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Iminophosphine ligands and their metal binding properties

A thesis presented in partial fulfilment of the requirements for the degree of

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In

Chemistry

At Massey University, Palmerston North
New Zealand

Kurt Allen McBeth
2003
Abstract

This work focuses on the complexes of two iminophosphine ligands, N-(2-diphenylphosphinobenzylidine)-aniline (NP) and N-(2-diphenylphosphinobenzylidine)-4'-(benzo-15-crown-5) (O₅NP), and their complexes with Cu(I), Ag(I), Au(I), Cr(0), Mo(0) and W(0). The cation binding properties of the complexes of O₅NP have been investigated.

Chapter One describes the aims of this work and also provides a brief introduction to ligands containing phosphorus and nitrogen donor atoms as well as crown ethers and their inclusion in transition metal complexes. The analytical technique of electrospray mass spectroscopy (ESMS) is introduced and its use in the study of cation binding to crown ethers and cryptands discussed.

Chapter Two looks at the Cu(I), Ag(I) and Au(I) complexes of NP and O₅NP, such as [M(L)₂][PF₆] (M = Cu, Ag, Au; L = NP, O₅NP), [M(NP)X]₂, [M(O₅NP)Cl]₂ (M = Cu, Ag), Au(NP)X and Au(O₅NP)Cl (X = Cl, Br, I). Reported in this chapter are the X-ray structural analyses of O₅NP, [Cu(NP)₂][PF₆], [Ag(NP)₂][PF₆], [Au(NP)₂][PF₆], [Cu(NP)Br]₂, Au(NP)Cl and Au(NP)Br. Far and Near IR, ¹H and ³¹P NMR and ESMS were used to investigate the nature of the complexes. The [M(L)₂][PF₆] complexes displayed a clear trend in which the number of coordinated imines decreased as the soft nature of the metal centre increased. Both the Far IR and crystal structure analyses showed the Cu(I) and Ag(I) halo complexes to be dimeric with bridging halides and the
Au(I) halo complexes to be monomeric with terminal halides. The $^{31}$P NMR signal was found to be dependent on the mass of the metal centre.

In Chapter Three the Cr(0), Mo(0) and W(0) carbonyl complexes of NP and O$_5$NP are discussed. To characterise the complexes, IR, ESMS and $^1$H, $^{31}$P and $^{13}$C NMR techniques were employed. X-ray structural analyses of Mo(CO)$_4$(NP) and Mo(CO)$_4$(O$_5$NP) were also used. It was found that the metal centres had an octahedral geometry with the ligands being bidentate via the P and N atoms and having a cis conformation. Upon coordination, the $^1$H NMR signal of the imine proton moves to lower frequencies, whereas the $^{31}$P NMR signal moves to higher frequencies. It was also demonstrated that the presence of the crown ether has no significant effect on the structure of the metal centre.

Cation binding to the complexes of O$_5$NP, the free ligand, and starting material, 4'-aminobenzo-15-crown-5 (O$_5$NH$_2$), is discussed in Chapter Four. Electrospray mass spectroscopy (ESMS) was used as a qualitative measure of the relative cation binding strengths. The X-ray structural analyses of the inclusion complexes W(CO)$_4$(O$_5$NP)Na(PF$_6$) and [Cu(O$_5$NP)$_2$]K[PF$_6$]$_2$ were determined, and provided information on the coordination of alkali cations by these complexes. W(CO)$_4$(O$_5$NP) binds Na$^+$ within the cavity of the benzo-15-crown-5 moiety which experiences significant change to its conformation. [Cu(O$_5$NP)$_2$][PF$_6$] binds K$^+$ in a sandwich formation suggesting that rotation of the ligands occurs about the Cu(I) centre. The starting material, O$_5$NH$_2$, and free ligand, O$_5$NP, were selective towards K$^+$, forming a 1:1 species. The complexes M(CO)$_4$(O$_5$NP) (M = Cr, Mo, W) and [M(O$_5$NP)$_2$][PF$_6$] (M = Cu, Ag, Au) were selective towards Na$^+$ and K$^+$ respectively with a 1:1 formation. The halide complexes, [Cu(O$_5$NP)Cl]$_2$, [Ag(O$_5$NP)Cl]$_2$ and Au(O$_5$NP)Cl, displayed different selectivities from each other. Both [Cu(O$_5$NP)Cl]$_2$ and [Ag(O$_5$NP)Cl]$_2$ dissociated in solution to give the monomers which selectively bound Li$^+$ and K$^+$ respectively in a 1:1 species. The Au(O$_5$NP)Cl complex was selective towards Na$^+$. 
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Abbreviations.

NP \quad N-(2-diphenylphosphinobenzylidine)-aniline
O_{5}NP \quad N-(2-diphenylphosphinobenzylidine)-4'-(benzo-15-crown-5)
2PCHO \quad 2-(diphenylphosphino)benzaldehyde.
ArNH_{2} \quad Aniline.
O_{2}NH_{2} \quad 4'-aminobenzo-15-crown-5.
Ph_{2}Ppy \quad 2-(diphenylphosphino)pyridine
NBD \quad 2,5-norbornadiene.
Pip \quad Piperidine.
Ph \quad Phenyl
Bz \quad Benzo group
Cy \quad Cyclohexyl
Me \quad Methyl
L \quad Ligand (chemical), Litre (measurement)
IR \quad Infrared
NMR \quad Nuclear magnetic resonance
ESMS \quad Electrospray mass spectrometry
FAB+ \quad Fast atom bombardment, positive mode
\delta \quad Chemical shift in ppm.
ppm \quad Parts per million
Hz \quad Hertz.
J_{xY}^{X} \quad Coupling constant over \chi bonds between atoms X and Y.
s \quad Singlet (spectral)
d \quad Doublet (spectral)
t \quad Triplet (spectral)
sep \quad Septuplet (spectral)
m \quad Multiplet (spectral)
\nu(X-Y) \quad Stretching frequency of X-Y bond.
m/z \quad Mass per charge.
ORTFEP The computer program used to produce illustrations of X-ray crystallography structural analyses.
MLCT Metal to ligand charge transfer
<table>
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