Diazenido-complexes of Molybdenum and Tungsten

By **Joseph Chatt,* Alan J. Pearman,** and **Raymond L. Richards,** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ

The diazenido-complexes $[MX(N_2H)(dppe)_2]$ (M = Mo or W; X = F, Cl, or Br; dppe = $Ph_2PCH_2CH_2PPh_2$) have been prepared by treatment of the corresponding diazene, $[MX_2(NH{:}NH)(dppe)_2]$, or hydrazido(2−), $[MF(N{\cdot}NH_2)(dppe)_2][BF_4]$, complexes with triethylamine or aqueous potassium carbonate. With 1 mol of anhydrous acid they regenerate the parent diazene or hydrazido(2−) complexes. The complex $[WBr(N_2H)(dppe)_2]$ reacts with organic bromides to give the known complexes $[WBr_2(N_2HR)(dppe)_2]$ (R = Me or MeCO). The N_2H ligand is not displaced by trialkylphosphines but nitrogen mono-oxide displaces it quantitatively to give the nitrosyl complexes $[MX(NO)(dppe)_2]$. Spectroscopic data for these complexes and their ^{15}N and ^2H derivatives are described.

WE recently briefly described the protonation and reduction of co-ordinated dinitrogen to ammonia and the preparation of complexes of ligands which are intermediate stages in the route from dinitrogen to ammonia.[1,2] The first stage is monoprotonation of ligating dinitrogen to give N_2H, the hitherto unknown diazenido or iminonitrosyl ligand.[2] Complexes of this ligand were obtained only in an impure state by direct protonation of ligating dinitrogen, but are readily obtained pure by the abstraction of a proton by base from diazene or hydrazido(2−) complexes,[3] resulting from the diprotonation of ligating dinitrogen. Here we describe this preparation of diazenido-complexes and some of their physical and chemical properties.

RESULTS AND DISCUSSION

The tungsten complexes $[WX_2(NH{:}NH)(dppe)_2]$ (X = Cl or Br; dppe = $Ph_2PCH_2CH_2PPh_2$) or $[WF(N{\cdot}NH_2)(dppe)_2][BF_4]$ [4] reacted in methanol solution with an excess of triethylamine or aqueous potassium carbonate, under dinitrogen or *in vacuo*, to deposit yellow crystals of the complexes $[WX(N_2H)(dppe)_2]$ (X = F, Cl, or Br), *e.g.* equation (1). Under similar conditions, the complexes $[MoBr_2(NH{:}NH)(dppe)_2]$ or $[MoF(N{\cdot}NH_2)(dppe)_2][BF_4]$ [5] regenerated the parent dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$ as a major product, but when they were treated in tetrahydrofuran (thf) suspension with exactly 1 mol of NEt_3 *in vacuo* the diazenido-complexes $[MoX(N_2H)(dppe)_2]$ (X = Br or F) were formed. Some ^{15}N and ^2H derivatives were similarly prepared and analytical data, *etc.*, for these complexes are shown in Table 1.

$$[WBr_2(NH{:}NH)(dppe)_2] + NEt_3 \longrightarrow [WBr(N_2H)(dppe)_2] + [NEt_3H]Br \quad (1)$$

The complexes are characterised by a strong sharp band at *ca.* 1 880 cm^{-1} (M = W) or *ca.* 1 940 cm^{-1} (M = Mo) which, since it shifts appropriately in the tungsten ^{15}N analogue (Table 1), is assigned to an N–N stretching mode. We were able to detect the N–H (N–^2H) i.r. absorptions and the N–H n.m.r. resonance only in the fluoride complexes (Tables 1 and 2). In the other halide complexes, perhaps because of an electronic effect, the i.r. (NH) absorption may be weak and broad and the (NH) n.m.r. resonance may coincide with other resonances or be very broad, so that neither was observed. Nevertheless, the otherwise similar spectral data for the series and the following chemical evidence establish that all these halido-complexes contain the diazenido-ligand. Thus the pyrolysis of $[WBr(N_2{}^2H)(dppe)_2]$ gave ^2HH together with H_2 and a trace amount of $^2H_2$. Also the tungsten N_2H complexes were quantitatively converted into the parent diazene complexes [3] by 1 mol of halogen acid [equation (2)], while treatment with HBF_4 yielded the hydrazido(2−) salt [equation (3)]. The complex

$$[WX(N_2H)(dppe)_2] + HX \xrightarrow[\text{thf}]{\text{vacuum}} [WX_2(NH{:}NH)(dppe)_2] \quad (2)$$
$$(X = \text{Cl or Br})$$

$$[WX(N_2H)(dppe)_2] + [Et_2OH][BF_4] \xrightarrow{\text{thf}} [WX(N{\cdot}NH_2)(dppe)_2][BF_4] \quad (3)$$
$$(X = \text{Cl, Br, or F})$$

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[1] J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39.

[2] J. Chatt, A. J. Pearman, and R. L. Richards, *J. Organometallic Chem.*, 1975, **101**, C45.

[3] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074.

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

[5] M. Hidai, T. Tatsumi, T. Hikita, T. Kodoma, and Y. Uchida, *Proc. 7th Internat. Conf. Organometallic Chem.*, Venice, 1975, p. 235.

$[MoF(N_2H)(dppe)_2]$ gave the parent hydrazido(2−) complex $[MoF(N{\cdot}NH_2)(dppe)_2][BF_4]$ on treatment with 1 mol of $[Et_2OH][BF_4]$, but its bromide analogue, while giving mainly its parent diazene complex with HBr, also underwent a side reaction with evolution of dinitrogen to yield $[MoBr_2(dppe)_2]$.

TABLE 1

Molybdenum and tungsten complexes

Complex	M.p. $(\theta_c/°C)$	Analyses (%) [a] C	H	N	Halogen	I.r. data (cm^{-1}) [b] $\nu(N{-}Z)$ [c]	$\nu(M{-}Cl)$ [d]	M [a,e]	Λ / $S\ cm^2\ mol^{-1}$	Appearance
$[WF(N{\cdot}NH_2)(dppe)_2]$-$[BF_4]$	254—258	55.8 (55.9)	4.6 (4.5)	2.5 (2.5)		3 255w [f] 3 335w [f]			90 [g]	Yellow crystals
$[WF(N_2H)(dppe)_2]$	decomp. >176	59.5 (60.7)	4.9 (4.8)	2.6 (2.7)		1 820m 3 365w [f] 2 495w [h]		828 (1 029)	32 [i]	Yellow solid
$[WF(NO)(dppe)_2]$	decomp. >174	60.6 (60.6)	4.8 (4.7)	1.4 (1.4)		1 510s		1 048 (1 030)		Yellow crystals
$[WCl(N_2H)(dppe)_2]$	decomp. >152	59.5 (59.8)	4.8 (4.7)	2.7 (2.7)	3.3 (3.4)	1 885s 1 855mw	260	753 (1 045)	15 [e]	Orange-yellow crystals
$[WCl(^{15}N_2H)(dppe)_2]$	decomp. >146	59.3 (59.6)	4.9 (4.7)	2.8 (2.9)		1 820s [j] 1 790mw [j]	265			Orange-yellow crystals
$[WCl(NO)(dppe)_2]$	247—251	59.6 (59.7)	4.8 (4.6)	1.3 (1.3)		1 530s	263	1 063 (1 046)		Yellow crystals
$[WCl(N{\cdot}NH_2)(dppe)_2]$-$[BF_4]{\cdot}thf$	decomp. >221	55.8 (55.8)	4.6 (4.9)	2.5 (2.3)		3 250w [f] 3 345w [f]	285		81 [g]	Pale brown solid
$[WBr(N_2H)(dppe)_2]$	decomp. >180	57.0 (57.3)	4.7 (4.5)	2.6 (2.6)	7.2 (7.3)	1 880s 1 850mw 1 890s [i]		731 (1 090)	15 [e]	Orange-yellow crystals
$[WBr(N_2{}^2H)(dppe)_2]$	decomp. >179	57.3 (57.3)	4.7 (4.6)	2.5 (2.6)		1 880s 1 850mw				Orange-yellow crystals
$[WBr(N_2H)(dmtpe)_2]$	decomp. >141	59.4 (60.0)	5.4 (5.5)	2.3 (2.3)		1 860s		835 (1 202)	21 [e] 23 [i]	Orange-yellow crystals
$[WBr(NO)(dppe)_2]$	260—264	57.3 (57.3)	4.9 (4.4)	1.3 (1.3)	7.2 (7.3)	1 520s		1 072 (1 091)		Yellow crystals
$[WBr(N{\cdot}NH_2)(dppe)_2]$-$[BF_4]{\cdot}thf$	decomp. >209	53.5 (53.8)	4.8 (4.7)	2.3 (2.2)		3 255w [f] 3 342w [f]			76 [g]	Pale brown solid
$[WBr_2(NH{\cdot}NCOMe)$-$(dppe)_2]$	decomp. >241	53.8 (53.5)	4.3 (4.3)	2.2 (2.3)		2 760w [f] 1 705s (C=O)			8 [i]	Pink crystals
$[MoF(N{\cdot}NH_2)(dppe)_2]$-$[BF_4]$	250—256	60.1 (60.7)	5.2 (4.9)	2.7 (2.7)		3 255w [f] 3 340w [f]			80 [g]	Orange crystals
$[MoF(N_2H)(dppe)_2]$	decomp. >151	65.9 (66.4)	5.4 (5.3)	2.8 (3.0)		1 915s [f] 3 357w [f] 2 490w [f]		692 (941)	11 [e]	Yellow solid
$[MoF(NO)(dppe)_2]$	decomp. >246	66.0 (66.3)	5.2 (5.1)	1.5 (1.5)		1 535s		927 (942)		Yellow crystals
$[MoBr(N_2H)(dppe)_2]$	decomp. >214	62.0 (62.4)	4.9 (4.9)	2.8 (2.8)	8.0 (8.0)	1 940s 1 905mw		719 (1 002)	13 [e]	Yellow crystals
$[MoBr(NO)(dppe)_2]$	223—226	62.3 (62.3)	4.9 (4.8)	1.4 (1.4)	8.0 (8.0)	1 550s		1 008 (1 003)		Yellow crystals

s = Strong, m = medium, and w = weak.

[a] Calculated values are given in parentheses. [b] Nujol mulls unless otherwise stated. [c] Z = N or O. [d] M = Mo or W. [e] In *ca.* 10^{-3} mol dm^{-3} $C_2H_4Cl_2$ solution. [f] $\nu(NH)$. [g] In *ca.* 10^{-3} mol dm^{-3} $MeNO_2$ solution. [h] $\nu(N^2H)$ in deuterio-analogue. [i] In *ca.* 10^{-3} mol dm^{-3} CH_2Cl_2 solution. [j] $\nu(^{15}N^{15}N)$.

Acetyl and methyl halides reacted under carefully anhydrous conditions with the tungsten diazenido-derivatives to give the known [6] organonitrogen complexes [equations (4) and (5)]. These properties are

$$[WX(N_2H)(dppe)_2] + MeCOX \longrightarrow [WX_2(NHNCOMe)(dppe)_2] \quad (4)$$
$$(X = Cl \text{ or } Br)$$

$$[WBr(N_2H)(dppe)_2] + MeBr \longrightarrow [WBr\{N_2(H)Me\}(dppe)_2]Br \quad (5)$$

therefore consistent with the formulation of all these complexes as containing the N_2H ligand.

The diazenido-group is formally analogous to nitrosyl, consequently it is smoothly and quantitatively displaced by nitrogen mono-oxide in benzene, dichloromethane, or thf solution at 20 °C, with evolution of 1 mol of dinitrogen. The fate of the hydrogen is not certain but it probably reacts with a second mol of NO (2 mol are necessary for the reaction to reach completion) [equation (6)]. A ^{15}N-labelling experiment showed that the evolved

$$[MX(N_2H)(dppe)_2] + 2NO \longrightarrow N_2 + [MX(NO)(dppe)_2] + \text{' HNO '} \quad (6)$$

dinitrogen was entirely from the diazenido-ligand. Under similar conditions, NO did not displace dinitrogen from the diazene or from the dinitrogen complexes.

The above reactions show that the N_2H group is an 'odd-electron' ligand like NO. The high value of $\nu(N_2)$ and effective atomic number of the metal suggests that the diazenido-ligand is most probably present as a linear three-electron donor corresponding to so-called

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[6] J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 444; J. Chatt, G. A. Heath, G. J. Leigh, and A. A. Diamantis, *J. Organometallic Chem.*, 1975, **84**, C11.

NO^+, as has been postulated for the analogous ligands in $[RuCl(N_2R)(bipy)_2][PF_6]_2$ (R = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$; bipy = 2,2′-bipyridine) which also have very high ν(N_2) values (at *ca.* 2 080 cm^{-1}).[7]

TABLE 2

N.m.r. spectra

Complex	Resonance[a] (p.p.m. ± 0.02)	Assignments and coupling constants[b]
(*a*) ^1H Data[c]		
$[WF(N{\cdot}NH_2)(dppe)_2][BF_4]$	2.50—2.85 (8)	P–CH_2 (m)
	6.86—7.48 (40)	P–Ph_2 (m)
	4.00[d] (2)	N–H_2 (br, s)
$[WF(N_2H)(dppe)_2]$	2.31—2.91 (8)	P–CH_2 (m)
	6.73—7.53 (40)	P–Ph_2 (m)
	9.60[d] (1)	N–H (br s)
$[WF(NO)(dppe)_2]$	2.30—2.96 (8)	P–CH_2 (m)
	6.92—7.50 (40)	P–Ph_2 (m)
$[WCl(N_2H)(dppe)_2]$	2.34—3.00 (8)	P–CH_2 (m)
	6.74—7.64 (40)	P–Ph_2 (m)
$[WCl(NO)(dppe)_2]$	2.11—2.90 (8)	P–CH_2 (m)
	6.90—7.46 (40)	P–Ph_2 (m)
$[WBr(N_2H)(dppe)_2]$	2.45—3.15 (8)	P–CH_2 (m)
	6.80—7.70 (40)	P–Ph_2 (m)
$[WBr(N_2H)(dmtpe)_2]$	2.04 and 2.08 (24)	*m*–CH_3 (s)
	2.22—3.02 (8)	P–CH_2 (m)
	6.78—7.30 (32)	aryl–H (m)
$[WBr(NO)(dppe)_2]$	2.24—2.98 (8)	P–CH_2 (m)
	6.94—7.40 (40)	P–Ph_2 (m)
$[WBr_2\{NHN(COMe)\}(dppe)_2]$	1.33 (3)	NCO–CH_3 (s)
	2.77—3.35 (8)	P–CH_2 (m)
	7.01—7.45 (40)	P–Ph_2 (m)
	11.71[d] (1)	N–H (br, s)
$[MoF(N{\cdot}NH_2)(dppe)_2][BF_4]$	2.44—2.95 (8)	P–CH_2 (m)
	6.88—7.50 (40)	P–Ph_2 (m)
	5.11[d] (2)	N–H (br, s)
$[MoF(NO)(dppe)_2]$	2.44—2.64 (8)	P–CH_2 (m)
	6.96—7.44 (40)	P–Ph_2 (m)
$[MoBr(NO)(dppe)_2]$	2.26—2.88 (8)	P–CH_2 (m)
	6.96—7.38 (40)	P–Ph_2 (m)
(*b*) ^{31}P Data[e]		
$[WF(N{\cdot}NH_2)(dppe)_2][BF_4]$[f]	−105.25	P–Ph_2 (d) with ^{183}W satellites ^2J(FWP) 41.5 J(WP) 288.1
$[MoF(N{\cdot}NH_2)(dppe)_2][BF_4]$[f]	−94.75	P–Ph_2 (d) ^2J(FMoP) 31.7
$[WBr(N_2H)(dmtpe)_2]$[g]	−104.67	P-$(C_6H_4Me\text{-}m)_2$ (s) with ^{183}W satellites J(WP) 300.3
(*c*) ^{19}F Data[h]		
$[WF(N{\cdot}NH_2)(dppe)_2][BF_4]$	−156.33 (4)	B–F_4 (s)
	−172.21 (1)	W–F (q), ^2J(PWF) 40.9
$[MoF(N{\cdot}NH_2)(dppe)_2][BF_4]$[f]	−156.29 (4)	B–F_4 (s)
	−160.14 (1)	Mo–F (q) ^2J(PMoF) 31.7

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

[a] Integration values are given in parentheses. [b] Coupling constants in Hz ± 0.1. [c] In $C^2H_2Cl_2$ solution, relative to $SiMe_4$ unless otherwise stated. [d] Disappeared on addition of ^2H_2O. [e] Relative to trimethyl phosphite, negative values to high field; measurements made in Fourier-transform mode with proton decoupling. [f] In MeOH solution. [g] In CH_2Cl_2 solution. [h] Relative to $CFCl_3$, negative values to high field; measurement made in Fourier-transform mode.

Probably the N_2H ligand receives more back donation into its π* orbitals from the low-valent uncharged M (M = Mo or W) atom than the N_2R group does from the ruthenium atom in its positively charged complex, thus ν(N_2) for N_2H is lower than for N_2R. The high degree of back donation from M (M = Mo or W) is particularly notable in the nitrosyl complexes where ν(NO) is so low as to be in the region observed when NO is a one-electron donor. The lowest values of ν(N_2) and ν(NO) in the molybdenum and tungsten series are observed for the fluoride complexes (Table 1) presumably because the π-electron releasing properties of fluoride induce the maximum back-donating capacity from the metal atoms.

A number of other reactions of the diazenido-complexes were also studied in attempts to oxidise or reduce the complexes and to substitute the co-ligands of the N_2H group. The course of oxidation of the diazenido-complexes varied according to the metal. Thus with anhydrous iron(III) chloride in thf $[MoBr(N_2H)(dppe)_2]$ gave the salt $[MoBrCl(dppe)_2][FeCl_4]$ and 1 mol of dinitrogen. Presumably the hydrogen atom was associated with an anion such as chloride or $FeCl_4^-$ and was not detected. The tungsten analogue did not react cleanly, however, 0.75 mol of N_2 being evolved, but no pure solid product could be isolated. Sodium dimethyldithiocarbamate, thiols, and tertiary phosphines did not react with the complexes in thf, even under reflux. On treatment with sodium tetrahydroborate, both the molybdenum and tungsten diazenido-complexes gave the corresponding tetrahydrido-complexes, but neither hydrazine nor ammonia were detected.

It seems very likely that the reactions in which co-ordinated dinitrogen is protonated and reduced to ammonia[1] occur in a stepwise fashion and that N_2H complexes result from the addition of the first proton. The second step is then a rapid protonation of the N_2H group at either nitrogen atom, depending on the final co-ordination number of the metal.[3,8] The basic character of the N_2H ligand results in its rapid further protonation but prevents the preparation of its complexes by addition of 1 mol of halogen acid to the bis-(dinitrogen) complexes. Mixtures of N_2H, N_2H_2, and starting dinitrogen complexes result and the only clean preparation of the diazenido-complexes is the deprotonation method we have described.

With the particular combination of halide and chelating phosphine ligands utilised here, protonation beyond the N_2H_2 stage does not occur at 20 °C.[2] However, when unidentate phosphines and oxygen-donor solvents or anions are employed reduction to ammonia is achieved[1] and details of this work will be reported separately.

EXPERIMENTAL

Air-sensitive compounds were handled under pure dinitrogen and gas handling involved standard vacuum techniques. All solvents were rigorously dried and distilled under dry dinitrogen.

A Jeol P.S. 100 spectrometer was used for n.m.r. measure-

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[7] W. L. Bowden, W. F. Little, and T. J. Meyers, *J. Amer. Chem. Soc.*, 1973, **95**, 508.

[8] B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J.C.S. Chem. Comm.*, 1972, 34.

ments and i.r. spectra were recorded on Unicam SP 1200, Grubb–Parsons D.M.4, and Unicam SP 2000 instruments. Mass spectra were obtained on 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 an Electrothermal melting-point apparatus. Analyses were by Mr. and Mrs. A. G. Olney of these laboratories, and those of new complexes are given in Table 1.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromodiazenidotungsten*, $[\mathrm{WBr(N_2H)(dppe)_2}]$.—To a solution of $[\mathrm{WBr_2(NH{:}NH)(dppe)_2}]$ (0.44 g) in methanol (40 cm^3) was added triethylamine (0.3 cm^3) with stirring. A yellow solid was rapidly produced, and the mixture was stirred for 2 h. The solid was then filtered, washed with water, methanol, and diethyl ether, and dried (0.33 g, 80%). Aqueous potassium carbonate can also be used as the base. The fluoro-, chloro-, dmtpe- [dmtpe = $(m\text{-}\mathrm{MeC_6H_4})_2\mathrm{PCH_2CH_2P(C_6H_4Me}\text{-}m)_2$], and $^{15}\mathrm{N_2H}$-derivatives were similarly prepared using the appropriate starting materials. The deuterio-analogues were obtained by exchange with $\mathrm{C^2H_3O^2H}$.

Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with* HBr.—Tetrahydrofuran (35 cm^3) and HBr (1 mol) were condensed *in vacuo* at −196 °C on to $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.23 g). The mixture was then warmed to 20 °C with stirring, during which time a red solution was produced, followed by precipitation of a pale brown solid. The mixture was stirred for 2 h and the solid then filtered off, washed with diethyl ether, and dried (0.23 g, 96%). The solid was identified as $[\mathrm{WBr_2(NH{:}NH)(dppe)_2}]$ (i.r. and m.p.) (Found: C, 53.7; H, 4.8; N, 2.3. $\mathrm{C_{52}H_{50}Br_2N_2P_4W}$ requires C, 53.4; H, 4.3; N, 2.4%).

Reaction of $[\mathrm{WCl(N_2H)(dppe)_2}]$ *with* HCl.—The reaction was performed as for the bromo-analogue; $[\mathrm{WCl_2(NH{:}NH)(dppe)_2}]$ was isolated in 91% yield and identified by its i.r. spectrum and m.p. (Found: C, 57.6; H, 4.6; N, 2.6. $\mathrm{C_{52}H_{50}Cl_2N_2P_4W}$ requires C, 57.7; H, 4.7; N, 2.6%).

Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with* $[\mathrm{Et_2OH}][\mathrm{BF_4}]$.—An excess of $[\mathrm{Et_2OH}][\mathrm{BF_4}]$ was added to a suspension of $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.36 g) in tetrahydrofuran (35 cm^3) *in vacuo*. There was an immediate reaction giving a red-orange solution, which was stirred for 12 h, during which time a pale brown precipitate of $[\mathrm{WBr(N{\cdot}NH_2)(dppe)_2}][\mathrm{BF_4}]$ was deposited. This was filtered off, washed with diethyl ether, and dried (0.29 g, 74%). The fluoro- and chloro-analogues reacted similarly to give $[\mathrm{WF(N{\cdot}NH_2)(dppe)_2}][\mathrm{BF_4}]$ and $[\mathrm{WCl(N{\cdot}NH_2)(dppe)_2}][\mathrm{BF_4}]$ respectively.

Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with* MeBr.—Benzene (40 cm^3) and MeBr (1.2 mol) were condensed *in vacuo* at −196 °C on to $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.25 g) and the mixture was warmed to 20 °C and stirred for 24 h with irradiation from two 150 W tungsten lamps. The mixture deposited pale brown $[\mathrm{WBr\{N_2(H)Me\}(dppe)_2}]\mathrm{Br}$ (0.17 g, 63%), identical with the product obtained by reaction of MeBr with $[\mathrm{W(N_2)_2(dppe)_2}]$, followed by treatment with HBr [6] (i.r., n.m.r., and m.p.). The complex is a 1 : 1 electrolyte in nitromethane (Λ 82 S cm^2 mol^{-1} in *ca.* 10^{-3} mol dm^{-3} solution) (Found: C, 53.5; H, 4.4; N, 2.3. $\mathrm{C_{53}H_{52}Br_2N_2P_4W}$ requires C, 53.7; H, 4.4; N, 2.4%).

Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with* MeCOBr.—Tetrahydrofuran (40 cm^3) and MeCOBr (5 mol) were condensed *in vacuo* at −196 °C on to $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.41 g). On warming, a red solution was produced followed by precipitation of pink $[\mathrm{WBr_2\{N_2H(COMe)\}(dppe)_2}]$ before 0 °C was reached. The mixture was stirred for 1 h, then the solid was filtered off and dried. Recrystallisation from $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$ gave pink crystals (0.39 g, 86%).

Reaction of $[\mathrm{WCl(N_2H)(dppe)_2}]$ *with* MeCOCl.—The reaction was carried out as above giving 83% yield of $[\mathrm{WCl_2\{N_2H(COMe)\}(dppe)_2}]$, identical with the product produced by reaction of MeCOCl with $[\mathrm{W(N_2)_2(dppe)_2}]$ [6] or $[\mathrm{WCl_2(NH{:}NH)(dppe)_2}]$ [3] in refluxing thf (i.r., n.m.r., and m.p.) (Found: C, 57.7; H, 4.9; N, 2.5. $\mathrm{C_{54}H_{52}Cl_2N_2OP_4W}$ requires C, 57.7; H, 4.7; N, 2.5%).

Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with Nitrogen Monooxide*.—Dichloromethane or benzene (30 cm^3) and nitrogen mono-oxide (2 mol) were condensed *in vacuo* at −196 °C on to $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.22 g). The mixture was stirred for 12 h during which time dinitrogen (4.85 cm^3, 1.0 mol) was evolved. No dihydrogen was detected. The resulting orange-brown solution was reduced to a quarter of its volume and methanol was added to precipitate a yellow solid. Recrystallisation from dichloromethane–hexane gave yellow crystals of *bis*[1,2-*bis*(*diphenylphosphino*)-*ethane*]*bromonitrosyltungsten*, $[\mathrm{WBr(NO)(dppe)_2}]$ (0.19 g, 81%). The chloro- and fluoro-analogues were similarly prepared. Reaction of $[\mathrm{WCl(^{15}N_2H)(dppe)_2}]$ with NO gave $[\mathrm{WCl(NO)(dppe)_2}]$ and $^{15}\mathrm{N_2}$ gas (1 mol).

Attempted Reaction of $[\mathrm{WX_2(NH{:}NH)(dppe)_2}]$ (X = Cl or Br) *with* NO.—Using similar conditions to those above, no gas was evolved and starting material was recovered in both cases.

Reaction of trans-$[\mathrm{W(N_2)_2(dppe)_2}]$ *with* NO.—The conditions were again as above; some dinitrogen was evolved but no nitrosyl complexes were formed.

Reaction of $[\mathrm{WX(N_2H)(dppe)_2}]$ (X = Cl *or* Br) *with* $\mathrm{FeCl_3}$.—Ethanol (40 cm^3) was condensed *in vacuo* at −196 °C on to $[\mathrm{WX(N_2H)(dppe)_2}]$ (0.2 g) and $\mathrm{FeCl_3}$ (varying amounts). The mixture was warmed to 20 °C and stirred for 4 h. Dinitrogen (up to 0.75 mol. equiv.) was evolved but no dihydrogen. No pure solid product was obtained.

Reaction of $[\mathrm{WX(N_2H)(dppe)_2}]$ (X = Cl *or* Br) *with* $\mathrm{Na[BH_4]}$.—Ethanol (40 cm^3) was condensed on to the tungsten complex (0.25 g) and sodium tetrahydroborate (0.2 g) at −196 °C *in vacuo*. The mixture was then stirred for 12 h at 20 °C. Then about one half of the solvent and other volatile materials were distilled into 1 N sulphuric acid (5 cm^3). This solution gave negative tests for ammonia (indophenol) and hydrazine (*p*-dimethylaminobenzaldehyde). The yellow solid in the residue was filtered off, washed with water and methanol, and dried, and was shown to be identical with an authentic sample of $[\mathrm{WH_4(dppe)_2}]$ (m.p. and i.r.) [8] (Found: C, 61.3; H, 5.3. $\mathrm{C_{52}H_{52}P_4W}$ requires C, 61.7; H, 5.1%).

Attempted Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with Dimethylphenylphosphine*.—The complex $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.38 g) was suspended in thf (35 cm^3) and $\mathrm{PMe_2Ph}$ (0.3 g) added, and the mixture was heated under reflux under dinitrogen for 4 h. The orange solution was then reduced in volume and diethyl ether was added giving a yellow solid, identified as starting material (i.r. and m.p.).

Attempted Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with* EtSH.—To $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.4 g) in thf (40 cm^3) was added EtSH (0.3 cm^3) and the mixture stirred under dinitrogen for 24 h. The yellow solid produced was filtered off, washed with diethyl ether, dried, and shown to be starting material (i.r. and m.p.).

Attempted Reaction of $[\mathrm{WBr(N_2H)(dppe)_2}]$ *with* $\mathrm{Na[S_2CNMe_2)]}$.—To $[\mathrm{WBr(N_2H)(dppe)_2}]$ (0.4 g) in methanol (50 cm^3)

was added Na[S_2CNMe_2] (0.2 g) and the mixture was heated under reflux under dinitrogen for 8 h. Some yellow solid was filtered off, washed with water and methanol, and shown to be starting material (i.r.). The orange-brown solution was reduced in volume and diethyl ether was added to give a red-brown powder (0.1 g) whose i.r. spectrum showed no ν(NN) band and no bands attributable to the complexed dithiocarbamate ligand.

Reaction of trans-[W(N_2)$_2$(dppe)$_2$] *with* HBr (1 mol).—Tetrahydrofuran (40 cm^3) and HBr (1 mol) were condensed *in vacuo* on to *trans*-[W(N_2)$_2$(dppe)$_2$] (0.4 g) and the mixture stirred at 20 °C for 4 d during which time a yellow solid was produced, and dinitrogen (5.6 cm^3, 0.6 mol) was evolved. The solid was filtered off, dried, and its i.r. spectrum showed it to be a mixture of *trans*-[W(N_2)$_2$(dppe)$_2$] together with [WBr(N_2H)(dppe)$_2$] and [WBr(N_2H_2)(dppe)$_2$]. The last complex was removed by washing with methanol but the resulting mixture, [WBr(N_2H)(dppe)$_2$] and *trans*-[W(N_2)$_2$(dppe)$_2$], could not be separated. Addition of diethyl ether to the mother liquor gave more solid, also a mixture of [WBr(N_2H)(dppe)$_2$] and *trans*-[W(N_2)$_2$(dppe)$_2$] (i.r.).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromodiazenidomolybdenum*, [MoBr(N_2H)(dppe)$_2$].—To a suspension of [MoBr$_2$(NH:NH)(dppe)$_2$] (0.4 g) in degassed thf (30 cm^3) was added NEt$_3$ (0.06 cm^3, 1 mol) and the mixture was stirred *in vacuo* for 1.5 h. The resulting yellow solid was filtered off under argon, washed with water, methanol, and diethyl ether, and dried (0.25 g, 68%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*diazenidofluoromolybdenum*, [MoF(N_2H)(dppe)$_2$].—Methanol (40 cm^3) was condensed on to [MoF(N·NH$_2$)(dppe)$_2$][BF$_4$] (0.2 g) and K$_2$[CO$_3$] (0.03 g, 1 mol) *in vacuo* at −196 °C. The mixture was warmed to room temperature with stirring, and was stirred for 18 h, producing a bright yellow solid. This was filtered off, washed (water and ethanol), and dried (0.15 g, 82%).

Reaction of [MoBr(N_2H)(dppe)$_2$] *with* HBr.—Dichloromethane (40 cm^3) and HBr (1 mol) were condensed *in vacuo* on to [MoBr(N_2H)(dppe)$_2$] (0.31 g) at −196 °C. The mixture was warmed to room temperature with stirring whereupon a red solution formed. This was stirred for 0.5 h and dinitrogen (3.05 cm^3, 0.4 mol) was evolved but no dihydrogen. The solvent was removed and methanol (40 cm^3) was added to give a yellow solid which was filtered off, dried, and recrystallised from CH$_2$Cl$_2$–MeOH to give yellow crystals of [MoBr$_2$(dppe)$_2$] (0.12 g, 37%) (m.p. 205—209 °C) (Found: C, 59.2; H, 4.4; Br, 15.2. $C_{52}H_{48}Br_2MoP_4$ requires C, 59.3; H, 4.6; Br, 15.2%). The red methanol solution was reduced in volume and diethyl ether was added to give a pale brown solid, identified as [MoBr$_2$(NH:NH)(dppe)$_2$] (0.18 g, 54%) (i.r. and m.p.) (Found: C, 56.9; H, 4.9; N, 2.5. $C_{52}H_{50}Br_2MoN_2P_4$ requires C, 57.7; H, 4.7; N, 2.6%).

Reaction of [MoF(N_2H)(dppe)$_2$] *with* [Et$_2$OH][BF$_4$].—To [MoF(N_2H)(dppe)$_2$] (0.08 g) in thf (20 cm^3) was added [Et$_2$OH][BF$_4$] (0.1 cm^3) with stirring, to give an immediate darkening of the orange solution to orange-brown. This was stirred for 2 h, then the solution was reduced in volume, and diethyl ether was added to give orange-brown crystals of [MoF(N:NH$_2$)(dppe)$_2$][BF$_4$] (0.068 g; 78%) (i.r. and m.p.) (Found: C, 60.3; H, 4.9; N, 2.6. $C_{52}H_{50}BF_5MoN_2P_4$ requires C, 60.7; H, 4.9; N, 2.7%).

Reaction of [MoBr(N_2H)(dppe)$_2$] *with* NO.—Tetrahydrofuran (30 cm^3) and NO (2 mol) were condensed *in vacuo* at −196 °C on to [MoBr(N_2H)(dppe)$_2$] (0.2 g) and the mixture stirred for 5 h at 20 °C. Dinitrogen (4.75 cm^3, 0.99 mol) was evolved, but no dihydrogen was detected. The resulting yellow solid was filtered off and dried *in vacuo*. Reduction in volume of the remaining solution followed by addition of Et$_2$O gave more yellow solid. Recrystallisation from CH$_2$Cl$_2$–MeOH gave yellow crystals of *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromonitrosylmolybdenum*, [MoBr(NO)(dppe)$_2$] (0.14 g, 70%). The fluoro-analogue was similarly prepared.

Reaction of [MoBr(N_2H)(dppe)$_2$] *with* FeCl$_3$.—Tetrahydrofuran (25 cm^3) was condensed *in vacuo* at −196 °C on to [MoBr(N_2H)(dppe)$_2$] (0.17 g) and FeCl$_3$ (0.18 g), and the mixture stirred at 20 °C for 2 h. A red solution was quickly produced and dinitrogen (4.0 cm^3, 0.98 mol) was evolved but no dihydrogen. On addition of diethyl ether, red needles of [MoBrCl(dppe)$_2$][FeCl$_4$] were produced which were filtered off and dried. The complex had ν(FeCl) at 380 cm^{-1} (Nujol mull) and was a 1 : 1 electrolyte in nitrobenzene (Λ 18.5 S cm^2 mol^{-1} in *ca.* 10^{-3} mol dm^{-3} solution) (Found: C, 51.5; H, 4.6. $C_{52}H_{48}BrCl_5FeMoP_4$ requires C, 51.8; H, 4.0%).

Reaction of [MoBr(N_2H)(dppe)$_2$] *with* Na[BH$_4$].—Tetrahydrofuran (25 cm^3) was condensed *in vacuo* at −196 °C on to [MoBr(N_2H)(dppe)$_2$] (0.25 g) and Na[BH$_4$] (0.2 g), and the mixture stirred for 12 h. About one third of the solvent and other volatile materials were distilled on to 0.1 N sulphuric acid (5 cm^3) and shown to contain neither ammonia nor hydrazine. The yellow solid in the residue was filtered off, washed with water and methanol, and dried. Addition of methanol to the mother liquor yielded more yellow solid, identical to the one above. The two solids were combined and recrystallised from thf, yielding yellow crystals of [MoH$_4$(dppe)$_2$] (0.16 g, 73%), identified by its i.r. and n.m.r. spectra[9] (Found: C, 69.8; H, 6.0. $C_{52}H_{52}MoP_4$ requires C, 69.6; H, 5.9%).

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