Organohydrazido(2−) Complexes of Molybdenum and Tungsten from α,ω-Dibromides; Crystal and Molecular Structures of (Azetidinylimido)bis[1,2-bis(di-*p*-tolylphosphino)ethane]bromotungsten Bromide–Dichloromethane (1/3)†

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The reactions of α,ω-dibromides, $Br(CH_2)_nBr$ (n = 3, 4, or 5), with a range of bis(diphosphine) complexes $[M(N_2)_2(L\text{–}L)_2]$ (L–L = diphosphine) have been investigated. The products are generally of the form $[MBr\{NN(CH_2)_{n-1}CH_2\}(L\text{–}L)_2]Br$ [M = Mo or W, n = 4 or 5, L–L = $R_2PCH_2CH_2PR_2$, where R = Et, Ph, or $4\text{-}XC_6H_4$ (X = Me, MeO, Cl, or CF_3)]. For n = 3 the products take the form $[MBr\{NNH(CH_2)_3Br\}(L\text{–}L)_2]^+$, but when X = Me, ring compounds are again formed, and the structure of the molecule with M = W was determined by *X*-ray structure analysis. The spectroscopic characteristics of the various complexes are discussed.

During our studies of the mono-[1] and di-alkylation[2] of dinitrogen in the complexes $[M(N_2)_2(dppe)_2]$ (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) we carried out a survey of the reactions with α,ω-dibromides, $Br(CH_2)_nBr$.[3] This showed that the reaction products depend upon n in the following way: n = 1, diazoalkane complex; n = 2, $[MBr_2(dppe)_2]$; n = 3, $[MBr(NNCH_2CH_2CH_2Br)(dppe)_2]$ and $[\{MBr(dppe)_2\}_2(\mu\text{-}NNCH_2CH_2CH_2NN)]$; n = 4 or 5, $[MBr\{NN(CH_2)_{n-1}CH_2\}(dppe)_2]^+$; and $n \geqslant 6$, $[MBr\{NN(CH_2)_nBr\}(dppe)_2]^+$ and $[\{MBr(dppe)_2\}_2\{\mu\text{-}NN(CH_2)_nNN\}]$. The reasons for the different products were reasonably well established. The formation of ring compounds by internal quaternization, rather than external reaction of the ω-bromide with more dinitrogen complex, was ascribed to the non-strained nature of the five-membered, $\text{-}N(CH_2)_3CH_2$, and six-membered, $\text{-}N(CH_2)_4CH_2$, rings. The presence of the rings was established by n.m.r. spectroscopy, and also by the formation of piperidine from $[WBr\{NN(CH_2)_4CH_2\}(dppe)_2]^+$ after reduction and treatment with acid.[4] However, no *X*-ray structural analyses were undertaken. This paper describes the effect on product type of varying the diphosphine in $[M(N_2)_2(L\text{–}L)_2]$ (L–L = diphosphine) in the reactions with α,ω-dibromides, $Br(CH_2)_nBr$ (n = 3, 4, or 5).

Results and Discussion

The recent availability of 4-substituted bis(diaryl) diphosphines, $R_2PCH_2CH_2PR_2$ (R = aryl) has enabled us to study the influence of a range of substituents on the properties of diphosphine derivatives, especially of dinitrogen complexes.[5] We discuss here compounds based on the diphosphines $(4\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}4)_2$, which are represented in the text by abbreviations as follows: X = CF_3, dfmppe; Cl, dcppe; H, dppe; Me, dtpe; MeO, dmppe; we also used $Et_2PCH_2CH_2PEt_2$, depe.

In general, the reactions of the dibromides $Br(CH_2)_nBr$ (n = 3, 4, or 5) with $[M(N_2)_2(dppe)_2]$ were carried out in benzene solution, with stirring and with tungsten-filament irradiation (the irradiation being absolutely necessary for M = W) for 6—8 h. The products, usually being ionic, tend to precipitate out of solution which facilitated work-up. For the reactions reported here, it was often found advisable to irradiate for 12—16 h, presumably to complete the primary alkylation, and stirring in the dark for a further 8 h improved the ultimate yield. This apparently facilitated the secondary alkylation. Often the compounds did not precipitate, and a general procedure involved evaporating the reaction mixture to dryness, extracting with methanol {leaving the insoluble $[MBr_2(L\text{–}L)_2]$ behind}, taking to dryness again, and finally recrystallizing from dichloromethane–hexane. For the reaction of dcppe it was advantageous to use neat dibromoalkane (n = 4 or 5) and no solvent; and for dfmppe the molybdenum derivatives with n = 4 or 5 were obtained in very low yields indeed, and the tungsten–bis(dinitrogen) complex, very difficult to prepare pure, yielded products which contained no nitrogen. Finally, reactions of $[Mo(N_2)_2(depe)_2]$ did not proceed unless the solvent was refluxed, and for $Br(CH_2)_3Br$ we obtained uncharacterizable oils.

Data for the compounds are given in Tables 1—3. Many of the analyses could only be rationalized satisfactorily by including some solvent in the formulations, which was confirmed by ^1H n.m.r. spectroscopy. The tendency of bis(diphosphine) complexes to retain small solvent molecules in the crystal has been recognized frequently during crystal-structure determinations,[6] so this observation is not surprising. The solvent was often lost upon exposure to air or under reduced pressure, which contributed to the inconsistencies in some of the analytical data.

The reactions of $Br(CH_2)_3Br$ yield diazenido complexes except with the derivatives of dtpe. These can be protonated by acid in the usual way to give hydrazido(2−) complexes. Very unexpectedly, the compounds $[M(N_2)_2(dtpe)_2]$ yielded products which, on the basis of i.r. and n.m.r. (^1H and ^{13}C) spectroscopy, appear to contain a ring, *viz.* $\text{-}N(CH_2)_2CH_2$, resulting from internal quaternization. This was confirmed by *X*-ray structural analysis of crystals of $[WBr\{NN(CH_2)_2CH_2\}(dtpe)_2]Br\cdot 3CH_2Cl_2$.

We have previously shown that the hydrazido(2−) complexes $[WBr(NNMe_2)(dppe)_2]Br$ and $[MBr\{NN(CH_2)_3CH_2\}(dppe)_2]Br$ (M = Mo or W) can be destructively reduced by $LiAlH_4$ to yield dimethylamine and pyrrolidine, respectively.[4] Further, we showed that chemical or electrochemical reduction of $[MoBr\{NN(CH_2)_4CH_2\}(dppe)_2]Br$ yields the five-co-ordinate molybdenum(II) species $[Mo\{NN(CH_2)_4CH_2\}(dppe)_2]$[7] which, upon treatment with HBr, produces piperidine and $[MoBr(NH)(dppe)_2]Br$.[8]

In order to determine whether similar reactions are feasible with the new complexes, we studied their cyclic voltammetry in tetrahydrofuran (thf) and in the novel electrolyte $[NBu^n{}_4][BF_4]\cdot 3MePh$. The data are presented in Table 4. All the complexes undergo irreversible two-electron reductions. There

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

Table 1. New organohydrazido(2−) complexes of molybdenum and tungsten

Complex	Form	M.p.[a]/°C	Yield (%)	Conductivity Λ_M (MeNN$_2$)/Ω^{-1} cm^2 mol^{-1}	ν(N=N)/ cm^{-1}	Analysis[b] (%) C	H	N
(**1**) $[\mathrm{MoBr\{NNH(CH_2)_3Br\}(dmppe)_2]BF_4}$	Brown-green solid	125—127	43	84	1 354	50.9 (51.9)	5.20 (4.85)	2.05 (1.90)
(**2**) $[\mathrm{WBr\{NNH(CH_2)_3Br\}(dmppe)_2]BF_4\cdot CH_2Cl_2}$	Brown solid	116—120	45	60	1 358	47.0 (47.1)	4.50 (4.50)	1.65 (1.70)
(**3**) $[\mathrm{MoBr\{N\overline{N(CH_2)_2CH_2}\}(dtpe)_2]Br\cdot 3CH_2Cl_2}$	Dark green crystals	197—198	15	40	1 313	53.1 (53.2)	5.35 (5.10)	2.10 (1.90)
(**4**) $[\mathrm{WBr\{N\overline{N(CH_2)_2CH_2}\}(dtpe)_2]Br\cdot CH_2Cl_2}$	Brown crystals	180	46	25	1 312	55.0 (54.6)	5.25 (5.10)	1.95 (2.00)
(**5**) $[\mathrm{MoBr\{NNH(CH_2)_3Br\}(dppe)_2]BF_4}$	Salmon-red solid	214—215	32	56	1 358	56.6 (54.6)	4.70 (4.55)	2.55 (2.30)
(**6**) $[\mathrm{MoBr\{NNH(CH_2)_3Br\}(dcppe)_2]BF_4}$	Green-brown crystals	238—240	38	92	1 357	43.9 (44.4)	3.10 (3.15)	1.80 (1.90)
(**7**) $[\mathrm{MoBr\{N\overline{N(CH_2)_3CH_2}\}(depe)_2]Br}$	Brown solid	176—177	72	59	1 322	38.4 (38.3)	7.00 (7.45)	3.75 (3.70)
(**8**) $[\mathrm{MoBr\{N\overline{N(CH_2)_3CH_2}\}(dmppe)_2]Br\cdot CH_2Cl_2}$	Green crystals	158—160	57	64	1 318	54.4 (53.4)	5.40 (5.45)	1.95 (1.90)
(**9**) $[\mathrm{WBr\{N\overline{N(CH_2)_3CH_2}\}(dmppe)_2]Br}$	Brown crystals	172—173	42	49	1 324	52.1 (52.4)	5.10 (4.90)	1.85 (1.90)
(**10**) $[\mathrm{MoBr\{N\overline{N(CH_2)_3CH_2}\}(dtpe)_2]Br\cdot 1.5CH_2Cl_2}$	Green crystals	143	72	81	1 320	57.6 (57.1)	5.25 (5.45)	2.05 (2.05)
(**11**) $[\mathrm{WBr\{N\overline{N(CH_2)_3CH_2}\}(dtpe)_2]Br}$	Brown crystals	180—182	53	54	1 325	58.8 (57.5)	5.80 (5.40)	1.85 (2.10)
(**12**) $[\mathrm{MoBr\{N\overline{N(CH_2)_3CH_2}\}(dcppe)_2]Br\cdot 3CH_2Cl_2}$	Green crystals	189—191	72	57	1 320	41.9 (42.4)	3.15 (3.25)	1.75 (1.70)
(**13**) $[\mathrm{WBr\{N\overline{N(CH_2)_3CH_2}\}(dcppe)_2]Br\cdot CH_2Cl_2}$	Pink-brown crystals	217—218	31	109	1 323	44.1 (43.2)	3.20 (3.15)	1.70 (1.75)
(**14**) $[\mathrm{MoBr\{N\overline{N(CH_2)_3CH_2}\}(dfmppe)_2]Br}$	Brown-green solid	245	46	74	Obscured by diphosphine	45.6 (45.7)	3.10 (2.85)	1.35 (1.65)
(**15**) $[\mathrm{MoBr\{N\overline{N(CH_2)_4CH_2}\}(depe)_2]Br}$	Brown solid	148—150	58	32	1 353	39.5 (39.2)	7.20 (7.55)	3.45 (3.65)
(**16**) $[\mathrm{MoBr\{N\overline{N(CH_2)_4CH_2}\}(dmppe)_2]Br}$	Green crystals	145	65	81	1 342	55.6 (56.1)	5.70 (5.30)	1.75 (2.00)
(**17**) $[\mathrm{WBr\{N\overline{N(CH_2)_4CH_2}\}(dmppe)_2]Br\cdot 0.5CH_2Cl_2}$	Red-brown crystals	142	78	100	1 340	51.5 (51.6)	5.15 (4.95)	1.95 (1.85)
(**18**) $[\mathrm{MoBr\{N\overline{N(CH_2)_4CH_2}\}(dtpe)_2]Br\cdot 3CH_2Cl_2}$	Dark green crystals	149—150	63	43	1 345	53.9 (53.8)	5.35 (5.25)	1.85 (1.85)
(**19**) $[\mathrm{WBr\{N\overline{N(CH_2)_4CH_2}\}(dtpe)_2]Br\cdot CH_2Cl_2}$	Brown crystals	208—210	58	42	1 346	55.1 (55.2)	5.10 (5.30)	1.95 (1.95)
(**20**) $[\mathrm{MoBr\{N\overline{N(CH_2)_4CH_2}\}(dcppe)_2]Br}$	Green solid	212—213	48	38	1 339	47.3 (48.0)	3.40 (3.50)	1.80 (1.95)
(**21**) $[\mathrm{WBr\{N\overline{N(CH_2)_4CH_2}\}(dcppe)_2]Br\cdot CH_2Cl_2}$	Pink solid	220	30	78	1 353	43.5 (43.5)	3.45 (3.25)	1.70 (1.75)
(**22**) $[\mathrm{MoBr\{N\overline{N(CH_2)_4CH_2}\}(dfmppe)_2]Br}$[c]	Orange solid							

[a] With decomposition. [b] Calculated values in parentheses. [c] Characterized spectroscopically, only trace amounts obtained.

were no obvious oxidations within the voltage range scanned. The significance of the data is discussed below.

Discussion

This paper is one of a number in which we have described the effect of changing the diphosphine in a series of complexes containing the basic skeleton $M(L\text{–}L)_2$ (L–L = diphosphine), and which consist of *trans*-bis(dinitrogen) complexes and some derivatives. The reactivity pattern with α,ω-dibromides $Br(CH_2)_nBr$ (n = 3, 4, or 5) largely follows the pattern established earlier. The compounds in Table 1 are listed in order of n and, within each value of n, in decreasing probable donor power of the diphosphines.

In general, the preparative reactions involved here are rather slow, and with the less strong donors (dcppe and dfmppe) loss of N_2 from $[Mo(N_2)_2(L\text{–}L)_2]$ seems to be much more favoured, causing low or zero yields of the desired products. It was generally possible to obtain better yields with Mo than with W, which is the converse of what was observed with the corresponding, faster protonation reactions.[9]

The most complete series was obtained for n = 4, for which we found no evidence of open-chain diazenido complexes. It is unlikely that open-chain diazenido complexes will form with n = 5, whereas we obtained no indication of ring formation in some preliminary experiments with n = 6. The extraordinary observation is that ring formation does occur with n = 3,

Table 2. 90-MHz ^{1}H and ^{31}P-{^{1}H} N.m.r. spectra of organohydrazido(2−) complexes of molybdenum and tungsten[a]

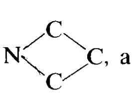
		^{1}H N.m.r.[c]				
Complex[b]	Solvent	Phenyl	PCH_2	CH_3	$\overline{N(CH_2)_{n-1}C}H_2$ or $N(H)CH_2CH_2CH_2Br$	^{31}P N.m.r.[d]
(1)	$CDCl_3$	7.46—6.53 (32)	3.16—2.34 (br, 10)	3.85, 3.76 (d, 25)	NH under Me; NCH_2, 2.11—1.77 (br, 2); CH_2, 1.33—1.03 (br, 2); CH_2Br under PCH_2	−98.3
(2)	$CDCl_3$	7.67—6.16 (32)	3.04—2.13 (br, 10)	3.85, 3.76 (d, 24)	NH, 4.04 (br s, 1); NCH_2, 1.98—1.67 (br, 2); CH_2, 1.03—0.76 (br, 2); CH_2Br under PCH_2	−114.2 (J_{WP} 282 Hz)
(3)	$CDCl_3$	7.17—6.48 (32)	3.07—2.37[e] (br, 10)	2.35, 2.30 (d, 24)	2.70[e] (m); 1.16 (qnt?, 4)	−98.5
(4)	$CDCl_3$	7.31—6.44 (32)	3.06—2.06[e] (br, 10)	2.40,[e] 2.31[e] (d, 24)	2.88[e] (t); 1.15 (t, 4)	−113.7 (J_{WP} 279 Hz)
(5)	$CDCl_3$	7.60—6.80 (40)	3.20—2.50 (br, 10)		NH, 5.09—4.88 (br, 1); NCH_2, 2.06—1.72 (q, 2); CH_2, 1.20—0.80 (qnt, 2); CH_2Br under PCH_2	−96.9
(6)	$CDCl_3$	7.32—6.66 (32)	3.03—2.42 (br, 10)		NH, 6.49—6.27 (br s, 1); NCH_2, 2.12—1.81 (m, 2); CH_2, 1.37—1.03 (m, 2); CH_2Br under PCH_2	−98.2
(7)	$CDCl_3$		2.09—1.52[e] (m, 28)	1.52—0.99[e] (m, 24)	3.46 (t, 4); under PCH_2	−96.9
(8)	$CDCl_3$	7.61—6.52 (32)	3.20—2.32 (br s, 8)	3.85, 3.75 (d, 24)	2.12 (br s, 4); 1.05 (br s, 4)	−98.7
(9)	CD_2Cl_2	7.57—6.46 (32)	3.06—2.33 (br s, 8)	3.83, 3.77 (d, 24)	2.16 (br m?, 4); 0.98 (br m?, 4)	−113.2 (J_{WP} 280.0 Hz)
(10)	$CDCl_3$	7.25—6.50 (32)	3.11—2.46[e] (br s, 8)	2.35,[e] 2.23[e] (d, 24)	1.97[e] (br m, 4); 0.94 (br m, 4)	−98.1
(11)	$CDCl_3$	7.66—6.33 (32)	3.18—2.26[e] (br s, 8)	2.40,[e] 2.31[e] (d, 24)	2.10 (br s, 4); 0.95 (br s, 4)	−114.4 (J_{WP} 279.6 Hz)
(12)	CD_2Cl_2	7.61—6.97 (32)	3.28—2.59 (br s, 8)		2.30 (br s?, 4); 1.13 (br s?, 4)	−95.0
(13)	$CDCl_3$	7.72—6.73 (32)	3.30—2.58 (br s, 8)		2.31 (br m?, 4); 1.10 (br m?, 4)	−114.5 (J_{WP} 287.2 Hz)
(14)	CD_2Cl_2	8.00—7.20 (32)	3.40—2.80 (br s, 8)		2.27 (br m?, 4); 1.18 (br m?, 4)	−93.9
(15)	CD_2Cl_2		2.60—1.42[e] (m, 32)	1.42—0.48[e] (m, 24)	3.80—3.36 (m, 2); under PCH_2	−98.4
(16)	$CDCl_3$	7.60—6.51 (32)	3.12—2.34 (br s, 8)	3.86, 3.76 (d, 24)	1.61 (br s, 4); 0.82 (br s, 6)	−99.7
(17)	CD_2Cl_2	7.40—6.21 (32)	2.96—2.31 (br s, 8)	3.83, 1.76 (d, 24)	1.63 (br m?, 4); 0.85 (br m?, 6)	−114.4 (J_{WP} 282.1 Hz)
(18)	$CDCl_3$	7.29—6.41 (32)	3.08—2.41[e] (br s, 8)	2.40,[e] 2.29[e] (d, 24)	1.54 (br s, 4); 0.77 (br s, 6)	−99.0
(19)	$CDCl_3$	7.61—6.70(32)	3.20—2.52[e] (br s, 8)	2.40,[e] 2.31[e] (d, 24)	1.50 (br s, 4); 0.75 (br s, 6)	−115.0 (J_{WP} 282.0 Hz)
(20)	CD_2Cl_2	7.74—6.95 (32)	3.28—2.48 (br s, 8)		1.84 (br s, 4); 0.90 (br s, 6)	−97.0
(21)	CD_2Cl_2	7.63—6.55 (32)	3.22—2.48 (br s, 8)		1.77 (br s, 4); 0.88 (br s, 6)	−113.9 (J_{WP} 282.0 Hz)
(22)	CD_2Cl_2	8.00—6.90 (32)	3.30—2.60 (br s, 8)		1.65 (br m?, 4); 0.90 (br m?, 6)	−93.2

[a] br = Broad; s = singlet; d = doublet; t = triplet; q = quartet; qnt = quintet. [b] For compound designations see Table 1. [c] Relative to $SiMe_4$. [d] Relative to trimethyl phosphite. [e] Overlapping peak.

Table 3. 90-MHz ^{13}C-{^{1}H} N.m.r. spectra of some cyclic organohydrazido(2−) complexes[a] relative to $SiMe_4$

Complex[b]	Solvent	$-C_6H_4-$	$-PCH_2-$	$N(CH_2)_n$	Other alkyls
(3)	$CDCl_3$	140.76—128.54 (m)	29.60 (m)	53.45 (s, 2); 13.90 (m, 1)	21.33 (s)
(4)	$CDCl_3$	141.53 128.48 (m)	32.36 (m)	56.31 (s, 2); 14.30 (s, 1)	21.33 (s)
(7)	$CDCl_3$		18.95 (q)	53.58 (s, 2); 24.31 (s, 2)	CH_2, 23.0—20.5 (sxt); Me, 9.36, 8.28 (d)
(8)	$CDCl_3$	161.67—113.52 (m)	29.56 (m)	50.30 (d, 2); 20.66 (s, 2)	55.90, 55.12 (d)
(9)	CD_2Cl_2	162.15—113.82 (m)	33.25 (m)	48.87 (s, 2); 23.84 (s, 2)	56.00, 55.50 (d)
(11)	$CDCl_3$	141.53—128.66 (m)	32.16 (m)	48.27 (s, 2); 23.72 (s, 2)	21.51, 21.57 (d)
(12)	CD_2Cl_2	138.30—129.00 (m)	30.20 (m)	Under CD_2Cl_2: 24.60 (m?, 2)	
(16)	$CDCl_3$	161.67—113.52 (m)	29.26 (m)	50.95 (s, 2); 24.67 (s, 2); 21.84 (s, 1)	55.78, 55.12 (d)
(19)	$CDCl_3$	141.65—128.66 (m)	32.94 (m)	49.76 (s, 2); 24.91 (s, 2); 22.17 (s, 1)	21.39, 21.27 (d)
(20)	CD_2Cl_2	138.43—128.28 (m)	29.71 (m)	52.62 (s, 2); 24.94 (s, 2); 21.99 (s, 1)	

[a] s = Singlet; d = doublet; q = quintet; sxt = sextet; m = multiplet. [b] For compound designations, see Table 1.

despite the likely strain in the ring , and with the diphosphine dtpe, which is intermediate in presumed donor power between dmppe and dppe, which both yield open-chain diazenido compounds. We have shown[2,10] that the second alkylation of co-ordinated dinitrogen in the sequence M–N≡N → M–N=NR → M=N–NR$_2$ by an alkyl halide, RX, involves nucleophilic (S_N2) attack of the monoalkylated nitrogen upon the halogen-bearing carbon of RX, and it may be assumed that a similar mechanism is operating here, too. However, there must be a complication in that a stronger donating diphosphine, while increasing the nucleophilicity of the nitrogen should also, to some degree, decrease the electrophilicity of the carbon to be attacked. This latter effect should diminish as *n*, in $Br(CH_2)_nBr$, increases, and we infer that it is not significant with $n = 4$. With $n = 3$ the balance of the two effects is enough to cause ring formation only with dtpe. For more strongly donating phosphines, the carbon is not electrophilic enough. For more weakly donating phosphines the nitrogen is not nucleophilic enough. It is hardly likely that differences in steric effects are important here since all the phosphine substituents are in *para* positions, well removed from the centres of reaction.

The values of ν(N=N) (Table 1) do not vary greatly, bearing in mind the admitted experimental error (±2 cm^{-1}) and the fact that these are unlikely to be pure N–N vibrations. For M = Mo and $n = 4$, in the series from depe to dcppe, ν(N=N) is invariant with diphosphine, which is very different from ν(N≡N) in the corresponding dinitrogen complexes.[5] For $n = 5$ the values are *ca.* 1 345 cm^{-1}, and for $n = 3$ are *ca.* 1 355 cm^{-1} for

Table 4. Electrochemical properties of some cyclic organohydrazido(2−) complexes $[MBr\{N\overline{N(CH_2)_{n-1}C}H_2\}(L\text{–}L)_2]Br$ (M = Mo or W, n = 3, 4, or 5)

Diphosphine (L–L)	n	E_p^{red}/V[a] Mo	E_p^{red}/V[a] W	Electrolyte[b]
depe	4	−2.105 (1.95)		(1)
dmpe	4	−1.815 (1.74)	−2.090	(1)
dmpe	4		−1.90	(2)
dtpe	3	−1.355	−1.890 (2.07)	(1)
dtpe	3		−1.76	(2)
dtpe	4	−1.715 (1.63)	−2.028	(1)
dtpe	4		−1.81	(2)
dtpe	5	−1.745 (1.70)	−2.002	(1)
dtpe	5		−1.79	(2)
dppe	4	−1.625 (2.00)	−1.985 (2.00)	(1)
dppe	4		−1.80	(2)
dcppe	4	−1.585 (1.68)	−1.805 (1.91)	(1)
dcppe	4		−1.66	(2)
dfmppe	4	−1.215		(1)

[a] Values in parentheses are numbers of electrons involved; data relative to s.c.e. [b] (1) = $[NBu^n{}_4]BF_4$–thf; (2) = $[NBu^n{}_4]BF_4 \cdot 3MePh$.

the diazenido complexes, and *ca.* 1 312 cm^{-1} for the ring compounds. These are not characteristic of diphosphine or metal, but of structural type, increasing in the series $n = 3 < 4 < 5$.

The ring compounds apparently all have the same general structure, being electrolytes (Table 1) and showing a single ^{31}P n.m.r. signal (Table 2) due to the presence of four phosphorus atoms in a plane and hence implying a *trans*-octahedral structure, already suggested for the dppe derivatives. The tungsten compounds show the usual tungsten satellites. All the compounds contain metal in the formal oxidation state IV, and we have shown previously[5] that the differences between ^{31}P chemical shifts for corresponding molybdenum and tungsten compounds decrease in oxidation state, and that J_{WP} values decrease in the same way. The observed values are precisely those to be expected of these oxidation states, independent of phosphine.

The ^{13}C n.m.r. spectra of the ring carbons (Table 3) show, for $n = 3$, two kinds of carbon, present in the ratio 2:1, for $n = 4$, two types of carbon present in equal amount, and for $n = 5$, three types of ring carbon, present in the ratio 2:2:1. The carbons joined to nitrogen have the largest shifts in every case (*ca.* 50 p.p.m.) but the unique carbon for $n = 3$ has a very small shift, which may indicate that it is particularly strained. In fact, the C–C–C angle is only *ca.* 96° (see below). However, the N–C–C angles are even smaller, and the corresponding carbon shifts more 'normal,' *cf.* azetidine itself for which ^{13}C shifts of 47.2 and 21.2 p.p.m. have been reported.[11a] The corresponding values for pyrrolidine and piperidine are 47.1 and 25.7 p.p.m.[12] and 47.9, 27.8, and 25.9 p.p.m.,[12] respectively.

The resonances of the methyl carbons of the dtpe complexes appear as doublets. The same is true of complexes of dmppe, the methoxy carbon giving rise to a doublet. This is not true in the cases $[MBr\{N\overline{N(CH_2)_2C}H_2\}(dtpe)_2]Br$. However, the corresponding proton spectra are all split into doublets, and a doublet is even observed in the ^{19}F-$\{^1H\}$ n.m.r. spectrum of $[MoBr\{N\overline{N(CH_2)_3C}H_2\}(dfmppe)_2]Br$. The splittings observed in the ^1H n.m.r. spectra of $[WBr\{N\overline{N(CH_2)_{n-1}C}H_2\}(dtpe)_2]Br$ increase with observation frequency, so this is not a coupling phenomenon. We have previously shown that the phenyl regions of the ^1H n.m.r. spectra are diagnostic of complex type [dinitrogen, diazenido, or hydrazido(2−)]. The new observations may be related. However, similar splittings are not observed in the spectra of the corresponding diazenido complexes $[MBr(NNEt)(dtpe)_2]$.

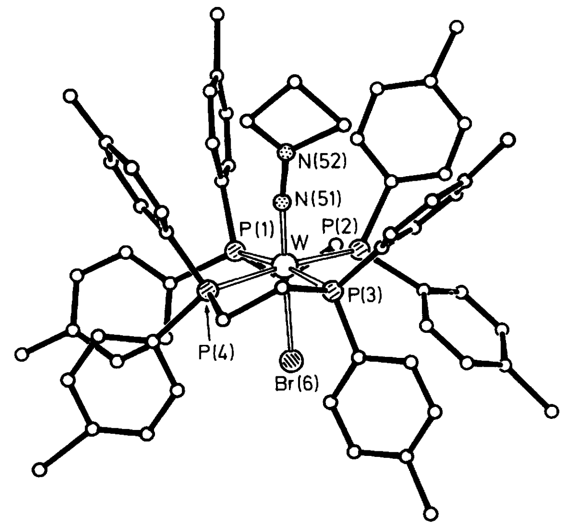


Figure 1. Molecular structure of $[WBr\{N\overline{N(CH_2)_2C}H_2\}(dtpe)_2]^+$

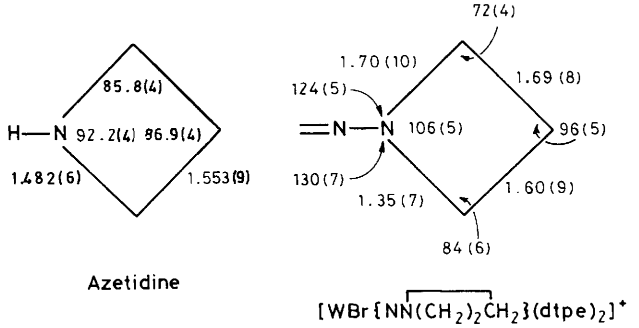


Figure 2. Comparison of the dimensions of the rings in azetidine (determined by electron diffraction)[11b] and $[WBr\{N\overline{N(CH_2)_2C}H_2\}(dtpe)_2]^+$ (angles in degrees, lengths in Å)

The crystal structure data for $[WBr\{N\overline{N(CH_2)_2C}H_2\}(dtpe)_2]Br$ in Tables 5 and 6, even though rather imprecise, confirm the structural predictions made from spectroscopy. The P atoms of the two chelating dtpe ligands form the equatorial plane of the co-ordination octahedron in the complex cation, Figure 1. The W atom is slightly displaced (0.14 Å) from this plane towards the hydrazido ligand. The Br–W–N system is almost linear (*ca.* 177°) but the quasi-linear W–N–N group is tilted slightly towards P(3) [P(3)–W $\cdots$ N(52) = 85(1)°]; the W–N–N angle is 171(5)°, W–N = 1.72(6) and N–N = 1.42(6) Å, all much as expected. The two N atoms and the connected C atoms are essentially coplanar, that is with the *exo*-N atom apparently sp^2 hybridized. However, the azacyclobutane system is very asymmetrical and strained. Figure 2 shows that the heterocyclic ring (which is only slightly puckered) is considerably distorted from the highly strained azetidine ring system (data taken from ref. 11*b*].

The NC_3 ring lies between the two dtpe ligands with the normal to its mean plane approximately parallel to the P(1) $\cdots$ P(4) and P(2) $\cdots$ P(3) vectors. Each of the two C atoms bonded to N(52) is in close contact with two dtpe phenyl rings. The P–W–P angle between the phosphorus atoms of the same diphosphine (*ca.* 80°) is smaller than that between the phos-

Table 5. Final fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	2 137(5)	2 071(2)	1 893(2)
C(11a)	1 882(46)	2 129(28)	−147(20)
C(11b)	1 963(46)	2 734(28)	−582(20)
C(11c)	1 195(46)	2 656(28)	−1 234(20)
C(11d)	346(46)	1 974(28)	−1 452(20)
C(11e)	264(46)	1 369(28)	−1 017(20)
C(11f)	1 032(46)	1 446(28)	−365(20)
C(11g)	−499(89)	1 905(32)	−2 110(34)
C(12a)	4 098(46)	3 160(22)	639(25)
C(12b)	5 165(46)	3 140(22)	289(25)
C(12c)	6 128(46)	3 787(22)	301(25)
C(12d)	6 025(46)	4 454(22)	661(25)
C(12e)	4 958(46)	4 474(22)	1 011(25)
C(12f)	3 995(46)	3 827(22)	1 000(25)
C(12g)	7 165(77)	5 199(28)	730(28)
P(1)	2 952(27)	2 242(10)	713(10)
C(1)	3 914(94)	1 407(33)	606(36)
C(2)	5 190(105)	1 565(38)	1 162(43)
P(2)	4 247(28)	1 649(10)	2 084(11)
C(21a)	5 638(45)	2 356(21)	2 619(23)
C(21b)	5 923(45)	3 082(21)	2 383(23)
C(21c)	6 834(45)	3 646(21)	2 785(23)
C(21d)	7 461(45)	3 484(21)	3 424(23)
C(21e)	7 177(45)	2 758(21)	3 661(23)
C(21f)	6 265(45)	2 194(21)	3 258(23)
C(21g)	8 815(106)	3 995(42)	3 714(42)
C(22a)	4 609(66)	729(18)	2 476(22)
C(22b)	5 616(66)	360(18)	2 486(22)
C(22c)	5 520(66)	−334(18)	2 787(22)
C(22d)	4 418(66)	−658(18)	3 080(22)
C(22e)	3 410(66)	−288(18)	3 070(22)
C(22f)	3 506(66)	405(18)	2 769(22)
C(22g)	4 367(86)	−1 520(32)	3 351(32)
C(31a)	305(59)	814(20)	3 169(34)
C(31b)	609(59)	531(20)	3 824(34)
C(31c)	109(59)	−221(20)	3 938(34)
C(31d)	−694(59)	−690(20)	3 397(34)
C(31e)	−998(59)	−407(20)	2 742(34)
C(31f)	−498(59)	346(20)	2 628(34)
C(31g)	−1 487(104)	−1 499(40)	3 606(40)
C(32a)	1 970(67)	2 166(20)	3 888(23)
C(32b)	1 527(67)	2 467(20)	4 480(23)
C(32c)	2 354(67)	2 712(20)	5 103(23)
C(32d)	3 625(67)	2 657(20)	5 134(23)
C(32e)	4 068(67)	2 356(20)	4 542(23)
C(32f)	3 240(67)	2 110(20)	3 919(23)
C(32g)	4 453(100)	3 028(38)	5 877(40)
P(3)	1 117(30)	1 773(10)	3 030(11)
C(3)	−158(88)	2 260(32)	2 986(31)
C(4)	−1 251(83)	2 139(29)	2 240(33)
P(4)	43(31)	2 350(9)	1 544(10)
C(41a)	−1 229(57)	1 959(33)	757(30)
C(41b)	−1 711(57)	2 297(33)	173(30)
C(41c)	−2 538(57)	1 856(33)	−377(30)
C(41d)	−2 883(57)	1 076(33)	−341(30)
C(41e)	−2 401(57)	737(33)	244(30)
C(41f)	−1 574(57)	1 178(33)	793(30)
C(41g)	−4 006(84)	803(31)	−1 059(32)
C(42a)	186(52)	3 390(16)	1 459(26)
C(42b)	855(52)	3 713(16)	917(26)
C(42c)	1 021(52)	4 486(16)	836(26)
C(42d)	518(52)	4 935(16)	1 297(26)
C(42e)	−152(52)	4 612(16)	1 839(26)
C(42f)	−318(52)	3 840(16)	1 919(26)
C(42g)	557(75)	5 790(27)	1 226(27)
N(51)	2 748(73)	2 976(34)	2 249(29)
N(52)	3 210(75)	3 679(35)	2 643(31)
C(53)	4 046(93)	3 787(36)	3 467(38)
C(54)	3 953(79)	4 653(29)	3 208(30)
C(55)	2 943(91)	4 360(38)	2 521(36)
Br(6)	1 317(11)	685(3)	1 352(4)
Br(7)	2 351(15)	4 125(5)	7 132(5)

Solvent CH_2Cl_2 molecules				s.o.f.*
C(8)	6 798(109)	5 260(39)	4 711(37)	0.85
Cl(8a)	6 156(35)	4 352(13)	4 831(12)	0.85
Cl(8b)	8 506(37)	5 483(11)	5 199(12)	0.85
C(9)	9 122(130)	3 691(53)	6 137(56)	0.80
Cl(9a)	8 053(54)	3 708(18)	6 712(18)	0.80
Cl(9b)	8 790(41)	2 849(15)	5 697(15)	0.80
C(10)	4 617(135)	3 064(56)	8 170(45)	0.80
Cl(10a)	4 148(42)	2 134(14)	8 215(16)	0.80
Cl(10b)	5 870(56)	3 531(19)	8 137(23)	0.80
C(11)	6 963(206)	352(90)	4 470(81)	0.55
Cl(11a)	6 667(53)	−344(20)	4 884(21)	0.55
Cl(11b)	7 575(58)	1 131(24)	4 779(22)	0.55

* Site occupancy factor, if different from 1.0.

phorus atoms of different diphosphines (*ca.* 100°). There are clearly at least two kinds of tolyl group, and this may account for the n.m.r. spectra. In addition, asymmetry is provided by the two PCH_2CH_2P bridges, which take up parallel conformations. Because of the ^1H n.m.r. spectra, we infer that this parallel conformation is probably common to all the dtpe complexes.

Table 7 lists some data from comparable compounds in the literature. Although the W–P and W–Br bond lengths are all similar, the W–N distance here is the shortest yet reported in compounds of this type, and N–N is the longest. The structure most similar is probably that of $[\mathrm{WF}\{\mathrm{NNCOCH_2CH_2CO}\}(\mathrm{dppe})_2]\mathrm{BF_4}$,[13] which contains a five-membered ring. This shows similar planarity around the *exo*-nitrogen and suggests similar sp^2 hybridization. The ring arrangement is rather different, presumably because the ring is less strained.

The bromide anion is quite separate from the cationic complex, but is surrounded by hydrogen atoms of CH_2Cl_2 molecules in three of the four solvent locations.

We have shown previously that $[\mathrm{MoBr}\{\mathrm{NN(CH_2)_4CH_2}\}(\mathrm{dppe})_2]\mathrm{Br}$ can be reduced chemically and electrochemically to give $[\mathrm{Mo}\{\mathrm{NN(CH_2)_4CH_2}\}(\mathrm{dppe})_2]$, which in turn reacts with HBr to yield $[\mathrm{MoBr(NH)(dppe)_2}]$ and piperidine.[7,8] The new complexes present the possibility of synthesizing piperidines, pyrrolidines, and even azetidines by similar routes. All the complexes undergo irreversible two-electron reductions, and the data are presented in Table 4.

The reduction peaks of the tungsten complexes, particularly with aryl diphosphines, with the more electron-donating substituents, MeO– and Me–, were observed as shoulders on the solvent reduction peaks in thf. We therefore undertook measurements in $[\mathrm{NBu^n_4}]\mathrm{BF_4}$·3MePh, although we had to make measurements above the freezing point (30 °C) in this case.[14] The data allow the following generalizations. (*i*) E_p^{red} are at more negative potentials for tungsten complexes than for molybdenum complexes. (*ii*) E_p^{red} becomes more negative in the sequence $CF_3 > Cl > H > Me > OMe$ for substituents X in the diphosphines $(4\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}4)_2$. (*iii*) E_p^{red} also varies slightly with ring size, generally becoming more negative in the sequence $n = 3 > 5 > 4$. This implies that the smallest rings make the complexes less difficult to reduce.

The reduction peaks for derivatives of $4\text{-}ClC_6H_4$ and $4\text{-}CF_3C_6H_4$ were often broad and the maxima more difficult to define. This may be due to impurities, because the parent dinitrogen complexes are difficult to obtain pure, or to reduction of the substituent. We did not attempt to determine which.

The values of E_p^{red} are clearly solvent dependent, but the spread of values in thf is not very different from that in $[NBu^n{}_4]BF_4{\cdot}3MePh$. In addition, a plot of E_p^{red} values in thf against E_p^{red} in $[NBu^n{}_4]BF_4{\cdot}3MePh$ is linear, with a correlation coefficient of 0.98. We infer that the solvents are not significantly involved in solvating the species in either case.

Table 6. Selected molecular dimensions, bond lengths (Å) and angles (°), with e.s.d.s in parentheses

(*a*) About the W atom

W–P(1)	2.488(20)	W–P(4)	2.46(3)
W–P(2)	2.555(30)	W–N(51)	1.72(6)
W–P(3)	2.545(22)	W–Br(6)	2.610(7)
P(1)–W–P(2)	77.4(8)	P(3)–W–N(51)	89.1(19)
P(1)–W–P(3)	173.6(8)	P(4)–W–N(51)	92.1(25)
P(2)–W–P(3)	104.6(8)	P(1)–W–Br(6)	82.2(5)
P(1)–W–P(4)	96.9(8)	P(2)–W–Br(6)	82.3(5)
P(2)–W–P(4)	171.3(6)	P(3)–W–Br(6)	92.0(5)
P(3)–W–P(4)	80.4(8)	P(4)–W–Br(6)	90.6(5)
P(1)–W–N(51)	96.8(19)	N(51)–W–Br(6)	177.3(25)
P(2)–W–N(51)	95.1(25)		

(*b*) In the hydrazido ligand

N(51)–N(52)	1.42(6)	W–N(51)–N(52)	171.4(46)
N(52)–C(53)	1.70(10)	N(51)–N(52)–C(53)	124.1(52)
N(52)–C(55)	1.35(7)	N(51)–N(52)–C(55)	129.5(70)
C(53)–C(54)	1.69(8)	C(53)–N(52)–C(55)	105.7(54)
C(54)–C(55)	1.60(9)	N(52)–C(53)–C(54)	72.0(42)
		C(53)–C(54)–C(55)	95.7(46)
		N(52)–C(55)–C(54)	84.4(60)

(*c*) Torsion angles in the ligands

P(1)–C(1)–C(2)–P(2)	56(5)
P(3)–C(3)–C(4)–P(4)	–51(6)
N(51)–N(52)–C(53)–C(54)	177(7)
N(52)–C(53)–C(54)–C(55)	10(5)
C(53)–C(54)–C(55)–N(52)	–12(6)
C(54)–C(55)–N(52)–C(53)	12(6)
C(55)–N(52)–C(53)–C(54)	–12(6)
N(51)–N(52)–C(55)–C(54)	–178(8)

We also obtained linear least-squares fits of tungsten data against molybdenum data for the reductions, but a satisfactory correlation (0.98) was obtained only with the exclusion of the data for $n = 3$. The slope of this line is *ca.* 0.5, which should also be evident from Table 4. The range of values for molybdenum is twice that observed for tungsten. This type of variation has been observed with both ethyldiazenido[2] and dinitrogen[5] complexes, and is presumably a reflection of the greater polarizability of tungsten compared to molybdenum. This difference in polarizability has been noted before.[5] However, we infer that the same general mechanisms operate for both sets of metal derivatives.

For each metal, we also obtained linear least-squares plots against the Hammett constants σ_p and $\sigma_p{}^+$. For tungsten, the best correlation was found against σ_p in both cases (0.98, *cf.* 0.84 for $\sigma_p{}^+$). This implies that the phosphine substituents are affecting the lowest unoccupied molecular orbital (l.u.m.o.) inductively. This is consistent with our observations on the dinitrogen[5] and ethyldiazenido complexes.[2] However, with the molybdenum complexes the situation is less clear cut.

For E_p^{red} and molybdenum the correlation is marginally better for σ_p (0.96) than for $\sigma_p{}^+$ (0.92). Consequently we cannot distinguish between the two cases. However, if the interaction were not primarily inductive, it would be the only case we have yet identified.

In summary, there would appear to be exceptional circumstances associated with the reduction of the molybdenum and tungsten compounds with $n = 3$. In the latter case, it may be associated with strain in the azetidine type ring. In any case, these complexes are easier to reduce than might have been predicted, and we currently hope to investigate the use of these complexes to synthesize azetidine and substituted azetidines.

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, where 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

Table 7. Comparison of bond lengths and bond angles in some dinitrogen-derived complexes of tungsten

	Bond lengths (Å)					Bond angles (°)			
Compound	W–P[a]	W–X[b]	W–N(1)	N(1)–N(2)	N(2)–C	X–W–N(1)[b]	W–N(1)–N(2)	N(1)–N(2)–C	Ref.
$[WBr\{NN{=}CH(CH_2)_3OH\}(dppe)_2]PF_6$	2.526(5)	2.569(2)	1.772(13)	1.32(2)	1.30(3)	177.3(4)	172.6(12)	116.2(15)	*c*, *d*
$[WBr(NN{=}CMe_2)(dppe)_2]Br$	2.533(2)	2.585(2)	1.724(12)	1.355(18)	1.90(17)	179.9(3)	171.3(7)	123.9(11)	*d*
$[WCl(NNH_2)(dppe)_2]BPh_4$	2.522(4)	2.421(4)	1.73(1)	1.37(2)			171(1)		*e*
$[WBr(NNH_2)(depe)_2]Br$[f] (*i*)	2.595(5)	2.654(2)	1.739(15)	1.325(26)		179.2(4)	175.1(13)		*g*
(*ii*)	2.620(7)	2.641(2)	1.773(11)	1.340(18)		178.6(5)	177.2(12)		
$[WBr(NNHMe)(dppe)_2]Br$	2.52	2.61	1.768(14)	1.32(2)	1.48		174(1)	121	*h*
$[WF(NNCOCH_2CH_2CO)(dppe)_2]BF_4$			1.75(2)	1.39(3)	1.37(4) 1.43(4)		174(2)	120.5 125.9	14
$[WBr\{NN(CH_2)_2CH_2\}(dtpe)_2]Br$	2.512(3)	2.610(7)	1.72(6)	1.42(6)	1.70(10) 1.35(7)	177.3(25)	171.4(46)	124.1(52) 129.5(70)	This work

[a] Average bond length. [b] X = F, Cl, or Br, as shown in compound list (Table 1). [c] P. C. Bevan, J. Chatt, R. A. Head, P. B. Hitchcock, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1976, 509. [d] J. Chatt, R. A. Head, P. B. Hitchcock, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, 1977, **133**, C1; R. A. Head and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1980, 1150. [e] G. A. Heath, R. Mason, and K. M. Thomas, *J. Am. Chem. Soc.*, 1974, **96**, 259. [f] Two asymmetric molecules in unit cell. [g] D. L. Hughes, G. J. Leigh, and H. Mohd.-Ali, unpublished work. [h] F. C. March, R. Mason, and K. M. Thomas, *J. Organomet. Chem.*, 1975, **96**, C43.

analysis, C, H and N, was carried out by Mrs. G. Olney and Ms. K. Plowman of the University of Sussex and by Mr. C. A. Macdonald of the A.F.R.C. Unit of Nitrogen Fixation. 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. N.m.r. spectra: Bruker WM360 (360 MHz), JEOL FX90Q (90 MHz), and Bruker WP80 (80 MHz).

All of the solvents used were dried by standard methods or otherwise, as recommended by Perrin *et al.*[15] α,ω-Dibromoalkanes, Br(CH$_2$)$_n$Br (n = 3, 4, 5, or 6), were obtained commercially from Aldrich Chemical Co. These were made into stock solutions of known concentration in benzene.

The diphosphines R$_2$PCH$_2$CH$_2$PR$_2$ were prepared according to the published methods, where R = Cl,[5,16] Et,[16] 4-MeOC$_6$H$_4$,[5] 4-MeC$_6$H$_4$,[5] 4-ClC$_6$H$_4$,[5] 4-CF$_3$C$_6$H$_4$,[5] or C$_6$H$_5$.[17] The corresponding bis(dinitrogen) complexes of tungsten and molybdenum were prepared as described in the literature.[5]

The cyclic organohydrazido(2−) complexes $[\mathrm{MBr}\{\mathrm{N}\overline{\mathrm{N(CH_2)_3C}}\mathrm{H_2}\}(\mathrm{dppe})_2]\mathrm{Br}$ (M = Mo or W) were prepared by the method of Chatt *et al.*[3]

Bis{1,2-*bis*[*bis*(*methoxyphenyl*)*phosphino*]*ethane*}*bromo*[N-*bromopropylhydrazido*(2−)]*molybdenum Tetrafluoroborate* (**1**).—*trans*-[Mo(N$_2$)$_2$(dmppe)$_2$] (0.67 g, 0.56 mmol) and an equimolar amount of 1,3-dibromopropane in benzene (40 cm^3) was stirred vigorously for 2 h under irradiation by 2 × 100-W tungsten-filament bulbs each placed *ca.* 30 cm from the reaction vessel. The dark brown solution obtained was further stirred in the dark for 4—5 h. Removal of benzene solution to dryness left an orange-brown residue. This was redissolved in benzene (25 cm^3) and HBF$_4$·Et$_2$O (0.5 cm^3) was added with vigorous stirring for 10 min. An immediate colour change from orange-brown to green was observed. The excess of solvent was removed to dryness and to the residue was added diethyl ether (50 cm^3). Stirring for 2 h gave a green *precipitate* which was separated by filtration. The green solid product was recrystallized using methanol–diethyl ether–n-pentane. Yield 0.35 g.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-*bromopropylhydrazido*(2−)]*molybdenum Tetrafluoroborate* (**5**).—*trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (1.16 g, 1.18 mmol) was suspended in benzene (100 cm^3) and, together with an equimolar amount of 1,3-dibromopropane, was stirred under irradiation for 4.5 h. The reaction mixture was then filtered over Celite and to the filtrate was added HBF$_4$·Et$_2$O (1.25 cm^3) with stirring for 1 h. The colour changed immediately from dark brown to deep red. The excess of solvent was evacuated leaving a deep red oily liquid. This was extracted with dichloromethane (30 cm^3). The addition of an excess of diethyl ether to the dichloromethane extract afforded a salmon-red *solid* after filtration and drying *in vacuo*. Yield 0.44 g.

Bis{1,2-*bis*[*bis*(*chlorophenyl*)*phosphino*]*ethane*}*bromo*[N-*bromopropylhydrazido*(2−)]*molybdenum Tetrafluoroborate* (**6**).—*trans*-[Mo(N$_2$)$_2$(dcppe)$_2$] (0.75 g, 0.62 mmol) was suspended in 1,3-dibromopropane (10 cm^3) and stirred for 8 h under irradiation, during which time all the solid dissolved and a brown solution formed. The reaction mixture was further stirred in the dark for 12—16 h. Removal of the excess of solvent and stirring the residue in methanol (100 cm^3) gave an orange solid after filtration. The orange solid was suspended in benzene (80 cm^3) and HBF$_4$·Et$_2$O (0.5 cm^3) was added with vigorous stirring for 10 min. The solvent was removed to dryness and the residue was stirred in diethyl ether (50 cm^3) for 0.5 h to give a purplish brown solid. This solid was extracted exhaustively with methanol (*ca.* 3 × 100 cm^3). The *residue* after removal of the excess of methanol from the filtrate was recrystallized from dichloromethane–n-pentane to give brown-green crystals. Yield 0.36 g.

(*Azetidinylimido*)*bis*[1,2-*bis*(*di*-p-*tolylphosphino*)*ethane*]-*bromomolybdenum Bromide–Dichloromethane* (1/3) (**3**).—*trans*-[Mo(N$_2$)$_2$(dtpe)$_2$] (0.68 g, 0.64 mmol) and an equimolar amount of 1,3-dibromopropane in benzene (50 cm^3) was stirred for 22 h under irradiation. The excess of solvent was evacuated to dryness and the brown residue extracted with methanol. Removal of methanol from the extract gave a yellow-green *residue* which was redissolved in dichloromethane and an excess of n-hexane was added. This was then stored at 0 °C for 2 months whereupon dark green crystals gradually appeared. Yield 0.14 g.

Alternatively, the reaction mixture was stirred under irradiation at room temperature for the first 4—5 h. Then stirring and irradiation was continued at reflux temperature (*ca.* 70 °C) for 7 d. Some grey precipitate was observed. This was filtered off and discarded (insoluble in methanol). The benzene filtrate was reduced to dryness and the green residue was extracted with methanol. The brown-green methanolic extract was taken to dryness and the residue was recrystallized from dichloromethane–n-hexane, affording dark green crystals. Yield 0.63 g from 1.26 g of *trans*-[Mo(N$_2$)$_2$(dtpe)$_2$].

Bis{1,2-*bis*[*bis*(4-*methoxyphenyl*)*phosphino*]*ethane*}*bromo*-[N-*bromopropylhydrazido*(2−)]*tungsten Tetrafluoroborate–Dichloromethane* (1/1) (**2**).—*trans*-[W(N$_2$)$_2$(dmppe)$_2$] (0.40 g, 0.32 mmol) and an equimolar amount of 1,3-dibromopropane in benzene (40 cm^3) was vigorously stirred for 18 h under irradiation. The green-brown solution was further stirred in the dark for 5 h. The solvent was removed to dryness and the residue redissolved in benzene (20 cm^3). HBF$_4$·Et$_2$O (0.5 cm^3) was then added with vigorous stirring for 10 min. The solvent was removed to dryness and the residue stirred in diethyl ether (50 cm^3) for 2—3 h, affording a grey solid after filtration and drying *in vacuo*. The solid was extracted with methanol and the extract evacuated to dryness. To the residue was added diethyl ether (30 cm^3) and this was stirred overnight (12—16 h) to give a brown *solid* after filtration and drying, which recrystallized from dichloromethane–diethyl ether. Yield 0.23 g.

(*Azetidinylimido*)*bis*[1,2-*bis*(*di*-p-*tolylphosphino*)*ethane*]-*bromotungsten Bromide–Dichloromethane* (1/1) (**4**).—*trans*-[W(N$_2$)$_2$(dtpe)$_2$] (0.88 g, 0.77 mmol) and an equimolar amount of 1,3-dibromopropane in benzene (50 cm^3) was irradiated for 22 h with vigorous stirring. The dark brown solution obtained was reduced to dryness and the resultant orange-brown residue was extracted with methanol. A brown *residue* was obtained from the methanolic extract and recrystallized from dichloromethane–n-pentane to give 0.47 g of brown crystals.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*pyrrolidinylimido*)*molybdenum Bromide* (**7**).—*trans*-[Mo(N$_2$)$_2$(depe)$_2$] (1.13 g, 2.0 mmol) and an equimolar amount of 1,4-dibromobutane in benzene (50 cm^3) was stirred vigorously under irradiation at reflux temperature (*ca.* 75 °C) for 16 h. The reaction mixture was further stirred in the dark for 4 h, with the precipitate appearing after 2 h. The dark brown *precipitate* was filtered and washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. Yield 1.08 g.

Bis{1,2-*bis*[*bis*(*methoxyphenyl*)*phosphino*]*ethane*}*bromo*-(*pyrrolidinylimido*)*molybdenum Bromide–Dichloromethane* (1/1) (**8**).—*trans*-[Mo(N$_2$)$_2$(dmppe)$_2$] (3.55 g, 2.99 mmol) was suspended in benzene (150 cm^3). An equimolar amount of 1,4-dibromobutane was syringed into the stirred suspension and the reaction mixture irradiated for 18 h. The brown-green solution obtained was further stirred in the dark for 8 h. The excess of solvent was then removed and the *residue* extracted with methanol (100 cm^3). Removal of methanol and recrystallization of the residue from dichloromethane–n-hexane yielded 2.46 g of green crystals.

Bis[1,2-*bis*(*ditolylphosphino*)*ethane*]*bromo*(*pyrrolidinylimido*)*molybdenum Bromide–Dichloromethane* (2/3) (**10**).—*trans*-[$Mo(N_2)_2(dtpe)_2$] (3.25 g, 3.05 mmol) and an equimolar amount of 1,4-dibromobutane in benzene (150 cm^3) was stirred under irradiation for 5 h, and for a further 14 h in the dark. Removal of the excess of benzene left a green residue which was extracted with methanol. The extract was reduced in volume to *ca.* 5 cm^3 and diethyl ether (20 cm^3) added to give a green *precipitate*. Recrystallization from dichloromethane–n-hexane yielded 3.04 g of green crystals.

Bis{1,2-*bis*[*bis*(*chlorophenyl*)*phosphino*]*ethane*}*bromo*(*pyrrolidinylimido*)*molybdenum Bromide–Dichloromethane* (1/3) (**12**).—*trans*-[$Mo(N_2)_2(dcppe)_2$] (0.74 g, 0.60 mmol) in 1,4-dibromobutane (10 cm^3) was stirred vigorously under irradiation for 8 h and a further 12—16 h in the dark. To the greenish brown reaction mixture was added benzene (30 cm^3) and the mixture stirred for *ca.* 1 h to bring about precipitation. Filtration and washing of the *precipitate* with benzene and recrystallization from dichloromethane–n-pentane gave 0.62 g of green crystals.

Bis{1,2-*bis*[*bis*(*trifluoromethylphenyl*)*phosphino*]*ethane*}-*bromo*(*pyrrolidinylimido*)*molybdenum Bromide* (**14**).—*trans*-[$Mo(N_2)_2(dfmppe)_2$] (0.93 g, 0.62 mmol) was stirred with an equimolar amount of 1,4-dibromobutane in benzene (50 cm^3) under irradiation for 48 h and for a further 16 h in the dark. The suspension was filtered and washed with benzene (2 × 10 cm^3). The yellow-orange solid was then extracted with methanol. Removal of excess solvent from the methanolic extract afforded a brown-green *solid*. Yield 0.5 g.

Bis{1,2-*bis*[*bis*(*methoxyphenyl*)*phosphino*]*ethane*}*bromo*(*pyrrolidinylimido*)*tungsten Bromide* (**9**).—*trans*-[$W(N_2)_2(dmppe)_2$] (1.01 g, 0.79 mmol) and an equimolar amount of 1,4-dibromobutane was vigorously stirred in benzene (40 cm^3) under irradiation for 48 h. The excess of solvent was then removed and the brown residue extracted with methanol. The brown methanolic filtrate was reduced in volume to *ca.* 2 cm^3 and addition of an excess of diethyl ether and n-hexane brought about precipitation. 0.50 g of brown *solid* was obtained after filtration and drying. The solid was recrystallized from the above solvents or from dichloromethane–n-pentane–diethyl ether.

Bis[1,2-*bis*(*ditolylphosphino*)*ethane*]*bromo*(*pyrrolidinylimido*)*tungsten Bromide* (**11**).—*trans*-[$W(N_2)_2(dtpe)_2$] (1.93 g, 1.68 mmol) and 1,4-dibromobutane in benzene (125 cm^3) was irradiated with stirring for 16 h and then left in the dark for a further 12—16 h. The residue left behind after removal of the benzene was extracted with methanol. The methanolic filtrate was reduced in volume to *ca.* 5 cm^3 and addition of an excess of diethyl ether gave a brown *precipitate*. Recrystallization from dichloromethane and n-pentane afforded 1.19 g of brown crystals.

Bis{1,2-*bis*[*bis*(*chlorophenyl*)*phosphino*]*ethane*}*bromo*(*pyrrolidinylimido*)*tungsten Bromide–Dichloromethane* (1/1) (**13**).—*trans*-[$W(N_2)_2(dcppe)_2$] (0.87 g, 0.66 mmol) in 1,4-dibromobutane (15 cm^3) was stirred vigorously for 24 h under irradiation. Benzene (50 cm^3) was then added to the dark brown solution, and during stirring for 2—3 h a golden-brown precipitate appeared. The precipitate was filtered and washed with benzene (2 × 10 cm^3). The precipitate was recrystallized from dichloromethane–n-pentane. A mixture of pink-brown crystals and a fluffy yellow solid was obtained. The latter was removed by repeated decantation in n-pentane. The pink-brown *crystals* were recrystallized again from dichloromethane–n-pentane to yield 0.31 g of product.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*piperidinylimido*)*molybdenum Bromide* (**15**).—*trans*-[$Mo(N_2)_2(depe)_2$] (1.33 g, 2.35 mmol) and an equimolar amount of 1,5-dibromopentane in benzene (50 cm^3) was stirred under irradiation at reflux temperature (*ca.* 75 °C) for 16 h, with a further 24 h in the dark. No precipitation occurred. The benzene was removed to dryness and the residue was extracted with methanol. The methanolic filtrate was reduced to dryness and the final *residue* was stirred in diethyl ether (50 cm^3) to give 1.08 g of a brown solid.

Bis{1,2-*bis*[*bis*(*methoxyphenyl*)*phosphino*]*ethane*}*bromo*(*piperidinylimido*)*molybdenum Bromide* (**16**).—*trans*-[$Mo(N_2)_2(dmppe)_2$] (3.53 g, 2.97 mmol) was suspended in benzene (150 cm^3) together with an equimolar amount of 1,5-dibromopentane. The reaction mixture was stirred and irradiated for 14 h, with a further 16 h in the dark. Removal of the excess of benzene and extraction with methanol afforded a brown-green solution. Removal of the solvent from the extract and recrystallization of the residue from dichloromethane–diethyl ether–n-pentane gave 2.98 g of green *crystals*.

Bis[1,2-*bis*(*di*-p-*tolylphosphino*)*ethane*]*bromo*(*piperidinylimido*)*molybdenum Bromide–Dichloromethane* (1/3) (**18**).—*trans*-[$Mo(N_2)_2(dtpe)_2$] (3.25 g, 3.06 mmol) and an equimolar amount of 1,5-dibromopentane in benzene (150 cm^3) was irradiated with vigorous stirring for 5 h. The reaction mixture was further stirred in the dark for 14 h. The solution obtained was reduced to dryness and the green residue was then extracted with methanol. The methanol extract was reduced in volume to *ca.* 5 cm^3 and diethyl ether (20 cm^3) was added, affording a dark green *precipitate*. The precipitate was recrystallized from dichloromethane–n-hexane. Yield 2.85 g.

Bis{1,2-*bis*[*bis*(*chlorophenyl*)*phosphino*]*ethane*}*bromo*(*piperidinylimido*)*tungsten Bromide–Dichloromethane* (1/1) (**20**).—*trans*-[$Mo(N_2)_2(dcppe)_2$] (0.65 g, 0.53 mmol) in neat 1,5-dibromopentane (10 cm^3) was stirred vigorously under irradiation for 18 h, and for a further 8 h in the dark. The reaction mixture was filtered and to the filtrate was added benzene (30 cm^3) with stirring. The precipitate obtained was filtered off and washed with benzene (2 × 10 cm^3). The green product was recrystallized from dichloromethane–diethyl ether–n-pentane. Yield 0.36 g.

Bis{1,2-*bis*[*bis*(*methoxyphenyl*)*phosphino*]*ethane*}*bromo*(*piperidinylimido*)*tungsten Bromide–Dichloromethane* (2/1) (**17**).—*trans*-[$W(N_2)_2(dmppe)_2$] (0.55 g, 0.43 mmol) and an equimolar amount of 1,5-dibromopentane in benzene (40 cm^3) were vigorously stirred under irradiation for 36 h. The benzene was then removed to dryness and the residue extracted with methanol. The methanolic filtrate was evacuated to dryness and the residue stirred in diethyl ether (40 cm^3) for 4 h, affording a red-brown *precipitate*. The precipitate was filtered and dried under vacuum. Yield 0.5 g.

Bis[1,2-*bis*(*di*-p-*tolylphosphino*)*ethane*]*bromo*(*piperidinylimido*)*tungsten Bromide–Dichloromethane* (1/1) (**19**).—To *trans*-[$W(N_2)_2(dtpe)_2$] (1.27 g, 1.10 mmol) in benzene (120 cm^3) was added an equimolar amount of 1,5-dibromopentane and this was stirred under irradiation for 16 h. The excess of benzene was removed and the residue extracted with methanol. The methanol extract was reduced to *ca.* 15 cm^3 and an excess of diethyl ether and n-hexane added to give brown *crystals*. The crystals were recrystallized from methanol–diethyl ether–n-hexane. Yield 0.92 g.

Bis{1,2-*bis*[*bis*(*chlorophenyl*)*phosphino*]*ethane*}*bromo*(*piperidinylimido*)*tungsten Bromide–Dichloromethane* (1/1) (**21**).—*trans*-$[W(N_2)_2(dcppe)_2]$ (0.78 g, 0.60 mmol) in 1,5-dibromopentane (15 cm^3) was stirred under irradiation for 72 h and for a further 16 h in the dark. Benzene (15 cm^3) was then added to the reaction mixture and stirring continued for 1—2 h. The precipitate obtained was filtered off and washed with benzene (2 × 10 cm^3) and dried under vacuum to give a golden brown solid. The final product was obtained as pink *crystals* of total yield 0.29 g after similar decantation and recrystallization treatment as described above for compound (**13**).

X-*Ray Structural Analysis of* $[WBr\{N\overline{N(CH_2)_2C}H_2\}(dtpe)_2]Br\cdot 3CH_2Cl_2$.—*Crystal data*. $C_{63}H_{70}Br_2N_2P_4W\cdot 3CH_2Cl_2$, $M = 1\,577.6$, triclinic, $a = 10.822(5)$, $b = 18.179(5)$, $c = 18.877(4)$ Å, $\alpha = 92.59(2)$, $\beta = 96.05(2)$, $\gamma = 102.20(3)°$, $U = 3\,600.8$ Å^3, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.455$ g cm^{-3}, $F(000) = 1\,584$, $\mu(Mo\text{-}K_\alpha) = 30.9$ cm^{-1}, $\lambda(Mo\text{-}K_{\bar{\alpha}}) = 0.710\,69$ Å.

After several unsuccessful attempts to mount 'dry' the pale brown rectangular prisms (the encapsulated crystals always deteriorated rapidly), some dichloromethane was included in the Lindemann glass capillary along with the chosen crystal (0.12 × 0.26 × 0.43 mm) before sealing.

The crystal was examined photographically, then accurate cell parameters (refined from the settings of 25 reflections having $10 < \theta < 11°$) and intensity data were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated radiation. To record the extent of crystal deterioration, two reflections were monitored regularly during the data collection, and were found to decrease steadily in intensity; before the data set to $\theta_{max.} = 15°$ was complete, these intensities had dropped by more than 40%, and the data collection was terminated. Since no further suitable crystals were available, this limited data set was used for the structure analysis.

After correction for Lorentz-polarization effects and for deterioration, 2 091 independent reflections [302 with $I < 2\sigma(I)$] were read into the SHELX program,[18] where an absorption correction was applied. The structure was determined by the heavy-atom method, and refined by full-matrix least-squares methods. Atoms of the phenyl rings were refined in rigid idealized groups and the dimensions in the four, disordered solvent molecule sites were constrained towards ideal values. Only the W, Br, and P atoms were allowed anisotropic thermal parameters, and some of these were not sensible. No hydrogen atoms were included. Refinement was terminated with $R = 0.136$ and $R' = 0.128$, for 1 787 reflections weighted $w = \sigma_F^{-2}$. The refinement and a final difference map showed that the tungsten complex cation is complete (if rather poorly defined in places), and that there are approximately three molecules of CH_2Cl_2 disordered over four separate sites. From the limited data set, the resulting dimensions must be considered rather imprecise and inaccurate.

Scattering factors were taken from ref. 19. Programs used in this analysis are listed in Table 4 of ref. 20, and were run on the VAX 11/750 computer at the Glasshouse Crops Research Institute, Littlehampton.

Final atomic co-ordinates are in Table 5 and selected molecular dimensions are presented in Table 6. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Electrochemical Measurements.—These were carried out in a standard three-electrode cell in conjunction with a scanning potentiostat (Princeton Applied Research Corp., model 362) and an XY/t recorder (J.J. Instruments, model PL4). All solvents and electrolytes were dried by standard techniques before use, and the cell was blanketed with dry dinitrogen. The electrolyte $[NBu^n{}_4]BF_4\cdot 3MePh$ was synthesized as described in the literature.[14] Otherwise 0.2 mol dm^{-3} $[NBu^n{}_4]BF_4$ in thf was used. Potentials were measured against the $E_{\frac{1}{2}}$ value for ferrocene {+0.535 V *vs.* s.c.e. (saturated calomel electrode) in $[NBu^n{}_4]BF_4$–thf}.

The surface areas of the electrodes were determined using ferrocene in acetonitrile with lithium perchlorate as supporting electrolyte.[21–23] This value was used, in turn, to calculate the diffusion coefficients of $[MBr\{N\overline{N(CH_2)_3C}H_2\}(dppe)_2]Br$, which were taken as representative of all the complexes. This assumes, of course, that a two-electron reduction is involved for the dppe complexes. On this basis, the numbers of electrons involved in the other process were calculated.[22,23]

The cyclic voltammograms were run at scan rates varying from 200 to 10 mV s^{-1}.

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