Redox Potential–Structure Relationships in Metal Complexes. Part 2.[1] The Influence of *trans*-Substituents upon the Redox Properties of Certain Dinitrogen Complexes of Molybdenum and Tungsten and Some Carbonyl Analogues: Inner-sphere *versus* Outer-sphere Electron Transfer in the Alkylation of Co-ordinated Dinitrogen

By **Joseph Chatt, G. Jeffery Leigh,* Heinrich Neukomm, Christopher J. Pickett,*** and **David R. Stanley,** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ

The preparation of some new anionic dinitrogen complexes of the type *trans*-$[M(N_2)X(dppe)_2]^-$ is described (M = Mo or W; X = SCN, CN, or N_3; dppe = $Ph_2PCH_2CH_2PPh_2$) together with their monocarbonyl analogues (M = Mo). Relationships between $E_{\frac{1}{2}}^{ox}$, $\nu(N_2)$, and $\nu(CO)$ of these complexes and those of $[M(N_2)(NCR)(dppe)_2]$ and the standard series $[Cr(CO)_5(L\text{ or }X^-)]$ have allowed us to identify the formation of a labile ammine complex $[Mo(N_2)(NH_3)(dppe)_2]$ in tetrahydrofuran and to predict $E_{\frac{1}{2}}^{ox}$ and $\nu(N_2)$ for as yet unsynthesised complexes related to those described. Furthermore, aspects of the reactivity of the co-ordinated dinitrogen ligand have been correlated with the ' electron-richness ' of the complex (as measured by $E_{\frac{1}{2}}^{ox}$) with particular reference to (*a*) inner-sphere *versus* outer-sphere electron-transfer alkylation of co-ordinated dinitrogen to give organodiazenido-complexes and (*b*) the protonation of $[M(N_2)(NCR)(dppe)_2]$ complexes which give the new hydrazido(2−)-salts, $[M(N_2H_2)(NCR)(dppe)_2][HSO_4]_2$, with retention of the *trans*-RCN ligand.

SIMPLE replacement of one ligand by another in a closed-shell metal complex often has a substantial influence upon the energies of the redox orbitals,[1,2] especially when it involves the exchange of a neutral ligand (*e.g.* CO) by a charged ligand (*e.g.* Cl^-).[2] In any *molecule*, the energy of the highest occupied molecular orbital (h.o.m.o.) is related to the oxidation potential, $E_{\frac{1}{2}}^{ox}$,[3] and in a series of isoelectronic complexes obtained by the substitution of one ligand by each of a series of other ligands, $E_{\frac{1}{2}}^{ox}$ is a measure of the relative ' electron-richness ' of the members of that series. The $E_{\frac{1}{2}}^{ox}$ of each member can be correlated with the effect of its particular substituent ligand upon the energy of the h.o.m.o. A change in $E_{\frac{1}{2}}^{ox}$ is often reflected by concomitant changes in other molecular parameters such as vibrational and electronic transition frequencies[4] and also in the *chemical reactivity*.[5]

In this paper we report the effects of ligands L or X^- on the redox properties of the complexes *trans*-$[M(N_2)(L\text{ or }X^-)(dppe)_2]$ (M = Mo or W; L = uncharged ligand, and X^- = an anionic ligand) and *trans*-$[Mo(CO)(L\text{ or }X^-)(dppe)_2]$ [dppe = 1, 2-bis(diphenylphosphino)ethane], also the correlation of the redox properties with $\nu(N_2)$, $\nu(CO)$, and with the susceptibility of the complexes towards attack by electrophilic reagents.

RESULTS AND DISCUSSION

(*a*) *Preparation of Complexes.*—The complexes $[M(N_2)L(dppe)_2]$ and $[M(N_2)X(dppe)_2]^-$ were prepared by reactions (1) and (2). When M = W, irradiation of the reaction mixture with a tungsten-filament lamp is necessary. Monocarbonyl analogues, $[Mo(CO)(L\text{ or }X^-)(dppe)_2]$ of the dinitrogen complexes were synthesised from *trans*-$[Mo(N_2)(CO)(dppe)_2]$ in reactions similar to (1) and (2). Tatsumi *et al.*[6,7] have reported the preparation of $[Mo(CO)L(dppe)_2]$ and $[Mo(N_2)L(dppe)_2]$ where L = RCN (R = alkyl or aryl) and we have briefly reported the preparation of some tungsten analogues.[8] The anionic complexes are all new and their preparation is detailed in the Experimental section.

The ^{31}P n.m.r. spectrum of $[Mo(N_2)(CN)(dppe)_2]^-$ and of $[Mo(CO)(NCPh)(dppe)_2]$ show single phosphorus resonances in tetrahydrofuran (thf) at $\delta = 70.8$ and 69.4 p.p.m., respectively, upfield from trimethyl phosphite. This clearly indicates a *meridional* arrangement of the four phosphorus atoms, as was found for the organonitrile dinitrogen complexes.[6]

$$[M(N_2)_2(dppe)_2] \xrightarrow[\text{thf or toluene}]{L} [M(N_2)L(dppe)_2] + N_2 \quad (1)$$

$$[M(N_2)_2(dppe)_2] + [NBu_4]X \xrightarrow{\text{thf}} [NBu_4][M(N_2)X(dppe)_2] + N_2 \quad (2)$$

(*b*) *Electrochemical Reactions of the Above Series of Mono(dinitrogen) and Monocarbonyl Complexes: Correlations between* $E_{\frac{1}{2}}^{ox}$ *and* $\nu(N_2)$ *and* $\nu(CO)$.—The electrochemical properties of the complexes were studied in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a platinum electrode. Figure 1 shows a typical cyclic voltammogram for $[NBu_4][Mo(N_2)(SCN)(dppe)_2]$. The behaviour of this complex is analogous to that of $[M(N_2)(NCR)(dppe)_2]$ with two successive one-electron reversible and diffusion-controlled oxidations [reaction (3)].[9]

$$[M(N_2)X(dppe)_2]^- \underset{+e}{\overset{-e}{\rightleftharpoons}} [M(N_2)X(dppe)_2] \underset{+e}{\overset{-e}{\rightleftharpoons}} [M(N_2)X(dppe)_2]^+ \quad (3)$$

Both the dinitrogen and the carbonyl complexes exhibit the same oxidation pattern, but the secondary oxidation process for the carbonyl complexes is decidedly less reversible than for their N_2 analogues. Whereas N_2 loss primarily accounts for the instability of the metal(II) dinitrogen complexes,[8] attack at the metal by F^- (from $[BF_4]^-$) *probably* accounts for the irreversibility of the secondary oxidation in the carbonyl series [reaction (4)].

In an earlier paper[8] we reported that $[M(N_2)(NCR)$-

(dppe)$_2$] is considerably easier to oxidise than [M(N$_2$)$_2$(dppe)$_2$] whilst the higher-oxidation-state metal complexes [M(N$_2$)(NCR)(dppe)$_2$]$^+$ and [M(N$_2$)(NCR)(dppe)$_2$]$^{2+}$ have substantially longer half-lives than their bis(dinitrogen) counterparts. We attributed this to the greater net-donor effect of the RCN ligands in strengthening the M–N$_2$ bonding interaction. With the anionic ligands [N$_3$]$^-$, [CN]$^-$, and [SCN]$^-$ these effects are even more marked. Thus the primary oxidation potential, $^1E_{\frac{1}{2}}{}^{ox}$, of [Mo(N$_2$)(N$_3$)(dppe)$_2$]$^-$ was found to be −1.22 V versus the saturated calomel electrode (s.c.e.) compared with $^1E_{\frac{1}{2}}{}^{ox} = -0.16$ V for the bis(dinitrogen) complex. Oxidation of [Mo(N$_2$)(SCN)(dppe)$_2$]$^-$ by air or PhCH$_2$Cl yields [Mo(N$_2$)(SCN)(dppe)$_2$] [reaction (5)].

$$[\mathrm{Mo(CO)X(dppe)_2}] \underset{+e}{\overset{-e}{\rightleftharpoons}} [\mathrm{M(CO)X(dppe)_2}] \underset{+e}{\overset{-e}{\rightleftharpoons}} [\mathrm{Mo(CO)X(dppe)_2}]^+ \quad (4)$$

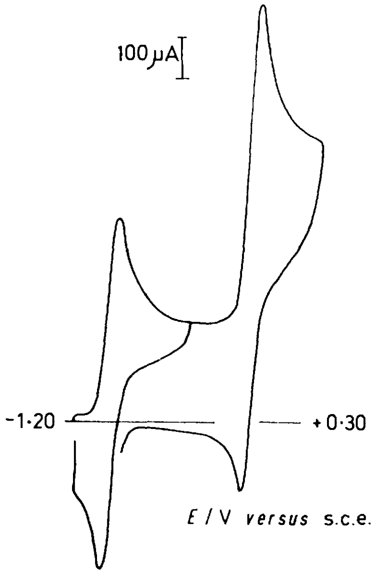


FIGURE 1 Cyclic voltammogram of [Mo(N$_2$)(SCN)(dppe)$_2$]$^-$ in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–thf at a platinum electrode. Scan rate 0.3 V s^{-1}

$$[\mathrm{Mo(N_2)(SCN)(dppe)_2}]^- \xrightarrow[\text{thf}]{\text{oxidation}} [\mathrm{Mo(N_2)(SCN)(dppe)_2}] \quad (5)$$

red
ν(N$_2$) at 1 890 cm^{-1}
ν(SCN) at 2 080 cm^{-1}

yellow
ν(N$_2$) at 1 970 cm^{-1}
ν(SCN) at 2 040 cm^{-1}

The air-oxidation of a solution of [Mo(N$_2$)(SCN)(dppe)$_2$]$^-$ in thf—0.2 mol dm^{-3} [NBu$_4$][BF$_4$] was monitored by cyclic voltammetry which showed that the anion is definitely oxidised to the neutral molydenum(I) species.[9] The tungsten complex [W(N$_2$)(SCN)(dppe)$_2$]$^-$ reacts with air in a similar way but substantial amounts of [W(SCN)$_2$(dppe)$_2$], which we were unable to separate from the tungsten(I) species, are also formed [reaction (6)].

$$[\mathrm{W(N_2)(SCN)(dppe)_2}]^- \xrightarrow[\text{thf}]{\text{oxidation}} x[\mathrm{W(N_2)(SCN)(dppe)_2}] + y[\mathrm{W(SCN)_2(dppe)_2}] \quad (6)$$

ν(N$_2$) at 1 860 cm^{-1}
ν(SCN) at 2 080 cm^{-1}

ν(N$_2$) at 1 920 cm^{-1}
ν(SCN) at 2 040 cm^{-1}

ν(SCN) at 2 000 cm^{-1}

The complexes [Mo(N$_2$)L(dppe)$_2$] and [Mo(N$_2$)X(dppe)$_2$]$^-$ are easier to oxidise than their carbonyl analogues (Figure 2). Thus CO exerts an electron-withdrawing effect when *trans* to L or X$^-$ somewhat stronger than N$_2$. Figure 2 shows a plot of $^1E_{\frac{1}{2}}{}^{ox}$(N$_2$) *versus* $^1E_{\frac{1}{2}}{}^{ox}$(CO). The linear relationship with a dimensionless slope of 1.2 demonstrates that the ligand, L or X$^-$, has the same gross influence upon the metal h.o.m.o. whether bound to Mo(CO)(dppe)$_2$ or Mo(N$_2$)(dppe)$_2$. That the slope is not unity, *i.e.* the difference in the oxidation potentials of the carbonyl and dinitrogen analogues *increases* somewhat with decreasing oxidation potential, suggests that in similar environments the N$_2$ ligand is less able than CO to accommodate extra electronic charge, *via* the metal from the *trans* ligand.

The uncharged Cr(CO)$_5$ moiety can bind a very wide range of ligands L or X$^-$ such as RCN, pyridine, I$^-$, Cl$^-$, or Br$^-$ to give complexes which undergo *reversible* one-electron oxidations,[2,10] and which provide a useful standard series against which we can compare the influence of L or X$^-$ upon the variation of oxidation potential in the [M(N$_2$ or CO) (L or X$^-$) (dppe)$_2$] series. Figures 3(*a*) and 3(*b*) show plots of $^1E_{\frac{1}{2}}{}^{ox}$(CO) and $^1E_{\frac{1}{2}}{}^{ox}$(N$_2$) for the molybdenum complexes discussed above *versus* $^1E_{\frac{1}{2}}{}^{ox}$ for the corresponding complexes derived

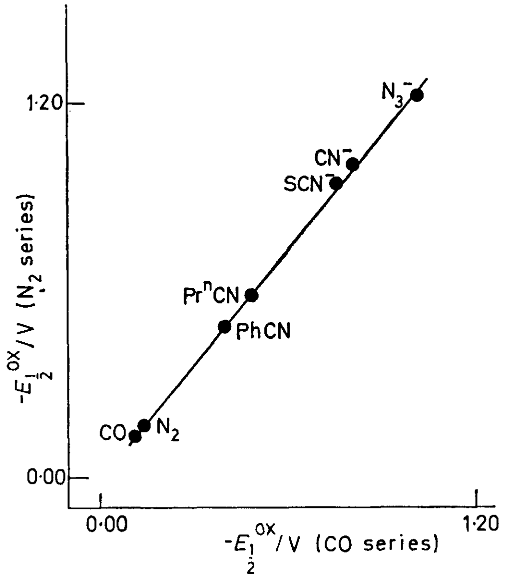


FIGURE 2 Relationship between the oxidation potentials of the [Mo(N$_2$)(L or X$^-$)(dppe)$_2$] and [Mo(CO)(L or X$^-$)(dppe)$_2$] *trans* complexes. Potentials are quoted *versus* the s.c.e. The oxidation potential of [Mo(N$_2$)(CO)(dppe)$_2$] was estimated from $\frac{1}{2}\{E_{\frac{1}{2}}{}^{ox}[\mathrm{Mo(CO)_2(dppe)_2}] + E_{\frac{1}{2}}{}^{ox}[\mathrm{Mo(N_2)_2(dppe)_2}]\}$

from the $Cr(CO)_5$ moiety. Reasonably linear correlations are observed but the slopes are *ca.* 0.72 and 0.84 for the carbonyl and dinitrogen series respectively. This indicates that the energy of the h.o.m.o. of $[Cr(CO)_5(X^-$ or $L)]$ is increased or decreased to a greater extent for a given ligand change than are the h.o.m.o.s of the molybdenum series. The net change in oxidation potential, ΔE_L^{Cr}, for a given ligand change in the standard series[2] $[Cr(CO)_5(L$ or $X^-)]$ can be related to that, $\Delta E_L^{M(N_2 \text{ or } CO)}$, for the two dppe series by equation (7) where β is a constant, which for the above two series is

$$\Delta E_L^{Cr} = \beta[\Delta E_L^{M(N_2 \text{ or } CO)}] \qquad (7)$$

ca. 0.72 (CO) and 0.84 (N_2). Each constant β will apply only to the two series of complexes related here because electron-withdrawing and -donating effects of a given ligand are a function of the circumstances of its coordination as the above results emphasise. Nevertheless the degree of constancy of β will be an interesting parameter as an indication of how much electron-withdrawing and -donating effects depend on the metal centre and its associated ligands.

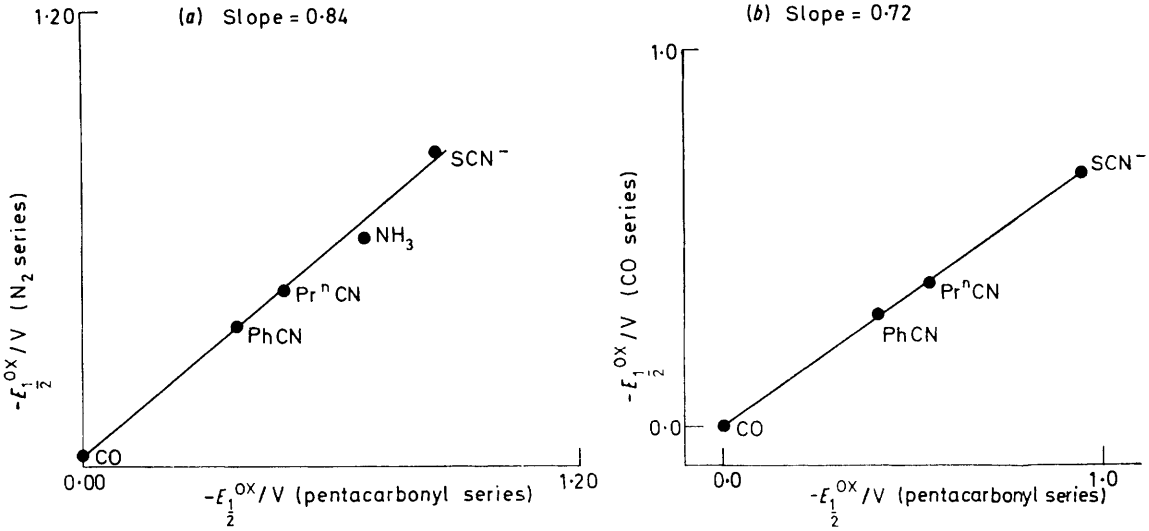


FIGURE 3 Relationship between the oxidation potentials of (*a*) the dinitrogen and (*b*) the carbonyl dppe complexes and the oxidation potentials of the $[Cr(CO)_5(L$ or $X^-)]$ series. Potentials are *versus* the $[Mo(CO)_2(dppe)_2]$–$[Mo(CO)_2(dppe)_2]^+$ couple for the dppe complexes and *versus* the $[Cr(CO)_6]$–$[Cr(CO)_6]^+$ couple for the pentacarbonyl series

A comparison of the oxidation potentials of the molybdenum diphosphine complexes with those of $[Mo(CO)_5(L$ or $X^-)]$ is less rigorous because the latter series tend to oxidise irreversibly. Nevertheless, the peak oxidation potentials, $^1E_p^{ox}$, as measured by cyclic voltammetry for the members of the molybdenum pentacarbonyl series, differ only marginally from $^1E_p^{ox}$ of their chromium analogues.[2,10]

$^1E_{\frac{1}{2}}^{ox}$ is a measure of the 'electron-richness' of the complexes and as such would be expected to follow the same trend as $\nu(CO)$ and $\nu(N_2)$ if these are determined primarily by electron flow from the metal into ligand π-antibonding orbitals. Empirically, the second-order correlations between $^1E_{\frac{1}{2}}^{ox}$ and $\nu(N_2)$ and $\nu(CO)$ are reasonably linear over the range *ca.* −0.1 to −1.2 V, as shown in Figure 4, and may be expressed in the form of equations (8a) and (8b). These empirical relationships

$$\Delta E_L^{M(N_2)}/\Delta\nu(N_2)_L = 9.4 \pm 0.5 \text{ mV cm} \qquad (8a)$$

$$\Delta E_L^{M(CO)}/\Delta\nu(CO)_L = 8.1 \pm 0.5 \text{ mV cm} \qquad (8b)$$

can be compared with those for the closed-shell series $[Cr(CO)_2(\eta\text{-}C_6H_5Me)(PR_3)]$ and $[Mn(CO)_2(\eta\text{-}C_5H_4Me)(PR_3)]$, calculated from the data of ref. 4. In these, the redox orbitals and $\nu(CO)$ frequencies have been perturbed by changing R (R = alkyl or aryl), to give the values $\Delta E_L^{Cr}/\Delta\nu_L(CO) \doteqdot 9.0$ mV cm and $\Delta E_L^{Mn}/\Delta\nu_L(CO) \doteqdot 11.0$ mV cm. These parameters are of the same order as those of equation (8) and suggest that generally for a 1 V change in oxidation potential of a closed-shell

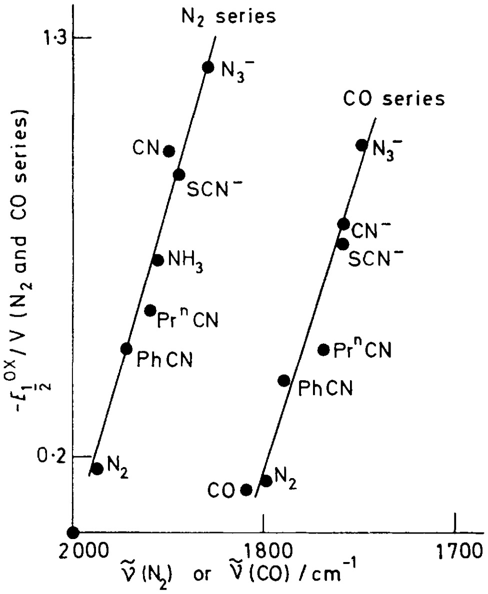


FIGURE 4 Plots of $E_{\frac{1}{2}}^{ox}$ for the N_2 and CO series against the $\nu(N_2)$ and $\nu(CO)$ frequencies

complex, incurred by ligand substitution, ν(CO) changes by *ca.* 100 ± 20 cm^{-1}.

Equations (7) and (8) can be used to predict redox potentials and ν(CO) or $\nu(N_2)$ of complexes as yet unsynthesised or unstable. For example, by measuring the oxidation potential of $[Cr(CO)_5I]^-$ we predict that $[Mo(N_2)I(dppe)_2]^-$ would oxidise at *ca.* −0.95 V *vs.* s.c.e. [equation (7)] and have $\nu(N_2)$ at *ca.* 1 880 ± 5 cm^{-1}. Neither of these parameters lies outside of the range of known dinitrogen complexes, *e.g.* for $[Mo(N_2)(N_3)(dppe)_2]^-$ $^1E_{\frac{1}{2}}^{ox} = -1.22$ V and $\nu(N_2)$ occurs at 1 860 cm^{-1}, and would infer a stable Mo–N_2 bond. The complex cannot be synthesised from $[Mo(N_2)_2(dppe)_2]$ plus iodide ion and its instability must be attributed to the inability of the weakly d_π-accepting (or even π-donating) iodide ion with its negative charge to bind to this electron-rich metal core, rather than to any lability of the Mo-N_2 bond.[11]

On the other hand, ammonia-saturated thf reacts slowly with *trans*-$[Mo(N_2)_2(dppe)_2]$ to give a dark red solution. Dinitrogen reverses this reaction, regenerating the orange solution of the starting material. Evaporation of the solvent from the red solution gives a material which shows i.r. bands assignable to a mixture of $[Mo(N_2)_2(dppe)_2]$ [$\nu(N_2)$ at 1 975 cm^{-1}] and a new dinitrogen complex [$\nu(N_2)$ at 1 910 cm^{-1}]. Examination of $[Mo(N_2)_2(dppe)_2]$ by cyclic voltammetry in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ *before* and *after* reaction with NH_3 reveals a new species characterised by a *reversible* one-electron oxidation at $E_{\frac{1}{2}}^{ox} = -0.71$ V *vs.* s.c.e. From the measured oxidation potential of $[Cr(CO)_5(NH_3)]$ and equation (7) we predict $E_{\frac{1}{2}}^{ox}$ of $[Mo(N_2)(NH_3)(dppe)_2]$ to be −0.75 ± 0.05 V *vs.* s.c.e. and $\nu(N_2)$ to be at 1 910 ± 5 cm^{-1} from equation (8). Evidently the new complex in the red solution is the labile $[Mo(N_2)(NH_3)(dppe)_2]$ species.

(*c*) *Chemical Reactivity and Redox Potential.*—Finally, we consider whether there is a correlation between the redox potentials of the complexes and the chemical reactivity of the co-ordinated dinitrogen. The complex *trans*-$[Mo(N_2)_2(dppe)_2]$ reacts with alkyl halides, RX′, *via* an *inner-sphere* redox process [reaction (9), L = N_2]. The rate-controlling step in this sequence is the initial loss of N_2.[12] It is possible that the more electron-rich

$$[Mo(N_2)(L\text{ or }X^-)(dppe)_2] \xrightarrow[-L\text{ or }X^-]{k_1}$$

$$[Mo(N_2)(dppe)_2] \xrightarrow{RX'} \underset{(A)}{[Mo(N_2)X'(dppe)_2]} + R\cdot \longrightarrow$$

$$[Mo(N_2R)X'(dppe)_2] \quad (9)$$

organonitrile or anionic complexes $[Mo(N_2)(L\text{ or }X^-)(dppe)_2]$ could form a reactive molybdenum(I) dinitrogen intermediate analogous to (A) *via* an *outer-sphere* electron transfer to RX′ (X′ = Br or I).[13]

$$[Mo(N_2)(L,X^-)(dppe)_2]^{0,-} + RX' \xrightarrow{k_2}$$

$$[Mo(N_2)(L,X^-)(dppe)_2]^{+,0} + R\cdot + X'^- \quad (10)$$

We therefore determined the lability of the L or X^- ligand in the complexes where L = Pr^nCN and X = SCN, and also the rate dependence of the alkylation reaction with Bu^nI which forms $[Mo(N_2Bu^n)I(dppe)_2]$ and $[Mo(SCN)(N_2Bu^n)(dppe)_2]$, respectively. Values of k_1 [reaction (9)] were obtained by electrochemically monitoring the substitution of L or X^- by PhCN in the complexes under pseudo-first-order conditions. The complexes in which L = N_2[14] or Pr^nCN and X = SCN span a range in redox potential of *ca.* 1 V and the rate-controlling steps in the *substitution* reactions were first order in complex concentration and zero-order in [PhCN] with $10^4k_1 = 1.2 \pm 0.1$,[9] 0.4 ± 0.1, and 0.8 ± 0.1 s^{-1} respectively [reaction (9)]. Moreover, the rates of alkylation of $[Mo(N_2)L(dppe)_2]$ (L = N_2 or Pr^nCN) with Bu^nI showed a similar dependence upon metal complex and substrate with k_1 close to the rate constants measured for the substitution reactions.[14] Thus the alkylation when L = Pr^nCN probably also proceeds *via* an *inner-sphere* redox pathway [reaction (9)].

By contrast, the alkylation of the more reducing thiocyanato-complex $[Mo(N_2)(SCN)(dppe)_2]^-$ showed a rate which was first order in complex concentration *and* first order in $[Bu^nI]$. Under similar first-order conditions, $10^4k_1(\text{app.}) = 120$ s^{-1} (Figure 5). In addition, the product retained the thiocyanato-ligand. This is clearly inconsistent with ligand loss as the rate-controlling step and suggests either an outer-sphere electron-transfer reaction (10) or a nucleophilic attack of co-ordinated N_2 upon the alkyl halide. However, the latter pathway is unlikely since the reaction of $[Mo(N_2)(SCN)(dppe)_2]^-$ with $PhCH_2Cl$ yields the neutral molybdenum(I) species [reaction (5)]. The benzyl radical is known not to attack N_2 in a molybdenum(I) dinitrogen complex, whereas an associative mechanism involving nucleophilic attack of N_2 on $PhCH_2Cl$ would yield a benzyldiazenido-complex which, prepared indirectly, is known to be stable.[14]

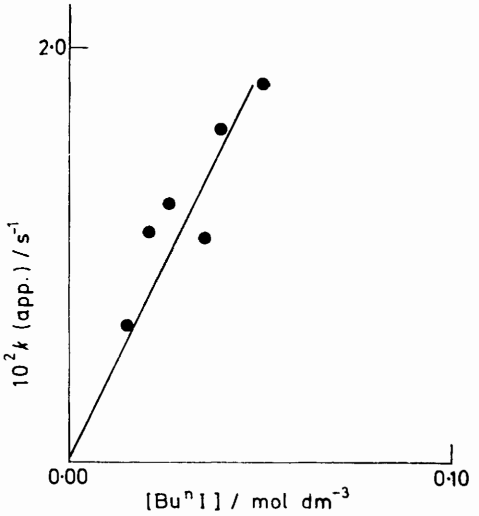


FIGURE 5 Plots of *k*(app.) for the reaction of $[Mo(N_2)(SCN)(dppe)_2]^-$ with Bu^nI in 0.2 mol dm^{-3} $[NBu_4][BF_4]$ at 19.5 ±0.5 °C *versus* $[Bu^nI]$. The *k*(app.) values were determined by electrochemically monitoring the concentration of the anionic complex as previously described [14]

The complex $[NBu_4][Mo(N_2)(CN)(dppe)_2]$ also reacts with Bu^nI to give $[Mo(N_2Bu)(CN)(dppe)_2]$ and the *retention* of the CN ligand is consistent with outer-sphere electron-transfer as the initiating step. The complex $[NBu_4][Mo(N_2)(N_3)(dppe)_2]$ is the most electron-rich of all the N_2 complexes we have prepared. It has a particularly labile $[N_3]^-$ ligand which is rapidly displaced by N_2 or PhCN; its preparation and manipulation is difficult and we have not studied its reactions.

In summary, the formation of the Mo^I–N_2 and radical precursors to the diazenido-products appears to take place *via* two initiating pathways. Those complexes with sufficiently negative oxidation potentials can undergo a simple outer-sphere electron-transfer reaction (10), whilst those complexes with a labile ligand undergo an inner-sphere electron-transfer reaction (9). In complexes which are both reducing and possess a labile ligand both pathways could co-exist, and may possibly do so in the reaction of Bu^nI with $[Mo(N_2)(N_3)(dppe)_2]^-$.

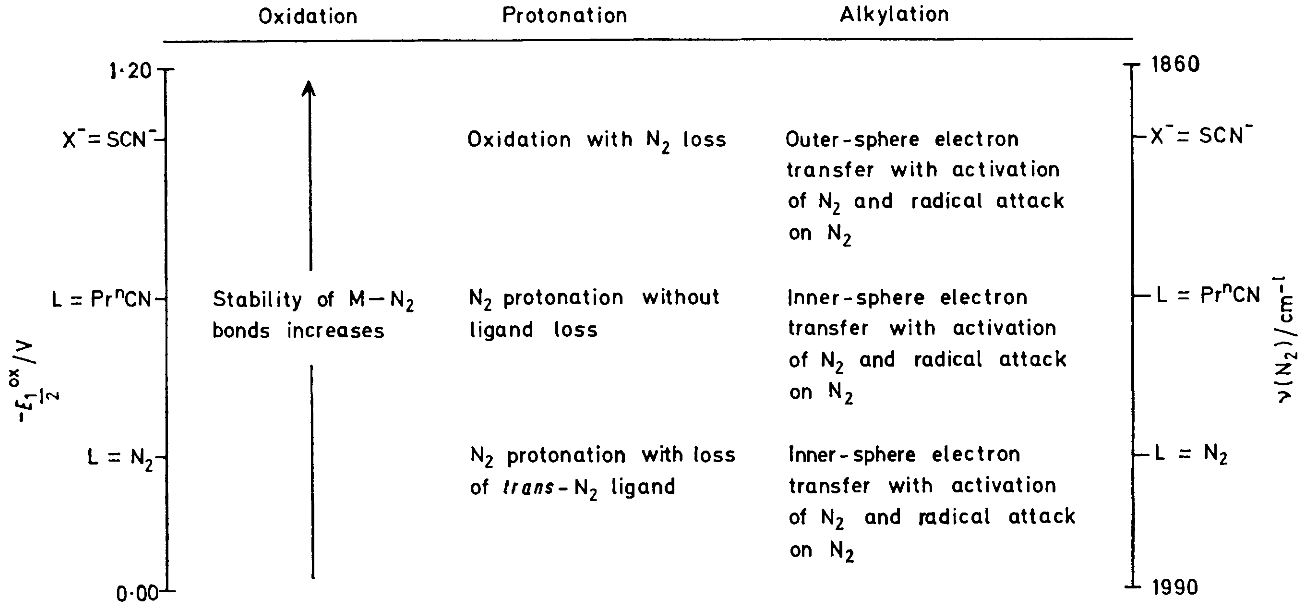
In contrast to the alkylation reactions of co-ordinated dinitrogen the detailed mechanisms of the initial stages of protonation of N_2 in its molybdenum(0) and tungsten(0) phosphine complexes are less well defined. The reaction of $[Mo(N_2)_2(dppe)_2]$ with H_2SO_4 in thf gives $[Mo(N_2H_2)(HSO_4)(dppe)_2][HSO_4]$ [15] whereas we find that both $[Mo(N_2)(NCPr^n)(dppe)_2]$ and $[W(N_2)(NCPr^n)(dppe)_2]$ protonate at the N_2 ligand *without* loss of the *trans*-Pr^nCN ligand. Protonation of the N_2 ligand [reaction (11)] is essentially an oxidation because the addition of a

$$[M(N_2)(NCPr^n)(dppe)_2] \xrightarrow[\text{thf, 0 °C}]{H_2SO_4} [M(N_2H_2)(NCPr^n)(dppe)_2][HSO_4]_2 \quad (11)$$

proton to the terminal nitrogen atom withdraws electronic charge from the metal and the co-ligands; formally the oxidation state of the metal is raised by four units. In the more electron-rich propyl cyanide complexes this shift in electron density from the metal is accommodated without ligand loss, but in $[Mo(N_2)_2(dppe)_2]$ protonation at one N_2 weakens the remaining M–N_2 bond causing the second N_2 to be substituted by the electron-releasing HSO_4 ligand. Reaction of H_2SO_4 in thf with the molybdenum thiocyanato-complex leads to loss of dinitrogen. It appears that the more reducing thiocyanato-complex reduces the solvated protons to dihydrogen to produce unstable $Mo^{II}(N_2)$ products rather than undergoing simple protonation at the N_2.

In the alkylation reactions discussed, the mechanism and products depend upon the redox potential of the complex, the nature of the alkyl halide, the solvent,[14] the lability of N_2 or other ligands and the change in this lability with the oxidation state of the complex. In the protonation reactions similar factors must also apply. It may be that the product(s) will depend upon acid strength and hence oxidising potential as is suggested by the fine dependence of the reaction products obtained from monophosphine dinitrogen complexes of Mo^0 and W^0 upon the specific protonation conditions employed.[15]

In summary, the variation of *reactivity* with redox potential of the $Mo^0(N_2)$ complexes as we understand the various reactions is shown in the Scheme below.



EXPERIMENTAL

Preparation of Complexes and Their Derivatives.—(*a*) *General procedures.* All reactions, unless otherwise stated, were carried out under an atmosphere of dinitrogen or argon in Schlenk-type glassware. Solvents were distilled under dinitrogen from appropriate drying agents.

Infrared spectra were recorded as Nujol mulls on a Unicam SP 200G spectrometer. Phosphorus-31 n.m.r. data were obtained in thf against trimethyl phosphite as external standard on a JEOL HS100 spectrometer. Melting points were recorded in sealed tubes under dinitrogen or argon.

(*b*) *Carbonyl and dinitrogen complexes.* The complexes *trans*-$[Mo(N_2)(NCR)(dppe)_2]$ and *trans*-$[Mo(CO)(NCR)(dppe)_2]$ were prepared according to the methods of ref. 6.

The *trans*-[W(N$_2$)(NCR)(dppe)$_2$] complexes were prepared in an analogous manner; however, irradiation with a tungsten-filament lamp (40 W) was necessary to promote the substitution reactions. As yet we have no synthetic route to the [W(CO)(NCR)(dppe)$_2$] complexes. Yields were generally high (80—90% based upon the parent complex). All the complexes are air-sensitive: *trans*-[Mo(N$_2$)(NCPr^n)(dppe)$_2$], scarlet *needles*, m.p. 107—108 °C, ν(N$_2$) at 1 925 cm^{-1}, ν(C≡N) at 2 200 cm^{-1} (Found: C, 67.95; H, 5.95; N, 4.50. Calc.: C, 67.95; H, 5.60; N, 4.25%); *trans*-[W(N$_2$)(NCPr^n)(dppe)$_2$], red *needles*, m.p. 173—175 °C, ν(N$_2$) at 1 900 cm^{-1}, ν(C≡N) at 2 175 cm^{-1} (Found: C, 62.85; H, 5.60; N, 3.75. Calc.: C, 62.45; H, 5.05; N, 3.90%); *trans*-[Mo(CO)(NCPr^n)(dppe)$_2$], yellow *solid*, m.p. 248—255 °C, ν(CO) at 1 745 cm^{-1}, ν(C≡N) at 2 225 cm^{-1} (Found: C, 70.85; H, 6.00; N, 1.40. Calc.: C, 69.15; H, 5.60; N, 1.40%); *trans*-[W(N$_2$)(NCPh)(dppe)$_2$], very dark green *crystals*, m.p. 199—202 °C, ν(N$_2$) at 1 925 cm^{-1}, ν(C≡N) at 2 100 cm^{-1} (Found: C, 65.8; H, 5.30; N, 3.45. Calc.: C, 63.75; H, 4.80; N, 3.80%); and *trans*-[Mo(CO)(NCPh)(dppe)$_2$], dark red-purple *solid*, ν(CO) at 1 770 cm^{-1}, ν(C≡N) at 2 175 cm^{-1} (Found: C, 67.7; H, 5.45; N, 1.35. Calc: C, 70.1; H, 5.20; N, 1.35%).

The anionic complexes [M(N$_2$)X(dppe)$_2$]$^-$ and [Mo(CO)X(dppe)$_2$]$^-$ were prepared as their quaternary ammonium salts by the reaction of 1 equivalent of the appropriate [NBu$_4$]X salt with [M(N$_2$)$_2$(dppe)$_2$] or [Mo(CO)(N$_2$)(dppe)$_2$] in thf at room temperature. The reactions of [M(N$_2$)$_2$(dppe)$_2$] complexes with the anions required *ca.* 15 h and the tungsten complex also required illumination to assist the substitution (40 W, tungsten-filament lamp). The carbonyl dinitrogen complex reacts rapidly in thf with the anions, *ca.* 5 min. The preparation of [Mo(N$_2$)(SCN)(dppe)$_2$]$^-$ is described in detail; the other complexes were prepared in an analogous manner. Yields were generally 50—60% based upon the parent complex. All the complexes are *extremely* air-sensitive.

[NBu$_4$][Mo(N$_2$)(SCN)(dppe)$_2$]. The complex [Mo(N$_2$)$_2$(dppe)$_2$] (300 mg, 0.31 mmol) was dissolved in *degassed* thf (25 cm^3). The salt [NBu$_4$][SCN] (93 mg, 0.31 mol) was added and the reaction was stirred under 1 atm dinitrogen for 15 h.* The solution changed colour during this period from orange to a very deep red. At the end of the reaction toluene (30 cm^3, degassed) was added to the solution under strictly anaerobic conditions. Dark red-black *needles* appeared after a few minutes. These were filtered from the mother-liquor, washed with fresh degassed toluene (5 cm^3), and dried *in vacuo*. Yield 295 mg (*ca.* 75%), m.p. 204—205 °C, ν(N$_2$) at 1 890 cm^{-1}, ν(SCN) at 2 080 cm^{-1} (Found: C, 67.6; H, 7.05; N, 4.45. Calc.: C, 67.85; H, 6.95; N, 4.60%).

The other anionic complexes prepared were as follows: [NBu$_4$][W(N$_2$)(SCN)(dppe)$_2$], black *needles*, m.p. 180—181 °C, ν(N$_2$) at 1 860 cm^{-1}, ν(SCN) at 2 080 cm^{-1} (Found: C, 62.8; H, 6.25; N, 4.65. Calc: C, 63.3; H, 6.45; N, 4.30%); [NBu$_4$][Mo(N$_2$)(CN)(dppe)$_2$], dark red *crystals*, m.p. 94 °C (decomp.), ν(N$_2$) at 1 900 cm^{-1}, ν(CN) at 2 050 cm^{-1} (Found: C, 69.75; H, 7.05; N, 4.80. Calc.: C, 69.75; H, 7.05; N, 4.70%); [NBu$_4$][W(N$_2$)(CN)(dppe)$_2$], dark red *crystals*, m.p. 89 °C (decomp.), ν(N$_2$) at 1 870 cm^{-1}, ν(CN) at 2 030 cm^{-1} (Found: C, 64.55; H, 7.15; N, 4.40. Calc.: C, 64.9; H, 6.60; N, 4.40%); [NBu$_4$][Mo(CO)(CN)(dppe)$_2$], orange *crystals*, m.p. 205 °C (decomp.), ν(CO) at 1 720 cm^{-1}, ν(CN) at 2 030 cm^{-1} (Found: C, 70.65; H, 7.00; N, 2.80. Calc.: C, 70.7; H, 7.10; N, 2.35%); [NBu$_4$][Mo(CO)(SCN)(dppe)$_2$], scarlet-red *crystals*, ν(CO) at 1 725 cm^{-1}, ν(SCN) at 2 090 cm^{-1} (Found: C, 67.45; H, 7.05; N, 2.55. Calc.: C, 68.85; H, 6.95; N, 2.30%); [NBu$_4$][Mo(N$_2$)(N$_3$)(dppe)$_2$] *and* [NBu$_4$][Mo(CO)(N$_3$)(dppe)$_2$] must be prepared under an atmosphere of argon; they appear to react reversibly with dinitrogen and preparation of analytically pure samples proved to be difficult, carbon analyses being particularly poor; [NBu$_4$][Mo(N$_2$)(N$_3$)(dppe)$_2$], very dark red *needles* stored under argon, m.p. 100 °C (decomp.), ν(N$_2$) at 1 850 cm^{-1}, ν(N$_3$) at 2 080 cm^{-1} (Found: C, 63.1; H, 6.70; N, 7.05. Calc.: C, 67.75; H, 7.00; N, 6.95%); [NBu$_4$][Mo(CO)(N$_3$)(dppe)$_2$], dark red *crystals* stored under argon, ν(N$_3$) at 2 065 cm^{-1}, ν(CO) at 1 690 cm^{-1} (Found: C, 65.0; H, 7.25; N, 4.55. Calc.: C, 68.75; H, 7.05; N, 4.65%).

(*c*) *Reactions of dinitrogen complexes*. (*i*) *Oxidation of* [NBu$_4$][Mo(N$_2$)(SCN)(dppe)$_2$] *by air*. The anionic complex (0.100 g) was dissolved in thf (15 cm^3) under dinitrogen. Air was admitted to the reaction flask and the dark red solution turned instantly bright yellow. The reaction vessel was rapidly evacuated and dinitrogen re-introduced. Methanol (15 cm^3) was added to the stirred solution whereupon a yellow microcrystalline *solid* [Mo(N$_2$)(SCN)(dppe)$_2$] deposited. This was filtered off, washed with methanol (2 × 5 cm^3), and dried *in vacuo*. Yield *ca.* 70%, m.p. 176 °C, ν(N$_2$) at 1 970 cm^{-1}, ν(SCN) at 2 040 cm^{-1} (Found: C, 64.45; H, 5.45; N, 4.00. Calc.: C, 65.0; H, 4.90; N, 4.30%). The complex showed a discrete one-electron reversible reduction at a potential corresponding to the [Mo(N$_2$)(SCN)(dppe)$_2$]$^{-/0}$ couple. The complex *trans*-[Mo(SCN)$_2$(dppe)$_2$], which was independently synthesised as a green crystalline material, shows a single ν(SCN) band at 2 010 cm^{-1} (Found: C, 64.55; H, 5.25; N, 2.65. Calc.: C, 64.3; H, 4.75; N, 2.70%). This material is also formed during air oxidation of the anion when the reaction mixture is stirred under air for long periods.

(*ii*) *Oxidation of* [NBu$_4$][W(N$_2$)(SCN)(dppe)$_2$]. Air-oxidation of the anion was attempted under similar conditions to (*i*) above. In every case a material was obtained which had i.r. bands characteristic of a mixture of [W(N$_2$)(SCN)(dppe)$_2$] [ν(N$_2$) at 1 920 cm^{-1}, ν(SCN) at 2 040 cm^{-1}] and *trans*-[W(SCN)$_2$(dppe)$_2$] [ν(SCN) at 2 005 cm^{-1}].

(*iii*) *Protonation of* [M(N$_2$)(NCPr^n)(dppe)$_2$]. The complex (*ca.* 200 mg) was dissolved in degassed thf (25 cm^3) and cooled to *ca.* 0 °C in an ice-bath. Concentrated sulphuric acid (25 µl; B.D.H. Ltd., AristaR) was added dropwise whilst the solution was stirred rapidly under dinitrogen. A bright green precipitate formed which was filtered off and washed with thf (2 × 5 cm^3). The product was recrystallised twice from methanol–diethyl ether under dinitrogen as bright green *crystals*: [Mo(N$_2$H$_2$)(NCPr^n)(dppe)$_2$][HSO$_4$]$_2$, yield 71%, m.p. 103 °C (decomp.), ν(CN) at 2 260 cm^{-1} (Found: C, 56.6; H, 5.40; N, 3.20. Calc.: C, 56.7; H, 5.00; N, 3.55%); [W(N$_2$H$_2$)(NCPr^n)(dppe)$_2$][HSO$_4$]$_2$, yield *ca.* 60%, m.p. 128 °C (decomp.), ν(CN) at 2 260 cm^{-1} (Found: C, 52.85; H, 5.00; N, 3.25. Calc.: C, 52.9; H, 4.50; N, 3.30%).

In one experiment the gas evolved during the protonation reaction was measured for the molybdenum complex and was found to be less than 0.2 mol nitrogen per mol of complex. Both of the protonation products give dark green solutions in MeOH which are readily deprotonated with NEt$_3$ to the neutral *parent* complexes which precipitate as bright red solids.

*** Throughout this paper: 1 atm = 101 325 Pa.**

(*iv*) *Alkylation of anionic complexes.* The salt $[NBu_4][Mo(N_2)(CN)(dppe)_2]$ (200 mg, 0.17 mmol) was dissolved in freshly distilled and degassed tetrahydrofuran (10 cm^3) under argon. n-Butyl iodide (19.4 μl, 0.17 mmol) was added and the reaction mixture stirred for *ca.* 0.5 h during which the colour changed from dark red to dark orange. At the end of this period the solution was cooled to 4 °C and the precipitated $[NBu_4]I$ was filtered off. The filtrate was concentrated to *ca.* 2 cm^3 and acetone (8 cm^3; B.D.H. Ltd., AnalaR) was added. Yellow-orange *crystals* of $[Mo(N_2Bu^n)(SCN)(dppe)_2]$ were formed which were filtered off and recrystallised from acetone. Yield 62%, m.p. 186 °C (decomp.), ν(N=N) at 1 525 and 1 550 cm ^{1}, ν(SCN) at 2 060 cm^{-1} (Found: C, 66.05; H, 6.60; N, 3.75. Calc.: C, 66.05; H, 5.50; N, 4.05%).

The anion, $[Mo(N_2)(SCN)(dppe)_2]^-$, was treated with Bu^nI under similar conditions to give the diazenido-product $[Mo(N_2Bu^n)(CN)(dppe)_2]$, ν(N=N) at 1 535 cm^{-1}, ν(CN) at 2 080 cm^{-1} (Found: C, 69.55; H, 6.30; N, 3.95. Calc.: C, 68.2; H, 5.70; N, 4.20%).

Electrochemical and Kinetic Measurements.—The electrochemical and kinetic measurements were made using a Hi-Tek Instruments DT2101 potentiometer, a Chemical Electronics (Birtley) Ltd. type 01 waveform generator, and a Philips PM 8041 X–Y recorder, as previously described.[8,12,14] All potentials quoted were internally referenced to the $[Mo(N_2)_2(dppe)_2]^{0/+}$ couple in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf to which an $E_{\frac{1}{2}}^{ox}$ of −0.16 V *vs.* s.c.e. has been assigned.

All the complexes studied showed one-electron reversible and diffusion-controlled oxidation as evidenced by the agreement with the usual electrochemical criteria, *i.e.* 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 aniodic and cathodic peak currents were close to unity, the peak oxidation current/concentration functions were within ±10% of that for the standard $[Mo(N_2)_2(dppe)_2]$, and the separations in the anodic and cathodic peak potentials were in the range 60—70 mV. Secondary, more or less reversible, oxidation processes were observed for the dinitrogen and carbonyl complexes at potentials *ca.* +0.9 V more positive than their primary oxidation potential.[8]

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