The Protonation of Molybdenum and Tungsten Bis(diphosphine)bis(dinitrogen) Complexes: the Crystal and Molecular Structure of Bis[1,2-bis(diethylphosphino)ethane]bromo[hydrazido(2−)]tungsten Bromide–Methanol (2/1) *

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The reactions of $[M(N_2)_2(L\text{–}L)_2]$ [M = Mo or W; L–L = diphosphine = $Et_2PCH_2CH_2PEt_2$ (depe) or $(4\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe\text{-}4)_2$ (dmppe)] with acids HX (X = Cl or Br) yield various products. Those containing nitrogen include $[MHX(NNH_2)(L\text{–}L)_2]^{2+}$, and $[MX(NNH_2)(L\text{–}L)_2]^+$, but the course of the reaction is also solvent dependent. The crystal structure of the complex $[WBr(NNH_2)(Et_2PCH_2CH_2PEt_2)_2]Br{\cdot}0.5MeOH$ is described.

Molybdenum and tungsten bis(dinitrogen) complexes of the form $[M(N_2)_2(L\text{–}L)_2]$ (L–L = diphosphine) react with acids HX to form hydrazido(2−) complexes (M = Mo or W; X = Cl, Br, or I; diphosphine = $Ph_2PCH_2CH_2PPh_2$, dppe).[1] These hydrazido(2−) complexes $[MX(NNH_2)(dppe)_2]^+$ cannot normally be protonated further to yield ammonia. However, hydrazido(2−) complexes containing monodentate phosphines do react with proton acids to yield ammonia and/or hydrazine.[2] The exception to these generalizations is $[W(NNH_2)(4\text{-}MeC_6H_4SO_3)(dppe)_2]^+$, which can be made to yield ammonia by coupled protonation and reduction, and can give rise to a cyclic system for the protonation of dinitrogen to ammonia.[3] Protonation of dinitrogen complexes also containing tertiary monophosphines give rise to ammonia, generally with complete decomposition of the complex structure, making catalytic cycling of the system at best very difficult. A system with two diphosphines has only been cycled in the specific case cited,[3] although the basic structure is much more robust than the system with four monophosphines.[4] It is a general aim of our research to overcome this dichotomy of properties.

It is already clear that the mechanism of protonation depends in detail on the acid strength, the solvent, and the metal,[5,6] although the ultimate nitrogen-containing product in the case of the bis[bis(diphenylphosphino)ethane] complexes is always the hydrazido(2−) complex. Relatively little attention has been paid to changing the diphosphine, although there are reports on the protonation of $[Mo(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) by HX (X = Cl or Br) in tetrahydrofuran (thf) to yield $[MoX(NNH_2)(depe)_2]^+$.[1,5,6] This paper describes a detailed investigation of the protonation of $[M(N_2)_2(depe)_2]$ (M = Mo or W) by the acids HX (X = Cl or Br), in the solvents MeOH, thf, or benzene. This last was selected because benzene has hitherto not been used in these reactions. The diphosphine, depe, was selected because its complexes are expected to be much more electron-rich than those of dppe.[7] For comparison, we also investigated some complexes of the strong electron-donating aryl diphosphine dmppe $[(4\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe\text{-}4)_2]$.[8]

We show that complexes $[M(N_2)_2(L\text{–}L)_2]$ can react with acids HX (X = Cl or Br) to give $[MX(NNH_2)(L\text{–}L)_2]X$, $[MHX(NNH_2)(L\text{–}L)_2]X_2$ or $[MX(NNH_2)(L\text{–}L)_2][HX_2]$. In addition, HBF_4 can give rise to $[MX(NHNH_2)(L\text{–}L)_2][BF_4]_2$.[9] Finally, it has been shown elsewhere[5] that the complex $[MH(N_2)_2(L\text{–}L)_2]X$ is also a product under certain conditions. Thus, there are at least five possible nitrogen-containing products in these reactions, and, in addition, products have been reported[1,5,6] which involve complete nitrogen loss, *viz.*, $[MoH_2Cl_2(dppe)_2]$. We can now begin to discuss the factors which cause particular products to form.

Results

Reactions of $[Mo(N_2)_2(depe)_2]$.—The results are summarized in the Scheme. It was originally reported that $[Mo(N_2)_2(depe)_2]$ reacts with hydrogen chloride or hydrogen bromide in thf to yield $[MoCl(NNH_2)(depe)_2]Cl$ (a product which was not completely characterized, due to its high solubility) and solvated $[MoBr(NNH_2)(depe)_2]Br$ (which was well characterized, and, indeed, was also characterized as the NND_2 derivative).[1] We have repeated the preparation of the bromo species in thf and have isolated the solvent-free species.

The reaction of $[Mo(N_2)_2(depe)_2]$ with ten molar equivalents of HX (X = Cl or Br) in benzene causes complete loss of N_2 from the complex, and, in the case of HBr, 2 moles of N_2 were recovered, within the limits of experimental error. The yellow, crystalline complex isolated in this case has a low but significant molar conductivity in nitromethane, and has a ^1H n.m.r. spectrum in CD_2Cl_2 suggestive of a paramagnetic species. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum gives rise to a sharp singlet at δ −96.78 p.p.m. and the analysis is consistent with the product being a Mo^{III} species, $[MoBr_2(depe)_2]Br$. The reaction with HCl allowed the isolation of a yellow solid, in high yield, but it could not be adequately characterized, though it would appear not to be $[MoCl_2(depe)_2]Cl$ from the analysis.

Reactions of $[W(N_2)_2(depe)_2]$.—In contrast, the reaction of $[W(N_2)_2(depe)_2]$ with HCl or HBr yields products, of which the constitution appears to depend upon the reactant proportions and the solvent. The reaction with HBr in thf in the mol ratio of 1:4 (complex:acid) produces pink, needle-shaped crystals of $[WBr(NNH_2)(depe)_2]Br$. This has bands in the i.r. spectrum at 3 100 cm^{-1}, and a resonance in the ^1H n.m.r. spectrum at δ 6.0 p.p.m., both characteristic of an NNH_2 group. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum is a singlet which is consistent with the presence of four, strongly coupled, equivalent phosphorus atoms (δ −112.26 p.p.m., J_{WP} = 271.8 Hz). We confidently assign this material the structure shown below, which has already been suggested[1] for the molybdenum analogue. This was confirmed by *X*-ray structure analysis (see later).

If ten molar equivalents of HBr are used, the reaction mixture produces a pink solid within 5 min. However, it slowly changes over 0.5 h to a yellow solid. The pink, air-sensitive solid loses

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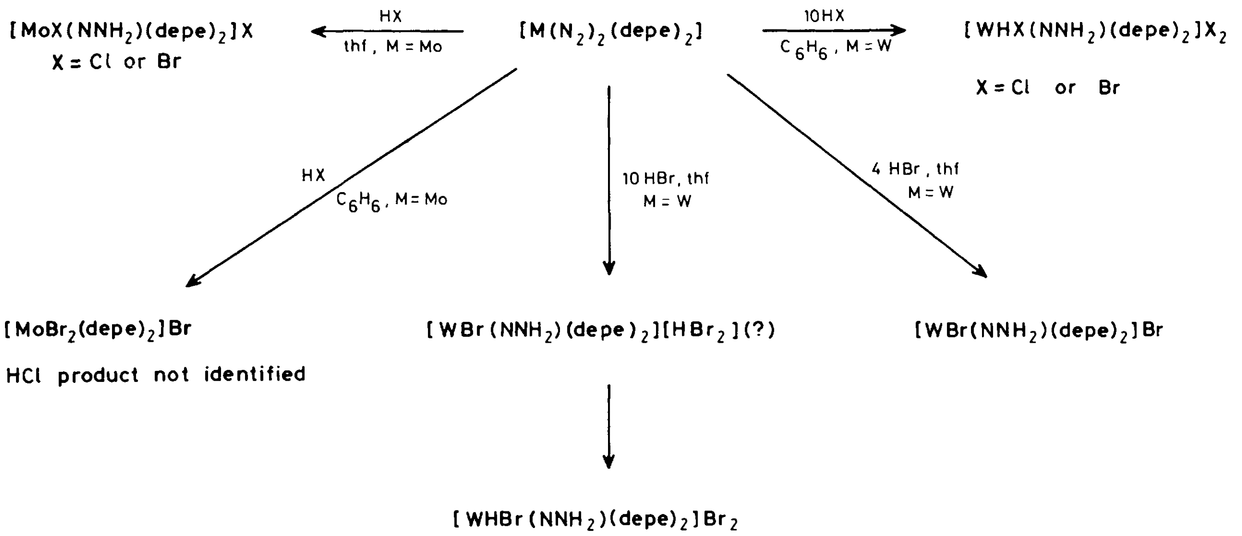
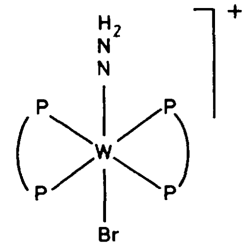
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans*, 1988, Issue 1, pp. xvii—xx.

Table 1. Analytical data for hydrazido(2 –) complexes

Complex	Colour	M.p. (°C)	Yield (%)	Λ_M/ Ω^{-1} cm^2 mol^{-1}	Analyses[a] (%) C	H	N
$[WCl(NNH_2)(depe)_2]Cl\cdot0.5Et_2O$	Red-brown	190—195 (decomp.)		66.8	36.4 (36.0)	6.75 (7.50)	4.05 (3.80)
$[WBr(NNH_2)(depe)_2]Br$	Red		60	74.9	30.7 (30.5)	6.85 (6.35)	3.50 (3.55)
$[MoBr(NNH_2)(depe)_2]Br$	Violet	252	84	71.7	34.5 (34.4)	7.40 (7.15)	4.10 (4.00)
$[WHCl(NNH_2)(depe)_2]Cl_2$	Pale yellow		76		36.2 (36.0)	7.30 (7.50)	4.20 (3.85)
$[WHBr(NNH_2)(depe)_2]Br_2$[b]	Yellow	192—193 (decomp.)	52	72.9	28.0 (27.7)	6.60 (5.90)	3.25 (3.25)
$[WDBr(NND_2)(depe)_2]Br_2$	Yellow		23	69.0	28.2 (27.6)	5.45 (6.20)	3.25 (3.20)
$[WBr(NNH_2)(dmppe)_2][HBr_2]$	Brown	170—173 (decomp.)	69	69.1	48.3 (48.4)	4.55 (4.50)	1.70 (1.90)
$[MoBr(NNH_2)(dmppe)_2][HBr_2]$	Brown	224—225	30	44.6	51.8 (51.5)	5.20 (4.80)	1.90 (2.00)
$[WBr(NNH_2)(dmppe)_2][BPh_4]$	Brown	220—221 (decomp.)	54	42.4	65.0 (61.2)	6.60 (5.25)	1.00 (1.70)
$[MoBr(NNH_2)(dmppe)_2][BPh_4]$	Yellow-green	202—204 (decomp.)	37	53.2	62.1 (64.7)	5.35 (5.40)	1.50 (1.80)

[a] Calculated values in parentheses. [b] Br analysis: 27.7 (27.7)%.



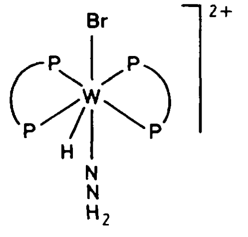


HBr even when dry, to yield the hydrazido(2 –) complex described above. It has a band assignable ν(NH) in its i.r. spectrum at 3 030 cm^{-1}. We have no further data apart from analyses on this particular labile material, but, by comparison with the dmppe analogues described below, we believe this to be a salt $[WBr(NNH_2)(depe)_2][HBr_2]$. The difference in the frequencies assigned to ν(NH) between this compound and the simple bromide could be due to changes in hydrogen bonding, known to be extensive in this class of complex[10,11] (see also crystal structure).

In contrast, the yellow compound shows a band assignable to ν(WH) in its i.r. spectrum at 1 865 cm^{-1}, but no band assignable to ν(NH). The hydride ligand also gives rise to a triplet of triplets of appropriate intensities (δ 4.02—5.07 p.p.m., J_{PWH} = 63.3 and 3.2 Hz), due to coupling with inequivalent pairs of phosphorus atoms.

The ^{31}P-{^1H} n.m.r. spectrum is of the AA′BB′ type, consisting of two six-line multiplets, with additional tungsten satellites. Such a spectrum has already been observed in, for example, $[WH(N_2)_2(dppe)_2][HCl_2]$.[1]

The data are fully consistent with a seven-co-ordinate pentagonal-bipyramidal structure (below) for the cation. The salt is an electrolyte in $MeNO_2$. This complex thus represents a rare class of materials, a hydrido–hydrazido(2 –) complex. The only other extensive report on such materials describes complexes of monodentate phosphines.[10] The inferences were confirmed by synthesis of $[WHBr(NND_2)(depe)_2]Br_2$, which produced the expected spectral changes compared to $[WHBr(NNH_2)(depe)_2]Br_2$ (see Tables 1, 2, and 3).



The reactions of HCl and HBr with $[W(N_2)_2(depe)_2]$ in benzene solution in the molar ratios of 10:1 or greater result in

Table 2. ^{31}P N.m.r.[a] and i.r. spectra of the new compounds

Complex	$\delta(^{31}P)$/p.p.m., J/Hz	ν/cm^{-1} (KBr discs)
$[WCl(NNH_2)(depe)_2]Cl\cdot 0.5Et_2O$	-106.52, $J_{WP} = 269.3$	ν(NH) 2 932
$[WBr(NNH_2)(depe)_2]Br$	-112.26, $J_{WP} = 271.8$ ($CDCl_3$)	ν(NH) 3 100
$[MoBr(NNH_2)(depe)_2]Br$	-98.4 ($CDCl_3$)	ν(NH) 3 180
$[WHCl(NNH_2)(depe)_2]Cl_2$	-75.56 (A,A′), -107.26 (B,B′), $J_{WP}(A,A') = 145$, $J_{WP}(B,B') = 186$, $J_{AA'} = 31.59, J_{AB} = J_{A'B'} = -32.33, J_{A'B'} = J_{A'B} = 71.72, J_{BB'} = -1.72$	ν(NH) 2 965, ν(WH) 1 881
$[WHBr(NNH_2)(depe)_2]Br_2$	-79.00 (A,A′), -112.00 (B,B′), $J_{WP}(A,A') = 140$, $J_{WP}(B,B') = 188$ $J_{AA'} = 30.62$, $J_{AB} = J_{A'B'} = -31.47$, $J_{AB'} = J_{A'B} = 69.50$, $J_{BB'} = -0.54$	ν(NH) 2 965, ν(WH) 1 872
$[WDBr(NND_2)(depe)_2]Br_2$	AA′BB′X pattern, not simulated	ν(ND) 2 200, ν(WD) 1 340
$[WHF(NNH_2)(depe)_2[BF_4]_2$[b]	-69.20 (A,A′), -98.26 (B,B′), $J_{AA'} = 31.1$, $J_{AB} = J_{A'B'} = -31.88$, $J_{AB'} = J_{A'B} = 79.55$, $J_{BB'} = -3.28$, $J_{AX} = J_{A'X} = 29.41$, $J_{BX} = J_{B'X} = 43.26$	
$[WBr(NNH_2)(dmppe)_2][HBr_2]$	-114.2, $J_{WP} = 282.1$	$\nu(NH_2)$ 2 932
$[MoBr(NNH_2)(dmppe)_2][HBr_2]\cdot 0.5Et_2O$	-98.5	$\nu(NH_2)$ 2 931
$[WBr(NNH_2)(dmppe)_2][BPh_4]$	-113.7, $J_{WP} = 279.5$	$\nu(NH_2)$ 2 926
$[MoBr(NNH_2)(dmppe)_2][BPh_4]$	-97.8	$\nu(NH_2)$ 2 626

[a] Solvent CD_2Cl_2 unless otherwise stated. [b] This compound will be discussed in more detail in a later paper.[9]

Table 3. ^1H N.m.r. spectra of the new complexes[a]

Complex	Solvent	CH_3	PCH_2	NH_2[b]	WH and phenyl
$[WCl(NNH_2)(depe)_2]Cl\cdot 0.5Et_2O$	CD_2Cl_2	0.91—1.47 (m, br, 24)	1.38—1.57 (m, br, 24)	7.15—7.98 (s, br, 2)	
$[WBr(NNH_2)(depe)_2]Br$	$CDCl_3$	1.20—1.85 (m, br, 24)	1.96—2.35 (m, br, 24)	6.05 (s, br, 2)	
$[MoBr(NNH_2)(depe)_2]Br$	$CDCl_3$	1.02—1.22 (m, br, 24)	1.11—1.60 (m, br, 24)	6.50—6.90 (s, br, 2)	
$[WHCl(NNH_2)(depe)_2]Cl_2$	CD_2Cl_2	1.00—1.76 (m, br, 24)	1.76—3.32 (m, br, 24)	10.03 (s, br, 2)	3.99, 4.69, 5.39 (tt, $J_{PH} = 2.2$, $J_{WH} = 62.6$)
$[WHBr(NNH_2)(depe)_2]Br_2$	CD_2Cl_2	1.11—1.58 (m, br, 24)	1.80—3.32 (m, br, 24)	8.40—10.70 (s, br, 2)	3.71, 4.42, 5.12 (tt, $J_{PH} = 3.6$, $J_{WH} = 62.7$)
$[WDBr(NND_2)(depe)_2]Br_2$	CD_2Cl_2	1.08—1.55	1.76—2.85 (m, br, 24)		
$[WBr(NNH_2)(dmppe)_2][HBr_2]$	$CDCl_3$	3.77 (s, 24)	2.22—3.00 (s, br, 8)	3.83 (s, br, 2)	6.40—7.32 (m, 32)
$[MoBr(NNH_2)(dmppe)_2][HBr_2]$	$CDCl_3$	3.76[c] (s, 26)	2.36—3.24 (s, br, 8)	*c*	6.80—7.80 (m, 32)
$[WBr(NNH_2)(dmppe)_2][BPh_4]$	CD_2Cl_2	3.78 (s, 24)	2.30—3.10 (s, br, 8)	3.31 (s, 2)	6.36—7.36 (m, 52)
$[MoBr(NNH_2)(dmppe)_2][BPh_4]$	CD_2Cl_2	3.77 (s, 24)	2.30—2.90 (s, br, 8)	3.64 (s, 2)	6.30—7.20 (m, 52)

[a] m = Multiplet, t = triplet, s = singlet, br = broad; shifts in δ/p.p.m., coupling constants in Hz. [b] All these signals disappear if D_2O is added to the sample. [c] NH_2 resonance obscured by CH_3 resonance.

the formation of the yellow complexes $[WHX(NNH_2)(depe)_2]X_2$ (X = Cl or Br). These compounds, one of which has already been described above, were characterized by the usual methods. The chloro complex decomposes slowly, even in the solid state under N_2, and HX was lost upon attempted double decomposition with $NaBPh_4$, yielding the hydrazido(2−) complexes, $[WX(NNH_2)(depe)_2]X$. There is some ^{31}P n.m.r. evidence that the reaction sequence (1) occurs, since we observe in the spectra

$$[WHCl(NNH_2)(depe)_2]Cl_2 \longrightarrow [WCl(NNH_2)(depe)_2][HCl_2] \longrightarrow [WCl(NNH_2)(depe)_2]Cl \quad (1)$$

of the final product an 'impurity' band at δ −108.06 p.p.m. ($J_{WP} = 269.3$ Hz) which could be due to the $[HCl_2]^-$ salt, but further work is required to prove this.

Reactions of Dmppe Complexes.—The reactions of $[M(N_2)_2(dmppe)_2]$ with HBr were investigated in some detail. Under no circumstances were we able to prepare hydrido–hydrazido(2−) complexes, the only isolable products being $[MBr(NNH_2)(dmppe)_2][HBr_2]$. We formulate these materials as $[HBr_2]^-$ salts chiefly on the basis of analysis. There is a difference between the resonance positions of the NH_2 protons and of the phosphorus for these salts and the $[BPh_4]^-$ salts, and also between Mo and W homologues. This is presumably connected with hydrogen bonding between the hydrazide and the counter anion. The single ^{31}P n.m.r. resonance is consistent with a *trans* structure.

X-*Ray Crystal-structure Analysis of* $[WBr(NNH_2)(depe)_2]Br\cdot 0.5MeOH$.—*X*-Ray crystal structure determination yielded the structures shown in Figure 1. Atomic co-ordinates are presented in Table 4; selected bond lengths and angles are given in Table 5. The crystals contain two independent complex cations, two bromide ions, and a methanol molecule. Both cations have approximately octahedral co-ordination about the tungsten atom, a *trans*-bromo–hydrazido(2−) configuration, and two depe ligands forming a four-phosphorus atom equa-

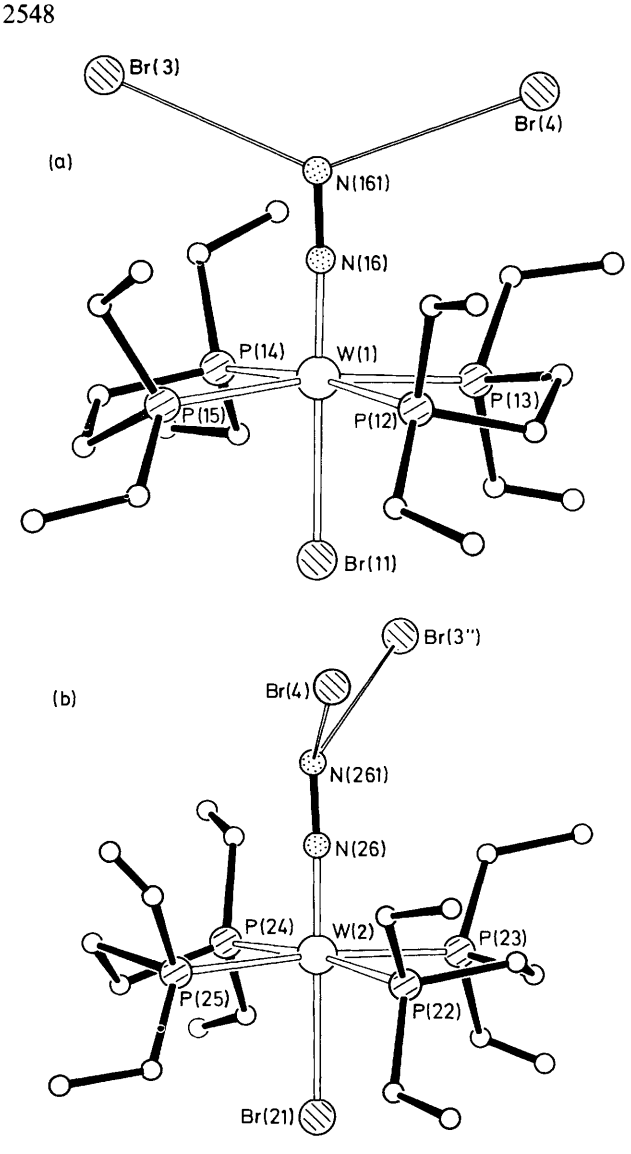


Figure 1. Views of the two independent $[WBr(NNH_2)(depe)_2]^+$ cations and adjacent bromide ions

torial plane. The two cations differ in the conformations of the ethyl groups (in one cation all eight ethyl groups are turned away from the centre, whereas in the other, one pair of ethyl groups folds inwards) and in the orientations of the hydrazido groups with respect to the depe molecules. Only one of the four N–H hydrogen atoms was clearly resolved, but all four N–H hydrogen atoms are clearly involved in N–H • • • Br hydrogen bonds, in a fashion now familiar from many other structures, Table 6. However, in one case [Figure 1(*a*)] the plane defined by the NNH_2 atoms bisects each of the two depe ligands, whereas in the other case [Figure 1(*b*)] it separates the depe ligands (Figure 1).

At the resolution obtained in this analysis, the dimensions of the depe ligands and the methanol molecules were not very satisfactory. However, the N_β atoms, N(161) and N(261), are each *ca.* 3.4 Å distant from two bromide ions, in an arrangement that allows the formation of chains of hydrogen bonds parallel to the *a* axis in the crystal (involving *a*-glide symmetry operations) (Figure 2). The methanol molecules are also hydrogen bonded to one of the bromide ions, forming branches to the main chains. The bromo ligands are not involved in hydrogen bonding.

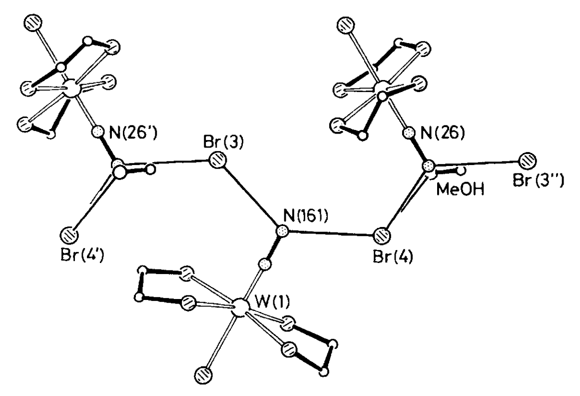


Figure 2. Hydrogen-bonding connections, in chains parallel to the *a* axis; the molecules of N(26) and N(26') are related by a glide-plane symmetry. Ethyl group atoms have been omitted for clarity

This structure is one of a number of unsubstituted hydrazido(2–) complexes to be analysed, but the first containing depe. The linear W–N–N system and W–N and N–N bond distances are all very similar to those previously reported (Table 6),[10–16] and are consistent with the normal formulation $W\overset{\cdots}{-}N\overset{\cdots}{-}NH_2$ postulated for the other structures.

Discussion

The data reported here constitute an extensive investigation of the protonation of co-ordinated dinitrogen in depe and dmppe complexes (see Scheme). The only comparable studies are on complexes of dppe, and on the related, but not precisely similar, complexes containing $P(CH_2CH_2PPh_2)_2Ph$, reported by George and co-workers.[17]

It might be expected that the N_2 in $[M(N_2)_2(depe)_2]$ would be more tightly bound and more negative than in $[M(N_2)_2(dppe)_2]$, and there is alkylation evidence to support this.[7] Consequently, one might expect protonation to be more rapid, and N_2 loss less significant, in the depe complexes, and also, consistent with the general electron-donating power of the metals, the tungsten-bound dinitrogen to be more basic than the molybdenum-bound one.[5,18] This is generally found to be true, though the rate of loss of N_2 is remarkably high in the molybdenum reactions reported here.

Henderson[5] has shown that the reaction between $[Mo(N_2)_2(depe)_2]$ and HCl in thf leads to products $[MoH_2Cl_2(depe)_2]$ or $[MoCl(NNH_2)(depe)_2][HCl_2]$ *via* the same intermediate, $[MoH(N_2)_2(depe)_2][HCl_2]$, depending upon the concentration of HCl. High concentrations of HCl favour the latter product. On the other hand, reaction with HBr in thf is believed to proceed *via* an adduct $[Mo(N_2)(N_2H)(depe)_2]Br{\cdot}HBr$ to form $[MoBr(NNH_2)(depe)_2]^+$. Complexes $[M(N_2)_2(dppe)_2]$ also show greater tendency to form non-nitrogen-containing products with M = Mo than with M = W, and with HCl than with HBr.

Our results in benzene (in which the concentration of HX is high but that of H^+ must be exceedingly low) are generally consistent with this. However, the products from benzene solution, although containing no nitrogen, were not hydrido complexes. This alternative route, to give, apparently, molybdenum(III) complexes, is presumably forced by the absence of polar solvent and hence of an ionic pathway. In thf with HBr we isolated $[MoBr(NNH_2)(depe)_2]Br$.

The reactions of $[W(N_2)_2(depe)_2]$ do not proceed with complete loss of N_2, and two kinds of product can be isolated, $[WX(NNH_2)(depe)_2]^+$ and $[WHX(NNH_2)(depe)_2]^{2+}$ (X = F, Cl, or Br; for a discussion of the fluoro derivatives, see a later

Table 4. Final fractional atomic co-ordinates (× 10^4); estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	2 572.6(4)	1 006.1(7)	3 808.5(2)	W(2)	3 627.5(4)	3 582.2(7)	1 202.3(3)
Br(11)	2 361(1)	435(2)	4 601.8(7)	Br(21)	2 660(1)	4 247(3)	429.7(8)
P(12)	3 586(3)	2 140(5)	4 302(2)	P(22)	2 949(3)	1 666(5)	1 211(2)
C(12)	4 256(12)	1 003(20)	4 560(8)	C(22)	3 346(14)	395(27)	955(10)
C(121)	3 986(14)	3 176(25)	3 961(9)	C(221)	3 012(10)	1 110(17)	1 787(7)
C(122)	4 523(16)	3 982(31)	4 142(13)	C(222)	2 819(15)	−229(20)	1 859(10)
C(123)	3 594(10)	3 063(18)	4 819(7)	C(223)	1 972(14)	1 751(26)	930(10)
C(124)	4 254(11)	3 358(31)	5 197(8)	C(224)	1 573(20)	670(46)	859(13)
P(13)	3 414(3)	−746(5)	3 995(2)	P(23)	4 044(3)	2 172(6)	709(2)
C(13)	4 251(12)	−51(24)	4 242(9)	C(23)	3 623(19)	759(34)	639(13)
C(131)	3 532(12)	−1 637(23)	3 489(8)	C(231)	4 935(12)	1 851(24)	930(9)
C(132)	4 182(15)	−2 350(29)	3 584(12)	C(232)	5 244(13)	711(28)	735(11)
C(133)	3 176(22)	−2 254(49)	4 380(13)	C(233)	3 931(27)	2 862(45)	9(16)
C(134)	3 691(25)	−2 674(61)	4 577(15)	C(234)	3 799(25)	2 097(50)	−246(24)
P(14)	1 518(3)	−190(5)	3 404(2)	P(24)	4 178(3)	5 582(6)	1 125(3)
C(14)	801(12)	805(22)	3 369(9)	C(24)[a]	3 660(23)	6 827(26)	1 281(12)
C(141)	1 313(12)	−1 678(22)	3 603(9)	C(241)	5 129(21)	5 548(42)	1 408(17)
C(142)	621(13)	−2 260(26)	3 347(15)	C(242)	5 521(20)	6 185(63)	1 434(16)
C(143)	1 333(11)	−538(21)	2 782(7)	C(243)	4 112(21)	6 177(34)	511(13)
C(144)	1 760(14)	−1 442(33)	2 663(9)	C(244)	4 231(23)	7 207(44)	413(14)
P(15)	1 715(3)	2 654(5)	3 755(2)	P(25)	3 100(3)	4 991(6)	1 635(2)
C(15)	899(13)	1 843(24)	3 683(9)	C(25)[a]	3 557(27)	6 498(26)	1 750(16)
C(151)	1 722(12)	3 667(21)	4 236(8)	C(251)	2 176(11)	5 192(25)	1 432(10)
C(152)	1 088(11)	4 493(24)	4 202(8)	C(252)	1 891(15)	6 220(29)	1 649(13)
C(153)	1 509(13)	3 738(22)	3 257(9)	C(253)[a]	3 217(23)	4 473(31)	2 251(8)
C(154)	2 046(13)	4 615(23)	3 286(11)	C(254)	3 430(27)	4 820(52)	2 572(15)
N(16)	2 720(6)	1 366(12)	3 290(5)	C(24x)[b]	4 099(42)	6 410(89)	1 647(22)
N(161)	2 812(9)	1 737(20)	2 898(6)	C(25x)[b]	3 335(42)	6 537(61)	1 465(36)
				C(255)[b]	3 576(47)	5 507(102)	2 234(18)
				N(26)	4 292(6)	3 153(12)	1 716(5)
				N(261)	4 797(8)	2 887(16)	2 110(5)
Br(3)	1 373(1)	2 605(3)	2 049.9(8)	C(5)	5 348(24)	−428(47)	2 163(21)
Br(4)	4 437(1)	1 011(3)	2 952.5(9)	O(5)	4 875(22)	−843(36)	2 198(15)

[a] Denotes site occupancy factor of 0.7. [b] Denotes site occupancy factor of 0.3.

paper).[9] This is the first time that protonated hydrazido(2−) complexes have been isolated amongst bis(diphosphine) complexes, though $[WHX_2(NNH_2)(PMe_2Ph)_3]X$ (X = Cl or Br) and $[WHCl_3(NNH_2)(PMe_2Ph)_3]$ have been characterized,[10,12] as has a series of more stable phenylhydrazido(2−) complexes containing monodentate phosphines.[10] The stability of our complexes shows quite clearly that protonation of a hydrazido(2−) complex at the metal does not necessarily lead to production of ammonia or hydrazine. The factors which govern protonation at the metal are not clear, but they do not necessarily include high acid strength. However, a strongly donating phosphine does seem to be a requirement. The diphosphine, dmppe, which is as strongly a donating aryl diphosphine as we have synthesized, does not permit protonation at the metal. We suppose that the relatively greater base strength of the N_2 in $[W(N_2)_2(depe)_2]$ as compared to that in $[Mo(N_2)_2(depe)_2]$ has some influence on the reaction pathways.

The i.r. and n.m.r. spectra in Tables 2 and 3 are consistent with the structures and are also generally self consistent. The ^{31}P n.m.r. spectra of the hydrazido(2−) complexes show progressively increasing shifts to higher field of trimethyl phosphite in the sequence F < Cl < Br. In addition, the tungsten shifts are *ca.* 12 p.p.m. to higher field than the molybdenum shifts. This is entirely consistent with our previous reports on compounds $[MBr(N_2Et)(L-L)_2]$[7] where the phosphorus shifts are in the same sense, but where the difference is *ca.* 15 p.p.m., and complexes $[M(N_2)_2(L-L)_2]$[19] where the difference is *ca.* 20 p.p.m. In fact, the difference decreases as the formal oxidation state increases from 0 to IV. The values of J_{WP} are *ca.* 320 Hz in the W^0 complexes, falling to 300 Hz in the W^{II} complexes,[7] and are *ca.* 270 Hz in the case of W^{IV}. These empirical correlations may be of some diagnostic value. The halide dependence of the shifts is what might be expected: F produces a more 'oxidized' product than Br in terms of the ^{31}P n.m.r. chemical shifts.

The dmppe complexes obey a similar pattern, but the superficial interpretation of the shifts is that dmppe is rather more 'reducing' than depe. However, comparison of $[Mo(N_2)_2(depe)_2]$ with $[Mo(N_2)_2(dmppe)_2]$ (shifts −84.5 and −78.2 p.p.m., respectively)[17] would suggest the opposite. Clearly, these facile interpretations need to be treated with care.

The complexes $[WHX(NNH_2)(depe)_2]^{2+}$ show chemical shifts for the AA′BB′ pattern which move to higher field in the order F < Cl < Br, which is the same sequence as observed for the hydrazido(2−) complexes, but the centre of a given pattern is about 15 p.p.m. to lower field than for the hydrazides. Thus the ^{31}P n.m.r. shifts reflect the more oxidized nature of the complex once the proton has added to the metal. The i.r. frequency, ν(WH) does not change much with X, and the values of the chemical shifts and J_{WH} are not easily rationalized.

We conclude that protonation of the metal is more likely to occur using HBr rather than HF or HCl. Depe is apparently a stronger base than dmppe, and facilitates protonation at the metal. However, the factors which control metal–phosphorus binding are clearly complex, and consequently the nett electron-donor power of dmppe in a complex may be rather different

Table 5. Selected molecular dimensions; bond lengths (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Cations

W(1)–Br(11)	2.654(2)	W(2)–Br(21)	2.641(2)
W(1)–P(12)	2.469(5)	W(2)–P(22)	2.485(5)
W(1)–P(13)	2.494(5)	W(2)–P(23)	2.468(7)
W(1)–P(14)	2.490(5)	W(2)–P(24)	2.463(7)
W(1)–P(15)	2.471(6)	W(2)–P(25)	2.473(7)
W(1)–N(16)	1.739(15)	W(2)–N(26)	1.773(11)
N(16)–N(161)	1.325(26)	N(26)–N(261)	1.340(18)
N(161)–H(161)	0.83(11)		
W(1)–N(16)–N(161)	175.1(13)	W(2)–N(26)–N(261)	177.2(12)
N(16)–N(161)–H(161)	109(7)		

(*b*) Methanol molecule

C(5)–O(5)	1.12(6)

(*c*) Hydrogen bonding

Br(3) ··· N(161)	3.383(19)	Br(4) ··· N(261)	3.509(16)
Br(3) ··· N(261′)	3.398(15)	Br(4) ··· O(5)	3.36(4)
Br(4) ··· N(161)	3.433(19)	Br(4) ··· H(161)	2.60(10)
N(16)–N(161) ··· Br(3)	114.2(11)	Br(3″) ··· N(261) ··· Br(4)	113.2(4)
N(16)–N(161) ··· Br(4)	108.8(11)	N(161 ··· Br(3) ··· N(261′)	123.6(4)
Br(3) ··· N(161) ··· Br(4)	135.8(6)	N(161) ··· Br(4) ··· N(261)	106.3(4)
N(161)–H(161) ··· Br(4)	173(9)	N(161) ··· Br(4) ··· O(5)	125.7(8)
N(26)–N(261) ··· Br(3″)	118.6(10)	N(261) ··· Br(4) ··· O(5)	70.5(7)
N(26)–N(261) ··· Br(4)	118.4(10)		

(*d*) Torsion angles in the depe

P(12)–C(12)–C(13)–P(13)	−50(2)	P(24)–C(24)–C(25)–P(25)	−61(3)
P(14)–C(14)–C(15)–P(15)	41(3)	P(24)–C(24x)–C(25x)–P(25)	84(5)
P(22)–C(22)–C(23)–P(23)	37(4)		

Symmetry operations: ′, $x - \frac{1}{2}, \frac{1}{2} - y, z$; ″, $\frac{1}{2} + x, \frac{1}{2} - y, z$.

Table 6. Crystal-structure data from hydrazido(2−) complexes of Mo and W[a] (Y = hydrogen bond acceptor)

Complex	M–N$_\alpha$	N$_\alpha$–N$_\beta$	M–N–N	M–X(*trans*)[b]	M–P	N$_\beta$ ··· Y	Ref.
[WCl(NNH$_2$)(dppe)$_2$][BPh$_4$]	1.73(1)	1.37(2)	171(1)	2.421	2.514(4)—2.540(4)		13
[MoF(NNH$_2$)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$	1.76(1)	1.33(2)	176(1)	1.992(8)	2.52(1) (mean)	2.82(2), 2.93(2)	14
[WBr(NNH$_2$)(NC$_5$H$_4$Me-4)-(PMe$_2$Ph)$_3$]Br	1.75	1.34	177				16
[WHBrCl(NNH$_2$)(PMe$_2$Ph)$_3$]-Br	1.80(4)	1.24(6)	177(5)	2.54(1)[c]	2.51(2)—2.61(2)	3.37(6), 3.24(5)	12
[W(quin)(NNH$_2$)(PMe$_2$Ph)$_3$]-I·0.5Hquin[d]	1.75(1)	1.36(2)	174.7(9)		2.475(3)—2.517(3)	3.604, 3.716	11
[Mo(quin)(NNH$_2$)(PMe$_2$Ph)$_3$]-I[d]	1.743(4)	1.347(7)	172.3(5)		2.500(2)—2.526(2)	3.637, 3.689	11
[Mo(quin)(NNH$_2$)(PMe$_2$Ph)$_3$]-Br[d]	1.735(8)	1.34(1)	168.3(8)		2.476(3)—2.519(4)	3.342, 3.411	11
[WCl$_3$(NNH$_2$)(PMe$_2$Ph)$_2$]	1.75(1)	1.30(2)	178.7(9)	2.508(4)	2.500(2)	3.35(1), 3.43(1)	10
[W(OMe)(NNH$_2$)(dppe)$_2$]-[FeCo$_3$(CO)$_{12}$][e]	1.76(2)	1.25(3)	174.7		2.52(1) (mean)		15
[WBr(NNH$_2$)(depe)$_2$]Br·0.5MeOH[f]	1.739(15)	1.33(3)	175(1)	2.654(2)	2.469(5)—2.494(5)	3.38(2), 3.43(2)	This work
	1.773(11)	1.34(2)	177(1)	2.641(2)	2.463(7)—2.485(5)	3.40(2), 3.51(2)	

[a] Bond lengths in Å, angles in °; average values quoted where appropriate. [b] X = F, Cl, or Br, as shown for any given compound. [c] Br and Cl ligands disordered. [d] quin = Quinolin-8-olate. [e] With some (unspecified) disorder. [f] Two independent molecules in the crystal.

from that which a simple proton base strength prediction might suggest. The unexpected lability of N$_2$ in [Mo(N$_2$)$_2$(depe)$_2$] is a token of this.

Experimental

All experimental manipulations were carried out under an inert atmosphere of dry dinitrogen or argon. Standard Schlenk-tube, vacuum-line, and syringe techniques were employed throughout, as appropriate.

The melting points were determined by an Electrothermal melting point apparatus in sealed tubes and all values obtained are uncorrected. Conductivity measurements were performed in nitromethane using a Portland Electronics bridge. Elemental analyses (C, H, and N) were carried out by Mrs. G. Olney and Ms. K. Plowman of the University of Sussex and by Mr. C. Macdonald of the A.F.R.C.–I.P.S.R. Nitrogen Fixation Laboratory.

Spectral measurements were carried out on the following machines. Infrared spectra (KBr disc): Perkin-Elmer 1710 FTIR in conjunction with Perkin-Elmer PP-I printer-plotter, and Perkin-Elmer 357. N.m.r. spectra: Bruker WM360, JEOL FX90Q, and Bruker WP80. The AA′BB′ spectra were simulated using a Digital VAX 11/75 computer employing the program LAOCOON-5 assuming magnetic equivalence of pairs of phosphorus atoms. The AA′BB′ spectra (AA′BB′X in the case of the fluoro derivative) consist of 2 multiplets centred at *ca.* $(\nu_A - \nu_B)/2$. No double-resonance or double-quantum experiments were carried out, and therefore the signs of the *J* values in Table 2 are not absolute, neither can ν_A and ν_B be correlated with molecular structure. The A,A′ transitions were arbitrarily assigned to the low-field multiplet in each case. Because $|J_{AB'}| > |J_{AB}|$ and $|J_{AA'}| > |J_{BB'}|$ in the results of our simulation, and $L > N, K, M$, the spectrum shows closely spaced doublets. The chloro-complex spectrum shows 10 lines. Overlapping lines arise because of the following equivalence of transitions: $E_{10} - E_{13} = E_9 - E_{12}, E_8 - E_{12} = E_7 - E_{13}, E_{10} - E_{14} = E_3 - E_8$, and $E_3 - E_9 = E_7 - E_{14}$. Similarly, the bromo spectrum shows 11 lines, with equivalences $E_7 - E_{12} = E_8 - E_{13}$ and $E_3 - E_8 = E_{10} - E_{14}$. The root mean square (r.m.s.) deviations of the calculated lines were 0.20 (chloro complex), 0.72 (bromo complex), and 0.46 Hz (fluoro complex). The large error in the case of the bromo complex arises because of difficulty in determining the frequencies of some of the lines in the spectrum.

All solvents were dried by standard methods. The following compounds were prepared by literature methods: dmppe,[8] depe,[8] dinitrogen complexes.[19] Other materials were obtained commercially.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*chloro*[*hydrazido*(2−)]-*hydridotungsten Dichloride*.—*trans*-$[W(N_2)_2(depe)_2]$ (0.64 g, 0.97 mmol) was dissolved in benzene (50 cm^3). Gaseous HCl (0.36 g, 9.74 mmol) was condensed into the solution at −196 °C. The flask was warmed to room temperature and the reaction mixture was stirred for 2 h. The resultant pale yellow suspension was separated by filtration and washed with benzene (2 × 3 cm^3). The pale yellow *solid* was obtained in 0.54 g yield after recrystallization from dichloromethane–diethyl ether.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*chloro*[*hydrazido*(2−)]-*tungsten Chloride*.—A mixture of $[WHCl(NNH_2)(depe)_2]Cl_2$ and $[WCl(NNH_2)(depe)_2]Cl$ was produced as described immediately above. To this mixture (0.28 g) in thf (20 cm^3) was added $NaBPh_4$ (0.13 g). The reaction mixture was stirred for *ca.* 12 h and then filtered. The orange filtrate was evacuated to dryness leaving an oily residue. The residue was extracted with dichloromethane (3 cm^3). Brown *crystals* (0.09 g) were obtained after the addition of an excess of diethyl ether and a few drops of n-hexane to the dichloromethane extract.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*[*hydrazido*(2−)]-*hydridotungsten Dibromide*.—To a solution of $[W(N_2)_2(depe)_2]$ (1.03 g, 1.58 mmol) in thf (20 cm^3) held at −196 °C was added HBr (gaseous, 11.3 mmol) on a vacuum line. On warming the reaction flask to 20 °C, a pink solid was precipitated immediately. This was probably $[WBr(NNH_2)(depe)_2][HBr_2]$. The mixture was stirred continuously for 0.5 h, and the resulting pale yellow *solid* was filtered off, washed with thf, and recrystallized from methanol–diethyl ether as yellow crystals. Yield 0.9 g, 66%.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*[*hydrazido*(2−)]-*hydridotungsten Dibromide–Methanol* (2/1).—*trans*-$[W(N_2)_2(depe)_2]$ (1.33 g, 2.03 mmol) was dissolved in benzene (25 cm^3). Gaseous HBr (1.64 g, 20.2 mmol) was condensed into the solution at −196 °C. The flask was warmed to room temperature and the reaction mixture was stirred for 0.5 h. The suspension was filtered off after washing with portions (2 × 5 cm^3) of benzene and diethyl ether consecutively. The canary-yellow *solid* was dried under vacuum. A yield of 0.93 g of yellow crystals was obtained after recrystallization from methanol–diethyl ether.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromodeuterido*{[$^2H_2$]-*hydrazido*(2−)}*tungsten Dibromide*.—DBr was generated from $SiMe_3Br$ (0.53 g, 3.5 mmol) and MeOD (0.13 g, 3.5 mmol). The mixture was added to a solution of $[W(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$ (0.3 g, 0.35 mmol) in thf (20 cm^3). A pink solid was formed at once and the mixture was stirred for 2 h. The now pale yellow *solid* was filtered off and dried *in vacuo* as $[WDBr(NND_2)(depe)_2]Br_2$. Yield 0.07 g.

A mixture of $[WBr(N_2H_2)(depe)_2]Br$ together with $[WBr(N_2D_2)(depe)_2]Br$ was obtained from the filtrate as red needle-shaped crystals after standing at 20 °C for 16 h. Yield 0.16 g, 58%.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*[*hydrazido*(2−)]-*tungsten Bromide*.—A mixture of $[W(N_2)_2(depe)_2]$ (0.5 g, 0.77 mmol) with HBr (4 mmol) in thf, stirred for 2 h, yielded some yellow solid characterized as $[WHBr(NNH_2)(depe)_2]Br_2$. The solid was filtered off and the filtrate was left to stand at 20 °C for 16 h. Red needle-shaped *crystals* of $[WBr(NNH_2)(depe)_2]Br$ were obtained. Yield 60%.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*[*hydrazido*(2−)]-*molybdenum Bromide*.—To a solution of $[Mo(N_2)_2(depe)_2]$ (1.52 g, 2.70 mmol) in thf (40 cm^3) held at −196 °C was added HBr (gaseous, 27 mmol) using a vacuum line. The reaction flask was warmed to 20 °C and the mixture was stirred for 2.5 h. The *solid* was filtered off, washed with thf, and recrystallized from methanol–diethyl ether yielding violet crystals. Yield 0.85 g.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*dibromomolybdenum Bromide*.—*trans*-$[Mo(N_2)_2(depe)_2]$ (0.85 g, 1.51 mmol) was dissolved in benzene (30 cm^3). The solution was then frozen at *ca.* −196 °C and gaseous HBr (1.21 g, 15 mmol) was added by flask-to-flask condensation. The reaction mixture was warmed to room temperature followed by vigorous stirring for 1 h. The suspension was filtered and washed with diethyl ether (2 × 5 cm^3). The yellow-green solid obtained was recrystallized from dichloromethane or methanol–diethyl ether. The bright yellow *crystals* were collected by filtration and dried *in vacuo*. Yield 1.24 g, 90%. The product shows a singlet in the ^{31}P n.m.r. spectrum at δ −96.78 (relative to trimethyl phosphite) (Found: C, 31.6; H, 6.20. $C_{20}H_{48}Br_3MoP_4$ requires C, 32.0; H, 6.40%). $\Lambda_M(MeNO_2) = 21.1\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Reaction of trans-$[Mo(N_2)_2(depe)_2]$ *with* 10 *Equivalents of* HCl(g).—*trans*-$[Mo(N_2)_2(depe)_2]$ (0.80 g, 1.42 mmol) was dissolved in benzene (50 cm^3). Gaseous HCl (0.53 g, 14.5 mmol) was added at −196 °C by flask-to-flask condensation. The reaction mixture was warmed to room temperature. After stirring for 2 h, the excess of benzene was evacuated to dryness leaving an oily brown residue. The residue was extracted with dichloromethane. Addition of an excess of diethyl ether to the dichloromethane extracts gave a yellow precipitate. The canary yellow solid was obtained after filtration and drying *in vacuo*. Yield 0.75 g, *ca.* 85% {Found: C, 32.7; H, 6.05. $C_{20}H_{48}Cl_3MoP_4$ requires C, 39.0; H, 7.80%. The formulation $[MoCl_2(depe)_2]Cl{\cdot}2CH_2Cl_2$ requires C, 33.6; H, 6.60%}).

Bis{1,2-*bis*[*bis*(4-*methoxyphenyl*)*phosphino*]*ethane*}*bromo*[*hydrazido*(2−)]*molybdenum Hydrogendibromide*.—To *trans*-[Mo(N_2)$_2$(dmppe)$_2$] (1.28 g, 1.08 mmol) suspended in benzene (30 cm^3) was added gaseous HBr (0.87 g, 10.7 mmol) at −196 °C. The reaction mixture was stirred for 1 h after warming at room temperature. It was then filtered and the filtrate was evacuated to dryness. The residue was extracted with methanol. Addition of an excess of diethyl ether to the methanolic extracts gave a brown *precipitate*. The product was filtered off and dried *in vacuo*. Yield 0.29 g.

Bis{*bis*[1,2-*bis*(4-*methoxyphenyl*)*phosphino*]*ethane*}*bromo*[*hydrazido*(2−)]*tungsten Hydrogendibromide*.—*trans*-[W(N_2)$_2$(dmppe)$_2$] (1.03 g, 0.81 mmol) was suspended in benzene (30 cm^3). Gaseous HBr (0.74 g, 0.91 mmol) was added by flask-to-flask condensation at −196 °C. After warming to room temperature, the reaction mixture was stirred for 2.5 h. The clear brown solution was reduced in volume to *ca.* 20 cm^3 followed by the addition of an excess of diethyl ether to give a golden brown precipitate. The *precipitate* was filtered off and washed with diethyl ether (2 × 5 cm^3). The product (yield, 0.83 g) was obtained after drying *in vacuo*.

Bis{1,2-*bis*[*bis*(4-*methoxyphenyl*)*phosphino*]*ethane*}*bromo*[*hydrazido*(2−)]*tungsten Tetraphenylborate*.—[WBr(NNH_2)(dmppe)$_2$][HBr_2] (0.29 g, 0.19 mmol) and $NaBPh_4$ (0.13 g, 0.38 mmol) were stirred in thf (25 cm^3) for 16 h. The reaction mixture was filtered and the filtrate was reduced in volume to *ca.* 5 cm^3. Addition of an excess of methanol afforded a brown *solid*. The product (0.17 g) was obtained after filtration and drying *in vacuo*.

Bis{1,2-*bis*[*bis*(4-*methoxyphenyl*)*phosphino*]*ethane*}*bromo*[*hydrazido*(2−)]*molybdenum Tetraphenylborate*.—[MoBr(NNH_2)(dmppe)$_2$][HBr_2] (0.10 g, 0.07 mmol) and $NaBPh_4$ (0.05 g, 0.15 mmol) were stirred in thf (15 cm^3) for 12 h. The reaction mixture was then filtered and the filtrate was reduced in volume to *ca.* 5 cm^3. Addition of an excess of methanol afforded a yellow-green *precipitate*. The precipitate was filtered off, washed with diethyl ether (2 × 5 cm^3) and vacuum dried. Yield 0.04 g.

X-*Ray Analysis of* [WBr(NNH_2)(depe)$_2$]Br·0.5MeOH.—*Crystal data*. $C_{20}H_{50}Br_2N_2P_4W\cdot0.5CH_4O$, $M = 802.2$, monoclinic, $a = 20.893(5)$, $b = 10.620(2)$, $c = 30.320(4)$ Å, $\beta = 109.09(2)°$, $U = 6\,357.2$ Å^3, space group $P2_1/a$ (equivalent to no. 14), $Z = 8$, $D_c = 1.676$ g cm^{-3}, $F(000) = 3\,176$, $\mu(\text{Mo-}K_\alpha) = 64.2$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

From a flask containing minute opaque yellow and pink crystals and a few brown, square-plate crystals, some of the last type were mounted on glass fibres and coated in epoxy resin. After photographic examination, accurate cell parameters (refined from the settings of 25 reflections having $\theta \sim 10°$) and intensity data were measured on an Enraf-Nonius CAD4 diffractometer with monochromated radiation. During processing of the data, corrections were made for Lorentz-polarization effects, crystal deterioration (the intensities of 2 control reflections dropping *ca.* 15% during the data collection), absorption (by ψ-scan methods) and negative intensities (by Bayesian statistical methods). 5 920 Independent reflections with $\theta_{max.} = 20°$ were entered into the SHELX program,[20] for structure determination by the heavy-atom method, and refinement by full-matrix least-squares methods.

There are two independent W-complex cations in the crystal, two bromide ions, and one molecule of solvent MeOH. The W, Br, P, and N atoms were refined anisotropically. Three C atoms of one depe ligand were considered disordered over two sites, with occupancies 0.7 and 0.3; in that ligand, all the C atoms (except those in the minor sites) were refined anisotropically. In the three other depe ligands the methylene C atoms were refined isotropically with two H atoms 'riding' on each in idealized positions, and the methyl C atoms were refined anisotropically (with no H atoms included). The refined thermal parameters suggest that there is considerable vibration in several of the ethyl groups, and that there may be further examples of site disorder. Also, the solvent MeOH molecule, allowed anisotropic thermal parameters, has not refined well. The bond dimensions in the methanol molecule and in some of the depe ligands were constrained towards normal values. The refinement was terminated with $R = 0.069$ and $R' = 0.065$ for 5 112 reflections [those with $I > \sigma(I)$] weighted $w = (\sigma_F^2 + 0.001\,12\,F^2)^{-1}$.

A final difference map showed features between *ca.* −1.0 and 1.0 e Å^{-3} with the major peaks indicating further inadequacies in the resolution of some of the depe ligands.

Scattering curves for W^{6+}, Br^-, and the other, neutral atoms were from ref. 21. All computations were made on the A.F.R.C.s VAX 11/750 machine at the Glasshouse Crops Research Institute, Littlehampton, using programs listed in Table 4 of ref. 22.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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