Protonation of Isonitriles Ligating Molybdenum(0) and Tungsten(0) at Nitrogen giving Complexes of Carbyne and Carbene Ligands

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Treatment of the complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (1: M = Mo or W; R = Me, Bu^t, or 4-MeC$_6$H$_4$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with mineral acids causes protonation at one or both nitrogen atoms to give the compounds *trans*-[M(CNHR)(CNR)(dppe)$_2$]X (2: M = Mo, R = Me, X = BF$_4$, HSO$_4$, or SFO$_3$; M = W, R = Me, X = BF$_4$, HSO$_4$, SFO$_3$, or H$_2$PO$_4$; R = Bu^t, X = BF$_4$, HSO$_4$, or SFO$_3$) and *trans*-[M(CNHR)$_2$(dppe)$_2$]X$_2$ (3: M = Mo, R = Me, X = BF$_4$; M = W, R = Me, X = BF$_4$, HSO$_4$, SFO$_3$, or SClO$_3$; R = 4-MeC$_6$H$_4$, X = BF$_4$). Deuterio-analogues have been prepared. Treatment of *trans*-[W(CNMe)$_2$(dppe)$_2$] with Al$_2$Et$_6$ in benzene gives an unstable adduct *trans*-[W{CN(AlEt$_3$)Me}$_2$(dppe)$_2$]. With HX (X = BF$_4$ or HSO$_4$), *cis*-[Mo(CO)$_2$(dppe)$_2$] gives, under dinitrogen, *trans*-[M(CO)$_2$(dppe)$_2$]X. Spectroscopic (i.r. and n.m.r.) data for these compounds are discussed in terms of their structure.

THE attack of nucleophilic reagents at the carbon atom of isonitriles ligating transition metals in their normal or higher oxidation states is well documented.[1] In such complexes, the metal centres are somewhat electron deficient with the result that there is little π character in the metal–carbon bond, the MCNR system is essentially linear and nucleophilic attack at carbon is promoted. If, however, an electron-rich site such as M(dppe)$_2$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) is ligated, the metal–carbon bond can have considerably more π character as a result of electron release from the metal, with the result that bending of the MCNR system at the nitrogen atom is induced.[2] For example, the CNMe angle is reduced to 156° in *trans*-[Mo(CNMe)$_2$(dppe)$_2$][2] and the CNBu^t angle is only 130(2)° in [Ru(CNBu^t)$_4$(PPh$_3$)].[3] In this condition, the nitrogen atom of the isonitrile becomes susceptible to electrophilic attack and here we describe in detail such an attack, by protons, on the complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (1: M = Mo or W, R = Me, Bu^t, or 4-MeC$_6$H$_4$) which leads to the formation of ligands which have carbene or carbyne-like character. A preliminary account has already appeared.[2]

The products of such reactions which can be isolated depend upon the nature of M and of R, with tungsten showing the greatest variety. Thus, although complexes protonated at one or both isonitrile nitrogen atoms have been isolated for both metals when R = Me, only products for M = W have been obtained when R = Bu^t (protonated at one N atom) and R = 4-MeC$_6$H$_4$ (protonated at both N atoms).

RESULTS AND DISCUSSION

Monoprotonation of Isonitrile Complexes.—Addition of 1 mol of mineral acid (HX) to (1: M = Mo, R = Me; M = W, R = Me or Bu^t) in benzene at 20 °C precipitates the green, crystalline, diamagnetic monocarbyne complexes *trans*-[M(CNHR)(CNR)(dppe)$_2$]X (2) [equation (1); M = Mo, X = BF$_4$, HSO$_4$, or SFO$_3$; M = W, X = BF$_4$, HSO$_4$, SFO$_3$, or H$_2$PO$_4$].

Analytical and spectroscopic data for these complexes are shown in Tables 1 and 2. The complexes (2) are stable in the solid state and in solution at low temperature but slowly rearrange at 20 °C in solution to hydrido-complexes which have been described.[4] The site of protonation is shown to be the nitrogen atom in complexes (2: R = Me) by the appearance of an N–H absorption in their i.r. spectra, appropriately shifted on deuteriation (Table 1), and of a quartet resonance for the N–H proton in their n.m.r. spectra. The N–H resonance could only be observed at low temperature, presumably because of rapid proton exchange between nitrogen atoms at higher temperatures, and its coupling [^3J(HH) = 4.7 Hz] with the methyl protons was demonstrated by decoupling and deuteriation experiments (Table 2). At low temperatures the N–CH_3 resonance of the protonated isonitrile is a doublet and that of the other isonitrile a singlet. The doublet resonance collapses to a broad singlet at higher temperatures when rapid proton exchange occurs. The value of ^3J(HH) = 4.7 Hz observed for the protonated isonitrile is in the range observed for ^3J(HCNH) in carbene ligands containing the NHCH$_3$ group (4.4—4.0 Hz) in such complexes as [Os(CNMe)$_4${C(NHMe)$_2$}$_2$][ClO$_4$]$_2$ [5] and *trans*-[PtCl{C(NHPh)NHMe}(PEt$_3$)$_2$][ClO$_4$].[6]

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

The value of ν(NC) for (2; M = Mo or W) is increased by 230—330 cm^{-1} relative to that for (1; M = Mo or W). A singlet ^{31}P n.m.r. resonance is observed for (2; M = Mo or W) indicating a *trans* structure for these compounds (Table 2). The ^{13}C n.m.r. spectra of (2; R = Me) show a signal at 242—248 p.p.m. to low field of SiMe$_4$, which is assigned to the protonated (carbyne) ligand because this value is in a similar range to those observed for carbyne ligands in complexes such as [WY(CNR$_2$)(CO)$_4$] (Y = Br or I, R = Me or Et).[7] Unfortunately the broadness of the resonance of (2; M = W, R = Me) (due to coupling with phosphorus) did not allow determination of ^1J(WC) (Table 2). The isonitrile-carbon resonance (155—160 p.p.m.) is to high field of the carbyne resonance, and both the isonitrile and the carbyne resonances of (2; M = Mo) are to low field of those for (2; M = W). A similar metal-dependent trend is shown by the related complexes [MBr(CNPh)(CO)$_4$] (M = Mo or W) and is commonly observed for carbene and carbonyl resonances in pentacarbonyl complexes of the Group 6 transition metals.[7] The opposite trend is shown for the CH_3 resonance of the carbyne and the isonitrile ligands of (2; R = Me) however, and for the carbene methyl resonance in $[M(CO)_5\{C(OCH_3)CH_3\}]$ (M = Mo or W).[8]

Diprotonation of Isonitrile Complexes.—The compounds $[M(CNHR)_2(dppe)_2]X_2$ (3: M = Mo or W, R = Me; M = W, R = 4-MeC_6H_4), in which both isonitrile nitrogen atoms are protonated, are obtained by the rapid addition of an excess of HX (X = BF_4, HSO_4, SFO_3, or $SClO_3$) to (1: M = Mo or W, R = Me; M = W, R = 4-MeC_6H_4) in dichloromethane, methanol, or tetrahydrofuran (thf) [equation (2); M = Mo, R = Me, X = BF_4; M = W, R = Me, X = BF_4, HSO_4, SFO_3, or $SClO_3$; M = W, R = 4-MeC_6H_4, X = BF_4].

Like the monocarbyne complexes (2), compounds (3) show N–H bands in their i.r. spectra which shift appropriately in their deuterio-analogues. They have no

$$\textit{trans-}[M(CNR)_2(dppe)_2] + HX(\text{excess}) \xrightarrow{CH_2Cl_2} [M(CNHR)_2(dppe)_2]X_2 \quad (2)$$

C≡N band, but bands in the region 1 615—1 645 cm^{-1}, assigned to vibrations of a $C\overset{+}{\equiv}N$ system. Immonium salts ($R_2CHCR{=}\overset{+}{N}R_2$) have a CN i.r. absorption in the range 1 644—1 691 cm^{-1}.[9] These bands are some 100 cm^{-1} to higher frequency than bands assigned to CN in the monocarbyne complexes (2) (Table 2). When HBF_4 is the acid used the compounds $[M(CNHMe)_2(dppe)_2][BF_4]_2$ (M = Mo or W) are isolated as a mixture of two isomers, one yellow and one red, whose crystals may be separated by hand. Both crystalline isomers have corresponding N–H and CN bands in their i.r.

TABLE 1

Physical properties of the complexes $[M(CNHR)(CNR)(dppe)_2]X$, $[M(CNHR)_2(dppe)_2]X_2$, and $[Mo(CO)_2(dppe)_2]X$

M	R	X	Colour	Λ_M [a]/ S cm^2 mol^{-1}	M.p.[b] (θ_c/°C)	Yield (%)	Analysis (%) [c] C	H	N	ν(NH) [d] [ν(ND)]	ν(C≡N) [d]	ν(C=N) [d]
(*a*) Complexes (1)												
W	Me	BF_4	Green	92	227—230	91	58.8 (58.5)	4.8 (4.8)	2.4 (2.4)	3 315	2 168	1 524
		HSO_4	Green	61	209—211	92	57.6 (57.9)	5.3 (4.9)	2.3 (2.4)	3 210 [2 360]	2 165	1 533
		SFO_3	Green	94	216—218	80	57.9 (57.8)	4.8 (4.8)	2.6 (2.4)	3 312	2 168	1 525
		H_2PO_4 [e]	Green							3 315	2 180	1 515
	Bu^t	BF_4 [f]	Greenish brown	92	232—234	88	57.2 (57.3)	5.3 (5.3)	2.0 (2.1)	3 260 [2 405]	2 135	
		HSO_4 [g]	Green	71	173—175	68	60.8 (60.8)	5.6 (5.6)	2.2 (2.2)	3 260	2 135	
		SFO_3 [h]	Green	86	221—223	85	62.0 (61.6)	5.7 (5.6)	2.2 (2.1)	3 267	2 132	
		BPh_4 [i,j]	Greenish brown	68	102—111	52	70.0 (70.3)	6.1 (6.1)	2.0 (1.9)	3 270	2 120	
Mo	Me	BF_4	Green	86	238 241	81	63.4 (63.3)	5.2 (5.2)	2.6 (2.6)	3 320 [2 320]	2 163	1 518
		HSO_4	Green	55	174—176	71	62.7 (62.7)	5.7 (5.3)	2.6 (2.6)	3 200	2 170	1 530
		SFO_3	Green	88	208—211	84	62.2 (62.6)	5.3 (5.2)	2.3 (2.6)	3 318	2 177	1 515
(*b*) Complexes (2)												
W	Me	BF_4 [k]	Red [i]	129 [l]	238—240	92	54.9 (54.6)	4.8 (4.8)	2.5 (2.2)	3 407 [2 525]		1 630
			Golden [m]	132 [l]	260—264	93	55.3 (54.9)	5.2 (4.9)	2.4 (2.1)	3 422		1 630
		HSO_4	Pink	110 [l]	173—175	57	53.0 (53.4)	4.6 (4.6)	2.2 (2.2)	3 400		1 632
		SFO_3 [n]	Brownish	101		77	54.9 (54.5)	5.0 (5.4)	2.3 (2.0)	3 415		1 628
		$SClO_3$ [e]	Brown							3 405		1 634
	4-MeC_6H_4	BF_4	Red	114	250—252	48	58.8 (58.7)	4.8 (2.0)	2.0 (2.0)	3 360 [2 500]		1 606
Mo	Me	BF_4 [k]	Red	113 [l] 148	244—245	88	58.6 (58.5)	5.0 (4.9)	2.5 (2.4)	3 392 [2 510]		1 645
			Yellow							3 410		1 645
(*c*) Complexes $[Mo(CO)_2(dppe)_2]X$												
		BF_4 [o]	Rose	89	236—245	85	60.5 (60.7)	4.9 (4.6)			1 878 [p]	
		HSO_4 [q]	Rose	86 [r]	203—204	85	56.8 (56.8)	4.7 (4.4)			1 878 [p]	

[a] In *ca.* 10^{-3} mol dm^{-3} nitrobenzene solution unless otherwise stated. [b] In sealed evacuated tubes. [c] Calculated values in parentheses. [d] Nujol mull spectra. [e] Impure compound, characterised only by spectrum, see text. [f] Contains CH_2Cl_2 of crystallisation. [g] Contains $\frac{1}{2}C_6H_6$ of crystallisation. [h] Contains C_6H_6 of crystallisation. [i] Contains $\frac{1}{2}Et_2O$ of crystallisation. [j] After substitution of of $[BF_4]^-$ by $[BPh_4]^-$, see Experimental section. [k] Two isomers, see text. [l] In *ca.* 10^{-3} mol dm^{-3} methanol solution. [m] Contains Et_2O of crystallisation. [n] With $2Et_2O$ of crystallisation. [o] Contains $\frac{1}{2}CH_2Cl_2$ of crystallisation, $\mu_{eff.}$ = 2.06 B.M. (22 °C). [p] ν(C≡O). [q] Contains 1.5 CH_2Cl_2 of crystallisation, $\mu_{eff.}$ = 2.10 B.M. (22 °C). [r] In *ca.* 10^{-3} mol dm^{-3} dimethylformamide solution.

spectra but the red isomers have higher values for ν(NH) (Table 1). In solution, the yellow isomers are rapidly converted into the red ones, so that n.m.r. data refer only to the red isomers.

At 25 °C the $\mathrm{CNC}H_3$ ^{1}H n.m.r. resonances of (**3**; R = Me, X = $\mathrm{BF_4}$) are singlets and there are also broad resonances at *ca.* 4—5 p.p.m. (Table 2) which integrate for two protons. Upon lowering the temperature, the

TABLE 2

N.m.r. data for *trans*-$[\mathrm{M(CNHR)(CNR)(dppe)_2}][\mathrm{BF_4}]$ (2) and *trans*-$[\mathrm{M(CNHMe)_2(dppe)_2}][\mathrm{BF_4}]_2$ (3) complexes

M	R	Temperature (θ_c/°C)	δ/p.p.m. (±0.22)	Integration [a]	Assignment	Coupling constant ^3J(HNCH)/Hz (±0.2)
(*a*) ^{1}H data [b]						
(*i*) Complexes (2)						
W	Me	−40	7.8—5.9 (m)	40 (40)	dppe aromatic	
			3.50 (q, br) [c]	1 (1)	CN*H*Me	4.7
			2.9—1.9 (m, br)	11 (11)	dppe methylenes	
			2.57 (d) [d]		CNH*Me*	4.7
			2.16 (s)	3 (3)	CN*Me*	
Mo	Me	−40	7.9—6.3 (m)	40 (40)	dppe aromatic	
			4.37 (q, br) [e]	1 (1)	CN*H*Me	4.7
			2.8—2.1 (m, br)	11 (11)	dppe methylenes	
			2.48 (d) [f]		CHN*Me*	4.7
			2.17 (s)	3 (3)	CN*Me*	
(*ii*) Complexes (3)						
W	Me [g]	−35	7.6—6.7 (m)	40 (40)	dppe aromatic	
			4.25 (q, br) [h]	2 (2)	CN*H*Me	4.2
			3.1—2.3	8 (8)	dppe methylenes	
			2.38 (d) [i]	6 (6)	CNH*Me*	4.2
	$\mathrm{4\text{-}MeC_6H_4}$	25	7.8—6.6 (m)	40 (40)	dppe aromatic	
			6.07 (d) [j]	4 (4)	Isocyanide aromatic *ortho* to $\mathrm{CH_3}$	
			4.62 (d) [j]	4 (4)	Isocyanide aromatic *ortho* to N	
			4.24 (br)	1.8 (2)	CN*H*R	
			2.9—2.0 (m, br)	7.8 (8)	dppe methylenes	
			1.93 (s)	6(6)	$\mathrm{CNHC_6H_4C}H_3$	
Mo	Me [k]	−20	7.6—6.7 (m)	40 (40)	dppe aromatic	
			4.74 (q, br) [l]	2 (2)	CN*H*Me	4.7
			3.50 (q)	4 (4)	$\mathrm{O(C}H_2\mathrm{CH_3)_2}$	
			3.1—2.2 (m, br)	8 (8)	dppe methylenes	
			2.29 (d) [m]	5.8 (6)	CHN*Me*	4.7
			1.20 (t)	6.2 (6)	$\mathrm{O(CH_2C}H_3\mathrm{)_2}$	
(*b*) ^{31}P data [n]						
(*i*) Complexes (2)						^1J(W–P)
W	Me	−42	86.8 (s)		dppe	271.0
W	Bu^t	−42	89.3 (s)		dppe	271.0
Mo	Me	−40	69.1 (s)		dppe	
(*ii*) Complexes (3)						
W	Me	−70	102.8		dppe	231.9
			104.1		dppe	229.5
		−55	103.1		dppe	231.9
			104.3		dppe	231.9
W	$\mathrm{4\text{-}MeC_6H_4}$	−40	113.8		dppe	229.5
			115.0		dppe	229.5
		+25	112.3		dppe	229.5
			113.5		dppe	
Mo	Me	−20	91.3		dppe	
			92.6		dppe	
(*c*) ^{13}C data [b]						
(*i*) Complexes (2)						
W	Me	25	242.4 (m, br) [o]		*C*NHMe	
			155.3 (m, br) [o]		*C*NMe	
			142.2—128.2 (m)		dppe aromatic C	
			33.0 (s, br) 29.8 (m, br)		dppe-$C\mathrm{H_2}$ + $\mathrm{CN}C\mathrm{H_3}$ +$\mathrm{CNH}C\mathrm{H_3}$	
Mo	Me	25	247.8 (m, br) [o]		*C*NHMe	
			159.2 (m, br) [o]		*C*NMe	
			139.4—128.3 (m)		dppe aromatic C	
			30.7 30.3 29.9		dppe-$C\mathrm{H_2}$ + $\mathrm{CN}C\mathrm{H_3}$ +$\mathrm{CNH}C\mathrm{H_3}$	

TABLE 2 (*Continued*)

M	R	Temperature (θ_c/°C)	δ/p.p.m. (±0.22)	Assignment
(*ii*) Complexes (3)				
W	Me	−36	194.5 (m, br) [o]	*C*NHMe
			137.3—128.3	dppe aromatic C
			39.2 (s)	CNH*C*H$_3$
			39.6 (s, br) [o]	dppe-*C*H$_2$
Mo	Me	25	204.7 (m, br) [o]	*C*HNMe
			136.7—125.2 (m)	dppe aromatic
			65.7 (s) [p]	O(*C*H$_2$CH$_3$)$_2$
			38.7 (s) [q]	CNH*C*H$_3$
			27.2 (s, br) [o]	dppe-*C*H$_2$
			15.2 (s) [r]	O(CH$_2$*C*H$_3$)$_2$
(*c*) ^{19}F data [s]				
W	Me	25	151.4 (s)	BF$_4^-$

s = Singlet, d = doublet, q = quartet, br = broad, m = multiplet.

[a] Required values in parentheses. [b] In CDCl$_2$ solution, relative to internal SiMe$_4$. [c] Sharpens on irradiation at δ 2.57, disappears on D$_2$O addition. [d] Coalesces into a singlet upon irradiation at δ 3.50 or on D$_2$O addition. [e] Sharpens on irradiation at δ 2.48, disappears on D$_2$O addition. [f] Sharpens on irradiation at δ 4.37, disappears on D$_2$O addition. [g] Apparently only red isomer, see text. [h] Sharpens on irradiation at δ 2.38, disappears on D$_2$O addition; at 25 °C, δ 4.8—4.0 (m, br). [i] Coalesces into a singlet on irradiation at δ 4.25 or on D$_2$O addition at 25 °C, δ 2.20 (s). [j] ^3J(H$_A$–H$_B$) = 8.0 ± 0.2 Hz. [k] Contains Et$_2$O of crystallisation. [l] Sharpens on irradiation at δ 2.29, disappears on D$_2$O addition; at 25 °C, δ 4.9—4.6 (m, br). [m] Coalesces into a singlet on irradiation at δ 4.74 or on D$_2$O addition; at 25 °C, δ 2.27 (s, br). [n] In CD$_2$Cl$_2$, p.p.m. upfield from P(OMe)$_3$ taken as positive. Both resonances of complexes (3) have same intensity. Bu^t complex run as BPh$_4$ salt. [o] Broadened due to coupling with P. [p] Triplet with off-resonance continuous-wave proton spin decoupling (c.w.s.d.), apparent *J*(CH) = 21.4 Hz. [q] Quartet with c.w.s.d., apparent *J*(CH) = 29.0 Hz. Quartet with c.w.s.d., apparent *J*(CH) = 27.5 Hz. [s] In CD$_2$Cl$_2$ relative to CFCl$_3$, upfield positive, only one resonance observed in range −289 to +339 p.p.m.

C*H*$_3$ resonance splits into a doublet and the broad resonance sharpens to a quartet with the same coupling constant as the methyl doublet (M = Mo, 4.7 Hz; M = W, 4.2 Hz). Thus the quartet signal, which disappears on addition of D$_2$O, is assigned to the NH resonance. Its coupling to the CH$_3$ resonance was confirmed by the collapse of the CH$_3$ doublet into a singlet on addition of D$_2$O and by decoupling experiments. Compounds (3) are therefore protonated at both nitrogen atoms and the loss of fine structure in their n.m.r. spectra at 25 °C is presumably caused by rapid N–H proton exchange, which is slowed at lower temperatures. Because of this susceptibility of the N–H protons to exchange, especially in the presence of a protic solvent, n.m.r. spectra of both (2) and (3) were only determined in rigorously dried dichloromethane.

The N–H resonances of the diprotonated complexes (3) are to high field of those of the carbyne complexes (2). The N–H resonance for [W{CNH(C$_6$H$_4$Me-4)}$_2$(dppe)$_2$]-[BF$_4$]$_2$ is sharper at 25 °C than that of (3; R = Me); evidently the exchange process is slower for this compound than for (3; R = Me) because of the steric and/or electronic effect of the 4-MeC$_6$H$_4$ group compared to CH$_3$.

The ^{13}C n.m.r. spectra of (3; R = Me) (Table 2) show low-field resonances for the (*C*NHMe) carbons (M = W, 194.5 p.p.m.; M = Mo, 204.7 p.p.m. relative to SiMe$_4$) which are to high field of the corresponding resonances in (2; R = Me). These signals are also to higher field for M = W than for M = Mo, as was seen for the analogous resonances of (2; R = Me). The broadness of the resonances precluded determination of ^1J(WC). The ^{31}P n.m.r. spectrum of this complex and of its molybdenum analogue consist of a doublet resonance (Table 2). Thus the phosphorus atoms appear to form two non-equivalent sets. The splitting does not appear to be due to coupling to a fluorine atom at the metal because the [BF$_4$]$^-$ ^{19}F resonance for (3; M = W, R = Me, X = BF$_4$) is a sharp singlet, no other ^{19}F resonances are observed, and these compounds are 1 : 2 electrolytes. Unfortunately complexes of other anions were insufficiently soluble for n.m.r. measurements. A *cis* configuration of phosphine ligands also seems to be unlikely because an AA'XX'-type ^{31}P spectrum would be expected, and, moreover, two CN i.r. bands would also be expected. In addition, the ^{1}H n.m.r. spectra of (3; M = Mo or W, R = Me, X = BF$_4$) do not show the triplet pattern normally exhibited in the phenyl region by *cis*-dppe complexes.[10] Thus a *trans* configuration is assigned to complexes (3). The inequivalence of the phosphorus atoms therefore is most probably due to the configuration of the NHMe groups about the linear NCMCN system, as is discussed below in more detail.

Two doublets of an AB pattern are observed for *trans*-[W{(CNH)(C$_6$H$_4$Me-4)}$_2$(dppe)$_2$][BF$_4$]$_2$ at 6.07 and 4.62 p.p.m., assigned to the aromatic protons of the protonated isonitrile ligands. The higher-field resonance probably corresponds to the protons which are *ortho* to nitrogen.

Structure of Mono- and Di-protonated Complexes.—The monoprotonated complexes, since they are clearly protonated at one nitrogen atom, have a carbyne (methylaminomethylidyne) ligand, CNHR (R = Me or Bu^t), so that their structures can be written in valence-bond terms as in Figure 1.

The structures of the analogous complexes [MX-(CNR$_2$)(CO)$_4$] (M = Cr or W; X = Cl, Br, or I; R = Me or Et) have been discussed on the basis of a similar scheme. In these the canonical form (b) has a large weight because the complex $[CrBr(CNEt_2)(CO)_4]$ (M = Cr or W) has a C–N distance of 129 ± 1 pm (in the normal range of C=N bond distances), a short Cr–C distance (172 ± 1 pm), and a trigonal-planar nitrogen atom.[7] The fairly high frequency CN band in the i.r. spectra of compounds (2) and their low-field ^{13}CNHR signal are consistent with a similar significant contribution of form (b) to their structure. The increase of ν(NC) of the ligating isonitrile of (2) relative to the ν(NC) value for (1) is a result of the contribution of metal *d* electrons to the metal–carbyne multiple-bond system at the expense of their use in π bonding to isonitrile.

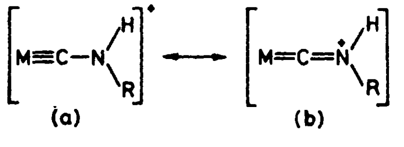

FIGURE 1

The two protons of the diprotonated complexes (3) clearly reside at the nitrogen atoms, so that a delocalised NCMCN system is produced. One description of this system is as in Figure 2, the implication of which is that relative to the complexes with a carbyne ligand (2) the diprotonated complexes (3) have greater π character in their C–N bond and less in their M–C bond. This follows since the metal contribution to the M–C π system in (3) must be shared between two strongly electron-withdrawing ligands. In (2) the CNHR ligand is evidently more strongly electron-withdrawing than is isonitrile, so its M–C bond has greater π character than of those of (3). This strong π withdrawal is reflected in the high value of ν(N≡C) of (2). As would be expected from this scheme the diprotonated complexes (3) have a higher value of ν(C$\overset{...}{=}$N) and a high-field shift of their ^{13}C resonance position, relative to those of the monocarbyne complexes. The diprotonated compounds are therefore best regarded as bis(iminiocarbene) compounds.

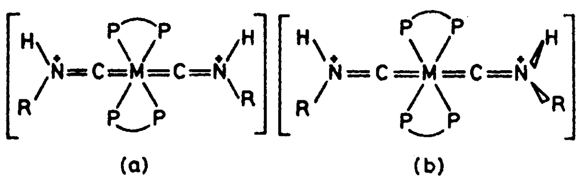

FIGURE 2

The structures shown in Figure 2 could lead to the occurrence of isomers, if the system is planar [Figure 2 (a)], with the NR and NH groups either *cis* or *trans* to each other. Thus a *cis* isomer as drawn in Figure 2(a) would have inequivalent phosphorus atoms, giving the observed ^{31}P spectrum for the red isomers. The yellow isomers observed in the solid state could therefore be the *trans* configuration. The two isomers would presumably have slightly different energies because of steric forces. Alternatively, the structure could resemble that of allene [Figure 2(b)], so that the NHR groups lie in planes at right angles. This again would lead to inequivalent phosphorus atoms, but a simple doublet only occurs if the nitrogen substituents are coplanar with the phosphorus atoms, and moreover, only one isomer is possible. A planar structure therefore is favoured by this discussion. Nevertheless, *X*-ray data are necessary to satisfactorily distinguish these alternatives but as yet suitable crystals have not been obtained.

Other Reactions.—(a) (1; M = W, R = Me) *with* Al_2Et_6. The red colour of a solution of (1; M = W, R = Me) in benzene darkened immediately on addition of an excess of Al_2Et_6 and the solution then had no C≡N band, but had bands in the 1 576—1 588 cm^{-1} region. These observations are consistent with the formation of an adduct, probably $[W\{CN(AlEt_3)Me\}_2(dppe)_2]$ or related species which is an analogue of the adduct $[W\{CO(AlMe_3)\}_2(dppe)_2]$.[11] It was very unstable, however, and decomposed on attempted isolation.

(b) cis-$[Mo(CO)_2(dppe)_2]$ *with* HX. In an attempt to produce complexes of the ≡C–OH ligand, *cis*-$[Mo(CO)_2(dppe)_2]$ was treated in anhydrous conditions under dinitrogen with HX (X = BF_4 or HSO_4). Although the terminal carbonyl group in this complex is sufficiently nucleophilic to form the adduct with $AlMe_3$ noted above, protic attack appeared to be initially at the metal, finally giving the oxidised complexes *trans*-$[Mo(CO)_2(dppe)_2]X$ (Table 1) with the release of some dihydrogen, but most of the protons could not be accounted for. The same products were obtained using attack of acids upon the above carbonyl complex in air, but protonation at the metal was achieved by treating them, in absence of air, with a slight excess of $HSFO_3$.[12] If an intermediate hydride was formed in our experiments, it was too unstable to be detected by n.m.r. measurements at temperatures down to −60 °C. The *trans* structure of the paramagnetic molybdenum(I) dicarbonyl products is assigned from their single C≡O stretching i.r. band (Table 1).

Attempts to alkylate *cis*-$[Mo(CO)_2(dppe)_2]$ with $MeSO_3F$ were unsuccessful.

Conclusions.—The ligands (XY = CO, N_2, or CNR) in the complexes $[M(XY)_2(dppe)_2]$ receive so much electron density from the electron-rich site $M(dppe)_2$ that they are susceptible to attack by electrophilic reagents. For XY = N_2, this susceptibility has led to preparation of complexes of the =N–NH_2 ligand [13] and for XY = CO to adducts containing the –$CO(AlMe_3)$ group,[11] but protonation at oxygen has not been observed. Ready protonation at nitrogen, for XY = CNR, has been the feature of this study. The lack of protonation at oxygen in the carbonyl is probably due to the greater electronegativity of this element compared to nitrogen. Other examples of greater basicity of N compared to O are known. Thus, iminocarbene groups, C(R′)=NR, are more easily protonated than the acyl ligands, C(R)=O, and may accept a proton from a weak acid such as $[NH_4]^+$ or even during work-up after their preparation by nucleophilic attack on a co-ordinated isonitrile.[14] Attempted protonation at the oxygen of carbamoyl ligands, C(NHR)=O, leads to the formation of allene by preferential protic attack at N.[15] Some further examples of protic attack at the nitrogen atom of ligating isonitrile are in iron complexes such as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ where the products have a bridging CNHR group, for example $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(H)Me\}]^+$, where again the nitrogen atom of the isonitrile is the protonated entity, rather than the oxygen atom of bridging carbon monoxide.[16]

An alternative site for an electrophilic attack in low-valent metal complexes is the metal itself, with the production of hydride complexes. Such an attack may well occur in the carbonyl case and hydride complexes have been isolated using $HSFO_3$,[12] although no transient intermediate was observed in our reactions. This type of attack can, however, occur on compounds (1) under our conditions to give hydrido-complexes which have been described elsewhere.[4]

EXPERIMENTAL

All air-sensitive materials were handled using standard nitrogen-flow or high-vacuum techniques. The complexes *trans*-$[M(CNR)_2(dppe)_2]$ [17] and *cis*-$[Mo(CO)_2(dppe)_2]$ [18] were prepared by published methods. Mineral acids were analytical grade (B.D.H.) and these and $[Et_2OH][BF_4]$ (Aldrich) were used as supplied. Tetrahydrofuran (thf) 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 Unicam SP 2000 or Perkin-Elmer 577 instruments and n.m.r. spectra with a JEOL PS100 spectrometer equipped with a 546 J digital signal averager, a JEOL PFT 100 Fourier-transform instrument or Varian EM 360 instruments. The solvents used for n.m.r. spectroscopy were scrupulously dried, degassed, and the solutions were prepared under vacuum directly in the n.m.r. tubes which were sealed in a vacuum.

Conductivities were measured using a Portand Electronics P310 conductivity bridge and melting points with an Electrothermal melting-point apparatus. Magnetic susceptibilities were determined with a Faraday balance and mass spectra with an A.E.I. MS10 instrument. Microanalyses were by Mr. and Mrs. Olney of the University of Sussex.

Protonation Reactions of Isonitrile Complexes.—Freshly prepared solutions of purchased acids were used unless otherwise stated. Since the methods used are general, only examples using HBF_4 (as $[Et_2OH][BF_4]$) are given. Analytical details *etc.*, of all compounds prepared are in Table 1 and n.m.r. spectroscopic data are shown in Table 2.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*](*methylaminocarbyne*)(*methyl isonitrile*)*tungsten*(IV) *tetrafluoroborate*,* trans-$[W(CNHMe)(CNMe)(dppe)_2][BF_4]$. Tetrafluoroboric acid (0.167 mmol, 0.489 cm^3 of an ether solution obtained by 1 : 21 dilution of commercial $[Et_2OH][BF_4]$) was added dropwise to a stirred solution of *trans*-$[W(CNMe)_2(dppe)_2]$ (0.188 g, 0.177 mmol) in benzene (20 cm^3). The resulting shiny green needles of *trans*-$[W(CNHMe)(CNMe)(dppe)_2][BF_4]$ (0.187 g, 92%) were filtered off, washed with benzene, and dried (10^{-3} mmHg, 20 °C).†

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bis*(*methylaminocarbene*)*tungsten*(IV) *bis*(*tetrafluoroborate*), trans-$[W(CNHMe)_2(dppe)_2][BF_4]_2$ (*red and yellow isomers*). Tetrafluoroboric acid (0.356 mmol, 0.197 cm^3 of an ether solution obtained by 1 : 4 dilution of commercial $[Et_2OH][BF_4]$) was rapidly (*ca.* 15 s) added dropwise to a solution of *trans*-$[W(CNMe)_2(dppe)_2]$ (0.172 g, 0.163 mmol) in CH_2Cl_2 (30 cm^3). (Methanol or thf could also be used as solvent.) During the acid addition the red colour of the solution darkened to brown, then lightened again to a final red colour. Concentration of the solution in a vacuum to *ca.* $\frac{1}{3}$ volume followed by slow addition of diethyl ether gave a small amount of precipitate which was filtered off. The solution was then cooled to *ca.* −20 °C and allowed to stand whereupon pink *platelets* of *trans*-$[W(CNHMe)(dppe)_2][BF_4]_2$ (0.19 g, 92%) deposited, as a mixture with varying amounts of the yellow isomer. The product was filtered off, washed with Et_2O–CH_2Cl_2 (5 : 2), and dried. The small amount of yellow crystalline isomer could be separated from the pink one by hand.

Reaction of trans-$[W(CNMe)_2(dppe)_2]$ *with* Al_2Et_6.—The compound Al_2Et_6 (10 mmol) in benzene (20 cm^3) was added to a solution of *trans*-$[W(CNMe)_2(dppe)_2]$ (1 mmol) in benzene (40 cm^3) with stirring. The colour of the solution darkened immediately to very dark red. The i.r. spectrum of this solution showed no band in the ν(C≡N) region but two strong absorptions at 1 588 and 1 578 cm^{-1} assigned to C=N vibrations of an adduct formulated as $[W\{CN(AlEt_3)Me\}_2(dppe)_2]$, the analogue of *cis*-$[W\{CO(AlMe_3)\}_2(dppe)_2]$ reported elsewhere.[11] The $AlEt_3$ adduct was very unstable and attempts to isolate it from solution merely caused its decomposition into parent isonitrile complex and unidentified yellow species.

Attempted Protonation of cis-$[Mo(CO)_2(dppe)_2]$.—Tetrafluoroboric acid (0.266 mmol, 0.656 cm^3 of an ether solution of 1 : 21 dilution of commercial $[Et_2OH][BF_4]$) was added dropwise to a solution of *cis*-$[Mo(CO)_2(dppe)_2]$ (0.107 g, 0.113 mmol) in CH_2Cl_2 (12 cm^3). The solution colour changed from pale yellow to pink and addition of diethyl ether gave *trans*-$[Mo(CO)_2(dppe)_2][BF_4]$ (0.1 g, 85%). The same complex precipitated from a benzene solution a few minutes after the addition of acid. The ^1H n.m.r. spectrum of a reaction mixture in a sealed tube under vacuum between 25 and −60 °C gave no detectable hydride resonance. A similar reaction occurred when H_2SO_4 (0.256 cm^3 of 98% acid, 4.71 mmol) was added to *cis*-$[Mo(CO)_2(dppe)_2]$ (0.149 g, 0.157 mmol) in methanol (30 cm^3) to give *trans*-$[Mo(CO)_2(dppe)_2][HSO_4]$ (0.139 g, 85%). These cationic complexes were identified by analysis (Table 1) and their spectroscopic properties, which were identical to those previously reported for these cations, prepared by a similar route in air.[19] In these latter reactions and those reported here, the fate of the hydrogen ion of the acid is uncertain. A small amount (*ca.* 0.2 mol per Mo atom) of hydrogen gas was evolved in our reaction but the remainder of the hydrogen could not be located.

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* More systematically, *trans*-bis[1,2-bis(diphenylphosphino)-ethane](methylaminomethylidyne)(methyl isocyanide)tungsten(IV) tetrafluoroborate.

† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.274 096 × 10^{-24} A m^2.

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