Hydrido-complexes of Molybdenum and Tungsten with Isonitrile and Carbyne-type Ligands

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Addition of acids, HX (X = BF_4, FSO_3, HSO_4, $ClSO_3$, Cl, or Br) to the complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (A) (M = Mo or W; R = Me, Bu^t, Ph, or C_6H_4Me-*p*; dppe = $Ph_2PCH_2CH_2PPh_2$) under carefully controlled conditions has given the hydride complexes [MH(CNR)$_2$(dppe)$_2$][X] (B) and the hydrido-carbyne complexes [MH{CN(H)R}(CNR)(dppe)$_2$][X]$_2$ (C). The i.r. and n.m.r. spectra of (B) and (C) are discussed with regard to their structures and compared with those of related complexes. A detailed analysis of the ^{31}P spectra of these complexes and of *trans*-[WH(N$_2$)$_2$(dppe)$_2$][HCl$_2$] is also given.

WE have recently described the preparation of the complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (A) (M = Mo or W; R = Me, Bu^t, Ph, or C_6H_4Me-*p*; dppe = $Ph_2PCH_2CH_2PPh_2$), where electron release from the electron-rich metal is sufficient to induce electrophilic attack at the nitrogen atoms of the isonitrile ligands.[1,2] Generally this attack, by reagents such as acids HX (X = BF_4, FSO_3, HSO_4, $ClSO_3$, Cl, or Br), has given complexes containing carbyne-type [CN(H)R] ligands.[2] Nevertheless, since the metal atom in such complexes is electron-rich, it might be expected also to be susceptible to electrophilic attack. We have found that this is indeed the case and under the appropriate conditions we have been able to isolate two series of hydride complexes containing isonitrile, or isonitrile and carbyne-like ligands, which are described below.

RESULTS AND DISCUSSION

Preparations.—(a) *Hydrido-isonitrile complexes* (B). These complexes were obtained either by the slow addition of 1 mol of HX to complexes (A) in dichloromethane solution or, for X = Cl or Br, by the addition of 2 mol of the gaseous acid to (A) in a vacuum (see Experimental section) [equation (1)] (M = Mo or W; R = Me, Bu^t, C_6H_5, or C_6H_4Me-*p*; X = BF_4, FSO_3, BPh_4, HSO_4, $ClSO_3$, or Br; for HX = HCl, the product anion is HCl_2).

$$trans\text{-}[M(CNR)_2(dppe)_2] + HX \rightarrow [MH(CNR)_2(dppe)_2][X] \quad (1)$$

A variety of acids were used to give these yellow, diamagnetic complexes in high yields. Analytical data, *etc*,, are shown in Table 1.

(b) *Hydrido-carbyne complexes* (*C*). If slightly more than 2 mol of HX are very slowly added dropwise, over a period of at least 10 min, to complexes (A) in CH_2Cl_2, then the hydrido-carbyne complexes (C) are formed, which may be isolated at *ca.* −20 °C [equation (2)].

$$trans\text{-}[M(CNR)_2(dppe)_2] + 2HX \rightarrow [MH\{CN(H)R\}(CNR)(dppe)_2][X]_2 \quad (2)$$

These yellow, diamagnetic compounds were also obtained in high yields and analytical data, *etc.*, are shown in Table 1.

These protonation reactions are very dependent upon the solvent used and on the rate of addition of acid. Thus slow addition of acid [or relatively slow reaction at low temperature using gaseous acid (see Experimental section)] is necessary to give the hydride and hydrido-carbyne complexes. If the acid is added very quickly or benzene is used as solvent, dicarbene or mono-carbyne complexes are produced respectively, which have been described elsewhere.[2]

Spectroscopic Properties and Structure.—(a) *Infrared spectra.* Both the complexes (B) and (C) display ν(CN) values which are higher than those of complexes (A), the order of frequency being (C) > (B) > (A) for corresponding complexes; *e.g.* an increase of ν(CN) relative to (A; M = W, R = Me)[1] of 366 cm^{-1} and 184 cm^{-1} respectively for (C; M = W, R = Me, X = BF_4) and (B; M = W, R = Me, X = BF_4). Such relative increases are to be expected in view of the decreased availability of metal *d*-electrons for back-bonding to π^*-RNC orbitals in (B) [formally M^{II}] and (C) [formally M^{VI}] as compared to (A) [formally M^0]. In addition, the intensity of the CN-stretching band is less in the complexes (C) than in complexes (B), again a result expected in view of the lower degree of electron release into the π^*-(CNR) orbitals in the former complexes, which results in their having a lower change of group dipole moment with symmetry co-ordinate.[3] The hydrido-carbyne complexes (C) also show a band in the region 1 555—1 580 cm^{-1} and a band in the region 3 140—3 250 cm^{-1} (which shifts appropriately in the deuterio-analogue shown in Table 1), which are assigned to ν(C=N) and ν(NH), respectively, of the carbyne ligand, CN(H)R (Table 1).

The M–H stretching vibration absorbs as a weak, broad band in the region 1 910—1 945 cm^{-1} for complexes (B) {ν(M–D) occurs at 1 405 cm^{-1} in [MoD(CNMe)$_2$(dppe)$_2$][BF$_4$]} but the M–H band in (C) appeared to be too weak to be assigned.

(b) *N.m.r. spectra.* (i) ^{1}H *Spectra.* Both the complexes (B) and (C) showed temperature-dependent spectra due to the fluxional behaviour of their M–H (and N–H) protons. Details of their ^{1}H n.m.r. spectra are shown in Table 2. Because of the fluxional behaviour, resonances are most clearly seen at lower temperatures. Thus the resonance due to CN(H)CH_3 protons is clearly seen as a doublet at −30 °C for [WH{CN(H)Me}-

TABLE 1

Hydride complexes of molybdenum and tungsten

M [a]	R [a]	X [a]	Colour	Λ_M [b] $S\ cm^2\ mol^{-1}$	M.p.[c] (°C)	Yield (%)	Analyses (%) [d]			ν(M–H) [e] [ν(M–D)]	ν(C≡N) [e]	ν(C=N) [e]
							C	H	N	cm^{-1}		
(a) Complexes $[MH(CNR)_2(dppe)_2][X]$ (B)												
W	Me	BF_4 [f]	Yellow	101	142 (decomp.)	62	57.1 (56.9)	4.8 (4.7)	2.5 (2.4)	1 935w,br	2 018s,br	
		FSO_3	Light green	96	106 (decomp.)	58	57.5 (57.8)	4.5 (4.8)	2.6 (2.4)	1 945w,br	2 030s,br	
		BPh_4	Brown	77	220—226	47	69.1 (69.5)	5.5 (5.5)	2.0 (2.0)	1 925w,br	2 035s,br	
		HCl_2 [g]	Yellow	80	162—164	80	60.0 (59.7)	5.0 (5.3)	2.5 (2.3)	1 930m,br	2 010s,br	
	Bu^t	BF_4 [h]								1 910w,br	2 009s,br	
		BPh_4 [h]									2 000s,br	
	p-MeC_6H_4	BF_4 [a]	Yellow	91	263—236	31	61.3 (61.2)	4.8 (4.8)	2.1 (2.1)		1 935s,br	
Mo	Me	BF_4 [h]	Yellow	95	270—277	60	62.1 (62.2)	5.4 (5.1)	2.6 (2.6)	1 930 [1 405]w,br	2 036s,br	
		HSO_4	Yellow	84	170 (decomp.)	45	62.9 (62.7)	5.8 (5.3)	2.6 (2.6)	1 925w,br	2 038s,br	
	p-MeC_6H_4	BF_4 [i]	Yellow	99	114 (decomp.)	34	66.1 (66.3)	5.2 (5.2)	2.5 (2.3)		1 951s,br	
		HCl_2 [j]	Yellow	65	172 (decomp.)	83	67.7 (68.1)	5.6 (5.8)	2.2 (2.3)		1 953s,br	
		Br	Yellow	75	170 (decomp.)	86	67.1 (67.6)	5.4 (5.3)	2.0 (2.3)		1 953s,br	
	Ph	Br [g]	Yellow								1 930s,br	
(b) Complexes $[MH(CNHR)(CNR)(dppe)_2][X_2]$ (C)												
W	Me	BF_4	Yellow	152 [k]	282—283	81	54.0 (54.3)	4.6 (4.6)	2.4 (2.3)	3 250 [2 400]m,br [l]	2 200s	1 568s,br
		HSO_4	Yellow	97	190 (decomp.)	58	53.0 (53.4)	4.7 (4.6)	2.2 (2.2)	3 140m,br	2 200s	1 570s,br
		FSO_3	Yellow	144	120 (decomp.)	50	52.8 (53.3)	4.7 (4.5)	2.3 (2.2)	3 147w,br [l]	2 200s	1 560s,br [l]
		$ClSO_3$ [m]	Yellow	220 [k]	155	32	53.9 (53.4)	5.0 (5.0)	2.1 (1.9)	3 150m,br [l]	2 200s	1 580s,br [l]
Mo	Me	BF_4	Yellow	117	275—280	48	58.3 (58.5)	4.7 (4.9)	2.4 (2.4)	3 245m,br [l]	2 200s	1 555s,br [l]

[a] M = Mo or W; R = Me, Bu^t, Ph, or C_6H_4Me-p; X = various anions as appropriate. [b] In *ca.* 10^{-3} mol dm^{-3} $PhNO_2$ solution unless otherwise stated. [c] In sealed, evacuated tubes. [d] Calculated values in parentheses. [e] Nujol mull spectra. [f] Contains $0.5CH_2Cl_2$ of crystallisation. [g] Contains thf of crystallisation, Cl analysis 5.8 (5.9). [h] Impure complex; other anions were used, but complexes impure, see text. [i] Contains 0.25 CH_2Cl_2 of crystallisation. [j] Cl analysis 5.6 (5.9). [k] In *ca.* 10^{-3} mol dm^{-3} dimethylformamide solution. [l] Value of ν(N–H) [ν(N–D)]. [m] Contains 2thf of crystallisation. s = Strong, m = medium, w = weak, br = broad.

(CNMe)]$[BF_4]_2$ but is unresolved at 25 °C (Table 2). The doublet structure collapses to a singlet on addition of D_2O, with a corresponding elimination of the resonance at 5.9 p.p.m. due to the N–H proton, confirming the assignment of a carbyne ligand in this complex and its analogues, which have similar spectral properties (see Tables 1 and 2).

The resonance due to the CH_2 groups of the dppe ligands is a very broad doublet for (B; R = Me or C_6H_4-Me-p) (J = 20—22 Hz, Table 3), which may be due to coupling with phosphorus, since the same apparent coupling constant is also seen in the spectrum determined at 60 MHz. The corresponding resonances in complexes (C) are much broader and could not be adequately resolved from the resonances of the $CHCH_3$ groups. The complexes (B; R = C_6H_4Me-p) show a doublet resonance (J = 8.0 Hz) which appears to be the high-field half of an AB pattern, due to the aromatic protons which are *ortho* to N[4] in the isonitrile ligands.

The low-temperature-limit hydride resonance in complexes (B) and (C) is a triplet of triplets due to coupling with four phosphorus atoms of the AA′XX′ type (see below). On raising the temperature this pattern broadens before finally collapsing into a quintet, the four phosphorus atoms then appearing to be equivalent. The chemical shift of the hydride resonance of complexes (B) (δ −5.1 to −6.3) is to slightly higher field of the hydride resonance of $[WH(N_2)_2(dppe)_2]$-$[HCl_2]$ (δ −3.50) and to still higher field of that of the hydride-carbyne complexes (C) (δ −0.82 to −2.3). This trend may reflect a decreasing electron density at the metal, since both N_2 and the carbyne ligand are able to withdraw electron density more effectively from the metal than does isonitrile.

(ii) ^{31}P *Spectra.* These spectra are also temperature dependent for both complexes (B) and (C) and are shown in Table 3 together with spectral data for $[WH(N_2)_2$-$(dppe)_2][HCl_2]$ which are included for comparison.[5] The chemical shift of the dppe ligand is to lower field for molybdenum complexes than for their tungsten analogues as is generally observed in phosphine complexes of these metals.[6] The chemical shift for the complexes $[WH(XY)_2(dppe)_2]^+$ (XY = CNMe or N_2) and (C; M = W, R = Me) fall within the range (δ 89.3—94.6) but do not show the same relative order as is observed for the hydride resonances.

In the low-temperature limit, the spectra of complexes (B), (C), and $[WH(N_2)_2(dppe)_2][HCl_2]$ consist of an AA′-XX′ pattern which coalesces to a singlet on heating, with average chemical shifts δ_{av} as shown in Table 3. The low-field half of the low-temperature-limit spectra is attributed to the phosphorus with the greater coupling to the hydride, since it is broader than the high field half in the proton undecoupled spectra and in spectra obtained by selective proton irradiation. The spectra were analysed according to the method of Abraham [7] using the notation shown in Figure 1.

The values of the coupling constants shown in Table 3 are, of course, not the only solutions, 32 combinations being possible, the only restriction being that J and J' must have opposite signs. The values of the coupling constants (assuming the signs as shown) were refined using a LAME iterative programe (Table 3).[7] The unrefined values show a maximum deviation of 0.7 Hz from the computed ones and therefore the coupling constants for all complexes are considered to have an error of about ±0.7 Hz. The computed spectra were

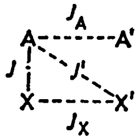

FIGURE 1

TABLE 2

^{1}H n.m.r. data [a]

M [b]	R [b]	X [b]	Temperature (°C)	δ (±0.02)	Integration [c]	Assignment	^2J(PMH) [d] (±1 Hz)
(*a*) Hydride complexes $[MH(CNR)_2(dppe)_2][X]$ (B)							
Mo	Me	BF_4 [e]	−70	8.0—6.0(m)	40 (40)	dppe aromatic	
				3.50(q)	1.8 (2)	$O(CH_2CH_3)_2$	
				2.82(s)	6 (6)	CN*Me*	
				2.57(d,br) [f]	7(8)	dppe methylenes	
				1.20(t)	3 (3)	$O(CH_2CH_3)_3$	
				−6.33(tt) [g]	1 (1)	M–*H*	68, 12
			25	−6.1(quin) [g]	1 (1)	M–*H*	42
	C_6H_4Me-*p*	HCl_2 [h]	25	7.4—6.6(m)	44 (44)	dppe aromatic + isonitrile aromatic *ortho* to Me	
				6.14(d) [i]	4 (4)	Isonitrile aromatic *ortho* to N	
				2.62(t,br) [j]	8 (8)	dppe methylenes	
				2.35(s)	6 (6)	$CNC_6H_4CH_3$	
				−5.53(quin)	1 (1)	M–*H*	42
W	Me	BPh_4 [k]	25	8.3—6.1(m)	60 (60)	dppe aromatic + BPh_4	
				2.84(s)	5 (6)	CN*Me*	
				2.52d(t,br) [j]	7.5 (8)	dppe methylenes	
				−6.1(quin)	1 (1)	M–*H*	44
		HCl_2	25	7.9—6.7(m)	40 (40)	dppe aromatic	
				2.85(s)	5.7 (6)	CN*Me*	
				2.6d(t,br)	8 (8)	dppe methylenes	
				−5.9(quin)	1 (1)	M–*H*	44
			−65	−6.4(tt)	1 (1)	M–*H*	71, 21
W	C_6H_4Me-*p*	BF_4	−30	7.9—6.5(m)	44 (44)	dppe aromatic + isonitrile aromatic *ortho* to CH_3	
				6.26(d) [i]	4 (4)	Isonitrile aromatic *ortho* to N	
				2.7d(t,br) [j]	7.6 (8)	dppe methylenes	
				2.43(s)	6 (6)	$CNC_6H_4CH_3$	
				−5.1(tt) [l]	1 (1)	M–*H*	72, 13
(*b*) Hydrido-carbyne complexes $[MH\{CN(H)R\}(CNR)(dppe)_2][X]_2$ (C)							
W	Me	BF_4	−30	7.8—6.7(m)	40 (40)	dppe aromatic	
				5.9(m,br) [m]	1 (1)	CN*H*Me	
				3.2—2.5(m,br)	8 (8)	dppe methylenes	
				2.50(s)	2.8 (3)	CN*Me*	
				2.03(d) [n]	3 (3)	CNH*Me*	
				−0.9(tt)	1 (1)	M*H*	68, 12
			+25	7.7—6.5(m)	40 (40)	dppe aromatic	
				3.4—1.5(m,br)B	14 (14)	dppe methylenes + CN*Me* + CHN*Me*	
				−0.8(quin)	0.9 (1)	M*H*	40 (±2)
Mo	Me	BF_4	−95	8.2—6.4(m)	40 (40)	dppe aromatic	
				3.7—2.1(m,br)	8 (8)	dppe methylenes	
				2.44(s)	3 (3)	CN*Me*	
				1.90(d) [o]	3 (3)	CHN*Me*	
				−2.3(tt)	1 (1)	M*H*	65, 12 (±2)
			+25	8.0—6.7(m)	40 (40)	dppe aromatic	
				3.2—1.7(m,br)	13 (14)	dppe methylenes + CN*Me* + CHN*Me*	
				−1.8(quin)	0.9 (1)	M*H*	38 (±2)

[a] In CD_2Cl_2, relative to $SiMe_4$. [b] M = Mo or W; R = Me, Bu^t, or C_6H_4Me-*p*; X = BF_4, HCl_2, or BPh_4 as appropriate. [c] Calculated values in parentheses. [d] $J(P_AH) = J(P_{A'}H)$ and $J(P_XH) = J(P_{X'}H)$ when ^{31}P resonance is an AA′XX′ pattern (see Table 3). Hydride resonance is then a tt. [e] Containing $0.5Et_2O$ of crystallisation. [f] $^2J(PH) = 22 \pm 1$ Hz. [g] At −30 °C intermediate pattern between qt and tt. [h] In $CDCl_3$ solution. [i] $^3J(HCCH) = 8.0$ Hz. [j] $^2J(PCH) = 20 \pm 1$ Hz. [k] In C_5D_5N. [l] At 25 °C, intermediate pattern between qt and tt. [m] Disappears on D_2O addition. [n] Collapses to singlet on D_2O addition, $^3J(HCNH) = 4.8 \pm 0.2$ Hz. [o] Not well resolved; $^3J(HCNH) = 3.2 \pm 0.5$ Hz.

m = Multiplet, quin = quintet, tt = triplet of triplets, br = broad, s = singlet, d = doublet.

TABLE 3

^{31}P N.m.r. data [a]

			High-temperature limit [c]			Low-temperature limit (AA'XX' type pattern) [d]										
M [b]	R [b]	X [b]	Temperature (°C)	δ	^1J(WP)	Temperature (°C)	δ_A	δ_X	δ_{av}	$\delta_A - \delta_X$	^1J (WP$_A$)	^1J (WP$_X$)	J_A	J	J'	J_X
(*a*) Hydrido-carbyne complexes, $[MH\{CN(H)Me\}(dppe)_2][X]_2$ (C)																
W	Me	BF_4 [e]				−55	80.4	100.5	(90.4)	20.1	146.5	195.3	30.7	35.7	−28.4	16.7
						+25 [f]	*ca.* 71.8	*ca.* 88.2								
Mo	Me	BF_4				−95	63.8	87.7	(75.8)	23.9			39.7	42.4	−42.4	15.9
(*b*) Hydride complexes, $[MH(CNR)_2(dppe)_2][X]$ (B)																
W	Me	HCl_2	72	89.9	193.4	−58	76.7	101.8	(89.3)	25.0	174.6	212.4	30.5	43.6	−33.9	13.4
			25	91.8br												
	C_6H_4Me-*p*	BF_4 [e]				−40	79.1	102.3	(90.7)	23.2	168.5	207.5	30.9	43.7	−34.0	14.2
Mo	Me	BF_4 [e]	25	68.9		−70	55.2	81.8	(68.5)	26.6			38.7	46.5	−46.6	13.4
(*c*) Complex $[WH(N_2)_2(dppe)_2][HCl_2]$ [g]																
						+32	80.6	108.6	(94.6)	28.0			28.4	55.3	−29.8	10.3

[a] In CD_2Cl_2, δ upfield from $P(OMe)_3$, J values in Hz ($\pm$2.4). [b] M = Mo or W; R = Me or C_6H_4Me-*p*; X = BF_4 or HCl_2. [c] Singlet for Mo complexes; triplet (including the two ^{183}W satellites) for W complexes. [d] See text for notation; δ_{av} = average resonance seen at higher temperatures. [e] J_A, J, J', J_X values refined by computation (see text). [f] Low- and high-field halves as two broad unresolved humps. [g] ^{1}H Spectrum reported in ref. 5, ^{31}P spectrum studied in present work, coupling constants refined by computation (see text).

in good agreement with experiment; examples for (B; M = W, R = C_6H_4Me-*p*, X = BF_4) and (C; M = W, R = Me, X = BF_4) are shown in Figure 2. In the only case where $^1J(^{183}W^{31}P)$ can be determined for comparable complexes it is greater for (B; M = W, R = Me, X = BF_4) than for (C; M = W, R = Me, X = BF_4).

(iii) ^{13}C *Spectra.* The ^{13}C n.m.r. spectrum of $[WH(CNHMe)(CNMe)(dppe)_2][BPh_4]_2$ in $CDCl_2$ shows a broad multiplet resonance at low field (δ 245.3 relative to $SiMe_4$) which is assigned to the carbyne-carbon since such resonances generally occur in the 230—290 p.p.m. range.[8] The *C*NMe resonance is at higher field (δ 147.3) and other resonances are at 133.0—129.5 (dppe aromatic-*C*) and δ 30.8 (dppe CH_2, $NHCH_3$, and $CNCH_3$). Unfortunately the broadness of the resonances prevented measurement of $^1J(^{183}W^{13}C)$ values.

Structures of the Complexes.—Three structures are likely for seven-co-ordinate complexes of this type, pentagonal bipyramidal {PB, *e.g.* $[WH(N_2)_2(dppe)_2][HCl_2]$};[5] capped octahedral {CAPO, *e.g.* $[TaH(CO)_2(dmpe)_2]$ [9] (dmpe = $Me_2PCH_2CH_2PMe_2$)}; and capped trigonal prismatic {CTP, *e.g.* $[MoCl(CO)_2(Me_2AsC_6H_4AsMe_2)_2]^+$}.[10] The latter structure seems unlikely for complexes (B) and (C) because they have only one CN stretching band in their i.r. spectra instead of the expected two for CTP(C_{2v}). It therefore remains to distinguish between the CAPO and PB structures.

The complex $[TaH(CO)_2(dmpe)_2]$ has been shown by *X*-ray crystallography to have the CAPO structure and $^2J(^{31}$P-hydride) values of 89.3 and 14.3 Hz.[9] The complexes $[MoH(CO)_2(dppe)_2][SO_3F]$,[11] $[WH(CO)(CS)(dppe)_2][CF_3SO_3]$,[12] and $[MoH(CO)_2(dmpe)_2][HCl_2]$,[13] also have ^2J(P-hydride) values in a similar range (66—72 and 8—14 Hz). They have also all been assigned the CAPO structure on the basis of the similarity of their n.m.r. spectral features to those of $[TaH(CO)_2(dmpe)_2]$ and also because of the common occurrence of this structure in seven-co-ordinate complexes of molybdenum(II) and tungsten(II), *e.g.* $[MoBr_2(CO)_3(dppe)]$.[14] It is therefore tempting to assign the CAPO structure to complexes (B) and (C), which have ^2J(P-hydride) values in the ranges 68—70 and 12—21 Hz and show the expected AA'XX' ^{31}P n.m.r. spectrum (Tables 2 and 3). However, the coupling constants observed for $[WH(N_2)_2(dppe)_2][HCl_2]$ [J(P-hydride) = 71.5 and 10 Hz; * AA'XX' ^{31}P pattern, Table 3] also fall in the same region, although it has the PB structure in the solid state.[5] Thus it does not appear possible to distinguish clearly the two structures on the basis of n.m.r. spectral parameters.

Nevertheless, there must be only a small energy difference between the two isomeric forms in solution so that they might easily undergo interconversion, especially if the temperature is raised. This sort of process, involving fluxionality of the molecule by proton migration, may account for the high-temperature ^{1}H-hydride spectra of (B) and (C), where the phosphorus atoms are apparently magnetically equivalent [Figure 3 shows the effect of temperature on the spectrum of (B; M = Mo, R = Me, X = BF_4) as an example]. Detailed lineshape calculations for a mutual phosphine exchange process in CAPO structures of the type $[MHL_2L_2']$ (M = metal,

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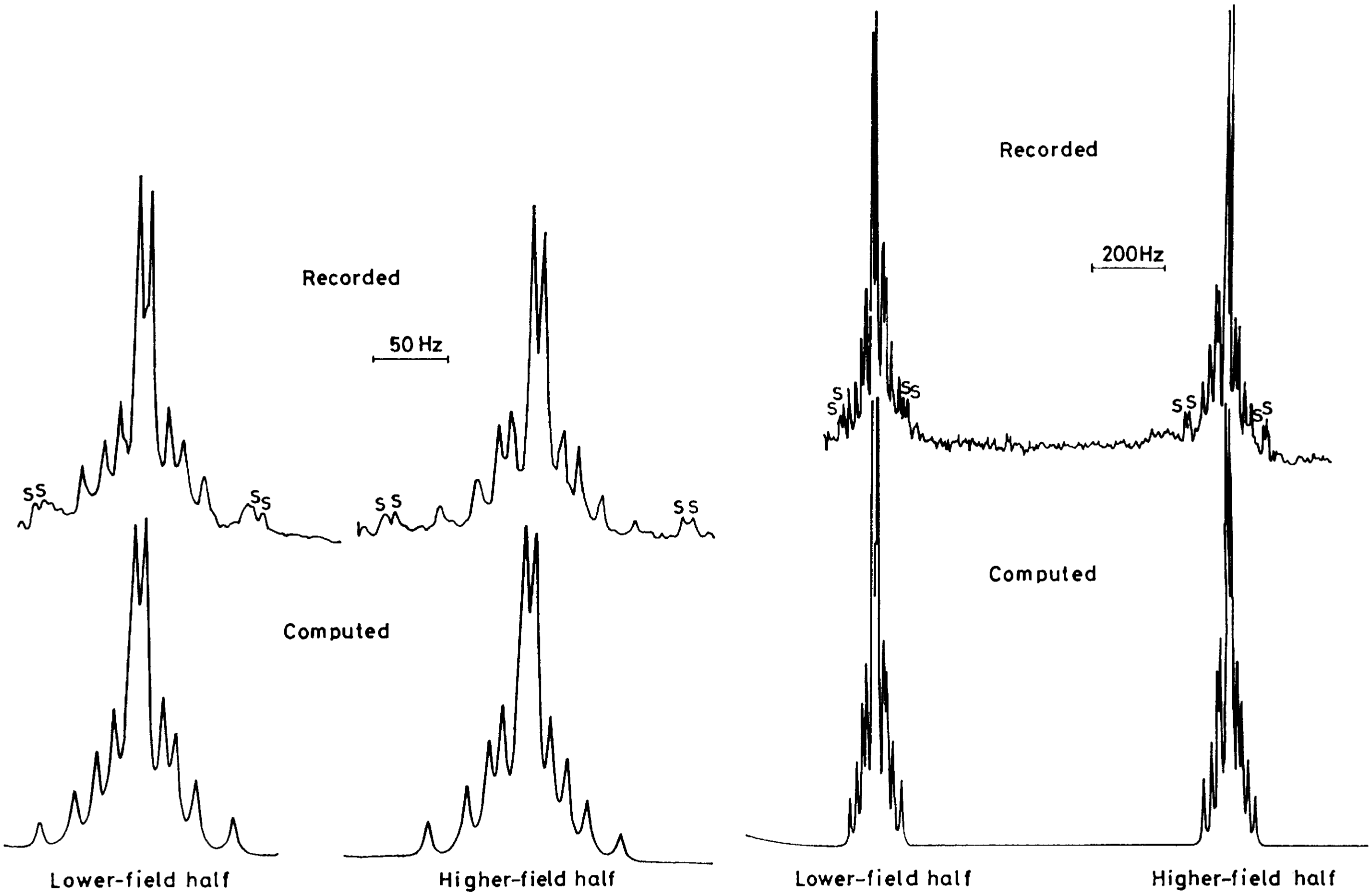
* These values replace those given in ref. 5, which are a factor of 10 too small owing to a misprint.

L = monodentate ligand, L_2' = bidentate ligand) have indicated that the outer lines of the hydride spectrum should remain sharp and the essential symmetry of the spectrum be retained over the temperature range.[9] This is the type of shape observed in the spectrum of complexes (B) and (C) (Figure 3). A fluxional process involving a CAPO structure in which the proton can move over the faces of the octahedron, above and below the P_4 plane, perhaps also involving a PB intermediate, has been suggested to account for the ^{1}H-hydride spectrum of $[MoH(CO)_2(dppe)_2][SO_3F]$,[11] which shows similar features to Figure 3. In the absence of more definitive structural data, such a CAPO structure and fluxional process appear also to account very reasonably for the n.m.r. spectra of complexes (B) and (C).

Because of the electron-rich nature of the $M(dppe)_2$ site, it is susceptible to attack by protons even when it carries electron-withdrawing ligands, *e.g.* in the complexes (A), *trans*-$[M(N_2)_2(dppe)_2]$,[5] $[M(C_2H_4)_2(dppe)_2]$,[15] and *cis*-$[M(CO)_2(dppe)_2]$.[11] Susceptibility to protic attack may also be induced in a ligand without attack at the metal, *e.g.* the complexes $[MX(NNH_2)(dppe)_2][X]$ (X = Cl or Br) have been obtained by treating *trans*-$[M(N_2)_2(dppe)_2]$ with HX. Complexes (A) are, however, exceptional in that attack at both the metal atom and a ligand can occur in the same complex, to give the hydride-carbyne complexes (C). Attack of other potential electrophiles, such as alkylating reagents, can also occur on complexes (A) but not at the metal, to give complexes with dialkylcarbyne ligands, which will be described separately.



(a) $[WH(CN(H)Me)(CNMe)(dppe)_2][BF_4]_2$ (b) $[WH(CNC_6H_4Me\text{-}p)_2(dppe)_2][BF_4]$

S = ^{183}W satellites

FIGURE 2 Comparison of actual and computer-simulated ^{31}P n.m.r. spectra of some tungsten complexes (low-temperature limit)

EXPERIMENTAL

All air-sensitive materials were handled using standard nitrogen-flow or high-vacuum techniques. The complexes (A) were prepared by published methods.[1] Mineral acids were analytical grade (B.D.H.) and were used as supplied. Tetrahydrofuran was distilled from sodium benzophenone-ketyl before use and all other solvents were dried and distilled under dinitrogen prior to use. Infrared spectra were determined with a Unicam SP 2000 or Perkin-Elmer 577 instruments, and n.m.r. spectra with a JEOL PS100 spectrometer equipped with a 546J digital signal averager, JEOL PFT 100 Fourier-transform, or Varian EM360 instruments. The solvents used for n.m.r. spectroscopy were scrupulously dried and degassed before use. Conductivities were measured using a Portland Electronics P310 conductivity bridge and melting points with an electrothermal melting point apparatus. Microanalyses were by Mr. and Mrs. Olney of the University of Sussex.

Preparation of Hydride Complexes.—Since preparations are general only one specific example is given for each type of complex. Analytical data, *etc.*, for all complexes are shown in Table 1.

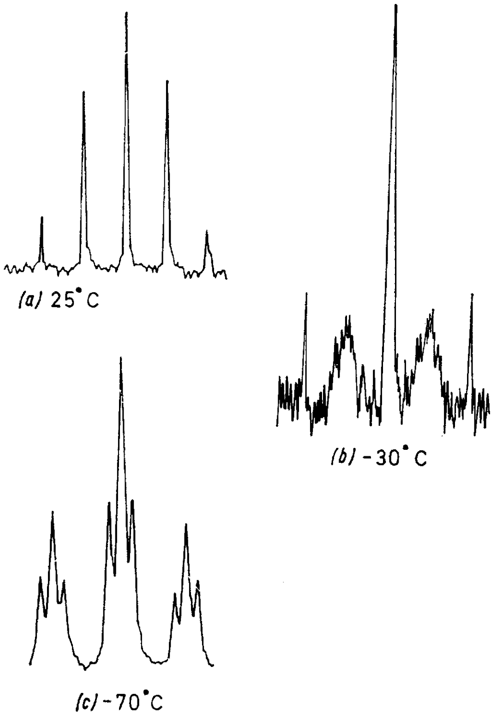


FIGURE 3 Hydride resonances of $[MoH(CNMe)_2(dppe)_2][BF_4]$ in CD_2Cl_2

Bis[1,2-*bis(diphenylphosphino)ethane*]*hydrido(methylaminocarbyne)(methyl isonitrile)tungsten*(VI) *Bis(tetrafluoroborate)*,* $[WH\{CN(H)Me\}(CNMe)(dppe)_2][BF_4]_2$.—Fluoroboric acid ($1.17\ cm^3$ of an ether solution prepared by 1 : 21 dilution of $[Et_2OH][BF_4]$, 0.402 mmol acid) was slowly added dropwise (total addition lasting *ca.* 10 min) to a solution of *trans*-$[W(CNMe)_2(dppe)_2]$ (0.195 g, 0.183 mmol) in CH_2Cl_2 ($40\ cm^3$). During the addition the solution darkened initially to a brown colour which changed slowly to yellow. The solution was concentrated in a vacuum followed by addition of ether and cooling to *ca.* −20 °C to give the product as *light yellow needles*, which were filtered, washed with ether, and dried (10^{-3} mmHg, 20 °C) (0.184 g, 81%).

Bis[1,2-*bis(diphenylphosphino)ethane*]*hydridobis(methyl isonitrile)molybdenum*(II) *Tetrafluoroborate*, $[MoH(CNMe)_2(dppe)_2][BF_4]$.—$[Et_2OH][BF_4]$ ($0.025\ cm^3$, 0.182 mmol) was added slowly to a solution of *trans*-$[Mo(CNMe)_2(dppe)_2]$ (0.178 g, 0.182 mmol) in CH_2Cl_2 ($25\ cm^3$). The solution darkened initially to a brown colour then lightened slightly. It was then refluxed for a few minutes, when its colour lightened further. The resulting solution was concentrated to *ca.* $10\ cm^3$, then ether ($20\ cm^3$) was added and the mixture filtered. Further concentration of the solution *in vacuo* gave *green-yellow needles* of the product which were filtered, washed with ether, and dried (10^{-3} mmHg, 20 °C). A further crop of product was obtained by concentration of the mother-liquor and addition of ether, giving a total yield of 0.118 g (60%).

Bis[1,2-*bis(diphenylphosphino)ethane*]*hydridobis*(p-*tolyl isonitrile*)*molybdenum*(II) *Hydrogendichloride*, $[MoH(CNC_6H_4Me\text{-}p)_2(dppe)_2][HCl_2]$.—Gaseous HCl (0.434 mmol) was condensed onto *trans*-$[Mo(CNC_6H_4Me\text{-}p)_2(dppe)_2]$ (0.237 g, 0.210 mmol) and tetrahydrofuran (thf) ($12\ cm^3$) in a vacuum at −196 °C. On warming to room temperature a red solution was obtained, from which precipitated *greenish yellow crystals* which were filtered off under dinitrogen, washed with thf, and dried (10^{-3} mmHg, 20 °C). Concentration of the filtered solution gave a further crop of the product (total yield 0.21 g, 83%). The same procedure was adopted to give the bromide analogues.

We thank the Instituto de Alta Cultura, Portugal for a maintenance grant (to A. J. L. P.), and Mr. M. Siverns for n.m.r. spectral measurements.

[8/1884 *Received, 27th October*, 1978]

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* More systematically (albeit only formally), bis[1,2-bis(diphenylphosphino)ethane]hydrido(methylaminomethylidyne)(methyl isocyanide)tungsten(VI) bis(tetrafluoroborate).