Bimetallic Systems. Part 9.[1] The Synthesis of and Nuclear Magnetic Resonance Studies on 10-Membered Ring Complexes of Type $[(OC)_4M^1(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2M^2(CO)_4]$ (M^1, M^2 = Cr, Mo, or W)

Jonathan A. Iggo and Bernard L. Shaw *
School of Chemistry, University of Leeds, Leeds LS2 9JT

The $Ph_2PCH_2CH_2PPh_2$ (dppe) bridged, bimetallic 10-membered ring complexes $[(OC)_4M^1(\mu\text{-dppe})_2M^2(CO)_4]$ have been synthesised by treating a complex of type *cis*-$[M^1(CO)_4(PPh_2H)_2]$ with one of type *cis*-$[M^2(CO)_4\{PPh_2(CH{=}CH_2)\}_2]$ in the presence of potassium t-butoxide as catalyst. The new precursor complexes *cis*-$[M(CO)_4\{PPh_2(CH{=}CH_2)\}_2]$ were prepared by displacement of norbornadiene (nbd) from $[M(CO)_4(nbd)]$. The fluxional processes in the 10-membered $M^1(\mu\text{-dppe})_2M^2$ rings have been studied by variable-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy and are characterised by a change from a second-order AA'XX' system at 20 °C to an essentially first-order AMPX system at −90 °C. The spectra have been fully interpreted and values for ^2J(*cis*-PMP) obtained. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the homonuclear $M(\mu\text{-dppe})_2M$ systems change from A_4 at 20 °C to AA'BB' at −90 °C. The low-temperature (−100 °C) ^1H and $^1H\text{-}\{^{31}P\}$ spectra were not resolved. These binuclear complexes are remarkably inert towards disproportionation to mononuclear chelate species and to attack by HCl or halogens.

The diphosphine ligand $Ph_2PCH_2PPh_2$ (dppm) will act as a chelating ligand to give four-membered rings but is particularly important as a bridging group. Many examples of complexes containing the eight-membered ring moiety $M^1(\mu\text{-dppm})_2M^2$ in a variety of stereochemistries are known. Such complexes may show a rich and varied chemistry, reacting, for example, with CO to give the associated 'A frame' complexes with a third group bridging the two metals.[2]

In contrast, the chemistry of the ligand $Ph_2PCH_2CH_2PPh_2$ (dppe) is dominated by the formation of stable, five-membered ring chelate complexes which, of course, one would expect to be thermodynamically more favoured than compounds containing the 10-membered ring moiety $M^1(\mu\text{-dppe})_2M^2$. Even metals which have a strong preference for linear (two-) co-ordination, such as gold(I), form five-membered ring chelates with dppe, *e.g.* $[Au(dppe\text{-}PP')_2]^+$,[3] although the 10-membered ring, binuclear complex $[ClAu(\mu\text{-dppe})_2AuCl]$ is well established and a 14-membered ring complex with two dppe ligands bridging two Au_2Fe triangles has been prepared.[4] Interestingly, and somewhat surprisingly, however, the related ligand $Ph_2PCH_2CH_2AsPh_2$ reacts with the hexacarbonyls of Group 6 metals to give an easily separable mixture of the mononuclear chelate complexes $[M(CO)_4(Ph_2PCH_2CH_2AsPh_2)]$ (M = Cr, Mo, or W) and the binuclear complexes *cis,cis*-$[M_2(CO)_8(\mu\text{-}Ph_2PCH_2CH_2AsPh_2)_2]$ apparently containing 10-membered rings. It was not established whether the binuclear product was a mixture of two isomers, *viz.* one isomer with both P atoms bound to one metal and the other with one P and one As bound to each metal.[5] There is no evidence that, when $Ph_2PCH_2CH_2PPh_2$ reacts with a Group 6 metal carbonyl, binuclear species of the type $[(OC)_4M(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2M(CO)_4]$ are formed, suggesting that they are less stable than the mononuclear complexes $[M(CO)_4(Ph_2PCH_2CH_2PPh_2)]$. However, it seemed possible that such complexes might be synthesised by treating a secondary phosphine complex *cis*-$[M^1(CO)_4(PPh_2H)_2]$ with a vinylphosphine complex *cis*-$[M^2(CO)_4\{PPh_2(CH{=}CH_2)\}_2]$ in the presence of a base. It has been shown by Keiter and co-workers[6] that treatment of a mixture of the monosubstituted derivatives $[M^1(CO)_5(PPh_2H)]$ and $[M^2(CO)_5\{PPh_2(CH{=}CH_2)\}]$ with potassium t-butoxide as a catalyst gives the bimetallic complexes, $[(OC)_5M^1(\mu\text{-}Ph_2PCH_2CH_2PPh_2)M^2(CO)_5]$ (M^1, M^2 = Cr, Mo, or W), containing the two metals singly bridged by $Ph_2PCH_2CH_2PPh_2$.

Results and Discussion

The known complexes *cis*-$[M(CO)_4(PPh_2H)_2]$[7] and the new complexes *cis*-$[M(CO)_4\{PPh_2(CH{=}CH_2)\}_2]$ were prepared by displacement of diolefin from the corresponding norborna-2,5-diene (bicyclo[2.2.1]hepta-2,5-diene) complexes $[M(CO)_4(nbd)]$.[8,9] The PPh_2H complexes were characterised by comparison of their i.r. and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra with published data and the new complexes by i.r. [ν(CO)], $^1H\text{-}\{^{31}P\}$ and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy, and microanalysis (Table 1 and 2). The vinylphosphine–chromium complex was obtained as a variable mixture of *cis* and *trans* isomers that could be separated only with difficulty. The isomeric mixture was therefore used in all reactions involving the chromium complexes and may account for the low yields of binuclear, ring complexes obtained starting from $[Cr(CO)_4\{PPh_2(CH{=}CH_2)\}_2]$.

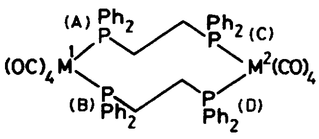
We find that treatment of an equimolar mixture of *cis*-$[Cr(CO)_4(PPh_2H)_2]$ and *cis*-$[Mo(CO)_4\{PPh_2(CH{=}CH_2)\}_2]$ in tetrahydrofuran with potassium t-butoxide immediately gives a yellow solution from which, after *ca.* 3 h stirring at room temperature, the desired heterobimetallic complex *cis,cis*-$[(OC)_4Cr(\mu\text{-dppe})_2Mo(CO)_4]$ was isolated in 49% yield. The five other homo- or hetero-bimetallic complexes were prepared similarly in yields of 21—66%. The reaction conditions were not optimised and undoubtedly some of the yields could be improved. Preparative details are given in the Experimental section.

The complexes were characterised by elemental analysis (C, H, and P) and i.r. and ^1H and ^{31}P n.m.r. spectroscopy (Tables 1 and 2). Molecular ions were observed in the mass spectra of the CrW and MoW complexes at *m/z* = 1 256 ($^{52}Cr^{184}W$) and 1 302 ($^{98}Mo^{184}W$) respectively, as were fragmentation ions due to loss of up to eight CO ligands. The *M* − 8CO fragmentation peak was observed at *m/z* = 1 164 (^{184}W) in the mass spectrum of the W_2 complex. The measured isotope intensity pattern of this fragmentation ion and those of the CrW and MoW spectra are in good agreement with calculated patterns. Molecular ions were not observed for the Cr_2, Mo_2, and MoCr complexes presumably due to fragmentation into mononuclear species in

Table 1. Infrared and analytical data for the complexes

	Infrared (cm^{-1})[a]		Analysis (%)[b]		
Complex	ν(CO)	$\delta(CH_2CH_2)$[c]	C	H	P
(1a)	2 000m, 1 912s, 1 906 (sh), 1 890s, 1 873s, 1 870 (sh)	1 443m, 1 438m	63.9 (64.1)	4.0 (4.3)	11.4 (11.0)
(1b)	2 015m, 1 922s, 1 914m, 1 905s, 1 887s, 1 880s, 1 872m	1 439m, 1 432m	59.0 (59.4)	3.9 (4.0)	10.1 (10.2)
(1c)	2 014m, 1 919s, 1 910m, 1 895s, 1 877s, 1 869s	1 440m, 1 435m	51.9 (51.9)	3.3 (3.5)	9.0 (8.9)
(1d)	2 022m, 2 006m, 1 924s, 1 911 (sh), 1 906s, 1 900s, 1 883s, 1 876 (sh), 1 870 (sh)	1 441m, 1 437m	61.5 (61.7)	4.0 (4.1)	10.8 (10.6)
(1e)	2 012m, 2 002m, 1 913s, 1 906 (sh), 1 892s, 1 875s, 1 867s	1 440m, 1 436m	57.2 (57.3)	3.6 (3.8)	10.2 (9.9)
(1f)	2 017m, 2 001m, 1 915 (sh), 1 892 (sh), 1 875s, 1 865 (sh), 1 855s	1 440m, 1 436m	55.4 (55.7)	3.6 (3.7)	9.2 (9.5)
[Cr(CO)$_4$(dppe-*PP′*)]	2 001m, 1 907s, 1 888 (sh), 1 883s, 1 871 (sh), 1 865s	1 482m, 1 432m, 1 419m			
[Mo(CO)$_4$(dppe-*PP′*)]	2 015m, 1 922s, 1 897 (sh), 1 893s, 1 882 (sh), 1 877s	1 481m, 1 437m, 1 419m	59.6 (59.4)	4.0 (4.0)	10.5 (10.2)
[W(CO)$_4$(dppe-*PP′*)]	2 010m, 1 911s, 1 888 (sh), 1 882s, 1 868s	1 483m, 1 437m, 1 419m			
cis-[Cr(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$]	2 028m, 2 020 (sh), 1 956m, 1 940s, 1 919s		65.3 (65.3)	4.3 (4.5)	10.6 (10.5)
cis-[Mo(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$]	2 014m, 2 002 (sh), 1 918m, 1 900s, 1 867s		60.5 (60.8)	4.1 (4.1)	
cis-[W(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$]	2 011m, 2 001 (sh), 1 913m, 1 891s, 1 862s		53.1 (53.4)	3.7 (3.6)	

[a] Recorded as Nujol mull. [b] Calculated values in parentheses. [c] Tentative assignment.



	M^1	M^2
(1a)	Cr	Cr
(1b)	Mo	Mo
(1c)	W	W
(1d)	Cr	Mo
(1e)	Cr	W
(1f)	Mo	W

the mass spectrometer source. In the i.r. absorption spectra the strong absorption bands due to ν(CO) (Table 1) were indicative of a *cis* geometry for both metals.[10] Interestingly all six bimetallic complexes gave two closely spaced medium-intensity bands at *ca.* 1 440 cm^{-1} (Table 1) whereas the chelates [M(CO)$_4$(dppe-*PP′*)] gave three bands at *ca.* 1 480, 1 435, and 1 420 cm^{-1}: these bands are tentatively assigned to $\delta(CH_2CH_2)$. The six complexes are thus formulated as binuclear species each with a 10-membered ring and *cis* geometry around each metal, *viz.* as **(1a)**—**(1f)**.

The ^{31}P-{^1H} n.m.r. spectral data for complexes **(1a)**—**(1f)** are given in Table 2. At ambient temperature the resonance of each of the homobimetallic complexes is a sharp singlet at δ 48.7 **(1a)**, 29.6 **(1b)**, and 10.0 p.p.m. **(1c)**, the last with satellites due to coupling to tungsten-183. On cooling the solutions the resonances first broaden then split into two with a coalescence temperature of *ca.* 60—65 °C. At −90 °C the spectrum of complex **(1a)** consists of an AA′BB′ (almost an AA′XX′) system with $|N|$ = 28 Hz, Figure 1. At this temperature the spectra of **(1b)** and **(1c)** each show two broad resonances with chemical shifts similar to those found for the corresponding nuclei in the low-temperature-limiting spectra of complexes **(1d)**—**(1f)**.

The heterobimetallics **(1d)**—**(1f)** at ambient temperature show AA′XX′ ^{31}P-{^1H} patterns which were fully analysed. Each *cis*-*PMP* moiety seems to behave almost independently of the second metal. Thus the chemical shifts of the *P* nuclei co-ordinated to tungsten in **(1e)** (δ 10.8 p.p.m.) and **(1f)** (δ 11.1 p.p.m.) are almost the same as that found for the ditungsten complex **(1c)** (δ 10.0 p.p.m.). The chromium-containing (at *ca.* 49 p.p.m.) or molybdenum-containing (at *ca.* 29 p.p.m.) complexes show similar relationships (Table 2). Making the reasonable assumption that the coupling constants $^2J(PMP)$ are also almost independent of the other metal in the complex we can assign $|N|$, $|L|$, $|K|$, and $|M|$ unambiguously (Table 3) (where these letters have their usual designations)[11] and in this way obtain values for $^2J(cis\text{-}PMP)$. The values of $^2J(PMP)$ obtained (Table 2) show that this parameter drops in going from Cr to W, *viz. ca.* 28.5 (Cr), 24.0 (Mo), and 21.5 Hz (W). The values of $^3J(PCH_2CH_2P)$ vary from 32.5 to 35.5 Hz (Table 2). When a solution of one of these heterobimetallics is cooled the resonances broaden and then split further until at −90 °C an essentially first-order AMPX spectrum is obtained, see Figure 2 for complex **(1d)**. Examination of the resonances of **(1d)** shows that the chemical shifts of two of the resonances, 51.8 and 45.1 p.p.m., are very close to those obtained for the dichromium complex, 52.7 and 43.8 p.p.m., and the other two resonances, at 33.3 and 23.5 p.p.m., are very close in chemical shift to those of the dimolybdenum complex, 33.3 and 26.1 p.p.m.: the other n.m.r. parameters for these heterobimetallics are very similar to those found for the homobimetallics and clearly therefore each M is behaving almost independently of the nature of the second metal. Hence in the heterobimetallics, P(A), P(B), P(C), and P(D) are chemically non-equivalent and in the homobimetallics P(A) and P(B) or P(C) and P(D) are chemically inequivalent.

The $^2J(PMP)$ coupling constants at low temperature show a similar trend to that found at ambient temperature, decreasing in magnitude from 30.5 Hz (M = Cr) through 26.5 Hz (M = Mo) to 23.5 Hz (M = W); average values, Table 2. McFarlane

Table 2. Proton (methylene or vinyl) and ^{31}P n.m.r. data for the complexes

Complex	^1H-{^{31}P} (δ)[a,b]	^{31}P-{^1H} (δ)[a,c]	
		25 °C	−90 °C
(1a)	2.03 (s)	48.7 (s)	52.7 ($\lvert N \rvert = 28$), 43.8
(1b)	2.07 (s)	29.6 (s)	33.3 (br), 26.1 (br)
(1c)	2.16 (s)	10.0 [$J(WP) = 213$]	14.1 (br), 6.3 (br)
(1d)	2.05 (s)	49.9 [$^3J(PC_2P) = 32.5$, $^2J(PCrP) = 28.0$, $^2J(PMoP) = 24.0$, CrP], 29.6 (MoP)	51.8 [dd, $^2J(P_ACrP_B) = 30$, $^3J(P_AC_2P_B) = 30$, CrP_A], 45.1 [dd, $^3J(P_BC_2P_D) = 35$, CrP_B], 33.3 [dd, $^2J(P_CMoP_D) = 27$, MoP_C], 23.5 (dd, MoP_D)
(1e)	2.09 (s)	49.1 [$^3J(PC_2P) = 33.5$, $^2J(PCrP) = 29.5$, $^2J)(PWP) = 22.0$, CrP], 10.8 [$J(WP) = 230$, WP]	52.0 [dd, $^2J(P_ACrP_B) = 31$, $^3J(P_AC_2P_C) = 31$, CrP_A], 45.0 [dd, $^3J(P_BC_2P_D) = 35$, CrP_B], 15.0 [dd, $^2J(P_CWP_D) = 24$, $J(WP) = 223$, WP_C], 4.9 (dd, WP_D)
(1f)	2.11 (s)	29.3 [$^3J(PC_2P) = 35.5$, $^2J(PMoP) = 24.0$, $^2J(PWP) = 20.5$, MoP], 11.1 [$J(WP) = 230$,WP]	32.5 [dd, $^2J(P_AMoP_B) = 26$, $^3J(P_AC_2P_C) = 30$, MoP_A], 24.5 [dd, $^3J(P_BC_2P_D) = 35$, MoP_B], 13.7 [dd, $^2J(P_CWP_D) = 23$, $J(WP) = 223$, WP_C], 6.7 [dd, $J(WP) = 216$, WP_D]
[$Cr(CO)_4$(dppe-*PP′*)]		79.4 (s)	
[$Mo(CO)_4$(dppe-*PP′*)]		55.4 (s)	
[$W(CO)_4$(dppe-*PP′*)]		40.6 [$J(WP) = 239$]	
cis-[$Cr(CO)_4\{PPh_2(CH{=}CH_2)\}_2$]	6.39 [dd, $^3J(H^1H^2) = 17$, $^3J(H^1H^3) = 11$, 1 H, H^1], 5.73 [dd, $^2J(H^2H^3) = 1.5$, 1 H, H^2], 4.99 (dd, 1 H, H^3)	47.4	
cis-[$Mo(CO)_4\{PPh_2(CH{=}CH_2)\}_2$]	6.37 [dd, $^3J(H^1H^2) = 18$, $^3J(H^1H^3) = 12$, 1 H, H^1], 5.74 [dd, $^2J(H^2H^3) = 1.5$, 1 H, H^2], 5.04 (dd, 1 H, H^3)	29.1	
cis-[$W(CO)_4\{PPh_2(CH{=}CH_2)\}_2$]	6.36 [dd, $^3J(H^1H^2) = 17$, $^3J(H^1H^3) = 12$, $^3J(WH) = 94$, 1 H, H^1], 5.68 [dd, $^2J(H^2H^3) = 1.5$, $^4J(WH) = 34$, 1 H, H^2], 5.03 (dd, 1 H, H^3)	11.6 [$J(WP) = 232$]	

[a] Recorded in CD_2Cl_2 solution. [b] $^3J(H^1H^2)$ is *trans* coupling constant, $^3J(H^1H^3)$ *cis*. [c] Positive shifts downfield from external 80% H_3PO_4; br = broad, s = singlet, d = doublet. Coupling constants in Hz.

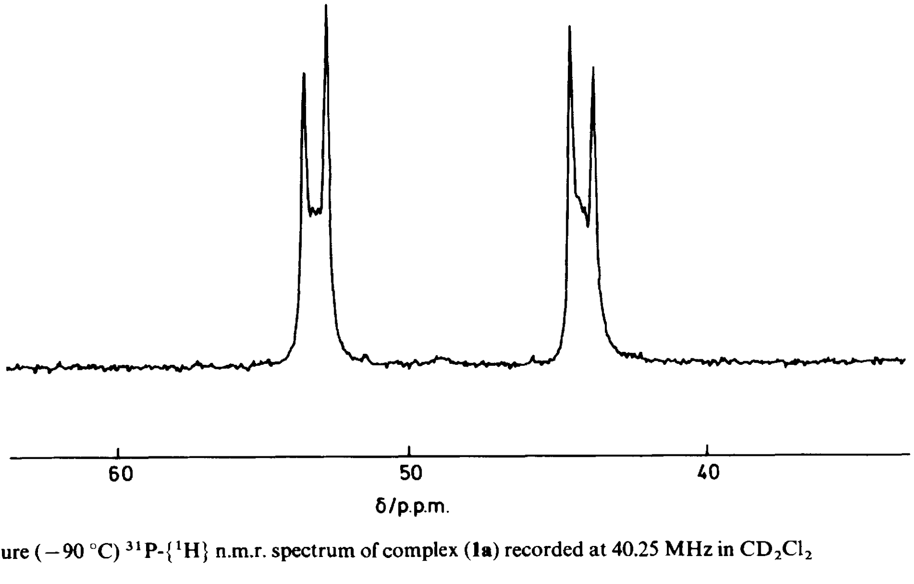


Figure 1. Low-temperature (−90 °C) ^{31}P-{^1H} n.m.r. spectrum of complex (**1a**) recorded at 40.25 MHz in CD_2Cl_2

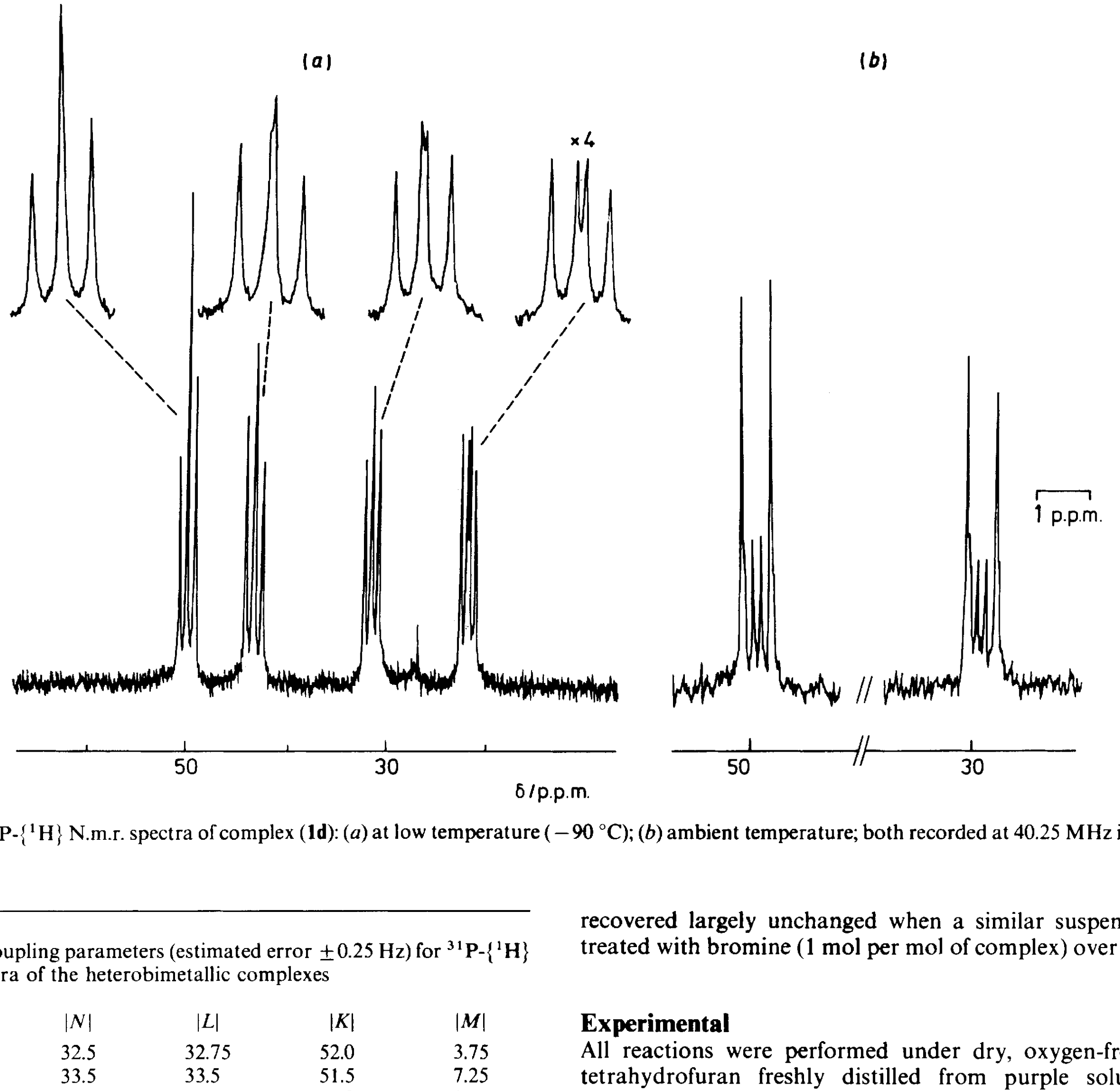


Figure 2. ^{31}P-{^{1}H} N.m.r. spectra of complex (**1d**): (*a*) at low temperature (−90 °C); (*b*) ambient temperature; both recorded at 40.25 MHz in CD_2Cl_2

Table. 3. Coupling parameters (estimated error ±0.25 Hz) for ^{31}P-{^{1}H} n.m.r. spectra of the heterobimetallic complexes

Complex	$\|N\|$	$\|L\|$	$\|K\|$	$\|M\|$
(**1d**)	32.5	32.75	52.0	3.75
(**1e**)	33.5	33.5	51.5	7.25
(**1f**)	35.5	35.5	44.25	3.75

and co-workers[12] have studied the $^{2}J(PMP)$ coupling constants in the mononuclear complexes *cis*-[M(CO)$_4$(L–L)] (M = Cr, Mo, or W; L–L = chelating diphosphine) and have found that the absolute value increases as the metal is changed from Cr to Mo to W and spans a range of values from +84 Hz [M = W; L–L = $(Ph_2P)_2C{=}CH_2$] to −38 Hz [M = Cr, L–L = $(Ph_2P)_2NH$]. For the largest rings studied by McFarlane, *cis*-[M(CO)$_4${$(Ph_2P)_2C_4H_8$}], values of −27.0, −21.5, and −15.0 Hz were obtained for M = Cr, Mo, and W respectively. Although we have not measured the sign of $^{2}J(PMP)$ for our complexes, Colquhoun and McFarlane's results suggest that it is negative.

The ^{1}H or ^{1}H-{^{31}P} n.m.r. spectra of the complexes were not particularly informative. At ambient temperature all six complexes (**1a**)—(**1f**) gave a singlet in the ^{1}H or ^{1}H-{^{31}P} n.m.r. spectra: the ^{1}H spectra were broader (*ca.* 50% more) than the ^{1}H-{^{31}P} spectra. At very low (−103 °C) temperatures and high field (4.7 T) the ^{1}H-{^{31}P} n.m.r. spectra were a broad quartet similar in intensity to an AB quartet.

The complexes (**1a**)—(**1f**) are rather insoluble and seem difficult to attack chemically. Thus a suspension of the CrMo complex (**1d**) in dichloromethane was resistant to treatment with an excess of dry hydrogen chloride over 2 d and was recovered largely unchanged when a similar suspension was treated with bromine (1 mol per mol of complex) over 17 h.

Experimental

All reactions were performed under dry, oxygen-free N_2 in tetrahydrofuran freshly distilled from purple solutions of sodium–benzophenone. Infrared spectra were recorded for Nujol mulls between KBr discs on a Perkin-Elmer 257 grating spectrometer. Unless indicated otherwise, n.m.r. spectra were recorded on a JEOL FX100 instrument at 99.55 MHz (^{1}H) or 40.25 MHz (^{31}P) using the solvent resonances as internal standards and referenced to external $SiMe_4$ or 80% H_3PO_4 as appropriate. Mass spectra were recorded on an AEI MS902 instrument.

The complexes [M(CO)$_4$(nbd)][13,14] and all phosphine ligands were prepared by literature methods and characterised by ^{31}P n.m.r. and i.r. spectroscopy as appropriate.

Preparation of cis-[M(CO)$_4$(PR$_3$)$_2$] *Complexes*.—*cis*-[Mo(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$]. A solution of PPh$_2$(CH=CH$_2$) (4.2 g, 20 mmol) in benzene (100 cm^3) was added to a stirred solution of [Mo(CO)$_4$(nbd)] (3.0 g, 10 mmol) over a period of 40 min at 0 °C. The solution was stirred for a further 2 h and allowed to warm to room temperature. After stirring for a further 1 h, the volatiles were removed at reduced pressure, the grey residue redissolved in Et_2O, and filtered under N_2 through alumina. Removal of the ether solvent gave a yellow-green oil which on trituration with absolute alcohol gave a white solid. This was collected by filtration, washed with alcohol and light petroleum (b.p. 40—60 °C), and dried. Yield 5.72 g, 90%. The product so obtained was sufficiently pure for most purposes but could be recrystallised from Et_2O–EtOH if desired.

cis-[Mo(CO)$_4$(PPh$_2$H)$_2$]. This was prepared similarly as lime-green platelets after recrystallisation from Et$_2$O. Yield 4.43 g, 85%.

cis-[W(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$]. The complex [W(CO)$_4$(nbd)] (0.388 g, 1.0 mmol) and PPh$_2$(CH=CH$_2$) (0.414 g, 2.0 mmol) were refluxed in light petroleum (b.p. 40—60 °C) (25 cm^3) for 2 h. The volatiles were removed and the residue redissolved in the minimum of Et$_2$O. Addition of EtOH–MeOH (1:1) precipitated the desired product as a yellow powder. Yield 0.622 g, 86%.

cis-[W(CO)$_4$(PPh$_2$H)$_2$]. This was prepared similarly and recrystallised from light petroleum (b.p. 40—60 °C)–MeOH. Yield 83%.

[Cr(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$]. This complex was obtained from an analogous procedure utilising [Cr(CO)$_4$(nbd)]. On cooling the reaction mixture a yellow precipitate comprising a *cis,trans* mixture was obtained in 73% yield. Careful recrystallisation from hexane, manual separation of the crystal forms, and final recrystallisation from hexane afforded pure *cis*-[Cr(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$] as orange blocks in *ca.* 10% yield.

cis-[Cr(CO)$_4$(PPh$_2$H)$_2$]. This was obtained as yellow-green crystals on cooling the light petroleum reaction solution. Yield 80%.

Preparation of [M^{1}M^2(CO)$_8$(dppe)$_2$] *Complexes.*—Since the preparations of all these complexes are similar in all important respects only that for [CrMo(CO)$_8$(dppe)$_2$] (**1d**) from *cis*-[Cr(CO)$_4$(PPh$_2$H)$_2$] and *cis*-[Mo(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$] will be given in detail.

Potassium t-butoxide (0.07 g) was added to a solution containing *cis*-[Cr(CO)$_4$(PPh$_2$H)$_2$] (0.54 g, 1.0 mmol) and *cis*-[Mo(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$] (0.63 g, 1.0 mmol) in dry tetrahydrofuran (20 cm^3). The resultant yellow solution was stirred at 20 °C for 2.5 h. The solvent was then removed under reduced pressure and the residue treated with CH$_2$Cl$_2$ and water. The dichloromethane layer was then evaporated to dryness and the residue taken up in the minimum of dichloromethane, filtered, and methanol added. Most of the dichloromethane was then removed under reduced pressure to give complex (**1d**) as analytically pure yellow microcrystals. Yield 49%. A similar procedure using [Cr(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$] and [Mo(CO)$_4$(PPh$_2$H)$_2$] gave a 40% yield.

The following were prepared similarly: (**1a**) as yellow microcrystals, m.p. 270—273 °C (decomp.), yield 21%; (**1b**) as cream microcrystals, m.p. 274—278 °C (decomp.), yield 66%; (**1c**) as pale yellow microcrystals, m.p. 253—254 °C (decomp.), yield 45%; (**1e**), using [Cr(CO)$_4$(PPh$_2$H)$_2$] and [W(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$], as pale yellow microcrystals, yield 60%, m/z = 1 256 (^{52}Cr^{184}W); and (**1f**), using [Mo(CO)$_4$(PPh$_2$H)$_2$] and [W(CO)$_4${PPh$_2$(CH=CH$_2$)}$_2$], as off-white microcrystals, yield 35%, m/z = 1 302 (^{98}Mo^{184}W).

Acknowledgements

We thank the S.E.R.C. for financial support and the Edinburgh high field n.m.r. service for the ^{1}H-{^{31}P} n.m.r. spectrum.

References

1 Part 8, C. R. Langrick and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 511.

2 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99 and refs. therein.

3 S. J. Berners-Price, M. A. Mazid, and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1984, 969.

4 C. E. Briant, K. P. Hall, and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 843.

5 S. C. Trapathi, S. C. Srivastava, and A. K. Shrimal, *J. Organomet. Chem.*, 1974, **73**, 343.

6 R. L. Keiter, S. K. Keiter, N. P. Hansen, J. W. Brodack, and L. W. Cary, *Inorg. Chem.*, 1981, **20**, 283.

7 P. M. Treichel, W. K. Dean, and W. M. Douglas, *J. Organomet. Chem.*, 1972, **42**, 145.

8 J. G. Smith and D. T. Thompson, *J. Chem. Soc. A*, 1967, 1694.

9 R. B. King and T. F. Korenowski, *Inorg. Chem.*, 1971, **10**, 1188.

10 G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 1.

11 'NMR Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer, Berlin, 1971, vol. 5, p. 111.

12 G. T. Andres, I. J. Colquhoun, and W. McFarlane, *Polyhedron*, 1983, **2**, 783.

13 R. B. King, 'Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1.

14 R. B. King, *J. Organomet. Chem.*, 1967, **8**, 139.

Received 27*th July* 1984; *Paper* 4/1325