to the bpy-based ancillary ligands is likely to lead to lower spin density on the carbon chain and temper the reactivity, a suggestion that is consistent with the results of DFT calculations on structurally simplified model complexes [89].



Scheme 7 Oxidation of diynyl complexes $\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CR})\text{L}_2(\eta\text{-C}_7\text{H}_7)$ ($\text{R} = \text{SiMe}_3, \text{H}$; $\text{L}_2 = \text{bpy, dppe}$). Whilst $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{bpy})(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$ can be isolated, the analogous *dppe* complex undergoes a C-C coupling reaction to give the dimer shown [89].

Further examples of the use of ancillary ligands to influence the energy and occupancy of the metal *d*-orbital manifold and in turn the extent of overlap with the alkynyl ligand fragment in half-sandwich complexes are found in the deceptively similarly structured cyclopentadienyl complexes $[\text{Mo}(\text{C}\equiv\text{CR})(\text{CO})(\text{dppe})\text{Cp}']$ and *trans*- $[\text{Mo}(\text{C}\equiv\text{CR})(\text{CO})(\text{PMe}_3)_2\text{Cp}']$ ($\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{-4-Me}$), both of which undergo a facile, electrochemically reversible one-electron oxidation. These complexes are spectroscopically rich; the $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ bands are sensitive reporters of the metal electron density and the bonding electron density in the alkynyl moiety respectively, whilst the spin active $^{95,97}\text{Mo}$, ^{31}P and ^1H nuclei can couple with the unpaired electron that results from one-electron oxidation to give informative EPR spectra. In the case of *trans*- $[\text{Mo}(\text{C}\equiv\text{CR})(\text{CO})(\text{PMe}_3)_2\text{Cp}']^{0/+}$, a combination of electrochemical measurement, UV-vis-NIR and IR spectroelectrochemical studies and EPR spectra collected from solutions of the radical cation prepared by *in situ* chemical oxidation indicate that the redox process can satisfactorily be described in terms of a predominantly metal-centred process (e.g. $\Delta\nu(\text{C}\equiv\text{C}) < -11 \text{ cm}^{-1}$). This is consistent with results of DFT calculations on model systems, which give the HOMO of *trans*- $[\text{Mo}(\text{C}\equiv\text{CR})(\text{CO})(\text{PMe}_3)_2\text{Cp}']$ as principally composed of the metal d_{z^2} -orbital, the *z*-axis of the local coordinate system being directed to the centroid of the cyclopentadienyl ring (**Figure 12**). The HOMO-1

is comprised of a geometrically restricted weak anti-bonding (filled-filled) interaction between d_{xz} and the alkynyl π -orbitals. The d_{yz} and d_{xz} are involved in π -bonding interactions with the e_1 -level of the Cp ligand and lowered considerably from the frontier orbital region. The HOMO of these systems is therefore strongly metal centred (59%) with minor components on CO (16%). The poor symmetry match of the alkynyl π -orbital with the metal d_{z^2} -orbital and competing bonding overlap with the CO π^* -level, prescribes only a weak metal alkynyl interaction. Overall the electronic structure, redox and spectroscopic properties of *trans*-[Mo(C≡CR)(CO)(PMe₃)₂Cp'] resemble [Mo(C≡CR)(dppe)(η -C₇H₇)] complexes.

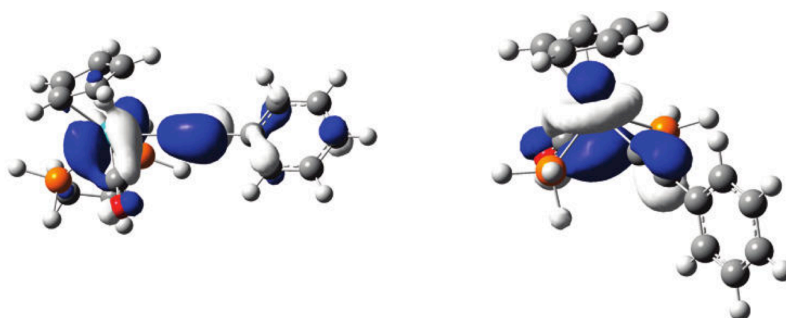


Figure 12 Plots ($0.04 (e/\text{bohr}^3)^{1/2}$) of the HOMO of the model systems [Mo(C≡CR)(CO)(dHpe)Cp] (left) and *trans*-[Mo(C≡CR)(CO)(PH₃)₂Cp]

In contrast, the HOMO of [Mo(C≡CR)(CO)(dppe)Cp'] is more like that of [Ru(C≡CR)(dppe)Cp'] systems, with DFT calculations indicating relatively large alkynyl (51%) and small metal (34%) contributions to the HOMO (**Figure 12**). With the electron-accepting CO and electron-donating alkynyl ligands *cis* to each other, there is a strong driving force to re-hybridise the metal d -orbitals that is not possible in the *trans*-conformation where the CO acceptor and C≡CR donor ligands must compete for the same metal orbital. A distortion of the structure from the idealised square-based pyramidal (pseudo- C_{4v}) geometry towards pseudo- C_{2v} allows a mixing and re-hybridisation of d_{z^2} and $d_{x^2-y^2}$ orbitals to give two new hybrid orbitals oriented along the yz and xz axes. In turn, this permit better metal-ligand back-bonding with the CO and phosphine *trans* to CO ligands that bend down out of the idealised square plane, and an enhanced alkynyl ligand-to-metal forward bonding interaction in the xz plane with the alkynyl and phosphine *trans* to alkynyl ligands. These results are entirely consistent with the experimental spectroelectrochemical data, which reveal a substantially larger negative shift in the $\nu(\text{C}\equiv\text{C})$ band position ($\Delta\nu(\text{C}\equiv\text{C})$ ca. -50 cm^{-1}) on oxidation.

The work conducted here has employed a combination of synthetic, spectroscopic, spectroelectrochemical and computational approaches to explore the physical and electronic structures of a wide variety of mononuclear metal complexes bearing 'carbon rich' vinyl, ynyl and poly(ynyl) ligands. The relationships between chemical structure and electronic structure that have been established allow the rational exploration of the chemistry of these species, and used with explanations of the properties of bimetallic complexes featuring these structural motifs, including the electronic structures and charge-transfer characteristics of putative 'mixed-valence' derivatives (*vide infra*).

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Group 8 complexes

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Carbene, vinylidene and allenylidene and related complexes

Bertrand, Arduengo and others have dramatically advanced the chemistry of the carbene ligand, :CR_2 , through the development of stable examples. The chemical flexibility offered by the carbene fragment, where the steric, stereochemical and electronic properties can be tuned through the choice of substituent design, has allowed the development of this species as an ancillary ligand in a wide range of powerful catalytic processes. However, carbene ligands and unsaturated (vinylidene) derivatives enjoy a long history that predates these examples, and have featured prominently in the development of Organometallic chemistry. More recently, synthetic routes to complexes bearing allenylidene [B11], butatrienyliidene [B3, B6, B7, B14] and higher unsaturated carbene ligands have been developed, allowing entry to the chemistry of these species.

Metal acetylide complexes, typified here by the Group 8 half-sandwich compounds $[\text{M}(\text{C}\equiv\text{CR})(\text{PP})\text{Cp}']$, are nucleophilic at $\text{C}(\beta)$, reacting readily with electrophiles, E^+ , (subject to steric constraints) to give vinylidene complexes $[\text{M}\{\text{C}=\text{C}(\text{E})\text{R}\}(\text{PP})\text{Cp}']^+$. For example, as part of a search for entry to compounds bearing cyano-acetylide and cyanovinylidene ligands, complexes $[\text{M}(\text{C}\equiv\text{CR})(\text{PP})\text{Cp}']$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{-4-Me}$; $\text{M}(\text{PP})\text{Cp}' = \text{Fe}(\text{dppe})\text{Cp}, \text{Ru}(\text{PPh}_3)_2\text{Cp}$) were reacted with BrCN in the presence of NH_4PF_6 but found to give bromovinylidenes $[\text{M}\{\text{C}=\text{C}(\text{Br})\text{R}\}(\text{PP})\text{Cp}']\text{PF}_6$ via formal electrophilic addition of Br^+ . In the case of $\text{R} = \text{SiMe}_3$, the unusual dibromovinylidenes $[\text{M}(\text{C}=\text{CBr}_2)(\text{PP})\text{Cp}']\text{PF}_6$ were obtained [61].

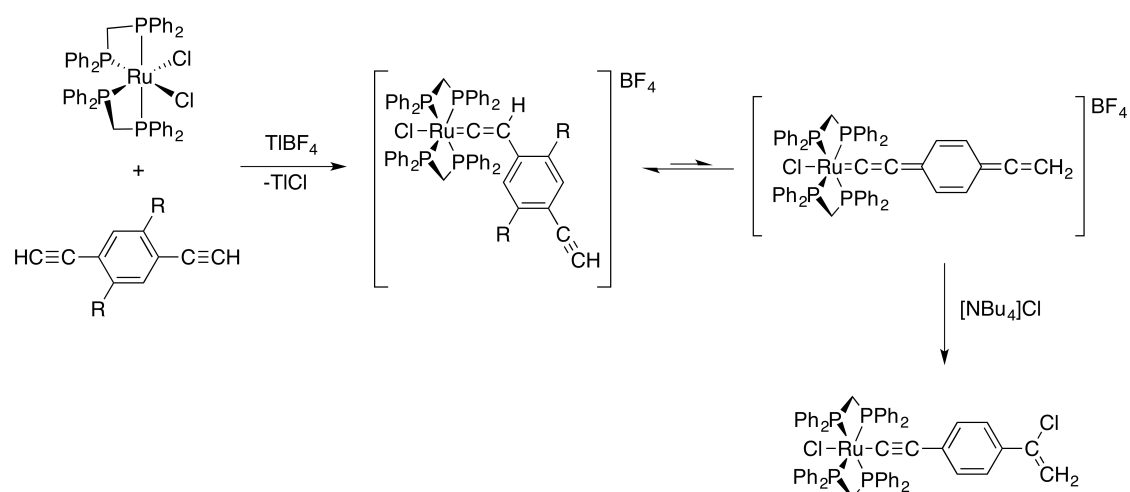
Vinylidenes, allenylidenes and higher cumulenes display patterns of alternating electrophilic / nucleophilic character along the carbon chain. This permits C-C bond formation between the electron-rich $\text{C}(\alpha)$ carbon of the acetylide ligand and electrophilic $\text{C}(\alpha)$ carbon of the vinylidene ligands in *cis*- $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-R})\{\text{C}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-R}\}(\text{dppm})_2]\text{BF}_4$ to give butenylnyl complexes [131]. In the case of reactions of the parent vinylidenes $[\text{M}(\text{C}=\text{CH}_2)(\text{PP})\text{Cp}']\text{PF}_6$ [$\text{M}(\text{PP})\text{Cp}' = \text{Fe}(\text{dppe})\text{Cp}, \text{Ru}(\text{dppe})\text{Cp}, \text{Ru}(\text{PPh}_3)_2\text{Cp}, \text{Ru}(\text{dppe})\text{Cp}^*$], reaction with NH_3 proceed readily (r.t., CH_2Cl_2) to give complexes $[\text{M}\{\text{C}(\text{Me})\text{NH}_2\}(\text{PP})\text{Cp}']\text{PF}_6$ from addition of the nucleophile to the electrophilic carbene-like $\text{C}(\alpha)$ carbon in good to excellent yield [127]. Despite the well-known stability of acyclic amino carbenes, these compounds are rare examples of metal complexes bearing an acyclic amino carbene ligand. Structural and electronic structure calculations indicate that the ligand acts as a simple singlet carbene, with good σ -donor character but little $\text{M}(\text{d})\text{-C}(\text{p})$ π -interaction. Further computational investigations of free acyclic amino carbenes, such as $\text{:C}(\text{tBu})=\text{N}(\text{iPr})_2$ also predict singlet character ($\Delta E_{\text{S-T}} = 35.8 \text{ kcal mol}^{-1}$), but a more linear structure ($\text{N-C-C } 122.62^\circ$) due to steric constraints. The difficulties obtaining metal complexes of mono(amino) carbenes directly from the free carbene and a metal complex precursor therefore seems to be due to the significant steric bulk of the supporting groups necessary to stabilise the singlet carbene. 'On-complex' synthetic methods therefore appear a more suitable entry point for further explorations of such compounds [127].

Although nucleophilic attack at $\text{C}(\alpha)$ in vinylidene complexes is often sterically restricted by the ancillary ligands of the metal and the vinylidene substituents, the more remote carbon atoms of allenylidenes and butatrienyliidenes are more available sites for

reaction. The terminal diyne $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ has proven a convenient entry point to butatrienyliene species such as $[\text{Mo}\{\text{C}=\text{C}=\text{C}=\text{C}(\text{H})\text{R}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ ($\text{R} = \text{H}$ or SiMe_3 , undefined) which in keeping with the high reactivity of such species could not be isolated but rather was trapped by reaction with NHET_2 in situ to give the formal hydroamination product, formulated on the basis of a single-crystal X-ray diffraction study and NMR data as $[\text{Mo}\{\text{C}\equiv\text{CC}(=\text{NET}_2)\text{Me}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{BPh}_4$ [144], with only a small contribution from the allenylidene resonance contributor, consistent with the limited π -donor capacity of the $\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}$ fragment noted earlier (*vide supra*). The strongly metal-centred nature of the redox processes of $\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}$ complexes brings the advantage that interpretation of the IR spectroscopic data can essentially be simplified to a consideration of the expected decrease in π -back donation and increase in iminium alkynyl character following one-electron oxidation. Spectroelectrochemical investigations on the redox pair $[\text{Mo}\{\text{C}\equiv\text{CC}(=\text{NET}_2)\text{Me}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^{+/2+}$ reveal an increase in the IR active $\nu(\text{CCC})$ stretching frequency of ca. 70 cm^{-1} following one-electron oxidation, which contrasts the shift of $\nu(\text{CCC})$ to lower wavenumber on oxidation of $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NET}_2\}\text{Cl}(\text{dppm})_2]^+$ due to the greater $\text{Ru}=\text{C}=\text{C}=\text{C}$ character in the redox-active orbital. These observations highlight the highly flexible bonding character of the aminoallenylidene ligand, which can also bind as a special case of an alkynyl ligand with additional π -acceptor capability in the case of metal complexes with limited π -donor capacity.

The high reactivity of butatrienyliene and longer cumulated ligands prompted consideration of stabilised forms of these species that would be more amenable to study. Although reactions of 1,4-diethynylbenzenes with $[\text{RuCl}(\text{PP})\text{Cp}']$ and similar metal reagents are known to give (4-ethynylphenyl)vinylidene complexes [B15], our calculations on the isomeric vinylidene and quinoidal cumulene complexes *trans*- $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{C}\equiv\text{CH}\}\text{Cl}(\text{dppm})_2]^+$ and *trans*- $[\text{Ru}(\text{C}=\text{C}=\text{C}_6\text{H}_4=\text{C}=\text{CH}_2)\text{Cl}(\text{dppm})_2]^+$ revealed the quinoidal cumulene form to lie only some 41 kJ mol^{-1} higher in energy [131]. Duly, reactions of *trans*- $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}_6\text{H}_2\text{-2,5-R}_2\text{-C}\equiv\text{CH}\}\text{Cl}(\text{dppm})_2]\text{BF}_4$ ($\text{R} = \text{H}, \text{Me}$) with $[\text{NBu}_4]\text{Cl}$ resulted in rapid formation of a single new compound, characterised spectroscopically and crystallographically as the Markovnikov addition products *trans*- $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}_6\text{H}_2\text{-2,5-R}_2\text{-C}\equiv\text{CH}\}\text{Cl}(\text{dppm})_2]\text{BF}_4$ (**Scheme 8**) Control reactions of $[\text{NBu}_4]\text{Cl}$ with *trans*- $[\text{RuCl}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{dppm})_2]\text{BF}_4$ and *trans*- $[\text{RuCl}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})(\text{dppm})_2]$ gave no evidence of reaction, consistent with the steric protection of $\text{C}(\alpha)$ in the vinylidene and the exceptionally slow reaction addition of HCl to alkynes in uncatalysed reactions. Careful computational investigation of the addition of Cl^- to $\text{C}(\alpha)$ in *trans*- $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{C}\equiv\text{CH}\}\text{Cl}(\text{dppm})_2]^+$ and the *pseudo*- $\text{C}(\gamma)$ in the proposed quinoidal cumulene isomer *trans*- $[\text{RuCl}(\text{C}=\text{C}=\text{C}_4\text{H}_4=\text{C}=\text{CH}_2)(\text{dppm})_2]^+$ revealed similar kinetic barriers to the initial addition. However, whilst the barrier to reverse reaction was small in the case of the vinylidene isomer, there is a great thermodynamic preference for formation of the Markovnikov vinyl chloride from the quinoidal cumulene [131]. The proposal of a quinoidal cumulene isomer existing as a small equilibrium component in solutions of (4-ethynylphenyl)vinylidene complexes is consistent with the previously unexplained observation of facile Markovnikov addition of HBr to the pendant alkyne in

[Mn{C=C(H)C₆H₄C≡CH}(CO)₂Cp] by Kolobova.¹ The identification of further examples of such ‘spaced’ cumulenes and studies of their reactivity are current topics of investigation in the group.



Scheme 8 Reactions of ruthenium 4-ethynylphenylvinylidene complexes ($R = H, Me$) with nucleophiles proceed via a quinoidal cumulene to give Markovnikov addition products [131].

In summary, the manipulation of the electronic and steric properties of the metal, ancillary ligands and substituents on acetylide, vinylidene and the longer unsaturated carbene ligands allow for reaction products of metal complexes bearing these ligands to be predicted and rationalised. Whilst higher cumulenes with small end-groups are too reactive to be isolated, the identification of reaction products and computational studies of reaction pathways provides a route to establish the existence of these species.

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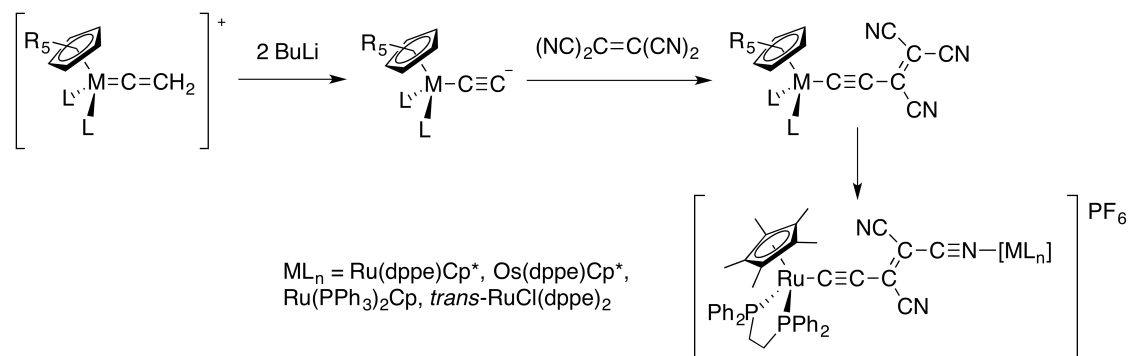
¹ N.E. Kolobova, O.S. Zhvanko, L.L. Ivanov, A.S. Batsanov, Yu. T. Struchkov, *J. Organomet. Chem.*, 1986, **302**, 235 – 242.

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Cyanide, cyanoacetylide, cyanovinylidene and other cyanocarbon complexes

As part of a broader interest in the chemistry of metal complexes bearing acetylide, vinylidene and cumulated carbon ligands, we have been drawn to the chemistry of such ligands incorporating cyano moieties, $C\equiv N$, which are isoelectronic and isolobal with $C\equiv CH$ [B8, B9, B15, 18, 26, 34, 65]. Within this body of work, a distinct theme concerning the preparation and chemistry of cyanovinylidene and cyanoacetylide complexes can be identified, and which forms the subject of this section.

The lithiated acetylides obtained from $[M(C=CH_2)(PP)Cp'] [PF_6]$ [$M(PP)Cp' = Ru(PPh_3)_2Cp, Os(PPh_3)_2Cp, Ru(dppe)Cp^*$] and 2 equivalents of BuLi or MeLi react with TCNE to give tricyanovinylethynyl $[M\{C\equiv CC(CN)=C(CN)_2\}(PP)Cp']$ complexes (**Scheme 9**), whilst direct reactions of $[M(C\equiv CH)(PP)Cp']$ or $[Ru(C\equiv CC\equiv CH)(dppe)Cp^*]$ with TCNE gave the conventional tetracyanobutadienyl products. On the basis of structural, NMR and IR spectroscopic data, the tricyanovinylethynyl compounds are best formulated with a degree of the allenylidene tautomer. Coordination of a second metal centre to the CN moiety *trans* to the metal fragment in $[Ru\{C\equiv CC(CN)=C(CN)_2\}(dppe)Cp^*]$ was readily achieved to give bimetallic complexes, although there is only limited delocalisation between the metal fragments [83].

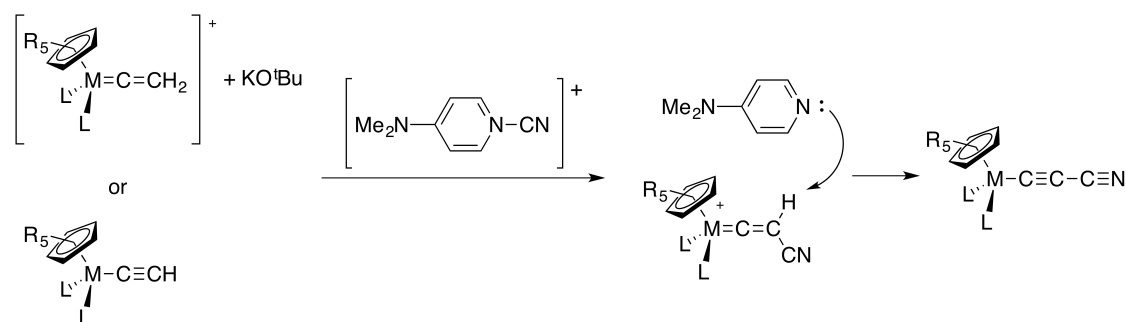


Scheme 9 The tricyanovinylethynyl complexes $[M(C\equiv CC(CN)=C(CN)_2)(PP)Cp']$, readily formed from acetylide anions and TCNE, serve as metalloligands [83].

In extending these studies, cyanoacetylenes appeared to offer considerable potential to assemble a diverse range of metal centres around a single ligand through the use of both $C\equiv C$ and $C\equiv N$: fragments. In early studies of the coordination chemistry of the prototypical cyanoacetylene $PhC\equiv CC\equiv N$ it was shown that either the nitrile-like lone pair or the alkyne π -system could enter into usual coordination reactions with $[RuCl(PPh_3)_2Cp] / NH_4PF_6$, to give $[Ru(N=CC=CPh)(PPh_3)_2Cp]PF_6$, or $[Co_2(CO)_6(dppe)]$, to give $[Co_2(\mu-PhC_2CN)(CO)_4(dppe)]$. The pendant nitrile moiety in $[Co_2(\mu-PhC_2CN)(CO)_4(dppe)]$ is also available for coordination, undergoing reaction with $[RuCl(PPh_3)_2Cp]/NH_4PF_6$ to give the heterobimetallic complex $[Co_2(\mu-PhC_2CN\{Ru(PPh_3)_2Cp\}(CO)_4(dppe))]PF_6$ [13]. However, the $\eta^1-N=CC\equiv CPh$ ligand in $[Ru(N=CC=CPh)(PPh_3)_2Cp]PF_6$ proved to be quite labile, being displaced by both

NCMe and TCNE to give mononuclear $[\text{Ru}(\text{NCMe})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ and binuclear $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-TCNE})][\text{PF}_6]_2$ [13].

Attention was next turned to $\eta^1\text{-C}\equiv\text{CC}\equiv\text{N}$ complexes, $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{N})\text{L}_n]$, which have obvious analogies with both metal cyanide complexes $[\text{M}(\text{C}\equiv\text{N})\text{L}_n]$ and butadiynyl complexes $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{CH})\text{L}_n]$. At the commencement of our studies, preparations of the very few metal cyanoacetylide complexes known involved the use of the rather noxious parent cyanoacetylene, $\text{HC}\equiv\text{CC}\equiv\text{N}$, or trialkyltin derivatives. Gratifyingly, the use of these reagents could be avoided by generating metal acetylide anions from reaction of $[\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}]$ with BuLi [13], or $\text{Fe}(\text{C}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}$ with MeLi [29], followed by treatment with PhOCN to give $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$ and $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}]$, respectively. Alternatively, the use of lithium reagents can be avoided completely and the acetylide complex $[\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*]$ converted smoothly to $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}^*]$ on reaction with 1-cyano-4-dimethyl-amino pyridinium tetrafluoroborate ($[\text{CAP}]\text{BF}_4$) or bromide ($[\text{CAP}]\text{Br}$) (**Scheme 10**) [47]. The reaction proceeds via the intermediate cyanovinylidene $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{CN}\}\{\text{dppe}\}\text{Cp}^*]^+$ which is deprotonated by the dimethylaminopyridine liberated from the $[\text{CAP}]^+$ reagent. Similar reactions have been used to generate a number of cyanovinylidene complexes $[\text{M}\{\text{C}=\text{C}(\text{CN})\text{R}\}(\text{PP})\text{Cp}'^+]$ [82]. Even more conveniently, $[\text{M}\text{C}\equiv\text{CC}\equiv\text{N}](\text{PP})\text{Cp}'$ complexes can be prepared in one-pot reactions from either the vinylidenes $[\text{M}(\text{C}=\text{CH}_2)(\text{PP})\text{Cp}']\text{PF}_6$ with KO^tBu , or $[\text{M}(\text{C}\equiv\text{CR})(\text{PP})\text{Cp}']$ ($\text{R} = \text{H}, \text{SiMe}_3$), and 1-cyano-4-dimethyl-amino pyridinium tetrafluoroborate ($[\text{CAP}]\text{BF}_4$) [94, 105]. In keeping with various studies of extended carbon chains noted above, $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PP})_2\text{Cp}']$ [$\text{Ru}(\text{PP})\text{Cp}' = \text{Ru}(\text{PPh}_3)_2\text{Cp}, \text{Ru}(\text{dppe})\text{Cp}^*$] also reacts exclusively at C(δ) to give the 2,4-pentadiynyl nitrile complexes $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N})(\text{PP})_2\text{Cp}'$ after desilylation in situ [94].



Scheme 10 Schematic of the one-pot preparation of cyanoacetylide complexes [47, 94, 105]

In contrast to the labile coordination of organic cyanoacetylenes, metalcyanoacetylide complexes, $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{N})\text{L}_n]$ proved to be exceptional metalloligands, readily able to coordinate to a wide variety of other metal centres to give stable bimetallic $[\{\text{L}_n\text{M}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{ML}_n\}]^{x+}$ complexes [13, 29]. The well-known capacity of the cyanide ligand to promote electron delocalisation between metal centres prompted consideration of the electronic structures and electron-transfer characteristics of cyanoacetylide bridged complexes. The spectroscopically rich

derivative $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$ was studied using a combination of spectroelectrochemical methods, ps-time-resolved infrared (ps-TRIR) and transient absorption (TA) spectroscopies, and DFT calculations. The HOMO of this species is largely Fe in character, but contains appreciable contributions from the $\pi(\text{C}\equiv\text{CC}\equiv\text{N})$ and $\text{Re}(d)$ orbitals (**Figure 13**). The HOMO-1 is similarly composed and structured, but lies approximately orthogonal to the HOMO. The small $\text{Re}(d)$ contribution is an important feature of the HOMO-1, allowing better orbital overlap with the $\text{bpy}(\pi^*)$ -based LUMO. Consequently the lowest energy excitation of significant intensity (HOMO-1 \rightarrow LUMO) results in a significant transfer of electron density from Fe to bpy, via the delocalised Fe-C \equiv C \equiv N-Re chain. This $\{\text{Fe}^+\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{bpy}^{\cdot-})\}$ charge separated state is clearly evinced by the characteristic shifts in the $\nu(\text{CO})$ band pattern to lower wavenumbers due to an increase in electron density at the $\text{Re}(\text{CO})_3(\text{bpy})$ fragment on photoexcitation at 490 nm [53]. The Re-bpy MLCT charge transfer transition occurs at rather shorter wavelengths. There is efficient back-electron transfer, and the lifetime of the excited state can be estimated to be 30 ± 4 ps from analysis of the TA and ps-TRIR decay.

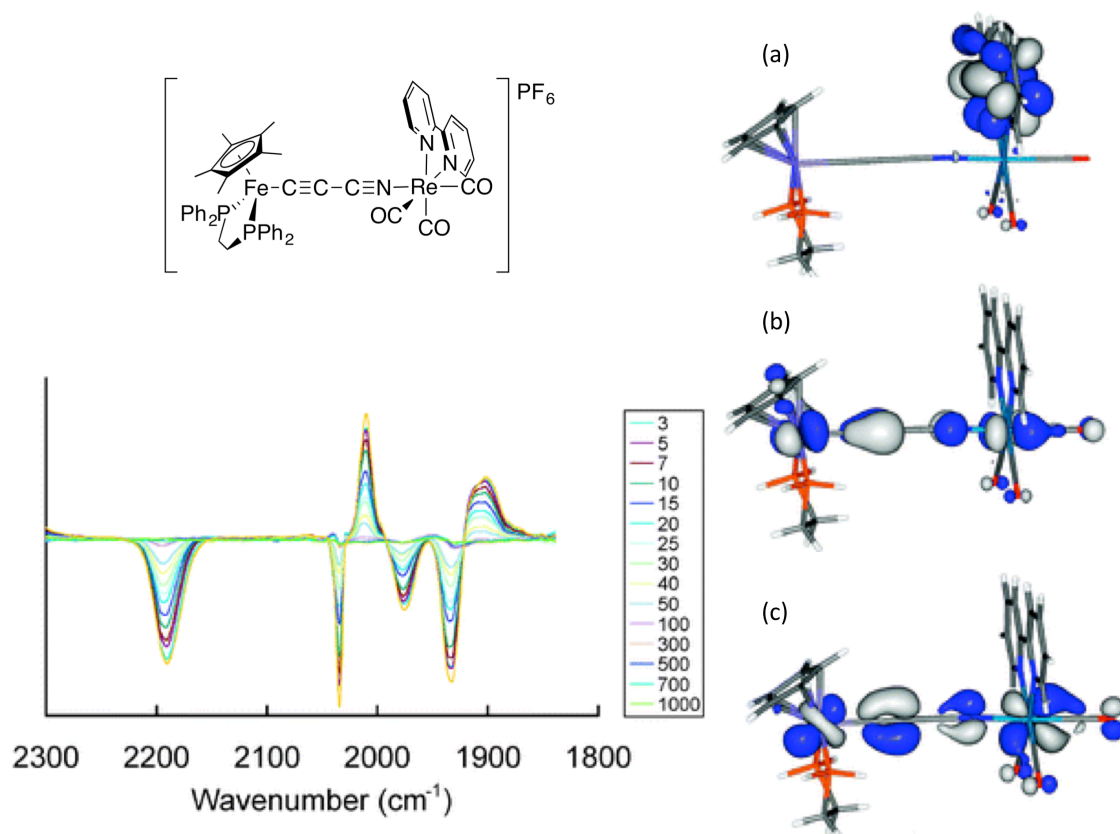


Figure 13 The difference ps-TRIR spectrum of $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$ in CH_2Cl_2 measured after 490 nm excitation. The legend shows the delay times (ps) for each spectral acquisition. Plots of the (a) LUMO (b) HOMO and (c) HOMO-1 are also shown [53].

Further figurative and literal extension of this chemistry to linear trimetallic complexes *trans*-[Fe{N≡CC≡CFe(dppe)Cp}₂(dppx)₂][BF₄]₂ (dppx = dppe, dppm) is achieved through reaction of [Fe(NCMe)₂(dppx)₂]BF₄ with two equivalents of [Fe(C≡CC≡N)(dppe)Cp] [105]. These complexes undergo three, one-electron oxidation processes arising from sequential oxidation of the outer iron-cyanoacetylide moieties and finally the central {Fe(dppe)₂} fragment, the assignments being made on the basis of IR spectroelectrochemical investigations. The formally Fe(II/II/III) mixed-valence tricationic complexes feature two distinct IVCT transitions, one associated with charge transfer from the central 18-electron {Fe(N≡CR)₂(dppx)₂}²⁺ to the terminal {Fe(C≡CR)(dppe)Cp}⁺ moiety, and a lower energy transition involving charge transfer between the terminal Fe fragments separated by the redox active 9-atom, 10-bond -C≡CC≡N{Fe(dppe)₂}N≡CC≡C- bridge (**Figure 14**). Consistent with this assignment, the tetracationic complexes generated by a further stepwise oxidation exhibit a single {Fe(N≡CR)₂(dppx)₂}²⁺-to-{Fe(C≡CR)(dppe)Cp}⁺ IVCT transition.

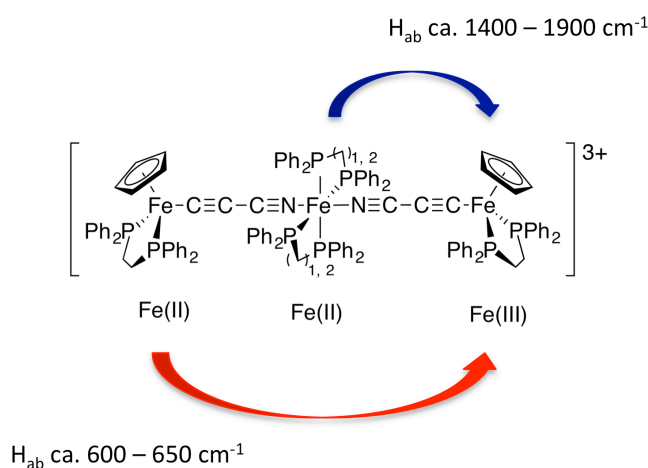


Figure 14 The tris(iron) cyanoacetylide bridged complexes in the Fe(II,II,III) mixed-valence state exhibit two distinct electron transfer processes [105].

The redox non-innocent character of the iron cyanoacetylide metalloligands and ambiguity over the precise charge transfer distance complicates the extraction of coupling information from these metal-to-metal charge transfer bands. Nevertheless, using the metal-metal distances as proxy for the electron transfer distance, spectral parameters derived from Gaussian deconvolution of the IVCT bands can be used within the Hush relationships derived for the two-state case to give coupling parameters H_{ab} in the trications of 610 cm⁻¹ (dppx = dppe) or 665 cm⁻¹ (dppx = dppm) between the external Fe centres linked through the 9-atom, 10-bond -C≡CCN-Fe-N≡CC≡C- bridge. Larger couplings of 1845 cm⁻¹ (dppx = dppe) and 1469 cm⁻¹ (dppx = dppm) are calculated from the centre-to-outer Fe(II)-Fe(III) IVCT bands [105]. Despite the over-estimation of the electron transfer distance, these values compare well with analogous data from the trimetallic, cyanide-bridged complexes such as [(py)₅Ru]-CuN-[Ru(py')₄]-NuC-[Ru(py)₅] (700–800 cm⁻¹, 1100 cm⁻¹).²

² G. E. Pieslinger, P. Albores, L. D. Slep, B. J. Coe, C. J. Timpson and L. M. Baraldo, *Inorg. Chem.*, 2013, **52**, 2906–2917.

The studies summarised here present novel, facile synthetic routes to mono-, di- and trimetallic cyanoacetylide complexes, and illustrate the capacity of the cyanoacetylide ligand to serve as a efficient conduit for electronic effects between metal centres located at the C and N termini in a manner comparable with shorter cyanide ligands, and highlights the great potential of the C≡CC≡N moiety in the assembly of electro-optically active polymetallic structures. A more detailed summary of the mixed-valence characteristics and assignments of UV-vis-NIR and IR spectra of open shell, 35-electron $[\{\text{Cp}'(\text{PP})\text{M}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{M}(\text{PP})\text{Cp}'\}]^{2+}$ (M, M' = Fe, Ru) is given below.

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Cross-conjugated carbon-rich ligands and compounds

In addition to studies of metal complexes of linear carbon fragments, a line of investigation concerning the preparation of branched or cross-conjugated carbon-rich molecules and metal complexes incorporating these unusual species and fragments as ligands has been conducted. Cross-conjugated systems can be defined as those systems containing three unsaturated systems linked through a common atom in which any two are conjugated with each other, but not the third. The molecular structure of 1,1-diethynylethenes serves as a simple illustrative example. Cross-conjugated structures have attracted attention as the HOMO and LUMO can be selectively and independently localised along different linearly conjugated paths across the molecular backbone, or delocalised over the entire structure. This in turn allows control over the both the HOMO-LUMO gap and potentially the singlet-triplet energy gap, which can lead to designs for materials with useful thermally activated delayed fluorescence (TADF) behaviour. Cross-conjugated systems are also attracting attention as scaffolds through which to explore quantum interference effects in molecular electronics.

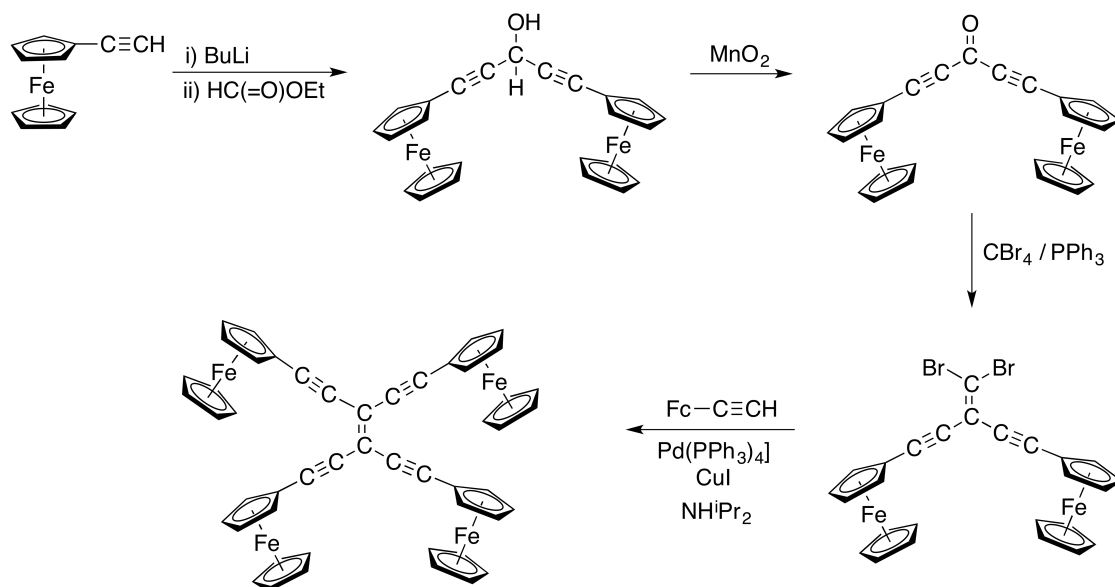
This section summarises work directed to the synthesis of cross-conjugated systems, the use of such compounds as ligands in organometallic chemistry and the reactivity profiles of the resulting complexes. A combination of electrochemical measurements, spectroelectrochemical studies and calculations of electronic structure have been used to explore the accessible charge transfer pathways through these systems as part of larger bodies of work concerning the descriptions of electronic structures of mixed-valence complexes and the development of molecular scaffolds with unusual electronic properties for use in molecular electronic systems.

Our initial forays into molecular systems with cross-conjugated architectures were drawn from our studies of mixed-valence complexes, and inspired by an interest in how three or more electrophores or chromophores might interact through a common bridging ligand. We were pleased to find that a number of terminal alkynes bearing less-electron donating groups ($\text{HC}\equiv\text{CSiMe}_3$, $\text{HC}\equiv\text{CPh}$, $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-CN}$) smoothly cross-coupled ($\text{Pd}(\text{PPh}_3)_4$ / CuI / NEt_3) with tetrachloroethene to give tetraethynylethenes in 30 – 60% yield [9], which compare most favourably with the ca. 25% overall yield from multistep routes developed by Diederich.³ The tetrakis(trimethylsilyl) tetraethynylethene proved to be a convenient reagent for the preparation of metal complexes through coordination of metal carbonyl clusters to the alkyne π -systems [9, 37], desilylation and auration to give the tetra(gold) complex $\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_2\text{C}=\text{C}\{\text{C}\equiv\text{CAu}(\text{PPh}_3)\}_2$ and subsequent gold-mediated cross-coupling reactions [37].

Although the direct coupling of more electron-rich alkynes, including ethynylferrocene, with tetrachloroethene did not proceed smoothly, tetraferrocenylolethene could be prepared from the sequence of reactions shown in **Scheme 11** [148]. Whilst the sequential oxidation of the ferrocene moieties could not be resolved in 0.1M $[\text{NBu}_4]\text{PF}_6$ (CH_2Cl_2) solution, in an electrolyte solution containing the weakly coordinating anion $[\text{B}(\text{C}_6\text{H}_3\text{-3,5}-(\text{CF}_3)_2)]$ ($[\text{BAr}^{\text{F}}_4]^-$) anion the ferrocenyl

³ J. Anthony, A.M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C.B. Knobler, P. Seiler, D. Diederich, *Helv. Chim. Acta*, 1995, **78**, 13 – 45.

redox waves were resolved with a consistent $\Delta E_{1/2}$ ca. 70 mV. This indicates an appreciable ‘through-space’, but more limited through-bond, electronic interactions between the ferrocene moieties.⁴ This conclusion was further supported by IR spectroelectrochemical studies and DFT based calculations of electronic structure [148].

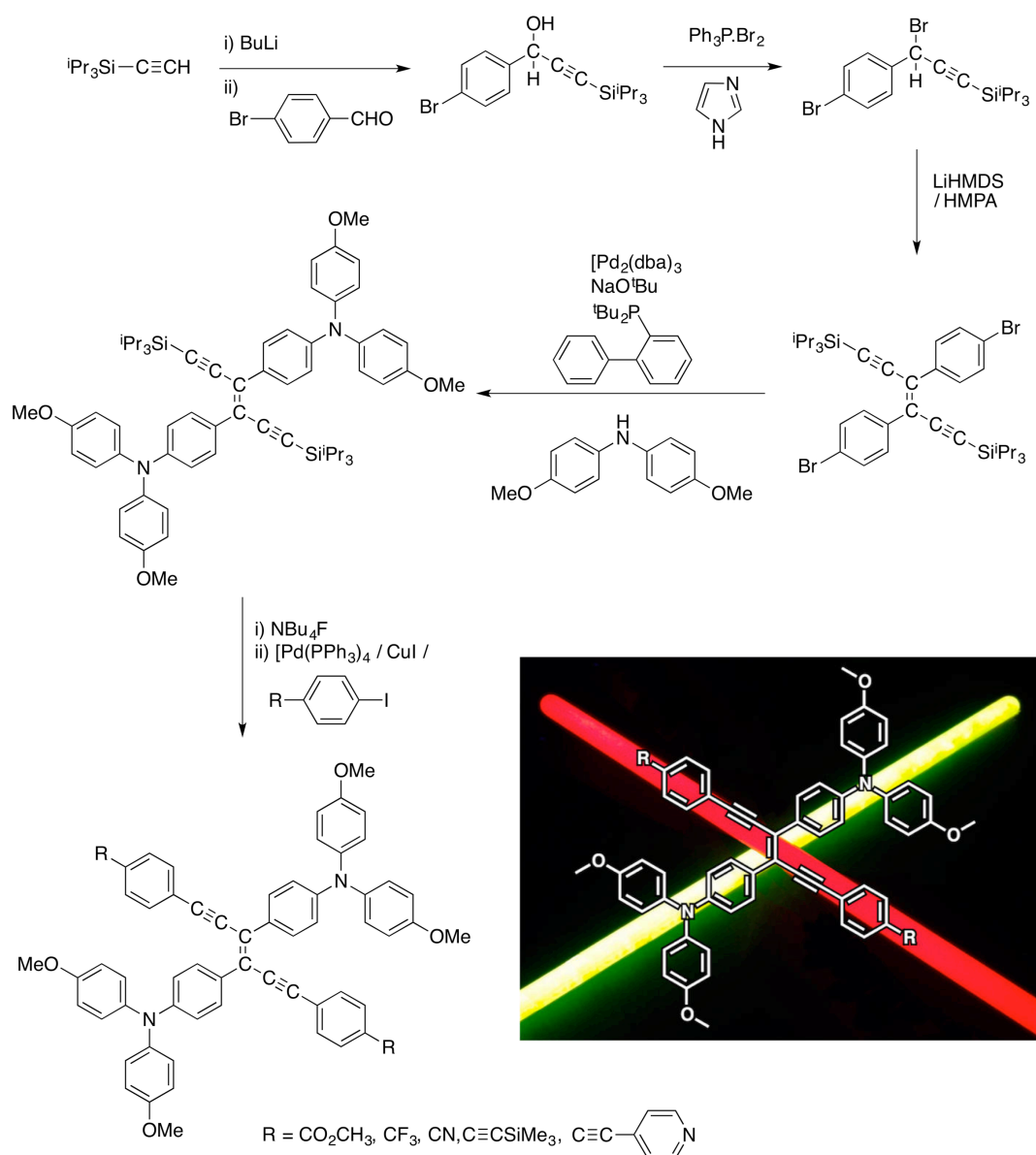


Scheme 11 The preparation of tetraferrocenylethene [148].

More highly functional tetra-substituted ethenes bearing a wider range of donor/acceptor groups were prepared by dimerisation of propargyl bromides using a LiHMDS-HMPA-mediated carbenoid coupling-elimination strategy (**Scheme 12**) [130]. The use of the triisopropylsilyl moiety allowed better regiocontrol of the dimerisation reaction, with the *E*-configured triisopropylsilyl-substituted hexa-3-ene-1,5-diyne backbone being obtained in good (56%) yield. The ability to introduce both an arylbromide and a protected alkyne makes this an excellent strategy for the further construction of cross-conjugated hexa-3-ene-3,4-diaryl-1,5-diynes. Hartwig-Buchwald coupling with diaryl amines was used to install electron donating and redox-active triarylamine groups to the molecular backbone, and subsequent fluoride-induced desilylation exposed the terminal alkyne for further elaboration through Sonogashira cross-couplings with a variety of aryl iodides (**Scheme 12**). The cross-conjugated π -system proved to allow unusual interactions between the donor triarylamine groups and the acceptor substituents on the alkynes. The optical spectra of these cross-conjugated species contained low energy (434 – 494 nm) transitions of significant intensity ($\epsilon = 10,000 - 30,000 \text{ M}^{-1} \text{ cm}^{-1}$) arising from charge transfer from the diarylaminostilbene-like HOMO to the hexa-3-ene-1,5-diyne LUMO. At cryogenic temperatures where thermal motion is suppressed the compounds become significantly fluorescent with emission from the CT state. The introduction of the electron-withdrawing groups to the bis(diarylamine) substituted stilbene backbone decreases the ground-state electronic

⁴ F. Barriere, W.E. Geiger, *J. Am. Chem. Soc.* 2006, **128**, 3980 - 3989

coupling between the amine electrophores, and the one-electron oxidation products are characterised as Class II mixed-valence compounds, with rather symmetrically shaped, solvatochromic IVCT bands. Infra-red spectroelectrochemical studies using the $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})$ bands as markers indicated that redox state changes in the bis(amino)stilbene moiety affect the entire cross-conjugated molecular backbone [130]. This finding confirmed our initial thoughts that the electronic characteristics of the wire-like *E*-hexa-3-en-1,5-diyne moiety should be sensitive to the oxidation state of the pendant triarylamine moieties, and opens further design strategies for multi-mode switchable components in molecular electronics based on these motifs.



Scheme 12 The preparation of luminescent cross-conjugated hexa-3-ene-3,4-diaryl-1,5-diynes using a sequence of carbenoid, Hartwig-Buchwald and Sonogashira coupling reactions. The inset illustrates the fluorescence of the triisopropylsilyl protected precursor and the R = CN derivative [130].

Returning to organometallic derivatives, although desilylation-metallation reactions of $[\text{RuCl}(\text{PP})\text{Cp}']$ with $(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{C}=\text{O}$ were unsuccessful, the direct reaction of $[\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*]$ with one-half equivalent of oxalyldichloride $[\text{ClC}(=\text{O})\text{C}(=\text{O})\text{Cl}]$ gave the bis(metalla-ethynyl)ketone, $[\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}_2\text{C}=\text{O}]$ in good (72%) yield [97]. The carbonyl moiety in the cross-conjugated diethynyl ketone ligand could be converted via a Knoevenagel condensation to give a 1,1-dicyano-2,2-diethynyl cross-conjugated bridge. Related compounds were also obtained from $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{CN})=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*]$ via nucleophilic displacement of the cyano moiety *gem* to the metal centre on reaction with the lithiated derivative obtained from $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*]$ / BuLi. Although a sequence of two oxidation and one reduction processes that were reversible on the electrochemical timescale were observed by cyclic voltammetry for the complexes $[\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{C}(=\text{E})\{\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}^*\}]$ [$\Delta E_{1/2}(\text{ox}) = 0.20$ V ($\text{E} = \text{O}$), 0.30 V ($\text{E} = \text{C}(\text{CN})_2$)] indicating appreciable thermodynamic stability of the one-electron oxidation state, the redox products proved unstable on the longer timescale of spectroelectrochemical experiments. DFT calculations with a series of model structures revealed the sensitivity of the composition of the HOMO to the electron donating or withdrawing nature of substituents on the methylene moiety, with more electron-donating groups increasing the electron density at $\text{C}(\gamma)$, and in principle increasing the degree of electronic interactions between the metal centres.

These synthetic studies, combined with a proposal from Grozema describing a chemically gated quantum-interference-based molecular transistor architecture based on a donor-acceptor substituted 1,1-diethynylethene (**Figure 15**)⁵ prompted a further investigation of related species. In particular we targeted derivatives featuring electron-donating and redox-switchable pendants to the 1,1-diethynylethene core in the search for systems that could display redox-switchable quantum interference effects, and hence ‘gate’ the electronic interactions between remote molecular sites analogous to the ‘source’ and ‘drain’ of a conventional transistor architecture.

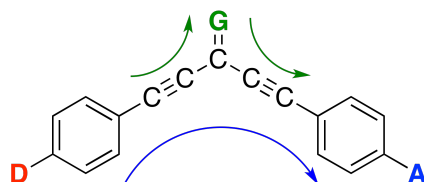
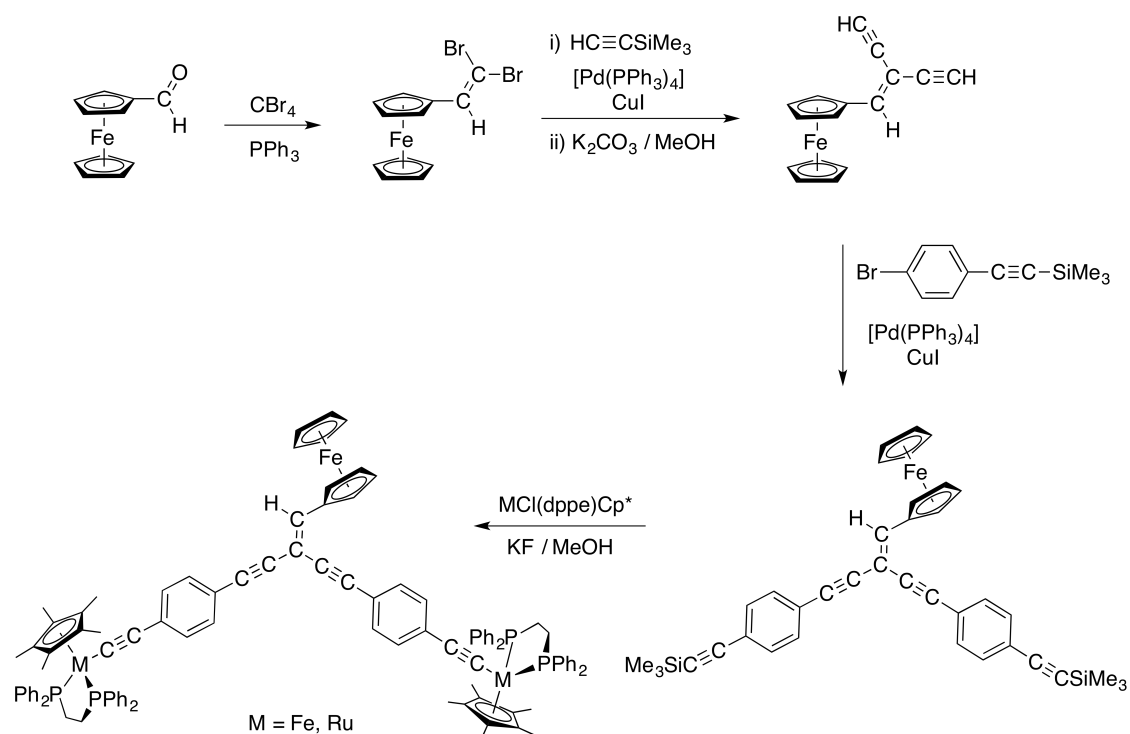


Figure 15 A schematic of the Grozema gate quantum interference transistor. The coupling of the donor (D) to the acceptor (A) through the cross-conjugated bridge is weak due to destructive quantum interference (DQI). The introduction of a charge (e.g. by protonation in the original proposal⁵ or oxidation of a pendent ferrocene moiety described in our work [101]) changes the energy of the pendent gate group (G), and the side chain, reducing the DQI and more effectively coupling D and A.

⁵ A.A. Kocherzhenko, L.D.A. Siebbeles, F.C. Grozema, *J. Phys. Chem. Lett.*, 2011, **2**, 1753 – 1756.

A general synthetic route to such systems with a ferrocene pendant was developed [101], building on earlier studies of multiferrocene derivatives [148] and extended to complexes $[\text{FcCH}=\text{C}\{1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CM}(\text{dppe})\text{Cp}^*\}_2]$ (Fc = ferrocenyl; M = Fe, Ru) (**Scheme 13**) [162]. Although the half-sandwich fragments underwent sequential oxidation before the pendant ferrocene gate, the extended, trimetallic complexes provided rare opportunities to explore the electronic differences and characteristics of putative mixed-valence complexes derived from the half-sandwich $\{\text{M}(\text{dppe})\text{Cp}^*\}$ moieties, through a cross-conjugated bridging ligand.



Scheme 13 The preparation of bimetallic cross-conjugated complexes bearing a redox-active ferrocene pendant group.

In the case of the ruthenium species (**Scheme 13**), the mixed-valence mono-cation obtained by one-electron oxidation could be detected by UV-vis-NIR and IR spectroelectrochemistry in a comproportionated mixture, leading to a description in terms of a polarized, but still rather extensively delocalized, system with substantial spin density over the bridging ligand framework. Electron-exchange between the ruthenium complex ‘branches’ is fast on the timescale of EPR spectroscopy, with spectra also confirming significant contributions from the carbon chain and organic-like singlet character in this monocation. In contrast, the iron complex gives rise to much more metal localized redox behaviour. Apparently the more limited delocalization into the carbon-rich bridging ligand lowers the thermodynamic stability of the mixed-valence iron complex, which cannot be detected spectroscopically using the methods available here. The results here support the notion that 3d orbitals of metals such as Fe, which are exceptionally compact due to the lack of a radial node, undergo limited d- π mixing, in turn promoting localized behaviour in mixed-valence

complexes featuring carbon- rich bridging ligands. In contrast, analogues formed with heavier metals such as Ru, which offer 4d orbitals mix more extensively with the ligand π system, give more bridge-based character [162]. These findings are in line with those made from studies of iron and ruthenium complexes bridged by linearly conjugated ligands and form a basis for much of the interpretation of the mixed-valence characteristics of these species discussed elsewhere in this Thesis.

In summary, a suite of convenient synthetic routes that permit access to cross-conjugated organic compounds and organometallic complexes have been developed. The electronic structure and distribution of electron density along the molecular backbone has been shown to be sensitive to the donor / acceptor character of the substituents. In this manner, it is possible to design systems, which vary in electronic character from strongly localised to quite delocalised. The potential for this character to be tuned through redox processes of the substituents hints at possible roles for such systems in designs of molecular electronic components.

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Further aspects of electron transfer processes and mixed-valence chemistry: within and beyond the Marcus-Hush model

Mixed-valence compounds can be most simply defined as those that contain an element in more than one formal oxidation state. Classical examples of mixed-valence species include the framework material Prussian Blue $[\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}]$ and the molecular Creutz-Taube ion $[\{(\text{NH}_3)_5\text{Ru}\}(\mu\text{-pz})\{\text{Ru}(\text{NH}_3)_5\}]^{5+}$. Mixed-valence compounds typically feature a characteristic intervalence charge transfer (IVCT) transition that arises from photo-induced electron transfer between the reduced and oxidised sites as well as a ground state pathway for thermal electron transfer. Mixed-valence compounds are therefore ideal species with which to explore intramolecular electron-transfer processes, and consequently have attracted attention for many decades. Whilst many theoretical approaches have been developed to describe the electronic structures of mixed valence compounds, and provide interpretation and assignment of their spectroscopic features, these are largely all drawn from the seminal works of Rudolph Marcus and Noel Hush.

Marcus-Hush theory describes the inner-sphere electron transfer reaction taking place in a mixed-valence complex $[\text{M}]\text{-bridge-}[\text{M}]^+$ in terms of two unlike point charges separated by a distance, d . Importantly, Hush's work showed how experimentally observable parameters from the shape of the IVCT band could be related to the underlying electronic coupling term, H_{AB} , linking the two sites. Whilst variations of Marcus-Hush theory have been developed that include descriptions of the effects of vibronic coupling on the electron-transfer reaction (PKS theory) and extensions to include explicit bridge states in the electron-transfer process (three-state models), the two-state Marcus-Hush theory remains the workhorse model for the interpretation of a very wide variety of mixed-valence compounds, due in no small measure to the simplicity of its application. The analytical expressions derived from Marcus-Hush approaches have immense value in the extraction of electronic information from systems that conform well to the approximations on which the theory is based (i.e. exhibit electron transfer between two well-defined minima along a well-defined reaction coordinate) and for which the IVCT band can be correctly identified and its band-shape accurately observed.

It is important to recognise from the outset the terminology used in this field, such as "intervalence charge transfer", was developed from studies of classical mixed-valence coordination complexes, $[\{L_n\text{M}\}(\mu\text{-bridge})\{\text{ML}_n\}]^{+/-}$. Much of the language presupposes metal-centred redox processes and assignment of well-defined metal d -electron counts. However, as described in more detail below, in many cases the metal, supporting and bridging ligand orbitals are extensively mixed, and arguably makes such terms less appropriate. The combination of computational methods that satisfactorily model the electronic structures of complexes that fall across the continuum from localized to delocalised cases, verified by agreement of calculated parameters with readily accessible spectroscopic information, including IR data, may be used to provide an alternative, molecular orbital basis for discussion. However, the conventional lexicon will be employed in the discussions below, where appropriate for clarity or brevity.

Our interests in the determination of the electronic structure of molecules using a combination of spectroelectrochemical methods and density functional theory has

driven, and in turn largely been driven by, studies of mixed-valence complexes. In many ‘real’ systems, the application of Hush-style expressions is complicated by the challenges of correctly assigning the nature and composition of the electrophore, the determination of the electron-transfer distance using readily available methods, the challenges of observing and correctly identifying the IVCT band which is often weak in intensity (in weakly coupled systems) and of low energy (extending into the IR region) and overlapped by other electronic transitions and the distribution of molecular geometry. The situation is further complicated by the fact that many molecular systems are not well described in terms of a single (lowest energy) geometry, but rather exist in fluid solution as an ensemble of molecular conformers. These conformers can have quite distinct electronic structures, preventing accurate descriptions in terms of a single electronic coupling parameter.

Our efforts to explore the electronic structures and describe the charge transfer character of mixed-valence complexes using a combination of UV-vis-NIR and IR spectroelectrochemical measurements and various DFT-based computational methods as alternative to the classical Hush-based methods of analysis are described in the summary below. The examples chosen range from systems with strongly localised electronic structures (weakly-coupled Class II mixed-valence systems) to those with substantial delocalised structures (strongly coupled Class III ‘mixed-valence’ systems), and those in which the bridging ligand plays a significant role in the redox properties of the assembly. A particular point of note is the use of hybrid- and local-hybrid DFT functionals and conformational minima sampled from across the potential energy hypersurface to arrive at a more complete model of the real system in solution.

Infra-red spectroelectrochemistry allows convenient access to a body of data related to the molecular structures of members in a redox series, which for the purposes of this initial discussion can be considered as $[\{L_nM\}(\mu\text{-bridge})\{ML_n\}]^{x+}$. In comparison with the rather broad nature of electronic transitions in solution, IR spectra are much better resolved, with narrower bands falling in characteristic frequency ranges for each functional group. These IR data can give direct insight into the underlying electronic character of individual compounds, at least on the relatively fast IR timescale (ca. 10^{-13} s), and becomes especially powerful when redox active modes on the bridging ligands (typically $\nu(\text{C}\equiv\text{C})$ or $\nu(\text{C}=\text{C})$ modes in our work) are combined with additional vibrational reporters on the metal fragments (e.g. $\nu(\text{CO})$) [87]. In addition to giving information concerning the symmetry of the molecular framework in each redox state (i.e. localisation or delocalisation on the IR timescale), the various $\nu(\text{C}\equiv\text{C})$, $\nu(\text{C}=\text{C})$, $\nu(\text{CO})$ etc. bands also contain information about the site of the redox process as these modes are sensitive to the local electron density. The data from IR spectroelectrochemistry can be further used to verify the geometry models obtained from DFT optimisations, through comparison with results from frequency calculations, corrected for anharmonicity as appropriate to the functional employed. With a satisfactory computational model in hand, TD DFT calculations using an appropriate hybrid, range-separated or local hybrid density functional can be used to assign and explore further detail of the less well-resolved electronic transitions with emphasis typically being directed towards the low-energy IVCT-type processes. These approaches have been used together with various metal and organic electrophores and conjugated bridging ligands to establish structure-property relationships in mixed-valence compounds and protocols for the investigation of the optoelectronic properties of these fascinating systems.

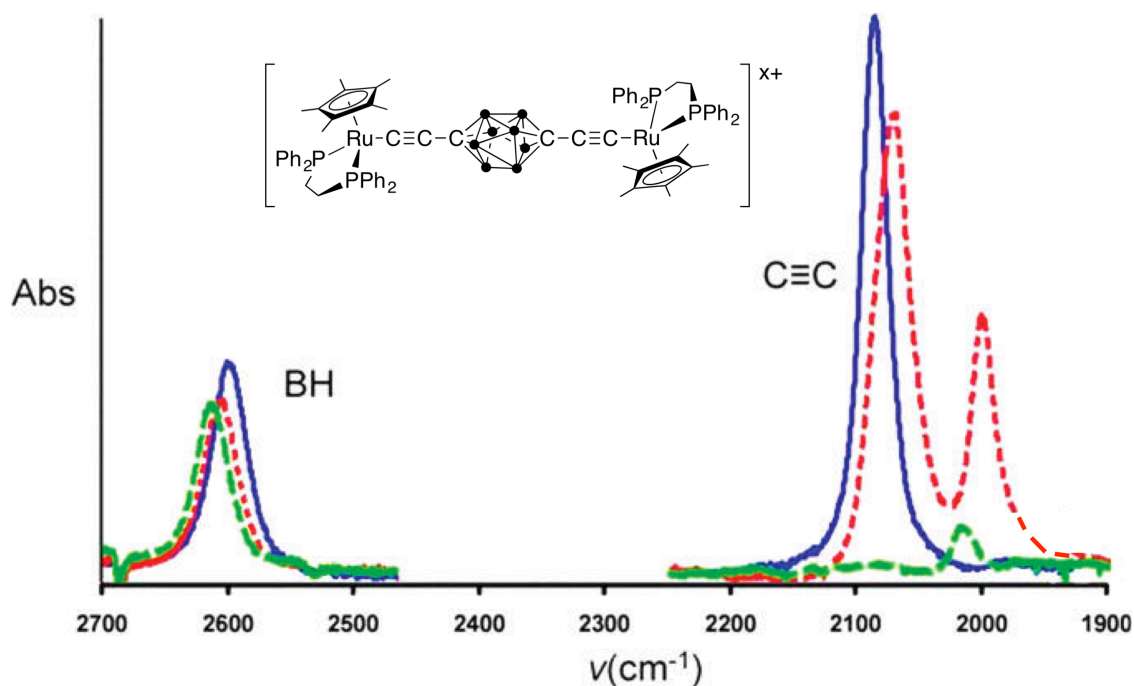


Figure 16 The IR spectra of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_8\text{H}_8\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})\text{Cp}^*\}]^{x+}$ ($x = 0$ (blue), 1 (red), 2 (green)). The two $\nu(\text{C}\equiv\text{C})$ bands in the mixed-valence ($x = 1$) complex clearly indicate an electronic structure that is localised on the IR timescale [50].

The development of a facile route to *para*-*C,C*-bis(ethynyl)carboranes which offer a degree of ‘three-dimensional’ aromaticity around the carborane cluster scaffold (*vide supra*) allowed the preparation of bimetallic complexes $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_n\text{H}_n\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})\text{Cp}^*\}]$ ($n = 8, 10$) [50] and $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_{10}\text{C}\equiv\text{C})\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}]$ [72]. These systems are almost ideally suited to analysis using Hush-based approaches with weak coupling, well defined electrophores and a small, but tuneable, mixing of the metal *d*-orbitals and the bridge π -system. Infra-red spectroelectrochemical investigations clearly established the localised electronic structures of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_n\text{H}_n\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})\text{Cp}^*\}]^+$ (**Figure 16**) and $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_{10}\text{C}\equiv\text{C})\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}]^+$, whilst NIR spectroelectrochemical measurements gave convoluted IVCT band envelopes (**Figure 17**, **Figure 18**).

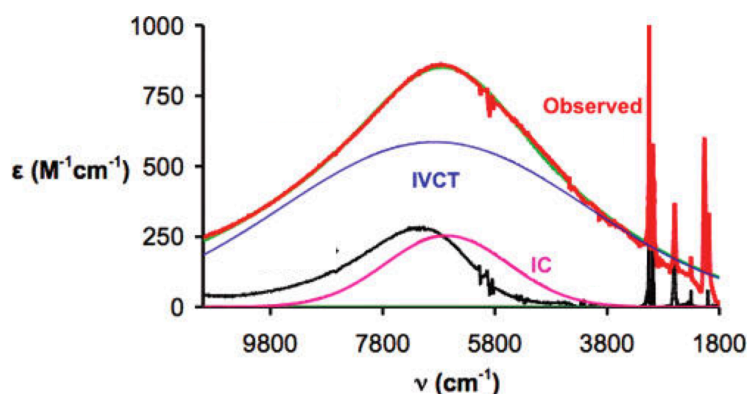


Figure 17 The NIR spectrum of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_8\text{H}_8\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})\text{Cp}^*\}]^+$ (red) and deconvolution into the IVCT (blue) and IC (pink) components. The IC band of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_8\text{H}_8\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})\text{Cp}^*\}]^{2+}$ (black) is shown for reference and to assist in assignment [50].

In the case of the Ru systems, a Gaussian shaped IVCT band could be readily deconvoluted from an interconfigurational (dd) transition and conformed with reasonable precision to the predictions of the two-state model, giving expected low coupling constants [$H_{AB} = 260 \text{ cm}^{-1}$ ($n = 8$), 140 cm^{-1} ($n = 10$)]. For the Mo based system with the larger symmetry induced splitting of the d -orbital manifold, the low energy electronic absorption region was more complex, with all three possible IVCT and two dd transitions expected from a *pseudo*-octahedral d^5 - d^6 mixed valence complex⁶ observed following spectral deconvolution (Figure 18).

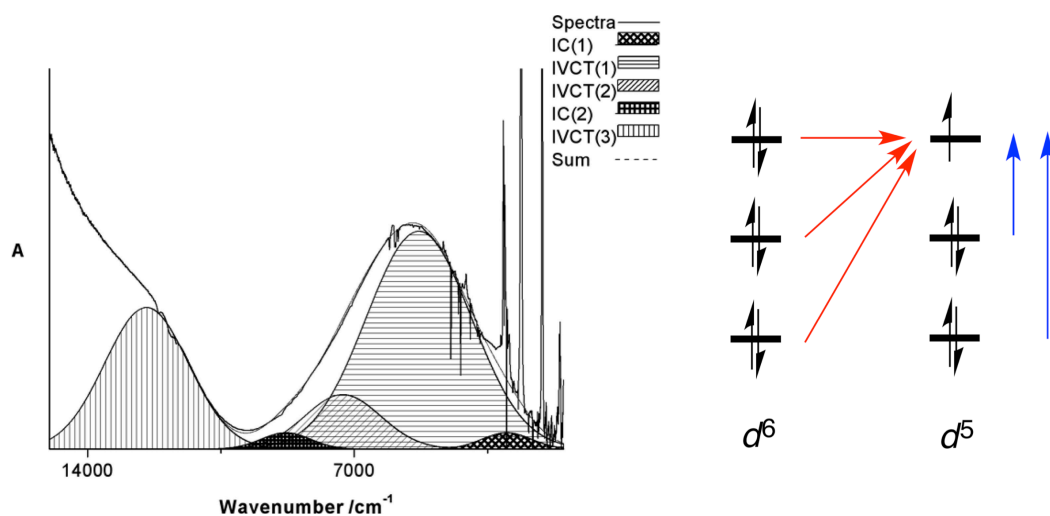


Figure 18 The NIR spectrum of $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}(\mu\text{-C}\equiv\text{CC}_2\text{B}_{10}\text{C}\equiv\text{C})\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}]^+$ showing the deconvolution into the three IVCT (schematic, red) and two interconfigurational (IC) transitions (schematic, blue) [72].

The observation and resolution of the three IVCT bands allowed the some early constrained DFT approaches to explore the character, composition and distribution of the principal orbitals responsible for each transition. The lowest energy IVCT transition arises from electron exchange between the d_{z^2} -type MOs at each Mo centre

⁶ K.D. Demadis, C.M. Hartshorn, T.J. Meyer, *Chem. Rev.*, 2001, **101**, 2655 – 2685.

has a band-shape in excellent agreement with the predictions of the two-state model. The higher energy IVCT transitions involve lower-lying orbitals that are more extensively mixed with the ethynyl π -system. As with the Ru analogues, the band shape of these higher-energy IVCT bands arising are in less good agreement with the Hush model due to the breakdown of the two-state approximation through the greater involvement of the bridge-based orbitals in those transitions. These works illustrate the strengths and limitations of the two-state model and motivate further efforts to develop alternative methods of analysis of mixed-valence complexes.

A broad range of mixed-valence molecular systems have been explored using similar strategies. For examples, studies of systems with well-defined ferrocene / ferricenium redox markers bridged by a chalcogenophene and silole moieties [96, 102, 107, 126] have established the dominant role of the *trans-cis-cis-trans*-diene in the electron transfer pathway, leading to the identification of such systems as relatively accessible polyacetylene models [153]. Whilst radical cations have been the principal research vehicle, mixed-valence radical anions are also accessible, drawing on our interests in boron-containing species allowing stabilisation of the pyrene radical anion by B(mes)₂ fragments [122]. Compounds with well-defined localised electronic character in which the bridge plays an important role in stabilising the unpaired electron / hole, such as 1,3-diethynylbenzene [60], or is better described as an insulating spacer, such as *trans*-Pt(PR₃)₂ [104, 114] and 1,1'-ferrocenediyl [22], provide further important benchmark data that help to 'fingerprint' the spectroscopic characteristics of 'mixed-valence' complexes from localised to delocalised examples, and those that are better thought of in terms of the redox properties of the bridge.

Alternatively, one can design models that explore the limits of the two-state model at the delocalised extreme. The Mo₂-Mo₂ dimer-of-dimer systems [Mo₂(DAniF)₃](μ -E₂CCE₂)[Mo₂(DAniF)₃] (DAniF = N,N'-di(p-anisyl)-formamidinate; E₂ = OO, OS, SS) offer a unique electronic structure in which the δ -orbital of the quadruply bonded Mo₂ moieties is non-degenerate with the other σ - and π -type metal and ancillary ligand orbitals and creates something of a 'super atom' with fragment frontier orbitals that can only mix with the π -orbitals of the oxalate-derived bridge (**Figure 19**) [156]. The electron delocalization between the Mo₂ cores increases with increasing number of soft sulfur atoms, E, in the bridge, and the well-resolved and well-separated metal-to-ligand (MLCT) and IVCT absorption bands that result also permit accurate observation of the band shape. The electronic coupling matrix elements (H_{ab}) estimated from the IVCT transition energy within the two-state model ($H_{ab} = 2000\text{--}2500\text{ cm}^{-1}$) are in excellent agreement with results from the Hush-like expressions modified for Class III systems ($2400\text{--}3000\text{ cm}^{-1}$),⁷ and place the oxalate-bridged complex (E₂ = O₂) on the Class II–III borderline, whilst the two thiolated species (E = OS, SS) are lie deep into Class III. However, in contrast to the predictions from the two-state model, the IVCT band becomes more symmetric in shape as the electronic coupling constant increases beyond the Class III border, $2H_{ab}/\lambda \gg 1$ (**Figure 19**). Therefore, the very strongly coupled E₂ = OS and SS based systems behave more like molecular radicals, rather than a 'strongly coupled' system in the framework of the two-state model. This study illustrates the first observation of a systematic transition from a strongly coupled MV complex near the Class II–III border (E₂ = O₂), through Class III, and to systems in

⁷ B.S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.*, 2002, **31**, 168- 184.

which the underlying ground state is better described in terms of simple delocalized electronic states ($E_2 = \text{OS}, \text{SS}$) rather evolving from strongly coupled diabatic states which define Class III.

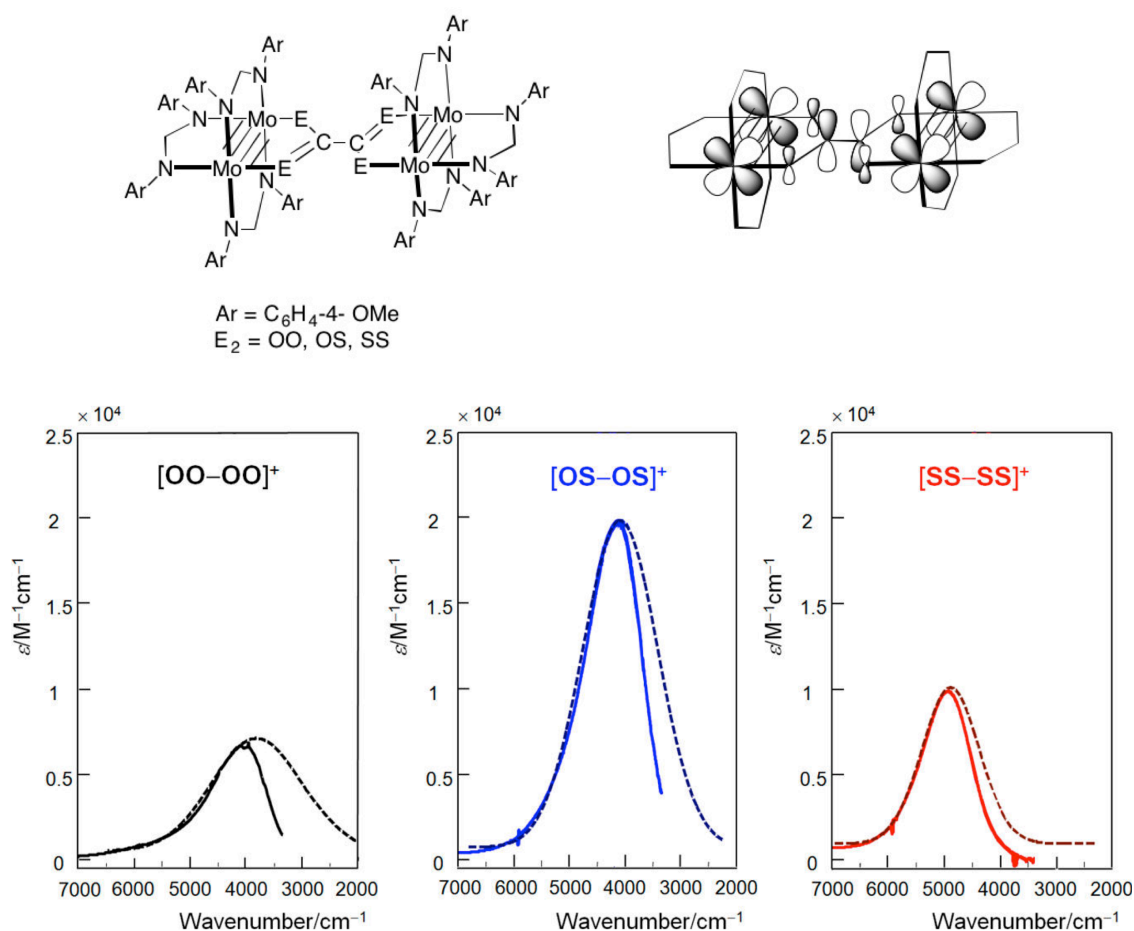
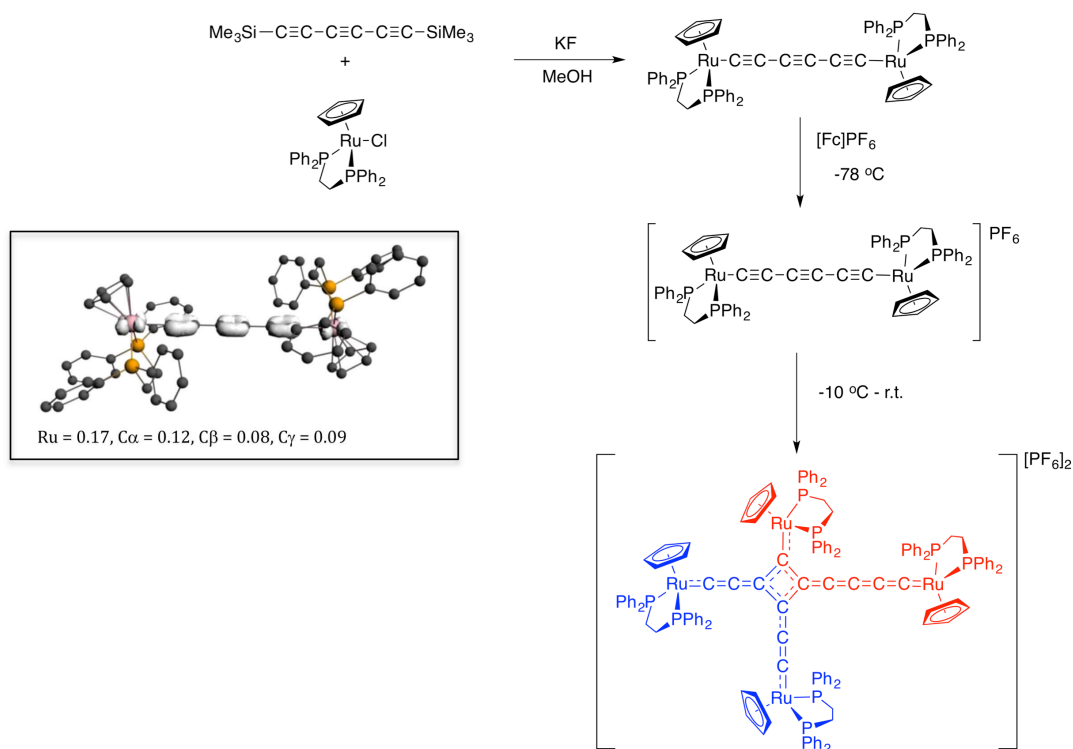


Figure 19 The Mo₂-Mo₂ dimers-of-dimers [Mo₂(DAniF)₃](μ-E₂CCE₂)[Mo₂(DAniF)₃] (DAniF = N,N'-di(p-anisyl)-formamidinate; E₂ = OO, OS, SS), a representation of the HOMO and the NIR spectra of the resulting one-electron oxidised products illustrating the change in band shape of the IVCT (or charge resonance) transition with increasing coupling [156].

The compounds and complexes described above illustrate the extremes of weakly coupled (Class II), strongly coupled (Class III) and 'fully delocalised'. Complementing these works are studies of compounds derived from one-electron oxidation of bimetallic complexes featuring {Mo(dppe)(η-C₇H₇)} and {M(PP)Cp'} [Fe(dppe)Cp, Fe(dppe)Cp*, Ru(PPh₃)₂Cp, Ru(dppe)Cp, Ru(dppe)Cp*] moieties linked by (poly)ynediyl, -(C≡C)_n-, and diethynylarylene, -C≡C-Ar-C≡C-, bridges. These have proven fertile ground for explorations of the 'mixed-valence' landscape, especially systems that do not conform well to the two-state model or derivatives. This work has led to new understanding of the significance of molecular conformation as well as composition, and provided new methods for the analysis of the spectroscopic properties and electronic structures of mixed valence complexes.



Scheme 14 The synthesis, oxidation and dimerisation of $[\{Cp(dppe)Ru\}(\mu-C\equiv CC\equiv CC\equiv C)\{Ru(dppe)Cp\}]$. The inset shows the calculated spin-density distribution in the one-electron oxidation product [98].

To the simplest approximation, and most general description, for bimetallic complexes with acetylide-based bridging ligands, the poor symmetry match of the d_{z^2} -like frontier orbital of the $\{Mo(dppe)(\eta-C_7H_7)\}$ fragment with the $C\equiv C$ π -system ensures that mixed-valence complexes derived from this metal fragment and ethynyl-based bridging ligands will be examples of weakly-coupled mixed-valence systems [81], whilst the better symmetry and energy match of the d_{xz} and d_{yz} based frontier fragment orbitals of $\{Ru(PP)Cp'\}$ [B16, 12] and $\{Os(dppe)Cp^*\}$ [43] systems with the $C\equiv C$ π -system leads to extensively delocalised systems in which an appreciable portion of the spin-density is supported on the bridge. Indeed, inspection of the low energy electronic transitions in the group 8 radical cations $[\{Cp(dppe)M\}(\mu-C\equiv C)\{M(dppe)Cp'\}]^+$ and supporting (TD-)DFT calculations reveal these systems to also be examples better described as molecular radicals with $(d-\pi-d)^1$ electronic character and extensive carbon-character in the SOMO [42]. Whilst the steric protection offered by the metal-ancillary ligand sphere stabilises the carbon-chain bridging ligand in these C_2 [42] and analogous C_4 [12] mixed-valence examples, the more exposed carbon atoms in the C_6 -bridged analogue $[\{Cp(dppe)Ru\}(\mu-C\equiv CC\equiv CC\equiv C)\{Ru(dppe)Cp'\}]^+$ undergoes rapid intermolecular dimerisation above -10 °C, with the formation of new C-C bonds between $[C(\alpha)-C(\beta)]$ and $[C(\gamma)-C(\delta)']$ [98], clearly evincing the distribution of radical character over the carbon-chain (**Scheme 14**). The high regiochemistry of the coupling is driven by competition between the high spin density at $C(\alpha)$ and $C(\beta)$, and the steric congestion at these sites brought about by the ancillary ligands. In the case of heterometallic systems such as $[\{Cp^*(dppe)Fe\}(\mu-C\equiv CC\equiv C)\{Ru(PP)Cp'\}]^+$ the ground state electronic structure is rather polarised towards and Fe(III)/Ru(II) structure

as would be expected based on the nature of the two metal fragments, [25] strongly contrasting with the ‘delocalised’ electronic structures of the homobimetallic Ru derivatives. As will be discussed below, this observation together with the reassignment of the electronic structure of the homobimetallic iron derivatives to localised systems finally creates consistency in the structure-property relationships in all-carbon-bridged bimetallic complexes.

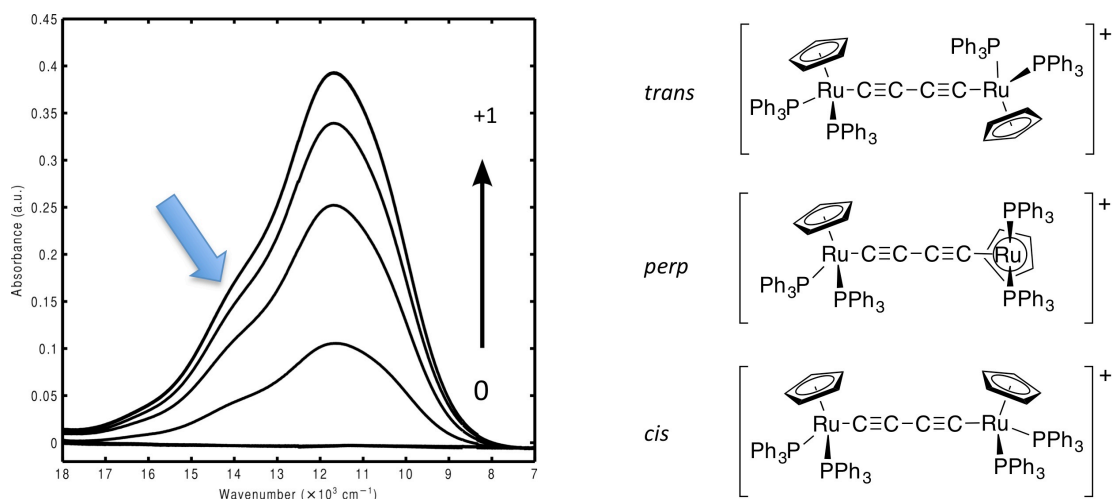


Figure 20 The NIR spectrum of $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$ recorded during oxidation of the neutral parent in a spectroelectrochemical cell. The large blue arrow indicates the high energy shoulder arising from MLCT transitions in the *perp*-conformers. The principal *trans*, *perp* and *cis* conformers are also illustrated [100].

Closer inspection of the IVCT (or charge resonance) band and the $\nu(\text{C}\equiv\text{C})$ bands in the IR spectra of the delocalised radical cation $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$ revealed a more complex NIR band-shape than would be expected based predictions of the two- or three-state models and DFT calculations using the global minimum structure, with a high-energy shoulder clearly apparent (**Figure 20**) [100]. The crystallographic characterisation of a number of rotamers of $[\{\text{Cp}'(\text{PP})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PP})\text{Cp}'\}]$ complexes prompted consideration of the influence of different conformers on the electronic structure of the ground and excited states of the one-electron oxidation products. In collaboration with the Kaupp group at Technische Universität Berlin, a relaxed rotamer scan identified a number of low-lying minima that differ in the relative orientation of half-sandwich fragments around the long molecular axis, sweeping from the most *trans*-like conformers through systems where the M-Cp' vectors are approximately perpendicular (*perp*) to *cis*-like structures. The observed NIR absorption profile of $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$ is in good agreement with the Boltzmann-weighted summation of transitions arising from the three fully optimised structures *trans*- $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$, *perp*- $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$ and *cis*- $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$. The NIR band envelope observed for the simple diyndiyl complexes $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$ can therefore be attributed to two transition envelopes with distinct electronic character (charge resonance or $d\pi\text{-}d\pi^*$, and MLCT) arising from a distribution of conformers in solution. The MLCT component contributes to the higher energy shoulder of the IVCT

band envelope, and was predicted on the basis of the computational work to be most intense for the *perp*-style minima. This suggestion was confirmed by the preparation and study of the *pseudo*-macrocyclic complex $[\{\text{RuCp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2\}_2]^+$ which is restricted to a narrow range of *cis*-like conformers and is characterised by an almost idealised Class III style IVCT (or charge-resonance) band with the expected low-energy cut off predicted by the two-state model [100].

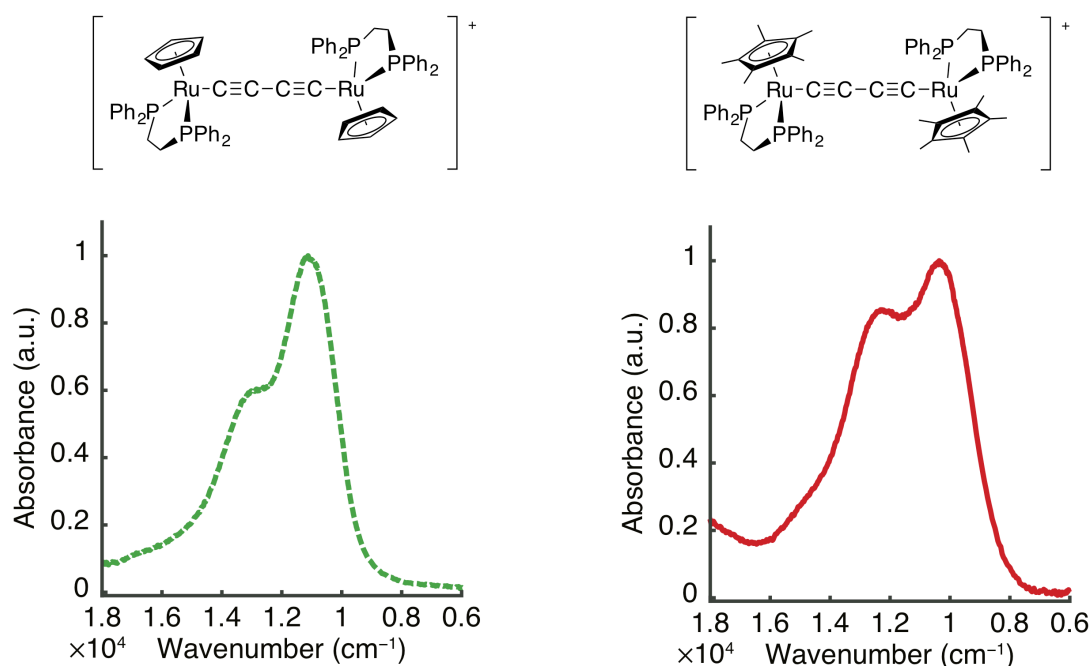


Figure 21 The normalised NIR spectra of $[\{\text{Cp}'(\text{dpe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{dpe})\text{Cp}'\}]^+$ ($\text{Cp}' = \text{Cp}, \text{Cp}^*$). The increased stability of the perpendicular conformers due to inter-ligand interactions lead to the more pronounced MLCT transitions which appear as a band to higher energy than the IVCT or charge resonance transition [142].

Critically, these results show that an accurate interpretation of the NIR spectrum of the prototypical complex $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}]^+$ must allow for the different spectroscopic properties of the various thermally accessible rotameric forms. As shown in numerous other examples, these conclusions apply to many other examples of “mixed-valence” complexes with low axial symmetry and relatively free rotational elements and a distribution of rotamers is required to accurately describe the spectroscopic profiles (**Figure 21**) [142]. The inclusion of dispersion effects adds to the accuracy of the computationally derived description of the relative energies and structures of the conformational minima. The detailed analyses of the NIR (IVCT) spectra of such systems should therefore consider not only the contributions to the band shape that can arise from vibronic coupling and transitions from lower-lying filled metal orbitals that gain intensity through low local coordination symmetry and/or spin orbit coupling, but also the potential for rotamers with distinct spectroscopic profiles. The latter will not be adequately treated by interpretations drawn from a single lowest energy conformer.

The introduction of an additional arylene ‘rotor’ within the bridging ligand increases the complexity of the conformational space and the diversity of electronic character of the various rotamers. Solutions of these systems feature a distribution of conformers with quite distinct character ranging from highly localised to highly delocalised electronic structures. These different parts of the conformational population can be detected most clearly from the presence of additional bands in relatively well resolved $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}=\text{C})_{\text{arylene}}$ vibrational modes in the IR spectra characteristic of different conformers, but are also apparent in the electronic spectra [80, 106]. In the case of heterobimetallic complexes such as $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{C-1,4-C}_6\text{H}_4\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}]^+$, the conformational dependence of the electronic structure leads to observation of Fe(III)/Mo(0):Fe(II)/Mo(I) redox isomers in solution [79].

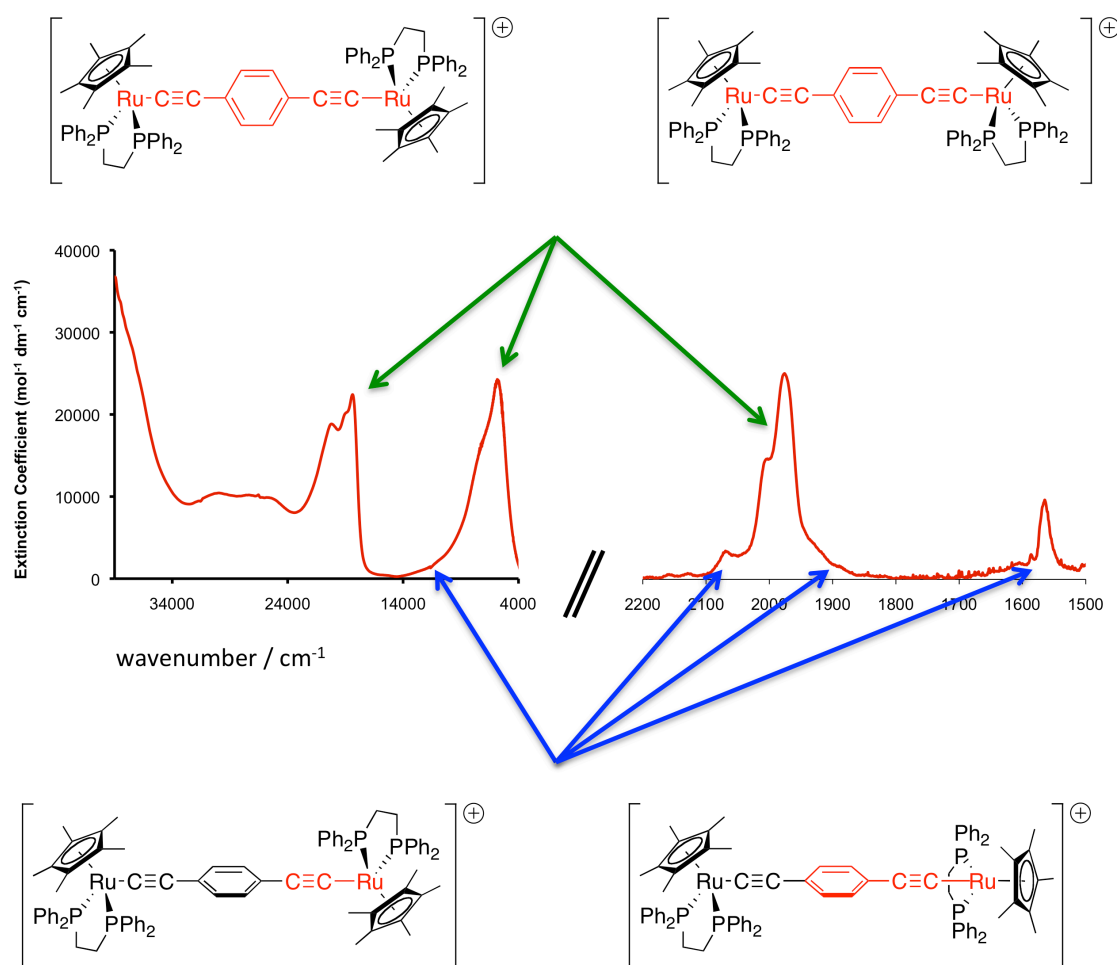


Figure 22 The UV-vis-NIR and IR spectra of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})\{\text{Ru}(\text{dppe})\text{Cp}^*\}]^+$ with indications of the characteristic features of the delocalised forms with substantial diethynyl benzene radical character (top) and the more metal-centred localised forms (bottom) [80, 106].

Beyond the role that IR spectroscopy can play in the identification of distributions of conformers within solutions of mixed-valence complexes lies a more fundamental basis for the identification of electronic character based on the IR activity of bridge vibrational modes, especially those active along the electron-transfer coordinate. The bimetallic buta-1,3-diyne-1,4-diyl-bridged radical cation complexes $[\{Cp'(PP)M\}(\mu-C\equiv CC\equiv C)\{M(PP)Cp'\}]^+$ ($M(PP)Cp' = Fe(dppe)Cp^*$,⁸ $Ru(PPh_3)_2Cp$ [B16, 100], $Ru(dppe)Cp^*$ [12, 142]) have been widely considered benchmark examples of strongly delocalised mixed-valence complexes, the IR activity and significant intensity of both the symmetric and asymmetric $\nu(C\equiv CC\equiv C)$ bands in $[\{Cp'(dppe)Fe\}(\mu-C\equiv CC\equiv C)\{Fe(dppe)Cp'\}]^+$ ($Cp' = Cp, Cp^*$) [159] contrasts with barely detectable symmetric stretches for the delocalized ruthenium (and closely related rhenium examples⁹), where the symmetric stretch only gains some intensity due to the larger symmetry breaking in the most perpendicular conformers (**Figure 23**).

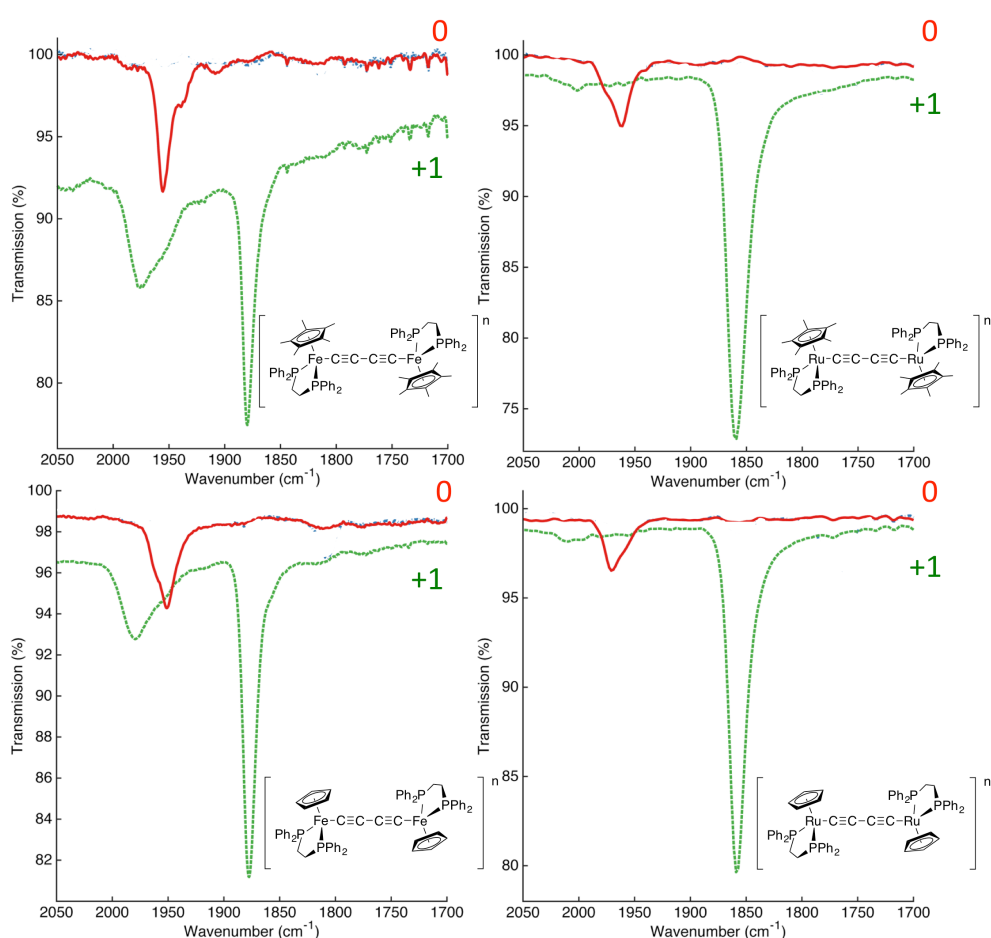


Figure 23 The mid-IR spectra showing the $\nu(C\equiv CC\equiv C)$ bands in $[\{Cp'(PP)M\}(\mu-C\equiv CC\equiv C)\{M(PP)Cp'\}]^+$ complexes. The higher frequency symmetric mode apparent in the iron complexes clearly indicates the localised electronic structure of these compounds [159].

⁸ N. Le Narvor, L. Toupet, C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129 – 7138.

⁹ M. Brady, W. Wang, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Bohme, G. Frenking, J.A. Gladysz, *J. Am. Chem. Soc.*, 1997, **119**, 775 – 788.

The iron compounds are therefore now reclassified as localized (Class II) mixed-valence complexes, in contrast to the ruthenium (and rhenium) complexes, which are delocalized (Class III) systems, with the true IVCT band being detected as a very weak, low energy band in accord with the two-state model (**Figure 24**) [159]. Of course, the description of “localized” or “delocalized” character is intricately related to the time-scale of the observation, and whilst appearing localized on the IR timescale, on the longer time scale of ESR and Mossbauer spectroscopies, $[\{\text{Cp}^*(\text{dppe})\text{Fe}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Fe}(\text{dppe})\text{Cp}^*\}]^+$ appears to be more fully delocalized. The effective electron transfer rate between the two iron centres can therefore be estimated as between 10^{-9} and 10^{-13} s. The previously unrecognised electronic-structure counterpoint of the Fe and Ru based complexes highlights the differences in metal–ligand overlap for 3d and 4d systems and indicates a general result that in the case of “all-carbon” or “carbon-rich” bridged bimetallic complexes first row metals are more likely to result in “localized” behaviour while second row metals likely give more delocalized structures.

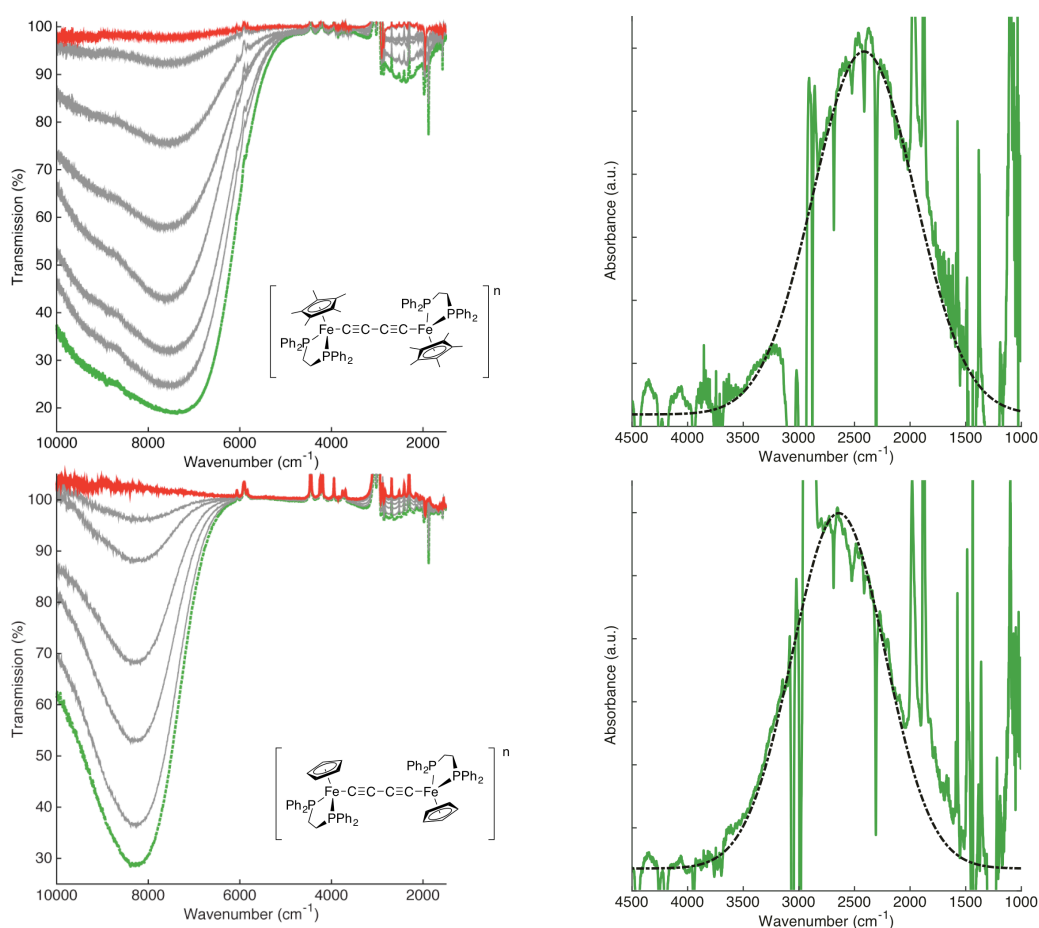


Figure 24 The NIR-IR spectra of $[\{\text{Cp}'(\text{dppe})\text{Fe}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{Fe}(\text{dppe})\text{Cp}'\}]^+$ ($\text{Cp}' = \text{Cp}, \text{Cp}^*$) showing the true IVCT band (expanded with Gaussian fitting) and the higher energy MLCT/IVCT band originally observed and analysed by Lapinte⁸ [159].

Regardless of the electronic character, members of the series $[\{\text{Cp}'(\text{PP})\text{M}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\{\text{M}(\text{PP})\text{Cp}'\}]^+$ exist as a thermally populated distribution of conformers in solution, and the overlapping spectroscopic profiles that reflect the rich conformational landscape make the accurate extraction of the parameters necessary for the analysis within the framework of the Marcus–Hush model extremely challenging. Analysis of the spin-density distributions from a range of conformational minima provides an alternative representation of the degree of charge localization, and a comparison between members of the series. While the spectra for the diruthenium complexes are well reproduced with BLYP35-D3, this is not the case for the mixed-valence diiron systems, due to the onset of significant spin contamination. Here the use of a novel type of exchange-correlation functionals, known as local hybrids, with position-dependent exact-exchange admixture, provided the necessary improvements. Thus, whilst the electronic structure and spectra are essentially unchanged compared to BLYP35-D3 for ruthenium complexes, the calculated electronic spectra of the iron complexes were decisively improved by the local hybrid Lh-SsirPW92-D3, allowing their detailed interpretation. Computations therefore help explain some intriguing features of the spectra, such as the identification of a new, low-energy IVCT band in the IR region (for both the iron and ruthenium systems). Further electronic absorptions in the NIR region originally observed and analysed arise from higher energy, overlapping MLCT and IVCT-like transitions in each of the thermally accessible conformers.

In summary, these investigations have conclusively demonstrated that conformational factors play a significant role in the appearance of spectra in mixed-valence compounds, and account for the increased complexity of the spectral band envelopes of many mixed-valence complexes beyond the predictions of the two-state model and related theories. The presence of multiple conformers in all but the most symmetric of “mixed-valence” systems, all of which offer subtly different electronic transitions, making application of band shape analysis within the framework of Marcus–Hush theory fraught with difficulty. The apparent band envelope maxima and molar extinction coefficients of the experimental absorption spectra arise from overlapping transitions from different conformers and cannot necessarily be attributed to any single conformer. Uncertainties in the precise composition of the equilibrated conformational mixture mean that accurate deconvolution and attribution of components of the band envelope to any individual conformer or electronic transition is not possible. Therefore, in cases in which spectroscopic evidence points to the presence of multiple conformers, it is necessary to move beyond analyses derived from exclusive consideration of the global minimum.

The work described here highlights how the presence of multiple conformers can be detected from the appearance of both IR and NIR spectral envelopes. These spectroscopic features are well modelled though the molecular and electronic structures of the most significant conformers determined by quantum-chemical methods using a suitably balanced global or local hybrid functionals, and modestly sized basis set. Therefore, with even modest computational resources, the study of mixed-valence compounds in a manner that accounts for a distribution of conformers within a sample is achievable. By combining spectroscopic observation and quantum-chemical methods, a more complete description of mixed-valence compounds and indeed, of intramolecular charge-transfer processes in general, is achieved.

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Molecular electronics

The field of molecular electronics is often considered in terms of the design of molecules that can mimic the electrical properties of conventional solid-state electronic components such as wires, rectifiers and transistors. Whilst this may reflect the popular perception of this area of research, molecular electronics research is more broadly directed towards understanding and controlling the transfer of charge between macroscopic interfaces via a molecular conduit and the electrical properties of these electrode|molecule|electrode structures or *molecular junctions* [R12]. Single molecule molecular junctions are immensely powerful research tools, providing great insight into the molecular structure-electrical property relationships (**Figure 25**). For example, molecular junctions based on mechanically controlled or STM break junctions, STM-based current-distance spectroscopy ($I(s)$ methods) or STM current-time (telegraphic blinking) methods all correlate electrical characteristics with the separation of the macroscopic electrodes and hence give some information concerning molecular geometry within the junction. The experimental platforms are compatible with a range of different solvents, allowing medium effects to be explored whilst the introduction of an additional external counter electrode allows electrochemical and electrolytic control of the molecule within the junction independent of the bias applied across the junction. Typically results from many hundreds or thousands of individual junctions are used to give a statistically significant data set. The combined current-distance ($I-s$) traces can be represented in a heat map, or 2-D histogram, to highlight the stability of the junction to the mechanical forces arising from increasing the separation of the electrodes, and the dimension of the junction at the point of rupture of the molecule-electrode contact. The data from the $I(s)$ traces can also be binned in small current steps and the data used to plot 1-D histograms in which the most probable conductance values appear as one or more peaks.

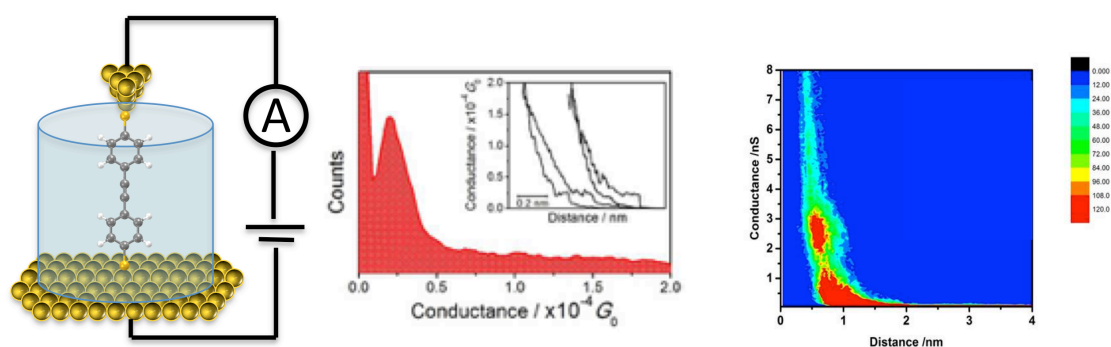


Figure 25 A schematic of a STM-based single molecule junction, a plot of current-distance ($I-s$) traces, the analogous 1-D conductance histogram and a 2-D $I-s$ 'heat map'.

Multi-molecule junctions are similar sandwich-like structures but formed from monolayer films sandwiched between a conducting substrate and a top contacting nanoparticle, conducting-AFM (c-AFM) tip, liquid metal (Hg, e-GaIn) or deposited electrode provide information and avenues for investigation complementary to those of single molecule junctions. These 'large area' (nm^2) monolayer junctions provide an electrical response averaged from across the individual molecular environments within the junction but are more commensurate with device construction methods. However,

the fabrication of the top electrode on top of the monolayer without interpenetration or damage to the monolayer remains a significant challenge.

The electrical conductance, G , arising from tunnelling through a molecule in a junction can be described in general terms by a simplified form of the Landauer-Büttiker model

$$G = \frac{2e^2}{h} \frac{4\Gamma^2}{(E_F - E_{MO}) + 4\Gamma^2}$$

The conductance through the junction therefore depends on the energy offset of a critical molecular orbital that mediates charge transfer with the electrode Fermi level ($E_F - E_{MO}$), with better alignment leading to increased conductance, becoming idealised when in resonance. The conductance through the molecule is also critically dependent on the nature of the molecule-electrode coupling (Γ) and hence the nature of the molecular anchor group that links the molecule to the electrode and the surface states on the electrode through which contact is made. Strong molecule-electrode coupling leads to hybridisation of the molecular orbitals with the electrode, and hence a broadening of the molecular levels, an increase in the transmission probability through the junction and higher conductance. Molecular conductance within a molecular junction is therefore a complex function of the chemical composition of the molecular backbone, the anchor group, fine details of the molecule-surface contact and the precise molecular geometry within the junction [R13]. In the following summary, our contributions to the areas of single molecule and monolayer film based molecular electronics are described, including activities directed towards the properties of organic and organometallic compounds, explorations of different molecule-electrode contacting strategies, and steps towards solving the ‘top contact’ problem.

Polyynes, $R(C\equiv C)_nR$ and oligo(phenylene ethynylene)s (OPEs), $RC\equiv C\{(C_6H_4C\equiv C)_n\}R$ might be considered the simplest conceivable molecular components, offering linear, π -conjugated backbones of defined molecular length, terminated by an anchor group, R . However, due to the junction-to-junction variation in surface-molecule contacts, even these simple molecular backbones give rise to multiple conductance signatures that can span orders of magnitude (**Figure 26a**).¹⁰ Such multiple conductance values are particularly prevalent in STM BJ measurements due to the rougher electrode surfaces and greater array of binding sites. This inspires the search for new anchor groups that can limit the range of accessible, conductive molecular contact geometries and reduce the distribution of molecular conductance values. The capacity of the trimethylsilylethynyl moiety to form weak van der Waals contacts to gold surfaces, combined with the steric bulk of this moiety that might restrict the range of accessible binding conformations and the ready synthesis of bis(trimethylsilyl)-terminated polyynes, $Me_3Si(C\equiv C)_nSiMe_3$, and OPEs, $Me_3SiC\equiv C\{(C_6H_4C\equiv C)_n\}SiMe_3$, therefore made these systems appealing targets for exploration in molecular junctions.

¹⁰ (a) C. Wang, A.S. Batsanov, M.R. Bryce, S. Martin, R.J. Nichols, S.J. Higgins, V.M. Garcia-Suarez, C.J. Lambert, *J. Am. Chem. Soc.*, 2009, **131**, 15647 – 15654. (b) P. Moreno-García, M. Gulcur, D.Z. Manrique, T. Pope, W. Hong, W. Kaliginedi, C. Huang, A.S. Batsanov, M.R. Bryce, C. Lambert, T. Wanlowski, *J. Am. Chem. Soc.*, 2013, **135**, 12228 – 12240.

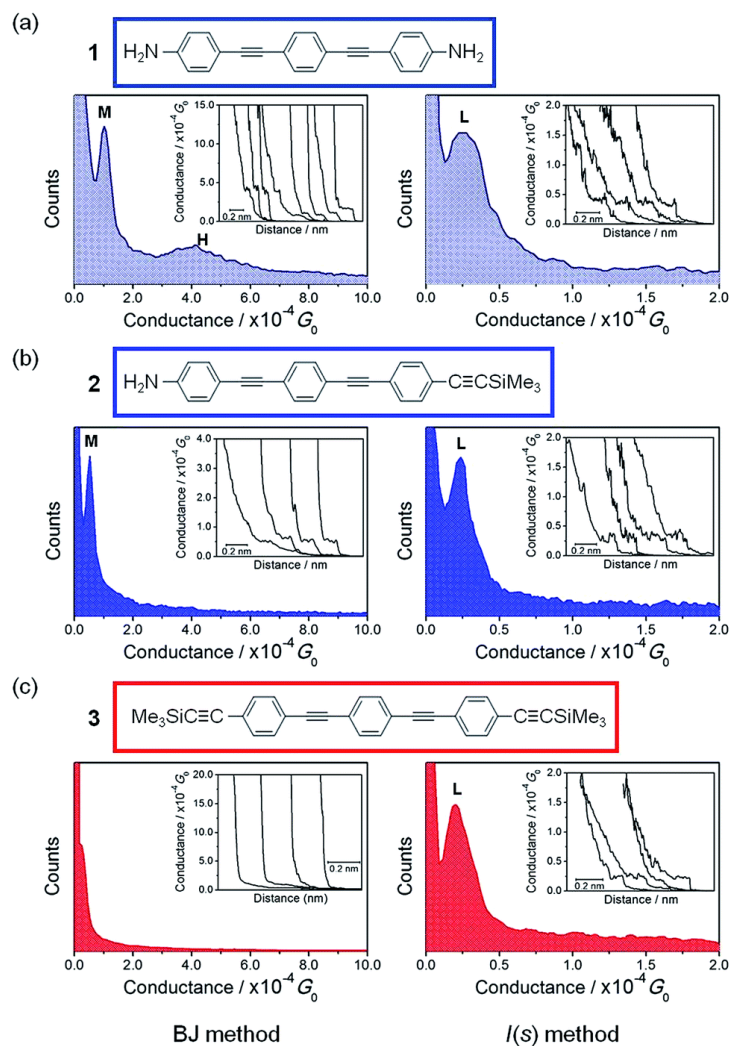


Figure 26 Conductance histograms built from summation of ca. 450 individual conductance traces featuring a current plateau which exceeds 0.1 nm in length for OPE molecules bearing NH_2 and / or SiMe_3 anchors using either the STM-BJ technique (left side) or the $I(s)$ method (right side). Conductance peaks are denoted high (H), medium (M) or low (L) for clarity. The insets feature examples of the $I-s$ curves used to construct the 1-D histograms. Conductance data are referenced to the conductance quantum $G_0 = 2e^2/h = 77.5 \mu\text{S}$. $U_{\text{iip}} = 0.6 \text{ V}$ [139].

A thorough study of the gold| $\text{Me}_3\text{SiC}\equiv\text{C}$ contact using OPE derivatives and data from quartz crystal microbalance measurements during SAM formation, Raman and SERS data, DFT calculations and single molecule conductance measurements with a range of model compounds conclusively demonstrated that $\text{Me}_3\text{SiC}\equiv\text{C}$ -terminated molecules can form weak van der Waals-type contacts with some ionic character at top, bridge and hollow sites on gold (111) terraces. However, the conductance of these configurations is lower than the detection limits of the single-molecule experiments. Instead, contacts at defect sites within a very narrow range of molecular orientations are necessary to increase the binding energy between the $\text{Me}_3\text{SiC}\equiv\text{C}$ - group and the gold substrate and stabilize the binding of the molecule to the surface in a manner that can be explained through an image charge or electrostatic model. The resulting

hybridization of the molecular levels and the metallic gold states increases the width of the resonances (from 5 meV to 8 meV) and enhances the overall transmission at the Fermi level [139]. Although this small range of binding geometries results in low probabilities for junction formation in STM BJ and STM $I(s)$ measurements, the very specific molecular orientation necessary for achieving significant molecular conductance greatly simplifies conductance histograms relative to more common anchor groups such as NH_2 , with for trimethylsilylethynyl-anchored compounds giving rise to a single conductance peak (**Figure 26**). Overall, the $-\text{C}\equiv\text{CSiMe}_3$ group is a useful molecule-electrode contact for use in fundamental studies of molecular junctions in cases where a single, well-defined conductance histogram is required, although the resulting molecular conductance and junction formation probabilities are low.

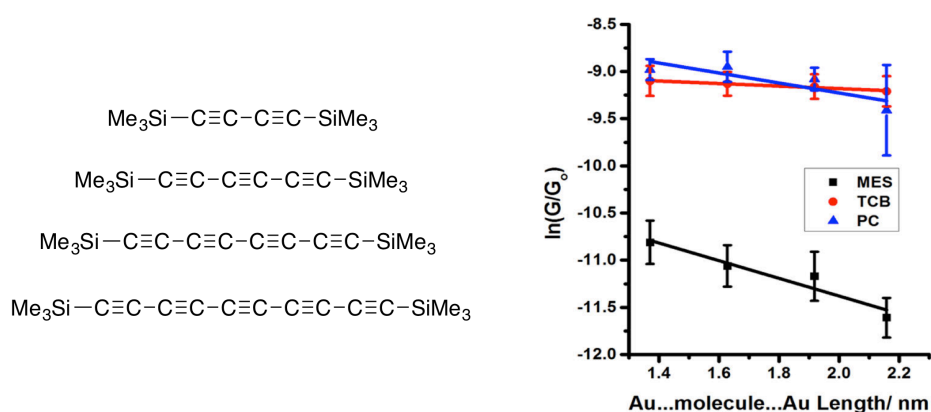


Figure 27 The polyynes $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ ($n = 2 - 5$) and a plot of conductance vs. molecular length in mesitylene (MES), 1,3,5-trichlorobenzene (TCB) and propylene carbonate (PC) [135].

As noted above, oligynes represent one of the simplest wire-like molecular structures, prompting a series of single-molecule $I(s)$ conductance measurements with the series $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ ($n = 2, 3, 4, 5$). Whilst the expected exponential decay in molecular conductance, G , with molecular length, l , was observed such that $G \propto e^{-\beta l}$ where β is the decay parameter, both G and β were found to be solvent dependent (**Figure 27**). In mesitylene, the series exhibits a lower conductance and higher length decay ($\beta \approx 1.0 \text{ nm}^{-1}$) than those measured in 1,2,4-trichlorobenzene ($\beta \approx 0.13 \text{ nm}^{-1}$) or propylene carbonate ($\beta \approx 0.54 \text{ nm}^{-1}$) [135].

Solvent effects in molecular junctions have rarely been examined, a situation that is surprising given that most contemporary laboratory STM-based single molecule conductance measurements are performed in a liquid or ambient environment rather than UHV conditions. The solvent dependent conductance behaviour of the polyynes series (**Figure 27**) has been rationalized with the aid of theoretical and computational investigations carried out in collaboration with Lambert. The computational work reveals that β values are higher when the contact Fermi energies are close to the middle of the molecular HOMO–LUMO gap, but decrease as the Fermi energies approach resonance with either the HOMO or LUMO. Further examination with DFT-based models of the molecular junction including explicit solvent molecules interacting with the oligoyne backbone have shown that the

electrostatic interactions between the solvent and the oligoyne have a profound impact on the computed electron transmission curves for the junctions, and hence the conductance and length dependence across the homologous series. This effect has been termed “solvent induced gating of the molecular junction electrical properties” and rationalizes the previously unexpected differences observed between different studies of oligoyne molecular conductance,¹¹ which can be now attributed to solvent effects.

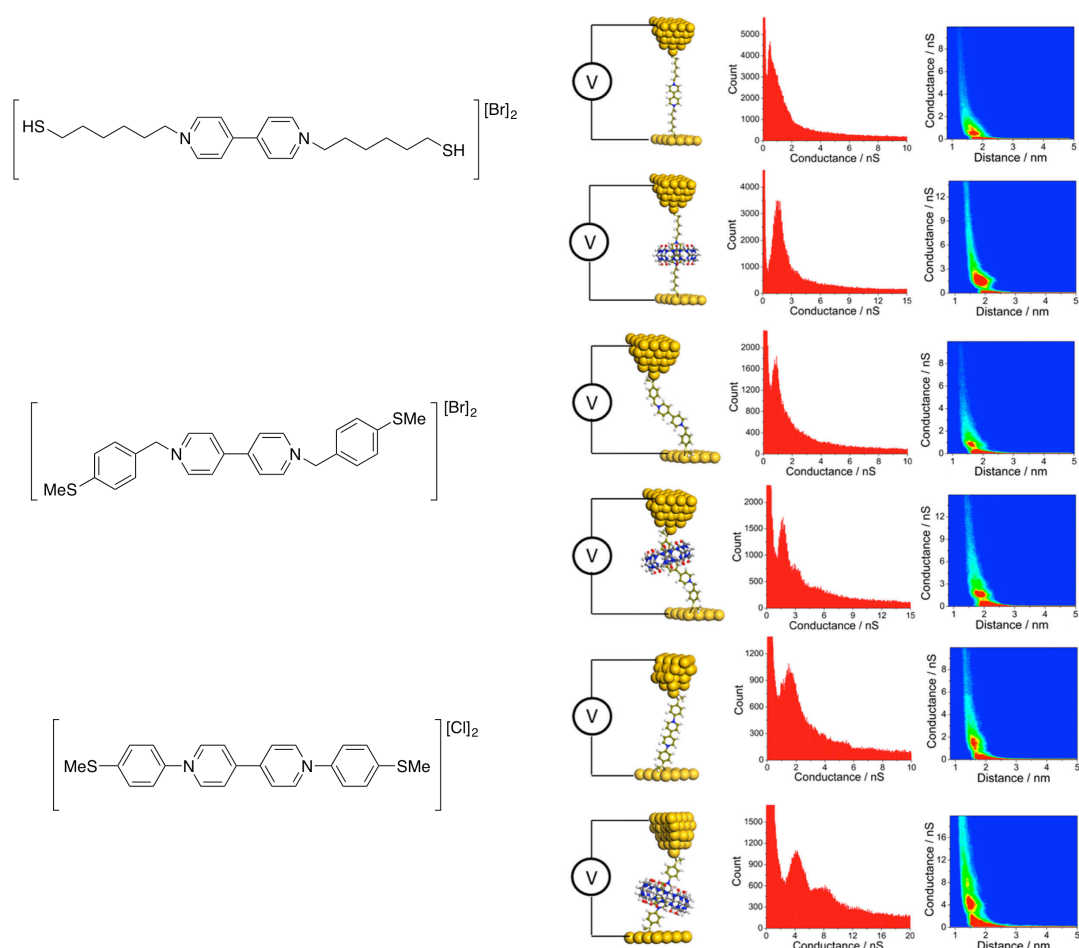


Figure 28 The viologen containing wire-like molecules used to explore supramolecular screening of solvent effects in redox-active molecular junctions. Schematics of the single molecule junctions are shown together with 1-D conductance histograms and 2-D current-distance plots for both the molecule and the 1:1 molecule: cucurbit[8]uril supramolecular complex [136].

Further evidence for such outer-sphere type contributions to the conductance of a molecular junction has been obtained from studies of redox-active viologen-based

¹¹ C.S. Wang, A.S. Batsanov, M.R. Bryce, S. Martin, R.J. Nichols, S.J. Higgins, V.M. Garcia-Suarez, C.J. Lambert, *J. Am. Chem. Soc.*, 2009, **131**, 15647 – 15654; P. Moreno-Garcia, M. Gulcur, D.Z. Manrique, T. Pope, W. Hong, V. Kaliginedi, C. Huang, A.S. Batsanov, M.R. Bryce, C. Lambert, T. Wandlowski, *J. Am. Chem. Soc.*, 2013, **135**, 12228 – 12240.

molecular wires and their 1:1 cucurbit[8]uril supramolecular complexes in aqueous solution [136]. Significant (2 – 3 fold) increases in the single molecule conductance of viologen-based wires are observed when the molecule is threaded through the hydrophobic cucurbit[8]uril cavity. Electron transfer across the viologen takes place via a Kuznetsov-Ulstrup (KU) style two-step hopping mechanism rather than direct tunnelling. Here, environmental and internal fluctuations pre-organise the molecular geometry to allow an electron to hop from one gold electrode to the viologen, leading electrochemical reduction and further structural relaxation of the system. A second sequence of pre-organisation, electron-transfer from the reduced viologen group to the other gold electrode of the junction and reorganisation back to the molecular starting geometry completes the electron-transfer process. The confinement of the viologen within the cucurbit[8]uril cavity reduces the outer-sphere component of the Marcus-type reorganisation energy and enhances the molecular conductance. This work has clearly demonstrated that control of the local microenvironment within a supramolecular complex encapsulating the molecular wire has a substantial impact on the molecule conductance, providing a rationale and motivation for future designs of supramolecular electronic devices and control of environment in molecular junction studies.

An extension of this work with solvent effects, outer-sphere effects and redox-active viologens within molecular junctions prompted the first studies of the electrochemical gating of such systems in ionic liquid media [129]. In this experiment, a viologen functionalised with surface binding groups is tethered as usual between the STM tip and substrate surface (**Figure 29**). The tip and substrates can be viewed as the drain and source electrodes of a transistor-like device, respectively. A counter and reference electrode are also introduced into the STM liquid cell, the combination of which acts as the gate electrode in this four-electrode bipotentiostat setup. The use of a bipotentiostat allows independent electrochemical potential control of the substrate (working electrode 1, or “source”) and the STM tip (working electrode 2, or “drain”). The potential difference between these two electrodes is the bias voltage applied to the molecular junction. The effect of the ‘gate’ electrode is relayed to, or coupled with, the molecule within the junction through the electrolyte. Contrary to the behaviour in aqueous electrolytes, a sharp, clear peak in the single molecule conductance versus electrochemical potential data was obtained in the ionic liquid 1-butyl-3-methylimidazolium triflate (BMIM-OTf). These data are rationalized in terms of the KU model, where the ionic liquid is modelled gate coupling parameter, ξ , of unity. This compares to a much lower gate coupling parameter of 0.2 for the equivalent aqueous gating system. This study shows that ionic liquids are far more effective media for gating the conductance of single molecules than either solid-state three-terminal platforms created using nanolithography, or aqueous media.

The biphenyl moiety of the viologen is also able to form contacts with electrode surfaces, evinced by the two distinct conductance features observed in single-molecule STM $I(s)$ conductance experiments with *N,N'*-di(4-(trimethylsilylethynyl)benzyl)-4,4'-bipyridinium bis(tetrafluoroborate) [155]. From the break-off distances and studies with model compounds, the higher conductance junctions ($G = 5.4 \pm 0.95 \times 10^{-5} G_0$, break-off distance 1.56 ± 0.09 nm) are attributed to molecular contacts between the molecule and the electrodes via the viologen moiety and one trimethylsilylethynyl group. The lower conductance junction ($G = 0.84 \pm 0.09 \times 10^{-5} G_0$, break-off distance 1.95 ± 0.12 nm) is consistent with an extended molecular conformation between the

substrate and tip contacted through the two trimethylsilylethynyl groups. However, when assembled into a Langmuir-Blodgett film only the higher conductance junctions are observed, due to the restricted range of molecular conformations within the tightly packed film.

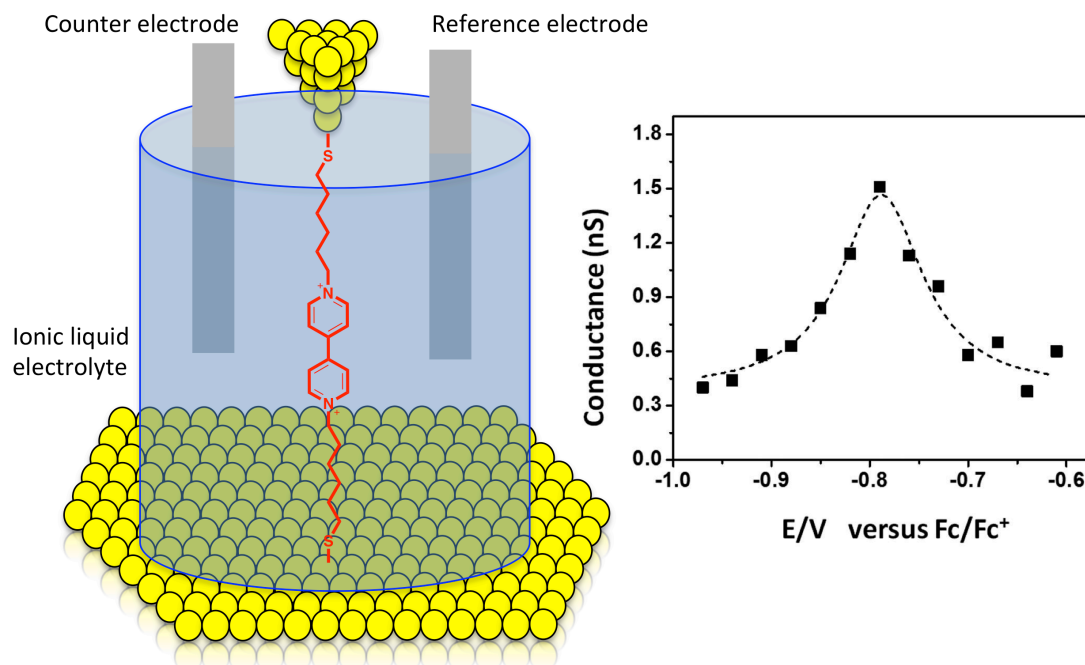


Figure 29 A schematic of the electrolytically gated single molecule junction, with a plot of the single-molecule conductance of 6-[1'-(6-mercaptohexyl)[4,4']bipyridinium]hexane-1-thiol versus electrochemical potential showing OFF-ON-OFF transistor-like behaviour [129].

Although the majority of molecules explored within single-molecule and monolayer-film based molecular junctions are organic in nature, the potential to design more highly functional junctions through the redox, photochemical and geometric features of organometallic compounds and inorganic complexes was highlighted in early discussions [R3, R8] and experiments. By way of example, a series of bis-2,2':6',2''-terpyridine complexes featuring Ru(II), Fe(II), and Co(II) metal ions and trimethylsilylethynyl (Me₃SiC≡C-) or thiomethyl (MeS-) surface contact groups were prepared, their redox chemistry explored using voltammetry and spectroelectrochemical methods, and the single molecule conductance determined using the STM-*I*(*s*) method. The absence of a strong correlation between the trends in solution-based redox potentials and the observed conductance behaviour indicate non-resonant tunnelling transport mechanisms. Further examination using non-equilibrium Green's function based methods in collaboration with Lambert indicate the major conduction channel to involve the terpy-based LUMO, which explains the limited influence of the metal ion on the single-molecule conductance values. The conductance properties of these compounds are therefore determined more by the strength of the electrode–molecule contact and the structure of the “linker” than the nature of the metal-ion or redox properties of the complex [123]. However an extended series of mono- and bimetallic complexes, the latter featuring the bis(tridentate) bridging ligand 2,3,5,6-tetra(pyridine-2-yl)pyrazine (tpp) allowed the determination of a tunnelling

decay constant (pseudo β -value) of 1.5 nm^{-1} , falling between decay factors for organic oligoynes and oligophenylenes, promoting further consideration of metal complexes within molecular junctions [134].

A comparative study of $trans$ -[Ru(C \equiv CC $_6$ H $_4$ C \equiv CSiMe $_3$) $_2$ (dppe) $_2$] with 1,4-bis(phenylethynyl)benzene derivatives XC $_6$ H $_4$ C \equiv CC $_6$ H $_4$ C \equiv CC $_6$ H $_4$ X (X = NH $_2$, C \equiv CSiMe $_3$) in $I(s)$ single molecule junctions demonstrated the improved through-molecule conductance of the ruthenium $trans$ -bis(acetylide) moiety vs. the 1,4-phenylene [91]. In this early demonstration, the improved conductance of an organoruthenium $trans$ -bis(acetylide) compound relative to the prototypical OPE system can be attributed to the better alignment of the HOMO of the organometallic compound with the electrode Fermi level. Extension of the acetylide ligand to ethynyltolan based moieties $trans$ -[M(C \equiv CC $_6$ H $_4$ C \equiv CC $_5$ H $_4$ N)L $_n$] and $trans$ -[M(C \equiv CC $_6$ H $_4$ C \equiv CC $_6$ H $_4$ SMe)L $_n$] [ML $_n$ = Ru(dppe) $_2$, Pt(PPh $_3$) $_2$] was readily achieved through an ‘on complex’ cross-coupling of the aryl contacting group with $trans$ -[M(C \equiv CC $_6$ H $_4$ C \equiv CH) $_2$ L $_n$] [140]. The introduction of the longer ‘linker’ resulted in a shift from HOMO-based conductance to tunnelling through the tail of the LUMO resonances of the more conjugated ligands, and hence a surprisingly similar conductance of both molecules.

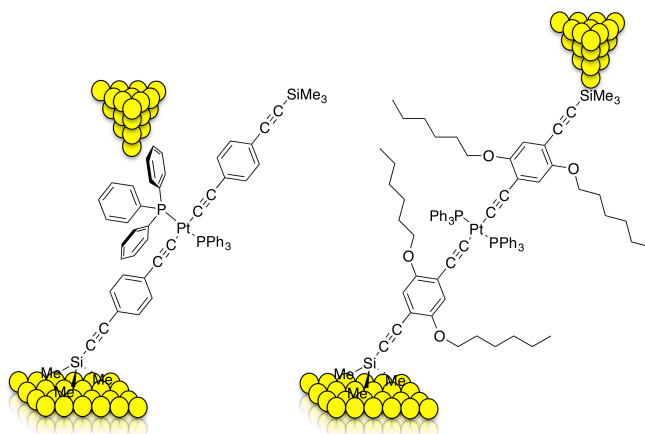


Figure 30 Cartoons depicting the ‘short circuit’ contacts to the PPh $_3$ ligands in a Pt-based molecular wire, and the analogous ‘insulated’ version [152].

Although thiolate-contacted Pt(II) bis(acetylide) complexes have been proposed as ‘molecular insulators’,¹² the discovery of efficient LUMO-based conductance mechanisms prompted further consideration of conductive platinum(II)-based molecular wires, $trans$ -[Pt(C \equiv CR) $_2$ L $_2$], revealing further design criteria for metal complexes within molecular junctions. The unusually high conductance and short break-off distances of complexes $trans$ -[Pt(C \equiv CC \equiv CSiMe $_3$) $_2$ (PPh $_3$) $_2$] and $trans$ -[Pt(C \equiv CC $_6$ H $_4$ C \equiv CSiMe $_3$) $_2$ (PPh $_3$) $_2$] in arise from unanticipated contacts to the aryl rings of the ancillary phosphine ligands. The introduction of hexyloxy side chains to the diethynylbenzene fragment limits these adventitious contacts and effectively insulates the molecular backbone. Similarly, the use of the trialkylphosphine PEt $_3$ ancillary ligands also prevents these orthogonal contacts directs molecular contacts within the

¹² M. Mayor, C. von Hanisch, H.B. Weber, J. Reichert, D. Beckman, *Angew. Chem. Int. Ed.*, 2002, **41**, 1183 - 1186

junction to the designated contact points and allows molecular conductance through the full length of the molecule to be reliably measured, and indeed demonstrating remarkably high conductance for molecules of this length [152].

Further design criteria for organometallic complexes are revealed through STM-BJ and STM- $I(s)$ studies of the molecular conductance of a series of 3-thiophene anchored acetylide complexes *trans*-[Ru(C≡C-3-C₄H₃S)₂(dppe)₂], *trans*-[Ru(C≡C-3-C₄H₃S)₂{P(OEt₃)₄}] and *trans*-[Pt(C≡C-3-C₄H₃S)₂(PEt₃)₂] made in comparison with the organic analogue 1,4-C₆H₄(C≡C-3-C₄H₃S)₂ [146]. The STM- $I(s)$ conductance data were used to rigorously test Albrecht's multi-parameter vector classification methods,¹³ with data compared with results from manual data selection. Both methods reveal remarkably consistent conductance data across the series, with little variation despite the rather substantial differences in the molecular backbone structure, which can be attributed to the uniformity of the thiophene-gold contact and the position of the electrode Fermi level close to the centre of the HOMO-LUMO gap. Thus, whilst the HOMO and LUMO transport resonances differ significantly between each of these molecules, transport in the vicinity of the middle of the HOMO-LUMO gap is similar, and in each case the molecular binding to the gold electrodes is similar. Data from STM-BJ junctions give the same conclusions, albeit that the rough or fractal nature of the cleaved gold contact points result in binding of the molecule at more under-coordinated sites and generally higher conductance.

Turning attention from single molecule to monolayer film based junctions prompted consideration of methods for forming high-quality films from representative tolan and OPE type molecular systems. Initial studies using Langmuir-Blodgett methods with alkyloxy-tailed tolan [39] and OPEs [44, 46, 51] featuring polar nitrile, carboxylate, ester or amine head-groups either as pure materials or mixtures with a supporting fatty acid matrix [48, 59] gave well-ordered films which, despite the polar nature of the assembly, gave symmetric I - V curves with little evidence of rectification. Interestingly, the alkyloxy-tail proved to be unnecessary in the formation of well-packed films [63]. These preliminary studies were important in establishing methods for fabrication of high-quality, defect free monolayer films and for expanding the array of functional groups that could be introduced to form the exposed top surface of the film, including groups such as trimethylsilylethynyl [68] and the terminal ethynyl moiety [85] that can be further used to form good contacts to a top electrode. The establishment of these molecular design strategies in turn allowed comparisons of electrical behaviour of the same species in both single-molecule and thin film junctions.

In this manner it can be shown that near-neighbour interactions play little role in the conductance of OPE-type wires where molecular conductance is dominated by non-resonant tunnelling mechanisms [76, 119]. In an interesting variation on this theme of near-neighbour interactions, films of 4,4'-[1,4-phenylene-bis(ethyne-2,1-diyl)]dibenzoic acid prepared on basic or pure water sub-phases showed different conductivity characteristics. Films of 4,4'-[1,4-phenylene-bis(ethyne-2,1-diyl)]dibenzoic acid prepared from basic sub-phases and featuring a Na-carboxylate top surface gave conductivity profiles similar to that of single-molecule junctions of the (deprotonated) 4,4'-[1,4-phenylene-bis(ethyne-2,1-diyl)]dibenzoic acid. In

¹³ M. Lemmer, M.S. Inkpen, K. Kornysheva, N.J. Long, T. Albrecht, *Nat. Commun.*, 2016, 7, 12922.

contrast, the hydrogen-bond network formed between the carboxylic acid functional groups on the top surface of films prepared from pure-water sub-phases substantially reduces the junction conductance [95].

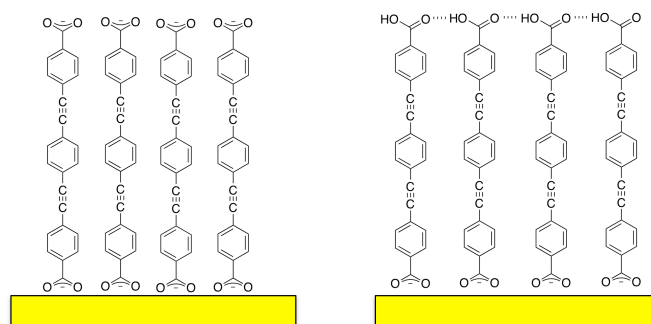
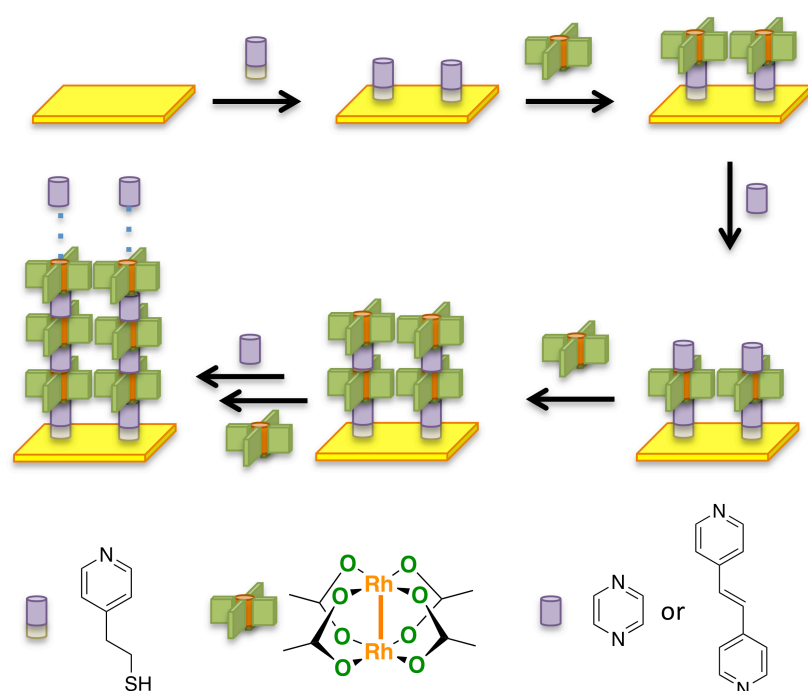


Figure 31 Cartoons illustrating the monolayer LB films of 4,4'-[1,4-phenylenebis(ethyne-2,1-diyl)]dibenzoic acid deposited onto a gold substrate from a basic water sub-phase (left) and a pure water sub-phase (right) [95].

Metal complexes have also attracted attention as building blocks for the assembly of monolayer films, primarily through layer-by-layer assembly methods. Interestingly, the inclusion of a gold(I) complex within the OPE-like backbone resulted in an increase in 2 – 4 fold increase in conductance of the resulting Langmuir-Blodgett films relative to films of other, similarly contacted OPE derivatives of comparable length, reinforcing the ideas expressed above from single-molecule junctions that metal complexes can give improvements in the conductance of molecular junctions [116]. By taking advantage of the facile axial coordination of $[\text{Rh}_2(\text{OAc})_4]$ by N,N' -bidentate ligands and layer-by-layer approaches, highly-ordered films of well-defined composition and thickness can be obtained (**Scheme 15**) [158]. The good alignment of the molecular HOMO with the gold Fermi level leads to excellent electrical characteristics. Further examination of conductance vs. length data gives a rare experimental demonstration of a change in mechanism from tunnelling to hopping, which occurs in this case around the tetramer-pentamer boundary. Curiously, the films formed from the longer 1,2-bis(4-pyridyl)ethene linker gave even lower decay values, β , than pyrazine bridged analogues in both the tunnelling (0.44 nm^{-1} vs. 1.0 nm^{-1}) and hopping (0.03 nm^{-1} vs. 0.35 nm^{-1}) regimes.

It is proposed that under a bias voltage, the $\{\text{Rh}_2(\text{OAc})_4\}$ redox sites in the wire are in mixed-valence $\text{Rh}_2(\text{II/II})\text{-Rh}_2(\text{II/III})$ states. In a donor-bridge-acceptor molecular system operating under a super-exchange mechanism, as is the case in the shorter monomer to tetramer systems, reducing the energy gaps between the donor and bridge and/or the bridge and acceptor increases charge transfer from the D (A) site to the bridge, and vice versa, increasing the rate of electron exchange and hence increasing conductance. In the case of the systems here, the lower π^* and higher π orbital energies of the longer, more conjugated ligand dipyridylethene ligand would lower this critical energy gap and improve tunnelling-based charge transport between two neighbouring $\{\text{Rh}_2(\text{OAc})_4\}$ centres. In the case of the longer (pentamer and beyond) complexes for which hopping mechanisms dominate the conductance mechanism, simultaneous and consecutive electron (or hole) self-exchange across the bridging ligand is responsible for the passage of current. In the shorter pyrazine-bridged complexes, hopping

mediated conductance is reduced relative to the dipyridylethene-bridged analogues by the higher MLCT gap. In addition, although the pyrazine bridge favours stronger coupling between the $\text{Rh}_2(\text{II/II})\text{-Rh}_2(\text{II/III})$ sites, delocalisation of charge over the $\{\text{Rh}_2\text{-pz-Rh}_2\}^+$ units works against hopping mediated conductance due to the additional strong electrostatic repulsion between the hopping sites. Therefore, somewhat counter-intuitively, molecular wires comprised of localized redox active hopping sites linked by bridges with small optical gaps present as a design strategy for molecular wires with excellent long-distance conductance characteristics [158]. This work has successfully brought ideas from mixed-valence chemistry and intramolecular electron transfer chemistry to bear on the design of metal-complexes in molecular electronics.

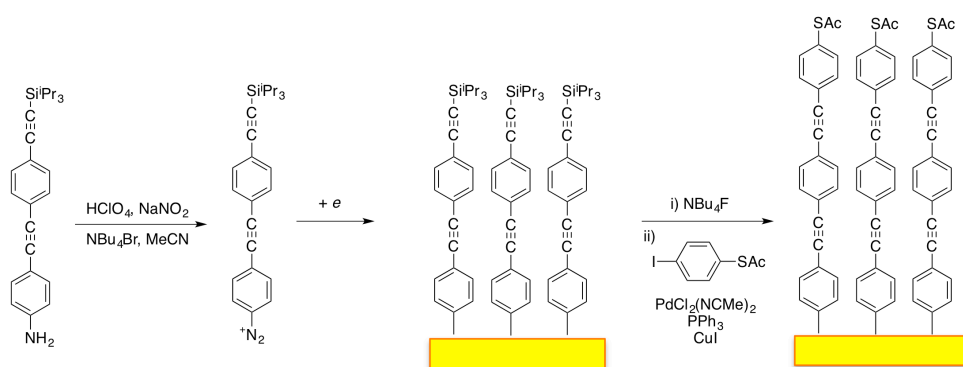


Scheme 15 A schematic description of the stepwise layer-by-layer assembly of metal-organic hybrid SAMs on Au substrates. A base layer of 2-(4-pyridyl) ethanethiol is self-assembled on the gold surface, to which the first $[\text{Rh}_2(\text{OAc})_4]$ building block is coordinated. A bridging pyrazine or 1,2-dipyridylethene is then introduced to give a new coordination site, and the cycle of coordination and ligand addition repeated to give films of desired thickness and composition [158].

In seeking to move beyond physisorbed and chemisorbed molecule-electrode contact, attention has been turned to methods of creating films with more robust films anchored through covalent contacts to electrode surfaces. McCreery and his team have pioneered the use of electrochemical grafting of diazonium derivatives to a range of surfaces. Whilst often leading to dendritic growth of multilayer molecular films, the resulting structures have been successfully employed in a range of device architectures.¹⁴ In order to prepare well-ordered, covalently grafted monolayers, the amino tolan, 4-(2-(4-(2-(triisopropylsilyl)ethynyl)phenyl)ethynyl)benzamine was prepared and converted to

¹⁴ R.L. McCreery, *Chem. Rec.*, 2012, **12**, 149 – 163.

the diazonium derivative *in situ* before being grafted to a gold substrate by cathodic electrochemical grafting [141]. The bulky triisopropylsilyl group effectively protected the growing film from adventitious attack of the arylene radicals, resulting in compact monolayers. Removal of the triisopropylsilyl group by treatment with fluoride to exposed the terminal acetylene moiety, which was further functionalisation through on surface Sonogashira coupling with 1-iodo-4-acetylthiobenzene to create surface sites bearing the strongly aurophilic thiolate top-contacting group, protected as the acetate (**Scheme 16**). The success of these surface reactions has been confirmed using Raman spectroscopy (gap-mode and SHINERS, employing gold nanoparticles and SiO₂ coated gold nanoparticles, respectively), taking advantage of the spontaneous deprotection of the thiolate group in presence of gold. Furthermore, contacting the thiolate groups with a gold-STM tip allowed creation of STM-based molecular junctions, with conductance values in the typical range for OPE derivatives (ca. $4 \times 10^{-5} G_0$).



Scheme 16 A schematic illustrating the electrografting of *in situ* formed diazonium salts onto a gold electrode surface to give high quality monolayers of wire-like OPE derivatives [141].

Carbon-contacted monolayers to gold were also achieved from 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne in remarkably efficient and simple fashion [161]. Stoichiometric reaction of the tetrayne with one equivalent of fluoride in the presence of a gold substrate, which ultimately serves as the bottom electrode, resulted in removal of one SiMe₃ group, and formation of a highly-ordered monolayer, Au|C≡CC≡CC≡CC≡CSiMe₃ (**Figure 32**). Further treatment of the gold-supported monolayer with excess fluoride removed the remaining SiMe₃ group on the top surface of the film to give a modified, ethynyl terminated monolayer Au|C≡CC≡CC≡CC≡CH. The reactive terminal C≡C–H moiety was able to be modified by ‘click’ reactions with (azidomethyl)ferrocene (FcCH₂N₃) to introduce a ferrocene redox probe, which in turn allowed assessment of electrochemical electron transfer rate between the ferrocene moiety and the gold substrate, through the C₈ chain. The value of k_{ET} determined ($3.2 \pm 0.1 \text{ s}^{-1}$) is similar those found in ferrocene-terminated monolayers of peptide nucleic acid of similar thickness ($k_{ET} \sim 3 \text{ s}^{-1}$). Incubation of the gold substrate supported monolayer Au|C≡CC≡CC≡CC≡CH in a solution of gold nanoparticles (GNPs) also resulted in reaction at the ethynyl top surface, and covalent attachment of GNPs on top of the film via a second alkynyl carbon–Au σ -bond, in a manner similar to earlier reports from ethynyl functionalised OPE based monolayers [112]. These remarkable Au|C₈|GNP structures in which the monolayer of linear C₈ chains is sandwiched

between two macroscopic gold contacts represent the first ‘all carbon’ molecular junctions whereby the carbon chain is contacted directly to the metallic electrodes without an intervening anchor group (**Figure 32**).

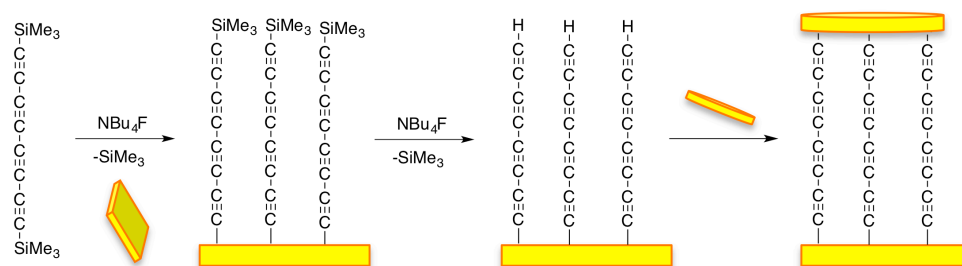


Figure 32 A cartoon schematic of the formation of the first ‘all-carbon’ molecular junctions [161].

The electrical properties of these metal|polyynediyl|metal junctions were characterised by contacting the GNPs with a conductive AFM (c-AFM) tip, from which sigmoidal-shaped $I-V$ curves, indicative of well-behaved junctions free of short circuits, were registered. As with the other measurements of nanoparticle-contacted films described below, a compromise has to be made in selecting the peak force that is applied by the tip to the nanoparticle during the measurement. If the tip is not contacted with sufficient force there will be inadequate electrical contact and the junction current will be underestimated. However, application of too great a force will result in a large deformation of the underlying monolayer. Therefore, before recording the $I-V$ curves, control experiments must be made across a range of set-points to determine the ‘Goldilocks zone’ for the most appropriate set-point force.

Although the deposition of pre-formed nanoparticles on a monolayer provides a conceptual soft route to the deposition of a metal on to a monolayer film and nascent ‘large area’ molecular junctions, attention has been more turned to alternative methods for the deposition of a metallic top contact on to a monolayer film in a manner that avoids interpenetration of the growing metal into the monolayer or damage to the constituent molecules and which might be viewed as compatible with conventional nanofabrication methodologies. The use of auric acid (HAuCl_4) in the sub-phase during formation of a Langmuir-Blodgett film of 4-{{4-{{4-{{(trimethylsilyl)ethynyl}phenyl}ethynyl}phenyl}ethynyl} benzenaminium chloride resulted in anion metathesis and formation of a monolayer contacted to the substrate via physisorption of the trimethylsilyl group and presenting a top surface of aurate anions [103]. Simple exposure to 254 nm light resulted in photoreduction of the aurate and formation of gold nanoparticles across the monolayer. The electrical properties of these nascent devices were determined from $I-V$ curves recorded using c-AFM in the PeakForce tunnelling AFM (PF-TUNA) mode. The PF-TUNA combines ‘tapping’ mode AFM with a conducting AFM tip and a low-noise current amplifier to probe current flow through the metal|molecule|GNI junctions. This gave consistent, sigmoidal-shaped $I-V$ curves indicative of well-behaved junctions free of metallic filaments and short circuits and confirming the applicability of the method, which was later extended to photoreduced silver contacts [143].

Gold nanoparticle based junctions were also prepared in a ‘single source’ fashion from complexes $[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NH}_2)(\text{NCC}_6\text{H}_4\text{-4-OMe})]$ and $[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-CO}_2\text{H})(\text{PPh}_3)]$ [110]. Well-ordered and tightly packed Langmuir-Blodgett monolayers of the gold precursors were prepared and subjected to a mild thermal annealing (ca. 150°C, 2 hrs) to promote decomposition of the gold head group with reduction to gold metal nanoparticles and presumably accompanying oxidation of the ancillary isocyanide or phosphine ligand. The I - V curves collected from these metal|monolayer|nanoparticle junctions are typical of metal-molecule-metal junctions over a wide range of set-point forces, with no low resistance traces characteristic of metallic short circuits observed. Plate-shaped palladium nanoparticle top-contacts were also prepared via a CO restricted growth processes on top of an amine functionalised monolayer giving comparable metal|monolayer|Pd junctions with similarly excellent electrical characteristics [147].

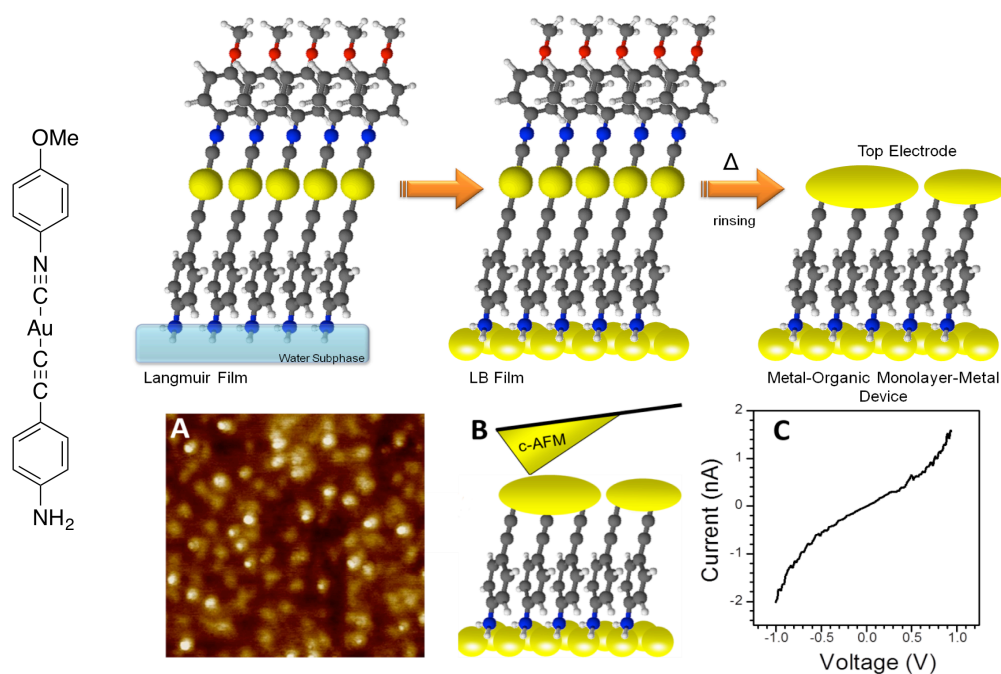


Figure 33 Photolysis of Langmuir-Blodgett films prepared from $[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NH}_2)(\text{NCC}_6\text{H}_4\text{-4-OMe})]$ results in decomposition of the gold moiety to give gold nanoparticle decorated films. The inset A shows an AFM image of the gold nanoparticles distributed over the film. Contacting these nanoparticles with a conducting AFM (inset B) gives well-behaved sigmoidal-shaped I - V curves indicative of molecular junctions (inset C) [110].

Finally, and perhaps most excitingly, nascent molecular electronic devices based on a monolayer OPE-type film sandwiched between two carbonaceous electrodes, have been prepared [147]. Tightly packed monolayers of 4-((4-ethynylphenyl)ethynyl)phenyl)ethynyl)benzoic acid were deposited onto a highly oriented pyrolytic graphite (HOPG) electrode using the Langmuir-Blodgett technique. An amorphous carbon top contact electrode was subsequently formed on top of the monolayer from a gaseous naphthalene precursor using the focused electron beam induced deposition (FEBID) technique. This allows the deposition of a carbon top-contact electrode with well-defined shape, thickness, and precise positioning on the

film with nm resolution. Devices prepared in this method displayed high reproducibility in their electrical properties. These prototype devices feature a metal-free, carbon-based top-contact electrode, deposited with nm precision, without the need of resists nor masks, with the location, shape, and size of the top electrode determined by the path of the e-beam. Since the FEBID technique is capable of very high (nm) lateral resolution, these results represent a substantial step toward the realization of integrated molecular electronic devices based on monolayers and carbon electrodes. Further advances toward ultraminiaturized devices should now be possible.

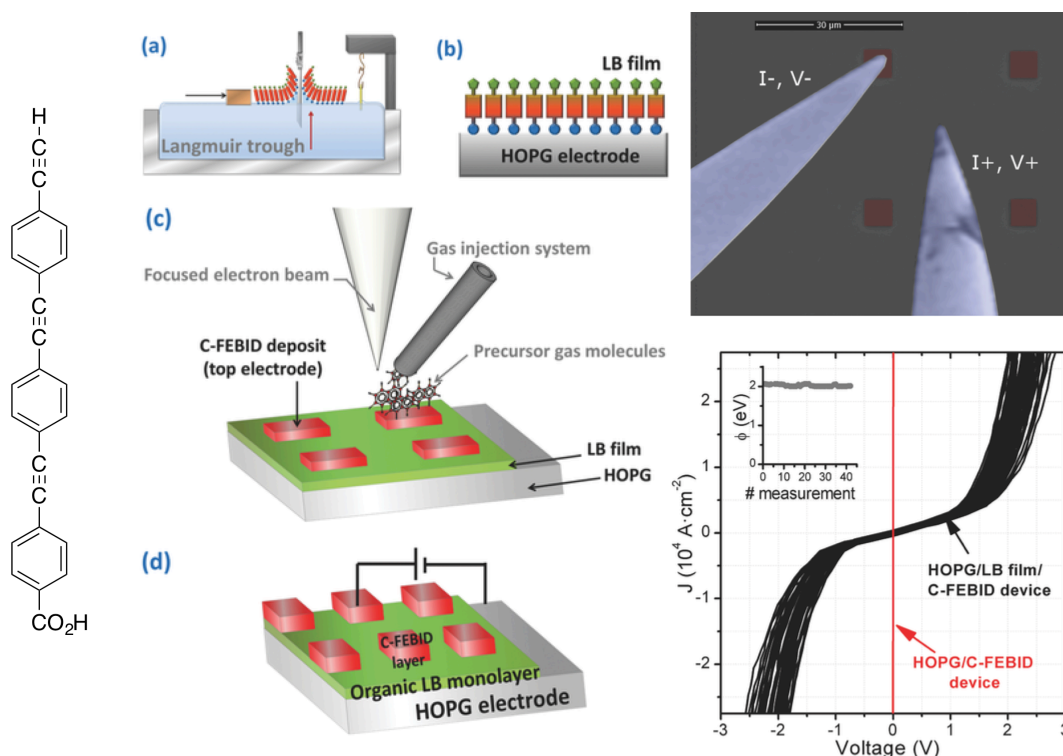


Figure 34 A schematic showing the deposition of carbon top-contact electrodes on Langmuir-Blodgett films of 4-((4-((4-ethynylphenyl)ethynyl)phenyl)ethynyl)benzoic acid. The false colour image (top right) shows four FEBID carbon pads as red squares, and the microcontact probes. At bottom right J - V curves from measurements of twenty-one different all-carbon electrode molecular electronic devices are shown with two curves collected per device (42 J - V curves in total). The red line corresponds to measurements from a HOPG/C-FEBID device, without the organic monolayer. The inset figure shows the values obtained for the effective barrier height of the tunnelling transport across the all-carbon electrode molecular electronic devices in all the measurements performed [147].

In summary, substantial advances have been made over the past decade in areas relating to the fabrication and study of molecular components within single-molecule and monolayer film molecular junctions. Studies with OPE based systems have permitted exploration of contacting group chemistry, whilst the use of metal complexes as components has demonstrated improved conductance behaviour as a result of better alignment of critical molecular orbitals with the junction electrode Fermi levels. Insights into the nature of the medium and outer-sphere contributions to electron transfer in single molecule junctions have been gained. A number of methods for the soft creation of top-contact metallic nanoparticles on molecular monolayers have been

developed and an exciting nanofabrication route to the reliable and reproducible creation of 'large area', metal free molecular junctions and nascent molecular devices with nm precision has been developed. Together, these studies serve to open routes that come ever closer to achieving the goals of a molecular electronic device, whilst also probing the fundamentals of electron transfer within molecular junctions.

References

Single-molecule electronics

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Miscellaneous studies

The pursuit of the major themes identified in the preceding sections has opened opportunities to contribute to studies led by others, and explore leads in other directions. Selected examples of these more miscellaneous works are summarised briefly here.

Spectroelectrochemical methods have been used to characterise bis[4,5-di(methylsulfanyl)1,3-dithiol-2-ylidene]-9,10-dihydroanthracene and the corresponding radical cation and dication in collaboration with Bryce (Durham University). This work included the design and construction of a unique spectroelectrochemical capillary flow cell suitable for use in time-resolved resonance Raman experiments, at the UK national Lasers for Science facility, Rutherford Appleton Laboratories [3].

Expertise in the organometallic chemistry of alkynes and preparations of acetylide complexes has contributed to the development of luminescent Rh complexes *mer,trans*-RhH(C≡CAr)(PMe₃)₃ (Ar = 9-anthracene, 1-naphthalene, C₆H₄-4-NMe₂, C₆H₄-4-C≡CC₆H₄-4'-NMe₂) by the Marder group at Durham [32], whilst with Humphrey (ANU) the combination of metal acetylide complexes with triarylamine moieties has led to N-cored organometallic dendrimers with promising two-photon absorption behaviour, and displaying some evidence for unusual three-photon absorption [57]. We have also made brief forays into the development of Ru-based photocatalysts for water splitting catalysts bearing phenylene ethynylene 'linkers' suitable for tethering proton reduction catalysts or surface immobilisation [125].

Interests in photo-induced charge transfer has led us to collaborate with Marder on unusual donor acceptor systems in which three-coordinate boron moieties serve as both π -donor (1,3-diethyl-1,3,2-benzodiazaborolyl, [C₆H₄-1,2-(NEt)₂B]) and π -acceptor (dimesitylboron, [B(mes)₂]) [84]. Photophysical studies and DFT calculations (CAM-B3LYP) show that the electron-donating effect of the benzodiazaborolyl group is between that of dimethylamino and methoxy groups, and reorganisation of the borolyl group in the S₁ state is thought responsible for the large Stokes shift (up to 9800 cm⁻¹) observed on emission.

We have extended our studies of thin-films and interests in the use of palladium-catalysed cross-coupling reactions with Li (Ningbo University) to develop layer-by-layer assembled multi-layer films of [PdCl₂(L)₂] (L = bridging bidentate ligand) immobilised on glass slides. These slides have been used as reservoirs of low concentrations (ca. 2.7 × 10⁻⁶ mol%) of catalytically active palladium in Suzuki and Heck reactions [99]. With the same group we have exploited our expertise in the preparation and surface coordination of gold nanoparticles to develop a simple colourmetric sensor for the insecticide pymetrozine, which can has been demonstrated in systems from tap and lake water to green teas and fruit juices with detection limits from ratiometric UV-vis absorption spectroscopy similar to that obtained from HPLC analysis [157]. We have also explored the use of chiral salen- and salen-based metallomacrocycles as sensors enabling the enantiorecognition of chiral bio-relevant guests with Cui (Shanghai Jiao Tong University) [149].

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Summary and Conclusion

The work presented here is derived from studies carried out in the Low group laboratory in the Universities of Durham (1999 – 2013) and Western Australia (2013 – present). These independent investigations have been largely concerned with the synthesis of linearly and cross-conjugated organic and organometallic compounds, and studies of the distribution and transfer of charge within and through these species as mixed-valence compounds in solution, and in molecular junctions. These interests have led to more general interests in molecular materials, particularly triarylamine-based hole-transport materials and emissive heavy-metal complexes, and surface chemistry, particularly the molecule-surface interface. These studies are characterised by the concerted application of bespoke molecular synthesis, and associated developments of novel synthetic strategies, combined with spectroscopic, spectroelectrochemical and computational methods to arrive at a comprehensive description of electronic structure and function.

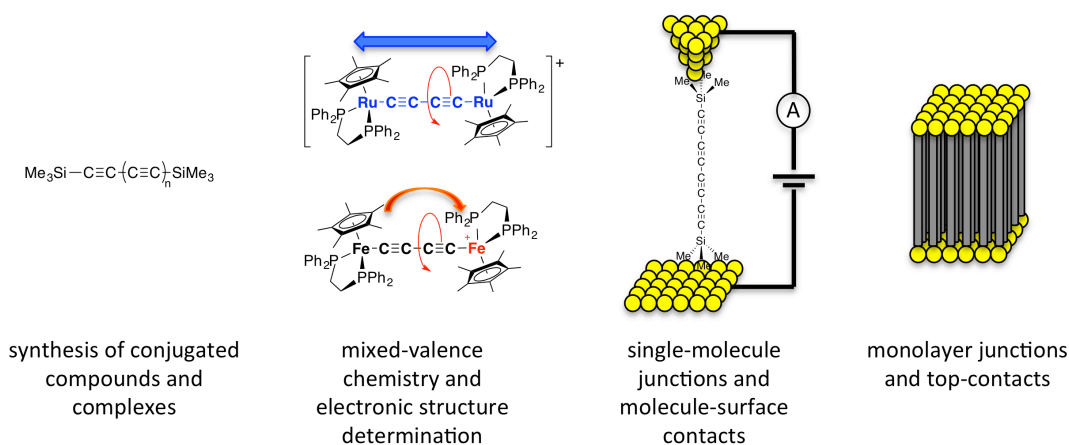


Figure 35 An overview of the principal themes of this Thesis.

Several recurring themes emerge from the body of work, principally the study of electron transfer through polyynyl-based structures, which exemplify links across the broad body of work from synthesis to mixed-valence chemistry and intramolecular electron transfer studies to through molecule conductance in molecular junctions (**Figure 35**). Thus, early work identifying the ‘delocalised’ or Class III mixed-valence character of ‘all-carbon’ bridged ruthenium complexes $[\text{Cp}'(\text{PP})\text{Ru}\{\mu\text{-}\{\text{C}\equiv\text{C}\}_n\}\{\text{Ru}(\text{PP})\text{Cp}'\}]^+$ has evolved to the use of spectroelectrochemical and computational methods for the identification and description of these systems in terms of a distribution of conformers. These conformers convolute the appearance of the Hush-style IVCT band, hampering the application of the methods of analysis drawn from the two-state model. Computational approaches in concert with UV-vis-NIR and IR data drawn from spectroelectrochemical studies have been developed to address these issues. The iron compounds $[\text{Cp}'(\text{dppe})\text{Fe}\{\mu\text{-}\text{C}\equiv\text{C}\text{C}\equiv\text{C}\}\{\text{Fe}(\text{dppe})\text{Cp}'\}]^+$, which offer more compact 3d orbitals that do not mix extensively with the buta-1,3-diyndiyl π -system, previously described as fully delocalised compounds (Class III), have been re-assigned with localised electronic structures (Class II) on the basis of IR data supported by local-hybrid DFT calculations. This work illustrates the essential role that

the choice of metal as well as bridging ligand plays in the determination of mixed-valence character in $[\{L_nM\}\text{-bridge-}\{ML_n\}]^+$ compounds. The bis(trimethylsilyl) polyynes are capable of contacting to gold electrodes to give single molecule molecular junctions, which have proven to be exceptional test objects for solvent effects in molecular electronics. By sequentially and selectively removing the trimethylsilyl protecting groups, ‘all-carbon’ self-assembled thin-film molecular junctions Au|C₈|Au can be constructed, allowing the conductivity of this linear carbon fragment to be studied directly for the first time.

The past 20-or so years of work with all-carbon ligands, polyynes and allied areas have been immensely rewarding, both personally and professionally. The results and methodologies developed, and the collaborative teams assembled, will hopefully continue to contribute to further study in these areas, and inspire new activity in molecular materials science. For example the recent predictions of design strategies for cumulated carbon chain compounds with unusual chiral helical orbital structures,¹⁵ building on the conformer dependent electronic structures derived from our mixed-valence studies with all-carbon ligands, suggest a fascinating new avenue concerning the coherent electron transport properties of such systems. Similarly, the identification of polyyne-based molecular thermoelectric materials¹⁶ as an exemplary ‘more than more Moore’ target for molecular electronic research prompts interest in the construction of thermal management and heat recovery devices. Such ideas are given further impetus given our demonstrations of methods to create large area thin film devices from these carbon fragments. Wherever such ideas might ultimately lead, the work carried out to date gives us confidence that future activity in the area of all-carbon and carbon-rich compounds will continue to be rewarding for those fortunate enough to be given the opportunity to explore.

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