Synthesis, Structure and Reactivity of the Later Transition Metal Complexes Containing a Multidentate Phosphorus-Nitrogen Hybrid Ligand

A dissertation presented in partial fulfilment of the requirements for the degree of
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Steven Michael Fornara Kennedy

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For Tracey

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Steven Kennedy
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Errata

Piii, line 5; pxiii, line 17 and -6; diphenylphosphino not diphenylphoshino
P4, line 3, metal's not metals
P6, line -5, nucleophilic not nucleophile
P10, Figure 1.8, complex should have a 1+ charge
P13, line 9, 'PN$_2$' ligand not ligand 'P$_2$N'
rcf 28, Wiley not Wily
P14, delete ref 29 (it is on the previous page)
P25, line -6, carried out not carried
P29, line -6, dependent not dependant
P31, line -6, has not as
P33, line 2, en route not on route
line 11, the molybdenum not molybdenum
P34, line 9, the π not the a π
line 14, from heating not from the heating
line -8 and elsewhere, methyl iodide or iodomethane not methyliodide
line -4, dication not diction
P36, line -3, delete "and"
P38, line -10, arbitrarily not arbitrary
P43, line 1, 2.2.3.2 not 2.2.2.2
P45/73/119/124/129/134/169, Table 2.4/3.1/4.1/4.3/4.5/4.7/4.8/5.1, delete "Completeness to theta = 0.50° ... 0.0%"
P47, first para, line 9, section 2.2.2 not 2.2.9
ref 14 and elsewhere, Thornton-Pett not Thorton-Pett
P48, line -10; p173, line -6: from not form
line -2, 2.4.5 not 2.2.8
P51, line 1; p126, line 10: ligand's not ligands
P55, line 9; p57, line 11; p87, last line: latter not later
P55, references: titles of books should be italicised
P56, Table 2.9, fourth entry under ν(P-C) should be 1090 not 1890 cm^{-1}
P57, line -3, cuvette not curvette
P62, line 2, trifluoroacetic not uifuroacetic
P68, line 12; p164, line -11: delete "the"
line -5, previously not previuosly
P69, line 13, "A least squares difference map..." not "A least differencc map..."
P70, delete lines 6 through 10 and "found in the title complex." of line 11
P73, Table 3.1, *mer*-[W(CO)$_3${PN(H)CHP-κ^2P,P-$\eta^2(N{=}C)$}]BF$_4$•2CH$_2$Cl$_2$ not , *mer*-[W(CO)$_3${PN(H)CHP-κ^2P,P-$\eta^2(N{=}C)$}]BF$_4$
Table 3.1, "Reflections collected...21461" not "Reflections collected...9391"
Table 3.1, R(int) = 0.0192 not R(int) = 0.0000
P79, line -1, delete "in"
P81, heading; p89, line 14: ...CHP... not ...CP...
P81, line 4, quaternised not quarternarised
P86, and elsewhere: *ca* not c.a.
P89, and elsewhere δ 66 not δ66
P93, line -6, replace "band splitting in the solid state" with "a ν(^{13}C-O) stretch"
P98, Table 3.10; p148, Table 4.12 "-" (minus) not "•"
P99, line 1, "...D$_2$,^{33} that is..." not "...D$_2$.^{33} That is ..."
P99, line 7; p105, line -10: CF$_3$SO$_3$H not CF$_3$SO$_2$H
P101, line 8, > 90% not < 90%
line -8, itself not its self
P104/105, Tables 3.9/3.10/3.11 are incorrectly referred to --should be 3.8/3.9/3.10 respectively
P107, ref 1, Inorganic not Iinorganic
line -3, readily not readly
P113, line 3, BF$_4^-$ not BF4$^-$
P115, line -4, being unable not unable
P121, line -8, triphenylphosphane not triphenylphosphino
line -4, ligand not ligands
P126, line 4, complex's not complexes
P132, line 14, basal plane not basal
line -8, previous not previuos
line -2, mirror plane not two-fold axis
P144, Table 4.10, all coupling constants are accurate only to the first decimal point
P149, line 5, phenanthroline not phenantroline
P150, line 11, 0.401 mmol not 401 mmol
P155, line 5, 0.164 g not 164 g
P158, line 8, than not then
P160, ref 116, C. Hahn not Hahn
P162, The complexes/ligands F.5.2-* refer to Figure 5.2 on the same page only
P163 The complexes/liugands F.5.2-* refer to Figure 5.2 on the same page only
P166, line -1, nucleophilicity not nucleophilcity
P168, line 4, two-fold axis not mirror plane
P174, Table legend, to be assigned not to assigned
P177, Table legend, delete legend
line -6 to -5, chloride ligand not chloride atom
P179, line -5, Schlenk not Schlenck
P181, ref 11 should be ref 1, 1982-1994
P185, line 4, replace "asymmetric unit" with "unit cell"
P187, line -2, Peak not Peck
P205 line 4, mixtures not solutions
P207, line 12, Merck not Merk

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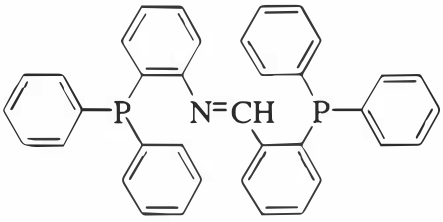
Abstract

Chapter 1 - This first part of the chapter aims to give the reader a flavour of the chemistry concerning phosphorus-nitrogen hybrid ligands containing both phosphorus and nitrogen donor atoms. This will be achieved by highlighting selected relevant examples from the literature. The second part will introduce the ligand 2-(diphenylphosphino)-N-[2-(diphenylphoshino)benzylidene]benzeneamine, (PNCHP), which is the subject of Chapters 2 through 6.



PNCHP

Chapter 2 - The ligand PNCHP reacts with [Mo(CO)$_3$(1,3,5-cycloheptatriene)] to give the complex *fac*-[Mo(CO)$_3$(PNCHP-κ^3*P,N,P*)] which readily isomerises to *mer*-[Mo(CO)$_3$(PNCHP-κ^3*P,N,P*)]. Kinetic studies on the isomerisation in acetone yielded the first-order forward rate constants (k_1) 1.22×10^{-5}, 4.18×10^{-5}, 1.72×10^{-4} and 4.89×10^{-4} s^{-1} at 19.5, 29.7, 40.0 and 49.5 °C respectively, with thermodynamic activation parameters $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ of 95 kJ mol^{-1} and –14.1 J mol^{-1} K^{-1} respectively. The related complex *fac*-[Mo(CO)$_3$(PNHCH$_2$P-κ^3*P,N,P*)] (PNHCH$_2$P = 2-(diphenylphosphino)-N-[(2-diphenylphosphino)benzyl]benzeneamine does not undergo isomerisation. The complex *cis*-[Cr(CO)$_4$(PNCHP-κ^2*N,P*)] reacts with sulfur to give *cis*-[Cr(CO)$_4$(SPNCHP-κ^2*N,P*)] and reacts with methyliodide under an atmosphere of carbon monoxide to yield the anion [Cr(CO)$_5$I]$^-$.

Chapter 3 - The complexes [M(CO)$_3$(PNCHP-κ^3*P,N,P*)] (M = Cr, Mo or W), containing a terdentate PNCHP ligand, react with H$^+$ to give the protonated products [M(CO)$_3${PN(H)CHP-κ^2*P,P*-η^2(*C*=*N*)}]$^+$, where the imino group has 'slipped' from a κ^1*N* to a η^2(*C*=*N*) coordination mode as a result of the protonation of the nitrogen atom. When

the acid is HCl the above cation [M(CO)$_3${PN(H)CHP-κ^2*P*,*P*-η^2(*C*=*N*)}]$^+$ (M = Mo or W) converts to *cis*-[M(CO)$_2$Cl$_2$(PNHCH$_2$P-κ^3*P*,*N*,*P*)]. In this unusual reaction the imine group of the PNCHP ligand has been reduced to an amine concurrently with the two electron oxidation of the metal. In contrast, on reaction of *cis*-[Cr(CO)$_4$(PNCHP-κ^2*N*,*P*)] with H$^+$, the bidentate PNCHP ligand dissociates from the metal resulting in cyclisation of the ligand to give a phosphonium salt.

Chapter 4 - PNCHP favours terdentate coordination with Pd(II) and Pt(II). The complexes [MCl(PNCHP-κ^3*P*,*N*,*P*)]Cl and [Pd(CH$_3$)(PNCHP-κ^3*P*,*N*,*P*)]Cl are synthesised starting with [MCl$_2$(1,5-cyclooctadiene)] and [M(CH$_3$)Cl(1,5-cyclooctadiene)], respectively. The ionic chlorides can be exchanged with BF$_4^-$ using AgBF$_4$. Abstraction of the covalent chloride with AgBF$_4$ in the presence of acetonitrile yields [Pt(CH$_3$CN)(PNCHP-κ^3*P*,*N*,*P*)]$^{2+}$. The acetonitrile ligand of this dication can be substituted with triphenylphosphane, 2-picoline, or 3-picoline. The reaction of [Pt(CH$_3$CN)(PNCHP-κ^3*P*,*N*,*P*)]$^{2+}$ with 1,10-phenanthroline, 2,2'-bipyridine, bis(diphenylphosphino)ethane or 2,2':6',2''-terpyridine (L-L) yields complexes of the type [Pt(L-L)(PNCHP-κ^3*P*,*N*,*P*)]$^{2+}$ - the first five-coordinate platinum(II) dications.

Chapter 5 - The complex [RhCl(PNCHP-κ^3*P*,*N*,*P*)] is synthesised by reacting the PNCHP ligand with 0.5 equivalents of [{RhCl(1,5-cyclooctadiene)}$_2$]. This extremely reactive compound undergoes oxidative addition of dichloromethane and chloroform to yield complexes of the type [RhCl$_2$(R)(PNCHP-κ^3*P*,*N*,*P*)] (R = CH$_2$Cl or CDCl$_2$). Addition of carbon monoxide to [RhCl(PNCHP-κ^3*P*,*N*,*P*)] results in the adduct [RhCl(CO)(PNCHP-κ^3*P*,*N*,*P*)] which is in equilibrium with square planar complex [Rh(CO)(PNCHP-κ^3*P*,*N*,*P*)]Cl. The coordinated chloride ligand of [RhCl(PNCHP-κ^3*P*,*N*,*P*)] can be substituted with tetrahydrofuran, acetonitrile or triphenylphosphane.

Chapter 6 - The triosmium clusters [Os$_3$(CO)$_{11}$(CH$_3$CN)] and [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] react with PNCHP to give [{Os$_3$(CO)$_{11}$}$_2$(PNCHP-κ^2*P*,*P*)] (containing PNCHP bridging equatorially two osmium triangles), two coordination isomers of [Os$_3$(CO)$_{11}$(PNCHP-κ^1*P*)] and 1,1-[Os$_3$(CO)$_{10}$(PNCHP-κ^2*P*,*P*)], respectively. When 1,1-[Os$_3$(CO)$_{10}$(PNCHP-κ^2*P*,*P*)] is reacted with one equivalent of trimethylamineoxide the major product is [Os$_3$(μ-

$H)(CO)_7(\mu_3$-PNCP)], in which the imine hydrogen of PNCHP has migrated to the osmium cluster and PNCP is left to act as a triply bridging nine-electron donor. Two geometrical isomers of [$Os_3(\mu$-$H)(CO)_8(\mu_2$-PNCP)] are found as minor products, with PNCP acting as a doubly bridging seven-electron donor ligand.

Table of Contents

Abbreviations

Ar	aryl
CHT	1,3,7-cycloheptatriene
COD	1,5-cyclooctadiene
CP/MAS	cross polarisation/magic angle spinning
dec	decomposition
diphos	1,2-bis(diphenylphosphino)ethane
Et	ethyl
Hz	hertz
IR	Infrared
${}^{X}J$	coupling constant over X bonds (Hz)
M^+	molecular ion
Me	methyl
MeCN	acetonitrile
M.p.	melting point
m/z	mass to charge ratio
NMR	nuclear magnetic resonance
PNCHP	2-(diphenylphosphino)-N-[2-(diphenylphoshino)benzylidene]-benzeneamine
$PNHCH_2P$	2-(diphenylphosphino)-N-[(2-diphenylphosphino)benzyl]-benzeneamine
2-pico	2-picoline
3-pico	3-picoline
Ph	phenyl
phen	1,10-phenanthroline
ppm	parts per million
SPNCHP	2-(diphenylphosphinothioyl)-N-[2-(diphenylphoshino)-benzylidene]-benzeneamine
terpy	2,2':6',2''-terpyridine
THF	tetrahydrofuran
tlc	thin layer chromatography
UV-vis	ultraviolet-visible

δ	chemical shift in ppm
$\nu(XY)$	stretching frequency of X-Y bond (cm^{-1})]