Diazene-*N*- (Di-imide) and Hydrazido-(2—)*N*- (Aminoimido) Complexes: The Addition of Acids to Dinitrogen Complexes

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The protonation and reduction of dinitrogen in a mononuclear complex are described. The diazene compounds $[MX_2(N_2H_2)(dpe)_2]$ (I; M = W, X = Cl or Br; M = Mo, X = Br; dpe = $Ph_2PCH_2CH_2PPh_2$), and hydrazido-(2−)*N* complex salts, $[Mo(N_2H_2)(depe)_2]X$ (X = Cl or Br; depe = $Et_2PCH_2CH_2PEt_2$) and *trans*-$[WCl(N_2H_2)(PMe_2Ph)_4]Cl$ were prepared by the reaction of *trans*-$[M(N_2)_2(diphos)_2]$ (M = Mo or W; diphos = dpe or depe) or *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with an excess of the appropriate hydrogen halide. Compounds (I) contain labile halogen and are converted into the hydrazido-(2—)*N* complex salts $[MX(N_2H_2)(dpe)_2]Y$ (Y = BPh_4, ClO_4, or PF_6, M = W; Y = BF_4, M = Mo) by treatment with $NaBPh_4$, $LiClO_4$, $NaPF_6$, or $[NEt_4]BF_4$ as appropriate. The structural implications of the i.r., ^1H, and ^{31}P n.m.r. spectroscopic properties of the N_2H_2 compounds and of their ^{15}N analogues are discussed.

With only 2 mol equiv. of HCl, *trans*-$[W(N_2)_2(dpe)_2]$ gives the hydride $[WH(N_2)_2(dpe)_2]HCl_2$ and *trans*-$[Mo(N_2)_2(dpe)_2]$ gives the dihydride $[MoH_2Cl_2(dpe)_2]$. $[WH(N_2)_2(dpe)_2]HCl_2$ is converted into $[WH_2Cl_2(dpe)_2]$ in refluxing methanol and $[WCl_2(N_2H_2)(dpe)_2]$ gives $[WCl_2\{N_2H(COCH_3)\}(dpe)_2]$ with acetyl chloride or acetic anhydride.

This work provides the first chemical evidence that dinitrogen is as likely to be reduced at a mono- as at a bi-metal site in nitrogenase.

It is believed that the two molybdenum atoms in the Mo–Fe protein of nitrogenase [1] provide the sites which bind dinitrogen prior to its reduction to ammonia.[2] Circumstantial evidence also suggests that the two molybdenum atoms react independently. Dinitrogen complexes are often presented as models for the enzyme site with bound nitrogen, but apart from one brief communication [3] of the work detailed in this paper, there is no experimental evidence that dinitrogen

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[1] T. C. Huang, W. H. Zumft, and L. E. Mortenson, *J. Bact.* 1973, **113**, 884.

[2] J. Chatt in ' Proceedings of the Climax First International Conference on the Chemistry and Uses of Molybdenum,' University of Reading, September 1973. Ed. P. C. H. Mitchell, Climax Molybdenum Company Limited (an affiliate of Amax), London, 1973, p. 224.

[3] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Chem. Comm.*, 1972, 1010.

attached to only one transition-metal atom can be reduced to a hydride of nitrogen.

Whenever the dinitrogen in a complex has been observed to undergo protonation and reduction to hydrazine or ammonia, μ-dinitrogen complexes have been invoked in explanation.[4] Generally the treatment of mononuclear complexes with acid leads to the evolution of dinitrogen, often together with dihydrogen, but sometimes the metal may be protonated to form a hydride complex without loss of dinitrogen.[4] Here we describe the first example of the protonation of the dinitrogen in a well defined mononuclear dinitrogen complex. In our example it yields stable mononuclear complexes of diazene (HN=NH) or hydrazido-(2−)*N*(H_2N–N^{2-}), the first to be described, although diazene was recently synthesised as a bridging ligand.[5]

When *trans*-[$W(N_2)_2(dpe)_2$] (dpe = $Ph_2PCH_2CH_2PPh_2$) is treated with only 2 mol. equiv. of hydrogen chloride in thf (thf = tetrahydrofuran), it undergoes protonation at the metal and retains both dinitrogen molecules to form the salt [$WH(N_2)_2(dpe)_2$]HCl_2. However, if more than 5 mol. equiv. of hydrogen chloride are used, one of the ligating dinitrogen molecules is protonated and reduced to yield ligating N_2H_2. The corresponding molybdenum bis-dinitrogen complex undergoes an analogous reaction with hydrogen bromide, but not with hydrogen chloride, as described below.

Preparation of N_2H_2 *Complexes*.—When *trans*-[$W(N_2)_2(dpe)_2$] in thf solution is treated with an excess (>5 mol. equiv.) of anhydrous HX (X = Cl or Br) *in vacuo* it reacts as in equation (1). The reaction is

$$\textit{trans}\text{-}[W(N_2)_2(dpe)_2] + 2HX \longrightarrow [WX_2(N_2H_2)(dpe)_2] + N_2 \quad (1)$$

quite rapid at 0 °C and appears to be faster when X = Br. The N_2H_2 complex is also formed when aqueous hydrochloric acid is added to a tetrahydrofuran solution of the bis-dinitrogen complex, but the experiments described in this paper were carried out under anhydrous conditions *in vacuo* so that dinitrogen and/or dihydrogen evolution could be monitored. A reaction analogous to equation (1) occurs when *trans*-[$Mo(N_2)_2(dpe)_2$] is treated with hydrogen bromide, but hydrogen chloride displaces all the dinitrogen from the molybdenum complex in accord with equation (2).

$$\textit{trans}\text{-}[Mo(N_2)_2(dpe)_2] + 2HCl \longrightarrow [MoH_2Cl_2(dpe)_2] + 2N_2 \quad (2)$$

One of the halide ligands in the compounds [$MX_2(N_2H_2)(dpe)_2$] (see Table) is labile and the compounds, in 1,2-dichloroethane, behave as weak electrolytes and give rather low molecular weights. In nitrobenzene they undergo about 75% electrolytic dissociation. The bromides are more dissociated than the corresponding chlorides. By reaction with salts such as $NaBPh_4$, $LiClO_4$, $NaPF_6$, or [NEt_4]BF_4, as appropriate, salts of the cations *trans*-[$MX(N_2H_2)(dpe)_2$]$^+$ are obtained, *e.g.* as in equation (3). Similarly [$MoBr(N_2H_2)(dpe)_2$]-

$$[WCl_2(N_2H_2)(dpe)_2] + NaBPh_4 \longrightarrow [WCl(N_2H_2)(dpe)_2][BPh_4] + NaCl \quad (3)$$

[BF_4] is obtained by the reaction of [NEt_4][BF_4] with [$MoBr_2(N_2H_2)(dpe)_2$] in dichloromethane.

Hydrogen chloride reacts with *cis*-[$W(N_2)_2(PMe_2Ph)_4$] in dichloromethane to give *trans*-[$WCl(N_2H_2)(PMe_2Ph)_4$]Cl which is a 1 : 1 electrolyte in dichloroethane and nitrobenzene (see Table 1). Its ^1H n.m.r. spectrum (singlet P-CH_3 resonance) and ^{31}P spectrum in dichloromethane [^2H] (Table 2) are consistent with a symmetrical arrangement of the phosphine ligands[6] with the Cl and N_2H_2 groups in mutually *trans*-positions about the octahedral cation.

It is interesting that *trans*-[$Mo(N_2)_2(depe)_2$] (depe = $Et_2PCH_2CH_2PEt_2$) in contrast to its dpe analogue, is protonated to give the N_2H_2 complexes by both hydrogen chloride and hydrogen bromide, but the products are very soluble and except for the bromide have not yet been obtained pure. This greater ease of *N* protonation may be caused by the greater basic strength of the aliphatic diphosphine or by its greater restriction of access to the molybdenum atom, or both.

The N_2H_2 compounds which we have prepared are listed in Table 1 together with their analytical and pertinent physical data. Some tend to retain tenaciously their solvent of crystallisation.

Spectroscopic Properties.—The N–H stretching frequencies and N–^{1}H resonance values of the N_2H_2 complexes (see Tables 1 and 2) fall into two groups. The solid-state i.r. spectra of the seven-co-ordinate compounds [$MX_2(N_2H_2)(dpe)_2$] show two N–H bands separated by *ca.* 350 cm^{-1}, whereas the solid salts containing the six-co-ordinate cations *trans*-[$MX(N_2H_2)(dpe)_2$]$^+$ generally show two or three bands of overall separation *ca.* 200 cm^{-1}. The *trans*-[$WCl(N_2H_2)(PMe_2Ph)_4$]Cl and [$MoX(N_2H_2)(dpe)_2$]X compounds fall in this latter category. The ^1H n.m.r. spectra of the seven-co-ordinate compounds show the N–H resonance at *ca.* 5·8—6·5 p.p.m. depending on the solvent, and this resonance is split in the $^{15}N_2H_2$ derivative only below *ca.* −70 °C, when an asymmetric multiplet is observed. In contrast, the N–H resonance of the cationic complexes occurs at higher field (≈3·1 p.p.m.), which in the $^{15}N_2H_2$ complex is split into a doublet, independent of temperature, over the range −100 to +20 °C. Half the doublet is masked by the P–CH_2 absorption. Thoroughly dry solvents are essential to observe these resonances—evidence of rapid proton exchange with water.

The N_2H_2 group may be bound to the metal as a hydrazido-(2−)*N* group as in (a), as a diazene-*N* ligand as in (b), or as a diazene-*N*,*N*^{1} as in (c). Structure (a) has been clearly established in the cationic complex

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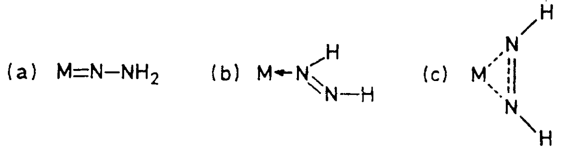
[4] J. Chatt and R. L. Richards, in ‘ Chemistry and Biochemistry of Nitrogen Fixation,’ ed. J. R. Postgate, Plenum Press, London, 1971, p. 57.

[5] D. Sellman, *J. Organometallic Chem.*, 1972, **44**, C 46.

[6] M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741.

$[WCl(N_2H_2)(dpe)_2]BPh_4$ by *X*-rays[7] and is in accord with its spectroscopic data; in particular the separation



of the N–H stretching frequencies (100 cm^{-1}) is similar to that of primary amines.[8] The N–^{1}H n.m.r. resonance occurs at 3 p.p.m. (C^2HCl_3). The N_2H_2 group in the seven-co-ordinate $[WX_2(N_2H_2)(dpe)_2]$-type complexes shows quite different spectroscopic properties. Its ν(N–H) frequencies are widely separated (*ca.* 350 cm^{-1}), its ^{1}H n.m.r. resonance occurs at lower field (*ca.* 6 p.p.m.) and in the ^{15}N analogues is not split at temperatures down to *ca.* −70 °C when an asymmetric multiplet pattern develops. These facts suggest an asymmetrical mode of bonding for the N_2H_2 group in the seven-co-ordinate complexes as in (b) rather than as in (c).

TABLE 1

Tungsten and molybdenum compounds

Compound	M.p.^{a} (t/°C)	Analyses (%)^b C	H	N	Cl or Br	ν(N–Z)^c	ν(M–Cl)^d	M^e	Λμ Ω^{-1} cm^{-2} mol^{-1}
$[WCl_2(N_2H_2)(dpe)_2]$	243—246	57·5 (57·7)	4·8 (4·6)	2·6 (2·6)	6·7 (6·6)	3270,^{f} 3330^g 2920,^{f} 2960^g 1590^h	280	864 (1084)	6,^{e} 18^i
$[WCl_2(N_2H_2)(dpe)_2]\cdot CH_2Cl_2$	230—232	54·7 (54·6)	4·4 (4·5)	2·4 (2·4)	12·4 (12·1)	3290	280		
$[WCl_2(^{15}N_2H_2)(dpe)_2]$	248—251	57·7 (57·7)	4·6 (4·5)	2·5 (2·6)		3270 2920	280		
$[WCl_2(N_2{}^2H_2)(dpe)_2]$	245—250	56·9 (57·7)	4·8 (4·4)	2·5 (2·6)	6·8 (6·6)	2450 2120 1360^{f,h}	280		
trans-$[WCl(N_2H_2)(dpe)_2]BPh_4$	241—248	66·8 (66·8)	5·1 (5·1)	2·1 (2·1)	2·3 (2·6)	3340 3240	285		16^i
trans-$[WCl(^{15}N_2H_2)(dpe)_2]BPh_4$	238—248	66·4 (66·8)	5·0 (5·1)	2·1 (2·1)		3340 3240	285		
trans-$[WCl(N_2{}^2H_2)(dpe)_2]BPh_4$	234—239	66·2 (66·8)	5·3 (5·1)	1·9 (2·1)		2515vw 2380	285		16^i
trans-$[WCl(N_2H_2)(dpe)_2]ClO_4$	152—153	54·5 (54·5)	4·8 (4·4)	2·4 (2·5)	6·2 (6·2)	3330, 1590^h 3230 3130	278		21^i
trans-$[WCl(N_2{}^2H_2)(dpe)_2]ClO_4\cdot thf$	152—153	55·1 (55·2)	4·9 (4·8)	2·3 (2·3)		2490 2370 2255	278		21^i
trans-$[WCl(N_2H_3)(dpe)_2]PF_6$	dec. >250	52·6 (52·4)	4·4 (4·2)	2·4 (2·4)		3360 3270			20^i
$[WBr_2(N_2H_2)(dpe)_2]$	224—227	53·4 (53·4)	4·3 (4·2)	2·4 (2·4)	13·8 (13·7)	3270 2930, 1590^h		826 (1254)	13,^{e} 19^i
$[WBr_2(N_2H_2)(dpe)_2]\cdot CH_2Cl_2$	235—240	50·3 (50·7)	4·2 (4·1)	2·4 (2·2)		3295, 3300^f 2940,^{f} 1590^h			
$[WBr(N_2{}^2H_2)(dpe)_2]$	236—242	53·6 (53·4)	4·8 (4·2)	2·4 (2·4)		2470 3190, 1375^{f,h}			
$[WBr_2(^{15}N_2H_2)(dpe)_2]\cdot CH_2Cl_2$	235—237			2·2 (2·2)		3290			
trans-$[WBr(N_2H_2)(dpe)_2]BPh_4\cdot CH_2Cl_2$	140—142	61·4 (61·6)	5·0 (4·9)	1·9 (1·9)		3340 3230			23^i
trans-$[WCl(N_2{}^2H_2)(PMe_2Ph)_4]Cl$	177—195			3·1 (3·0)		2473^f 2313^f 2267w^f			
trans-$[WBr(N_2H_2)(PMe_2Ph)_4]Br$	124—135			2·7 (2·9)		3265 3180 3110w			
$[WH_2Cl_2(dpe)_2]$	250—255	59·1 (59·3)	4·9 (4·8)		6·6 (6·7)	1970^j 1760^j 1740	289, 241		
$[MoBr_2(N_2H_2)(dpe)_2]$	287—290	57·3 (57·7)	4·5 (4·6)	2·6 (2·6)	14·3 (14·8)	3300 2720, 1570^h		Insoluble	18^i
$[MoBr_2(N_2{}^2H_2)(dpe)_2]$	286—289	57·7 (57·7)	4·2 (4·5)	2·4 (2·6)		2470^f 2190—2065,vbr 1370^h			
trans-$[MoBr(N_2H_3)(dpe)_2]BF_4\cdot HCOMe_2$	275—285	56·6 (56·8)	4·9 (4·9)	3·3 (3·6)		3340, 1690 3230 (C=O) 3130			19^i
$[MoCl(N_2H_2)(depe)_2]Cl$	n.p.			4·6 (4·6)					
$[MoBr(N_2H_2)(depe)_2]Br\cdot thf$	254—250	36·1 (36·2)	6·6 (6·9)	3·7 (3·8)		3174 3078, 1565^h			18·1^i
$[MoBr(N_2{}^2H_2)(depe)_2]Br\cdot thf$	240—250			3·6 (3·8)		2405 2312 2190w			
$[MoH_2Cl_2(dpe)_2]$	dec. >220	64·5 (64·7)	5·4 (5·2)		7·4 (7·4)	1880w^j	304, 262	1000 (965)	
$[Mo^2H_2Cl_2(dpe)_2]$	dec. >220	64·4 (64·7)	5·3 (5·2)			1355^k	304, 262		
$[WH(N_2)_2(dpe)_2]HCl_2\cdot 2thf$	dec. >200	57·4 (57·5)	5·1 (5·3)	4·6 (4·5)	6·0 (5·7)	1995^l			40,^{e} 60^m
$[WH(^{15}N_2)_2(dpe)_2]HCl_2\cdot 2thf$	dec. >200	57·0 (57·5)	5·2 (5·3)	4·5 (4·5)		1935^n			
trans-$[Mo(N_2)_2(depe)_2]$	dec. >180	42·4 (42·6)	8·6 (8·5)	10·1 (9·9)		1936^l			

^{a} In sealed, evacuated tubes. ^{b} Required value in parentheses. ^{c} Z = H or ^{2}H. Nujol mulls unless otherwise stated. ^{d} M = Mo or W. ^{e} In *ca.* 10^{-3} molar $C_2H_4Cl_2$ solution. ^{f} Hexachlorobutadiene mull. ^{g} CH_2Cl_2 solution. ^{h} N–H or N–^{2}H deformation frequency. ^{i} In *ca.* 10^{-3} molar $PhNO_2$ solution. ^{j} ν(M–H). ^{k} ν(Mo–^{2}H). ^{l} ν(N_2). ^{m} $MeNO_2$ solution. ^{n} ν($^{15}N_2$). br = broad; v = very; w = weak; thf = tetrahydrofuran; dpe = $Ph_2PCH_2CH_2PPh_2$; depe = $Et_2PCH_2CH_2PEt_2$; n.p. = not obtained pure; dec. = decomposed.

Sellman[9] has pointed out that the hydrogen atom attached to a nitrogen atom adjacent to a transition-metal ion has a ^{1}H n.m.r. resonance at much lower fields than 6 p.p.m. He observed it at 14·27 p.p.m. in his μ-diazene complex *trans*-$[(C_5H_5)(CO)_2Mn–NH=NH–Mn(CO)_2(C_5H_5)]$,[5] and it occurs at 15·1 p.p.m. in the complex $[PtCl(3\text{-}FC_6H_4N=NH)(PEt_3)_2]BF_4$.[10] Taken alone, these facts suggest that even in our seven-co-ordinate complexes, the N_2H_2 might have structure (a) as Sellman has suggested.[9] However, the wide ν(N–H) separation, and absence of

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[7] G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 259; G. A. Heath and R. Mason, personal communication.

[8] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, New York, 1962, p. 250.

[9] D. Sellman, *J. Organometallic Chem.*, 1973, **49**, C 22.

[10] G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822.

^{15}N–H coupling above −70°C, are inconsistent with (a) (see above).

The facts can be explained by supposing that the N$_2$H$_2$ group in the seven-co-ordinate complexes has structure (b) and that a rapid exchange of protons between the two nitrogen atoms occurs. The position of the proton shift is very sensitive to any trace of protic substance (*e.g.* MeOH) in the dichloromethane solvent and scrupulously dried solvent is necessary to observe the splitting which occurs below −70 °C in the ^{15}N$_2$H$_2$ analogue, indicating rapid proton exchange also with a protic solvent. The seven-co-ordinate complexes show a slight electrolytic conductivity in dichloromethane solution suggesting that the form, *e.g.* [WCl$_2$(NH=NH)(dpe)$_2$], is in equilibrium with a small concentration of the salt, [WCl(N–NH$_2$)(dpe)$_2$]Cl with which it could

TABLE 2

N.m.r. spectra[a]

Compound	Resonance (p.p.m. ±0·02)[b]	Assignment and coupling constants[c]
(*a*) ^{1}H Data		
[WCl$_2$(N$_2$H$_2$)(dpe)$_2$]	2·4—3·05 (8)	P–CH_2 multiplet
	6·50,[d] 5·85[d,e] (2)	N–H_2[f] broad singlet
	6·8—7·4 (40)	P–Ph multiplet
[WCl$_2$(^{15}N$_2$H$_2$)(dpe)$_2$][e]	2·55—3·10 (8)	P–CH_2 multiplet
	5·32[d] (2)	N–H_2 broad singlet, multiplet at −70 °C
	6·8—7·3 (40)	P–Ph multiplet
[WBr$_2$(N$_2$H$_2$)(dpe)$_2$]·CH$_2$Cl$_2$[e, g]	2·4—3·1 (8)	P–CH_2 multiplet
	5·15 (2)	CH_2Cl$_2$ singlet
	6·3[d] (2)	N–H_2[f] broad singlet
trans-[WCl(NNH$_2$)(dpe)$_2$]BPh$_4$[e]	2·24—2·84 (8)	P–CH$_2$ multiplet
	3·02[d] (2)	N–H_2 broad singlet
	6·6—7·4 (60)	P–Ph B–Ph } multiplets
trans-[WBr(NNH$_2$)(dpe)$_2$]BPh$_4$	2·2—3·0 (8)	P–CH_2 multiplet
	3·26[d] (2)	N–H_2 broad singlet
	6·6—7·4 (60)	P–Ph B–Ph } multiplets
trans-[WCl(NNH$_2$)(dpe)$_2$]ClO$_4$[e,g]	2·2—3·05 ~2·90[d] } *h* (10)	P–CH_2 N–H_2 } *h*
	6·6—7·9 (40)	P–Ph multiplet
trans-[WCl(NNH$_2$)(dpe)$_2$]PF$_6$[e]	2·5—3·0 (8)	P–CH_2 multiplet
	3·40[d] (2)	N–H_2 singlet
	6·5—7·9 (40)	P–Ph multiplet
trans-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]Cl[e]	1·70 (24)	P–CH_3 broad singlet
	2·0—2·6 (~2)	N–H_2 possibly, but v. broad
	5·18 (2)	CH_2Cl$_2$ singlet
	7·1—7·8 (20)	P–Ph multiplet
trans-[MoBr(NNH$_2$)(depe)$_2$]Br·½thf[i]	0·6—1·0 (~13)	P–CH_3 multiplet[j]
	1·2—1·85 (~11)	P–CH_2 multiplet[j]
	3·2—3·4 (~2)	thf multiplet
[MoH$_2$Cl$_2$(dpe)$_2$]	1·5—3·5 (~4)	P–CH_2 multiplet
	6·9—7·8 (40)	P–Ph multiplet
	−4·55 (~2)	Mo–H quintet ^2J(PMoH) = 48
[WH(N$_2$)$_2$(dpe)$_2$]HCl$_2$·2thf[e]	2·8 2·6 } (8)	P–CH$_2$ v. broad doublet
	1·4 3·3 } (16)	C$_4$$H_8$O multiplets
	6·6—7·9 (40)	P–Ph multiplet
	−3·50 (1)	W–H triplet of triplets[k] ^2J(PWH)$_A$ = 7·0; ^2J(PWH)$_B$ = 0·5
	~9·5—11·5 (1)	Cl$_2$$H$ singlet[l]
(*b*) ^{31}P Data[m]		
[WH(N$_2$)$_2$(dpe)$_2$]HCl$_2$[e]	79·05—83·26 (1) 106·97—112·27 (1)	PPh$_2$ multiplets of AA′XX′ system
[WCl$_2$(N$_2$H$_2$)(dpe)$_2$][e]	107·63 (1)	PPh$_2$ singlet with ^{183}W satellites J(WP) = 278·2
	182·27 (~0·06) 130·18 (~0·06)	probably A′A′XX′-type pattern
trans-[WCl(N·NH$_2$)(PMe$_2$Ph)$_4$]Cl[e]	107·45	PMe$_2$Ph singlet with ^{183}W satellites J(WP) = 279·8
[MoBr$_2$(N$_2$H$_2$)(dpe)$_2$][e]	95·99 (1)	probably PPh$_2$ singlet
	102·50 (0·3) 130·12 (0·3)	probably PPh$_2$ AA′XX′-type pattern
trans-[WBr(NNH$_2$)(dpe)$_2$]BPh$_4$	115·99	PPh$_2$ singlet with ^{183}W satellites J(WP) = 277·7
[WBr$_2$(N$_2$H$_2$)(dpe)$_2$][n]	115·07 (1)	PPh$_2$ singlet
	115·47 (~0·8) 127·87 (~0·8)	probably PPh$_2$ AA′XX′-type pattern

[a] In C^{2}HCl$_3$ solution, relative to tetramethylsilane unless otherwise stated. [b] Integration values in parentheses. [c] Coupling constants in Hz ±0·1. [d] Disappears on treatment with ^{2}H$_2$O. [e] C^{2}H$_2$Cl$_2$ solution. [f] Position somewhat variable, very sensitive to traces of moisture. [g] Computer accumulated spectrum because of low solubility. [h] Overlapping resonances. [i] N–H$_2$ Resonance could not be assigned, possibly obscured by other resonances. [j] Tentative assignment, probably overlapping resonances. [k] Two coupling constants which cannot be assigned to particular phosphorus atoms but in accord with known structure (see text). [l] Position variable, probably moisture sensitive. [m] Relative to trimethyl phosphite, positive value is to high field, measurements made in Fourier transform mode with proton decoupling. [n] In MeOH solution.

undergo proton exchange. Thus the observed shifts of *ca.* 6 p.p.m. are an average of the *ca.* 14 p.p.m. expected for the hydrogen on the nitrogen adjacent to the metal, and the *ca.* 3 p.p.m. expected for the hydrogen on the terminal nitrogen in the (NH=NH) complex and in the equilibrium concentration of the ($N-NH_2$) complex.

If the form (a) of N_2H_2 occurred in the neutral seven-co-ordinate complexes the ^1H resonance would be expected at higher fields than 3 p.p.m., where it occurs in the cationic complexes, and not at lower fields (*ca.* 6 p.p.m.), as is observed.

The form (c) of the ligand N_2H_2 would give only a small splitting of ν(N–H) [*cf.* PhNH–NHPh ($\Delta\nu < 20$ cm^{-1}) and PhNH–NHCOCH$_3$ ($\Delta\nu \approx 50$ cm^{-1})], and certainly does not occur in any of the complexes obtained in the above reactions. However some organodiazene complexes of the later transition metals have this symmetrically bonded form, *e.g.* [Ni(PhN=NPh)-{P(*p*-tolyl)$_3$}$_2$].[11]

The tungsten in the salt $[WH(N_2)_2(dpe)_2]HCl_2$ has a pentagonal bipyramidal co-ordination with a dinitrogen molecule at each apex and the four phosphorus and one hydrogen atoms occupying the equatorial positions.[7] In accord with this structure the ^1H n.m.r. spectrum of $[WH(N_2)_2(dpe)_2]HCl_2$ shows the hydride resonance as a triplet of triplets (Table 2), and the ^{31}P n.m.r. shows an AA′XX′-type pattern.

The ^{31}P spectra of *trans*-$[WCl(N_2H_2)(PMe_2Ph)_4]Cl$ and *trans*-$[WBr(N_2H_2)(dpe)_2]BPh_4$ show the expected singlet (with ^{183}W satellites). Those of $[MX_2(N_2H_2)(dpe)_2]$ (M = W, X = Cl or Br; M = Mo, X = Br) also have a singlet main peak, but there are two subsidiary peaks, apparently an AA′XX′ pattern, whose intensity relative to the main peak varies somewhat depending upon the solvent or compound (see Table 2). Thus there appear to be two isomers of the seven-co-ordinate compounds in solution: the main isomer has equivalent phosphorus atoms, and in the minor one the phosphorus atoms are arranged as in $[WH(N_2)_2(dpe)_2]HCl_2$.

Reactions. The above hydride slowly loses dinitrogen in thf or methanol solution at 20 °C in the presence of an excess of hydrogen chloride, and no $[WCl_2(N_2H_2)_2(dpe)_2]$ is formed. Under reflux the reaction rapidly goes to completion according to equation (4). In contrast the

$$[WH(N_2)_2(dpe)_2]HCl_2 \xrightarrow[HCl]{\text{thf or MeOH}} [WH_2Cl_2(dpe)_2] + 2N_2 \quad (4)$$

complex $[WCl_2(N_2H_2)(dpe)_2]$ is stable under the conditions of reaction (4). It is evident that the cationic hydride is not an intermediate in the formation of the N_2H_2 complexes.

The complex $[WCl_2(N_2H_2)(dpe)_2]$ is readily acetylated by acetyl chloride or acetic anhydride in boiling thf solution to give a monoacetyl derivative [equation (5)].

$$[WCl_2(N_2H_2)(dpe)_2] + CH_3COCl \xrightarrow{\text{thf}} [WCl_2\{N_2H(COCH_3)\}(dpe)_2] + HCl \quad (5)$$

The acetyl derivative is identical with that obtained by direct acetylation of $[W(N_2)_2(dpe)_2]$ using acetyl chloride with traces of hydrogen chloride.[12]

Attempts to free the ligating N_2H_2 from $[WCl_2(N_2H_2)(dpe)_2]$ or $[WCl(N_2H_2)(dpe)_2]^+$ as a nitrogen hydride have not so far been successful. The N_2H_2 complexes are readily oxidised, *e.g.* by $AgBF_4$, to give dinitrogen, silver, and unidentified products, or electrochemically in dichloromethane to form $N_2 + H_2$ and unidentified tungsten species, but no ammonia or hydrazine. The N_2H_2 compounds show no reduction wave down to −1·6 V (in 10 : 1 CH_2Cl_2/MeOH) and such reagents as H_2SO_4, CH_3SO_3H, CF_3CO_2H, $TiCl_3$/HCl, $TiCl_3$/KOH, $SnCl_2$, Zn/CH_3CO_2H, Adams catalyst/H_2, and $AlMe_3$ have not led to the production of any hydrazine or ammonia. Sodium tetrahydroborate liberated dinitrogen according to equation (6).

$$[WX_2(N_2H_2)(dpe)_2] + NaBH_4 \xrightarrow{\text{EtOH}} [WH_4(dpe)_2] + N_2 \quad (6)$$
$$(X = Cl \text{ or } Br)$$

The molybdenum compound behaved analogously but $[MoH_n(dpe)_2]$ (n = 2 or 4)[13] being more labile, it was possible to carry out the following cycle of reactions (7).

$$\begin{tikzcd}
{[MoBr_2(N_2H_2)(dpe)_2]} \arrow[r, "NaBH_4", "thf"'] & {[MoH_n(dpe)_2] + N_2} \arrow[d, "C_6H_6\ N_2\ (slow)"] \\
 & {trans\text{-}[Mo(N_2)_2(dpe)_2] + \frac{n}{2}H_2} \arrow[ul, "thf\ excess\ HBr"]
\end{tikzcd} \quad (7)$$

Tin(II) chloride abstracted halide ion from the tungsten compound [equation (8)].

$$[WCl_2(N_2H_2)(dpe)_2] + SnCl_2 \xrightarrow{\text{thf}} [WCl(N_2H_2)(dpe)_2][SnCl_3] \quad (8)$$

Alkali generally deprotonates the diazene ligand to give back the original or a new dinitrogen complex. An excess of triethylamine in benzene gives reactions as follows:

$$2[MoBr_2(N_2H_2)(dpe)_2] + 4NEt_3 \xrightarrow[Ar]{\text{thf}} trans\text{-}[Mo(N_2)_2(dpe)_2] + \text{other Mo species} + 4[NEt_3H]Br \quad (9)$$

$$[MoBr_2(N_2H_2)(dpe)_2] + 2NEt_3 \xrightarrow[N_2]{\text{thf}} trans\text{-}[Mo(N_2)_2(dpe)_2] + 2[NEt_3H]Br \quad (10)$$

$$2[MoBr_2(N_2H_2)(dpe)_2] + 4NEt_3 \xrightarrow[CO]{\text{thf}} trans\text{-}[Mo(N_2)_2(dpe)_2] + trans\text{-}[Mo(CO)_2(dpe)_2] + 4[NEt_3H]Br \quad (11)$$

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[11] See S. D. Ittel and J. A. Ibers, *J. Organometallic Chem.*, 1973, 389 and references therein.

[12] J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 44.

[13] See A. Frigo, G. Puosi, and A. Turco, *Gazzetta*, 1971, **101**, 637 for a discussion of the formulation of this compound.

The products of the similar abstraction of hydrogen halide from $[WX_2(N_2H_2)(dpe)_2]$ contain only two nitrogen atoms to each tungsten atom, and their exact nature is still under investigation.

This work shows that dinitrogen in a mononuclear complex can be protonated, despite good theoretical reasons for thinking otherwise.[4] The products are the first stable monohapto N_2H_2 complexes to be described, either of the diazene (di-imide) or hydrazido(2-) (amino-imido or aminonitrene) types. In view of the great instability of N_2H_2 as a molecule, it is surprising that its monohapto-complexes are so stable, and especially that they resist reduction to hydrazine complexes.

Whether the N_2H_2 ligand takes up the linear imido-type structure (a) or the bent diazene-type structure (b) probably depends entirely on the electronic requirement of the metal. The seven-co-ordinate $[WCl_2(N_2H_2)(dpe)_2]$ is an 18-electron system with the N_2H_2 ligand as a formal 2-electron donor, *i.e.* in the diazene form (b). The removal of a chloride ligand would reduce the complex to a 16-electron system, $[WCl(N_2H_2)(dpe)_2]^+$, if it was not that the neutral N_2H_2 ligand can adjust itself to become a formal 4-electron donor by adopting the formally dianionic imido-form (a) and co-ordinating by an essentially triple bond [7] as is found in organoimido-complexes, *e.g.* $[ReCl_3(NPh)(PEt_2Ph)_2]$.[14,15]

We have not investigated the mechanism of the protonation of the dinitrogen ligand but it is worth some speculation. Since the ligating dinitrogen can receive its electron donor property only by back donation of electrons from the metal, one would expect that the electron-donor character of the metal would be greater than that of the ligating dinitrogen. This must normally be the case since the action of acids on monohapto-dinitrogen complexes generally yields hydride complexes with loss of dinitrogen, and also of dihydrogen if the derived hydride complex is sensitive to protic acid. The ' normal ' reaction occurs when $[Mo(N_2)_2(dpe)_2]$ is treated with hydrogen chloride, but the diazene complex is formed when it is treated with hydrogen bromide. The tungsten bis-dinitrogen complex also gives the diazene complex more rapidly and exclusively with hydrogen bromide as compared with hydrogen chloride. This suggests that the halide plays a decisive part in the reaction. We suggest therefore that the first important step is the attack on the metal by halide ion or hydrogen halide. From here one can speculate whether the next step is protonation or loss of one molecule of ligating dinitrogen, but we have no evidence on this point.

We have shown that monohapto-dinitrogen can be protonated and reduced to monohapto-diazene even in the presence of water, but in the system which we have examined it can be reduced no further in a protic solvent. Nevertheless our experiments suggest that dinitrogen in the enzymic system is just as likely to be reduced at a mono-metal as at a bi-metal site.

EXPERIMENTAL

The dinitrogen complexes were obtained by substantially improved methods, based on those originally developed in these laboratories,[16] as given below.

Gas handling involved standard vacuum techniques and air-sensitive materials were handled under pure dinitrogen. All solvents were rigorously dried and distilled under dry dinitrogen. Acetyl chloride and acetic anhydride were purified by distillation.

Jeol P.S. 100 and Varian H.A. 100 spectrometers were used for the n.m.r. measurements, and i.r. spectra were measured with Unicam SP 1200 and Grubb–Parsons D.M. 4 instruments. Mass spectra were obtained with an A.E.I. MS 10 spectrometer, electrolytic conductivities with a Portland Electronics conductivity bridge, molecular weights with a Hitachi–Perkin-Elmer 115 osmometer, and m.p.s. with a Kofler hot stage. Analyses (Table 1) were by Mr. A. G. Olney of these laboratories.

The dinitrogen complexes were prepared, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ from *trans*-$[WCl_4(PPh_3)_2]$, *trans*-$[W(N_2)(dpe)_2]$ from $[WCl_4(dpe)]$, and *trans*-$[Mo(N_2)_2(dpe)_2]$ from $[MoCl_3(thf)_3]$. The preparations and states of the starting materials are important and are also given together with the preparations of the appropriate dinitrogen complexes.

cis-*Tetrakis(dimethylphenylphosphine)bis(dinitrogen)tungsten.*—Dimethylphenylphosphine (5·6 g) was added to *trans*-$[WCl_4(PPh_3)_2]$ [17] (5 g) in dichloromethane (150 cm^3) and the solution was heated under reflux for 10 min. The resultant wine red solution was concentrated to one-third volume *in vacuo* and a brown oil was precipitated from it by addition of hexane (20 cm^3). The solution was decanted from the oil and concentrated *in vacuo* to give fine orange-red crystals of $[WCl_4(PMe_2Ph)_3]$ which were removed, washed with hexane, and dried at 20 °C *in vacuo* (3·6 g). This material (3·6 g) in thf (200 cm^3) was treated with magnesium turnings (10 g) and dimethylphenylphosphine (3·6 g) with vigorous stirring under dinitrogen for 18 h. The resultant yellow-brown solution was filtered, concentrated *in vacuo* to small volume, and ether (30 cm^3) was added to precipitate a white solid which was filtered off. The filtrate was taken to dryness *in vacuo* and the yellow residue extracted with ether. The ether solution, washed with water then concentrated, gave fine yellow platelets of the bis-dinitrogen complex which were filtered off, washed with ether, and dried at 20 °C *in vacuo* (1·5 g, 40%).

trans-*Bis[bis(diphenylphosphino)ethane]bis(dinitrogen)tungsten.*—Tungsten(VI) chloride (10 g), triphenylphosphine (6 g), and zinc (20 g) were mixed as solids, and dichloromethane (60 cm^3) was added. The mixture was shaken for 10 min then filtered and the residue (10 g) dried by suction (N_2 at 2 mmHg). It was then mixed with a further 5 g of dpe suspended in toluene (100 cm^3) and the mixture heated at 80 °C with stirring for 3 h. The greenish yellow $[WCl_4(dpe)]$ (11 g) was filtered off, washed with hexane, and dried at 20 °C *in vacuo*. To this material (11 g) was added dpe (6 g), magnesium (6 g), and thf (200 cm^3), and

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[14] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019; J. Chatt, J. D. Garforth, W. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

[15] D. A. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703 and references therein.

[16] B. Bell, J. Chatt, and G. J. Leigh, *J.C.S. Dalton*, 1972, 2492; J. Chatt and A. G. Wedd, *J. Organometallic Chem.*, 1971, **27**, C 15.

[17] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J.C.S. Dalton*, 1972, 1064.

the mixture vigorously stirred under dinitrogen with two crystals of iodine. The solution rapidly darkened and after being stirred for 18 h was filtered and concentrated *in vacuo* to give orange crystals of the product (8 g, 51%) which were filtered off, washed with ether, and dried.

trans-*Bis[bis(diphenylphosphino)ethane]bis(dinitrogen)-molybdenum*.—Amalgamated zinc (10 g) was added to $[MoCl_4(thf)_2]$ [18] (9 g) and dichloromethane–thf (200 cm^3 1 : 1 mixture) at 0 °C and the solution was stirred until it became blue. It was then filtered, the solvent removed *in vacuo*, and the *pinkish brown* $[MoCl_3(thf)_3]$ (8·6 g, 87%) precipitated by the addition of cold thf, filtered off, and dried at 20 °C *in vacuo* (Found: C, 34·2; H, 5·9. Calc. for $C_{12}H_{24}Cl_3O_3Mo$: C, 34·4; H, 5·8%). The solid has $\mu_{eff} = 3{\cdot}59$ B.M. This material (5·9 g) suspended in thf (175 cm^3) was treated with dpe (13·4) and magnesium turnings (7·5 g) and a crystal of iodine added. The mixture was vigorously stirred for 3 h under dinitrogen and the resulting yellow precipitate and magnesium were filtered off and extracted with thf. The orange-yellow extract was filtered and the two filtrates combined and concentrated *in vacuo* to give the product (11·4 g, 88%) as yellow prisms which were removed, washed with ether, and recrystallised from thf–ether.

trans-*Bis[bis(diethylphosphino)ethane]bis(dinitrogen)-molybdenum*.—To $[MoCl_3(thf)_3]$ (2·7 g) in thf (130 cm^3) was added magnesium (3 g) and depe (2·5 g) in thf (29 cm^3). The mixture was stirred for 5 min with a fast stream of dinitrogen passing through the solution, and was then stirred under dinitrogen. An orange precipitate formed after 15 min but redissolved, and the solution was stirred for a further 10 h. The magnesium was then filtered off, the solution reduced to one-third volume *in vacuo* and degassed methanol (30 cm^3) was added to give a yellow-orange precipitate which was recrystallised from thf–ether as yellow-orange *rhombs* (1·5 g, 41%).

Diazenebis[bis(diphenylphosphino)ethane]dibromotungsten, $[WBr_2(N_2H_2)(dpe)_2]$.—Tetrahydrofuran (40 cm^3) and hydrogen bromide (6 mol. equiv.) were condensed at $-196°$ *in vacuo* onto *trans*-$[W(N_2)_2(dpe)_2]$ (0·66 g). On warming the mixture to *ca.* 0 °C with stirring, an orange solution formed and dinitrogen (12·9 cm^3, 1·0 mol. equiv.) was rapidly evolved. The solution was then stirred at room temperature for 1 h and then concentrated to half volume *in vacuo*. Addition of diethyl ether (20 cm^3) then gave golden-yellow *crystals* which were filtered, washed with ether, and dried (0·6 g, 80%). Recrystallisation from dichloromethane–ether gave orange-yellow *prisms* of the dichloromethane solvate. The analogues shown in Table 1 were similarly prepared.

Bis[bis(diphenylphosphino)ethane]bis(dinitrogen)hydridotungsten Hydrogendichloride, $[WH(N_2)_2(dpe)_2]HCl_2$.—Tetrahydrofuran (50 cm^3) and HCl (2 mol) were condensed at -196 °C onto *trans*-$[W(N_2)_2(dpe)_2]$ (1·0 g) and the mixture was warmed to room temperature. A yellow solution was formed which was allowed to stand for 12 h when bright yellow *crystals* formed which were filtered off, washed with ether, and dried (0·55 g, 51%). The $^{15}N_2$ derivative was similarly prepared.

Bis[bis(diphenylphosphino)ethane]dichlorodi- or tetrahydridomolybdenum, $[MoH_nCl_2(dpe)_2]$ (n = 2 or 4).—Tetrahydrofuran (50 cm^3) and hydrogen chloride (2·5 mol) were condensed at -196 °C onto *trans*-$[Mo(N_2)_2(dpe)_2]$ (0·4 g) and the mixture was allowed to warm to room temperature when dinitrogen (18·8 cm^3, 1·99 mol. equiv.) was evolved with the formation of a yellow solution. The solution was stirred for 8 h and then concentrated to half volume *in vacuo*. Addition of ether (20 cm^3) gave a yellow solid which crystallised from tetrahydrofuran–ether as yellow *prisms* (0·3 g, 73%).

trans-*Bis[bis(diphenylphosphino)ethane](chloro)[hydrazido-(2−)N]tungsten Tetraphenylborate*, trans-$[WCl(N_2H_2)(dpe)_2]BPh_4$.—(*a*) To $[WCl(N_2H_2)(dpe)_2]$ (0·11 g) in dichloromethane (10 cm^3) was added a filtered solution of $NaBPh_4$ (0·1 g) in CH_2Cl_2–thf (20 cm^3 of 1 : 1 mixture). A cloudy precipitate rapidly formed and after the solution had been allowed to stand for 1 h it was filtered, taken to dryness *in vacuo*, and the residual solid was extracted with CH_2Cl_2 (20 cm^3). After filtration of a white solid, a yellow-orange solution resulted to which ether was added to give, after 10 h, orange-yellow *needles* which were filtered off, washed with ether, and dried (0·88 g, 89%). The bromo-analogue was similarly prepared.

trans-*Bis[bis(diphenylphosphino)ethane](chloro)[hydrazido-(2−)N]tungsten Perchlorate*, trans-$[WCl(N_2H_2)(dpe)_2]ClO_4$ followed procedure (*a*) above using $[WCl_2(N_2H_2)(dpe)_2]$ (0·1 g), CH_2Cl_2–thf (60 cm^3; 1 : 1 mixture), and $LiClO_4$ (0·1 g); yield 0·06 g (60%).

trans-*Bis[bis(diphenylphosphino)ethane](chloro){hydrazido-(2−)N[²H]}tungsten Tetraphenylborate*, trans-$[WCl(N_2{}^2H_2)(dpe)_2]BPh_4$.—*trans*-$[WCl(N_2H_2)(dpe)_2]BPh_4$ (0·1 g) was dissolved in dry deuteriochloroform (20 cm^3) and ^2H_2O (0·3 cm^3) was added under dinitrogen. The solution was stirred vigorously for 1 h and then taken to dryness *in vacuo*; dry ether (10 cm^3) was added to it to give a yellow *solid* which was filtered off, washed with ether, and dried. The perchlorate was similarly prepared.

trans-*Bis[bis(diphenylphosphino)ethane](bromo)[hydrazido-(2−)N]molybdenum Tetrafluoroborate*, trans-$[MoBr(N_2H_2)(dpe)_2]BF_4$.—To $[MoBr_2(N_2H_2)(dpe)_2]$ (1 g) in suspension in CH_2Cl_2 (50 cm^3) was added $[NEt_4]BF_4$ (1 g) in CH_2Cl_2–MeOH (20 cm^3; 1 : 1 mixture). The mixture was stirred for 3 h when a yellow precipitate was deposited which was filtered off, washed with CH_2Cl_2 (2 × 10 cm^3) and ether (2 × 20 cm^3), and dried; it crystallised from dimethylformamide–ether as yellow-brown *prisms* containing 1 mol. equiv. of dimethylformamide of crystallisation (0·6 g, 60%).

trans-*Chlorotetrakis(dimethylphenylphosphine)[hydrazido-(2−)N]tungsten Chloride*, trans-$[WCl(N_2H_2)(PMe_2Ph)_4]Cl$.—Dichloromethane (50 cm^3) and HCl (6 mol. equiv.) were condensed at $-196°$ onto *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (1·01 g) and the mixture allowed to warm to 0 °C when a yellow solution formed with evolution of dinitrogen (26·4 cm^3, 1·08 mol. equiv.). The solvent was removed *in vacuo* and ether was added to give a yellow oil and a yellow-orange solution which was decanted and, after being filtered, gave orange-yellow *prisms* on standing which contained one dichloromethane of crystallisation (0·5 g, 52%). The deuterio- and bromo-analogues were prepared similarly using ^2HCl and HBr.

Conversion of $[WH(N_2)_2(dpe)_2]HCl_2$ *into* $[WH_2Cl_2(dpe)_2]$.—Methanol or thf (60 cm^3) and HCl (4 mol. equiv.) were condensed *in vacuo* at -196 °C onto $[WH(N_2)_2(dpe)_2]HCl_2$ (0·3 g) in a glass vessel carrying a break-seal and the vessel was sealed by fusion. After the vessel had been heated at 70 °C for 2 h a yellow precipitate was obtained and dinitrogen (11·2 cm^3, 1·85 mol. equiv.) was recovered after opening the break-seal. The yellow *crystals* were filtered

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[18] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531.

off, washed with ether (20 cm³), and dried (0·25 g, 86%). A repeat of this reaction without HCl gave identical products in similar yields.

Reaction of $[\mathrm{WCl_2(N_2H_2)(dpe)_2}]$ (I) *with* $\mathrm{CH_3COCl}$.—To (I) (0·5 g) in thf (50 cm³) was added distilled $\mathrm{CH_3COCl}$ (10 cm³) and the mixture was heated under reflux for 6 h. A pink precipitate of $[\mathrm{WCl_2\{NNH(COCH_3)\}(dpe)_2}]$ was deposited and this was filtered off, washed with ether, and dried (0·4 g, 75%). The same product resulted when acetic anhydride was used instead of $\mathrm{CH_3COCl}$.

Reaction of $[\mathrm{WCl_2(N_2H_2)(dpe)_2}]$ (I) *with* $\mathrm{AgClO_4}$—With (I) (0·06 g) and $\mathrm{AgClO_4}$ (0·08 g), in a glass tube carrying a break-seal, was condensed *in vacuo* at −196 °C thf (15 cm³) and the tube was sealed by fusion. When the tube was warmed a rapid evolution of gas occurred with deposition of a black solid which was not identified but contained silver metal. The gas was removed by opening the break-seal (1·37 cm³, 1·03 mol. equiv.) and was shown by its mass spectrum to be dinitrogen with a small amount of dihydrogen. Presumably the dihydrogen of the $\mathrm{N_2H_2}$ ligand was liberated as $\mathrm{H^+}$.

Preparation of the Diazene Complexes using Aqueous Acid.—Aqueous hydrogen bromide (12 cm³, 48% solution) was added to *trans*-$[\mathrm{W(N_2)_2(dpe)_2}]$ (5·4 g) in thf (75 cm³). Immediate reaction ensued with vigorous effervescence and the resulting red solution was stirred for 4 h. The solution, concentrated to one-third volume *in vacuo*, gave a brown precipitate (3·7 g, 61%) which was removed, washed with water and ether, and dried *in vacuo*. It was identical (i.r., m.p.) with $[\mathrm{WBr_2(N_2H_2)(dpe)_2}]$ prepared under anhydrous conditions. Its molybdenum analogue was similarly prepared in 57% yield.

Electrochemical Oxidation of $[\mathrm{WBr_2(N_2H_2)(dpe)_2}]$ (A) *and* $[\mathrm{WBr_2(^{15}N_2H_2)(dpe)_2}]$ (B) (*with Dr. C. M. Elson*).—In both experiments the tungsten compound (0·005 g) was dissolved in $\mathrm{CH_2Cl_2}$–MeOH (5 cm³ of 10 : 1 mixture) which was 0·1M in $[\mathrm{Et_4N}]\mathrm{Cl}$. The electrochemical apparatus was as previously described [19] but with a 5 cm³ Luggin cell which could be made gas-tight. The sample solution was degassed and saturated with argon before use. (A) Was non-reducible over the range +0·5 to −1·6 V (*versus* S.C.E.). At −1·6 V the electrolyte was discharged at the dropping mercury electrode. Both (A) and (B) were irreversibly oxidised $[n(1 - a) \simeq 0{\cdot}4]$ on a platinum electrode at +0·68 V and the electrode process was diffusion controlled. Controlled-potential oxidations of (A) and (B) were carried out at +0·85 V and any gases evolved were led into an evacuated flask mounted above the solution and were analysed by mass spectrometry. The oxidation of (A) proceeded to negligible background current ($i <$ 100 μA) and gave dinitrogen plus dihydrogen. Oxidation of (B) gave $\mathrm{^{15}N_2}$ confirming that the source of dinitrogen in the oxidation of (A) was the $\mathrm{N_2H_2}$ group. The possibility that at least some of the dihydrogen produced was from reduction of solvent at the counter electrode of the Luggin cell could not be ruled out. In a similar experiment using $[\mathrm{MoBr_2(N_2H_2)(dpe)_2}]$, no wave corresponding to reduction of the metal complex was observed.

Reaction of $[\mathrm{WX_2(N_2H_2)(dpe)_2}]$ (X = Cl *or* Br) *with* $\mathrm{NaBH_4}$.—Ethanol (70 cm³) was distilled onto the tungsten compound (0·3 g) and sodium tetrahydroborate (0·1 g) *in vacuo*, then the vessel was filled with argon. All subsequent work was under argon. The mixture was stirred overnight, then about one-third of the solvent and other volatile materials were distilled into 0·1N-sulphuric acid (5 cm³). The residue deposited yellow $[\mathrm{WH_4(dpe)_2}]$ identical with an authentic specimen (i.r. and m.p.) [20] (Found: C, 62·1; H, 5·4. Calc. for $\mathrm{C_{52}H_{52}P_4W}$: C, 61·7; H, 5·1%). The sulphuric acid solution gave negative tests for ammonia (indophenol test) and hydrazine (*p*-dimethylaminobenzaldehyde test) as did the mother liquors and washings from the solid product.

Reaction of $[\mathrm{MoBr_2(N_2H_2)(dpe)_2}]$ *with* $\mathrm{NaBH_4}$.—This was performed using 0·88 g of the molybdenum compound and 0·3 g of sodium tetrahydroborate exactly as its tungsten analogue above. No ammonia or hydrazine was found and the hydride product $[\mathrm{MoH}_n\mathrm{(dpe)_2}]$ (n = 2 or 4) was identified by its i.r. spectrum [13] (Found: C, 70·4; H, 5·9. Calc. for $\mathrm{C_{52}H_{52}P_4Mo}$: C, 69·7; H, 5·8%).

Reaction of $[\mathrm{MoH}_n\mathrm{(dpe)_2}]$ *with Dinitrogen.*—Dinitrogen was passed through a benzene (50 cm³) solution of the hydride (0·8 g) for 14 days. The solvent was removed *in vacuo* and hexane added to yield a precipitate of *trans*-$[\mathrm{Mo(N_2)(dpe)_2}]$ mixed with the original hydride (both identified by i.r. spectroscopy) (Found: N, 2·3. Calc. for $\mathrm{C_{52}H_{48}N_4P_4Mo}$: N, 5·9%).

Reaction of $[\mathrm{WCl_2(N_2H_2)(dpe)_2}]$ *with Tin*(II) *Chloride.*—Tetrahydrofuran (50 cm³) was distilled onto the tungsten complex (0·2 g) and tin(II) chloride (0·2 g) *in vacuo*. After 1 h with stirring at 20 °C the solution was filtered, concentrated to one-third volume *in vacuo*, and trans-*bis*[*bis*(*diphenylphosphino*)*ethane*](*chloro*)[*hydrazido*-(2−)N]*tungsten trichlorostannate*(II) crystallised from the filtrate by addition of dry ether (20 cm³). This recrystallised from thf–ether as fine yellow needles whose i.r. spectrum (Nujol) showed the typical ν(NH) pattern of bands at 3300, 3210, and 3025 cm⁻¹ of the $[\mathrm{WCl(N_2H_2)(dpe)_2}]^+$ cation and was a 1 : 1 electrolyte in nitrobenzene (Λ_m, 19 Ω^{-1} cm² mol⁻¹ in *ca.* 10^{-3}M solution) (Found: C, 49·1; H, 4·2; Cl, 10·9; N, 1·9. $\mathrm{C_{52}H_{50}Cl_4N_2P_4SnW}$ requires C, 49·2; H, 3·8; Cl, 11·2; N, 2·2%).

Reactions of $[\mathrm{MoBr_2(N_2H_2)(dpe)_2}]$ *with Triethylamine.*—(a) *Under argon.* Tetrahydrofuran (70 cm³) was condensed in a vacuum system onto $[\mathrm{MoBr_2(N_2H_2)(dpe)_2}]$ (0·5 g) followed by triethylamine (0·3 g), and the reaction vessel was filled with argon and warmed to 20 °C. The resultant dark brown-red solution was stirred for 12 h when it became greenish yellow. It was filtered under argon, concentrated to one-third volume *in vacuo*, and argon-saturated ether (20 cm³) was added to precipitate a yellow solid (0·2 g). This solid contained $[\mathrm{Mo(N_2)(dpe)_2}]$ and $[\mathrm{NEt_3H}]\mathrm{Br}$ (i.r.) and was washed with water, dried, and thrice recrystallised from thf–$\mathrm{Et_2O}$ to give slightly impure *trans*-$[\mathrm{Mo(N_2)_2(dpe)_2}]$ (Found: N, 4·3. Calc. for $\mathrm{C_{52}H_{48}N_4P_4Mo}$: N, 5·9%).

(b) *Under dinitrogen.* The above experiment repeated under dinitrogen gave, from 0·5 g of the diazene complex, 0·3 g of the pure dinitrogen complex (Found: N, 5·6%).

(c) *Under carbon monoxide.* Experiment (a), repeated under carbon monoxide, gave solid products showing strong i.r. bands at 1975 cm⁻¹, characteristic of *trans*-$[\mathrm{Mo(N_2)(dpe)_2}]$ and at 1815 cm⁻¹. On repeated crystallisation (thf–$\mathrm{Et_2O}$) there was no separation but the 1815 cm⁻¹ band split into two bands at 1780 and 1855 cm⁻¹, consistent with the isomerisation of a *trans*-$[\mathrm{Mo(CO)_2(dpe)_2}]$

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complex [ν(CO) = 1815 cm^{-1}] into its known *cis*-isomer [21,22] in solution. The product which thus appears to be a mixture of *trans*-[Mo(N$_2$)$_2$(dpe)$_2$] and *trans*-[Mo(CO)$_2$(dpe)$_2$] was not further investigated.

Attempted Reduction of Diazene and Hydrazido(2—) *Complexes*.—The appropriate reducing agent was added in large excess to the diazene or hydrazido(2—) complex ($\approx$0·1 g) in a suitable solvent (where necessary). The gases evolved were swept through 0·1N-sulphuric acid (5 cm^3) in a stream of argon. When reaction was complete, an excess of aqueous potassium hydroxide was added to the reaction mixture and about half its volume distilled into the sulphuric acid. Organic solvents were distilled from the trap and the resultant sulphuric acid solution was tested for ammonia (indophenol) and hydrazine (*p*-dimethylaminobenzaldehyde). The residual solution was also tested for hydrazine. In no case was a significant increase over background traces found.

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