STUDIES OF HEXAARYL[3]RADIALENE LIGANDS: SYNTHESIS, COORDINATION CHEMISTRY AND ANION INTERACTIONS

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Declaration

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Courtney A. Hollis
18th June 2013

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Abbreviations

$\sum_{vdw}$	sum of the van der Waals radii
bpy	4,4’-bipyridine
n-BuLi	n-butyllithium
Cp	cyclopentadiene
Cp*	pentamethyl-cyclopentadiene
CSD	Cambridge Structural Database
DCM	dichloromethane
DFT	density functional theory
dppe	1,2-bis(diphenylphosphino)ethane
DMF	N,N’-dimethylformamide
DMSO	dimethylsulfoxide
EI-MS	electron impact mass spectroscopy
en	1,2-ethylenediamine
ESI-HRMS	electrospray ionisation high resolution mass spectrometry
ESI-MS	electrospray ionisation mass spectrometry
EtOAc	ethyl acetate
EtOH	ethanol
h	hour/s
HAT	1,4,5,8,9,12-hexaazatriphenylene
HOMO	highest occupied molecular orbital
IR	infrared
LUMO	lowest unoccupied molecular orbital
M	molar
MeOH	methanol
min	minutes
NCE	normalised collision energy
NDI	napthalenediimide
NMR	nuclear magnetic resonance
ppm	parts per million
Q_{zz}	quadropole moment along the z-axis
RCSR	Reticular Chemistry Structure Resource
tccp	tetrachlorocyclopropene
TEBB	1,3,5-tris(4-ethynylbenzonitrile)benzene
THF	tetrahydrofuran
TLC	thin layer chromatography
UV-Vis	ultra violet-visible

Abstract

This thesis describes the synthesis and study of three nitrile substituted hexaaaryl[3]radialene ligands, two of which are new compounds, and three new flexible bis-pyridyl ligands produced as precursors in the attempted synthesis of extended hexaaryl[3]radialenes. The coordination and metallo-supramolecular chemistry of these compounds were investigated with a variety of different metal atoms, primarily silver(I) and copper(I) due to the nature of the soft nitrile donors. Five different coordination modes were observed for hexakis(4-cyanophenyl)[3]radialene with silver(I) and copper(I) including bidentate, tetradentate, and also the first example of this compound acting as a hexadentate ligand. The flexible bis-pyridyl ligands were observed to form predominantly 1-D coordination polymers but also on occasion led to the production of 2-D networks.

Mononuclear ruthenium(II) complexes of hexakis(4-cyanophenyl)[3]radialene and hexakis(3-cyanophenyl)[3]radialene are also described, although di- and tri-nuclear complexes were unable to be obtained and thus the nature of any metal-metal interactions within such complexes were unable to be examined. Visible absorption and fluorescence spectroscopy, as well as cyclic voltammetry, were used to examine the properties of the mononuclear radialene complexes as well as dinuclear ruthenium(II) complexes of the [3]radialene precursors 4,4’-dicyanodiphenylmethane and 3,3’-dicyanodiphenylmethane.

Close contacts between anions and the [3]radialene core were first observed in solid-state structures of hexakis(4-cyanophenyl)[3]radialene and silver(I). In order to determine whether these interactions were predominately due to anion-hydrogen bonding, or whether anion-π interactions with the [3]radialene core were also involved, a three pronged study involving computational, mass spectrometric, and X-ray crystallographic techniques was undertaken. The combined evidence from each of these methods provides a strong case for the existence of anion-π interactions between anions and the [3]radialene core in both the gas phase and the solid-state.

In conjunction with infrared spectroscopy and elemental analysis, X-ray crystallography was used to characterise the majority of metal complexes and coordination polymers produced during the course of this work. The crystal structures of six precursor compounds or ligands and 25 complexes are described.