Reactions of ligating Dinitrogen to form Carbon–Nitrogen Bonds

By **Joseph Chatt,* Alex A. Diamantis, Graham A. Heath, Norman E. Hooper,** and **G. Jeffery Leigh**, School of Molecular Sciences and A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ

The reactions of $[M(N_2)_2(dppe)_2]$ [M = Mo or W; dppe = 1,2-bis(diphenylphosphino)ethane] with alkyl bromides, acyl chlorides, or aroyl chlorides, under irradiation, lead to organohydrazido(2−)- and organodiazenido-complexes. Complexes $[ReCl(N_2)(PMe_2Ph)_4]$ and $[ReCl(N_2)(py)(PMe_2Ph)_3]$ (py = pyridine) can be acylated but not alkylated at the dinitrogen, but in $[OsCl_2(N_2)(PMe_2Ph)_4]$ dinitrogen is inactive even to acid chlorides. The reactivity of dinitrogen in its complexes decreases along the third Transition Series in the order W > Re > Os.

CO-ORDINATED dinitrogen is generally inert, despite the weakening of the N–N bond in its complexes indicated by the lowering of $\nu(N_2)$ and the slight increase in the N–N distance. Most reactions of dinitrogen complexes involve decomposition with loss of N_2, or nitriding under very strongly aprotic reduction. The only well defined complexes in which dinitrogen shows any sign of direct reaction apart from reactions with other co-ordination centres,[1] are $[M(N_2)_2(PR_3)_4]$ ($M = Mo$ or W; $PR_3 =$ tertiary phosphine or half a ditertiary phosphine),[2-5] $[Mo(N_2)(NCPh)(Ph_2PCH_2CH_2PPh_2)_2]$,[6] $[ReCl(N_2)(PR_3)_3L]$ ($L =$ pyridine or PR_3),[4] $[(N_2)(Me_5C_5)_2Zr(N_2)Zr(C_5Me_5)_2(N_2)]$,[7] various less well defined titanium complexes,[8,9] and $[Ni(N_2)\{P(C_6H_{11})_3\}_2]$.[10]

The reaction of co-ordinated dinitrogen in a well defined manner to form organonitrogen ligands was first noted in the reaction of organic acid halides with $[M(N_2)_2(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] and $[ReCl(N_2)(PMe_2Ph)_3L]$ to form acyl- and aroyl-diazenido-complexes.[3] Since then there have been brief reports of the reactions of the molybdenum and tungsten bis(dinitrogen) complexes with alkyl halides under irradiation to give alkyldiazenido- and related complexes,[4,5,11,12] and with tetrahydrofuran (thf) to form complexes which were tentatively described as tetrahydropyridazido-complexes [13] but were recently shown to be ω-diazobutanol complexes.[14] Here we describe in detail the work briefly reported in refs. 3 and 4.

RESULTS

Acyldiazenido- and Aroyldiazenido-complexes and their Derivatives.—Acyl and aroyl halides react with the complexes $[M(N_2)_2(dppe)_2]$, $[ReCl(N_2)(PR_3)_4]$, or $[ReCl(N_2)(py)(PR_3)_3]$ (py = pyridine) to form acyldiazenido- and aroyldiazenido-complexes.[3] The products containing molybdenum or tungsten are most easily isolated as the hydrochlorides, formulated $[MCl_2(N_2HCOR)(dppe)_2]$ (R = alkyl or aryl). One mol of hydrogen chloride can be removed by

$$[M(N_2)_2(dppe)_2] + RCOCl + HCl \longrightarrow [MCl_2(N_2HCOR)(dppe)_2] \underset{HCl}{\overset{NEt_3}{\rightleftharpoons}} [MCl(N_2COR)(dppe)_2] \quad (1)$$

bases, as shown in (1). Acylation and aroylation of the rhenium dinitrogen complexes analogously yield $[ReCl_2(N_2COR)(PR_3)_3]$, but the resulting diazenido-ligand is not protonated by hydrogen chloride. These complexes (with R = aryl) have been obtained previously from aroylhydrazines,[15] but the acyldiazenido-complex is the first of its type. The complexes $[OsCl_2(N_2)(PR_3)_3]$, which are isoelectronic in the valence shell with the rhenium, molybdenum, and tungsten complexes, do not react with acyl or aroyl halides, even in toluene under reflux.

Tungsten and molybdenum. Dinitrogen complexes of these metals react analogously, and the tungsten diazenido-complexes, which have been most thoroughly investigated, are described here in detail. Details of the molybdenum analogues are given in the Experimental section. Very recently Hidai *et al.*[6] described the synthesis of $[MoCl(N_2COPh)(dppe)_2]$ from $[Mo(N_2)(NCPh)(dppe)_2]$ and benzoyl chloride. This complex was previously obtained by us from the bis(dinitrogen) complex.[3]

The reaction of *trans*-$[W(N_2)_2(dppe)_2]$ with acid chlorides RCOCl (R = Me, Ph, or *p*-$MeOC_6H_4$) in thf or benzene solution occurs with quantitative evolution of 1 mol of dinitrogen [sequence (2)]. The products (A) of the reactions of

$$[W(N_2)_2(dppe)_2] + RCOCl \longrightarrow \underset{(A)}{[WCl(N_2COR)(dppe)_2]} + N_2 \xrightarrow{HCl} \underset{(B)}{[WCl_2(N_2HCOR)(dppe)_2]} \quad (2)$$

the dinitrogen complexes with aroyl chlorides are yellow, crystalline, diamagnetic complexes, but acyl chlorides invariably produce the hydrochlorides (B). The hydrogen chloride is presumably provided by adventitious moisture. The t-butyl derivative (A; $R = Bu^t$) also was obtained directly, but only in low yield. In all cases (A) is rapidly converted into (B) by the addition of hydrogen chloride.

Complexes (B) can also be obtained by the reaction of organic acid chlorides with $[WCl_2(N_2H_2)(dppe)_2]$,[2] but the replacement of both imino-hydrogen atoms to form $[WCl_2\{N_2(COR)_2\}(dppe)_2]$ was never achieved. Aromatic sulphonyl chlorides oxidize the bis(dinitrogen) complexes without attacking the dinitrogen, and 1,2-bis(diphenylphosphoryl)ethane was the only compound isolated from the reaction mixture. This is of no particular significance, as sulphonyl halides, RSO_2Cl, oxidize tertiary phosphines to the oxide and are reduced to the disulphides, R_2S_2, even in the absence of transition metals.

We have no definitive evidence regarding the mechanism of formation of complexes (A) and (B). It appears to involve a reactive intermediate which may be $[M(N_2)(dppe)_2]$ or $[M(N_2)(RCOCl)(dppe)_2]$. In such intermediates, with four strongly electron-donating phosphine ligands and no good electron acceptors except dinitrogen [16] on the metal, strong back bonding to the dinitrogen would occur, so rendering the latter susceptible to electrophilic attack by RCO^+ or H^+.

Because of the novelty of these acylation and aroylation reactions it was important to establish the presence of C–N bonds in the products. Hidai *et al.*[6] showed by *X*-ray

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[1] J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Comm.*, 1970, 955.

[2] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074; J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39.

[3] J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 444.

[4] A. A. Diamantis, J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Organometallic Chem.*, 1975, **84**, C11.

[5] V. W. Day, T. A. George, and S. D. A. Iske, *J. Amer. Chem. Soc.*, 1975, **97**, 4127.

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[7] J. M. Manriquez and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1974, **96**, 6229.

[8] A. E. Shilov, A. K. Shilova, E. F. Kvashina, and T. A. Vorontsova, *Chem. Comm.*, 1971, 1590.

[9] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1972, **94**, 1219.

[10] P. W. Jolly and K. Jonas, *Angew. Chem. Internat. Edn.*, 1968, **7**, 731.

[11] J. Chatt, A. A. Diamantis, G. A. Heath, G. J. Leigh, and R. L. Richards, *Proc. First Internat. Symp. Nitrogen Fixation*, eds. W. E. Newton and C. J. Nyman, Interdisciplinary Discussion, Washington 1974, State University Press, Pullman, Washington, 1975, vol. 1, p. 17; T. A. George and S. D. A. Iske, *ibid.*, p. 27; J. Chatt, A. A. Diamantis, G. J. Leigh, and G. A. Heath, *Proc. 17th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, paper 4.8.

[12] J. Chatt, *J. Organometallic Chem.*, 1975, **100**, 17.

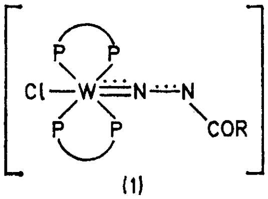
[13] A. A. Diamantis, J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1975, 27.

[14] P. C. Bevan, J. Chatt, R. A. Head, P. B. Hitchcock, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1976, 509.

[15] J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, *J. Chem. Soc. (A)*, 1971, 2631.

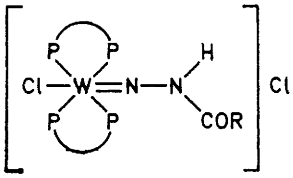
[16] See for example, J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1975, 7392.

structural analysis of $[\mathrm{MoCl_2(N_2HCOC_6H_4Me)(dppe)_2}]$ that the complex contains an essentially linear Mo–N–N group with the carbonyl carbon atom attached to the terminal nitrogen atom. We have equally convincing spectroscopic evidence for the presence of a C–N bond in our tungsten complexes. Thus the mass spectrum of (B; R = Me) gives a weak but definite parent ion and the most abundant ion corresponds to the parent after loss of hydrogen chloride. This, in turn, loses $\mathrm{RCON_2}$ or $\mathrm{RCON_2H}$ to yield $[\mathrm{WCl(dppe)_2}]^+$, confirmed by the appropriate metastable ions. The spectrum also contains intense peaks corresponding to RCN^+. These assignments are supported by ^{15}N substitution. The mass spectra of complexes (A; R = Me or Ph) correspond with the fragmentation of $[\mathrm{WCl(N_2COR)(dppe)_2}]^+$ as noted above.

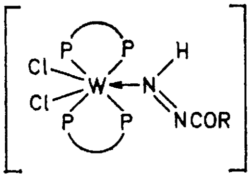


(1)

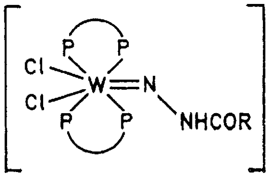
The acylhydrazido(2–)- and aroylhydrazido(2–)-complexes (B) all have a band in their i.r. spectra (Table 1) at *ca.* 1 700 cm^{-1}, not affected by substitution of ^{14}N by ^{15}N and assigned to ν(CO). Each also shows a broad band assigned to ν(NH) at 2 750 cm^{-1}, which shifts to 2 150 cm^{-1} on ^{2}H substitution. The ^{1}H n.m.r. spectrum of (B; R = Me) has well defined resonance at τ = 3.8 which becomes a doublet [$|J(^{15}\mathrm{N{-}H})|$ 95 Hz] on substitution of ^{14}N by ^{15}N. The binding of both H and COR to ligating dinitrogen is thus unequivocally established, and *X*-ray structural analysis of analogues containing hydrazido(2–)- and methylhydrazido(2–)-ligands suggest that they are both bound to a terminal nitrogen atom.



(2)



(3)

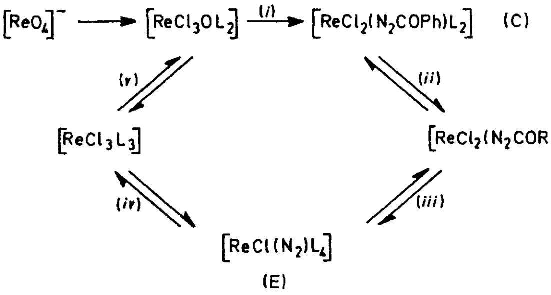


(4)

The complexes (A), after Hidai *et al.*,[6] probably contain a linear W–N–N system and are best described by the structural formula (1). They have ν(CO) at 1 550—1 575 cm^{-1} (Table 1), lower than in (B) by *ca.* 150 cm^{-1}. Complex (A; R = Me) has a band in the i.r. spectrum at 1 334 cm^{-1} (1 298 cm^{-1} in the ^{15}N complex) assigned to ν(N=N). Complexes (B) could have formal 18-electron structures (2), (3), or (4), but the chlorides are non-electrolytes thus eliminating (2). Structures (3) and (4) are tautomers in which both nitrogen atoms will be weakly basic, and in view of the fact that $[\mathrm{WCl_2(N_2H_2)(dppe)_2}]$ has the diazene structure corresponding to (3) it seems likely that our complexes have that structure, perhaps in tautomeric equilibrium with (4) in solution. The higher value of ν(CO) in complexes (B) than in (A) can be attributed to electron withdrawal from the carbonyl by the additional proton. In our preliminary note[3] we suggested that the lower carbonyl frequency in (A) was evidence of chelation, but this view is untenable in view of Hidai's structure of the molybdenum analogue of (A) which shows a free carbonyl[6] despite its low frequency. The low frequency must reflect the mesomeric spread of a very high electron density from the metal.

Rhenium and osmium. The reactions of organic acid halides with a rhenium dinitrogen complex offer the first direct route to rhenium acyldiazenido-complexes, *e.g.* (D; R = Me) (see Scheme). The complexes $[\mathrm{ReCl(N_2)(PMe_2Ph)_4}]$ and $[\mathrm{ReCl(N_2)(py)(PMe_2Ph)_3}]$, preferably the latter because the pyridine is more labile, react with an excess of RCOCl (R = Me or Ph) to yield the red diazenido-complexes, *cis-mer*-$[\mathrm{ReCl_2(N_2COR)(PMe_2Ph)_3}]$. Complex (D; R = Ph) has been shown by *X*-ray diffraction to be identical with a sample of known structure[17] prepared by the original route, through (*i*) and (*ii*) using benzoylhydrazine.[15] Complexes (D; R = Me or Ph) are converted into the dinitrogen complex on reaction (*iii*) with an excess of dimethylphenylphosphine in the presence of methanol, but (D; R = Me) reacts at room temperature whereas (D; R = Ph) reacts only at reflux.

This new synthesis of rhenium benzoyldiazenido-complexes is essentially the reverse of the original preparation of rhenium(I) dinitrogen complexes.[18] We thus have a formally cyclic process with well defined steps (see Scheme) most of which can be reversed, although not all are realised using the same phosphine. Thus step (*i*) is realised only when L is triphenylphosphine but (*ii*) and (*iii*) require other ligands such as L = $\mathrm{PMe_2Ph}$ which allows all steps except (*i*).



SCHEME For reactions (*i*)—(*iv*) and the reverse of (*iv*), see ref. 18; (*v*), J. Chatt, H. P. Gunz, and G. J. Leigh, unpublished work; for the reverse of (*v*), see J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (*A*), 1968, **2637**; for the reverse of (*iii*), see this paper; reverse of (*ii*), J. Chatt, J. R. Dilworth, and G. J. Leigh, unpublished work.

The conversion (*iii*) of (E) into (D), like the corresponding reactions of molybdenum and tungsten bis(dinitrogen) complexes, involves the loss of a neutral ligand from the complex, in this case tertiary phosphine rather than dinitrogen. The replaced tertiary phosphine forms a quatern-

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[17] R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Amer. Chem. Soc.*, 1974, **96**, 260.

[18] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, 1973, 612.

ary salt, $[LCOR]Cl$, which was isolated in several instances. The loss of phosphine must be important because we could neither acylate nor aroylate $[ReCl(N_2)(dppe)_2]$ in which one phosphorus of a chelating diphosphine would need to dissociate from the metal or the product assume a positive charge as $[ReCl(N_2COR)(dppe)_2]^+$. However, if one assumes that ligand loss is rate determining the key intermediates would be $[ReCl(N_2)L_3]$ in the rhenium case and $[M(N_2)(dppe)_2]$ in the molybdenum or tungsten case, involving the loss of tertiary phosphine and of dinitrogen respectively. The loss of the electron-donating phosphine would reduce the electron density on the metal atom whereas the loss of the electron-withdrawing dinitrogen would increase it. Thus it seems unlikely that dissociative ligand loss can form the basis of a common electronic mechanism for the initiation of attack at the ligating dinitrogen. More probably the key intermediates are $[ReCl(ClCOR)(N_2)L_3]$ and $[M(N_2)(ClCOR)(dppe)_2]$ in which RCOCl is strongly polarized, RCO^+Cl^-, by co-ordination through the chlorine.

We were not able to acylate or aroylate the osmium dinitrogen complex $[OsCl_2(N_2)L_3]$. This may be, in part, because the phosphine does not easily dissociate from the metal. In the rhenium system there is considerable crowding of the four phosphine ligands which cannot take up an exactly square-planar configuration,[19] and the loss of a phosphine is thus assisted by steric overcrowding. There is no corresponding strain in the osmium complex. To introduce a better leaving ligand, pyridine, we attempted to synthesize $[OsCl_2(N_2)(py)L_2]$ for use as a starting material. However, heating $[OsCl_2(N_2)L_3]$ and pyridine in refluxing

TABLE 1

Infrared spectral assignments (cm^{-1}) for new molybdenum, tungsten, and rhenium complexes[a]

	Phase	ν(NH) (br)	ν(CO) (s)	ν(NN) (m)	Other(s)	ν(MCl) (M = Mo, Re, or W)
(*a*) *Acyl and aryl derivatives:* (*i*) hydrazido(2−)-complexes						
$[WCl_2(N_2HCOMe)(dppe)_2]$	Nujol	2 780, 2 700	1 690	1 368	1 225	280
	CH_2Cl_2	2 760, 2 680	1 700	1 370	1 223	
$[WCl_2(N_2DCOMe)(dppe)_2]$	Nujol	2 220, 2 130	1 690	1 368	1 225	280
$[WCl_2(^{15}N_2HCOMe)(dppe)_2]$	Nujol	2 760, 2 680	1 690	1 325	1 225	280
$[MoCl_2(N_2HCOMe)(dppe)_2]$	Nujol	2 700, 2 640	1 710	N.a.	1 205	270
$[WCl_2(N_2HCOEt)(dppe)_2]$	Nujol	2 650	1 685	1 365	1 170	290
$[MoCl_2(N_2HCOEt)(dppe)_2]$	Nujol	2 640	1 680	N.a.	1 160	290
$[WCl_2(N_2HCOBu^t)(dppe)_2]$	Nujol	2 700, 2 500	1 665	N.a.	1 142	290
$[WCl_2(N_2HCOPh)(dppe)_2]$	Nujol	2 650	1 675	N.a.	1 265	280
$[WCl_2(N_2HCOC_6H_4OMe)(dppe)_2]$	Nujol	2 700	1 660	N.a.	1 245	285
(*ii*) Diazenido-complexes						
$[WCl(N_2COMe)(dppe)_2]$	Nujol		1 570	1 338	1 268	270
$[WCl(^{15}N_2COMe)(dppe)_2]$	Nujol		1 570	1 298	1 262	N.a.
$[MoCl(N_2COMe)(dppe)_2]$	Nujol		1 575	N.a.	1 190	N.a.
$[WCl(N_2COEt)(dppe)_2]$	Nujol		1 570	1 330	1 272	275
$[MoCl(N_2COEt)(dppe)_2]$	Nujol		1 575	1 330	1 180	N.a.
$[WCl(N_2COPh)(dppe)_2]$	Nujol		1 550	N.a.	1 270	N.a.
$[WCl(N_2COC_6H_4OMe)(dppe)_2]$	Nujol		1 550	N.a.	1 280, 1 245	N.a.
$[ReCl_2(N_2COMe)(PMe_2Ph)_3]$	Nujol		1 625	N.a.	1 210	290, 262
$[ReCl_2(N_2COPh)(PMe_2Ph)_3]$	Nujol		1 615	1 505	1 235	286, 258

(*b*) *Alkyl derivatives:* (*iii*) hydrazido(2−)-complexes	Phase[b]	ν(NH) (br)	ν(NN) region
$[WBr(N_2HMe)(dppe)_2]Br$	CH_2Cl_2	2 980, 2 820	1 485m, 1 435s, 1 360m, 1 315w
$[WBr(N_2DMe)(dppe)_2]Br$	hcb	2 300—2 180	1 485m, 1 435s, 1 360m, 1 315w
$[MoBr(N_2HMe)(dppe)_2]Br$	KBr		1 435m, 1 385s, 1 305m
$[WBr(N_2HEt)(dppe)_2]Br$	KBr	3 000, 2 850	1 488m, 1 438s, 1 420w, 1 350w, 1 330m, 1 315 (sh)
$[WBr(N_2DEt)(dppe)_2]Br$	hcb	2 300—2 200 (multiplet)	1 488m, 1 435s, 1 415w, 1 386w, 1 336m, 1 315w
$[MoBr(N_2HEt)(dppe)_2]Br$	hcb	2 860	1 485m, 1 432s, 1 322m
$[WBr(N_2HPr^n)(dppe)_2]Br$	Nujol		1 435s, 1 410w, 1 380m, 1 350w, 1 310w
$[WBr(N_2HPr^i)(dppe)_2]Br$	Nujol		1 435s, 1 410w, 1 380m, 1 310w
$[WBr(N_2HBu^t)(dppe)_2]Br$	KBr	3 080, 2 925	1 495m, 1 435s, 1 415 (sh), 1 370m, 1 340 (sh), 1 315w
$[WBr(N_2DBu^t)(dppe)_2]Br$	hcb	2 320, 2 290, 2 200	1 495m, 1 435s, 1 370m, 1 315w
$[WCl(N_2HBu^t)(dppe)_2]Cl$	KBr	2 860	1 480m, 1 430s, 1 410w, 1 330 (sh), 1 310w
$[WBr(N_2Me_2)(dppe)_2]Br$	KBr		1 485m, 1 435s, 1 380m, 1 315w
(*iv*) Diazenido-complexes			
$[WBr(N_2Me)(dppe)_2]$	KBr		1 525s, 1 485m, 1 435s, 1 420 (sh), 1 360s, 1 315w
$[MoBr(N_2Me)(dppe)_2]$	KBr		1 540s, 1 490m, 1 485 (sh), 1 440s, 1 420m, 1 360s, 1 320w
$[WBr(N_2Et)(dppe)_2]$	KBr		1 530—1 500s, 1 488m, 1 460w, 1 435s, 1 415 (sh), 1 372w, 1 305s
$[MoBr(N_2Et)(dppe)_2]$	KBr		1 560—1 540s, 1 485m, 1 432s, 1 305s
$[WBr(N_2Pr^n)(dppe)_2]$	Nujol		1 530—1 510s, 1 435s, 1 380s, 1 332s, 1 315w
$[WBr(N_2Pr^i)(dppe)_2]$	Nujol		1 520s, 1 380s, 1 320w
$[WBr(N_2Bu^t)(dppe)_2]$	KBr		1 485s, 1 435s, 1 385m, 1 360m, 1 310w

[a] N.a. = Not assignable; br = broad, sh = shoulder, s = strong, m = medium, and w = weak. [b] hcb = Hexachlorobutadiene.

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[19] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 578.

toluene resulted only in the slow displacement of dinitrogen and not of a phosphine, apparently to give $[OsCl_2(py)L_3]$.

Alkyldiazenido(2−)- *and Alkylhydrazido*(2−)-*complexes*.—In the course of our investigation we noted that the reaction of pivaloyl chloride with $[W(N_2)_2(dppe)_2]$ gave, in addition to the expected product, $[WCl(N_2COBu^t)(dppe)_2]$, a pink material which showed no carbonyl absorption in its i.r. spectrum, although the ^1H n.m.r. spectrum clearly showed the presence of a t-butyl group. The pink material analyzed for $[WCl_2(N_2HBu^t)(dppe)_2]$ suggesting that the carbon monoxide had been eliminated. We therefore attempted to obtain similar products from the bis(dinitrogen) complexes and alkyl halides.

Since we published our initial results[4] using alkyl bromides it has become clear that in the molybdenum series alkyl chlorides tend to oxidize the dinitrogen complexes without forming easily characterizable products,[6] and that alkyl iodides react similarly to the bromides but more easily.[5] The reactions of $[M(N_2)_2(dppe)_2]$ (M = Mo or W) with alkyl bromides are catalyzed by visible light, but the molybdenum complex, unlike its tungsten analogue, reacts slowly in the dark. Irradiation of $[W(N_2)_2(dppe)_2]$ in thf solution under dinitrogen in the absence of alkyl halides causes no change.

TABLE 2

Hydrogen-1 n.m.r. spectra(τ) [a]

Complex	Solvent	Phenyl	PCH_2-CH_2P	Alkyl	N*H*
$[WCl_2(N_2HCOMe)(dppe)_2]$	CD_2Cl_2	2.7—2.9 (m)	7.0 (br, s)	8.72 (s)	−3.0 (s) [b]
$[MoCl_2(N_2HCOMe)(dppe)_2]$	CD_2Cl_2	2.7—2.9 (m)	7.0 (br, m)	8.75 (s)	−2.0 (s)
$[WCl_2(N_2HCOEt)(dppe)_2]$	CD_2Cl_2	2.7—2.85 (m)	7.0 (br, s)	8.28 (q), 9.57 (t)	−2.3 (s)
$[MoCl_2(N_2HCOEt)(dppe)_2]$	CD_2Cl_2	2.8—2.9 (m)	7.0 (br, m)	8.42 (q), 9.65 (t)	−2.0 (s)
$[WCl_2(N_2HCOBu^t)(dppe)_2]$	CD_2Cl_2	2.6—2.8 (m)	6.5 (s), 6.9 (s)	9.15 (s)	−2.3 (s)
$[WCl_2(N_2HCOPh)(dppe)_2]$	CD_2Cl_2	2.7—2.9 (m)	6.6 (s), 7.0 (s)		−2.5 (s)
$[WCl_2(N_2HCOC_6H_4OMe\text{-}p)(dppe)_2]$	CD_2Cl_2	2.7—2.9 (m)	6.7 (s), 7.1 (s)	6.30 (s)	−2.5 (s)
$[WCl_2(N_2COMe)(dppe)_2]$	$CDCl_3$	2.5—3.0 (m)	7.2 (br, m)	8.75 (s)	
$[WCl_2(N_2COEt)(dppe)_2]$	$CDCl_3$	2.5—3.0 (m)	7.1 (br, m)	8.35 (q), 9.60 (t)	
$[WCl_2(N_2COC_6H_4OMe\text{-}p)(dppe)_2]$	$CDCl_3$	2.5—3.2 (m)	7.1 (br, m)	6.20 (s)	
$[WBr(N_2HMe)(dppe)_2]Br$	$CDCl_3$	2.7—2.9 (m)	6.8—7.4 (br, s)	8.49 (d)	4.1 (s)
$[WBr(N_2DMe)(dppe)_2]Br$	$CDCl_3$	2.7—2.9 (m)	6.8—7.4 (br, s)	8.49 (s)	
$[MoBr(N_2HMe)(dppe)_2]Br$	$CDCl_3$	2.6—3.0 (m)	6.8—7.5 (br, m)	8.66 (d)	1.5 (s)
$[WBr(N_2HEt)(dppe)_2]Br$ [c]	CD_2Cl_2	2.7—2.9 (m)	6.8—7.6 (br, m)	9.96 (t)	*d*
$[WBr(N_2DEt)(dppe)_2]Br$ [c]	CD_2Cl_2	2.7—2.9 (m)	6.8—7.6 (br, m)	9.96 (t)	
$[MoBr(N_2HEt)(dppe)_2Br$ [c]	CD_2Cl_2	2.6—3.0 (m)	6.8—7.5 (br, m)	9.87 (t)	4.1 (s)
$[WBr(N_2HPr^n)(dppe)_2]Br$	CD_2Cl_2	2.5—2.9 (m)	6.8—7.4 (br, s)	8.28 (t), 9.30—9.80 (tq)	*ca.* 6.0
$[WBr(N_2HPr^i)(dppe)_2]Br$	$CDCl_3$	2.5—2.9 (m)	6.7—7.9 (br, s)		
$[WBr(N_2HBu^t)(dppe)_2]Br$	CD_2Cl_2	2.9—3.3 (m)	7.2—7.8 (br, m)	9.90 (s)	7.6 (s)
$[WBr(N_2DBu^t)(dppe)_2]Br$	CD_2Cl_2	2.9—3.3 (m)	7.2—7.8 (br, m)	9.90 (s)	
$[WCl(N_2HBu^t)(dppe)_2]Cl$	CD_2Cl_2	2.5—3.0 (m)	7.2 (br, s)	9.93 (s)	6.8 (s)
$[WBr(N_2Me)(dppe)_2]$	$CDCl_3$	2.7—3.0 (m)	6.8—7.6 (br, m)	8.90 (s)	
$[MoBr(N_2Me)(dppe)_2]$	CD_2Cl_2	2.4—3.1 (m)	7.0—7.7 (br, m)	8.52 (s)	
$[WBr(N_2Et)(dppe)_2]$	CD_2Cl_2	2.7—2.9 (m)	6.9—7.7 (br, m)	7.76 (q), 9.80 (t)	
$[MoBr(N_2Et)(dppe)_2]$	CD_2Cl_2	2.6—3.1 (m)	6.9—7.7 (br, m)	8.10 (q), 9.78 (t)	
$[WBr(N_2Pr^n)(dppe)_2]$	CD_2Cl_2	2.4—3.0 (m)	6.9—7.7 (br, m)	7.70 (t), 9.40—9.60 (tq)	
$[WBr(N_2Pr^i)(dppe)_2]$	CD_2Cl_2	2.4—3.0 (m)	6.8—7.6 (br, m)	7.34 (q), 9.60 (d)	
$[WBr(N_2Bu^t)(dppe)_2]$	$CDCl_3$ CD_2Cl_2		6.9—7.6 (br, d)	9.77 (s)	
$[WBr(N_2Me_2)(dppe)_2]Br$	$CDCl_3$	2.4—3.0 (m)	6.8—7.4 (br, s)	8.38 (s)	
$[ReCl_2(N_2COMe)(PMe_2Ph)_3]$	$CDCl_3$	2.6—2.9 (m)	8.18 (t), 8.34 (t), 8.66 (d) [e]	8.22 (s)	
$[ReCl_2(N_2COPh)(PMe_2Ph)_3]$	$CDCl_3$	2.6—2.9 (m)	7.96 (t), 8.13 (t), 8.61 (d) [e]		

[a] s = Singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [b] A doublet in the ^{15}N analogue, $|J(N-H)|$ 95 Hz. [c] Resonances of ethyl group were partly obscured by phosphine methylenes. [d] N*H* resonance was obscured by the various methylene resonances. [e] Methyl resonances from PMe_2Ph.

The complex $[W(N_2)_2(dppe)_2]$, when irradiated in benzene solution in the presence of an alkyl bromide (RBr) during 4 h, produces $[WBr(N_2HR)(dppe)_2]Br$ as pink crystalline precipitates, the amounts of precipitate being increased by the addition of hydrogen bromide after the irradiation [reaction (3)]. The i.r. spectra (Table 1) of the products are

$$[W(N_2)_2(dppe)_2] + RBr \xrightarrow{h\nu} N_2 + [WBr(N_2R)(dppe)_2] \xrightarrow{HBr} [WBr(N_2HR)(dppe)_2]Br \quad (3)$$

characteristic of dppe complexes, with an additional band at *ca.* 1 435 cm^{-1} apparently associated with the N_2HR ligand, as well as NH bands, whose assignments were confirmed by deuteriation (see Table 1).

The ^1H n.m.r. spectra (Table 2) in CD_2Cl_2 solution show resonances at τ 2.5—3.3 (complex multiplet) due to the aromatic protons, a signal at τ 8.50—9.90 ascribed to the alkyl protons, and broad doublet at τ 6.8—7.8 due to the phosphine methylene protons. A resonance arising from an N–*H* proton is also observed (see Table 2). The structure of the cationic complexes is thus probably analogous to that of *trans*-$[WCl(NNH_2)(dppe)_2]^+$ and of *trans*-$[WBr(NNHMe)(dppe)_2]^+$ both of which have been determined by *X*-ray analysis.[20,21] They contain a linear X–W–N–N (X = Cl or Br) atomic arrangement.

The alkylhydrazido(2−)-complex cations, like the corres-

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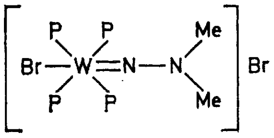
[20] G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 259.

[21] F. C. March, R. Mason, and K. M. Thomas, *J. Organometallic Chem.*, 1975, **96**, C43.

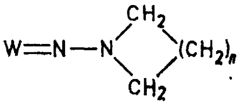
ponding acyl and aroyl cations, are deprotonated by potassium carbonate dissolved in water–ethanol to give the uncharged alkyldiazenido-complexes $[WBr(N_2R)(dppe)_2]$. These orange crystalline substances react with aqueous hydrogen bromide in dichloromethane to regenerate the alkylhydrazido(2−)-complex cations.

The lower alkyl halides (R = Me, Et, Pr^n, Pr^i, or Bu^t) react according to reaction (3) in benzene or in thf solutions. However methyl and ethyl bromide in thf solution give, in addition to the normal products, an ω-diazobutanol complex, $[WBr(N_2CHCH_2CH_2CH_2OH)(dppe)_2]Br$, in which the butanol chain has been derived from thf.[13,14] The principal product of reaction of MeBr with $[W(N_2)_2(dppe)_2]$ followed by treatment with hydrogen bromide in thf solution is the thf-derived complex; $[WBr(N_2HMe)(dppe)_2]Br$ is the minor product which is readily deprotonated by mild alkali to give $[WBr(N_2Me)(dppe)_2]$.

This methyldiazenido-complex is also obtained directly from *trans*-$[W(N_2)_2(dppe)_2]$ and 1 mol of MeBr irradiated with daylight or tungsten-filament light in benzene solution, but it is more difficult to isolate than the hydrobromide salt. Two or more moles of MeBr yield $[WBr(N_2Me_2)(dppe)_2]Br$ as an insoluble brown material. This shows no evidence of N–H in either the i.r. or the ^1H n.m.r. spectrum, and the ^1H n.m.r. spectrum shows the presence of two equivalent methyl groups. This equivalence was confirmed by the ^{13}C n.m.r. spectrum. The dimethylhydrazido-ligand was not protonated by acid and we formulate it as below (6). The molybdenum analogue of this complex was not obtained by an analogous reaction from $[Mo(N_2)_2(dppe)_2]$ nor was any other dialkyl derivative obtained in the tungsten or molybdenum series. However, both tungsten[22] and molybdenum[23] bis(dinitrogen) complexes formed heterocyclic ligands of the type (7) with α,ω-dibromoalkanes.



(6)



(7)

Most of the reactions of tungsten complexes discussed above have analogues in the molybdenum series, as will be clear from the Tables and the details which are given in the Experimental section. We have not yet succeeded in obtaining analogous alkyldiazenido-complexes from $[M(N_2)_2L_4]$ (M = Mo or W, L = monotertiary phosphine). Furthermore, we have not been able to alkylate dinitrogen in $[ReCl(N_2)(py)(PMe_2Ph)_3]$ or in $[OsCl_2(N_2)(PEt_2Ph)_3]$ despite trying a range of solvents and radical initiators and also irradiation.

DISCUSSION

It is likely that all the reactions of ligating dinitrogen in mononuclear complexes involve electrophilic attack at the terminal nitrogen atom, although this is probably not the first step because irradiation and the presence of a good leaving ligand (dinitrogen or pyridine) appear to be essential to produce organonitrogen products. The present work indicates that the reactivity of dinitrogen in analogous mononuclear d^6 complexes formed by transition metals from Groups 6, 7, and 8A decreases rapidly in that order.

Although protonation of dinitrogen in molybdenum and tungsten dinitrogen complexes has been achieved,[2] all attempts to protonate dinitrogen in rhenium complexes have led to the protonation of the metal and formation of hydride complexes. Thus $[ReH(N_2)(dppe)_2]$ in fluoroboric acid yields $[ReH_2(N_2)(dppe)_2]^+$.[24] The complexes $[ReX(N_2)(py)(PMe_2Ph)_3]$ (X = Cl or Br) with 2 mol of HX yield $[ReX_3H_2(PMe_2Ph)_3]$ essentially quantitatively; the use of only 1 mol of HX results in a reduced yield of the dihydrido-complex. The protonation[25] of $[Re(N_2)(PMe_2Ph)_3(S_2CNEt_2)]$ yields $[ReH_2(PMe_2Ph)_3(S_2CNEt_2)]^+$. Even the complex $[ReCl(N_2)(PMe_2Ph)_4]$, which is a close analogue of the bis(dinitrogen) complexes of molybdenum and tungsten, protonates only at the metal[18] to form the unstable hydride $[ReClH(N_2)(PMe_2Ph)_4]^+$.

However, acetylation and benzoylation of the dinitrogen occur in $[ReCl(N_2)(py)(PMe_2Ph)_3]$. The products $[ReCl_2(N_2COR)(PMe_2Ph)_3]$ (R = Me or Ph) readily lose their acetyl or benzoyl groups to regenerate the dinitrogen complex $[ReCl(N_2)(PMe_2Ph)_4]$ by reaction with the phosphine in methanol at 20 °C (R = Me) or at the boiling point (R = Ph). The N_2COR ligand in the rhenium complexes is not sufficiently basic to be protonated by HX to form the ligand N_2HCOR, in sharp contrast to the avidity with which it picks up protons in the corresponding complexes of molybdenum and tungsten. Alkylation of dinitrogen in its rhenium complexes was not obtained.

The dinitrogen in $[OsCl_2(N_2)(PMe_2Ph)_3]$ is not protonated, acetylated, benzoylated, or alkylated, but the complex does react with hydrogen chloride in the presence of dioxygen to form $[OsCl_3(PMe_2Ph)_3]$ possibly *via* an unstable hydridic intermediate.[26]

Mechanism.—The apparent fall in nucleophilicity of the terminal nitrogen atom along the series $[W(N_2)_2(dppe)_2] > [ReCl(N_2)(PMe_2Ph)_4] > [OsCl_2(N_2)(PMe_2Ph)_3]$ and $[WCl(N_2COR)(dppe)_2] > [ReCl_2(N_2)(N_2COR)(PR_3)_3]$ is probably caused by the increasing nuclear charge and associated increasing electron affinity of the metal, with consequent decrease in electron density on the nitrogens of the ligands. How the reaction with acid chlorides or alkyl halides occurs is uncertain. The reactions are sensitive to light, but dinitrogen is not evolved in the absence of the organic halide which must therefore play a definite role in assisting the evolution. Free radicals derived from the alkyl halides are undoubtedly involved in the alkyl-halide reactions because methane is a main product of the formation of the diazobutanol complexes from MeBr in thf. Also strong

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[22] R. Ben-Shoshan, J. Chatt, W. Hussain, and G. J. Leigh, *J. Organometallic Chem.*, 1976, **112**, C9.

[23] J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, work in progress.

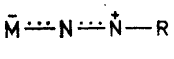
[24] M. E. Tully and A. P. Ginsberg, *J. Amer. Chem. Soc.*, 1973, **95**, 2042.

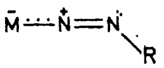
[25] J. Chatt, R. H. Crabtree, J. R. Dilworth, and R. L. Richards, *J.C.S. Dalton*, 1974, 2358.

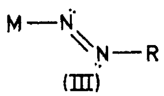
[26] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 895.

signals from methyl radicals are seen in the e.s.r. spectra of reaction solutions during the methylation of the bis(dinitrogen)-molybdenum and -tungsten complexes. This suggests that the reaction may be initiated by attack of bromine atoms, from homolytic dissociation of the alkyl bromide at the metal centre, so displacing the first dinitrogen ligand whilst the second picks up the free alkyl radical, or in thf the derived thf radical.[23] The mechanism is still under investigation.

Structure and Protonation.—There are three limiting structures for the alkyl-, acyl-, and aryl-diazenido-complexes of molybdenum and tungsten which we have prepared, (I)—(III). Of these (I) and (II) obey the inert-gas rule. The N–N stretching frequencies when amended by the rules developed for nitrosyl chemistry[27] appear to exclude form (I), and suggest that all the complexes have the diazenido-ligand at least singly bent (II). This is consistent with our finding that protonation occurs on the terminal nitrogen atom. Nevertheless the correlation of ν(NN), structure, and reactivity is not sufficiently firm to exclude entirely the other two possibilities. The reactivity of nitrogen in diazenido-complexes is affected by very small differences. Thus in $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ neither nitrogen atom can be protonated, whereas in $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2]$ the terminal one can.[17] It is unlikely that the diazenido-ligands in these two complexes have different structures but they must have different electron densities. The complex $[WBr(N_2H)(dppe)_2]$ has ν(NN) at 1 895 cm^{-1}, suggesting that it has the form (I), yet it protonates reversibly at either of the nitrogen atoms depending on the co-ordination number of the metal.[28] The form (III) should be capable of protonation at either of its nitrogen atoms. In practice, form (III) has been established only in closed-shell complexes where formulation as (I) or (II) would involve an effective atomic number greater than 18; in these circumstances protonation has been found only at the nitrogen atom bonded to the metal. Obviously the site of protonation of the diazenido-ligand is determined by the interdependent electronic states of the metal and of the diazenido-ligand.


(I)


(II)


(III)

EXPERIMENTAL

Experiments were carried out under dinitrogen or argon with purified dioxygen-free solvents. Carbon, hydrogen, and nitrogen analyses were by Mr. A. G. Olney, The Chemical Laboratory, The University of Sussex. Phosphorus and halogen analyses were by Dr. A. Bernhardt, West Germany. The following spectrometers were used: (i.r.) Perkin-Elmer 457, Grubb–Parsons DM4, and Unicam SP 1200; (u.v.) Unicam SP 1800; (n.m.r.) Varian T-60 and HA-100, Jeol PS-100. Melting points were measured in sealed tubes *in vacuo* or under dinitrogen on an Electrothermal apparatus. Molecular weights were determined in solution in 1,2-dichloroethane using a Hitachi–Perkin-Elmer 115 osmometer. Conductivities were measured with a Portland Electronics bridge and solutions were generally in nitromethane. Mass spectra were obtained using an A.E.I. MS9 mass spectrometer. Magnetic moments of solids were measured by the Faraday technique. Analytical and other data are in Table 3.

[*Acetylhydrazido*(2—)]*bis*[1,2-*bis*(*diphenylphosphino*)-*ethane*]*dichlorotungsten*(IV).—To a solution of acetyl chloride (0.5 cm^3) in thf (60 cm^3) was added *trans*-bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)tungsten(0)[29] (F) (1.0 g) and the mixture was allowed to stand overnight. A substantial pink crystalline precipitate formed. Concentrated hydrochloric acid (0.1 cm^3) was added and after stirring for 15 min the crystals were filtered off, washed with thf (5 × 5 cm^3), and dried at 10^{-3} mmHg.* The product was recrystallized from methylene chloride-isopropyl alcohol as deep pink *crystals* (0.75 g). *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*dichloro*[*propionylhydrazido*(2—)]*tungsten*(IV) was prepared similarly and recrystallized from methanol.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*dichloro*[*pivaloylhydrazido*(2—)]*tungsten*(IV) was prepared from (F) (1.0 g), pivaloyl chloride (0.5 cm^3), and thf (50 cm^3) during 12 h. The pink crystals (0.1 g) were filtered off, washed with thf (5 × 1 cm^3), and dried at 10^{-3} mmHg. The filtrate from this reaction was evaporated to 20 cm^3 on a vacuum line, and concentrated HCl (0.2 cm^3) was added. On stirring, a pink precipitate of *bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*[*t-butylhydrazido*(2—)]*tungsten*(II) *chloride* (0.2 g) formed, which was filtered off, washed with thf (5 × 1 cm^3), and dried at 10^{-3} mmHg.

[*Benzoylhydrazido*(2—)]*bis*[1,2-*bis*(*diphenylphosphino*)-*ethane*]*dichlorotungsten*(IV).—Benzoyl chloride (0.5 cm^3) and complex (F) (1.0 g) were heated in benzene (70 cm^3) under reflux for 1.0 h, and the solution was allowed to cool. Concentrated HCl (0.2 cm^3) was added to the mixture and the pink precipitate was collected, washed with thf (5 × 5 cm^3), and diethyl ether (2 × 5 cm^3) and dried at 10^{-3} mmHg. The crude product was recrystallized from methylene chloride-ethanol as deep pink crystals (0.6 g). The p-*methoxyphenyl derivative* was prepared similarly.

Acetyldiazenidobis[1,2-*bis*(*diphenylphosphino*)*ethane*]-*chlorotungsten*(II).—The acetylhydrazido(2—)-complex (0.4 g) was dissolved in dichloromethane (10 cm^3), and on addition of triethylamine (0.3 cm^3) to the stirred red solution the colour changed instantly to yellow. The solution was evaporated to dryness on a vacuum line and the powdery residue was extracted with water (5 × 2 cm^3) and washed with ethanol (2 × 2 cm^3) and finally diethyl ether (5 × 2 cm^3). The *product* was recrystallized from methanol as yellow needles (0.3 g). Alternatively, a suspension of the acetylhydrazido(2—)-complex in thf was treated with diazomethane (1.2 mol) in diethyl ether. This produced the crystalline yellow product directly.

The yellow analogues, the *propionyldiazenido*-, *benzoyldiazenido*-, and the p-*methoxybenzoyldiazenido-derivatives* were prepared similarly from the corresponding hydrazido(2—)-complexes. Alternatively, the benzoyl derivative was prepared by reaction of (F) (1.0 g) with benzoyl chlor-

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

[27] A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 6859.

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

[29] B. Bell, J. Chatt, and G. J. Leigh, *J.C.S. Dalton*, 1972, 2492.

TABLE 3

Characterization of the new complexes of molybdenum, tungsten, and rhenium

Complex	Colour	M.p. (θ_c/°C)	Yield (%)	Analyses (%) [a]				M [a,b]	Λ S cm^2 mol^{-1}
				C	H	N	Halogen		
$[WCl_2(N_2HCOMe)(dppe)_2]$ [c]	Pink	235	70	57.7 (57.8)	4.90 (4.60)	2.45 (2.50)	6.7 (6.3)	1 130 (1 123)	2 [d]
$[MoCl_2(N_2HCOMe)(dppe)_2]$	Violet	210	37	61.4 (61.6)	5.30 (5.10)	2.40 (2.70)			
$[WCl_2(N_2HCOEt)(dppe)_2]$	Pink	230	59	57.9 (58.1)	4.95 (4.70)	2.50 (2.45)	6.6 (6.2)		
$[MoCl_2(N_2HCOEt)(dppe)_2]$	Violet	213	45	61.3 (62.9)	5.30 (5.20)	2.60 (2.65)	6.0 (6.7)		
$[WCl_2(N_2HCOBu^t)(dppe)_2]$	Pink	221	9	58.5 (58.8)	5.40 (4.95)	3.40 (2.40)			
$[WCl_2(N_2HCOPh)(dppe)_2]$	Pink	255	53	59.5 (59.8)	5.20 (4.50)	2.35 (2.35)		1 205 (1 185)	3 [d]
$[WCl_2(N_2HCOC_6H_4OMe)(dppe)_2]$ [e]	Pink	275	56	59.4 (59.3)	5.20 (4.55)	2.30 (2.30)	6.0 (5.8)		
$[WCl(N_2COMe)(dppe)_2]$ [f]	Yellow	272	78	59.1 (59.7)	4.90 (4.75)	2.50 (2.60)	3.3 (3.3)	1 070 (1 087)	10 [g]
$[WCl(N_2COEt)(dppe)_2]$	Yellow	262	52	60.0 (60.0)	5.10 (4.85)	2.50 (2.55)			
$[WCl(N_2COPh)(dppe)_2]$	Yellow	265	41	61.8 (61.7)	5.05 (4.65)	2.45 (2.45)		1 160 (1 149)	8 [g]
$[WCl(N_2COC_6H_4OMe)(dppe)_2]$ [h]	Yellow	270	46	61.4 (61.1)	4.85 (4.70)	2.45 (2.40)	3.0 (3.0)		
$[ReCl_2(N_2COMe)(PMe_2Ph)_3]$	Deep red	128—134	16	42.1 (42.1)	4.90 (5.00)	3.75 (3.75)	10.1 (9.6)	720 (743)	
$[ReCl_2(N_2COPh)(PMe_2Ph)_3]$	Orange	204—206	70	45.8 (46.3)	4.90 (4.75)	3.35 (3.50)		780 (804)	
$[WBr(N_2HMe)(dppe)_2]Br{\cdot}thf$	Brown	253 (decomp.)	58	54.5 (53.7)	4.90 (4.75)	2.35 (2.35)	12.5 (12.7)		99 [g]
$[MoBr(N_2HMe)(dppe)_2]Br{\cdot}1.5CH_2Cl_2$	Brown	130 (decomp.)	30	52.7 (53.5)	4.35 (4.50)	2.25 (2.30)			
$[WBr(N_2HEt)(dppe)_2]Br{\cdot}2thf$	Pink	242—245	52	55.2 (55.5)	5.20 (5.25)	2.25 (2.10)	11.5 (11.9)		90 [g]
$[MoBr(N_2HEt)(dppe)_2]Br{\cdot}2CH_2Cl_2$	Brown	195—199	55	53.1 (52.7)	4.75 (4.55)	2.25 (2.20)			
$[WBr(N_2HPr^n)(dppe)_2]Br{\cdot}1.5CH_2Cl_2$	Orange-yellow	180—184	56	50.6 (50.7)	4.55 (4.45)	2.05 (2.10)	12.9 (11.9)		
$[WBr(N_2HPr^i)(dppe)_2]Br{\cdot}1.5CH_2Cl_2$	Orange-yellow	183—187	64	50.5 (50.7)	4.45 (4.45)	2.00 (2.10)	14.5 (11.9)		
$[WBr(N_2HBu^t)(dppe)_2]Br$	Pink	192—194	37	54.7 (54.8)	4.80 (4.75)	2.25 (2.30)	13.0 (13.0)	834 (1 225)	
$[WCl(N_2HBu^t)(dppe)_2]Cl$	Pink	204	*ca.* 10	59.2 (59.1)	5.50 (5.15)	2.50 (2.45)	6.1 (6.2)		
$[WBr(N_2Me)(dppe)_2]$	Yellow	257—260	65	57.8 (57.7)	4.75 (4.65)	2.30 (2.55)	7.5 (7.2)		16 [i]
$[MoBr(N_2Me)(dppe)_2]$	Yellow	208—211	75	61.8 (62.7)	5.00 (5.05)	2.80 (2.75)			
$[WBr(N_2Et)(dppe)_2]$	Orange	236 (decomp.)	75	58.0 (58.0)	4.85 (4.80)	2.55 (2.50)	7.2 (7.2)		9 [i]
$[MoBr(N_2Et)(dppe)_2]$	Orange	205	75	62.7 (63.0)	5.20 (5.20)	2.80 (2.70)			
$[WBr(N_2Pr^n)(dppe)_2]$	Orange	185—188	70	58.2 (58.3)	5.05 (5.45)	2.40 (2.45)	7.4 (7.1)	1 119 (1 131)	
$[WBr(N_2Pr^i)(dppe)_2]$	Orange	164—167	70	58.2 (58.3)	4.95 (5.45)	2.45 (2.45)	7.4 (7.1)	1 074 1 131)	
$[WBr(N_2Bu^t)(dppe)_2]$	Orange	184—186	75	58.5 (58.7)	5.25 (5.00)	2.45 (2.45)	7.0 (7.0)	944 (1 144)	4 [g]
$[WBr(N_2Me_2)(dppe)_2]Br$	Brown	212—215 (decomp.)	52	52.8 (54.1)	4.60 (4.55)	2.30 (2.35)			82 [g]
$[ReCl(N_2)(py)(PMe_2Ph)_3]$	Orange	183 (decomp.)	60	46.7 (46.9)	5.20 (5.15)	5.65 (5.65)		710 (742)	*j*
$[ReCl(N_2)(py)(PMePh_2)_3]$	Orange	176—181 (decomp.)	66	56.3 (56.9)	4.90 (4.80)	4.75 (4.50)	3.8 (3.2)	*k*	*j*
$[ReCl(N_2)(4Me\text{-}py)(PMe_2Ph)_3]$ [l]	Dark yellow	176—179 (decomp.)	66	48.2 (47.7)	5.60 (5.30)	5.30 (5.55)		*k*	*j*
$[ReCl(N_2)(3Me\text{-}py)(PMe_2Ph)_3]$	Orange	173—175 (decomp.)	64	47.9 (47.7)	5.70 (5.30)	6.45 (5.55)		*k*	*j*
$[ReCl(N_2)(pydz)(PMe_2Ph)_3]$ [m]	Brown-orange	157—160 (decomp.)	33	45.8 (45.2)	5.20 (5.00)	7.55 (7.55)		*k*	
$[ReBr(N_2)(PMe_2Ph)_4]$	Yellow	169—174 (decomp.)	75	45.7 (45.4)	5.70 (5.25)	3.25 (3.30)	9.5 (9.5)	760 (846)	*j*
$[ReBr(N_2)(py)(PMe_2Ph)_3]$	Orange	152—155 (decomp.)	62	44.8 (44.2)	5.05 (4.90)	5.10 (5.35)	10.3 (10.2)	735 (787)	*j*
$[ReCl_3H_2(PMe_2Ph)_3]$	Light yellow	*n*	39	40.5 (40.7)	5.00 (5.00)	0.00 (0.00)	15.3 (15.0)	*o*	
$[ReBr_3H_2(PMe_2Ph)_3]$	Light yellow	*n*	37	34.7 (34.2)	4.40 (4.20)	0.00 (0.00)	28.3 (28.5)	*o*	

[a] Calculated values are given in parentheses. [b] Determined in 1,2-dichloroethane. [c] O, 2.0 (1.4)%. [d] For a 5×10^{-3} mol dm^{-3} solution in CH_2Cl_2. [e] O, 3.1(2.6); P, 9.8(10.2)%. [f] P, 11.2(11.4)%. [g] For a 1×10^{-3} mol dm^{-3} solution in $MeNO_2$. [h] P, 11.6 (10.5)%. [i] For a 1×10^{-3} mol dm^{-3} solution in CH_2Cl_2. [j] Non-conductor in $PhNO_2$. [k] Solution is unstable. [l] 4Me-py = 4-Methylpyridine. [m] pydz = Pyridazine. [n] Loses H_2 at *ca.* 100 °C. [o] Insoluble.

ide (0.5 cm^3) in benzene (70 cm^3) at 60 °C during 1 h. The volume was reduced to 10 cm^3 at 10^{-3} mmHg and dropwise addition of hexane (15 cm^3) caused the separation of crude *product* from the cooled solution. The product was recrystallized from methylene chloride–ethanol (0.4 g). The *p*-methoxybenzoyl complex was obtained analogously.

[*Acetylhydrazido*(2—)]*bis*[1,2-*bis*(*diphenylphosphino*)-*ethane*]*dichloromolybdenum*(IV).—Acetyl chloride (0.25 cm^3) and *trans*-bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)molybdenum (G) (1.0 g) [30] were stirred in thf (40 cm^3) overnight. Concentrated HCl (0.1 cm^3) was then added and after stirring for 15 min the microcystalline violet *precipitate* was filtered off, washed with benzene (5 × 5 cm^3), and dried (0.2 g). The synthesis of the *propionylhydrazido*(2—)-*analogue* was similar.

Acetyldiazenidodichlorotris(*dimethylphenylphosphine*)-*rhenium*(III).—Acetyl chloride (0.4 cm^3) was heated with *trans*-chlorotetrakis(dimethylphenylphosphine)(dinitrogen)rhenium(I) [18] (1.0 g) under reflux in benzene (50 cm^3) for 1 h. The solution was then allowed to stand overnight, and the solid which separated ($PMe_2Ph{\cdot}MeCOCl$) was collected by filtration. The filtrate was taken to dryness on a vacuum line and the residue washed with hexane (10 × 2 cm^3) and dried at 60 °C (10^{-3} mmHg). The impure powder was extracted with diethyl ether (5 × 5 cm^3) and the residue was recrystallized from diethyl ether as deep red *needles* (0.15 g).

Better yields and more rapid reactions were obtained using chlorotris(dimethylphenylphosphine)(dinitrogen)pyridinerhenium(I). This complex (0.3 g) and acetyl chloride (0.5 cm^3), freshly distilled, dried, and degassed, were stirred in dry thf (25 cm^3) for 4 h. The brownish solution was reduced to an oil on the vacuum line, and dry benzene was added. A white solid precipitated and was separated by filtration. The solution was evaporated to dryness at 10^{-3} mmHg. Hexane (25 cm^3) and diethyl ether (5 cm^3) were added and the mixture was stirred vigorously until the oil solidified to give an orange-brown solid. The solid was recrystallized from benzene–hexane to give red-brown *crystals*, 0.17 g (57%).

Benzoyldiazenidodichlorotris(*dimethylphenylphosphine*)-*rhenium*(III).—Benzoyl chloride (0.5 cm^3) and $[ReCl(N_2)(PMe_2Ph)_4]$ (0.5 g) were heated under reflux in benzene (50 cm^3) for 2 h. The solution became red, and a white solid ($PMe_2Ph{\cdot}PhCOCl$) was deposited. The volume was reduced to 10 cm^3 on a vacuum line and hexane (10 cm^3) was added dropwise. The red-brown precipitate was recrystallized from dichloromethane–diethyl ether as deep red *needles* (0.35 g). *X*-Ray diffraction studies, including selected three-dimensional intensity data, showed that the crystals were identical with those prepared previously [17] from benzoylhydrazine: space group $P2_12_12_1$; $a = 14.50$, $b = 22.95$, $c = 9.93$ Å. The unit-cell dimensions obtained from a benzoylhydrazine product are $a = 14.56$, $b = 22.95$, and $c = 9.93$ Å.

The above product was also prepared in comparable yield by the reaction of $[ReCl(N_2)(py)(PMe_2Ph)_3]$ with benzoyl chloride in benzene at 20 °C.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[*t-butylhydrazido*(2—)]*tungsten*(IV) *Bromide*.—Complex (F) (0.7 g) was dissolved in thf (60 cm^3) and t-butyl bromide (0.3 cm^3) was added. The mixture was irradiated with two tungsten lamps, each of 150 W, placed *ca.* 15 cm from the reaction vessel. After 4 h a light pink precipitate had formed. Hydrobromic acid (0.25 cm^3, 50% aqueous) was added, and, after cooling at 0 °C for 48 h, a mixture of dark pink crystals and green crystals was filtered off. This mixture was heated to 65 °C in thf (60 cm^3) and filtered while hot. The solution was reduced to 25 cm^3 at 10^{-3} mmHg and dark pink *crystals* were obtained on cooling. The crystals, recrystallized from thf, always contained 2 mol of thf, yield 0.2 g. The green crystals [13] are sparingly soluble in thf. Their characterization will be described elsewhere.[14]

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[*methylhydrazido*(2—)]*tungsten*(IV) *Bromide*.—Complex (F) (0.5 g), methyl bromide (0.6 mol), and benzene (50 cm^3) were irradiated as above for 4 h. Dry hydrogen bromide (*ca.* 2 mol equiv.) was distilled into the reaction solution on a vacuum line. A pink-brown solid was obtained, and this was recrystallized from dichloromethane–hexane as brown *crystals* (0.35 g). Similarly were prepared the *ethyl-*, *n-propyl-*, and *isopropyl-hydrazido*(2—)-*analogues* of the above tungsten complex, and *bis*[1,2-*bis*(*diphenylphosphino*)-*ethane*]*bromo*[*methylhydrazido*(2—)]*molybdenum*(IV) *bromide* and its *ethylhydrazido*(2—)-*analogue*.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(*t-butyldiazenido*)*tungsten*(II).—The corresponding t-butylhydrazido-(2—)-complex (0.2 g) was dissolved in ethanol (5 cm^3) and treated with a solution of potassium carbonate (0.12 g) in water (1.0 cm^3). The yellow-orange *crystals* produced were filtered off, and washed with aqueous ethanol (5 cm^3), ethanol (5 cm^3), and diethyl ether (1 cm^3), yield 0.15 g. The *ethyl*, *n-propyl*, and *isopropyl analogues* were prepared similarly.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[*methyldiazenidotungsten*(II).—Methyl bromide (0.6 mmol) was distilled on a vacuum line into a solution of complex (F) (0.5 g) in benzene (50 cm^3). After irradiation as above, the insoluble brown precipitate [the hydrazido(2—)-complex] was filtered off, and the orange-yellow filtrate was reduced to 20 cm^3 on a vacuum line. On cooling, yellow *crystals* (0.35 g) appeared. These were filtered off and recrystallized from benzene.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromomethylhydrazido*(2—)]*molybdenum*(IV) *Bromide*.—Complex (G) (1.0 g) was dissolved in benzene (100 cm^3), MeBr (0.2 g) was added, and the mixture was irradiated and stirred overnight. Hydrogen bromide (0.25 g, 3 mmol) was then added and the solution was stirred for 8 h. The pink *solid* was filtered off, dissolved in dichloromethane, and crystallized by the careful addition of hexane (0.3 g). *Bis*[1,2-*bis*(*diphenylphosphino*)-*ethane*]*bromo*[*ethylhydrazido*(2—)]*molybdenum*(IV) *bromide* was prepared analogously.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(*methyldiazenido*)*molybdenum*(II).—The corresponding methylhydrazido-complex (0.29 g) was dissolved in methanol (10 cm^3). A solution of $K_2[CO_3]$ (0.4 g) in water (3 cm^3) was added and the precipitate was filtered off, washed with methanol, and recrystallized from ethanol as orange *microcrystals* (0.20 g). The *ethyldiazenido-complex* was prepared analogously.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[(N,N-*dimethylhydrazido*(2—)]*tungsten*(IV) *Bromide*.—Methyl bromide (5.0 mmol), dried over P_4O_{10}, was distilled on a vacuum line into a solution of complex (F) (1.0 g) in benzene (60 cm^3). The mixture was stirred and irradiated for 12 h. The buff *precipitate* was filtered off, washed with benzene

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[30] M. W. Anker, J. Chatt, G. J. Leigh, and A. G. Wedd, *J.C.S. Dalton*, 1975, 2639.

(5 × 5 cm^3), dried at 10^{-3} mmHg, and recrystallized from methylene chloride–hexane as orange needles (0.6 g).

Chlorotris(dimethylphenylphosphine)(dinitrogen)pyridinerhenium(I).[16]—Chlorotetrakis(dimethylphenylphosphine)(dinitrogen)rhenium(I) (0.5 g) [18] and pyridine (1 cm^3) were heated in methanol (25 cm^3) under reflux for 1.5 h. The solution was cooled to −18 °C and orange *crystals* separated. The crystals were recrystallized from ethanol–pyridine (yield 0.28 g). The complex showed ν(NN) at 1905 cm^{-1} (Nujol).

Chloro(dinitrogen)tris(methyldiphenylphosphine)pyridinerhenium(I).[16]— [Benzoylhydrazido(3−)-*ON′*]dichlorobis(triphenylphosphine)rhenium(V) [15] (3.0 g), methyldiphenylphosphine (4.0 g), and pyridine (2 cm^3) were heated under reflux in benzene–methanol (1 : 2, 50 cm^3) for 3 h. The orange solution was reduced to an oil at 10^{-3} mmHg. Diethyl ether (10 cm^3) was added, and the mixture was shaken and cooled to −18 °C. An orange *solid* was precipitated and recrystallized from benzene–pyridine–methanol as orange crystals (2.0 g). The complex exhibited ν(NN) at 1 905 cm^{-1} and ν(ReCl) at 254 cm^{-1} (Nujol).

With 4-methylpyridine (2 cm^3), dark yellow crystals (0.31 g) of *chlorotris(dimethylphenylphosphine)(dinitrogen)(4-methylpyridine)rhenium*(I) were obtained. The complex exhibited ν(NN) at 1 910 cm^{-1} (Nujol) and ν(ReCl) at 262 cm^{-1}. *Chlorotris(dimethylphenylphosphine)(dinitrogen)(3-methylpyridine)rhenium*(I) was prepared in analogous manner using 3-methylpyridine (2 cm^3). An orange solid was obtained and recrystallized from ethanol–3-methylpyridine to to give orange *crystals* (0.30 g). The complex showed ν(NN) at 1 910 cm^{-1} (Nujol).

Chlorotris(dimethylphenylphosphine)(dinitrogen)(pyridazine)rhenium(I).— Chlorotetrakis(dimethylphenylphosphine)(dinitrogen)rhenium(I) (0.5 g) and pyridazine (1 cm^3) were heated in benzene (30 cm^3) under reflux for 0.5 h. The red-violet solution was reduced in volume to 2 cm^3 at 10^{-3} mmHg and diethyl ether (15 cm^3) was added. A brown *solid* was precipitated. The solid was recrystallized from benzene–pentane to give orange-brown crystals (0.15 g). The complex exhibited ν(NN) at 1 915, 1 930, and 1 940 cm^{-1} (Nujol).

Bromotetrakis(dimethylphenylphosphine)(dinitrogen)rhenium(I).—[Benzoylhydrazido(3−)-*ON′*]dibromobis(triphenylphosphine)rhenium(V) [15] (1.0 g) and PMe$_2$Ph (1.0 g) were heated in benzene–ethanol (5 cm^3 + 50 cm^3) under reflux for 1.5 h. The yellow-brown solution was reduced to 5 cm^3 at 10^{-3} mmHg and a yellow solid precipitated. This was recrystallized from benzene–methanol to give the *product* as light yellow crystals (0.63 g). The complex has ν(NN) at 1 922 cm^{-1} (Nujol).

Bromotris(dimethylphenylphosphine)(dinitrogen)pyridinerhenium(I).[16]— Bromotetrakis(dimethylphenylphosphine)(dinitrogen)rhenium(I) (0.3 g) and pyridine (2 cm^3) were heated in benzene (40 cm^3) under reflux for 2 h. The orange solution was reduced to an oil at 10^{-3} mmHg and methanol (20 cm^3) was added. The orange solid which precipitated was recrystallized from benzene–pyridine–ethanol to give the *product* as orange crystals (0.17 g). The complex exhibited ν(NN) at 1 905 cm^{-1} (Nujol).

Trichlorotris(dimethylphenylphosphine)dihydridorhenium(V).— Chlorotris(dimethylphenylphosphine)(dinitrogen)pyridinerhenium(I) (0.4 g) was dissolved in thf (30 cm^3). Hydrogen chloride gas was passed through the solution at 0 °C during 0.5 h. The solution was reduced to 2 cm^3 at 10^{-3} mmHg and methanol (10 cm^3) was added. A light yellow *solid* (0.15 g), too insoluble for recrystallization, was precipitated (yield 39%). The complex *tribromotris(dimethylphenylphosphine)dihydridorhenium*(V) was prepared by the same method using bromotris(dimethylphenylphosphine)(dinitrogen)pyridinerhenium and hydrogen bromide gas. A light yellow *solid* was obtained (0.16 g).

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