Mechanism of Alkylation and Acylation of Dinitrogen Co-ordinated to Molybdenum and Tungsten

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The alkylation, acetylation, and aroylation reactions of $[M(N_2)_2(dppe)_2]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) by organic halides RX are shown to procede by the initial rate-determining dissociation of one N_2 from the complex to form $[M(N_2)(dppe)_2]$, addition of the halide through the halogen to the metal producing an unstable intermediate, $[M(N_2)(RX)(dppe)_2]$, homolysis of the carbon–halogen bond, and attack of the organic free radical generated on the remaining co-ordinated N_2 to produce $[Mo(N_2R)X(dppe)_2]$.

The reactions of co-ordinated dinitrogen in well defined compounds to give complexes containing N–H or N–C bonds are few. Protonation of co-ordinated N_2 to give ammonia and/or hydrazine has been observed in complexes of titanium,[1] zirconium,[2] molybdenum,[3] and tungsten.[3] The mechanisms of such protonations are not understood, although some preliminary suggestions have been made.[3] In the only mechanistic study of which we are aware the protonation of $[W(N_2)_2(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] with hydrobromic acid in tetrahydrofuran (thf) was found to be very fast (diffusion controlled).[4] The alkylation reactions, which have so far been reported only for complexes containing Mo and W,[5,6] as well as the acylation reactions,[5,7] which have also been found for N_2 co-ordinated to Re,[5] are, in contrast, relatively slow and take several hours to reach completion. In addition the rates of these reactions are apparently increased by irradiation with diffuse daylight or u.v. light. This paper is primarily concerned with the mechanism of alkylation of dinitrogen co-ordinated to Mo or W in the complexes $[M(N_2)_2(dppe)_2]$. A preliminary account has already appeared.[8]

RESULTS AND DISCUSSION

The complexes $[M(N_2)_2(dppe)_2]$ react with alkyl bromides, RBr, in benzene to form alkyldiazenido-complexes $[MBr(N_2R)(dppe)_2]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, or Bu^t) [equation (1)]. The diazenido-complexes in

$$[M(N_2)_2(dppe)_2] + RBr \longrightarrow [MBr(N_2R)(dppe)_2] + N_2 \quad (1)$$

turn react with hydrogen bromide to form hydrazido(2−) complexes $[MBr(N_2HR)(dppe)_2]^+$.[5] For aryl bromides (R′Br) only complexes $[MBr_2(dppe)_2]$ were isolated, but the conditions necessary to promote reaction (several hours at benzene reflux) are more severe than those used for reactions involving alkyl bromides (room temperature).[9] Benzyl bromide also yields $[MBr_2(dppe)_2]$, but under the same reaction conditions as for alkyl bromides. Reactions involving alkyl bromides or iodides appear most ready, and chlorides are generally unreactive in alkylation reactions at room temperature, although $ClCH_2CO_2Et$ and $ClCO_2Et$, with $[Mo(N_2)_2(dppe)_2]$ or $[W(N_2)_2(dppe)_2]$ produce $[MoCl(N_2CH_2CO_2Et)(dppe)_2]$[10] or $[WCl(N_2CO_2Et)(dppe)_2]$,[11] respectively. However, the reaction of Bu^nCl with $[W(N_2)_2(dppe)_2]$ in benzene with irradiation does in fact produce $[WCl(N_2Bu^n)(dppe)_2]$ if the reaction mixture is carefully warmed to *ca.* 45 °C.

Other reactions which will be pertinent to the subsequent discussion are those with α,ω-dibromides $Br[CH_2]_nBr$[12] and those with alkyl bromides but in thf as solvent.[13] For the simplest dibromide ($n = 1$), complexes $[MBr(N_2CH_2)(dppe)_2]^+$ were isolated,[12] whereas for $n > 3$ the major products were either $[MBr\{N_2(CH_2)_n\}(dppe)_2]^+$ or $[MBr\{N_2(CH_2)_nBr\}(dppe)_2]$ and $[(dppe)_2BrMN_2(CH_2)_nN_2MBr(dppe)_2]$, depending on n. For $n = 2$, $[MBr_2(dppe)_2]$ and C_2H_4 were formed. Alkylations in thf produced $[MBr(N_2R)(dppe)_2]$ sometimes together with greater or lesser amounts (and, for R = Me, exclusively) of $[MBr\{N_2\overline{CH(CH_2)_3O}\}(dppe)_2]$, which can be protonated to yield the open-chain compounds $[MBr\{N_2CH(CH_2)_3OH\}(dppe)_2]^+$ which have been characterised by *X*-ray structural analysis.[13] We can now explain how these various products arise.

The Initial Step.—Table 1 shows the rate constants for a variety of reactions of $[M(N_2)_2(dppe)_2]$ measured by two techniques. Cyclic voltammetry has been used to monitor concentrations of $[M(N_2)_2(dppe)_2]$ and, in some cases, of products, in thf solution, and we have used

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$\nu(N_2)$ in the i.r. spectrum of $[M(N_2)_2(dppe)_2]$ to monitor concentrations in thf and also in toluene. The results of both kinds of measurement, which were made under pseudo-first-order conditions up to at least 50% completion of reaction, are concordant. Individual data points were fitted to a best straight line using a least-squares computer programme. When using $[W(N_2)_2(dppe)_2]$, illumination by tungsten-filament light or sunlight was necessary for any reaction to occur, but because it was not necessary for our purposes to study the light dependence, we have done no more than ascertain that the alkylations and dinitrogen exchange are first order in the concentration of tungsten complex. However, the reactions of $[Mo(N_2)_2(dppe)_2]$, although accelerated by light, all proceed in the dark, and the data in Table 1 therefore generally refer to dark reactions of $[Mo(N_2)_2(dppe)_2]$. Under the same conditions of illumination, Mo reactions are about twice as fast as those of W.

TABLE 1

Rate constants for a series of reactions of $[M(N_2)_2(dppe)_2]$ with various substrates [a]

(*a*) N_2 exchange reactions (i.r. study)

Complex	10^5Concentration / mol dm^{-3}	Substrate	10^4k [b] / s^{-1}
$[Mo(^{15}N_2)_2(dppe)_2]$	2.5	$^{14}N_2$	1.22 (0.995)
	1.2	$^{14}N_2$	1.32 (0.996)
	2.1	$^{14}N_2$	7.23 (0.996) [c]
$[W(^{15}N_2)_2(dppe)_2]$	2.3	$^{14}N_2$	No reaction
	2.4	$^{14}N_2$	4.17 (0.998) [c]

(*b*) Other substrates (i.r. study) in reaction with $[Mo(N_2)_2(dppe)_2]$

10^5Concentration / mol dm^{-3}	Substrate	[Substrate] / [Complex]	
2.7	PhCN	3.6	1.19 (0.997)
2.9	PhCN	33.7	1.34 (0.994)
2.1	PhCN	93.3	1.12 (0.994) [d]
2.6	EtBr	5.0	1.08 (0.997)
2.9	EtBr	44.8	1.43 (0.989)
1.6	EtBr	162	1.40 (0.995) [d]
2.7	MeBr	59.3	1.28 (0.994)
2.7	BuCl	35.2	No reaction
2.7	BuBr	35.5	1.38 (0.990)
3.0	BuI	29.3	1.48 (0.998)
2.6	$PhCH_2Br$	3.2	0.76 (0.993)
2.6	$PhCH_2Br$	3.2	0.95 (0.994)
2.7	$PhCH_2Br$	31.1	1.17 (0.994)
(*c*) Electrochemical studies with $[Mo(N_2)_2(dppe)_2]$			
36	EtBr	121	1.06 (0.998)
14	EtBr	105	0.80 (0.995)
31	EtBr	96	1.38 (0.991)
22	EtI	178	1.47 (0.992)
ca. 50	BuCl	*ca.* 200	No reaction
54	$Br(CH_2)_4Br$	88	1.27 (0.994)
43	PhCN	84	1.21 (0.991), [e] 1.21 (0.998) [f]
(*d*) Alkylation of $[Mo(N_2)(NCPr^n)(dppe)_2]$			
47	EtBr	113	0.45 (0.999)
(*e*) Attempted alkylation of $[W(N_2)_2(dppe)_2]$			
16	EtBr	153	No reaction

[a] All reactions at 20 °C and in thf in the dark unless otherwise stated. [b] Correlation coefficients are given in parentheses. [c] In the light. [d] In toluene. [e] From decay of $[Mo(N_2)_2(dppe)_2]$. [f] From appearance of $[Mo(N_2)(NCPh)(dppe)_2]$.

The reactions are all first order in the concentration of molybdenum complex and the rates are all independent of the ratio of complex to reactant under pseudo-first-order conditions. The rate constants k_1 are independent of solvent, and for all the reactions (dinitrogen exchange, substitution of dinitrogen by benzonitrile, and the various alkylations by bromides and iodides, but not by chlorides which are unreactive) the rate constants fall within the range $10^4k_1 = 1.3 \pm 0.2$ s^{-1}. This is even true for the benzyl bromide reaction which results in complete loss of N_2 from the system and formation of $[MoBr_2(dppe)_2]$. This indicates a common rate-controlling step for all these reactions and this can only be the loss of N_2 according to equation (2).

$$[M(N_2)_2(dppe)_2] \xrightleftharpoons{\text{slow}} [M(N_2)(dppe)_2] + N_2 \quad (2)$$

An alternative initiating step involving electron transfer has been suggested,[14] namely equation (3) (RX = alkyl and substituted alkyl chlorides, bromides, or iodides). We consider this to be unlikely, even

$$[Mo(N_2)_2(dppe)_2] + RX \xrightarrow{h\nu} [Mo(N_2)_2(dppe)_2]^+ + R^{\bullet} + X^- \quad (3)$$

though an analogous electron-transfer reaction [equation (4)] has been described for a related dicarbonyl complex.[15] Our e.s.r. studies (see below) show that the

$$[Mo(CO)_2(Me_2PCH_2CH_2PMe_2)_2] + Ph_3CCl \longrightarrow [Mo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]^+ + Ph_3C^{\bullet} + Cl^- \quad (4)$$

reaction of $[Mo(N_2)_2(dppe)_2]$ with triphenylmethyl chloride does not produce intermediates of the kind which we observe with alkyl bromides. Further, reaction (1) (M = Mo) does not require light, as required for the suggested reaction (3).

Other arguments against charge transfer as an initial step are that the lowest-energy charge-transfer bands of $[M(N_2)_2(dppe)_2]$ are virtually identical (Mo 378, ε 8 700; W 380 nm, ε = 7 600 dm^3 mol^{-1} cm^{-1}) and that the redox potentials of $[M(N_2)_2(dppe)_2]$ are very similar [Mo, −0.16; W, −0.15 V; both *versus* the saturated calomel electrode (s.c.e.)].[16] This indicates a similarity of energy levels in both the tungsten and the molybdenum complexes which makes it unlikely that the differences in behaviour with respect to light initiation can arise here. Much more likely is that the effect of light on both complexes is to labilise an N_2 molecule.

Other reactions appear to fall into the activation pattern outlined above. The substitution reactions (5)

$$[M(N_2)_2(dppe)_2] + RCN \longrightarrow [M(N_2)(NCR)(dppe)_2] + N_2 \quad (5)$$

$$[M(N_2)_2(dppe)_2] + 2CO \longrightarrow [M(CO)_2(dppe)_2] + 2N_2 \quad (6)$$

and (6) in general proceed in the dark for M = Mo, but require light activation for M = W.

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If dissociation of N_2 is the common first step in all these reactions, $[M(N_2)(dppe)_2]$, or conceivably $[M(N_2)(dppe)_2(solvent)]$, would be generated. The solvated intermediate would have to lose solvent again in any subsequent reaction and so it does not represent a step in the main reaction sequence. The five-co-ordinate species $[M(N_2)(dppe)_2]$ has not been detected by us, although a solution of $[Mo(N_2)_2(dppe)_2]$ in thf slowly loses N_2 when a stream of argon passes through it. The molybdenum-containing products remaining after N_2 loss have not been characterised. In contrast, the stable five-co-ordinate carbonyl species $[Mo(CO)(dppe)_2]$ has been characterised by *X*-ray crystallographic analysis [17] and represents the structural analogue of our dinitrogen intermediate. The synthesis of the carbonyl complex is achieved under very specific conditions and it rapidly takes up additional ligands, including N_2, to become six-co-ordinate. The synthesis of the dinitrogen analogue is likewise expected to be rather difficult. Further support for the dissociative step in the substitution of $[M(N_2)_2(dppe)_2]$ is that substitution reactions of saturated metal carbonyls, such as $[Mo(CO)_6]$, whether heat- or light-activated, are commonly held [18] to proceed *via* an initial dissociation, and the appropriate intermediate, in this case $[Mo(CO)_5]$, has been detected. Table 1 also includes data from the reaction of EtBr with $[Mo(N_2)(NCPr^n)(dppe)_2]$ [7] in thf. The first-order rate constant for this reaction (0.45×10^{-4} s^{-1}) is *ca.* 30% of that for the analogous reaction with $[Mo(N_2)_2(dppe)_2]$, the molybdenum-containing products of both reactions being the same. We accordingly infer that in this case loss of Pr^nCN is rate determining, rather than loss of N_2. The slower rate of reaction is consistent with the tighter binding of both Pr^nCN and N_2 in $[Mo(N_2)(NCPr^n)(dppe)_2]$ compared with that of dinitrogen in $[Mo(N_2)_2(dppe)_2]$.[19] Furthermore, the one-electron oxidation of $[Mo(N_2)(NCPr^n)(dppe)_2]$ is easier than that of $[Mo(N_2)_2(dppe)_2]$ [$E_{\frac{1}{2}} = -0.57$ *versus* s.c.e., *cf.* -0.16 V for the bis(dinitrogen) complex] so that electron transfer as a rate-controlling step is again unlikely.[16]

TABLE 2

E.s.r.[a] data for mixtures of $[M(N_2)_2(dppe)_2]$ and RX [b] (X = Br or I) [c]

Irradiation conditions		Complex			
		$[Mo(N_2)_2(dppe)_2]$	$[Mo(N_2R)(dppe)_2X]$	$[W(N_2)_2(dppe)_2]$	$[W(N_2R)(dppe)_2X]$
		Species observed			
Total darkness	*d*	$R^{\cdot}$	none	none	none
	e	$R^{\cdot}$ and $\cdot\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$	none	none	none
Daylight	*d*	$R^{\cdot}$ (more intense)	trace $R^{\cdot}$	trace $R^{\cdot}$	none
	e	$R^{\cdot}$ and $\cdot\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$	small amount $R^{\cdot}$ and $\cdot\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$	trace $R^{\cdot}$, $\cdot\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}$	none
Tungsten-filament irradiation	*d*	$R^{\cdot}$ (slightly intensified)	strong signals	very strong signals	trace $R^{\cdot}$
	e	$R^{\cdot}$ and $\cdot\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$ (slightly intensified)			trace $R^{\cdot}$, $\cdot\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$
Mercury light (5 s)	*d*	signals slightly less intense	signals slightly more intense	signals slightly more intense	signals much more intense
	e				
Mercury light (continuous)	*d*	Signals markedly less intense	signals less intense	signals less intense	signals less intense
	e				

[a] All run at room temperature, with nitrosodurene as spin trap. [b] R = Me, Et, Pr^n, Bu^n, $(CH_2)_4Br$, or $\mathrm{CH_2}\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$. [c] In general, signals derived from RI are stronger than those from RBr. Under similar conditions chlorides do not give rise to any signals. [d] Benzene or toluene. [e] thf, $\cdot\overline{\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{O}}$ detected only when R = Me.

The Substitution Reaction and the Generation of Radicals.—The second step in the substitution reactions

$$[M(N_2)(dppe)_2] + L \longrightarrow [M(N_2)L(dppe)_2] \quad (7)$$

is believed to be represented by equation (7). The donors L include organonitriles, N_2, RBr, RI, RN_3, RNCS, $[N_3]^-$, $[NCS]^-$, or $[CN]^-$,[19] but other 'good' donors such as pyridine, thf, Br^-, or I^- show little if any affinity for the site. In certain cases (*e.g.* L = MeCN) reaction (7) is reversible. The alkyl halides in the alkylation reactions apparently ligate through the halogen; this kind of co-ordination has been postulated before, as in the oxidation of $[ReCl_3(NCMe)(PR_3)_2]$ to $[ReCl_4(PR_3)_2]$ (PR_3 = tertiary phosphine) by alkyl halides.[20]

For the simple substitution reactions this constitutes the end of the process, but in the alkylation reactions co-ordination of the organic halide is followed immediately by homolysis of the carbon–halogen bond forming a complex $[M(N_2)X(dppe)_2]$ and a radical $R^{\cdot}$. For alkyl chlorides RCl this homolysis apparently does not occur and the reverse of reaction (7) is observed. The evidence for this is as follows. When reaction of $[W(N_2)_2(dppe)_2]$ with methyl iodide was carried out in thf in the presence of a >100-fold molar excess of $[NBu^n_4]Br$ followed by protonation with HBF_4 the product was $[WI\{N_2CH(CH_2)_3OH\}(dppe)_2]^+$ exclusively and quantitatively, with

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[19] J. Chatt, G. J. Leigh, and C. J. Pickett, unpublished work.

[20] G. Rouschias and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 993.

no bromo-product. Since halide ions were shown in subsequent experiments not to interchange on tungsten and because bromide ions were present in great excess in the reaction medium, it follows that the iodine must become attached to the tungsten while it is still combined in the alkyl iodide. The species $[M(RX)(N_2)(dppe)_2]$ was never detected and this is not altogether surprising.

The evidence for the homolysis of the C–X bond (X = Br or I) is given in Table 2. From this it is clear that in tungsten reactions radicals are generated only on irradiation, whereas the molybdenum mixtures generate radicals in the dark. Such dark reactions require 4—5 h to reach completion under our conditions. Quantitative measurements of the dark reaction of $[Mo(N_2)_2(dppe)_2]$ with EtBr in benzene showed that the amount of trapped radicals increased steadily with time, and that after *ca.* 20 min radicals corresponding to *ca.* 50% of the calculated number produced by that time had been trapped, assuming the known reaction rate.

The generation of tetrahydrofuranyl radicals from the reactions in thf (see below) is clear evidence that free radicals are generated and are not artefacts caused by the inclusion of a radical trap in the mixture. Such radicals can only arise by reaction of thf with other radicals and are never produced by the trap alone with thf. We showed independently that radicals $R^{\bullet}$ are generated by mercury-lamp (not tungsten-lamp) photolysis of $[MX(N_2R)(dppe)_2]$ which are themselves products of the alkylation reactions. However, such diazenido-complexes cannot be the source of radicals in the dark reactions.

We confirmed that the radicals become free by studying the reaction of hex-5-enyl bromide with $[W(N_2)_2(dppe)_2]$ in benzene.[21] The hex-5-enyl radical is known to rearrange in a first-order reaction with a rate constant of 10^5 s^{-1} to give the cyclopentylmethyl radical.[22] The reaction produces, after protonation of the reaction mixture, a quantitative yield of $[WBr\{N_2HCH_2(C_5H_9)\}(dppe)_2]^+$, whose structure was confirmed by an independent synthesis from $[WBr(N_2CH_2)(dppe)_2]Br$ and cyclopentyl-lithium.[11] The possibility that the product was a cyclohexyldiazenido-complex was excluded by the synthesis of $[WBr\{N_2HCH(CH_2)_5\}(dppe)_2]^+$ from cyclohexyl bromide and $[W(N_2)_2(dppe)_2]$. This means that the cyclohexenyl radical must have been ' free ' for at least 10^{-4} s.

The Metal(I) *Species*.—Our mechanism requires the

$$[M(RX)(N_2)(dppe)_2] \longrightarrow \underset{(A)}{[MX(N_2)(dppe)_2]} + R^{\bullet} \quad (8)$$

formation of an intermediate metal(I) species $[MX(N_2)(dppe)_2]$ (A; X = Br or I) [reaction (8)]. At least two groups of workers [14,23] claim to have isolated $[MoX(N_2)(dppe)_2]$ (X = Cl or Br) as stable crystalline solids [$\nu(N_2)$ at *ca.* 1 966 cm^{-1}] so that we felt it necessary to pursue this matter further because molybdenum(I) species are uncommon and should have a characteristic e.s.r. spectrum.

We have repeated the preparation of $[MoCl(N_2)(dppe)_2]$ according to the literature method [14] and also from the reaction of Ph_3CCl and $[Mo(N_2)_2(dppe)_2]$ in benzene.[24] We do indeed isolate a crystalline material [presumably (A; X = Cl)] which looks different from either $[Mo(N_2)_2(dppe)_2]$ or $[MoCl_2(dppe)_2]$. It has $\nu(N_2)$ at 1 966 cm^{-1} and ν(Mo–Cl) at 311 cm^{-1}. Its C, H, and N analyses are consistent with a stoicheiometry $MoCl(N_2)(dppe)_2$. However, we find it to be a *ca.* 1 : 1 mixture of $[Mo(N_2)_2(dppe)_2]$ and $[MoCl_2(dppe)_2]$. Our evidence is as follows.

A solution of our material (A; X = Cl) in thf or in toluene–methanol (80 : 20) has a cyclic voltammogram characteristic of the mixture only. Therefore it is either a mixture or it disproportionates very rapidly in solution or at the electrode. However, since it was recrystallised from benzene–methanol the disproportionation must be reversible! Nevertheless, a 1 : 1 mixture of $[Mo(N_2)_2(dppe)_2]$ and $[MoCl_2(dppe)_2]$ co-crystallised from benzene–methanol yields a sample identical in appearance and i.r. spectrum to (A; X = Cl) and also with a voltammogram characteristic of the mixture. Finally, the reaction of (A; X = Cl) with methyl isocyanide yields a 1 : 1 mixture of $[Mo(CNMe)_2(dppe)_2]$ and $[MoCl_2(dppe)_2]$,[25] and with butyl bromide produces a mixture of $[MoBr(N_2Bu^n)(dppe)_2]$ and $[MoCl_2(dppe)_2]$. This evidence that complexes (A) are mixtures also accords with e.s.r. spectra and magnetic susceptibilities as follows.

The $Mo(3d_{\frac{5}{2}})$ binding energies of $[MoX(N_2)(dppe)_2]$ are 228.2 (X = Cl) and 228.1 eV (X = Br), respectively.[26,*] The complex $[Mo(N_2)_2(dppe)_2]$ has a value of 227.2 eV, which agrees with our determinations (227.0, 227.1; two independent determinations on samples from different preparations). The signals from (A) are rather broad [full width at half-maximum (f.w.h.m.) = 2.0 eV].[26] However, we have also found for $[MoCl_2(dppe)_2]$ (two independent determinations) $Mo(3d_{\frac{5}{2}})$ = 228.2 and 228.5 eV. This is certainly no different from (A; X = Cl) and is only marginally different, given the normal experimental errors, from the value for $[Mo(N_2)_2(dppe)_2]$. In addition, the nitrogen (1*s*) binding energies of $[Mo(N_2)_2(dppe)_2]$, 399.6 and 398.6 eV, are not different from the values quoted [26] for (A), *viz.* 399.9, 399.1 (X = Cl), and 400.1, 398.9 eV (X = Br). Evidently, *X*-ray photoelectron spectra provide no independent criterion for the integrity of complexes (A).

The e.s.r. spectra of $[MX(N_2)(dppe)_2]$ should also be characteristic. The spectrum of (A; X = Cl) in benzene solution shows lines which are identical in position and shape with the observed spectrum of $[MoCl_2(dppe)_2]$.

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[*] Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 cal = 4.184 J; 1 G = 10^{-4} T.

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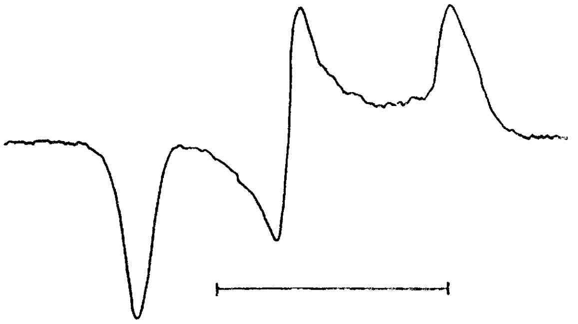
[25] A. Pombeiro and R. L. Richards, personal communication.

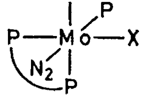
[26] P. Brant and R. D. Feltham, *J. Less Common Metals*, 1977, **54**, 81.

In CH_2Cl_2 these lines are again observed, together with three further unidentified signals, which are characteristic of a dichloromethane solution of $[Mo(N_2)_2(dppe)_2]$, consistent with (A; X = Cl) being the proposed mixture. The magnetic susceptibilities of $[MoCl_2(dppe)_2]$ (2.89, *cf.*[24] 2.83 B.M.), of (A; X = Cl) (1.67, *cf.*[24] 1.83 B.M.), and of the crystallised mixture (1.60 B.M.) also suggest that (A) is a mixture.

It was generally necessary to have the spin trap present in order to detect the organic radicals reported in Table 2. Only in the case benzyl and triphenylmethyl were we able to detect a signal assignable to the organic radical in the absence of a spin trap. However, in the absence of a spin trap and at −150 °C we observed a three-line spectrum (Figure) consistent with the presence of a non-symmetrical species *cis*-$[MoX(N_2)(dppe)_2]$ (I).



E.s.r. spectrum of a mixture of alkyl halide and $[Mo(N_2)_2(dppe)_2]$ in benzene at 12 K. The bar line represents 500 G. Representative *g* values: alkyl halide = Bu^nBr, $g_1 = 2.402$, $g_2 = 2.141$, $g_3 = 1.918$; $PhCH_2Br$, $g_1 = 2.392$, $g_2 = 2.135$, $g_3 = 1.918$; and CH_2Cl_2, $g_1 = 2.317$, $g_2 = 2.133$, $g_3 = 1.956$



(I)

We conclude that complexes (A) do not exist as stable species at room temperature. However, a carbonyl analogue, $[MoBr(CO)(dppe)_2]$, is much more stable. The complex $[Mo(CO)(N_2)(dppe)_2]$[27] reacts with benzyl bromide in benzene to form dibenzyl and a paramagnetic solid which analyses for $[MoBr(CO)(dppe)_2]$. In its cyclic voltammogram run in thf are found minor oxidation peaks corresponding to $[MoBr_2(dppe)_2]$ and to $[Mo(CO)_2(dppe)_2]$, and a major peak due to a third species which we believe to be $[MoBr(CO)(dppe)_2]$. Its paramagnetic nature is confirmed by its n.m.r. and e.s.r. spectra. The greater stability of the carbonyl as compared to the dinitrogen complex is not unexpected but the occurrence of a genuine molybdenum(I) complex is rare. We have preparative evidence that complexes related to $[MoX(N_2)(dppe)_2]$ can exist and are stable, because the complexes $[M(N_2)_2(dppe)_2]$ react with tetraalkylammonium salts of multiple bonded anions, such as $[NBu^n_4]NCS$ {but not $[NBu^n_4]X$ (X = Br, Cl, or I)} to form $[M(NCS)(N_2)(dppe)_2]^-$ which can be oxidised to the air-stable species $[M(NCS)(N_2)(dppe)_2]$ which will be described elsewhere.[19]

The Fate of the Radicals $R^\bullet$.—The radicals $R^\bullet$ must attack $[MoX(N_2)(dppe)_2]$ to form alkyldiazenido-complexes according to reaction (9), provided $R^\bullet$ is of the right stability and the solvent is unreactive.

$$[MoX(N_2)(dppe)_2] + R^\bullet \longrightarrow [MoX(N_2R)(dppe)_2] \quad (9)$$

Reaction (9) occurs when R = Me, Et, Pr, or Bu, but when R = CH_2Ph or CH_2CH_2Br, $[MoBr_2(dppe)_2]$ is the only complex product.

The reaction of $[Mo(N_2)_2(dppe)_2]$ with benzyl bromide in thf has the same rate as all the other reactions (Table 1) and produces benzyl radicals but the final products are $[MoBr_2(dppe)_2]$ and bibenzyl. Evidently the benzyl radicals are not reactive enough to attack the intermediate $[MoBr(N_2)(dppe)_2]$ or the solvent (see below) and eventually dimerise, even in benzyl methyl ether. The failure to isolate $[MoBr(N_2CH_2Ph)(dppe)_2]$ is not due to its lack of stability because it can be isolated as a stable crystalline product from the reaction of LiPh with $[MoBr(CH_2N_2)(dppe)_2]$.[8] In the reaction of $BrCH_2CH_2Br$ with $[M(N_2)_2(dppe)_2]$, $BrCH_2CH_2^\bullet$ radicals are produced and are so unstable[28] that they decompose before they react with any molybdenum species yielding $Br^\bullet$ and C_2H_4; the molybdenum-containing product is again $[MoBr_2(dppe)_2]$. In the reaction of methylene bromide, which with $[M(N_2)_2(dppe)_2]$ reacts to give diazomethane complexes $[MBr(CH_2N_2)(dppe)_2]^+$,[12] we have been able to trap $BrCH_2^\bullet$ and identify it by its e.s.r. spectrum. Evidently this attacks co-ordinated dinitrogen to give a bromomethyldiazenido-complex $[MBr(N_2CH_2Br)(dppe)_2]$ which then ionises, leaving the co-ordinated CH_2N_2. None of the chlorides or aryl halides under the conditions we used generate any radicals with $[M(N_2)_2(dppe)_2]$. By using more extreme conditions (benzene under reflux for several hours) we were able to form $[MX_2(dppe)_2]$ from aryl halides R′X,[9] but it is doubtful whether these reactions are related to the alkylation reactions.

The Scheme summarises the general features of the alkylation reactions.

The Influence of Solvent.—The rates of the reactions (Table 1) are independent of solvent but the products are not. This is evident from the e.s.r. data in Table 2, where the radical $R^\bullet$ from a halide RX is accompanied by the tetrahydrofuranyl radical when thf is the solvent. Our preparative experiments yielded, after protonation, a mixture of $[MBr(N_2HR)(dppe)_2]^+$ and $[MBr\{N_2CH(CH_2)_3OH\}(dppe)_2]^+$ from the reactions of $[M(N_2)_2(dppe)_2]$ and RBr in thf; the proportions of products in the mixture depend on R.[13] Evidently, when R· is sufficiently reactive to abstract hydrogen atoms from the solvent it forms RH and a solvent radical. This is

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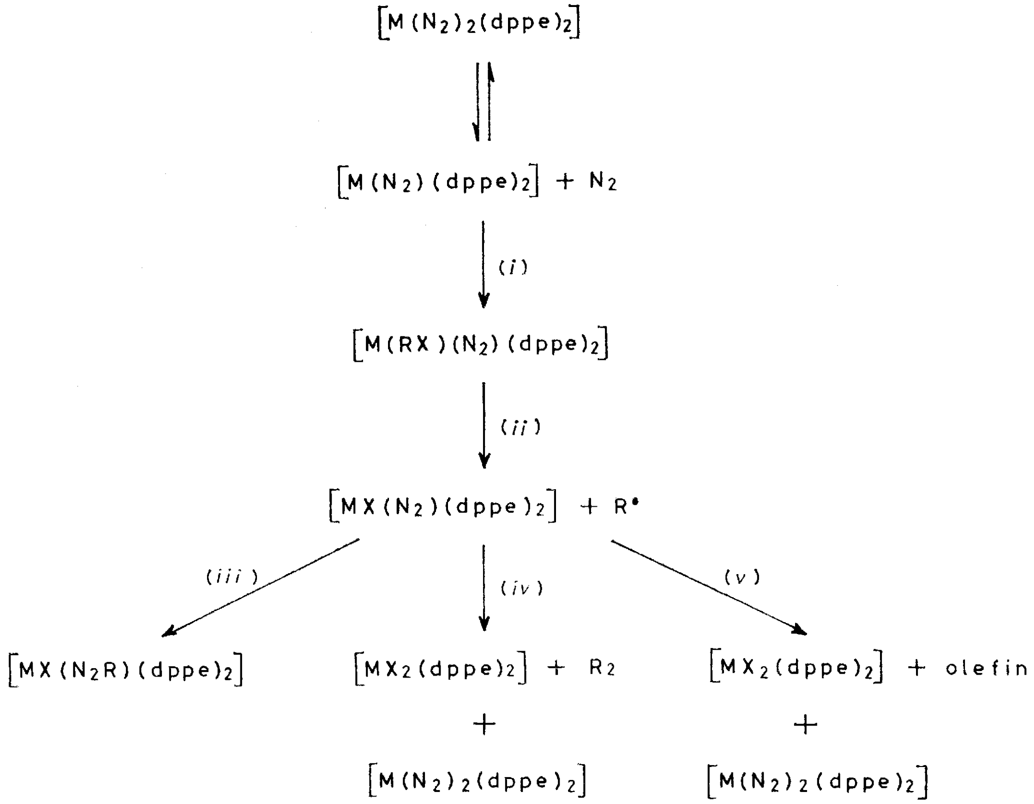
[27] T. Tatsumi, H. Tominaga, M. Hidai, and Y. Uchida, *J. Organometallic Chem.*, 1976, **114**, C27.

[28] P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 1960, 144.

confirmed by the detection of RH as a reaction product from reactions in thf. The fate of the thf radical is to form the normal organodiazenido-complexes, $[MBr\{N_2\overline{CH(CH_2)_3O}\}(dppe)_2]$, which can themselves be photolysed by u.v. irradiation to give tetrahydrofuranyl radicals. These tetrafuranyldiazenido-complexes react with acids, with ring opening to yield diazobutanol complexes $[MBr\{N_2CH(CH_2)_3OH\}(dppe)_2]^+$.[13]

Similar hydrogen abstractions and analogous cyclic products have been obtained from 2-methyltetrahydrofuran, tetrahydropyran, tetrahydrothiophene, *N*-methylpiperidine, and 1,4-dioxan.[29] Toluene as solvent yields methyldiazenido-complexes in reactions involving methyl bromide. Apparently only those solvents most reactive towards hydrogen abstraction[30] take part in these reactions.



SCHEME The generation and fate of radicals in the reactions of dinitrogen complexes and organic halides. (*i*) RX; (*ii*) homolysis; (*iii*) alkylation; (*iv*) radical coupling; (*v*) decomposition

The Reactivity of Organic halides in Alkylation and Acylation Reactions.—Alkylation of co-ordinated dinitrogen in the $[M(N_2)_2(dppe)_2]$ complexes under our conditions is achieved by alkyl bromides and iodides, but not chlorides, although more reactive organic chlorides such as $ClCH_2CO_2Et$ and $ClCO_2Et$ do undergo the alkylation reaction. Acyl and aroyl chlorides and bromides also react similarly. On the other hand $SiMe_3Cl$ yielded only the dichloro-complex $[MCl_2(dppe)_2]$, even after prolonged irradiation, and $SnBrMe_3$ did not react.[9]

Attempted arylation reactions were never successful. The initial loss of a ligating dinitrogen molecule must occur in all the systems studied, so the factors which are likely to control whether homolysis of the R–X bond occurs are the base strength of the organic halide for the metal site and the R–X bond dissociation energy. On this metal(0) site the base strengths of the halides are likely to decrease in the order I > Br > Cl. The bond-dissociation energies *D*(C–X) in the series MeX (X = Cl, Br, or I) are 84, 70, and 56 kcal mol^{-1}, respectively,[31] so we might conclude that 84 kcal mol^{-1} is too high to allow homolysis. However, the bond-dissociation energy is not the determining factor because chlorides, such as PhCOCl [*D*(C–Cl) 74 kcal mol^{-1}] and MeCOCl-[*D*(C–Cl) 81 kcal mol^{-1}] react normally with $[M(N_2)_2(dppe)_2]$ whereas PhI [*D*(C–I) 66 kcal mol^{-1}] does not react at all. More likely it is the low basicity of the aryl halides which controls their reactivity.

It is believed that a significant part of the driving force to homolytic fission in species such as $RX^{\bullet -}$, which may approximate to the condition of co-ordinated RX, is the energy of rearrangement of the liberated radical.[32] Thus homolytic fission to give $R^{\bullet} + X^-$ is considered to be much more likely if the product is a planar alkyl

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[29] J. Chatt, R. A. Head, and G. J. Leigh, unpublished work.

[30] T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, 1962, **27**, 3067.

[31] J. A. Kerr and A. F. Trotman-Dickenson in, ' The Handbook of Chemistry and Physics,' 53rd edn., Chemical Rubber Company, Cleveland, Ohio, 1972.

[32] M. C. R. Symons, *J.C.S. Chem. Comm.*, 1977, 408.

radical derived from a tetrahedral halide than if it is an aryl radical which has a geometry little different from that of its aryl halide precursor. In addition it should also be borne in mind that a halide which is oxidising enough might promote oxidation (simple electron transfer) prior to N_2 loss, although we have little evidence for this kind of reaction in the systems studied here.

We need finally to consider whether the acylation reactions are indeed of the same kind as the alkylations, or whether they parallel the protonations. The protonation reactions are very fast, whereas the alkylations and acylations are slow, and in the case of tungsten require irradiation. Complexes $[MX(NNH_2)(dppe)_2]^+$ react with acyl halides to form acylhydrazido(2—)-complexes $[MX\{N_2H(COR)\}(dppe)_2]^+$.[33] It is possible that, despite our efforts to exclude moisture, such NNH_2 complexes formed by trace amounts of acids with $[M(N_2)_2(dppe)_2]$ are essential intermediates in the reactions which generate the $N_2H(COR)$ derivatives. Such a complication does not arise in the interpretation of the alkylation reactions because alkyl bromides do not react with NNH_2 complexes.

We believe that the mechanism of acylation parallels that of alkylation rather than that of protonation for the following reasons. (*i*) Acylation is slow. (*ii*) It is accelerated by radiation, and the tungsten reactions *require* irradiation. (*iii*) Ligand loss to yield a co-ordinatively unsaturated species is a requirement. Thus, $[ReCl(N_2)(py)(PMe_2Ph)_3]$ yields $[ReCl_2(N_2COMe)(PMe_2Ph)_3]$ with MeCOCl and pyridine (py) is lost.[5] The protonation[19] of $[M(N_2)(NCR)(dppe)_2]$ proceeds to $[M(N_2H_2)(NCR)(dppe)_2]^{2+}$ without ligand loss, whereas alkylation[19] and acylation[7] yield $[MX(N_2R)(dppe)_2]$ and $[MX(N_2COR)(dppe)_2]$, respectively with a ligand loss. The alkylations of the nitrile complexes are considerably slower than the alkylations of the bis(dinitrogen) complexes despite their easier oxidation and lower $\nu(N_2)$ (see Table 1). This argues again against electron transfer and in favour of ligand loss as the rate-determining step. (*iv*) The reaction of 2,2-dimethylpropanoyl chloride with $[M(N_2)_2(dppe)_2]$ in benzene yields a t-butyldiazenido-complex.[5] We were not able to identify the radical $Bu^tCO^•$ by trapping it, but it is known to break down very rapidly to give $Bu^{t•}$ and CO.[34] There seems little doubt that acylation (and aroylation) are of the same general reaction type as alkylation.

The Metal Centre.—We have demonstrated that the generation of a co-ordinatively unsaturated intermediate is a prerequisite for the acylation and alkylation of dinitrogen co-ordinated to Mo and W, and that the nature of the radical generated determines whether N–C bond formation can occur. It remains to consider the kinds of metal atom which will allow such reactions to take place.

Most dinitrogen complexes so far synthesised are 18-electron systems. The most labile ligand is almost invariably dinitrogen. Hence it is not to be expected that alkylation would be a general reaction except in co-ordinatively unsaturated (or potentially unsaturated) systems such as $[M(N_2)_2(dppe)_2]$, $[IrCl(N_2)(PPh_3)_2]$, $[CoH(N_2)(PPh_3)_3]$, $[FeH_2(N_2)(PPh_3)_3]$, and $[(C_5H_5)_2Ti(N_2)Ti(C_5H_5)_2]$. Co-ordinative unsaturation to allow the addition of the alkyl halide to the metal is a necessary condition for alkylation by our proposed mechanism, but it is not a sufficient condition. A second is presumably that the metal should be sufficiently electron-releasing to cause homolysis of the R–X bond to produce $R^•$ and a ligating X^-. This process is reminiscent of the radical mechanism of oxidative addition proposed by Lappert and Lednor[35] for the reaction of alkyl halides with platinum(0) complexes. It must also be a sufficiently strong π-electron donor to retain the ligating dinitrogen molecule to be alkylated and this is probably a limiting condition. The metals to the left of the transition-metal series with their lower nuclear charges are more likely to promote this condition than are those to the right. The combination of the ligating N_2 with $R^•$ requires the induction of an unpaired electron on the terminal nitrogen atom. This obviously entails some activation energy because aliphatic radicals can combine with the N_2 whereas benzyl radicals cannot, somewhat reminiscent of general radical attack on olefins. In dinitrogen complexes of metals to the right of the transition-metal series with their higher electron affinities at the metal, it is more likely that the radical attack will occur on the metal, effecting oxidation and consequent loss of molecular nitrogen.*

EXPERIMENTAL

Infrared Kinetic Studies.—The rates of reaction of $[M(N_2)_2(dppe)_2]$ with reagents such as N_2 (isotopically labelled), PhCN, and alkyl halides were monitored using a pair of balanced solution i.r. cells (solvent thf or toluene) in a Unicam SP 2000 spectrometer set to scan the wavelength region of $\nu(N_2)$ (*ca.* 1 975 cm^{-1}, M = Mo; *ca.* 1 950 cm^{-1}, M = W). The compensating cell was a standard variable-pathlength solution cell and the test cell was fitted directly to a reaction vessel and to a syringe which allowed samples for measurement to be drawn into, or expelled from, the test cell as desired. During the exchange of $[Mo(^{15}N_2)(dppe)_2]$ with $^{14}N_2$ we observed the growth and decay of bands at *ca.* 1 940 cm^{-1} assignable to $\nu(N_2)$ in $[Mo(^{14}N_2)(^{15}N_2)(dppe)_2]$.

The room in which the measurements were carried out was thermostatted at 20 ± 1 °C, and the term 'light' used in Table 1 means irradiation with a single 60-W tungsten-filament bulb held at a fixed distance (*ca.* 25 cm) from the reaction vessel. The position of the bulb was the same in all the light reactions. The intensity of $\nu(N_2)$ was measured as a function of time and the best straight line, log (concen-

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* *Note added in proof*: In certain circumstances, N–C bonds can be formed from paramagnetic Mo and W dinitrogen complexes and organic radicals generated by electron-transfer.[19]

[33] J. Chatt, A. J. Pearman, and R. L. Richards, unpublished work.

[34] 'Free Radicals,' vol. 1, ed. J. K. Kochi, Wiley–Interscience, New York, 1973.

[35] M. F. Lappert and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 948.

tration) against time, obtained by a least-mean-squares curve-fitting computer program. The results are in Table 1.

Electrochemical Kinetic Studies.—The measurements were made using a Hi-Tek Instruments type DT2101 potentiostat, a Chemical Electronics type RB1 wave-form generator, and a Bryans type 2400 A4 recorder.

The reaction of $[M(N_2)_2(dppe)_2]$ with various substrates was followed by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ in thf at a platinum electrode. The primary oxidations occur with peak potentials at -0.16 (M = Mo) and -0.15 V (M = W) *versus* the s.c.e. The peak current, i_p, over scan rate, v, to the power one half, $i_p v^{-\frac{1}{2}}$/mA s$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$ is directly proportional to the concentration of the complex in solution. A silver-wire reference electrode contained in a solution of supporting electrolyte, but with no added silver ions, was employed. This avoided contamination of the system with water or foreign ions.

The electrochemical cell was placed in a light-tight box, and substrate was injected into the cell containing the solution of dinitrogen complex under dinitrogen *via* a septum cap. After stirring with dinitrogen for 10—15 s the cyclic voltammogram was recorded, and recorded again at 5—10 min intervals for 2—4 h.

In the course of reactions involving $[Mo(N_2)_2(dppe)_2]$ with EtX (X = Br or I) a single-product oxidation peak was observed to grow at *ca.* 200—250 mV positive of E_p for the starting material. At the end of the reaction with EtBr, the i_p of the product peak was >90% of i_p for the starting concentration of $[Mo(N_2)_2(dppe)_2]$. The redox characteristics of the product were those of $[MoBr\{N_2CHO(CH_2)_2CH_2\}(dppe)_2]$.

The reaction of $[Mo(N_2)_2(dppe)_2]$ and PhCN in the dark in the electrochemical cell allowed monitoring of the concentrations of both starting material and product, which produced a peak at $E_p = -0.48$ V *versus* s.c.e.[16] The sum of the peak currents, i_p, was essentially independent of time, indicating a clean stoicheiometric reaction.

The log i_p against time data were fitted to a best straight line using a least-mean-squares computer program. The results are in Table 1.

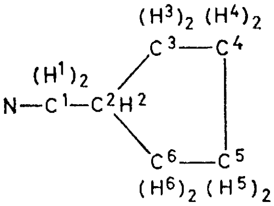
E.S.R. Studies.—All the experiments were carried out on Varian E9 and E104 spectrometers at *X*-band frequencies using quartz sample tubes and solvents distilled from suitable drying agents under N_2. Investigations were made with samples *in vacuo*, or under N_2 or Ar. Each test was carried out at least twice. Dark reactions were carried out in tubes coated externally with a matt-black spray paint which contains no paramagnetic centres. Appropriate blanks were run with alkyl halide, spin trap, and solvent and no dinitrogen complex, and gave no signals.

For quantitative measurements the e.s.r. spectrum of a standard solution of 1,1-diphenyl-2-picrylhydrazyl (0.852×10^{-3} mol dm^{-3}, benzene) was recorded under a variety of instrumental settings and the signal integrated by the method of Wyard.[36] A solution (0.3 cm^3) of $[W(N_2)_2(dppe)_2]$ (3.307×10^{-3} mol dm^{-3}, benzene) was introduced into an e.s.r. tube, and 110×10^{-3} cm^3 RX (*ca.* 1 mmol) added. The spectra were recorded and integrated as above; *g* values were determined against diphenylpicrylhydrazylmanganese and are accurate to $\pm 0.001\,5$.[37]

The general observations are recorded in Table 2, and the quantitative results are summarised in the Figure.

Preparative Studies.—All the reactions were carried out under an atmosphere of pure dry dinitrogen or argon using dry oxygen-free solvents and standard Schlenk-tube techniques. Magnetic moments were determined using an automatic Faraday balance and $Hg[Co(CNS)_4]$ as standard. Infrared spectra were recorded in KBr discs and Nujol mulls (CsI plates) using a Perkin-Elmer 577 spectrometer, ultraviolet spectra in solution in toluene using a Unicam SP 1800 spectrometer. Hydrogen-1 n.m.r. spectra were determined in solution in CD_2Cl_2 using a JEOL PS 100 spectrometer and tetramethylsilane as internal standard, ^{31}P and ^{13}C spectra in solution in CD_2Cl_2 or $CDCl_3$ using a JEOL PFT 100 instrument and trimethyl phosphite and $SiMe_4$ as internal standards. Melting points were obtained on a Kofler block in air. Microanalyses were by Mr. A. G. Olney, University of Sussex. *X*-Ray photoelectron spectral data were obtained by courtesy of Dr. J. A. Connor, University of Manchester, on an A.E.I. ES200 spectrometer using internal carbon (285 eV) as standard.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[*cyclopentylmethylhydrazido*(2—)-N′]*tungsten bromide–methanol* (1/2). (*a*) A solution of $[W(N_2)_2(dppe)_2]$ (0.68 g, 0.68 mmol) in benzene (150 cm^3) was treated with $CH_2{=}CH(CH_2)_4Br$ (0.21 g, 1.28 mmol) and the mixture stirred at 20 °C for 15 h under tungsten-filament irradiation. The orange solution was reduced to *ca.* 50 cm^3 at 10^{-3} mmHg and HBr (1.3 mmol) added *via* a vacuum line. On leaving to warm to 20 °C a light brown precipitate formed. The solvent was removed at 10^{-3} mmHg and the residue recrystallised from methanol–diethyl ether–hexane as large red-brown *crystals*, 0.59 g (70%), m.p. 157 °C (Found: C, 54.9; H, 5.08; Br, 12.2; N, 2.17. $C_{60}H_{68}Br_2N_2O_2P_4W$ requires C, 54.7; H, 5.20; Br, 11.7; N, 2.13%). N.m.r. spectra; ^{31}P in CD_2Cl_2, -26.53 (s) p.p.m., with tungsten satellites, $|^1J(W\text{-}P)|$ 278.3 Hz; ^{13}C, in CD_2Cl_2, 49.4 (C^1), 37.0 (C^2), 29.6 (C^3,C^6), and 24.8 p.p.m. (C^4,C^5); ^1H, in CD_2Cl_2, τ 7.0 (br s) disappearing on addition of MeOD (N–H), 8.44 (dd) collapsing to doublet on addition of MeOD, $|^3J(H^1\text{-}H^2)|$ 8, $|^3J(NH\text{-}H^1)|$ 5 Hz, otherwise complex characteristic pattern assignable to the other protons.



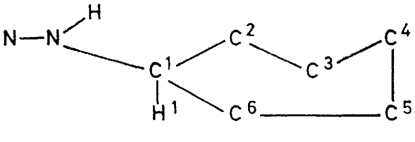
(*b*) Addition of an excess of cyclopentyl-lithium in diethyl ether to a suspension of $[WBr(CH_2N_2)(dppe)_2]Br$ (0.30 g, 0.25 mmol) in diethyl ether (10 cm^3) resulted in a rapid colour change from green to yellow. The solution was filtered and HBr (1.0 mmol) added to the filtrate using a vacuum line. The red-orange solution was reduced to dryness at 10^{-3} mmHg and the resulting brown oil recrystallised from methanol–diethyl ether–hexane as brown *crystals* (0.15 g,47%), identical in analysis and spectra to the sample obtained under (*a*).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[*cyclohexylhydrazido*(2—)-N′]*tungsten bromide–methanol* (1/2). To $[W(N_2)_2(dppe)_2]$ (0.62 g, 0.62 mmol) in benzene (150 cm^3) was added cyclohexyl bromide (0.011 g, 0.64 mmol) and the orange solution irradiated at 20 °C for 15 h. The solution was reduced to *ca.* 50 cm^{-3} at 10^{-3} mmHg and HBr (1.0

[36] S. J. Wyard, *J. Sci. Instr.*, 1965, **42**, 769.

[37] D. J. Lowe, R. M. Lynden-Bell, and R. C. Bray, *Biochem. J.*, 1972, **130**, 239.

mmol) condensed in on a vacuum line. After warming to 20 °C, solvent was removed at 10^{-3} mmHg and the resulting brown oil recrystallised from methanol–diethyl ether–hexane as large brown *crystals* (0.54 g, 68%), m.p. 166—167 °C (Found: C, 54.2; H, 5.18; N, 1.94. $C_{60}H_{68}Br_2N_2O_2P_4W$ requires C, 54.7; H, 5.20; N, 2.13%). N.m.r. spectra: ^{13}C, in CD_2Cl_2, 55.27 (C^1), 32.58 (C^2,C^6), 24.40 p.p.m. (C^3,C^4,C^5); ^1H, in CD_2Cl_2, 6.68(s, MeOH methyl), 7.26(s, NH) and a characteristic pattern for the other protons quite distinct from that of the cyclopentylmethyl derivative described above.



Reaction of $[W(N_2)_2(dppe)_2]$, MeI, *and an Excess of* $[NBu^n_4]Br$.—To a solution of $[W(N_2)_2(dppe)_2]$ (0.35 g, 0.35 mmol) and $[NBu^n_4]Br$ (0.98 g, 52.5 mmol) in thf (150 cm^3) was added MeI (0.52 g, 0.35 mmol) and the solution stirred at 20 °C without artificial irradiation for 40 h. The volume was reduced to *ca.* 40 cm^3 at 10^{-3} mmHg and a colourless solid filtered off. To the filtrate was added HBF_4 (0.70 mmol), the solvent removed at 10^{-3} mmHg, and the resulting brown oil recrystallised from methanol–diethyl ether–hexane as dark brown crystals (0.30 g, 74%), shown to be $[WI\{N_2CH(CH_2)_3OH\}(dppe)_2][BF_4]$ by spectra, analysis (zero bromide content), and comparison with an authentic sample.[13]

Reaction of $[W(N_2)_2(dppe)_2]$ *and Benzyl Bromide in Benzyl Methyl Ether.*—To a solution of $[W(N_2)_2(dppe)_2]$ (1.03 g, 1.0 mmol) in freshly distilled benzyl methyl ether was added benzyl bromide (0.34 g, 2.0 mmol) and the mixture irradiated for 48 h. The solvent was then removed at 10^{-3} mmHg leaving a pale yellow solid which was washed with hexane (3 × 10 cm^3), the hexane reduced to dryness at 10^{-3} mmHg, and the residue sublimed at 10^{-3} mmHg and 45 °C. The white sublimate was shown to be bibenzyl by its m.p. and by i.r. and ^1H n.m.r. spectroscopy. The yellow solid residue was dissolved in benzene and HBr (1.0 mmol) added using a vacuum line, and the product evaporated to dryness at 10^{-3} mmHg. Extraction with methanol (2 × 15 cm^3) afforded a pale orange solution, which, on reduction to *ca.* 10 cm^3 and addition of diethyl ether and hexane, afforded orange crystals of $[WBr_3(dppe)_2]\cdot 2MeOH$; 0.10 g (8%) (Found: C, 50.3; H, 4.63; N, 0.0. $C_{54}H_{56}Br_3O_2P_4W$ requires C, 50.5; H, 4.36; N, 0.0%). The methanol-insoluble fraction was recrystallised from benzene–hexane (1 : 1) as yellow platelets of $[WBr_2(dppe)_2]\cdot C_6H_6$, 0.87 g (71%) (Found: C, 57.2; H, 4.85; N, 0.0. $C_{58}H_{54}Br_2P_4W$ requires C, 57.2; H, 4.44; N, 0.0%).

Investigation of the Molybdenum(I) *Species.*—The material (A) alleged to be $[MoCl(N_2)(dppe)_2]$ was prepared by the method of George [24] from $[Mo(N_2)_2(dppe)_2]$ and Ph_3CCl, and also using methyl chloride.[14] It was also obtained by co-crystallising 1 : 1 mixtures of $[Mo(N_2)_2(dppe)_2]$ and $[MoCl_2(dppe)_2]$ from benzene–methanol.

Reaction of (A) *with n-butyl bromide.* To a solution of (A) (0.72 g, 0.76 mmol) in benzene (180 cm^3) was added Bu^nBr (85 × 10^{-3} cm^3; 0.76 mmol) and the mixture stirred at 20 °C without artificial irradiation for 55 h. The orange solution was reduced to dryness at 10^{-3} mmHg, the product dissolved in benzene (80 cm^3), and HBr (0.76 mmol) added from a vacuum line. The mixture was evaporated to dryness and the orange product extracted with methanol (2 × 20 cm^2), affording a red solution and a yellow solid. The solid was filtered off, washed with methanol, and recrystallised from benzene–hexane, and shown to be $[MoCl_2(dppe)_2]$ (0.28 g, 0.29 mmol) by analysis and comparison with an authentic sample. The solution was reduced to 15 cm^3 at 10^{-3} mmHg, and diethyl ether (15 cm^3) and hexane added to yield red crystals (0.38 g, 0.31 mmol). This was identical with the product obtained from $[MoBr(N_2Bu^n)(dppe)_2]$ and HBr (2 mol).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromocarbonylmolybdenum.* To a solution of $[Mo(CO)(N_2)(dppe)_2]$ (0.37 g, 0.38 mmol) in benzene (80 cm^3) was added benzyl bromide (0.05 cm^3) and the mixture stirred at 20 °C without artificial irradiation for 14 h, during which time a yellow precipitate had formed. The mixture was reduced to dryness at 10^{-3} mmHg and extracted with hexane (3 × 5 cm^3). The hexane extract was reduced to dryness at 10^{-3} mmHg and the residue sublimed at 50° C and 10^{-3} mmHg onto a probe cooled at −78 °C, and shown by i.r. and ^1H n.m.r. spectroscopy to be bibenzyl. The residue from the hexane extraction was dissolved in benzene (50 cm^3), and addition of hexane (20 cm^3) afforded lemon-yellow *crystals*, 0.31 g (83%) (Found: C, 63.3; H, 5.27; Br, 7.97; N, 0.0. $C_{53}H_{48}BrMoO$ requires C, 63.6; H, 4.84; Br, 7.99; N, 0.0%). The i.r. spectrum showed bands at 1 814(vs, sharp) and 1 746(vs, br) cm^{-1} in both Nujol and in solution in CH_2Cl_2, with which it does not readily react. The ^1H n.m.r. spectrum was typical of a paramagnetic species. The e.s.r. spectrum at −153 °C consisted of a strong broad signal at *g ca.* 2.118 ± 0.10. Electrochemically, the species shows an irreversible one-electron reduction, $E_{p/2} = -0.83$ V (*versus* the s.c.e.) ($E_p - E_{p/2}$ 90 mV) and a reversible one-electron oxidation at $E_{\frac{1}{2}} = 0.09$ V.

Samples of (A) were examined by cyclic voltammetry in thf—0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a platinum electrode. The various preparations *all* showed two reversible oxidation processes ($E_p^{ox} - E_p^{red}$ *ca.* 60 mV) in the ratio *ca.* 1 : 1 at $E_{\frac{1}{2}} = -0.16$ and -0.04 V *versus* the s.c.e., and a reversible reduction process at −1.65 V with an i_p in the same ratio. Authentic samples of $[MoCl_2(dppe)_2]$ and $[Mo(N_2)_2(dppe)_2]$ show primary oxidation waves at −0.04 and −0.16 V, respectively. The dichloride also has a reduction wave at −1.65 V. A 1 : 1 mixture of the dichloro- and the bis(dinitrogen) complexes gave a cyclic voltammogram indistinguishable from that of the supposed molybdenum(I) preparations (A). Addition of $[Mo(N_2)_2(dppe)_2]$ to the solution of (A) increased the more negative oxidation wave; addition of $[MoCl_2(dppe)_2]$ increased the other. A sample of (A) was examined in toluene–methanol (4 : 1), a solvent mixture more analogous to that recommended for recrystallisation. The cyclic voltammograms were similar to those obtained in thf. Disproportionation of (A) at the electrode surface seems unlikely; voltammograms using either vitreous-carbon or platinum electrodes were essentially identical.

We also searched for metal(I) species as intermediates in the alkylation reactions by e.s.r. spectroscopy. In the usual mixtures, no evidence for such species was detected between 20 and −140 °C. In the absence of a spin trap $R^{\bullet}$ was not observed (except in the case of Ph_3CCl and $PhCH_2Br$) but a broad signal was observed first at −80 °C, being a well defined three-line pattern at −150 °C (again except in the case of Ph_3CCl which gives rise to a more complex signal). The signal was retained on cycling the temperature between

20 and −150 °C. The *g* values are shown in the Figure. We attribute this signal to the unstable molybdenum(I) species [MoX(N_2)(dppe)$_2$].

Attempts to identify metal(I) species from u.v. irradiation of [WBr(N_2Me)(dppe)$_2$] failed and irradiation of [MoBr(N_2Et)(dppe)$_2$] afforded signals from at least two metal-centred species, neither of which could be properly identified.

Organic radicals were not identified from mixtures of PhCOCl or MeCOCl and [Mo(N_2)$_2$(dppe)$_2$] nor from MeCOCl and [W(N_2)$_2$(dppe)$_2$], nor from u.v. irradiation of [WCl(N_2COMe)(dppe)$_2$] all in the presence of a spin trap. In the absence of a trap, [Mo(N_2)$_2$(dppe)$_2$] and PhCOCl at room temperature gave two signals. One, which was weak, may be assigned to the benzoyl radical. The other was stronger and had *g* values of 1.967 and 1.937. On cooling to −153 °C an additional, weak, three-line pattern appeared, apparently in the same position as the signal attributed to [MoCl(N_2)(dppe)$_2$] formed from [Mo(N_2)$_2$(dppe)$_2$] and CH_2Cl_2.

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