CONVERSION OF COMPLEXES OF TYPE $[M(CO)_4(Ph_2PCH_2PPh_2\text{-}P,P')]$ TO $[M(CO)_4\{(PPh_2)_3CH\text{-}P,P'\}]$ $\{[M(CO)_4(tripod)]\}$ (M = Cr, Mo OR W) AND SUBSEQUENT CONVERSION TO PHOSPHINE OXIDES, PHOSPHINE SULPHIDES, AND COMPLEXES WITH PLATINUM(II)

SUBHI AL-JIBORI, and BERNARD L. SHAW*

*School of Chemistry, The University of Leeds, Leeds LS2 9JT (Great Britain)*

(Received April 12th, 1984)

Summary

Complexes of type $[M(CO)_4(PPh_2CH_2PPh_2)]$, when treated succesively with $LiBu^n$ and Ph_2PCl give complexes of type $[M(CO)_4\{(Ph_2P)_3CH\}]$ i.e. $[M(CO)_4(tripod)]$, in which the triphosphine is bidentate. These may be oxidized (H_2O_2) to the corresponding phosphine oxide $[M(CO)_4\{(Ph_2P)_2CHP(O)Ph_2\}]$ or converted with sulphur to the corresponding phosphine sulphide. The complexes of type $[M(CO)_4\{(PPh_2)_3CH\}]$ (L) react with K_2PtCl_4 to give what are probably complexes of type $PtCl_2L_2$, or with bridge complexes of type $[Pt_2Cl_4Q_2]$ ($Q = PPr^n_3$ or PMe_2Ph) to give heterobimetallic complexes of type *trans*-$[PtCl_2QL]$. IR and NMR data are given and discussed.

There is considerable interest in the triphosphine tris(diphenylphosphino)methane, $HC(PPh_2)_3$, known as tripod [1]. This triphosphine can act as a tridentate ligand across the face of a cluster e.g. in $[Co_4(CO)_9(tripod)]$ [2], or in $[Ni_3(CO)_6(tripod)]$ [3]. It can also act as a monodentate ligand as in $[Fe(CO)_4(tripod)]$ [4], or a bidentate ligand, as in $[Fe(CO)_3(tripod)]$ [4], or in $[Mo(CO)_4(tripod)]$ [4,5], in such cases the uncomplexed phosphorus atoms can subsequently be used to bond to a second metal atom, as in $[(OC)_4Fe(\mu\text{-tripod})Mo(CO)_4]$ [4], or [RhCl-(CO){Mo(CO)_4(tripod)}_2] [6]. Other examples of its use as a ligand have been reported [1].

In this paper we report another method of synthesizing bidentate and, subsequently, heterobimetallic complexes of tripod, from the readily synthesized complexes of type $[M(CO)_4(dppm)]$ [7], M = Cr, Mo, or W; dppm $= PPh_2CH_2PPh_2$. We have reported previously [8,9] that complexes of type $[M(CO)_4(dppm)]$ can be deprotonated by a strong base, such as n-butyllithium, and that the resultant
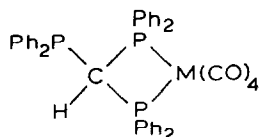
(**1a**, M = Cr,

1b, M = Mo,

1c, M = W)

TABLE 1

MELTING POINTS, COLOURS, MOLECULAR WEIGHTS, AND ELEMENTAL ANALYTICAL DATA FOR COMPLEXES OF THE TYPES 1 AND 2

| | M.p. ($^{\circ}$C) | Colour [a] | Analysis (Found (calcd.) (%)) | | M.wt. [b] |
			C	H	(Found (calcd.))
1a	256–258 [c]	y	67.15	4.35	706
			(67.2)	(4.3)	(733)
2a	260–263 [c]	py	65.6	4.05	[d]
			(65.8)	(4.2)	
2d	241–244	y	64.5	4.35	[d]
			(64.4)	(4.1)	
1b	221–222	py	63.45	3.95	785
			(63.4)	(4.0)	(777)
2b	218–225 [c]	ow	62.25	3.85	[d]
			(62.15)	(3.95)	
2f	224–226	y	54.9	3.5	[d]
			(54.6)	(3.6)	
1c	265 [c]	py	57.15	3.65	877
			(56.95)	(3.6)	(864)
2c	257–260	py	55.8	3.45	[d]
			(55.9)	(3.55)	

[a] y = yellow, py = pale yellow, ow = off white. [b] Measured osmometrically in $CHCl_3$ solution. [c] With decomposition. [d] Insufficiently soluble.
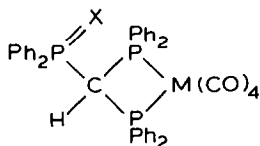
TABLE 2

^{31}P NMR [a] AND ^{1}H NMR [b] DATA FOR COMPLEXES OF TYPES **1a–1c** AND **2a–2f**

| | δ(P) | δ(P*) [c] | J(PP*) [c] | J(WP) | Methine hydrogen | |
					δ(H)	^{2}J(PH) [c]
1a	45.5	−23.4	20		6.24	8.5, 6.8*
2a	48.0 [d]	20.3 [d]	12 [d]		6.30	8.15, 11.6*
2d	49.0	34.0	10			
1b	23.3	−22.9	24		6.27	7.9, 6.6*
2b	27.0 [d]	20.2 [d]	12 [d]		6.38	7.6, 11.4*
2e	25.3	34.9	8			
1c	−2.5	−22.6	24	206	6.71	7.87, 6.6
2c	−2.0	22.3	10	217	6.83	7.8, unresolved
2f	−0.3	35.4	9	222		

[a] Measured in $CDCl_3$, unless stated otherwise, δ in ppm to high field of 85% H_3PO_4; error ±0.1 ppm, J values ±1 Hz. [b] Measured in $CDCl_3$. Chemical shifts (ppm) are relative to TMS error ±0.02 ppm, J values ±0.1 Hz. [c] Starred values are for the uncoordinated phosphorus nuclei. [d] Measured in C_6H_6/C_6D_6.

carbanion will attack electrophiles. We now find, that when treated with PPh_2Cl, these carbanions give complexes of bidentate tripod of type [M(CO)$_4$(tripod)] (1a–1c), in high yield; preparative details and IR data are in the Experimental, elemental analytical data in Table 1 and characterizing NMR data in Table 2. In all three cases the chemical shifts of the uncomplexd P-nuclei are at ca. −23 ppm, similar to that of uncoordinated dppm (−22.4 ppm) whilst the coordinated nuclei absorb at much higher frequency viz. 45.5, 23.3, −2.5 ppm for Cr, Mo, W, respectively. These three complexes have been prepared previously by the action of tripod on the hexacarbonyls but were not fully characterized [5]. In the ¹H NMR spectra the single aliphatic hydrogens absorb at ca. 6.3 ppm as a triplet of doublets (data in Table 2).

It was of interest to see if we could convert the free phosphine into a phosphine oxide or phosphine sulphide without affecting the rest of the molecule. Treatment of a solution of [Cr(CO)$_4${(PPh$_2$)$_3$CH}] in acetone with an excess of hydrogen peroxide at 40°C for 22 h gave the corresponding oxide complex 2a in 69% yield. The corresponding Mo and W complexes 2b and 2c were prepared in 80 and 73% yields respectively; details are in the Experimental section and characterizing NMR data are in Table 2. The infrared spectra showed in addition to the bands due to carbonyl stretch, a band at ca. 1200 cm⁻¹, corresponding to ν(PO). In the ³¹P{H} NMR spectra the chemical shift of the uncoordinated phosphorus (triplet) is shifted by about 43 ppm to high frequency of that of the uncoordinated phosphorus in the

(2a, M = Cr, X = O ;
2b, M = Mo, X = O ;
2c, M = W, X = O ;
2d, M = Cr, X = S ;
2e, M = Mo, X = S ,
2f, M = W, X = S)

non-oxidised complex, whilst the shifts of the coordinated phosphorus nuclei are shifted relatively little by the oxidation process (data in Table 2). Treatment of the chromium complex [Cr(CO)$_4${(PPh$_2$)$_3$CH}] with elemental sulphur in boiling benzene for 2 h gave the corresponding phosphine sulphide complex 2d in 66% yield. The corresponding W complex 2f was prepared similarly but the Mo complex was somewhat unstable and was not obtained pure but was identified in solution by its ³¹P{H} NMR spectrum (data in Table 2). The ³¹P NMR data are similar to those of the corresponding oxides. We were unable to identify the CH resonance in the proton spectrum, presumably because it was obscured by the aromatic resonances and were unable to identify ν(PS) in the infrared spectrum.

It seems likely that the free phosphine in complexes of type [M(CO)$_4${(Ph$_2$P)$_3$CH}] could be used to complex to a variety of metals. As a typical metal we have chosen to study platinum(II). Treatment of a suspension of [M(CO)$_4${(PPh$_2$)$_3$CH}] (M = Cr, Mo, or W) with K$_2$PtCl$_4$ in the ratio of 2/1, for several days at 45°C, gave very

TABLE 3

MELTING POINTS, COLOURS, MOLECULAR WEIGHTS, AND ELEMENTAL ANALYTICAL DATA FOR COMPLEXES OF THE TYPE trans-$[PtCl_2L(M(CO)_4\{Ph_2PCH(PPh_2)PPh_2\})]$, L = PR_3

	M.p. (°C)	Colour [a]	Analysis (Found (calcd.) (%))			M.wt. [b] (Found (calcd.))
			C	H	Cl	
4a	200–208 [c]	py	51.85	3.75	6.45	1112
			(51.8)	(3.7)	(6.25)	(1136)
4b	165–172 [c]	y	49.9	3.6	6.0	1163
			(49.85)	(3.6)	(6.0)	(1180)
4c	198–201 [c]	py	46.0	3.25	5.5	1299
			(46.4)	(3.35)	(5.6)	(1268)
4d	194–204	y	51.65	4.4	6.5	1160
			(51.5)	(4.5)	(6.15)	(1159)
4e	172–182 [c]	y	50.0	4.5	6.25	1232
			(49.95)	(4.35)	(6.0)	(1202)
4f	204–210 [c]	y	46.75	4.15	5.75	1243
			(46.55)	(4.05)	(5.5)	(1290)

[a] py = pale yellow, y = yellow. [b] Measured osmometrically in $CHCl_3$ solution. [c] With decomposition.

insoluble products, possibly of type **3** but which were too insoluble to recrystallize
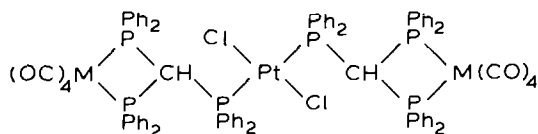
(**3**, M = Cr, Mo or W)

and were not obtained pure. The infrared spectrum of the Mo complex showed very strong bands at 2010, 1918, 1895, 1882 cm^{-1} indicating the presence of an $[Mo(CO)_4]$ moiety, and a very strong band at ca. 355 cm^{-1}, suggesting a trans-$PtCl_2$ moiety.

TABLE 4

^{31}P NMR DATA FOR COMPLEXES OF TYPE 4
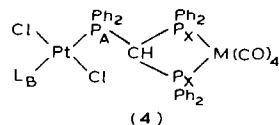
(4)

	$\delta(P_A)$	$\delta(P_B)$	$\delta(P_X)$	$^2J(P_AP_B)$	$^2J(P_AP_X)$	$^4J(P_BP_X)$	$^1J(PtP_A)$	$^1J(PtP_B)$	$^3J(PtP_X)$	$^1J(P_XW)$
	L = PMe_2Ph [a]									
4a	8.8	−21.4	47.0	490	14	6	2376	2634	34	
4b	12.1	−21.5	23.6	500	14	5	2396	2619	32	
4c	13.1	−21.5	−3.0	500	14	6	2396	2623	32	215
	L = PPr^n_3 [b]									
4d	23.7	6.2	60.2	475	13	4	2371	2554	32	
4e	26.7	6.1	36.6	475	13	4	2324	2607	28	
4f	27.6	6.2	9.8	475	13	4	2326	2608	31	215

[a] In $CDCl_3$; chemical shifts, δ, to high frequency of 85% H_3PO_4: error ±0.1 ppm; J in Hz. [b] In C_6H_6/C_6D_6; chemical shifts, δ, to high frequency of 85% H_3PO_4: error ±0.1 ppm; J in Hz.

TABLE 5

^{1}H NMR DATA ^{a} FOR COMPLEXES OF TYPE 4
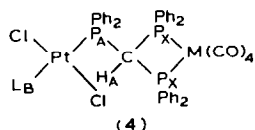
M	$\delta(CH_A)$	$\delta(CH_2)^d$	$\delta(CH_3)$	$^2J(P_XH_A)$	$^2J(P_AH_A)$	$^4J(P_BH_A)$	$^2J(P_BCH_3)$	$^4J(P_ACH_3)$	$^3J(PtH_A)$	$^2J(PtCH_3)$
L = PMe$_2$P										
4a 7.9		1.7	9	^{b}	^{c}	11	2	14	25	
4b 7.9		1.7	9	^{b}	2	11	3	15	25	
4c 8.2		1.7	9	15	2	11	3	16	25	
L = PPr$_3^n$										
4d 7.9	1.6	0.9	9	14				14		
4e 7.9	1.6	1.0	9	15				15		
4f 8.2	1.7	1.0	9	14				14		

^{a} In CDCl$_3$; chemical shifts, $\delta \pm 0.1$ ppm, to high frequency of 85% H$_3$PO$_4$; J in Hz. ^{b} Obscured by phenyl protons. ^{c} Coupling is very small, could not be measured. ^{d} CH$_2$ was unresolved multiplets.

Since we were unable to properly characterize this insoluble product we decided to attempt a bridge splitting reaction with complexes of type [Pt$_2$Cl$_4$(PR$_3$)$_2$]. Treatment of [M(CO)$_4$\{(PPh$_2$)$_3$CH\}] (M = Cr, Mo, or W) with [Pt$_2$Cl$_4$L$_2$] (L = PMe$_2$Ph, or PPr$^n_3$) in the ratio of 2/1 at room temperature gave complexes of type **4** readily. These complexes were characterized by elemental analysis (Table 3) and by NMR and IR spectroscopy (Tables 4 and 5). A strong far infrared band at around 340 cm^{-1} indicated a *trans*-arrangement of the two chlorines around platinum. Four strong infrared absorbtion bands in the carbonyl region were in agreement with presence of M(CO)$_4$ moieties (see Experimental). The ^{31}P\{H\} NMR spectrum of the Cr and Mo complexes showed ABX$_2$ patterns with platinum satellites and the W complex, an ABX$_2$ pattern with platinum and.tungsten satellites. The data are given in Table 4 and are in agreement with structures **4a–4f** in particular the very large
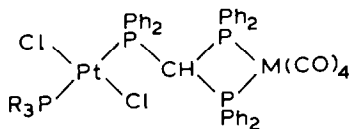
(**4a**, M = Cr, R$_3$P = PMe$_2$Ph ;
  4b, M = Mo, R$_3$P = PMe$_2$Ph ;
  4c, M = W , R$_3$P = PMe$_2$Ph ,
  4d, M = Cr, R$_3$P = PPr$^n_3$;
  4e, M = Mo, R$_3$P = PPr$^n_3$;
  4f, M = W , R$_3$P = PPr$^n_3$)

value of $^2J(P_AP_B)$ indicates a *trans*-arrangement of the P nuclei. It seems likely that complexes of type [M(CO)$_4$\{(PPh$_2$)$_3$CH\}] or their corresponding phosphine oxides and phosphine sulphides, described above could be complexed to many different metals to give heterobimetallic complexes. The ^{1}H NMR data are given in Table 5.

Experimental

The general techniques were the same as in other recent papers from this laboratory [10]. IR frequencies ± 2 cm^{-1}, the spectra were determined as Nujol mulls, unless stated otherwise.

[Cr(CO)$_4$ {(PPh$_2$)$_3$CH }] (1a)

A solution of n-butyllithium in diethyl ether (0.79 cm^3, 1.26 mmol) was added to a stirred solution of [Cr(CO)$_4$(dppm)] (0.462 g, 0.84 mmol) and TMEDA (1.26 mmol) in benzene (10 cm^3). The mixture was stirred for 1 h to give a turbid mixture. Diphenylchlorophosphine (0.3 cm^3, 1.68 mmol) was added dropwise with vigorous stirring and the mixture was stirred, during which a heavy precipitate formed. This was filtered off and washed with water to give a yellow solid. The mother liquor was evaporated to dryness to give some more of the product. The combined solid was recrystallized from CH$_2$Cl$_2$/MeOH to give the product as yellow needles (0.59 g, 0.805 mmol, 96%). IR data in 1,2-dichloroethane solution ν(CO) 2015, 1922, 1890, 1878.

The corresponding molybdenum and tungsten complexes were prepared similarly in 76 and 85% yield, respectively. IR data in 1,2-dichloroethane solution, **1b**: ν(CO) 2024, 1925, 1905, 1885 cm^{-1}; **1c**: ν(CO) 2018, 1913, 1892, 1875 cm^{-1}.

[Mo(CO)$_4$ { PPh$_2$)$_2$CHP(=O)PPh$_2$ }] (2b)

Hydrogen peroxide solution (30%) (0.059 cm^3, 0.52 mmol) was added to a solution of [Mo(CO)$_4${(PPh$_2$)$_3$CH}] (0.205 g, 0.26 mmol) in acetone (10 cm^3), the mixture was stirred at ca. 40°C for 22 h to give a white precipitate. The mixture was cooled to room temperature and the precipitate filtered off to give the product as a white solid (0.166 g, 0.22 mmol, 80%). ν(CO) 2024, 1923, 1980, 1864; ν(P=O) 1210 cm^{-1}.

The corresponding Cr and W complexes were prepared similarly in 69 and 79% yields respectively. **2a**: ν(CO) 2012, 1910, 1897, 1873; ν(P=O) 1207 cm^{-1}. **2c**: ν(CO) 2020, 1910, 1900, 1873 cm^{-1}; ν(P=O) 1205 cm^{-1}.

[Cr(CO)$_4$ { (PPh$_2$)$_2$CHP(=S)PPh$_2$ }] (2d)

Elemental sulphur (0.0193 g, 0.6 mmol) was added to a solution of [Cr(CO)$_4${(PPh$_2$)$_3$CH}] (0.221 g, 0.20 mmol) in benzene (ca. 10 cm^3). The mixture was refluxed for 2 h, then left to cool down, which gave the product as a yellow solid (0.15 g, 0.2 mmol, 66% yield). ν(CO) 2012, 1925, 1912, 1872 cm^{-1}.

The corresponding W complex **2f** was made in a similar fashion, yield 68%. ν(CO) 2020, 1915, 1898, 1855 cm^{-1}.

trans-[PtCl$_2$(PPr$^n_3$)(Cr(CO)$_4$(tripod)] (4d)

A solution of [Cr(CO)$_4${(PPh$_2$)$_3$CH}] (0.2 g, 0.27 mmol) in benzene (10 cm^3) was added to a stirred solution of [Pt$_2$Cl$_4$(PPr$^n_3$)$_2$] (0.116 g, 0.136 mmol) in benzene (4 cm^3). Methanol was added and upon evaporation of the solvent mixture, a yellow solid was obtained. On recrystallization from CH$_2$Cl$_2$/MeOH the product **4d** was obtained as a bright yellow solid (0.31 g, 0.27 mmol, 99%). ν(CO) 2010, 1920, 1900, 1876 cm^{-1}; ν(Pt–Cl) 343 cm^{-1}.

The corresponding Mo and W complexes were prepared and isolated similarly in

yields of 93 and 95%, respectively. IR data. **4e**: ν(CO) 2023, 1923, 1908, 1882 cm^{-1}; ν(Pt–Cl) 338 cm^{-1}; **4f**: ν(CO) 2020, 1915, 1889, 1875 cm^{-1}; ν(Pt–Cl) 341 cm^{-1}.

The compounds of type *trans*-[PtCl$_2$(PMe$_2$Ph)(M(CO)$_4$(tripod)], where M = Cr, Mo, or W, were prepared in 95, 92, and 98% yields respectively.

IR data. **4a**: ν(CO) 2012, 1919, 1900, 1867 cm^{-1}; ν(Pt–Cl) 338 cm^{-1}. **4b**: ν(CO) 2025, 1928, 1918, 1872 cm^{-1}; ν(Pt–Cl) 336 cm^{-1}; **4c**: ν(CO) 2025, 1922, 1911, 1867 cm^{-1}; ν(Pt–Cl) 337 cm^{-1}.

Acknowledgement

References

1 K. Issleib, and H.P. Abricht, J. Prakt. Chem., 312 (1970) 456.
2 A.A. Arduini, A.A. Bahsoun, J.A. Osborn, and C. Voelker, Angew. Chem. Int. Ed., 19 (1980) 1024.
3 J.A. Osborn, and G.G. Stanley, Angew. Chem. Int. Ed., 19 (1980) 1025.
4 J.T. Mague, and S.E. Dessens, J. Organomet. Chem., 262 (1984) 347.
5 G.T. Andrews, I.J. Colquhoun, and W. McFarlane, J. Chem. Soc., (1982) 2353.
6 A.A. Bahsoun, J.A. Osborn, P.H. Bird, D. Nucciarone, and A.V. Peters, J. Chem. Soc. Chem. Commun., (1984) 72.
7 J. Chatt, and H.R. Watson, J. Chem. Soc., (1961) 4980.
8 S. Al-Jibori, and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1982) 286.
9 S. Al-Jibori, and B.L. Shaw, Inorg. Chim. Acta, 74 (1983) 235.
10 J.R. Briggs, C. Crocker, W.S. McDonald, and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1982) 575