Dinitrogen Binding and Electrochemistry in Complexes of Molybdenum and Tungsten

Wasif Hussain, G. Jeffery Leigh, Hapipah Mohd. Ali, Christopher J. Pickett, and Douglas A. Rankin
A.R.C. Unit of Nitrogen Fixation and School of Chemical and Molecular Sciences, University of Sussex, Brighton BN1 9RQ

The preparation of a series of complexes $[M(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$ (M = Mo or W) is described. The variation of oxidation potential with phosphine substituents suggests that the electronic structures involve through-metal conjugation between the phosphine phosphorus and the dinitrogen, which contributes to the strength of the metal–dinitrogen bond. Electron-donating substituents on the phosphine make the compounds easier to oxidise. Studies of the rate of replacement of dinitrogen by benzonitrile show that electron-donating substituents also increase the metal–dinitrogen bond lability.

Although there are now many mononuclear dinitrogen complexes containing terminally bound dinitrogen, relative few of these undergo attack by protic reagents to form N–H bonds. In order to understand why this is so, and also to enable us to synthesise more complexes containing reactive dinitrogen, we have been attempting to understand how the metal and its auxiliary ligands modify the nucleophilic character of the ligating dinitrogen.

Recently, we described [1] the dinitrogen complexes $[M(N_2)L(dppe)_2]^{n-}$ (M = Mo or W, L = neutral or anionic ligand, dppe = $Ph_2PCH_2CH_2PPh_2$, n = 0 or 1) and found a linear correlation between the i.r. frequencies assigned to $\nu(N_2)$ and the reversible one-electron oxidation potentials, $E_{\frac{1}{2}}^{ox}$, determined by cyclic voltammetry. We concluded that the influence of the ligand L upon the redox orbital and upon the orbitals of the dinitrogen controlling the N–N stretching was probably inductive.[1]

The ability easily to synthesise [2] substituted aryldiphosphines $(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2$ has led to a range of new bis(dinitrogen) complexes. We describe here their preparation and properties, and discuss the transmission of electronic effects from the substituents X to the metal and to the co-ordinated dinitrogens. Some of the data have been published earlier in preliminary form.[3]

Results and Discussion

The complexes are detailed in Table 1. They are all of the form $[M(N_2)_2(diphosphine)_2]$, and the orange solids all have the usual *trans* stereochemistry since they exhibit a single resonance in their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, indicating the presence of four equivalent phosphorus atoms. They are soluble in tetrahydrofuran, benzene, and toluene and are air-stable in the solid state.

Influence of Diphosphines on $E_{\frac{1}{2}}^{ox}$.—We rationalised our previous data [1] using a model in which the orbital from which the electron in the oxidation process is removed (the highest occupied molecular orbital, h.o.m.o.) is principally metal-centred and non-bonding. The ligand L influences the h.o.m.o. by its ability to supply electron density to, or remove it from, the metal. Figure 1 shows a plot of $E_{\frac{1}{2}}^{ox}$ of the new complexes against the Hammett parameters σ^+ and σ for all the aryl derivatives. The linear correlation is significantly better for σ than for σ^+, the correlation coefficients being 0.995 and 0.913, respectively. Since the oxidation potentials of comparable molybdenum and tungsten species are virtually identical, then the correlation is equally valid for tungsten.

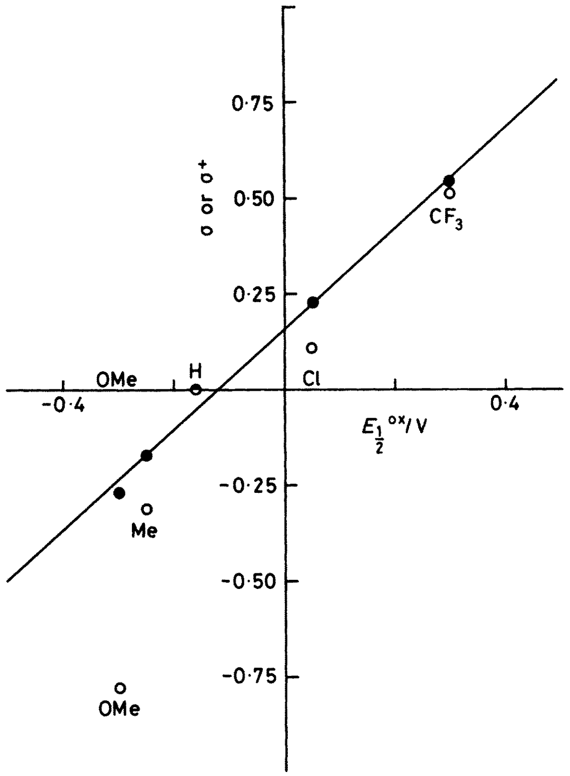


Figure 1. Plot of $E_{\frac{1}{2}}^{ox}$ *vs.* σ (●) and σ^+ (○) for $[Mo(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$. The line is a least-squares fit for the σ correlation and the substituents X are indicated. For X = H both curves coincide at the same point (◒)

We conclude that the h.o.m.o. is not conjugated to the aryl substituents of the phosphines, and that it is essentially non-bonding. This is consistent with our earlier inferences.[1]

Influence of Diphosphines on $\nu(N_2)$.—Figure 2 shows the relationship of $\nu(N_2)$ with σ^+ for both the molybdenum and tungsten complexes. The correlation coefficients for the best lines (0.999 for Mo and 0.993 for W) are better than for the relationship with σ (0.956 and 0.914, respectively). It is generally assumed that the principal determinant of $\nu(N_2)$ in complexes is back donation into the formally empty p_π–p_π antibonding orbital of the dinitrogen (for general information

Table 1. Dinitrogen complexes of molybdenum and tungsten

Complex	M.p. (°C)	Analysis[a] (%)			$E_{\frac{1}{2}}^{ox}$ (0 → 1)[b] /V	^{31}P N.m.r.[c] (p.p.m.)	I.r. (cm^{-1})[d]		Raman (cm^{-1})[e]
		C	H	N			ν(NN)	ν(MN)	ν(NN)
$[Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$	140	43.0	8.65	9.70	−0.43	−84.5	1 925	553	1 988
		(42.6)	(8.55)	(9.90)				548	
$[Mo(N_2)_2\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2\}_2]$	133	46.1	3.60	2.55	+0.30	−76.3	1 990		
	(decomp.)	(48.3)	(2.70)	(3.75)					
$[Mo(N_2)_2\{(p\text{-}ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl\text{-}p)_2\}_2]$	110	52.7	3.15	4.40	+0.05	−77.0	1 979[f]	593	
		(51.1)	(3.30)	(4.60)					
$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$	138				−0.16	−75.9	1 976	547	
$[Mo(N_2)_2\{(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2\}_2]$	148	67.1	5.95	4.70	−0.25	−77.5	1 967	547	
		(67.9)	(6.10)	(5.25)					
$[Mo(N_2)_2\{(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe\text{-}p)_2\}_2]$	147	60.1	7.75	4.45	−0.30	−78.2	1 956	552	2 022
		(60.6)	(5.40)	(4.70)					
$[W(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$	154	36.9	7.25	8.55	−0.42	−104.2	1 891	558	1 968
		(36.8)	(7.40)	(8.60)		(312)		552	
$[W(N_2)_2\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2\}_2]$	126	45.6	2.55	3.40	+0.23	−92.4	1 955		
	(decomp.)	(45.6)	(2.55)	(3.55)		(320)			
$[W(N_2)_2\{(p\text{-}ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl\text{-}p)_2\}_2]$	154	48.0	3.40	4.30	+0.06	−96.7	1 945		
	(decomp.)	(47.6)	(3.05)	(4.25)		(322.5)			
$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$	164				−0.15	−95.0	1 946	554	
						(322)			
$[W(N_2)_2\{(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2\}_2]$	167	62.4	5.95	4.75	−0.22	−97.3	1 940	554	
		(62.7)	(5.60)	(4.90)		(322)			
$[W(N_2)_2\{(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe\text{-}p)_2\}_2]$	159	56.9	5.80	4.10	−0.28	−98.1	1 930	557	1 992
		(56.4)	(5.05)	(4.40)		(332)			
$[W(N_2)_2\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}_2]$					−0.48		1 880		

[a] Calculated values in parentheses. [b] *Versus* s.c.e. [c] In tetrahydrofuran, *versus* trimethyl phosphite as external standard; ^{1}J(W−P)/Hz in parentheses. [d] Nujol, unless otherwise stated. [e] Crystalline samples in glass ampoules. [f] 1978 cm^{-1} in solution in thf.

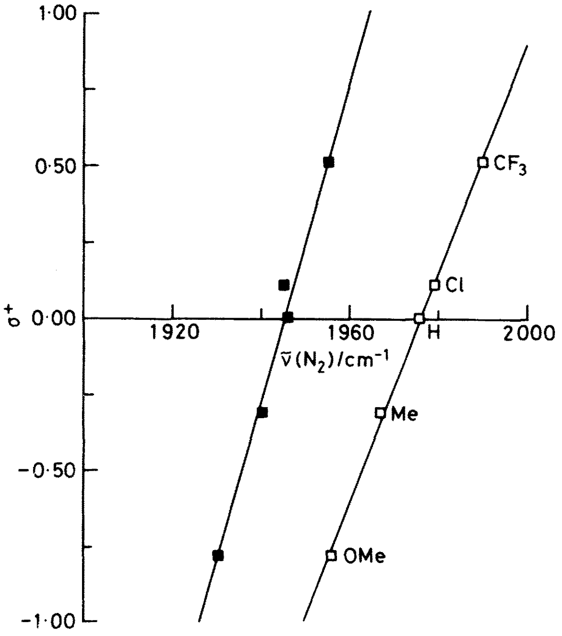


Figure 2. Plot of $\nu(N_2)$ *vs.* σ^+ for $[M(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$; M = Mo (□) or W (■)

and references concerning dinitrogen complexes see ref. 4). The data suggest that the substituents on the phosphines, which are located *cis* to the dinitrogens, are conjugated through the metal to the N_2 (see Figure 3).

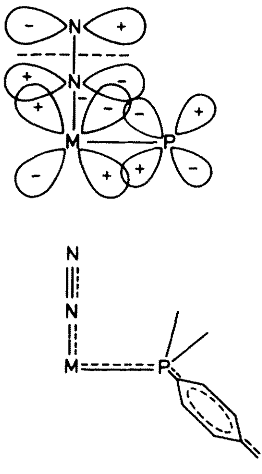


Figure 3. The through-metal conjugation between phosphine phosphorus and *cis*-situated dinitrogen in $[M(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$ (M = Mo or W)

Relationship of $E_{\frac{1}{2}}^{ox}$ *and* $\nu(N_2)$.—Since $E_{\frac{1}{2}}^{ox}$ correlates best with σ, and $\nu(N_2)$ with σ^+, it follows that there is no linear relationship of $E_{\frac{1}{2}}^{ox}$ and $\nu(N_2)$. The relationship is illustrated in Figure 4, which shows a relatively smooth curve for each metal. Figure 4 includes complexes outside the range of those previously considered [*viz.* compounds of $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$ and $Et_2PCH_2CH_2PEt_2$] and also data for the complexes $[Mo(N_2)L(dppe)_2]^{n-}$ [*trans* series (C_6H_5)] which have already been published.[1] In so far as we can identify ν(M−N) unequivocally, $E_{\frac{1}{2}}^{ox}$ is not linearly correlated with it, and neither, incidentally, with the ^{31}P n.m.r. chemical shifts (see below). The smooth curves obtained for the compounds synthesised by variation of X are very different from the linear relationship of $\nu(N_2)$ and $E_{\frac{1}{2}}^{ox}$ evident from our data on $[Mo(N_2)L(dppe)_2]^{n-}$ and established by other workers for $[Mo(N_2)(NCC_6H_4X)(dppe)_2]$.[5]

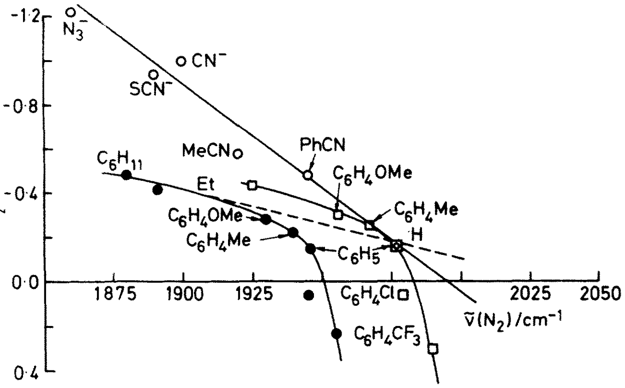


Figure 4. The relationship of $E_{\frac{1}{2}}^{ox}$ with $\nu(N_2)$ for a range of dinitrogen complexes: $[W(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$ (●), $[Mo(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$ (□), and $[Mo(N_2)L(dppe)_2]^{n-}$ (○); the various X and L are indicated. The curves were fitted by eye; the broken line is a linear extrapolation

The complexes of $(p\text{-}ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl\text{-}p)_2$ are a little distant from the smooth curve, for no apparent reason, but are slightly anomalous in other respects, too (see below). Analysis showed that no dehalogenation of the ligand had occurred during the reductive synthesis of the N_2 complexes, but in any case the departure from the $E_{\frac{1}{2}}^{ox}$ *vs.* $\nu(N_2)$ curve is not in the sense to be expected had dehalogenation occurred. The shapes of the $E_{\frac{1}{2}}^{ox}$ *vs.* $\nu(N_2)$ plots accommodate all the N_2 complexes we have synthesised, even $[W(N_2)_2\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}_2]$ which we were not able to obtain absolutely pure. The data of Figure 4 are not simply explained. Because of the empirical linear relationships, one can write equations (1) and (2) where C_1, C_2, k_1, and k_2 are constants.

$$E_{\frac{1}{2}}^{ox} = k_1\sigma + C_1 \qquad (1)$$

$$\nu(N_2) = k_2\sigma^+ + C_2 \qquad (2)$$

Clearly, $E_{\frac{1}{2}}^{ox}$ will be linearly related to $\nu(N_2)$ only if the term $(k_1\sigma + C_1)/(k_2\sigma^+ + C_2)$ is constant. So far, this has been shown to be true only for complexes of dppe,[1] although we would also expect it be true of analogous dinitrogen complexes of any other diphosphine. All the data we have presented so far appear self-consistent. Our earlier studies [1] on $[M(N_2)L(dppe)_2]^{n-}$ suggest that they have a metal-centred non-bonding h.o.m.o., although with no indication whether or not the ligands are conjugated with N_2. Since then, *ab initio* calculations [6] on N_2 complexes such as $[Mo(N_2)_2(PH_3)_4]$ have also shown that the h.o.m.o. is essentially non-bonding, with little P or N contribution. However, the metal–ligand bonding cannot easily be interpreted in terms of conventional σ and π contributions, and involves metal orbitals in shells of lower energy than of that normally regarded as the valence shell. Thus, all the data currently in hand seem to be consistent with a non-bonding h.o.m.o. (principally d_{xy}), with d_{xz} and d_{yz} involved in π bonding between metal, N_2, and the phosphorus atoms (Figure 5).

The energy scales of the axes in Figure 4 are very different since we are comparing changes in electronic energies with changes in vibrational energies. The slope of the linear correlation for the *trans* series is *ca.* 0.9 V per 100 cm^{-1}. Since 1 eV *ca.* 100 kJ mol^{-1} and 100 cm^{-1} *ca.* 1 kJ mol^{-1}, the energy changes observed in $E_{\frac{1}{2}}^{ox}$ are about one hundred times greater than those observed in $\nu(N_2)$. Consequently, it would be unwise to ascribe too much significance to the small energy changes implied by the range of $\nu(N_2)$. However, two points seem worth making. If the rate of change of $\nu(N_2)$ as the ring substituents vary were to be maintained so as to give a linear plot of $E_{\frac{1}{2}}^{ox}$ *vs.* $\nu(N_2)$ throughout the range of compounds (as shown by the extrapolation in Figure 4), $\nu(N_2)$ would reach values considerably higher than those normally associated with stable N_2 complexes. Since high values of $\nu(N_2)$ are normally taken to show weak metal–dinitrogen interactions,[4] such complexes would not be expected to exist under ambient conditions. The fact that they do exist implies that the relative importance of σ and π effects in $M\text{–}N_2$ and $N\equiv N$ bonding changes. The shape of Figure 4 implies that π bonding from phosphines through metal to dinitrogen is progressively less important in stabilising the $Mo\text{–}N_2$ system in moving from $[Mo(N_2)_2\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}_2]$ to $[Mo(N_2)_2\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2\}_2]$.

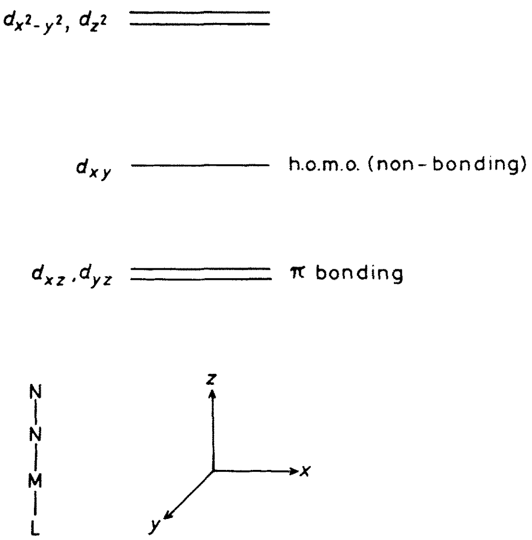


Figure 5. *d*-Orbital splitting in $[M(N_2)L(diphosphine)_2]^{n-}$ (M = Mo or W; L = anionic or neutral ligand, including N_2; *n* = 0 or 1)

The second point is that the linearity in the $\nu(N_2)$ *vs.* $E_{\frac{1}{2}}^{ox}$ relationship observed with ligands L *trans* to N_2 implies that the influence of L on either $E_{\frac{1}{2}}^{ox}$ or $\nu(N_2)$ is qualitatively the same throughout the series of complexes, that is to say, the relative proportion of σ and π effects remains constant. The magnitudes of the effects change with the metal and the *cis* ligands. This clearly distinguishes the consequences of changes in the *trans*-ligand L from those of changes in the tertiary phosphine substituents.

There is a considerable difference in $\nu(N_2)$ for comparable molybdenum and tungsten complexes, whereas the $E_{\frac{1}{2}}^{ox}$ values are very similar. In higher oxidation states, with far fewer formally non-bonding electrons (*e.g.* $[MF_6]^- \longrightarrow MF_6$) the tungsten complex is easier to oxidise by *ca.* 1.0 V.[7] This difference is difficult to rationalise and the similarity of potentials is clearly not generalisable to all oxidation states.

Tungsten is generally believed to be more electron-releasing than molybdenum in the d_π sense [8] and probably forms stronger metal–ligand bonds, *viz.* the M–CO dissociation energy in $[M(CO)_6]$ is 152 (Mo) and 181 (W) kJ mol^{-1} and the M–Cl energy in MCl_6 is 304 ± 7 (Mo) and 347 ± 1 (W) kJ mol^{-1}.[9] The bis(dinitrogen) complexes discussed in this paper fall into the same pattern. The ligands on a tungsten complex are more basic with respect to the proton than ligands on a homologous complex of molybdenum {pK_a of $[MF(NH)(dppe)_2]$ are 12.7 (Mo) and 15.5 (W)}.[10] However, this may not be true with acids in general, since $[Mo(N_2)_2(dppe)_2]$ is a

Table 2. Thermodynamic data [a] for the reactions $[Mo(N_2)_2L_4]^{n+} \longrightarrow [Mo(N_2)L_4]^{n+} + N_2$ where L = tertiary phosphine

Complex	n	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$k_{obs.}$ [b]/s^{-1}
trans-$[Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$	0	110(9)	+25(28)	5.2×10^{-6} (300)
	1	29(4)	−165(12)	1.7×10^{-1} (297)
trans-$[Mo(N_2)_2\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2\}_2]$	0	106(16)	+19(53)	2.8×10^{-3} (300)
	1	99(7)	+76(23)	3.0×10^{-1} (297)
trans-$[Mo(N_2)_2\{(p\text{-}ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl\text{-}p)_2\}_2]$	0	104(7)	+37(22)	3.5×10^{-4} (300)
	1	70(6)	−29(18)	2.4×10^{-1} (297)
trans-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$	0	116(4)	+75(12)	2.8×10^{-4} (300)
	1	92(4)	+43(11)	8.6×10^{-2} (297)
trans-$[Mo(N_2)_2\{(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2\}_2]$	0	115(8)	+70(44)	1.9×10^{-4} (300)
	1	91(3)	+36(9)	7.2×10^{-2} (297)
trans-$[Mo(N_2)_2\{(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe\text{-}p)_2\}_2]$	0	116(9)	+72(28)	1.4×10^{-4} (300)
	1	84(5)	+18(17)	9.4×10^{-2} (297)
cis-$[W(N_2)_2(PMe_2Ph)_4]$	0	109(8)	+38(24)	6.4×10^{-5} (300)
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	0	98(14)	+51(51)	2.6×10^{-2} (300)

[a] Estimated errors in parentheses, unless stated otherwise. [b] T/K in parentheses.

stronger base towards $AlMe_3$ than is $[W(N_2)_2(dppe)_2]$.[11] Clearly $\nu(N_2)$ is not necessarily an unequivocal measure of base strength. The difference between molybdenum and tungsten may also change with oxidation state. Indeed, the first ionisation potentials of the metals are 7.13 (Mo) and 7.98 (W) eV,[12] suggesting that the former should release charge more easily than the latter. However, in a complex the release of electrons onto ligands, by increasing the effective nuclear charge experienced by a non-bonding h.o.m.o., could lead to an increase in the difficulty of metal-centred oxidation. These disparate observations probably are simply rationalisable, but many more data are needed before this can be convincing.

Influence of Diphosphine on ^{31}P *N.M.R. Chemical Shifts.*—It can be seen from Table 1 that the ^{31}P n.m.r. chemical shifts vary with the phosphine substituents, although the overall range of the shifts is quite small. The coupling constants $^{1}J(W\text{-}P)$ are invariant. Tungsten complexes have shifts consistently some 20 p.p.m. to higher field than their molybdenum analogues and the shifts move to higher field as the substituent becomes more electron-donating. These are not unexpected trends.[13] Since the origin of chemical shifts in such complexes is not entirely understood, we shall not attempt to rationalise this further, except to say that the shifts reflect broadly the electron-releasing ability of the substituents. There is no acceptable correlation between ^{31}P n.m.r. shifts and $\nu(N_2)$ (correlation coefficient 0.96) and best-fit straight lines for the shifts and either σ or σ^+ are even worse. The complexes containing $p\text{-}ClC_6H_4$ are particularly anomalous.

There is also a poor correlation between $E_{\frac{1}{2}}^{ox}$ and the ^{31}P n.m.r. shifts. It has recently been shown [14] that for a series of complexes $[Cr(CO)_5L]$ (L = tertiary phosphine, halide, MeCN, C_5H_5N, or CO) there is a linear correlation between ^{13}C n.m.r. shifts and $E_{\frac{1}{2}}^{ox}$, especially for the *cis*-carbonyl shifts, but not for the ^{31}P shifts in the phosphine complexes. This was ascribed to the perturbation of charge effects by the steric constraints of the phosphines. We conclude, therefore, that in our complexes some complicating factor, possibly steric, is also important. It is noteworthy that the ^{31}P shifts of the free diphosphines do not correlate well with the Hammett substituent constants.

Kinetic Measurements.—It was clearly of interest to determine whether the effects of substituents in the phosphines would be reflected in changes in metal–dinitrogen bond energies. It is known [15] that substitution reactions of $[Mo(N_2)_2(dppe)_2]$ such as (3) proceed *via* a rate-determining step (4) which is dissociation of N_2 from the complex, followed by an association (5). The enthalpy of activation for such a substitution reaction is a measure of the $Mo\text{-}N_2$ bond-dissociation energy, provided the usual assumptions are made. We therefore determined the rates of reactions of displacement of N_2 by PhCN in the series of complexes shown in Table 2 by an electrochemical technique described elsewhere.[15]

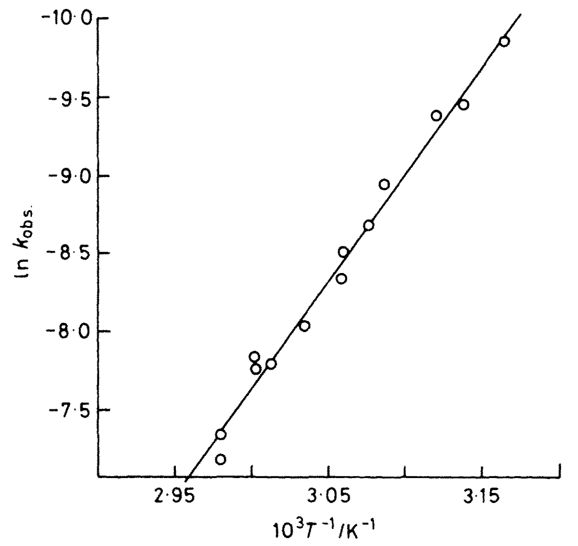


Figure 6. Plot of ln $k_{obs.}$ *vs.* $1/T$ for the reaction of $[Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$ with PhCN

$$[Mo(N_2)_2(dppe)_2] + PhCN \longrightarrow [Mo(N_2)(NCPh)(dppe)_2] + N_2 \quad (3)$$

$$[Mo(N_2)_2(dppe)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo(N_2)(dppe)_2] + N_2 \quad (4)$$

$$[Mo(N_2)(dppe)_2] + PhCN \xrightarrow{k_2} [Mo(N_2)(NCPh)(dppe)_2] \quad (5)$$

Further, since the species $[Mo(N_2)_2(diphosphine)_2]^+$ are of limited stability at room temperature and decompose by a rate-determining step which involves $Mo\text{-}N_2$ bond cleavage,[16] we were able by a double-potential-step method to determine the activation energies for $Mo\text{-}N_2$ bond cleavage in reaction

(6). This enabled us to obtain a comparable set of Mo–N_2 dissociation enthalpies for Mo^I. The results for both oxidation

$$[Mo(N_2)_2(\text{diphosphine})_2]^+ \longrightarrow [Mo(N_2)(\text{diphosphine})_2]^+ + N_2 \quad (6)$$

states are shown in Table 2 and a typical plot for ln $k_{obs.}$ *vs.* $1/T$ for $[Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$ is shown in Figure 6.

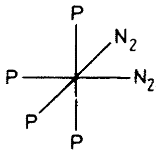
For the *trans* complexes in oxidation state zero, the value of $k_{obs.}$ at 300 K is in the following sequence as the phosphine substituents are varied: p-$CF_3C_6H_4$ > p-ClC_6H_4 > C_6H_5 > p-MeC_6H_4 > p-$MeOC_6H_4$ > Et. Least-squares plots of ln $k_{obs.}$ against σ and σ^+ show a better correlation with the latter, but since the correlation coefficient is only 0.94 this may not be very significant. Correlation is sensibly better with $\nu(N_2)$ (0.97) than with $E_{\frac{1}{2}}^{ox}$ (0.89), but again not very convincing. It is clear, however, that $\nu(N_2)$ in a closely related set of compounds such as ours is a rough measure of the relative strength of metal–dinitrogen binding.

Table 2 also includes the calculated values for the entropies and enthalpies of activation. The entropy contributions are large and positive, suggesting that there is a considerable rearrangement upon activation, but the associated experimental errors are inevitably so large that a detailed discussion is pointless. The values for $\Delta H^\ddagger$ accord roughly with the relative donor power of the phosphines, but still have rather large uncertainties associated with them. The values are of the same order as the few comparable data already in the literature, for example 117 kJ mol^{-1} for $[Ru(NH_3)_5(N_2)]^{2+}$.[17]

The data for the diphosphine complexes in oxidation state +1 are not so self-consistent. However, the same trends with donor power are evident. The p-chlorophenyl compound is again somewhat anomalous, and $\Delta H^\ddagger$ for the tetraethyldiphosphine is unexpectedly low. This may be because the reaction we are observing in oxidation state +1 is not simple N_2 loss.

Finally we consider the derivatives of PMe_2Ph. Dinitrogen is bound considerably more strongly in the case of tungsten than molybdenum. This is entirely consistent with previous data[8] on the relative abilities of these metals to release electron density to ligands.

The binding of N_2 in a *cis* complex is considerably weaker than that in the *trans* complexes. This is in accord with our experience of the reactivity of these complexes, but is nevertheless unexpected if one simply regards the fact that dinitrogens *trans* to each other should compete for π-electron density. However, the data discussed earlier show that *cis* delocalisation into N_2 is an important stabilising factor. Four *cis*-phosphine ligands binding two dinitrogens are apparently more effective than the arrangement in the *cis*-bis(dinitrogen) complexes (see below) where each N_2 is interacting with two common *cis*-phosphines (P) and with two further phosphines which are *cis* and *trans*, respectively. Presumably *trans*-phosphine metal–dinitrogen bond weakening *via* the σ system is significant here.



Experimental

All reactions and compound manipulations were carried out in Schlenk apparatus under dinitrogen or argon, as appropriate. The solvents were dried and distilled under dinitrogen before use. I.r. spectra were recorded for KBr discs (unless otherwise stated) on a Perkin-Elmer 527 spectrometer. Calibration with respect to indene for the M–N_2 stretching region suggests an accuracy of ±2 cm^{-1}. Raman spectra were obtained for sealed glass ampoules using a krypton laser (red line at 647.1 nm, power 24—85 mW) on a modified Cary 82 spectrometer, by courtesy of Professor I. R. Beattie and Dr. S. J. Ogden, University of Southampton. The accuracy of the data is ±1 cm^{-1}. Proton n.m.r. data were obtained in deuteriated solvents with tetramethylsilane as internal standard using Varian EM360 and JEOL PFT-100 spectrometers, and ^{31}P n.m.r. spectra using a JEOL-FX90Q spectrometer with trimethyl phosphite as external standard. Melting points were obtained *in vacuo* using an Electrothermal melting point apparatus, and are uncorrected. Oxidation potentials are quoted *versus* the saturated calomel electrode (s.c.e.) and were obtained in a two-compartment three-electrode cell with platinum electrodes and a silver-wire pseudo-reference electrode. The electrolyte was 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ in tetrahydrofuran (thf). The ferrocenium–ferrocene couple measured under our conditions was 0.535 V *versus* the s.c.e. Analyses were by Mr. A. G. Olney, University of Sussex.

The dinitrogen complexes of molybdenum and tungsten were generally prepared by direct reduction[18] of $MoCl_5$ or WCl_6 either by sodium amalgam or by magnesium in the presence of the appropriate phosphine. Derivatives of $R_2PCH_2CH_2PR_2$ (R = Ph or p-MeC_6H_4) have been described elsewhere.[19] The exceptions to the general method were the derivatives of $(ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl)_2$ and $(CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3)_2$.

Typically, 2—3 molar equivalents of diphosphine for each molar equivalent of $MoCl_5$ or WCl_6 were dissolved in thf (100 cm^3) and the metal halide (0.3—0.6 g) added in small quantities. Then magnesium turnings (1.0—3.0 g) which had been dried by flame heating *in vacuo* were added and the reactants stirred vigorously under N_2 for 16 h. The resulting dark red-orange solution was filtered through Celite to remove the excess of magnesium, reduced to *ca.* 20 cm^3 at 10^{-3} mmHg (0.134 Pa), and the complex precipitated from solution with methanol (20—60 cm^3). The orange-yellow (molybdenum) or orange (tungsten) complexes were filtered off and recrystallised from thf–methanol. Yields 20—60% of mildly air-sensitive material. In this way the following new compounds were obtained: *bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*bis*(*dinitrogen*)-*molybdenum* and -*tungsten*; *bis*[1,2-*bis*(*di*-p-*methoxyphenylphosphino*)*ethane*]*bis*(*dinitrogen*)-*molybdenum* and -*tungsten*; *bis*[1,2-*bis*(*di*-p-*tolylphosphino*)*ethane*]*bis*(*dinitrogen*)-*molybdenum* and -*tungsten*; the tungsten complex of $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$ was similarly prepared but never obtained pure.

Bis[1,2-*bis*(*di*-p-*chlorophenylphosphino*)*ethane*]*bis*(*dinitrogen*)*tungsten*.—To a solution of the appropriate phosphine (2.86 g, 5.33 mmol) in C_6H_6 (250 cm^3) was added $[WCl_4(PPh_3)_2]$[18] (4.07 g, 4.85 mmol) and the solution heated under reflux for 1 h. The greenish brown $[WCl_4\{(p\text{-}ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl\text{-}p)_2\}]$ was filtered off and dried *in vacuo* (yield 85%).

This complex (3.50 g, 4.06 mmol) and more diphosphine (2.40 g, 4.48 mmol) were then suspended in thf (200 cm^3) and an excess of magnesium turnings added. The mixture was stirred vigorously for 6 h, the dark red solution filtered through Celite, the filtrate reduced to dryness *in vacuo*, and methanol added to produce an orange-red solid which was recrystallised from thf–methanol, yield 65%. The new compound *bis*[1,2-*bis*(*di*-p-*trifluoromethylphenylphosphino*)*ethane*]-

bis(dinitrogen)tungsten was prepared similarly in comparable yield.

Bis[1,2-*bis*(*di*-p-*chlorophenylphosphino*)*ethane*]*bis*(*dinitrogen*)*molybdenum*.—To a solution of the diphosphine (2.0 g, 3.70 mmol) in thf (100 cm^3) were added three roughly equal portions of $MoCl_5$ (total 0.42 g, 1.50 mmol) over 10 min with vigorous stirring. An excess of 2% sodium amalgam was then added, and the reactants stirred vigorously for 16 h. The dark red-orange solution was filtered through Celite and the filtrate reduced *in vacuo* to 10 cm^3. An orange solid was precipitated using methanol, and was recrystallised from thf–methanol, yield 40%. The new compound *bis*[1,2-*bis*(*di*-p-*trifluoromethylphenylphosphino*)*ethane*]*bis*(*dinitrogen*)*molybdenum* was prepared in similar yield by the same method.

Kinetic Measurements.—Kinetic measurements were made in a two-compartment three-electrode cell fitted with a Luggin probe using a Hi-Tek potentiostat type DT2101 and waveform generator type PPRl in conjunction with a Philips PM8041 X-Y recorder. The cell was fitted with a platinum-wire working electrode, a platinum-wire-coil secondary electrode, and a silver-wire pseudo-reference electrode. The electrolyte was 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ in thf.

Potentials quoted were internally referenced to either the $[Mo(N_2)_2(dppe)_2]^{0/+}$ couple ($E_{\frac{1}{2}}^{ox}$ assigned as -0.16 V *versus* s.c.e.) or to that couple of one of the other molybdenum dinitrogen compounds whose cyclic voltammogram did not significantly overlap with that of the compound under study.

All the complexes studied showed one-electron reversible and diffusion-controlled oxidation as evidenced by the usual electrochemical criteria. The peak currents were proportional to the square root of the scan rate over the range 0.01—0.3 V s^{-1}, the ratios of the anodic to cathodic peak currents were close to unity, the peak oxidation/concentration functions were within 10% of that for the standard $[Mo(N_2)_2(dppe)_2]$, and the separations in the aniodic and cathodic peak potentials were in the range 60—70 mV.

Kinetic measurements were made by monitoring the concentration of the complexes (*via* the peak height of the oxidation wave of the cyclic voltammograms of the complexes) under pseudo-first-order conditions as a function of time at different temperatures. Measurements were made in a solution of supporting electrolyte (30 cm^3) under dinitrogen, the solution containing typically 20—40 mg (*ca*. 0.02—0.04 mmol) of complex. An excess of PhCN (0.5 cm^3, 4.9 mmol) was added under dinitrogen and measurements recorded after allowing the system to reach thermal equilibrium. Measurements were normally taken for at least two reaction half-lives. The reactions of PhCN with $[Mo(N_2)_2(diphosphine)_2]$ are first order in complex and zero order in PhCN concentration.

First-order rate constants ($k_{obs.}$) were determined from the slopes of the lines obtained by unweighted linear least-squares fits of the raw ln [complex] *versus* time data. Thermodynamic parameters were evaluated by using the Eyring equation (7).[20]

$$\log_{10}\left(\frac{k_{obs.}}{T}\right) = 10.32 - \frac{\Delta H^\ddagger}{4.57}\left(\frac{10^3}{T}\right) + \frac{\Delta S^\ddagger}{4.57} \qquad (7)$$

$\Delta H^\ddagger$ and $\Delta S^\ddagger$ values (in calories) were obtained from the slopes and intercepts respectively of the lines determined by unweighted linear least-squares fits of the $\log_{10}(k_{obs.}/T)$ *versus* $(10^3/T)$ data for the different complexes.

Double-potential-step measurements over a range of temperatures were used to study the decomposition rates of complexes $[Mo(N_2)_2(diphosphine)_2]^+$ in tetrahydrofuran. The procedure is described in ref. 21. The stepped potential applied was 0.84 V and the delay time 4 s. The thermodynamic parameters were evaluated as above.

Acknowledgements

We acknowledge the award of S.E.R.C. Postdoctoral Fellowships (to W. H. and D. A. R.).

References

1 J. Chatt, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1980, 121.
2 R. J. Burt, J. Chatt, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, 1979, **182**, 203.
3 J. Chatt, W. Hussain, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. A. Rankin, *J. Chem. Soc., Chem. Commun.*, 1980, 1024.
4 J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.
5 T. Tatsumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, 1975, **14**, 2530.
6 J. N. Murrell, A. H. Derzi, G. J. Leigh, and M. F. Guest, *J. Chem. Soc., Dalton Trans.*, 1980, 1425.
7 S. Brownstein, G. A. Heath, A. Sengupta, and D. W. A. Sharp, *J. Chem. Soc., Chem. Commun.*, 1983, 669.
8 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1982, 917; D. F. Shriver, *Acc. Chem. Res.*, 1970, **3**, 321.
9 G. Pilcher and H. A. Skinner, in 'The Chemistry of the Metal–Carbon Bond,' vol. 1, eds. F. R. Hartley and S. Patai, Wiley, Chichester, 1982, p. 43.
10 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1983, 51.
11 J. Chatt, R. H. Crabtree, E. A. Jeffery, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1973, 1167.
12 J. Kleinberg, W. J. Argersinger, and E. Griswold, 'Inorganic Chemistry,' D. C. Heath, Boston, 1960, p. 95.
13 S. Donovan-Mtunzi, M. Hughes, G. J. Leigh, H. Mohd. Ali, R. L. Richards, and J. Mason, *J. Organomet. Chem.*, 1983, **246**, C1.
14 A. M. Bond, S. M. Carr, R. Colton, and D. P. Kelly, *Inorg. Chem.*, 1983, **22**, 989.
15 J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1978, 1638.
16 C. M. Elson, *Inorg. Chim. Acta*, 1976, **18**, 209.
17 J. N. Armor and H. Taube, *J. Am. Chem. Soc.*, 1970, **92**, 6170.
18 T. A. George and M. E. Noble, *Inorg. Chem.*, 1978, **17**, 1678; S. N. Anderson, unpublished work.
19 L. J. Archer and T. A. George, *Inorg. Chem.*, 1979, **18**, 2079; J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074; G. J. Leigh, 'Preparative Inorganic Reactions,' vol. 6, ed. W. L. Jolly, Wiley-Interscience, London, 1971, p. 165.
20 H. Eyring, J. Walter, and G. E. Kimball, 'Quantum Chemistry,' Wiley, New York, 1944.
21 D. Pletcher, *Chem. Soc. Rev.*, 1975, **4**, 471.

Received 13*th October* 1983; *Paper* 3/1815