Hydrazido(2−)-complexes of Molybdenum and Tungsten formed from Dinitrogen Complexes by Protonation and Ligand Exchange

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

A number of new hydrazido(2−)-complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (A; M = Mo or W, X = Cl, Br, or I) and *trans*-$[MX(NNH_2)(PMe_2Ph)_4]X$ (B; M = W) have been prepared by reaction of concentrated HX with *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ in methanol. The addition of various ligands L to complexes (A) has given a series of complexes of the following types: (B; M = Mo or W), when L = PMe_2Ph; (C), $[MX(NNH_2)(PMe_2Ph)_3L]X$, when L = various pyridine bases or dimethylformamide; (D), $[M(NNH_2)(quin)(PMe_2Ph)_3]X$, when L = quinolin-8-olate ion (quin); and specifically $[WBr(NNH_2)(S_2CNMe_2)(PMe_2Ph)_2]$ (L = S_2CNMe_2) when M = W and X = Br. The (B)-type complex *trans*-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$ is obtained by treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with HF in methanol in a borosilicate-glass reaction vessel. The salts (E), $[WX(NNH_2)(PMe_2Ph)_3L][BPh_4]$ (M = W), are obtained by reaction of $Na[BPh_4]$ with (C; M = W) except for L = pyridine-2-thiol (2HS-py) when $[W(NNH_2)(2S\text{-}py)(PMe_2Ph)_3][BPh_4]$ results. The complexes *trans*-$[MI(NNH_2)(dppe)_2]I$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have been prepared by treatment of *trans*-$[M(N_2)_2(dppe)_2]$ with aqueous HI in tetrahydrofuran. Spectroscopic (i.r. and n.m.r.) data for these complexes are discussed in terms of their structures. In dichloromethane solution, complexes (A), (C), and (D) are electrochemically oxidised by one unit, but cannot be reduced.

IN our investigation of the reactions of ligating dinitrogen, particularly those which may be related to nitrogenase activity, we have described its protonation and reduction to ammonia in the complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W).[1] Hydrazido(2−)-complexes of the type $[MX_2(NNH_2)(PMe_2Ph)_3]$ (A; X = Cl, Br, or I) have been shown to represent an intermediate stage in the reduction process and have been briefly

---

[1] J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39; *J.C.S. Dalton*, 1977, 1852.

TABLE 1

Hydrazido(2−)-complexes of tungsten

Complex	Yield (%)	Analysis [a]			Colour	M.p. (θ_c/°C) [b]	Λ[c]/S cm^2 mol^{-1}	
		C	H	N			$MeNO_2$	$C_2H_4Cl_2$
trans-$[WCl(NNH_2)(PMe_2Ph)_4]Cl$	21	46.4 (45.9)	5.6 (5.5)	3.5 (3.3)	Yellow	99	92	4
trans-$[WBr(NNH_2)(PMe_2Ph)_4]Br$	29	41.4 (41.5)	5.0 (5.0)	3.1 (3.0)	Orange-yellow	92	110	4
trans-$[WI(NNH_2)(PMe_2Ph)_4]I$	10	37.7 (37.7)	4.5 (4.6)	2.6 (2.7)	Green-brown	91	102	9
trans-$[WI(NNH_2)(dppe)_2]I$	78	49.4 (49.4)	4.3 (4.0)	2.1 (2.2)	Yellow-brown	153	109	44
$[WI(NNH_2)(dmf)(PMe_2Ph)_3]I{\cdot}dmf$	55	34.8 (35.0)	4.8 (4.8)	5.2 (5.4)	Red-brown	127		2
trans-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$	67	43.3 (44.1)	5.2 (5.3)	3.3 (3.2)	Orange	166	95	33
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	63	41.0 (41.2)	5.4 (5.1)	4.1 (4.0) [d]	Red-brown	147		1
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	59	36.6 (36.6)	4.5 (4.5)	3.7 (3.6) [e]	Brown	156		1
$[WI_2(NNH_2)(PMe_2Ph)_3]$	75	32.8 (32.7)	4.2 (4.0)	3.1 (3.2) [f]	Brown	145		1
$[WCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	90	44.8 (44.7)	5.1 (5.2)	5.5 (5.4)	Red	166	86	3
$[WCl(NND_2)(py)(PMe_2Ph)_3]Cl$	85	44.7 (44.7)	5.1 (5.1)	5.3 (5.4)	Red	160		
$[WCl(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]Cl$	50	44.9 (45.5)	5.3 (4.5)	5.4 (5.3)	Red	156	98	4
$[WCl(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Cl$	44	45.5 (45.5)	5.6 (5.4)	5.5 (5.3)	Orange-red	149	78	3
$[WCl(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Cl$	71	45.5 (45.5)	5.2 (5.4)	5.5 (5.3)	Red	161	89	4
$[WBr(NNH_2)(py)(PMe_2Ph)_3]Br$	89	40.1 (40.2)	4.8 (4.7)	4.8 (4.8)	Red	149	100	5
$[WBr(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]Br$	64	41.0 (40.9)	4.8 (4.8)	5.0 (4.8)	Red	149	98	4
$[WBr(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Br$	90	40.9 (40.9)	4.9 (4.8)	4.9 (4.8)	Orange-red	153	97	4
$[WBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Br{\cdot}0.5\ (4Me\text{-}py)$	85	42.8 (42.7)	5.2 (5.0)	5.4 (5.3)	Red	156	103	4
$[WI(NNH_2)(py)(PMe_2Ph)_3]I{\cdot}0.5\ py$	87	37.7 (37.8)	4.3 (4.3)	4.8 (4.9)	Red	127	111	8
$[WI(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]I{\cdot}0.5\ (2Me\text{-}py)$	33	38.8 (38.8)	4.5 (4.5)	4.9 (4.8)	Red	114	111	9
$[WI(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]I{\cdot}0.5\ (3Me\text{-}py)$	64	39.0 (38.8)	4.7 (4.5)	4.8 (4.8)	Orange-red	124	104	7
$[WI(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]I{\cdot}0.5\ (4Me\text{-}py)$	71	38.8 (38.8)	4.9 (4.5)	4.9 (4.8)	Red	133	104	8
$[WCl(NNH_2)(py)(PMe_2Ph)_3][BPh_4]$	88	59.9 (59.9)	5.5 (5.7)	4.0 (4.0)	Red	157		31
$[WCl(NND_2)(py)(PMe_2Ph)_3][BPh_4]$	80	59.7 (59.9)	5.4 (5.6) [g]	3.9 (4.0)	Red			
$[WBr(NNH_2)(py)(PMe_2Ph)_3][BPh_4]$	71	58.0 (57.5)	5.8 (5.5)	4.0 (3.8)	Orange-red	146		44
$[WBr(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3][BPh_4]$	64	57.8 (57.9)	5.4 (5.6)	3.8 (3.8)	Orange-red	130		33
$[WBr(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3][BPh_4]$	52	57.9 (57.9)	5.6 (5.6)	3.8 (3.8)	Orange-red	141		37
$[WBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3][BPh_4]$	74	57.8 (57.9)	5.5 (5.6)	3.8 (3.8)	Yellow-orange	134		33
$[WI(NNH_2)(py)(PMe_2Ph)_3][BPh_4]$	85	55.5 (55.2)	5.3 (5.3)	3.7 (3.6)	Red	143		47
$[WCl(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]Cl{\cdot}(2HS\text{-}py)$	50	43.5 (44.3)	4.8 (4.9)	6.3 (6.1)	Dark red	120	72	5
$[WBr(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]Br{\cdot}(2HS\text{-}py)$	75	40.4 (40.4)	4.7 (4.5)	5.5 (5.5) [h]	Dark red	114	86	5
$[WI(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]I{\cdot}(2HS\text{-}py)$	53	37.7 (37.0)	4.6 (4.1)	5.1 (5.1)	Dark red	106	99	9
$[W(NNH_2)(2S\text{-}py)(PMe_2Ph)_3][BPh_4]$	80	58.9 (60.2)	5.7 (5.6)	3.8 (4.0) [i]	Pale red	132		35
$[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$	54	48.9 (49.1)	4.9 (5.1)	5.3 (5.2)	Deep purple	141	76	6
$[W(NNH_2)(quin)(PMe_2Ph)_3]Br$	63	46.4 (46.5)	4.9 (4.9)	4.0 (4.9) [j]	Deep purple	165	82	10
$[W(NNH_2)(quin)(PMe_2Ph)_3]I$	82	44.9 (44.1)	4.8 (4.6)	4.7 (4.7)	Deep purple	145	86	21
$[WBr(NNH_2)(S_2CNMe_2)(PMe_2Ph)_2]$	81	33.6 (33.1)	4.4 (4.4)	5.9 (6.1)	Red-brown	114		4

[a] Calculated values are given in parentheses. [b] Point at which decomposition occurred in sealed evacuated tubes. [c] In *ca.* 10^{-3} mol dm^{-3} solution. [d] Cl, 10.2 (10.1%); *M* in *ca.* 10^{-2} mol dm^{-3} $C_2H_4Cl_2$, 383 (699). [e] Br, 20.7 (20.3%); *M* in *ca.* 10^{-2} mol dm^{-3} $C_2H_4Cl_2$, 478 (788). [f] *M* in *ca.* 10^{-2} mol dm^{-3} $C_2H_4Cl_2$, 580 (882). [g] H + D expressed as H. [h] S, 6.6 (6.3%). [i] S, 2.7 (3.0%). [j] Br, 9.7 (9.4%).

reported.[2] Here we describe in detail the preparation of these complexes and their conversion into a variety of analogues by ligand substitution. The substituted products have been investigated electrochemically to determine the effect of ligands on the ease of oxidation and reduction of the complexes and hopefully of the hydrazido(2−) ligand.

TABLE 2

Hydrazido(2−)-complexes of molybdenum

Complex	Yield (%)	Analysis[a]			Colour	M.p.(θ_c/°C)[b]	Λ^c/S cm^2 mol^{-1}
		C	H	N			
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	88	47.5 (47.1)	5.8 (5.8)	4.6 (4.6)[d]	Light brown	93	32.3
$[MoCl_2(NND_2)(PMe_2Ph)_3]$	80	47.4 (47.1)	5.8 (5.7)	4.5 (4.6)	Light brown	90	30.1
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	67	40.8 (41.1)	5.0 (5.0)	4.0 (4.0)	Light brown	116	44.6
$[MoI_2(NNH_2)(PMe_2Ph)_3]$	47	35.8 (36.2)	4.2 (4.4)	3.4 (3.5)	Light brown	97	89.0
$[MoI(NNH_2)(dppe)_2]I$	63	53.3 (53.1)	4.8 (4.3)	2.3 (2.4)	Yellow	265	insoluble
$[MoCl(NNH_2)(PMe_2Ph)_4]Cl$	70	51.1 (51.3)	6.3 (6.2)	3.6 (3.7)	Orange	88	98.4
$[MoBr(NNH_2)(PMe_2Ph)_4]Br$	45	45.8 (45.8)	5.5 (5.5)	3.3 (3.3)	Red-orange	88	99.0
$[MoI(NNH_2)(PMe_2Ph)_4]I$	48	41.0 (41.2)	5.1 (4.9)	2.9 (3.0)	Brown-orange	90	114.0
$[MoCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	78	49.8 (49.7)	5.8 (5.7)	6.0 (6.0)	Golden-brown	148	
$[MoCl(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Cl$	70	50.8 (51.2)	5.9 (6.0)	6.0 (6.0)	Green-brown	150	58.0
$[MoCl(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Cl$	80	50.5 (51.2)	6.1 (6.0)	5.9 (6.0)	Brown	152	55.4, 7.1[e]
$[MoBr(NNH_2)(py)(PMe_2Ph)_3]Br$	70	44.5 (44.7)	5.2 (5.1)	5.0 (5.4)	Yellow-brown	158	
$[MoI(NNH_2)(py)(PMe_2Ph)_3I]$	50	39.8 (39.8)	4.6 (4.6)	5.0(4.8)	Green-brown	143	
$[MoBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Br$	60	45.8 (45.4)	5.8 (5.3)	5.3 (5.3)	Brown	160	56.4
$[MoI(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]I$	45	40.7 (40.6)	4.9 (4.7)	4.6 (4.7)	Green-brown	149	84.4
$[MoI(NNH_2)(dmf)(PMe_2Ph)_3]I$	20	37.0 (37.4)	4.9 (4.9)	4.7 (4.9)	Green-brown	138	98.0
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Cl$	50	54.8 (55.1)	5.8 (5.7)	5.7 (5.8)	Deep red	110	38.0, 5.1[e]
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Br$[f]	50	50.4 (49.9)	4.5 (5.2)	5.4 (5.2)	Deep red	115	52.6
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]I$	45	48.3 (48.8)	5.2 (5.1)	5.1 (5.2)	Deep red	126	72.8
$[MoBr(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]Br$	45	42.7 (42.9)	4.7 (4.9)	5.3 (5.2)	Red-brown	120	90[g]

[a] Calculated values in parentheses. [b] In sealed evacuated tubes, with decomposition. [c] In *ca.* 10^{-2} mol dm^{-3} dimethylformamide solution. [d] Cl, 11.7 (11.6%). [e] In *ca.* 10^{-2} mol dm^{-3} $C_2H_4Cl_2$ solution. [f] Contains $0.5CH_2Cl_2$ of crystallisation. [g] In *ca.* 10^{-2} mol dm^{-3} $MeNO_2$ solution.

RESULTS

Preparation of Hydrazido(2−)-complexes from Dinitrogen Complexes.—When treated with an excess of anhydrous or aqueous halogen acid (HX), under dinitrogen or *in vacuo* at 20 °C in methanol, *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ is converted into the hydrazido(2−)-complexes (A) [reaction (1)]. These

$$cis\text{-}[M(N_2)_2(PMe_2Ph)_4] + HX(excess) \xrightarrow{MeOH} \underset{(A)}{[MX_2(NNH_2)(PMe_2Ph)_3]} + N_2 + [PMe_2PhH]X \quad (1)$$

complexes are rather poorly soluble in the reaction solvent and are precipitated in high yields (47—88%, Tables 1 and 2). The addition of water to the mother liquor from reaction (1) precipitates a second type of hydrazido(2−)-complex, $[MX(NNH_2)(PMe_2Ph)_4]X$ (B) when M = W, but not when M = Mo, in low yields (10—29%). Higher yields of (B; X = Cl or Br) are obtained by treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with anhydrous HX in dichloromethane.[3] Some deuterio-analogues have also been prepared (Tables 1 and 2). The fluoro-complex *trans*-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$ results from the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with HF in methanol–diethyl ether over 14 d. The $[BF_4]^-$ anion is produced by reaction of the excess of hydrofluoric acid with the borosilicate glass walls of the reaction vessel. The complexes *trans*-$[MI(NNH_2)(dppe)_2]I$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have also been prepared as in (2). Their fluoride[4] and chloride and bromide[3] analogues have already been described (see below for further discussion of their structures).

$$trans\text{-}[M(N_2)_2(dppe)_2] + HI(aq)(excess) \xrightarrow{thf} trans\text{-}[MI(NNH_2)(dppe)_2]I + N_2 \quad (2)$$

Substitution Reactions of Hydrazido(2−)-complexes.—One halide ligand in complexes (A) is labile and is readily displaced by uncharged ligands (L) such as substituted pyridines or PMe_2Ph to give the cationic complexes (C) [equation (3):

$$[MX_2(NNH_2)(PMe_2Ph)_3] + L \longrightarrow \underset{(C)}{[MX(NNH_2)(PMe_2Ph)_3L]X} \quad (3)$$

[L = NC_5H_5, NC_5H_4Me (2-, 3-, or 4-isomers), NC_5H_4SH-2, or $HCONMe_2$; X = Cl, Br, or I]

When L = PMe_2Ph in reaction (3), complexes (A) are converted into (B). Reaction (3) for L = HCO-NMe_2 accounts for the high conductivity of complexes (A) in this solvent. The intensely purple cationic complexes $[W(NNH_2)(quin)(PMe_2Ph)_3]X$, (D), are obtained by treatment of complexes (A; M = W) with an excess of 8-hydroxyquinoline (Hquin) [equation (4)]. The hydrogen halide generated in this reaction is taken up by the excess of basic Hquin.

$$[MX_2(NNH_2)(PMe_2Ph)_3] + Hquin \longrightarrow \underset{(D)}{[M(NNH_2)(quin)(PMe_2Ph)_3]X} + HX \quad (4)$$

Metathetical replacement of the anion X in (C; M = W) with $Na[BPh_4]$ gives the complexes $[WX(NNH_2)(PMe_2Ph)_3L][BPh_4]$ (E) (Table 1). These are much more soluble than are (C; M = W), so much so in the case of $[W(NNH_2)(quin)(PMe_2Ph)_3][BPh_4]$ that it could not be isolated and was characterised spectroscopically in solution (Tables 3

---

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

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

[4] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1976, 1520.

and 4). Treatment of (C; M = W, L = NC_5H_4SH-2) with Na[BPh_4] not only caused replacement of one of the halide ions by PPh_4, but also dehydrohalogenation, generating the pyridine-2-thiolate ligand which presumably chelates the metal, as it does in [Ru(NC_5H_4S-2)$_2$(PPh_3)$_2$].[5] The HX generated in this reaction is removed by the molecule of NC_5H_4SH-2 present in the crystal of (C; M = W, L = NC_5H_4SH-2) (Table 1) [equation (5): X = Cl, Br, or I;

$$[\mathrm{WX(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]X{\cdot}2HS\text{-}py} + \mathrm{Na[BPh_4]} \xrightarrow{\mathrm{CH_2Cl_2\text{-}thf}} [\mathrm{W(NNH_2)(2S\text{-}py)(PMe_2Ph)_3][BPh_4]} + \mathrm{NaX} + [\mathrm{2HS\text{-}Hpy}]\mathrm{X} \quad (5)$$

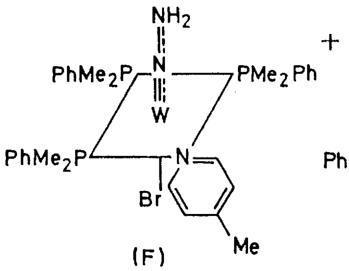
2HS-py = NC_5H_4SH-2, 2S-py = NC_5H_4S-2; thf = tetrahydrofuran].

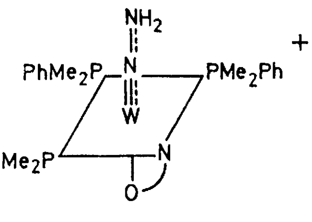
Only in one case [equation (6)] has treatment of complexes (A) with sodium dimethyldithiocarbamate given a characterisable product.

$$[\mathrm{WBr_2(NNH_2)(PMe_2Ph)_3}] + \mathrm{Na[S_2CNMe_2]} \longrightarrow [\mathrm{WBr(NNH_2)(S_2CNMe_2)(PMe_2Ph)_2}] + \mathrm{NaBr} + \mathrm{PMe_2Ph} \quad (6)$$

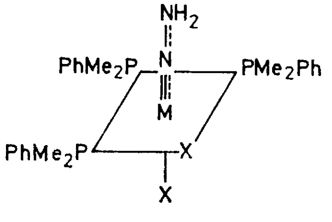
All the above hydrazido(2−)-complexes are thermally stable, stable in the solid state for several days on exposure to air, but much less stable in solution.

Structure and Spectroscopic Properties.—The structures of [WBr(NNH_2)(NC_5H_4Me-4)(PMe_2Ph)$_3$]Br (F)[6] and [W(NNH_2)(quin)(PMe_2Ph)$_3$]I (G)[7] have been determined by *X*-ray crystallography. By analogy, complexes (C) and (D) have been assigned structures corresponding to (F) and (G) respectively. They are also 1 : 1 electrolytes in solution (Tables 1 and 2). The spectroscopic properties and therefore structures of [WX(NNH_2)(PMe_2Ph)$_3$L][BPh_4] (E) and [W(NNH_2)(2S-py)(PMe_2Ph)$_3$][BPh_4] are also similar to that of (C).


(F)


(G) $\overset{\frown}{\mathrm{O\quad N}}$ = quin

The *mer* configuration of phosphine ligands in (D)—(F) gives rise to a pattern of two triplets and a doublet in their ^{1}H n.m.r. spectra[8] (Tables 3 and 4). Complexes (A) are poorly soluble except in solvents such as dimethylformamide (dmf), in which adduct formation occurs, as noted above. Nevertheless, in dmf solution they have a similar PMe ^{1}H n.m.r. pattern to (D) and (E) and so probably also have the *mer* configuration of PMe_2Ph groups. Complexes (A; M = Mo or W, X = Cl) also show two M–Cl bands in their i.r. spectra suggestive of a *cis*-chloride configuration. In view of these data and of the structures of (D) and (E), a likely structure for complexes (A) is as below.


(A)

Complexes (C) and (D) show the expected two singlets (one twice the intensity of the other) in their ^{31}P n.m.r. spectra (Tables 3 and 4).

Some complications occur in the ^{1}H n.m.r. spectra of the complexes (C; M = W; X = Cl, Br, or I, L = NC_5H_4Me-2 or -3). For L = NC_5H_4Me-3 two resonances are observed for the pyridine methyl group and four triplets and a doublet for the PMe_3 groups (Table 3). This presumably arises because the pyridine methyl group, regardless of its rotation about the W–N bond, lies in two different environments depending on whether it is above or below the plane of the phosphine ligands. Thus, twice the number of resonances are observed for this complex as are seen for its analogue where L = NC_5H_4Me-4, where no such inequivalence can occur. The ^{31}P n.m.r. spectrum of (C; M = W, L = NC_5H_4Me-3) shows two environments (a doublet) for the unique phosphorus atom, but only one for the mutually *trans*-phosphorus atoms and it is not clear why this should be. However, the ^{31}P n.m.r. spectrum of the complex [WBr(NNH_2)(NC_5H_4Me-3)(PMe_2Ph)$_3$][BPh_4] indicates two environments for both types of phosphorus atom (Table 3) suggesting an accidental equivalence of ^{31}P resonance positions in (C; M = W, L = NC_5H_4Me-3). The ^{1}H spectrum of (C; M = W, L = NC_5H_4Me-2) shows the normal doublet and two triplets for the PMe resonance, but the pyridine methyl group appears to show several resonances. Moreover, the ^{31}P n.m.r. spectrum indicates one environment for the unique phosphorus atom and two for the *trans*-phosphorus atoms. The reason for these spectral properties is as yet uncertain but they may be a result of the steric interactions of the 2-methyl group.

The *trans* structure of the complexes (B) and *trans*-[WF(NNH_2)(PMe_2Ph)$_4$][BF_4] follows from their singlet ^{31}P and ^{1}H (PMe) n.m.r. spectra and has already been discussed for (B; M = W, X = Cl or Br).[3] The complexes [MI(NNH_2)(dppe)$_2$] are also assumed to have the *trans* structure (see also below).

The complex [WBr(NNH_2)(S_2CNMe_2)(PMe_2Ph)$_2$] has a triplet PMe resonance pattern in its ^{1}H n.m.r. spectrum and a singlet ^{31}P resonance, therefore it has *trans* phosphines and so its structure is (H).

The structural parameters of the hydrazido(2−)-group in (F), (G), *trans*-[WBr(NNH_2)(dppe)$_2$][BPh_4], and in a number of related hydrazido(2−)-complexes appear to be little affected by the variation of co-ligand at the metal (Table 5). The corresponding parameters for *trans*-[MoF(NNH_2)(dppe)$_2$][BF_4] are also very similar to those of the tungsten complexes.[4,9]

The crystal structures of (F)[6] and (G)[7] also show that

---

[5] J. D. Gilbert, D. Rose, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 2765; S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 635.

[6] M. B. Hursthouse and M. Montevali, personal communication.

[7] I. R. Hanson, personal communication.

[8] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 1169 and refs. therein.

TABLE 3

N.m.r. data for hydrazido(2—)-complexes [a]

Complex	¹H data [b]					³¹P data [c]	
	NH_2	PMe	$\|{}^2J(PH) + {}^4J(PH)\|$ [d] or ${}^2J(PH)$	PPh and aromatic protons	Other resonances	PMe_2Ph	$J(WP)$
trans-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$	5.95 (s) [e]	1.55 (s, br)		7.24—7.58 (m)			
trans-$[WI(NNH_2)(PMe_2Ph)_4]I$	6.80 (s) [e]	1.79 (s)		7.24—7.62 (m)			
$[WCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	7.76 (s) [e]	1.42 (t), 1.60 (t) 1.83 (d)	7.1 8.3	7.10—7.64 (m) [f]	6.70, 6.99 8.29, 8.80 } (py)	−153.45 (str) −153.33 (su)	297.8 346.6
$[WCl(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]Cl$	8.04 (s) [e]	1.43 (t), 1.60 (t) 1.85 (d)	7.0 8.2	7.10—7.67 (m)	1.77, 1.85 1.93, 2.06 } (s)(2Me) 2.3 6.65, 6.91 8.30, 8.83 } (s)(2Me-py)	−153.15 (s, 2.5) −152.67 (s, 0.3) −153.39 (s, 0.1) −152.91 (s, 0.1)	297.8 346.6 297.8 } g
$[WCl(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Cl$	7.96 (s) [e]	1.39 (t), 1.49 (t) 1.61 (t), 1.63 (t) } 1.92 (d)	7.1 8.0	6.60—8.72 (m) [h]	1.74 (s) 2.10 (s) } (3Me)	−152.79 (str) −153.81 (0.5) −152.96 (0.5) } (su)	297.8 346.6
$[WCl(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Cl$	7.83 (s) [e]	1.42 (t), 1.59 (t) 1.83 (d)	7.0 8.3	7.05—7.63 (m)	2.34 (s) (4Me) 6.55, 6.89 8.16, 8.69 } (m)(4Me-py)	−153.45 (str) −153.03 (su)	297.8 346.6
$[WBr(NNH_2)(py)(PMe_2Ph)_3]Br$	ob	1.45 (t), 1.67 (t) 1.89 (t)	7.1 8.0	7.01—7.63 (m) [i]	6.63, 8.38 8.88 } (m)(py)	−157.49 (str) −157.79 (su)	215.4 341.8
$[WBr(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]Br$	ob	1.47 (t), 1.69 (t) 1.92 (t)	7.0 8.3	6.87—7.63 (m) [i]	6.61, 8.36 8.84 } (m)(2Me-py) 1.84, 1.94, 2.01 2.13, 2.34 } (s)(2Me)	−157.37 (1.5)(str) −156.95 (0.5)(str) } −157.67 (su)	297.8 339.4
$[WBr(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Br$	ob	1.47 (t), 1.70 (t) 1.95 (d)	7.2 8.0	6.53—8.80 (m) [j]	1.70 2.12 } (s)(3Me)	−156.95 (str) −158.22 (0.3)(su) −157.74 (0.7(su) }	295.4 341.2
$[WBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Br$ [k]	ob	1.47 (t), 1.70 (t) 1.95 (d)	7.2 8.0	6.53—8.80 (m) [i]	2.33, 2.36 (s) [l] (4-Me) 6.51, 6.94 [l] 8.25, 8.75 8.43 } (m)(4Me-py)	−157.61 (s)	{ 295.5 341.8
$[WI(NNH_2)(py)(PMe_2Ph)_3]I$ [k]	6.35 (s) [e]	1.56 (t), 1.80 (t) 2.02 (d)	7.1 7.9	7.12—7.60 (m) [b]	6.62, 8.80 8.60, 7.75 } (m)(py)	−164.31 (str) −165.09 (su)	293.0 334.5
$[WI(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]I$ [k]	6.27 (s) [e]	1.57 (t), 1.81 (t) 2.01 (d)	7.2 8.0	7.03—7.79 (m) [f]	1.94, 2.03 2.10 2.20, 2.37 } (s)(2Me) 6.63, 8.87 8.53 } (m)(2Me-py)	−164.46 (1.5) −167.05 (0.5) } (str) −165.13 (su)	293.0 339.4
$[WI(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]I$ [k]	6.60 (s) [e,m]	1.60 (t), 1.82 (t) 2.10 (d)	7.1 8.0	6.90—8.78 (m) [h]	1.73, 2.20 2.37 } (s)(2Me)	−163.88 (str) −165.51 (0.3) −165.33 (0.7) } (su)	295.4 334.5
$[WI(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]I$ [k]	6.28 (s) [e]	1.56 (t), 1.80 (t) 2.00 (d)	7.1 8.0	7.14—7.58 (m)	2.38 (s)(4Me) 6.50, 7.07 8.46, 8.74 } (m)(4Me-py)	−164.6 (str) −165.03 (su)	 332.0
$[MoCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	9.30 (s) [e]	1.29 (t), 1.48 (t) 1.65 (d)	6.5 8.1	6.90—7.70 (m) [n]	6.76, 8.56 8.92 } (m)(py)		
$[MoCl(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Cl$	9.01 (s) [e]	1.24 (t), 1.39 (t) 1.58 (d)	7.0 8.0	7.08—7.50 (m)	2.23 (s)(4Me) 6.61, 6.90 8.37, 8.74 } (m)(4Me-py)		

[MoBr(NNH$_2$)(py)(PMe$_2$Ph)$_3$]Br	8.63 (s) [e,m]	1.33 (t), 1.52 (t) 1.72 (d)	6.5 7.8	6.14—7.84 (m) [n]	6.68, 8.94 (m)(py)	−140.67 −141.03 } (dtr) −129.94 (tu)	14.6 [^2J(PP)] 14.6 [^2J(PP)]
[MoBr(NNH$_2$)(4Me-py)(PMe$_2$Ph)$_3$]Br	8.59 (s) [e,m]	1.32 (t), 1,53 (t) 1.69 (d)	6.5 7.5	7.10—7.61 (m)	2.17 (s)(4Me) 6.61, 7.0 8.90 } (m)(4Me-py)		
[MoI(NNH$_2$)(py)(PMe$_2$Ph)$_3$]I	8.11 (s)	1.43 (t), 1.67 (t) 1.82 (d)	6.5 8.0	7.18—7.60 (m) [n]	6.76, 8.75 9.05 } (m)(py)		
[WCl(NNH$_2$)(py)(PMe$_2$Ph)$_3$][BPh$_4$]	3.92 [e]	1.32 (t), 1.42 (t) 1.74 (d)	7.2 8.3	6.70—7.56 [o]	6.67, 8.28 (m)(py)	−154.3 (str) −155.08 (su)	293.0 346.6
[WBr(NNH$_2$)(py)(PMe$_2$Ph)$_3$][BPh$_4$]	3.79 [e]	1.38 (t), 1.48 (t) 1.82 (d)	7.3 8.3	6.71—7.57 [o]	7.72, 8.37 (m)(py)	−158.33 (str) −159.36 (su)	293.0 341.8
[WBr(NNH$_2$)(2Me-py)(PMe$_2$Ph)$_3$]-[BPh$_4$]	3.78 [e]	1.39 (t), 1.49 (t) 1.82 (d)	7.3 8.0	6.60—7.78 [o]	1.76, 1.84 1.91 } (s)(2Me) 8.38 (m)(2Me-py)	−158.39(1.6) −157.98(0.4) } (str) −159.24 (su)	293.0 344.2
[WBr(NNH$_2$)(3Me-py)(PMe$_2$Ph)$_3$]-[BPh$_4$]	3.87 [e]	1.40—1.60 [p] 1.91 (d)	 8.2	6.67—7.98 [o]	1.73 (s), 1.96 (s)(3Me) 8.42 (m)(3Me-py)	−158.15 (0.7) −157.91 (1.3) } (str) −159.84 (0.3) −159.24 (0.7) } (su)	293.0 336.9
[WBr(NNH$_2$)(4Me-py)(PMe$_2$Ph)$_3$]-[BPh$_4$]	3.75 [e]	1.37 (t), 1.49 (t) 1.80 (d)	7.5 8.2	6.87—7.67 [q]	2.39 (s)(4Me) 6.62, 6.73 8.29 } (m)(4Me-py)	−158.46 (str) −159.30 (su)	293.0 341.8
[WI(NNH$_2$)(py)(PMe$_2$Ph)$_3$][BPh$_4$]	3.67 [e]	1.45 (t), 1.54 (t) 1.88 (d)	7.0 8.0	6.53—7.55 [o]	7.81 8.53 } (m)(py)	−165.39 (str) −166.35 (su)	293.0 336.9
[WCl(NNH$_2$)(2HS-py)(PMe$_2$Ph)$_3$]Cl [k]	ob	1.67 [p] 1.81 (d)	 8.2	6.50—8.14 [r]	10.58 (s) [e] (*H*S-py) [s]	−158.61 (str) −157.65 (su)	283.2 358.9
[WBr(NNH$_2$)(2HS-py)(PMe$_2$Ph)$_3$]Br [k]	ob	1.71 [p] 1.89 (d)	 8.1	6.47—8.04 [r]	10.30 (s) [e] (*H*S-py) [s]	−163.68 (str) −162.84 (su)	283.2 356.4
[WI(NNH$_2$)(2HS-py)(PMe$_2$Ph)$_3$]I [k]	ob	1.81 [d] 1.98 (d)	 8.0	6.43—7.96 (m)	10.21 (s)(*H*S-py) [s]		
[W(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]Cl	ob	1.27 (ot) 1.75 (d)	6.5 8.0	6.70—7.74 [t]	8.64 (s)(quin)	−150.68 (str) −146.04 (su)	300.3 361.3
[W(NNH$_2$)(2S-py)(PMe$_2$Ph)$_3$][BPh$_4$]	3.70 [e]	1.32—1·60 (odt)	{ 7.0 8.0	6.23—7.47 [u]		−156.95(str) −148.57(su)	288.1 332.0
[W(NNH$_2$)(quin)(PMe$_2$Ph)$_3$[BPh]$_4$	4.08 [e]	1.04 (t), 1.11 (t) 1.64 (d)	7.0 8.0	6.56—7.62 [v]			
[Mo(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]Cl	8.23 [e]	1.33 (t), 1.42 (t) 1.64 (d)	6.3 7.5	6.70—7.85 [w]	8.72 (s) quin)	−135.85 −136.21 } (dtr) −126.08	14.7 [^2J(PP)] 14.7 [^2J(PP)]
[WBr(NNH$_2$)(S$_2$CNMe$_2$)(PMe$_2$Ph)$_2$]	3.43 [e]	1.93 (t)	16.0	7.25—6.67 (m)	3.36 (s)(NMe)		
[MoCl(NNH$_2$)(PMe$_2$Ph)$_4$]Cl	10.10 [e]	1.49 (s, br)		6.79—7.75 (m)			
[MoBr(NNH$_2$)(PMe$_2$Ph)$_4$]Br	9.40 [e]	1.48(s, br)		7.08—7.64 (m)			
[MoI(NNH$_2$)(PMe$_2$Ph)$_4$]I	8.32 [e]	1.60 (s, br)		7.00—7.80 (m)			

s = Singlet, t = triplet, str = singlet for *trans*-P nucleii, su = singlet for unique P nucleus, m = multiplet, br = broad, ob = obscured by other resonances, dtr = doublet for *trans*-phosphorus nucleii, tu = triplet for unique phosphorus nucleus, odt = overlapping doublet and pair of triplets, and ot = overlapping pair of triplets.

[a] In C^{2}H$_2$Cl$_2$ solution unless otherwise stated; resonance values in p.p.m. (±0.01), *J* values in Hz (±0.1). Integration values are as required unless given in parentheses. [b] Relative to SiMe$_4$. [c] Relative to P(OMe)$_3$, negative values to high field; resonances for tungsten complexes have tungsten satellites. [d] Spectrum shows P–P coupling. [e] Resonance, integrating for two protons, disappears on addition of ^{2}H$_2$O. [f] One py proton included. [g] Several resonances (see text). [h] Includes three protons of 3Me-py. [i] Includes NH$_2$ and one py proton. [j] Includes NH$_2$ and 3Me-py protons. [k] Contains 0.5 mol of substituted pyridine of crystallisation. [l] Includes resonances of uncoordinated substituted pyridine. [m] Includes one aromatic substituted-pyridine proton. [n] Includes two py protons. [o] Includes BPh$_4$ and three substituted-pyridine protons. [p] Two overlapping unresolved triplets. [q] Includes BPh$_4$ and one substituted-pyridine proton. [r] Includes NH$_2$, one (2*H*S-py) and (2HS-py) aromatic protons. [s] Uncoordinated ligand. [t] Includes NH$_2$ and (quin) protons. [u] Includes BPh$_4$ and 2S-py protons. [v] Includes BPh$_4$ and (quin) protons. [w] Includes (quin) protons.

TABLE 4

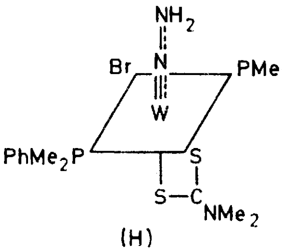
Infrared data (cm^{-1}) for hydrazido(2—)-complexes

Complex	ν(NH) [a]	ν(M–Cl) [b]	Other notable bands
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	3 140m, 3 220m, 3 300ms	245, 264s	
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	3 138m, 3 210m, 3 296ms		
$[WI_2(NNH_2)(PMe_2Ph)_3]$	3 132m, 3 205m, 3 295ms		
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	3 110m, 3 205m, 3 300ms	245ms, 264s	2 285m, 2 355m, 2 465ms (N–D) [c]
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	3 108m, 3 190m, 3 290ms		
trans-$[WCl(NNH_2)(PMe_2Ph)_4]Cl$	2 960ms, br, 3 090ms, br, 3 140w(sh)	265s	
trans-$[WBr(NNH_2)(PMe_2Ph)_3]Br$	2 940ms, br, 3 110ms, br, 3 203ms (sh)		
trans-$[WI(NNH_2)(PMe_2Ph)_4]I$	2 960ms, br, 3 110ms, br, 3 195mw (sh)		
trans-$[MoCl(NNH_2)(PMe_2Ph)_4]Cl$	3 360ms, br	275s	
trans-$[MoBr(NNH_2)(PMe_2Ph)_4]Br$	3 400ms, br		
trans-$[MoI(NNH_2)(PMe_2Ph)_4]I$	3 440ms, br		
trans-$[WI(NNH_2)(dppe)_2]I$	2 793mw, 3 293mw		2 063, 2 465 (N–D)
trans-$[MoI(NNH_2)(dppe)_2]I$	3 300mw		
trans-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$	3 201m, 3 290ms, 3 371m		
$[WI(NNH_2)(dmf)(PMe_2Ph)_3]\cdot dmf$	3 050ms, br, 3 180m, br		1 655s, 1 680s (C=O)
$[MoI(NNH_2)(dmf)(PMe_2Ph)_3]I$	3 100—3 190 mw [d]		1 645s, br (C=O)
$[WCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	2 870m, 2 975s, br, 3 205ms, br, 3 215w	268s	2 860w, 2 960m, br, 3 100w, br (N–D) [c]
$[WCl(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]Cl$	2 870m, 2 973s, br, 3 110ms, br, 3 213w	266s	
$[WCl(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Cl$	2 860m, 2 965s, br, 3 090ms, br, 3 200w	264s	
$[WCl(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Cl$	2 930s, br, 3 060ms, br	266s	
$[WBr(NNH_2)(py)(PMe_2Ph)_3]Br$	2 845m, 2 980s, br, 3 010ms, br, 3 130m, br		
$[WBr(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]Br$	2 855m, 2 985s, br, 3 020ms, br, 3 140m, br		
$[WBr(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Br$	2 850m, 2 985s, br, 3 020ms, br, 3 135m, br		
$[WBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Br\cdot 0.5\ (4Me\text{-}py)$	2 962s, br, 3 090mw, br		
$[WI(NNH_2)(py)(PMe_2Ph)_3]I\cdot 0.5\ py$	2 913m, 3 018s, br, 3 143ms, br, 3 198w		
$[WI(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3]I\cdot 0.5\ (2Me\text{-}py)$	3 005s, br, 3 140m, br		
$[WI(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]I\cdot 0.5\ (3Me\text{-}py)$	2 845w, 3 005s, br, 3 135ms, br, 3 175 (sh)		
$[WI(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]I\cdot 0.5\ (4Me\text{-}py)$	2 845w, 3 005s, br, 3 135ms, br		
$[MoCl(NNH_2)(py)(PMe_2Ph)_3]Cl$	2 850w, 2 920m, br, 3 060w, br, 3 170 w, br		
$[MoCl(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3]Cl$	*ca.* 3 000—3 200 [c]	266m	
$[MoCl(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Cl$	2 850mw, 2 930m, br, 3 060mw, br, 3 170w		
$[MoBr(NNH_2)(py)(PMe_2Ph)_3]Br$	2 825w, 2 950m, br, 3 080m, 3 180w, br		
$[MoBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Br$	*ca.* 3 000—3 200 [c]		
$[MoI(NNH_2)(py)(PMe_2Ph)_3]I$	2 860w, 2 960m, br, 3 100w, br		
$[MoI(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]I$	*ca.* 3 000—3 2000 [c]		
$[WCl(NNH_2)(py)(PMe_2Ph)_3][BPh_4]$	3 142mw, 3 228s, 3 302mw	276s	2 368s, 2 322mw (N–D) [c]
$[WBr(NNH_2)(py)(PMe_2Ph)_3][BPh_4]$	3 142mw, 3 230s, 3 302mw		
$[WBr(NNH_2)(2Me\text{-}py)(PMe_2Ph)_3][BPh_4]$	3 150mw, 3 232s, 3 310mw		
$[WBr(NNH_2)(3Me\text{-}py)(PMe_2Ph)_3][BPh_4]$	3 142mw, 3 230s, 3 303mw		
$[WBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3][BPh_4]$	3 154mw, 3 240s, 3 325m		
$[WI(NNH_2)(py)(PMe_2Ph)_3][BPh_4]$	3 140w, 3 224ms, 3 300mw		
$[WCl(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]Cl\cdot(2HS\text{-}py)$	2 980ms, br, 3 102m, br, 3 230mw	270s, 263(sh), 275(sh),	1 550s, 1 560(sh), 1 610m (2HS-py)
$[WBr(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]Br\cdot(2HS\text{-}py)$	2 970ms, br, 3 085m, br, 3 255w		1 552s, 1 585ms, 1 609m (2HS-py)
$[WI(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]I\cdot(2HS\text{-}py)$	3 000ms, br, 3 155m, br, 3 263w		1 555s, 1 585ms, 1 605m (2HS-py)
$[W(NNH_2)(2S\text{-}py)(PMe_2Ph)_3][BPh_4]$	3 135w, 3 230ms, 3 311w		
$[MoBr(NNH_2)(2HS\text{-}py)(PMe_2Ph)_3]Br$	3 290m		1 560s, 1 580ms, 1 610m (2HS-py)
$[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$	2 955ms, br, 3 090ms, br		1 565s, 1 585ms, 1 600w (quin)
$[W(NNH_2)(quin)(PMe_2Ph)_3]Br$	2 980ms, br, 3 110ms, br		1 568s, 1 588m, 1 602w (quin)
$[W(NNH_2)(quin)(PMe_2Ph)_3]I$	3 035ms, br, 3 145m, br, 3 203 (sh)		1 562s, 1 585m, 1 593mw (quin)
$[W(NNH_2)(quin)(PMe_2Ph)_3][BPh_4]$	3 161w, 3 246m, 3 310w		1 566s, 1 587s (quin)
$[Mo(NNH_2(quin)(PMe_2Ph)_3]Cl$	3 000—3 150 [c]		1 568s, 1 585m, 1 598m (quin)
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Br$	3 000—3 150 [c]		1 550s, 1 568s, 1 596m (quin)
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]I$	3 000—3 150 [c]		1 560s, 1 581m, 1 598w (quin)
$[WBr(NNH_2)(S_2CNMe_2)(PMe_2Ph)_2]$	3 285mw		1 530s (C=N), 1 155s (C=S)

m = Medium, w = weak, s = strong, br = broad, and sh = shoulder.

[a] Hexachlorobutadiene mulls unless otherwise stated. [b] M = Mo or W, Nujol mulls between Polythene plates. [c] In deuterio-analogue. [d] Broad series of bands, Nujol mulls.

there is considerable asymmetrical hydrogen bonding between the NNH_2 group and the bromide or iodide anions. A similar strong hydrogen-bonding interaction also occurs in the analogous complexes $[MoF(NNH_2)(dppe)_2][BF_4]$ [9] and $[MoI\{NN(C_8H_{17})H\}(dppe)_2]I$.[10] This type of hydrogen bonding cannot occur in the non-ionic complexes (A) which probably explains why their i.r. spectra (Table 4) in the N–H stretching region differ from those of (B)—(G). Complexes (A) have a characteristic sharp absorption pattern, whereas (B)—(D), (F), and (G) have a very broad, largely unresolved, absorption in this region.



(H)

TABLE 5

Structural parameters for hydrazido(2 –)-complexes

Complex	Bond/Å W–N	Bond/Å N–N	Angle/° W–N–N	Ref.
$[WBr(NNH_2)(4Me\text{-}py)(PMe_2Ph)_3]Br$	1.75	1.34	177	6
$[W(NNH_2)(quin)(PMe_2Ph)_3]I$	1.795	1.37	171	7
$[WCl(NNH_2)(dppe)_2][BPh_4]$	1.74	1.37	171	*a*
$[WBr(NNMeH)(dppe)_2]Br$	1.77	1.32	174	*b*
$[MoF(NNH_2)(dppe)_2][BF_4]$	1.76 [c]	1.33	176	9
$[MoI\{NN(C_8H_{17})H\}(dppe)_2]I$	1.80 [c,d]	1.26 [c]	174	10

[a] G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 259. [b] F. C. March, R. Mason, and K. M. Thomas, *J. Organometallic Chem.*, 1975, **96**, C43. [c] Mo–N distance. [d] Inaccurate values because of disorder in the crystal.

The NH_2 ^1H resonance positions (Table 3) of complexes (A; M = W) and (B; M = W) are also (when observed) at lower field (6.3—7.8 p.p.m. relative to $SiMe_4$) than those of *trans*-$[WX(NNH_2)(dppe)_2]Y$ (X = F, Cl, or Br; Y = BF_4, BPh_4, ClO_4, or PF_6) (2.90—4.0 p.p.m.) [3] and those of (A; M = Mo) and (B; M = Mo) (in the range 8.11—10.10 p.p.m.) are to low field of *trans*-$[MoF(NNH_2)(dppe)_2][BF_4]$ (5.11 p.p.m.).[4,9] This chemical-shift difference is unlikely to be due to the use of unidentate phosphines in one series and chelating diphosphines in the other. We consider it to be caused by a strong hydrogen-bonding interaction in CH_2Cl_2 between the NNH_2 group and halide anion in the unidentate phosphine series. As evidence, the complexes $[WX(NNH_2)(PMe_2Ph)_3L][BPh_4]$ (L = substituted pyridines), which contain monophosphines but do not have an anion capable of strong hydrogen bonding, have their NH resonance in the same region (3.67—3.92 p.p.m.) as does *trans*-$[WX(NNH_2)(dppe)_2]Y$.

In this paper we also describe the preparation of the poorly soluble complexes *trans*-$[MX(NNH_2)(dppe)_2]I$, whose structure is assigned on the basis of the similarity of their i.r. spectra to those of *trans*-$[WX(NNH_2)(dppe)_2]Y$ [1,3] and their conductivities in dmf (Tables 1 and 2). We have previously reported the preparation of their analogues $MX_2(N_2H_2)(dppe)_2$ (X = Cl or Br) [3] and have suggested that they might be seven-co-ordinate with the N_2H_2 ligand in the diazene form, NH:NH, because their NH i.r. pattern showed a large ν(NH) splitting (*ca.* 350 cm^{-1}) as compared with *trans*-$[WX(NNH)(dppe)_2]Y$ (100 cm^{-1}); also their NH resonance was at rather low field and they had low conductivity in CH_2Cl_2. In view of the data given in the previous paragraph, it now seems likely that they are salts, *trans*-$[MX(NNH_2)(dppe)_2]X$ (X = Cl or Br), with strong asymmetric hydrogen bonding between the NNH_2 group and X causing the shift of the NH resonance to low field and larger splitting of ν(NH). One problem with this new assignment, however, is that whereas *trans*-$[WX(NNH_2)(dppe)_2]Y$ and (B; M = W, X = Cl, Br, or I) have only a singlet resonance in their ^{31}P spectra, $MX_2(N_2H_2)(dppe)_2$ (X = Cl or Br) show additional resonances; moreover, an asymmetric multiplet is observed at –70 °C in the ^1H n.m.r. spectrum of their $^{15}N_2H_2$ analogue.[3] An *X*-ray structure of a member of the $MX_2(N_2H_2)(dppe)_2$ series is needed but so far suitable crystals have not been obtained. Pending a definitive structure, the hydrazido(2 –)-structure, *trans*-$[WX(NNH_2)(dppe)_2]X$ must be considered more likely than the diazene structure originally proposed.

Chemical and Electrochemical (*with Dr. C. Pickett*) *Oxidations.*—The complexes (A; M = W, X = Cl, Br, or I; M = Mo, X = Br), (B; L = NC_5H_5; M = W, X = Cl, Br, or I; M = Mo, X = Cl), and (D; M = W, X = Cl, Br, or I; M = Mo, X = Cl or Br) have been investigated electrochemically in dichloromethane solution, and the results are shown in Table 6. No reduction wave was observed for any complex at potentials above that of solvent discharge. All the complexes underwent oxidation by a single electron with the primary oxidation potentials for corresponding members of both the tungsten and molybdenum series having fairly similar values, the tungsten complexes being somewhat easier to oxidise. The oxidised species observed in solution were rather unstable, especially those of molybdenum, and decomposed on attempted isolation.

TABLE 6

Electrochemical data

Complex	E_p^{ox}/V [a]	Comments
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	–0.081	*b*, *c*
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	–0.060	*b*, *c*
$[WI_2(NNH_2)(PMe_2Ph)_3]$	–0.050	*b*, *c*
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	–0.048	*b*, *c*
$[WCl(NNH_2)(NC_5H_5)(PMe_2Ph)_3]Cl$	0.345	*b*, *c*
$[WBr(NNH_2)(NC_5H_5)(PMe_2Ph)_3]Br$	0.368	*b*, *c*
$[WI(NNH_2)(NC_5H_5)(PMe_2Ph)_3]I$	0.435	*b*, *c*
$[MoCl(NNH_2)(NC_5H_5))(PMe_2Ph)_3]Cl$	0.115	Irreversible at scan rates <0.3 V s^{-1}
$[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$	0.278	*b*, *c*, oxidised product decomposes in solution
$[W(NNH_2)(quin)(PMe_2Ph)_3]Br$	0.264	*b*, *c*, product decomposes in solution
$[W(NNH_2)(quin)(PMe_2Ph)_3]I$	0.250	*b*, *c*, product decomposes in solution
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Cl$	0.409	Irreversible, *c*
$[Mo(NNH_2)(quin)(PMe_2Ph)_3]Br$	0.410	Irreversible, *c*

[a] Refers to the peak oxidation potential of the complex *versus* the standard calomel electrode at a platinum-wire electrode, in 0.2 mol dm^{-3} $[NEt_4][BF_4]$–CH_2Cl_2, at a scan rate of 0.3 V s^{-1}. [b] Reversible. [c] One-electron oxidation.

---

[9] M. Hidai, T. Kodama, M. Sato, M. Harakawa, and Y. Uchida, *Inorg. Chem.*, 1976, **15**, 2694.

[10] V. W. Day, T. A. George, S. D. A. Iske, and S. D. Wagner, *J. Organometallic Chem.*, 1976, **112**, C55.

Complexes (A; X = Cl or Br) were also treated with silver nitrate or silver carbonate in an attempt to isolate oxidised hydrazido(2−)-species but in all cases quantitative evolution of dinitrogen occurred and no attempt was made to isolate the remaining metal-containing products.

DISCUSSION

The hydrazido(2−)-complexes described here and in previous papers represent the second step in the reduction of dinitrogen on molybdenum and tungsten to ammonia. In these hydrazido(2−)-complexes there is considerable multiple bonding between the ligating nitrogen atom and the metal, as demonstrated by the linearity of the M–N–N chain, and the hydrazido(2−)-group acts as a four-electron donor. This multiple bonding is responsible for the stability of the $M-N_2H_2$ moiety, and its stability aids the protonation and reduction process. For such a process to occur the metal must have available to it a range of oxidation levels so that it can act as a π donor at the dinitrogen binding stage and a π acceptor at the hydrazido(2−)-binding stage. Transition metals to the left of the transition-metal series with their relatively low electron affinities and tendency to multiple valency, in particular molybdenum and tungsten, are especially suited for this purpose. This accords with the generally accepted view of the function of molybdenum in nitrogenase.

The hydrazido(2−)-complexes are also capable of further protonation reactions leading to the production of ammonia and/or hydrazine, depending on the conditions. These aspects will be described in later papers.

EXPERIMENTAL

Air-sensitive materials were handled under dinitrogen or by vacuum techniques; non-condensible gases were determined by means of a Topler pump. N.m.r. spectra were recorded using a JEOL PS100 instrument (in the Fourier-transform mode for ^{31}P spectra) and i.r. spectra with a Unicam SP 2000 spectrometer. Mass spectra were determined with an A.E.I. MS10 instrument and conductivities with a Portland Electronics conductivity bridge. Analyses were by Mr. A. G. Olney of the University of Sussex. The complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) were prepared as previously described.[1,3] Pyridines were dried with molecular sieves before use and these and other chemicals were analytical grade and used without further purification.

Preparation of Complexes (A) *and* (B; M = W).—Since the methods are general, only one example for each metal is given.

Dibromotris(dimethylphenylphosphine)[hydrazido(2−)]-tungsten(IV), $[WBr_2(NNH_2)(PMe_2Ph)_3]$, *and* trans-*bromotetrakis(dimethylphenylphosphine)[hydrazido(2−)]tungsten*(IV) *bromide, trans*-$[WBr(NNH_2)(PMe_2Ph)_4]Br$. Hydrobromic acid (2.5 cm^3, 48% solution) was added with stirring under dinitrogen at 20 °C to a suspension of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (1.7 g) in methanol (40 cm^3). A rapid reaction ensued with gas evolution and formation of a red-brown solution, followed by precipitation of brown *crystals* of the tris(phosphine) product. The mixture was stirred for 4 h, then the solid was filtered off, washed with distilled water, methanol, and diethyl ether, and dried (10^{-3} mmHg, 20 °C).[*] Addition of distilled water (40 cm^3) to the mother liquor precipitated orange-yellow crystals of the tetrakis(phosphine) product, which were filtered off, washed with distilled water and a little chilled methanol, then dried (10^{-3} mmHg, 20 °C). The chloro- and iodo-analogues were similarly prepared.

The above preparations were also performed *in vacuo* so that the evolved gases could be measured. Methanol (35 cm^3) and hydrogen bromide (10.0 mol equivalents) were condensed *in vacuo* at −196 °C on to *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (1.23 g). On warming to 20 °C, dinitrogen (37.69 cm^3, 1.01 mol equivalent) was rapidly evolved with the formation of a brown-red solution followed by precipitation of brown crystals. The mixture was stirred for 4 h and then worked up as described above. The chloride analogue was similarly prepared.

Dichlorotris(dimethylphenylphosphine)[hydrazido(2−)]-molybdenum(IV), $[MoCl_2(NNH_2)(PMe_2Ph)_3]$. Hydrogen chloride (15.0 mol equivalents) was condensed at −196 °C *in vacuo* on to *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (0.132 g) in methanol (20 cm^3) and the mixture allowed to warm to 20 °C with stirring. Dinitrogen (1.02 mol equivalent) was rapidly evolved and a red-brown solution formed during 5 min which deposited an orange-brown *solid* on stirring for 3 h. The solid was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). This complex can also be prepared using an excess of concentrated aqueous hydrogen chloride either *in vacuo* or under dinitrogen. The bromide and iodide analogues were prepared using an excess of the corresponding aqueous halogen acids.

Deuterio-analogues of both the tungsten and molybdenum complexes were prepared *in vacuo* using anhydrous ^2HX (X = Cl or Br).

trans-*Bis[1,2-bis(diphenylphosphino)ethane][hydrazido-(2−)]iodotungsten*(IV) *iodide, trans*-$[WI(NNH_2)(dppe)_2]I$. Hydroiodic acid (0.4 cm^3, 55% solution) was added to a suspension of *trans*-$[W(N_2)_2(dppe)_2]$ (0.22 g) in methanol (35 cm^3) with stirring at 30 °C *in vacuo*. A red-orange solution slowly formed (*ca.* 15 min) with evolution of dinitrogen (5.15 cm^3, 1.01 mol equivalent). The solution was stirred for 18 h during which time a yellow-brown *solid* deposited which was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). The molybdenum analogue was similarly prepared.

trans-*Tetrakis(dimethylphenylphosphine)fluoro[hydrazido-(2−)]tungsten*(IV) *tetrafluoroborate, trans*-$[WF(NNH_2)(PMe_2Ph)_4][BF_4]$. Hydrofluoric acid (0.5 cm^3, 40% solution) was added to a suspension of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.27 g) in methanol (35 cm^3) with stirring in a borosilicate glass vessel *in vacuo* at 20 °C. Dinitrogen (7.42 cm^3, 0.91 mol equivalent) slowly evolved with formation of a red solution (*ca.* 0.5 h), and this solution was stirred for another 15 h. The solution was then concentrated *in vacuo* to about one third its volume, diethyl ether (75 cm^3) was added, and the solution allowed to stand at 0 °C for another 14 d during which time orange-brown *crystals* deposited. These were filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C).

Preparation of Complexes (C).—Where the method is a general one, *e.g.* for L = various pyridines, only one specific example is given.

Iodo(dimethylformamide)tris(dimethylphenylphosphine)-

---

[*] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[hydrazido(2—)]tungsten(IV) *iodide–dimethylformamide* (1/1), $[WI(NNH_2)(dmf)(PMe_2Ph)_3]I\cdot dmf$. Complex (A; M = W, X = I) (0.3 g) was dissolved in dmf (20 cm^3) under dinitrogen and diethyl ether (60 cm^3) was carefully added to the resulting red solution. The mixture was quickly filtered and slowly deposited red-brown *crystals* on standing at 0 °C which were filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). The molybdenum analogue was similarly prepared.

Chlorotris(dimethylphenylphosphine)[hydrazido(2—)]-pyridinetungsten(IV) *chloride*, $[WCl(NNH_2)(NC_5H_5)(PMe_2Ph)_3]Cl$. Pyridine (20 cm^3) was added to (A; M = W, X = Cl) (0.35 g) and the mixture stirred under dinitrogen at 20 °C until all the solid had dissolved (*ca.* 0.5 h). Diethyl ether (70 cm^3) was then slowly added to the resulting dark red solution and the mixture was quickly filtered. On standing, the filtrate deposited red *crystals* which were filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). Analogous complexes with the other substituted pyridines and those for M = Mo were prepared by a similar method.

trans-*Tetrakis(dimethylphenylphosphine)[hydrazido(2—)]-iodomolybdenum*(IV) *iodide*, *trans*-$[MoI(NNH_2)(PMe_2Ph)_4]I$. Complex (A; M = Mo, X = I) (0.53 g) and PMe_2Ph (0.1 g) were stirred together in methanol (30 cm^3). After a few minutes a red solution formed which was stirred for 3 h then kept at 0 °C for 16 h. Bright orange *crystals* deposited and were filtered off, dried (10^{-3} mmHg, 20 °C), and found to be analytically pure. The analogues for X = Cl and Br were similarly prepared.

Alternative preparation of trans-*bromotetrakis(dimethylphenylphosphine)[hydrazido(2—)]tungsten*(IV) *bromide*, *trans*-$[WBr(NNH_2)(PMe_2Ph)_4]Br$. Complex (A; M = W, X = Br) (0.17 g) and PMe_2Ph (0.03 g) were dissolved in CH_2Cl_2 (20 cm^3) and the solution was stirred for 60 h. The resulting solution was filtered through Celite to remove some blue solid deposit, and diethyl ether (20 cm^3) was added to the resulting clear red-brown solution. Orange *crystals* deposited which were filtered off and shown to be identical (i.r. spectrum and analysis) with (B; M = W, X = Br) prepared by acid treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ as described above.

Chlorotris(dimethylphenylphosphine)[hydrazido(2—)]-pyridinetungsten(IV) *tetraphenylborate*, $[WCl(NNH_2)(NC_5H_5)(PMe_2Ph)_3][BPh_4]$. Dichloromethane (20 cm^3) and tetrahydrofuran (20 cm^3) were added to a mixture of $[WCl(NNH_2)(NC_5H_5)(PMe_2Ph)_3]Cl$ (0.15 g) and $Na[BPh_4]$ (0.1 g) and the mixture was stirred under dinitrogen at 20 °C for 18 h. The red solution was then filtered and the solvent removed *in vacuo* at 20 °C. The residue was extracted with dichloromethane (10 cm^3) and diethyl ether (50 cm^3) slowly added to this extract. The mixture was then quickly filtered, and left to stand at 20 °C whereupon red *crystals* were deposited which were filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). The analogous complexes with various substituted pyridines were prepared in a similar manner.

Chlorotris(dimethylphenylphosphine)[hydrazido(2—)](pyridine-2-thiol)tungsten(IV) *chloride–pyridine-2-thiol*(1/1), $[WCl(NNH_2)(NC_5H_4SH\text{-}2)(PMe_2Ph)_3]Cl\cdot(NC_5H_4SH\text{-}2)$. Dichloromethane (35 cm^3) was added to a mixture of (A; M = W, X = Cl) (0.31 g) and NC_5H_4SH-2 (0.31 g) and the mixture was stirred for 30 h under dinitrogen at 20 °C. The resulting dark red solution was reduced to about one third its volume *in vacuo* and diethyl ether (50 cm^3) was added. The mixture was then quickly filtered and the filtrate, on standing at 20 °C, deposited dark red *crystals* which were filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). The bromo- and iodo-analogues were similarly prepared.

Tris(dimethylphenylphosphine)[hydrazido(2—)](pyridine-2-thiolato)tungsten(IV) *Tetraphenylborate*, $[W(NNH_2)(NC_5H_4S\text{-}2)(PMe_2Ph)_3][BPh_4]$.—Dichloromethane (20 cm^3) and thf (20 cm^3) were added to a mixture of $[WBr(NNH_2)(NC_5H_4SH\text{-}2)(PMe_2Ph)_3]Br\cdot(NC_5H_4SH\text{-}2)$ (0.12 g) and $Na[BPh_4]$ (0.1 g) and the mixture was stirred under dinitrogen at 20 °C for 18 h. The resulting red solution was filtered and the solvent removed *in vacuo*. The residue was extracted with dichloromethane (5 cm^3) and diethyl ether (40 cm^3) was carefully added to the extract. The mixture was quickly filtered and left to stand whereupon pale red *needles* were deposited which were filtered off, dried (10^{-3} mmHg, 20 °C), and recrystallised from CH_2Cl_2–Et_2O.

Tris(dimethylphenylphosphine)[hydrazido(2—)](quinolin-8-olato)tungsten(IV) *Chloride*, $[W(NNH_2)(quin)(PMe_2Ph)_3]Cl$.—Dichloromethane (35 cm^3) was added to a mixture of (A; M = W, X = Cl) (0.32 g) and quinolin-8-ol (0.32 g) and the mixture stirred for 18 h. The resulting deep purple solution was filtered and reduced to about one third its volume *in vacuo*. Diethyl ether (50 cm^3) was carefully added and the mixture quickly filtered. On standing the filtrate deposited very dark purple *prisms* of (D; M = W, X = Cl) which were filtered off, washed with diethyl ether, dried (10^{-3} mmHg, 20 °C), and recrystallised from CH_2Cl_2–Et_2O. The bromo- and iodo-analogues and the molybdenum analogues were similarly prepared.

Tris(dimethylphenylphosphine)[hydrazido(2—)](quinolin-8-olato)tungsten(IV) *Tetraphenylborate*, $[W(NNH_2)(quin)(PMe_2Ph)_3][BPh_4]$.—Dichloromethane (20 cm^3) and thf (20 cm^3) were added to a mixture of (D; M = W, X = Br) (0.1 g) and $Na[BPh_4]$ (0.1 g) and the mixture stirred for 18 h at 20 °C under dinitrogen. The resulting deep purple solution was filtered and the solvent removed *in vacuo*. The residue was extracted with dichloromethane (5 cm^3) and the solution again taken to dryness *in vacuo*. The i.r. and ^1H n.m.r. spectra of the dichloromethane solution of the residue showed the presence of the title complex. Attempts to crystallise it were unsuccessful.

Bromo(dimethyldithiocarbamato)bis(dimethylphenylphosphine)[hydrazido(2—)]tungsten(IV), $[WBr(NNH_2)(S_2CNMe_2)(PMe_2Ph)_2]$.—Dichloromethane (35 cm^3) was added to a mixture of (A; M = W, X = Br) (0.254 g) and $Na[S_2CNMe_2]$ (0.058 g, 1 mol equivalent) and the mixture stirred for 16 h at 20 °C under dinitrogen. The resulting red-brown solution was filtered and reduced to about half its volume *in vacuo*. After addition of hexane (50 cm^3) the mixture was quickly filtered then allowed to stand at 20 °C when red-brown crystals were deposited. These were filtered off, washed with hexane, and dried (10^{-3} mmHg, 20 °C). No solid product was obtained if an excess of $Na[S_2CNMe_2]$ was used.

Reactions of (A; M = W, X = Cl, Br, *or* I) *with* $Ag_2[CO_3]$.—The example given is for X = Cl.

Methanol (30 cm^3) was condensed on to (A; M = W, X = Cl) (0.096 g) and $Ag_2[CO_3]$ (0.1 g) at −196 °C *in vacuo*. The mixture was warmed to 20 °C with stirring whereupon it darkened rapidly and silver metal was deposited. The mixture was stirred for another 18 h and the gas evolved was found to be dinitrogen (3.20 cm^3, 0.98 mol equivalent). Further work-up of the metal-containing product was not attempted. Similar results were obtained for (A; M = W, X = Br or I).

Reaction of (A; M = Mo, X = Cl *or* Br) *with* Ag[NO_3].—Silver nitrate (0.1 g) in water (5 cm^3) was added to a suspension of (A; M = Mo, X = Cl) (0.095 g) in thf (30 cm^3) and the mixture rapidly stirred. A red colour rapidly formed, dinitrogen (1.0 mol equivalent) was evolved, and silver metal was deposited. No attempt was made to isolate the molybdenum-containing product. A similar result was obtained for (A; M = Mo, X = Br).

Electrochemical Method.—The supporting electrolyte, kinetic cell, and solvent-purification methods have been previously described.[11] Cyclic voltammograms were obtained using a HiTek Instruments type DT2101 potentiostat and a Chemical Electronics type RB1 waveform generator and were recorded on a Bryans type 26000AS XY recorder.

We thank Messrs. M. E. Fakley and S. N. Anderson for technical assistance.

[8/514 *Received*, 20*th March*, 1978]

---

[11] C. J. Pickett and D. Pletcher, *J.C.S. Dalton*, 1976, 749.