Synthesis, Structure and Relative Hydrolytic Stability of *cis*-$[PtCl_2L]$ and *cis*-$[W(CO)_4L]$ where L is the Bidentate Triaminophosphine Ligand $[MeNCH_2CH_2N(Me)PN(Me)CH_2]_2$*

John Powell, Alan Lough and Michael Raso
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 1A1, Canada

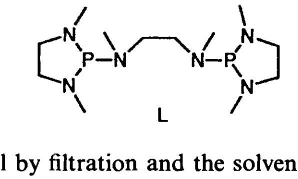
The ligand $MeNCH_2CH_2N(Me)PN(Me)CH_2CH_2N(Me)PN(Me)CH_2CH_2NMe$ (L) reacted with $[\{Pt(C_2H_4)Cl_2\}_2]$ to give a mixture of *cis*-$[PtCl_2L]$ and *trans*-$[\{PtCl_2(\mu\text{-}L)\}_2]$ and with $[W(CO)_4(nbd)]$ (nbd = norbornadiene) to give *cis*-$[W(CO)_4L]$ and $[\{W(CO)_4(\mu\text{-}L)\}_n]$ (n = 2–4). The ligand L and $[W(CO)_4L]$ are readily hydrolysed to give HPO_3^{2-}, $2MeNHCH_2CH_2NH_2Me^+$ and $MeNHCH_2CH_2NHMe$. In contrast the complex $[PtCl_2L]$ is considerably more resistant to ligand hydrolysis. The molecular structures of *cis*-$[PtCl_2L]$, *cis*-$[W(CO)_4L]$ and $[W(CO)_4(MeNHCH_2CH_2NHMe)]$ {a hydrolysis product of the reaction of $[W(CO)_4L]$ with water} have been determined by single-crystal X-ray diffraction studies. Crystal data (all monoclinic): *cis*-$[PtCl_2L]$, space group *Cc*, a = 17.986(2), b = 9.286(1), c = 12.059(1) Å, β = 91.07(1)°, Z = 4, R = 0.024 (R' = 0.028); *cis*-[W(CO)L], space group *Pn*, a = 15.611(3), b = 8.437(2), c = 27.604(6), β = 99.78(3)°, Z = 6, R = 0.036 (R' = 0.039); $[W(CO)_4(MeNHCH_2CH_2NHMe)]$, space group *C2/c*, a = 22.960(2), b = 7.456(1), c = 14.039(1) Å, β = 106.60(1)°, Z = 8, R = 0.040 (R' = 0.045).

Metal complexes of chelating bidentate tertiary phosphine ligands have been extensively studied for the last 25 years. Recently several groups have turned their attention to the chemical properties of metal complexes of bi- and multi-dentate phosphite ligands.[1–3] There is however very little published work relating to complexes of corresponding bidentate triaminophosphine ligands. This may be, in part, because of the known susceptibility of the P–N bond to undergo hydrolysis.[4] In this paper we report the synthesis of the bidentate triaminophosphine ligand $[MeNCH_2CH_2N(Me)PN(Me)CH_2]_2$ (L) and the synthesis and structures of the complexes $[PtCl_2L]$ and $[W(CO)_4L]$. Whilst free L and co-ordinated L in $[W(CO)_4L]$ are easily hydrolysed, the complex $[PtCl_2L]$ is considerably more resistant to ligand hydrolysis.

Results and Discussion

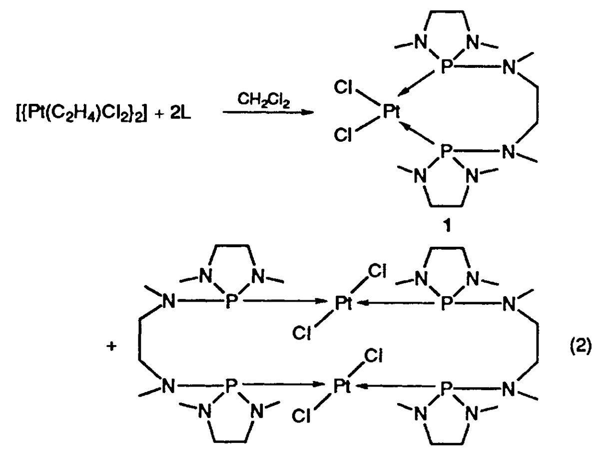
The compound L was obtained from the reaction of PCl_3 with *N,N'*-dimethylethane-1,2-diamine in dry benzene in the presence of triethylamine [equation (1)]. Removal of $[NEt_3H]Cl$ by filtration and the solvent *in vacuo* gave L as a white crystalline solid which was used in subsequent reactions without further purification.

$$2\,PCl_3 + 6\,MeNHCH_2CH_2NHMe + 6\,NEt_3 \longrightarrow$$



L + $6[NEt_3H]Cl$ (1)

The platinum compound *cis*-$[PtCl_2L]$ **1** was obtained from the addition of L to the stoichiometrically required amount of $[\{Pt(C_2H_4)Cl_2\}_2]$ [equation (2)]. Monitoring of the crude reaction product, which was pale yellow, by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy indicated the presence of *cis*-$[PtCl_2L]$ **1** [$\delta(^{31}P)$ 64.6, $^1J(^{195}Pt\text{-}^{31}P)$ 4967 Hz] and a second complex which is probably the *trans*-dimeric complex $[Cl_2Pt(\mu\text{-}L)_2PtCl_2]$ **2** [$\delta(^{31}P)$ 21.3, $^1J(^{195}Pt\text{-}^{31}P)$ 2432 Hz]. On standing in polar solvents **2** isomerizes to the monomeric complex **1** which recrystallizes from dichloromethane as white prisms.



1

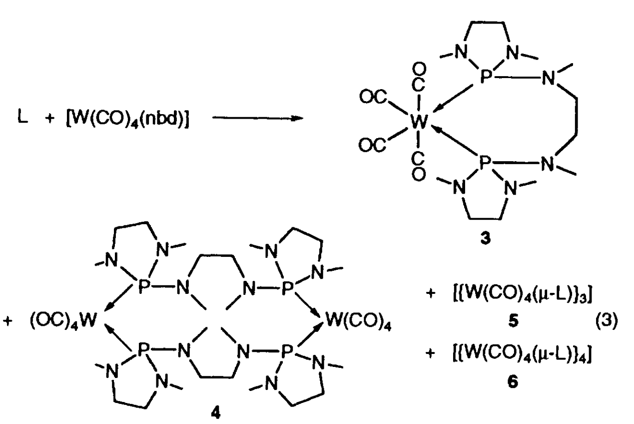
2

(2)

The tungsten complex $[W(CO)_4L]$ **3** was obtained by treating L with $[W(CO)_4(nbd)]$ (nbd = norbornadiene) in refluxing benzene for 48 h [equation (3)]. The infrared spectrum in the ν(CO) region of the crude product is consistent with the formulation $[W(CO)_4L]$. No absorptions associated with tri- or penta-carbonyl species were observed. However the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the crude product shows the presence of **3** as the major product (*ca.* 75%) together with three minor products (*ca.* 8% each) tentatively assigned as $[\{W(CO)_4L\}_n]$ (n = 2 **4**; 3 **5**; or 4 **6**) in which L functions as a bridging ligand. The complex *cis*-$[W(CO)_4L]$ was obtained as yellow prisms on recrystallization from CH_2Cl_2.

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



The molecular structure of $[PtCl_2L]$ **1** as determined by single-crystal X-ray diffraction is shown in Fig. 1. Bond lengths and angles are listed in Table 1. As expected the immediate co-ordination geometries of the Pt atom and the six nitrogen atoms are close to planar with very slight deviations from planarity occurring for five of the six N atoms. The sum of the C–N–C and C–N–P angles varies from 346° for N(5) to 358° for N(1). Atom N(5) lies almost in the $PtCl_2P_2$ plane and the $C_2N_2P_2Pt$ ring adopts a distorted boat configuration.

The molecular structure of $[W(CO)_4L]$ as determined by single-crystal X-ray diffraction is shown in Fig. 2. There are three molecules in the asymmetric unit. Bond lengths and angles for molecule A are given in Table 2. Molecules B and C have similar geometries. The complex exhibits the anticipated octahedral geometry at tungsten whilst the nitrogen atoms of the L ligand exhibit slight distortions from planar geometry. The sum of angles C–N–C and C–N–P varies from 349° for N(2) to 360° for N(6). The $C_2N_2P_2W$ ring adopts a distorted chair configuration.

A question of concern with respect to pursuing further studies of the co-ordination chemistry of the triaminophosphine L was the relative stability/reactivity of its complexes to hydrolytic cleavage of the P–N bonds. A qualitative assessment of the hydrolytic stabilities of **2** and **3** has been obtained by monitoring the $^{31}P-\{^1H\}$ NMR spectra of these complexes in CH_2Cl_2–MeCN in the presence of a small amount of added water at 20 °C. Solutions were *ca.* 0.02 mol dm^{-3} in complex and water was added in a *ca.* 50-fold excess. The $^{31}P-\{^1H\}$ NMR spectrum of the initially formed platinum complex indicated the presence of *cis*-$[PtCl_2L]$ **1** as the major solution species together with the *trans* dimer **2**. Within 1 h the signal of the *trans* complex had disappeared and the only signal observable was that of the *cis* complex **1**. This observation is consistent with a *trans* dimer to *cis* monomer isomerization in the relatively polar CH_2Cl_2–MeCN–water medium. The resulting spectrum remained unchanged after 7 d at 20 °C indicating that no hydrolysis of the P–N bonds had taken place. In contrast the tungsten complex $[W(CO)_4L]$ **3** and the presumed oligomers **4**–**6** are hydrolytically unstable. A $^{31}P-\{^1H\}$ NMR study of a mixture of complexes **3**–**6** in CH_2Cl_2–MeCN–water at 20 °C shows that concurrent with the loss of the signals of these complexes a new signal assignable to a tungsten intermediate is observed at δ 101 with $J(^{183}W-^{31}P)$ = 280 Hz. This peak reaches a maximum intensity after *ca.* 2 h reaction time and then disappears. A plausible structure for this intermediate is the anionic complex $[W(CO)_4\{[Me\overline{NCH_2CH_2N(Me)P}O]_2H\}]^-$ **7** which is structurally analogous to the known compound $[NEt_3H][Mo(CO)_4\{(PPh_2O)_2H\}]$.[5] Throughout the reaction a peak at δ 4 grows in and represents the sole phosphorus-containing product at the end of the reaction. The chemical shift and the observed $J(^1H-^{31}P)$ of 558 Hz are consistent with this species being the expected hydrolysis product HPO_3^{2-}.[6] Upon completion of the reaction a yellow crystalline material had formed in the NMR tube. It was identified as $[W(CO)_4(MeNHCH_2CH_2NHMe)]$ **8** by single-crystal X-ray diffraction.

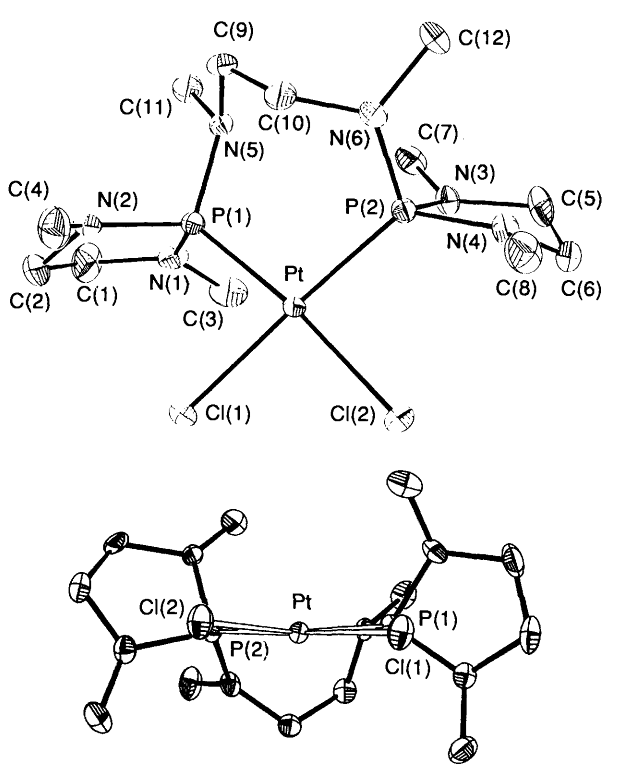


Fig. 1 Two views of the molecular structure of $[PtCl_2L]$ **1**

Table 1 Bond lengths (Å) and angles (°) for $[PtCl_2L]$ **1**

Pt–Cl(1)	2.378(3)	Pt–Cl(2)	2.365(3)
Pt–P(1)	2.230(3)	Pt–P(2)	2.228(3)
P(1)–N(1)	1.663(11)	P(1)–N(2)	1.680(11)
P(1)–N(5)	1.686(8)	P(2)–N(3)	1.685(11)
P(2)–N(4)	1.662(10)	P(2)–N(6)	1.654(12)
N(1)–C(1)	1.460(17)	N(1)–C(3)	1.419(17)
N(2)–C(2)	1.472(17)	N(2)–C(4)	1.438(17)
N(3)–C(5)	1.477(14)	N(3)–C(7)	1.413(16)
N(4)–C(6)	1.434(15)	N(4)–C(8)	1.455(17)
N(5)–C(9)	1.448(14)	N(5)–C(11)	1.468(14)
N(6)–C(10)	1.452(15)	N(6)–C(12)	1.465(17)
C(1)–C(2)	1.510(20)	C(5)–C(6)	1.499(18)
C(9)–C(10)	1.521(15)		
Cl(1)–Pt–Cl(2)	87.4(1)	Cl(1)–Pt–P(1)	85.0(1)
Cl(2)–Pt–P(1)	169.1(1)	Cl(1)–Pt–P(2)	177.0(1)
Cl(2)–Pt–P(2)	89.5(1)	P(1)–Pt–P(2)	98.0(1)
Pt–P(1)–N(1)	110.5(4)	Pt–P(1)–N(2)	120.2(4)
N(1)–P(1)–N(2)	94.4(5)	Pt–P(1)–N(5)	115.4(3)
N(1)–P(1)–N(5)	106.3(5)	N(2)–P(1)–N(5)	107.4(5)
Pt–P(2)–N(3)	114.3(4)	Pt–P(2)–N(4)	121.4(4)
N(3)–P(2)–N(4)	92.4(5)	Pt–P(2)–N(6)	112.1(4)
N(3)–P(2)–N(6)	112.1(6)	N(4)–P(2)–N(6)	102.8(5)
P(1)–N(1)–C(1)	112.5(9)	P(1)–N(1)–C(3)	125.1(9)
C(1)–N(1)–C(3)	120.8(11)	P(1)–N(2)–C(2)	111.9(8)
P(1)–N(2)–C(4)	122.3(8)	C(2)–N(2)–C(4)	117.0(10)
P(2)–N(3)–C(5)	111.4(8)	P(2)–N(3)–C(7)	124.7(8)
C(5)–N(3)–C(7)	118.8(10)	P(2)–N(4)–C(6)	112.9(8)
P(2)–N(4)–C(8)	123.0(8)	C(6)–N(4)–C(8)	119.9(9)
P(1)–N(5)–C(9)	117.6(7)	P(1)–N(5)–C(11)	116.6(7)
C(9)–N(5)–C(11)	111.9(9)	P(2)–N(6)–C(10)	122.9(8)
P(2)–N(6)–C(12)	120.4(8)	C(10)–N(6)–C(12)	116.4(10)
N(1)–C(1)–C(2)	107.3(11)	N(2)–C(2)–C(1)	105.9(10)
N(3)–C(5)–C(6)	106.0(9)	N(4)–C(6)–C(5)	104.0(9)
N(5)–C(9)–C(10)	113.1(9)	N(6)–C(10)–C(9)	111.5(9)

Table 2 Bond lengths (Å) and angles (°) for [W(CO)$_4$L] **3**

W(1A)–P(1A)	2.516(4)	W(1A)–P(2A)	2.525(4)	N(1A)–C(5A)	1.458(27)	N(1A)–C(9A)	1.372(24)
W(1A)–C(1A)	1.934(17)	W(1A)–C(2A)	1.976(17)	N(2A)–C(6A)	1.384(29)	N(2A)–C(10A)	1.399(25)
W(1A)–C(3A)	2.011(16)	W(1A)–C(4A)	2.017(16)	N(3A)–C(7A)	1.477(20)	N(3A)–C(11A)	1.457(22)
P(1A)–N(1A)	1.686(16)	P(1A)–N(2A)	1.724(14)	N(4A)–C(8A)	1.400(26)	N(4A)–C(12A)	1.455(24)
P(1A)–N(5A)	1.687(13)	P(2A)–N(3A)	1.683(14)	N(5A)–C(13A)	1.498(23)	N(5A)–C(15A)	1.424(21)
P(2A)–N(4A)	1.669(13)	P(2A)–N(6A)	1.642(14)	N(6A)–C(14A)	1.505(21)	N(6A)–C(16A)	1.415(26)
O(1A)–C(1A)	1.186(25)	O(2A)–C(2A)	1.144(21)	C(5A)–C(6A)	1.534(31)	C(7A)–C(8A)	1.468(25)
O(3A)–C(3A)	1.156(21)	O(4A)–C(4A)	1.162(20)	C(13A)–C(14A)	1.501(25)		
P(1A)–W(1A)–P(2A)	104.0(1)	P(1A)–W(1A)–C(1A)	84.1(5)	P(1A)–N(1A)–C(9A)	124.8(14)	C(5A)–N(1A)–C(9A)	117.5(17)
P(2A)–W(1A)–C(1A)	171.1(5)	P(1A)–W(1A)–C(2A)	170.2(5)	P(1A)–N(2A)–C(6A)	112.5(12)	P(1A)–N(2A)–C(10A)	120.2(13)
P(2A)–W(1A)–C(2A)	85.4(5)	C(1A)–W(1A)–C(2A)	86.3(7)	C(6A)–N(2A)–C(10A)	116.7(16)	P(2A)–N(3A)–C(7A)	111.7(9)
P(1A)–W(1A)–C(3A)	92.1(5)	P(2A)–W(1A)–C(3A)	88.2(5)	P(2A)–N(3A)–C(11A)	121.4(12)	C(7A)–N(3A)–C(11A)	118.3(13)
C(1A)–W(1A)–C(3A)	88.2(7)	C(2A)–W(1A)–C(3A)	85.7(7)	P(2A)–N(4A)–C(8A)	114.8(12)	P(2A)–N(4A)–C(12A)	123.0(12)
P(1A)–W(1A)–C(4A)	93.0(5)	P(2A)–W(1A)–C(4A)	90.4(5)	C(8A)–N(4A)–C(12A)	117.5(15)	P(1A)–N(5A)–C(13A)	116.8(10)
C(1A)–W(1A)–C(4A)	92.6(7)	C(2A)–W(1A)–C(4A)	89.3(7)	P(1A)–N(5A)–C(15A)	122.0(11)	C(13A)–N(5A)–C(15A)	114.1(13)
C(3A)–W(1A)–C(4A)	174.9(7)	W(1A)–P(1A)–N(1A)	117.0(5)	P(2A)–N(6A)–C(14A)	120.3(11)	P(2A)–N(6A)–C(16A)	125.7(12)
W(1A)–P(1A)–N(2A)	113.8(5)	N(1A)–P(1A)–N(2A)	92.5(7)	C(14A)–N(6A)–C(16A)	114.0(13)	W(1A)–C(1A)–O(1A)	177.4(14)
W(1A)–P(1A)–N(5A)	119.6(5)	N(1A)–P(1A)–N(5A)	101.7(7)	W(1A)–C(2A)–O(2A)	117.1(13)	W(1A)–C(3A)–O(3A)	173.1(16)
N(2A)–P(1A)–N(5A)	108.4(7)	W(1A)–P(2A)–N(3A)	118.1(5)	W(1A)–C(4A)–O(4A)	177.7(17)	N(1A)–C(5A)–C(6A)	105.6(18)
W(1A)–P(2A)–N(4A)	114.4(5)	N(3A)–P(2A)–N(4A)	90.7(7)	N(2A)–C(6A)–C(5A)	108.7(19)	N(3A)–C(7A)–C(8A)	103.9(14)
W(1A)–P(2A)–N(6A)	117.7(5)	N(3A)–P(2A)–N(6A)	102.5(7)	N(4A)–C(8A)–C(7A)	107.5(16)	N(5A)–C(13A)–C(14A)	111.3(14)
N(4A)–P(2A)–N(6A)	109.7(7)	P(1A)–N(1A)–C(5A)	113.2(12)	N(6A)–C(14A)–C(13A)	111.9(13)		

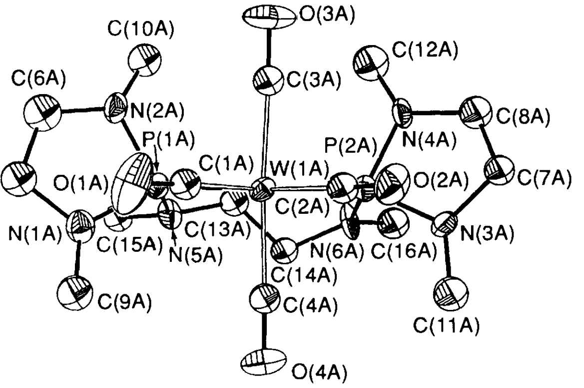
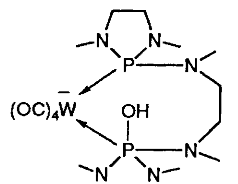


Fig. 2 The molecular structure of [W(CO)$_4$L] **3**



9

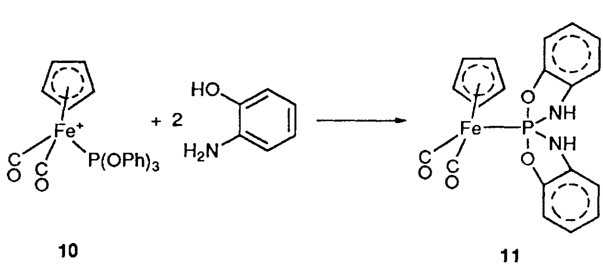
Table 3 Bond lengths (Å) and angles (°) for [W(CO)$_4$(MeNHCH$_2$-CH$_2$NHMe)] **8**

W–N(1)	2.297(8)	W–N(2)	2.308(11)
W–C(1)	1.947(10)	W–C(2)	1.986(12)
W–C(3)	2.017(10)	W–C(4)	2.023(9)
O(1)–C(1)	1.181(13)	O(2)–C(2)	1.141(16)
O(3)–C(3)	1.152(13)	O(4)–C(4)	1.142(12)
N(1)–C(5)	1.511(16)	N(1)–C(7)	1.487(18)
N(2)–C(6)	1.477(17)	N(2)–C(8)	1.495(14)
C(7)–C(8)	1.483(18)		
N(1)–W–N(2)	76.5(3)	N(1)–W–C(1)	173.4(4)
N(2)–W–C(1)	97.0(4)	N(1)–W–C(2)	95.9(4)
N(2)–W–C(2)	172.3(4)	C(1)–W–C(2)	90.7(5)
N(1)–W–C(3)	92.7(4)	N(2)–W–C(3)	91.2(4)
C(1)–W–C(3)	87.8(4)	C(2)–W–C(3)	88.9(5)
N(1)–W–C(4)	91.2(3)	N(2)–W–C(4)	92.1(4)
C(1)–W–C(4)	88.7(4)	C(2)–W–C(4)	88.3(4)
C(3)–W–C(4)	175.5(4)	W–N(1)–C(5)	114.1(6)
W–N(1)–C(7)	108.7(7)	C(5)–N(1)–C(7)	111.3(8)
W–N(2)–C(6)	115.6(8)	W–N(2)–C(8)	107.6(8)
C(6)–N(2)–C(8)	109.7(8)	W–C(1)–O(1)	177.1(9)
W–C(2)–O(2)	179.6(10)	W–C(3)–O(3)	175.4(10)
W–C(4)–O(4)	175.2(10)	N(1)–C(7)–C(8)	108.0(9)
N(2)–C(8)–C(7)	110.3(9)		

The molecular structure is shown in Fig. 3 and bond lengths and angles are given in Table 3.

For comparison purposes the hydrolysis of compound L under similar conditions to that of [W(CO)$_4$L] was also investigated. Initial hydrolysis of free L is essentially complete in *ca.* 20 min. Four new signals of similar magnitude and exhibiting one-bond $^1J(^{31}P-^1H)$ spin–spin coupling were observed at $\delta(^{31}P)$ 11.1 [$^1J(^{31}P-^1H) = 565$], 10.3 (556), 4.0 (558, HPO_3^{2-}) and −4.0 (648 Hz). After 24 h HPO_3^{2-} is the final hydrolysis product. The intermediate hydrolysis products were not structurally identified.

In conclusion the reaction of the bidentate triaminophosphine L with tungsten carbonyl and platinum chloro complexes has been investigated with a view to assessing the hydrolytic stability of L when co-ordinated to a transition metal. The platinum and tungsten complexes [PtCl$_2$L] and [W(CO)$_4$L] exhibit markedly different reactivities with L being rapidly hydrolysed when co-ordinated to W^0 whilst at 20 °C [PtCl$_2$L] is essentially inert with no evidence of hydrolysis after 7 d. This difference in reactivity is possibly a reflection of the relative degree of positive charge residing on the P atoms in the two complexes and/or the ease with which the respective metals can accommodate negative charge in an intermediate such as **9**. The proposed intermediate is structurally analogous to the recently reported iron complex **11** which was obtained *via* nucleophilic displacement of phenoxy groups from the co-ordinated P(OPh)$_3$ ligand of **10** [see equation (4)].[7] The results obtained



10 **11**

(4)

Table 4 Crystal data, details of intensity measurements and least-squares parameters

	1	**3**	**8**
Empirical formula	$C_{12}H_{30}Cl_2N_6P_2Pt$	$C_{16}H_{30}N_6O_4P_2W$	$C_8H_{10}N_2O_4W_4$
Crystal colour/habit	Colourless, block	Yellow, needle	Yellow, needle
Crystal size/mm	0.15 × 0.15 × 0.10	0.30 × 0.15 × 0.10	0.2 × 0.15 × 0.1
M_r	586.3	616.3	382.0
Crystal class	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	*Pn*	*C*2/*c*
a/Å	17.986(2)	15.611(3)	22.960(2)
b/Å	9.286(1)	8.437(2)	7.456(1)
c/Å	12.059(1)	27.604(6)	14.039(1)
β/°	91.07(1)	99.78(3)	106.60(1)
U/Å^3	2013.7(7)	3544.9(13)	2303.2(3)
Z	4	6	8
D_c/g cm^{-3}	1.934	1.732	2.203
μ(Mo-Kα)/cm^{-1}	73.99	50.56	100.27
F(000)	1144	1824	1424
ω Scan width/°	1.10 + 0.60 tan θ	0.52 + 0.57 tan θ	0.82 + 0.55 tan θ
Range 2θ collected/°	5.6–52.0	4.3–54.0	6.1–54.0
Absorption correction	Semiempirical	Semiempirical	Semiempirical
Minimum, maximum transmission coefficients	0.373, 0.485	0.347, 0.799	0.111, 0.606
Total no. reflections	2254	8535	2856
No. unique reflections	2089	7573	2371
R_{int}	0.000	0.000	0.036
No. observed data [$F > 3\sigma(F)$]	1901	5438	1900
Weighting g	0.0003	0.0003	0.0000
R	0.024	0.036	0.040
R'	0.028	0.039	0.045
Goodness of fit	0.96	1.26	2.53
Largest and mean Δ/σ	0.13, 0.02	0.00, 0.00	0.00, 0.00
Parameters refined	208	543	137
Maximimum, minimum density in ΔF map/e Å^{-3}	0.76, 0.51	1.09, 0.00	1.41, −1.14

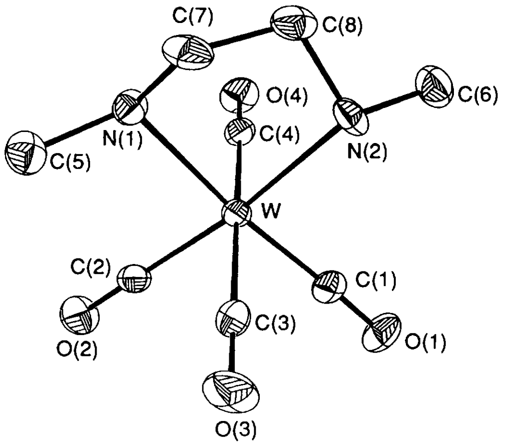


Fig. 3 The molecular structure of [W(CO)$_4$(MeNHCH$_2$CH$_2$NH-Me)] **8**

suggest that the rate of hydrolysis of co-ordinated bidentate triaminophosphines may be tuned by appropriate choice of metal, oxidation state and complementary ligands. Further studies of the chemistry of co-ordinated L and structurally related ligands are in progress.

Experimental

Proton NMR spectra were recorded on a Varian Gemini 200, ^{31}P-{^{1}H} NMR spectra on a Varian Gemini 300 spectrometer. All ^{1}H NMR spectra were recorded in CDCl$_3$ solution and referenced to SiMe$_4$, ^{31}P-{^{1}H} spectra in CDCl$_3$ and referenced to H$_3$PO$_4$. The IR spectra were recorded on a Nicolet 5DX Fourier-transform spectrometer using 0.5 mm NaCl solution cells. All reactions (unless otherwise specified) were done under a nitrogen atmosphere using dry degassed solvents. The complexes [{Pt(C$_2$H$_4$)Cl$_2$}$_2$][8] and [W(CO)$_4$(nbd)][9] were prepared as reported in the literature.

Table 5 Atomic coordinates for [PtCl$_2$L] **1**

Atom	*x*	*y*	*z*
Pt	0.133 30	0.020 8(3)	0.879 60
Cl(1)	0.232 5(2)	−0.123 5(3)	0.951 2(3)
Cl(2)	0.059 0(2)	−0.189 8(3)	0.880 5(3)
P(1)	0.210 1(2)	0.205 1(3)	0.910 9(3)
P(2)	0.036 5(2)	0.144 9(3)	0.813 1(3)
N(1)	0.228 4(6)	0.222 1(12)	1.045 9(9)
N(2)	0.299 9(6)	0.193 2(12)	0.876 0(9)
N(3)	−0.016 5(5)	0.220 2(13)	0.911 1(8)
N(4)	−0.036 2(5)	0.063 1(10)	0.753 8(9)
N(5)	0.178 6(4)	0.366 8(8)	0.867 1(7)
N(6)	0.061 1(5)	0.262 6(12)	0.717 6(9)
C(1)	0.307 9(7)	0.236 4(18)	1.070 4(12)
C(2)	0.348 9(6)	0.172 7(15)	0.973 9(12)
C(3)	0.177 7(8)	0.192 0(14)	1.131 5(11)
C(4)	0.322 8(7)	0.128 3(15)	0.773 9(11)
C(5)	−0.095 9(6)	0.185 5(16)	0.893 2(10)
C(6)	−0.097 9(6)	0.049 1(12)	0.826 7(11)
C(7)	0.002 6(7)	0.345 7(13)	0.971 5(10)
C(8)	−0.029 9(8)	−0.033 1(14)	0.659 1(12)
C(9)	0.178 0(6)	0.394 6(11)	0.749 0(9)
C(10)	0.137 3(6)	0.279 4(12)	0.681 9(9)
C(11)	0.203 6(7)	0.492 8(11)	0.931 2(14)
C(12)	0.006 9(7)	0.366 3(15)	0.673 0(12)

Preparations.—MeNCH$_2$CH$_2$N(Me)PN(Me)CH$_2$CH$_2$N(Me)PN(Me)CH$_2$CH$_2$NMe (L). To *syn*-*N*,*N'*-dimethylethane-1,2-diamine (25 cm^3) in benzene (600 cm^3) was added PCl$_3$ (15.4 cm^3) in benzene (15 cm^3). Then triethylamine (67.45 cm^3) was added quickly and the reaction allowed to stir for 2 h. The precipitate of [NEt$_3$H]Cl was filtered off and washed with benzene (2 × 75 cm^3). Removal of the solvent from the filtrate and washings gave the required product L as a moisture-sensitive white crystalline solid. Yield 52%. The ^{1}H NMR spectrum in CDCl$_3$ showed two doublets at δ 2.42 [J(^{31}P–^{1}H) = 14.4] and 2.54 (12.0 Hz) in the expected 6 : 12 ratio assignable

Table 6 Atomic coordinates for [W(CO)$_4$L] **3**

Atom	*x*	*y*	*z*
W(1A)	1.0	0.933 04(6)	1.0
P(1A)	0.987 4(2)	0.711 7(5)	1.060 3(2)
P(2A)	1.099 7(3)	0.819 2(5)	0.945 5(2)
O(1A)	0.869 1(10)	1.109 4(18)	1.055 3(7)
O(2A)	0.984 6(8)	1.232 3(13)	0.931 3(5)
O(3A)	0.835 9(9)	0.811 3(18)	0.925 9(7)
O(4A)	1.159 9(8)	1.091 8(16)	1.070 2(6)
N(1A)	0.973 3(10)	0.766 6(17)	1.117 2(5)
N(2A)	0.889 3(8)	0.611 9(18)	1.049 2(5)
N(3A)	1.158 1(7)	0.948 0(15)	0.917 4(5)
N(4A)	1.048 7(10)	0.752 3(16)	0.891 2(5)
N(5A)	1.067 6(8)	0.574 9(15)	1.072 8(5)
N(6A)	1.173 2(9)	0.688 4(17)	0.969 8(5)
C(1A)	0.917 4(10)	1.042 1(19)	1.033 3(6)
C(2A)	0.992 6(10)	1.122 9(20)	0.956 7(6)
C(3A)	0.898 9(11)	0.848 1(21)	0.951 9(7)
C(4A)	1.102 6(11)	1.033 5(20)	1.043 8(6)
C(5A)	0.888 1(13)	0.724 0(24)	1.128 1(8)
C(6A)	0.853 6(16)	0.591 6(28)	1.091 3(9)
C(7A)	1.119 2(10)	0.971 8(20)	0.865 3(6)
C(8A)	1.079 0(13)	0.816 6(22)	0.850 4(8)
C(9A)	1.017 6(13)	0.888 1(23)	1.144 0(8)
C(10A)	0.875 8(13)	0.488 3(24)	1.014 5(7)
C(11A)	1.204 7(12)	1.081 4(23)	0.943 9(7)
C(12A)	1.004 9(14)	0.597 9(24)	0.885 1(8)
C(13A)	1.111 3(11)	0.524 5(21)	1.030 9(7)
C(14A)	1.180 6(10)	0.641 4(21)	1.023 0(6)
C(15A)	1.067 7(11)	0.455 3(19)	1.109 6(6)
C(16A)	1.233 2(12)	0.609 8(24)	0.944 9(7)
W(1B)	0.959 56(5)	0.780 51(6)	0.670 95(3)
P(1B)	0.875 1(2)	1.007 0(5)	0.700 5(2)
P(2B)	1.018 0(2)	0.898 1(5)	0.599 2(2)
O(1B)	1.060 9(8)	0.469 9(14)	0.649 7(5)
O(2B)	0.903 4(10)	0.598 3(15)	0.760 2(5)
O(3B)	0.800 9(8)	0.637 7(16)	0.598 3(5)
O(4B)	1.130 7(8)	0.901 1(15)	0.740 3(5)
N(1B)	0.926 8(8)	1.089 3(15)	0.754 1(5)
N(2B)	0.788 9(7)	0.957 9(16)	0.724 8(5)
N(3B)	1.122 7(7)	0.961 8(18)	0.614 1(6)
N(4B)	1.045 8(10)	0.778 1(17)	0.556 3(6)
N(5B)	0.834 5(7)	1.155 9(14)	0.660 2(5)
N(6B)	0.955 7(8)	1.032 2(15)	0.566 0(5)
C(1B)	1.022 6(12)	0.587 0(22)	0.655 8(7)
C(2B)	0.924 8(10)	0.666 9(20)	0.726 6(7)
C(3B)	0.856 2(10)	0.693 3(19)	0.625 1(6)
C(4B)	1.066 8(9)	0.863 6(19)	0.713 5(6)
C(5B)	0.869 3(11)	1.109 5(22)	0.788 5(7)
C(6B)	0.803 2(13)	0.977 8(26)	0.777 7(8)
C(7B)	1.181 9(12)	0.895 2(23)	0.585 3(7)
C(8B)	1.137 2(11)	0.739 8(22)	0.563 7(8)
C(9B)	0.991 4(11)	1.210 0(20)	0.752 4(7)
C(10B)	0.724 5(11)	0.844 1(23)	0.704 6(7)
C(11B)	1.146 5(12)	1.108 3(23)	0.637 5(7)
C(12B)	0.987 7(13)	0.656 3(26)	0.533 9(8)
C(13B)	0.881 4(12)	1.199 1(21)	0.619 9(7)
C(14B)	0.872 3(10)	1.083 9(20)	0.578 8(6)
C(15B)	0.777 8(12)	1.275 1(21)	0.673 4(7)
C(16B)	0.983 1(13)	1.115 2(26)	0.524 8(7)
W(1C)	0.484 74(5)	0.282 71(7)	0.814 05(3)
P(1C)	0.606 0(2)	0.387 6(4)	0.877 4(2)
P(2C)	0.381 1(2)	0.516 3(5)	0.796 7(2)
O(1C)	0.590 1(8)	−0.033 1(12)	0.809 9(5)
O(2C)	0.343 8(8)	0.113 9(14)	0.735 6(5)
O(3C)	0.593 8(9)	0.399 7(16)	0.734 0(5)
O(4C)	0.401 6(8)	0.143 2(18)	0.901 1(5)
N(1C)	0.669 2(8)	0.255 9(15)	0.914 3(5)
N(2C)	0.693 2(7)	0.455 4(14)	0.855 6(5)
N(3C)	0.374 3(10)	0.588 1(18)	0.740 4(5)
N(4C)	0.273 1(8)	0.474 1(17)	0.786 4(5)
N(5C)	0.577 3(7)	0.516 3(15)	0.916 6(5)
N(6C)	0.386 0(7)	0.670 1(13)	0.837 6(5)
C(1C)	0.552 7(9)	0.083 4(18)	0.813 2(6)
C(2C)	0.397 7(10)	0.178 8(18)	0.762 9(6)
C(3C)	0.551 5(11)	0.363 1(22)	0.762 5(7)
C(4C)	0.431 1(11)	0.198 8(21)	0.868 6(7)
C(5C)	0.753 8(10)	0.233 5(19)	0.900 1(7)
C(6C)	0.775 2(9)	0.388 9(18)	0.879 1(6)
C(7C)	0.283 8(12)	0.605 3(25)	0.714 1(8)
C(8C)	0.236 0(14)	0.489 3(30)	0.736 9(8)
C(9C)	0.631 9(12)	0.120 7(23)	0.935 2(7)
C(10C)	0.695 8(11)	0.604 8(20)	0.830 9(7)
C(11C)	0.434 5(14)	0.701 6(26)	0.727 5(9)
C(12C)	0.237 3(12)	0.361 2(25)	0.819 0(8)
C(13C)	0.486 9(9)	0.578 6(19)	0.911 0(6)
C(14C)	0.465 8(11)	0.701 9(19)	0.870 6(6)
C(15C)	0.641 5(10)	0.603 7(20)	0.951 8(6)
C(16C)	0.324 6(11)	0.803 2(21)	0.827 9(7)

Table 7 Atomic coordinates for [W(CO)$_4$(MeNHCH$_2$CH$_2$NHMe)] **8**

Atom	*x*	*y*	*z*
W	0.375 14(2)	0.199 51(5)	0.966 15(3)
O(1)	0.448 3(4)	−0.154 8(10)	1.033 0(7)
O(2)	0.307 8(4)	0.147 7(12)	1.128 9(6)
O(3)	0.481 2(5)	0.387 9(14)	1.130 7(7)
O(4)	0.269 6(4)	−0.029 4(10)	0.824 0(6)
N(1)	0.328 4(4)	0.464 8(10)	0.905 0(7)
N(2)	0.418 0(5)	0.273 0(12)	0.841 3(6)
C(1)	0.419 4(5)	−0.023 6(14)	1.006 1(8)
C(2)	0.332 2(5)	0.166 8(13)	1.069 3(8)
C(3)	0.442 7(5)	0.325 5(14)	1.068 1(8)
C(4)	0.308 1(5)	0.057 0(12)	0.871 7(8)
C(5)	0.317 6(6)	0.588 3(15)	0.983 6(9)
C(6)	0.424 1(6)	0.123 7(19)	0.775 7(9)
C(7)	0.364 7(7)	0.554 9(14)	0.846 5(8)
C(8)	0.380 3(5)	0.419 0(16)	0.780 7(8)

to the NMe groups, together with multiplets at δ 2.95 and 3.20 assignable to the CH$_2$ protons; δ(^{31}P) 114 (s).[10]

[PtCl$_2$L] **1**. A solution of L (0.725 g) in CH$_2$Cl$_2$ (10 cm^3) was slowly added to [{Pt(C$_2$H$_4$)Cl$_2$}$_2$] (0.66 g) in CH$_2$Cl$_2$ (50 cm^3). After 1 h removal of the solvent gave a pale yellow solid which consisted of a mixture of complexes **1** and **2**. ^{31}P-{^{1}H} NMR: **1**, δ 64.6, $J(^{195}$Pt–^{31}P$)$ = 4967; **2**, δ 21.3, $J(^{195}$Pt–^{31}P$)$ = 2432 Hz. Recrystallization from CH$_2$Cl$_2$ by slow evaporation gave **1** as white prisms (72%, m.p. 166–167 °C). ^{1}H NMR: δ 2.47 [$J(^{31}$P–^{1}H$)$ 9.2, NMe (bridge)], 2.81 [$J(^{31}$P–^{1}H$)$ 11 Hz, NMe (ring)] and 3.25–3.51 (broad overlapping multiplets, CH$_2$) (Found: C, 25.30; H, 5.25; N, 14.00. Calc. for C$_{12}$H$_{30}$Cl$_2$N$_6$P$_2$Pt: C, 25.60; H, 5.15; N, 14.35%).

[W(CO)$_4$L] **3**. A solution of L (1.56 g) in benzene (80 cm^3) was slowly added to a refluxing solution of [W(CO)$_4$(nbd)] (1.72 g) in benzene (250 cm^3). The reaction was refluxed for 48 h. Removal of the solvent gave a yellow-green solid. IR[ν(CO) region]: 2010m, 1901 (sh, br) and 1882vs (br) cm^{-1}. The ^{31}P-{^{1}H} NMR spectrum in CH$_2$Cl$_2$ showed the presence of four products: δ 118 {$J(^{183}$W–^{31}P$)$ 315, [W(CO)$_4$L] **3**}, 121 {$J(^{183}$W–^{31}P$)$ 290, [{W(CO)$_4$(μ-L)}$_2$] *4*}, 124 {$J(^{183}$W–^{31}P$)$ 360, [{W(CO)$_4$(μ-L)}$_3$] **5**} and 124.5 {$J(^{183}$W–^{31}P$)$ 370 Hz, [{W(CO)$_4$(μ-L)}$_4$] **6**}. Recrystallization from CH$_2$Cl$_2$–hexane *via* slow evaporation gave [W(CO)$_4$L] as yellow prisms (42% yield, m.p. 170–171 °C). IR[ν(CO) region]: 2010m, 1909s and 1875vs cm^{-1}. ^{1}H NMR: δ 2.38 [$J(^{31}$P–^{1}H$)$ 6.8, virtual triplet, NMe (bridge)], 2.67 [$J(^{31}$P–^{1}H$)$ 11.5, virtual triplet, NMe (ring)], 3.18 [br m, NCH$_2$ (ring)] and 3.34 [$J(^{31}$P–^{1}H$)$ 23 Hz, virtual triplet, NCH$_2$ (bridge)] (Found: C, 31.50; H, 5.15; N, 13.35. Calc. for C$_{16}$H$_{30}$N$_6$O$_4$P$_2$W: C, 31.20; H, 4.90; N, 13.65%).

Hydrolysis Experiments.—A 0.02 mol dm^{-3} solution (5 cm^3) of [$PtCl_2L$], [$W(CO)_4L$] or L in CH_2Cl_2–MeCN (9 : 1 v/v) was placed in a NMR tube (diameter 5 mm) and water (1 cm^3) added. The sample was monitored by $^{31}P-\{^1H\}$ NMR spectroscopy.

X-Ray Structural Determinations.—Intensity data for compounds **1**, **3** and **8** were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The ω-scan technique was applied with variable scan speeds. Intensities of three standard reflections measured every 2 h, for each crystal, showed negligible variation. For all compounds the heavy-atom positions were solved by Patterson methods and the locations of all non-hydrogen atoms were determined from subsequent Fourier difference syntheses. In each case all non-hydrogen atoms were refined with anisotropic thermal parameters (except for **3** where carbon atoms were refined with isotropic thermal parameters) by full-matrix least squares to minimize $\Sigma w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F_o) + gF_o^2$. Hydrogen atoms were positioned on geometric grounds (C–H 0.96 Å) and included in the refinement as riding atoms with general thermal parameters for each structure [0.105(10) for **1**, 0.0800 for **3** and 0.073(12) Å^3 for **8**]. Crystal data, data collection, and least-squares parameters are listed in Table 4. All calculations were performed using SHELXTL PC[11] on a 486-66 personal computer. Relevant bond angles and distances are given in Tables 1–3 and atomic coordinates in Tables 5–7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

1 M. J. Baker, K. N. Harrison, A. G. Orpen, P. G. Pringle and G. Shaw, *J. Chem. Soc., Chem. Commun.*, 1991, 803.

2 T. J. Kwok and D. J. Wink, *Organometallics*, 1993, **12**, 1954.

3 M. J. Baker and P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, 1993, 314.

4 H. Goldwhite, *Introduction to Phosphorus Chemistry*, Cambridge University Press, Cambridge, 1981, p. 12.

5 G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem.*, 1978, **146**, 23.

6 J. R. Parks, *J. Am. Chem. Soc.*, 1957, **78**, 757.

7 H. Nakazawa, K. Kubo and K. Miyoshi, *J. Am. Chem. Soc.*, 1993, **115**, 5863.

8 J. Chatt and M. L. Searle, *Inorg. Synth.*, 1968, **17**, 210.

9 R. B. King and A. Fronzaglic, *Inorg. Chem.*, 1966, **5**, 1837.

10 F. Ramirez, A. V. Patwardham, H. J. Kayler and C. P. Smith, *J. Am. Chem. Soc.*, 1967, **89**, 6276.

11 G. M. Sheldrick, SHELXTL PC, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990.

Received 10*th November* 1993; *Paper* 3/06738F