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Iminophosphine ligands and their metal binding properties

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

Master of Science

In

Chemistry

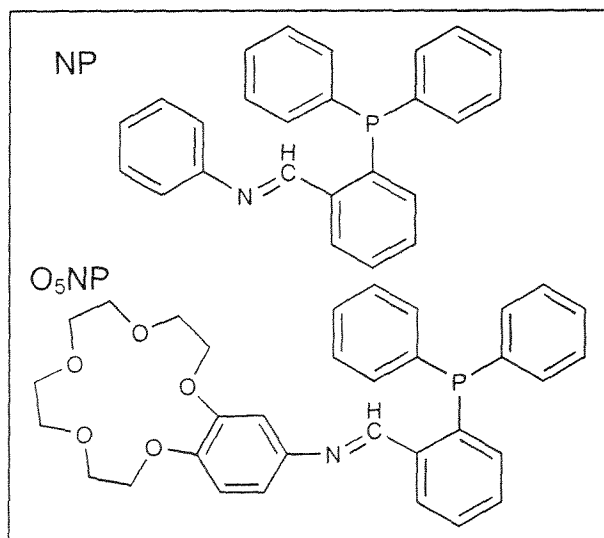
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Kurt Allen McBeth

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Abstract

This work focuses on the complexes of two iminophosphine ligands, *N*-(2-diphenylphosphinobenzylidene)-aniline (NP) and *N*-(2-diphenylphosphinobenzylidene)-4'-(benzo-15-crown-5) (O_5NP), 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 O_5NP 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 O_5NP , such as $[M(L)_2][PF_6]$ ($M = Cu, Ag, Au$; $L = NP, O_5NP$), $[M(NP)X]_2$, $[M(O_5NP)Cl]_2$ ($M = Cu, Ag$), $Au(NP)X$ and $Au(O_5NP)Cl$ ($X = Cl, Br, I$). Reported in this chapter are the X-ray structural analyses of O_5NP , $[Cu(NP)_2][PF_6]$, $[Ag(NP)_2][PF_6]$, $[Au(NP)_2][PF_6]$, $[Cu(NP)Br]_2$, $Au(NP)Cl$ and $Au(NP)Br$. Far and Near IR, 1H and ^{31}P NMR and ESMS were used to investigate the nature of the complexes. The $[M(L)_2][PF_6]$ 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_5NP are discussed. To characterise the complexes, IR, ESMS and ^1H , ^{31}P and ^{13}C NMR techniques were employed. X-ray structural analyses of $\text{Mo}(\text{CO})_4(\text{NP})$ and $\text{Mo}(\text{CO})_4(\text{O}_5\text{NP})$ 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 ^1H 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_5NP , the free ligand, and starting material, 4'-aminobenzo-15-crown-5 (O_5NH_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 $\text{W}(\text{CO})_4(\text{O}_5\text{NP})\text{Na}(\text{PF}_6)$ and $[\text{Cu}(\text{O}_5\text{NP})_2]\text{K}[\text{PF}_6]_2$ were determined, and provided information on the coordination of alkali cations by these complexes. $\text{W}(\text{CO})_4(\text{O}_5\text{NP})$ binds Na^+ within the cavity of the benzo-15-crown-5 moiety which experiences significant change to its conformation. $[\text{Cu}(\text{O}_5\text{NP})_2][\text{PF}_6]$ binds K^+ in a sandwich formation suggesting that rotation of the ligands occurs about the Cu(I) centre. The starting material, O_5NH_2 , and free ligand, O_5NP , were selective towards K^+ , forming a 1:1 species. The complexes $\text{M}(\text{CO})_4(\text{O}_5\text{NP})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[\text{M}(\text{O}_5\text{NP})_2][\text{PF}_6]$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) were selective towards Na^+ and K^+ respectively with a 1:1 formation. The halide complexes, $[\text{Cu}(\text{O}_5\text{NP})\text{Cl}]_2$, $[\text{Ag}(\text{O}_5\text{NP})\text{Cl}]_2$ and $\text{Au}(\text{O}_5\text{NP})\text{Cl}$, displayed different selectivities from each other. Both $[\text{Cu}(\text{O}_5\text{NP})\text{Cl}]_2$ and $[\text{Ag}(\text{O}_5\text{NP})\text{Cl}]_2$ dissociated in solution to give the monomers which selectively bound Li^+ and K^+ respectively in a 1:1 species. The $\text{Au}(\text{O}_5\text{NP})\text{Cl}$ complex was selective towards Na^+ .

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Abbreviations.

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

LLCT	Ligand to ligand charge transfer
logK	Formation constants
E_f	Redox potential
ΔE	Change in redox potential
$CDCl_3$	Deuterated chloroform
CD_3CN	Deuterated acetonitrile
TMS	Tetramethylsilane
RT	Room temperature
FW	Formula weight
μ	Gyromagnetic constant
$U(eq)$	Displacement parameters
g	Grams
mg	Milligrams
mmol	Millimoles
ml	Millilitres
h	Hours
$molL^{-1}$	Moles per litre