Dinitrogen Complexes of Tungsten with Bulky Phosphine Co-ligands. Preparation and Crystal Structures of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$, *trans*-$[W(N_2)_2(PEt_2Ph)_4]\cdot C_4H_8O$, and $[W(\eta^6\text{-}C_6H_5PPr^n{}_2)(N_2)(PPr^n{}_2Ph)_2]$[‡] and their Reactions to give Hydrazine or Ammonia

Stewart N. Anderson and Raymond L. Richards *
A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ
David L. Hughes *,[†]
Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts AL5 2JQ

Reduction of WCl_6 or $[WCl_4(PR_2Ph)_2]$ (R = Et or Pr^n) with Mg in the presence of PR_2Ph under N_2 in tetrahydrofuran (thf) gives a mixture of dinitrogen complexes: $[\{W(N_2)_2(PR_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1**), *trans*-$[W(N_2)_2(PR_2Ph)_4]$ (**2**), and $[W(\eta^6\text{-}C_6H_5PR_2)(N_2)(PR_2Ph)_2]$ (**3**) which can be observed in the ^{15}N n.m.r. spectra of the reaction solutions and isolated in most cases in moderate yield. Compound (**1a**) (R = Et) is shown to be a dimer by *X*-ray analysis but the structure could be refined only with constraints on interatomic distances. Compounds (**1**) react with anhydrous HCl (thf, 20 °C) to give hydrazine (0.2 mol/W atom) and dinitrogen (2 mol/W atom). Compound (**2a**) (R = Et) crystallises as a thf solvate with W–N = 1.986(6) and 1.994(6), N–N = 1.146(7) and 1.139(7) Å. Complex (**2a**) gives ammonia (1.8 mol/W atom) and N_2 (1 mol/W atom) on treatment with H_2SO_4–MeOH. Compound (**3b**) (R = Pr^n) has W–N = 1.980(8) and N–N = 1.126(10) Å and loses N_2 quantitatively on treatment with anhydrous HCl in thf.

In these laboratories, we have shown that dinitrogen, when ligating the electron-rich sites $M(PR_3)_4$ (M = Mo or W; PR_3 = PMe_2Ph or $PMePh_2$), can be reduced to ammonia or hydrazine and we have discussed these reactions with reference to the function of nitrogenase.[1,2] It is well known that bulky phosphine ligands can cause unusual reactions, co-ordination numbers, and stereochemistries in co-ordination compounds[3,4] and so we have investigated the preparation and properties of dinitrogen compounds with larger phosphines than those used in the studies mentioned above. This has led to the formation of new mono- and bi-nuclear dinitrogen complexes of tungsten, the latter having been briefly described,[5] and here we give full details of their preparation, structures, and some of their chemistry concerning the reactivity of their dinitrogen ligands.

Results and Discussion

Reduction of WCl_6 or $[WCl_4(PR_2Ph)_2]$ with Mg in tetrahydrofuran (thf) under N_2 in the presence of PR_2Ph gives a mixture of dinitrogen complexes having three major constituents. Figure 1 shows the ^{15}N n.m.r. spectrum of a reaction solution under $^{15}N_2$ (R = Et) where the resonances of the separate component dinitrogen complexes can be clearly seen. The assignments of the resonances in the spectrum to an approximately 1:1:1 mixture of *trans*-$[W(N_2)_2(PEt_2Ph)_4]$, $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$, and $[W(\eta^6\text{-}C_6H_5PEt_2)(N_2)(PEt_2Ph)_2]$ are based upon the separate isolation and characterisation of the component compounds as detailed below.

$[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1a**) is the first compound which can be isolated from the above reaction solution, in 10—15% yield, upon concentration and addition of methanol (see Experimental section). It shows the typical meridional ^{31}P n.m.r. pattern[6] of a doublet and a triplet (Table 1) and $\delta(^{15}N)$ for the bridging $^{15}N_2$ ligand of the ^{15}N analogue occurs at −21.3 p.p.m. (relative to CD_3NO_2), a position at the high-field end of the wide range (+299 to −120 p.p.m.) observed for bridging dinitrogen.[7] Its i.r. spectrum shows N_2 stretching bands at 1 890 and 1 895 cm^{-1} which shift appropriately in the ^{15}N analogue (Table 1) and are presumably mainly associated with the terminal ligands. No i.r. band associated with a μ-N_2 vibration could be identified.

The *X*-ray structure of compound (**1a**) is shown in Figure 2. Unfortunately the compound crystallised in fragile, extremely thin, red plates which did not diffract well so that the structure could not be refined below R = 0.15. Thus, although the structure is unequivocally as shown in Figure 2, accurate bond distances could not be obtained. It is interesting that the co-ordination octahedra of the pair of tungsten atoms are rotated about the W–W axis by 90°, so that, in every case, a terminal N_2 ligand on one W atom is eclipsed by a W–P bond on the other. This configuration is presumably the least sterically crowded arrangement of ligands. However, the 90° rotation may well arise because of the overlap of the two π^* orbitals on the μ-N_2 ligand with the one π-type d orbital on each metal which is not involved in π interaction with the terminal N_2 ligands. Since the two π^* orbitals on the μ-N_2 ligand are orthogonal, the 90° rotation maximises this overlap; a similar situation pertains in $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$.[8]

The analogue $[\{W(N_2)_2(PPr^n{}_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1b**) has similar spectroscopic properties to (**1a**) (Table 1) and is therefore assigned the same structure.

Compounds (**1**) react with anhydrous HCl in thf at 20 °C to give hydrazine (0.2 mol/W atom) and dinitrogen (2 mol/W atom). It is noticeable that of the binuclear dinitrogen complexes which have reactive dinitrogen ligands, *i.e.* $[\{M(\eta^5\text{-}$

[†] *Present address:* A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ.

[‡] μ-Dinitrogen-bis[tris(diethylphenylphosphine)bis(dinitrogen)tungsten(0)], *trans*-tetrakis(diethylphenylphosphine)bis(dinitrogen)-tungsten(0)–tetrahydrofuran (1/1), and dinitrogen[η^6-(di-n-propylphosphino)benzene]bis[phenyldi-n-propylphosphine]tungsten(0) respectively.

Supplementary data available (No. SUP 56377, 10 pp.): thermal parameters, H-atom co-ordinates for (**2a**) and (**3b**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Dinitrogen complexes of tungsten

Complex	Analysis (%)[a] C	H	N	$\nu(N_2)$[b]/cm^{-1}	$\delta(^{31}P)$[c,d]/p.p.m.	$\delta(^{15}N)$[d,e]/p.p.m.
(2a) *trans*-$[W(N_2)_2(PEt_2Ph)_4]$	53.9 (53.1)	7.2 (6.6)	6.3 (6.2)	1 900 1 830 ($^{15}N_2$)	143.1(s)	−30.5(d)[f] (N_β) −62.1(m) (N_α)
(1a) $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$	50.3 (49.9)	6.2 (6.0)	9.0 (9.3)	1 890 1 895 1 819 ($^{15}N_2$) 1 823 ($^{15}N_2$)	−134.5(t)[g] −138.6(d)[g]	−21.3(br s) (μ-N) −44.9(d)[h] (N_β) −64.6(br s) (N_α)
(3a) $[W(\eta^6\text{-}C_6H_5PEt_2)(N_2)(PEt_2Ph)_2]$[i]	52.0 (50.8)	6.4 (6.4)	4.5 (4.0)	1 970	n.d.	+9.0(d)[j] (N_β) −50.9(br s) (N_α)
(2b) *trans*-$[W(N_2)_2(PPr^n{}_2Ph)_4]$	56.2 (56.7)	7.3 (7.5)	5.3 (5.5)	1 915	−147.2(s)	n.d.
(1b) $[\{W(N_2)_2(PPr^n{}_2Ph)_3\}_2(\mu\text{-}N_2)]$[i]	52.9 (51.7)	7.5 (6.9)	7.9 (8.4)	1 885	−140.5(t)[g,k] −144.2(d)[g]	−25.9(s) (μ-N) −48.1(d)[l] (N_β) −66.7(br s) (N_α)
(3b) $[W(\eta^6\text{-}C_6H_5PPr^n{}_2)(N_2)(PPr^n{}_2Ph)_2]$[m]	54.9 (54.4)	7.0 (7.2)	3.1 (3.5)	1 945 1 872 ($^{15}N_2$)	−140.0(s)[n] −160.3(s)[p]	−7.2(d)[o] (N_β) −54.3(br s) (N_α)

[a] Calculated values in parentheses. [b] Nujol mulls. [c] Thf solution, reference $P(OMe)_3$. [d] s = singlet, br s = broad singlet, d = doublet, t = triplet, m = multiplet, n.d. = not determined. [e] Thf solution, reference CD_3NO_2. [f] $^1J(NN)$ = 6.0 Hz. [g] $^2J(PP)$ = 5.1 Hz. [h] $^1J(NN)$ = 5.5 Hz. [i] Difficult to purify, see text. [j] $^1J(NN)$ = 6.6 Hz. [k] $^1J(WP)$ = 335.4 Hz. [l] $^1J(NN)$ = 7.0 Hz. [m] ^1H N.m.r., C_6D_6 solution, reference $SiMe_4$ −4.28, −4.0, −3.75 (relative integrations 2:1:2), aromatic ring protons. [n] $^1J(WP)$ = 418 Hz. [o] $^1J(NN)$ = 6.3 Hz. [p] Non-ligating P atom.

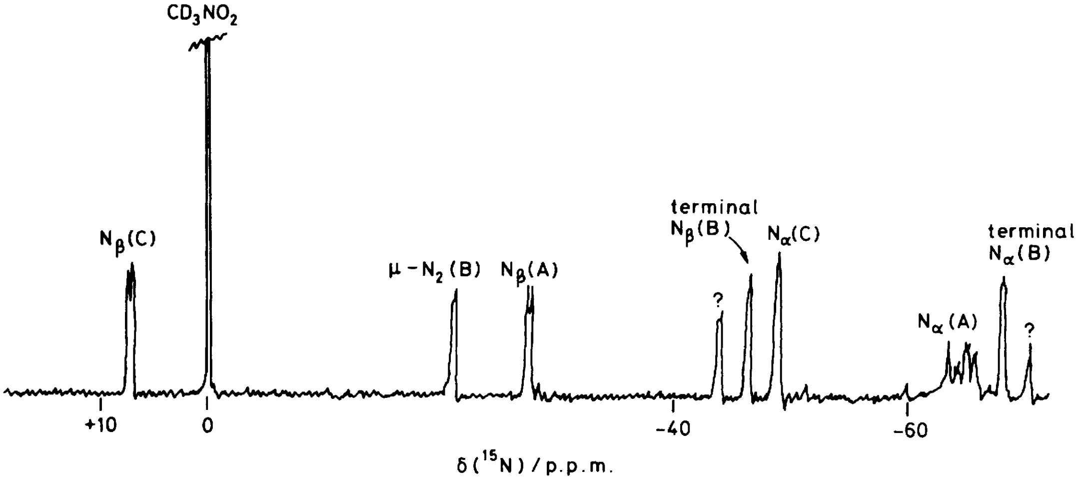

Figure 1. ^{15}N N.m.r. spectrum of the reaction WCl_6 + $^{15}N_2$ + Mg + PEt_2Ph in thf: (A) = *trans*-$[W(N_\alpha N_\beta)_2(PEt_2Ph)_4]$, (B) = $[\{W(N_\alpha N_\beta)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$, (C) = $[W(\eta^6\text{-}C_6H_5PEt_2)(N_\alpha N_\beta)(PEt_2Ph)_2]$, ? = unknown product

$C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ (M = Ti or Zr)[8] and $[\{TaX_3L_2\}_2(\mu\text{-}N_2)]$ [X = Cl, OBu^t, or H_2CCMe_3; L = thf, $P(CH_2Ph)_3$ or PEt_3],[9] all give hydrazine and no ammonia. For the Ti, Zr, and Ta compounds, this result is not too surprising because the number of electrons available for dinitrogen reduction in the compounds is only four. However, in compounds (**1**), 12 electrons are available and in view of the ease of production of ammonia from terminal dinitrogen,[1,2] some ammonia would have been expected. However, further discussion of this observation is postponed pending detailed examination of the reaction mechanism, which is in progress.

After separation of (**1a**) from the above reaction mixture, and allowing the solution to stand under N_2 at 0 °C, dark red, diamagnetic prisms of (**2a**) separated in 20% yield. The spectroscopic properties of (**2a**) (Table 1) are diagnostic[2] of the formulation *trans*-$[W(N_2)_2(PEt_2Ph)_4]$ and this is confirmed by its *X*-ray structure (Figure 3). As expected by analogy with its analogues with other phosphines,[1,2] (**2a**) gives ammonia (1.8 mol/W atom) on treatment with H_2SO_4 in MeOH (Experimental section).

Figure 3 shows (**2a**) to have good pseudo-$\bar{4}$ symmetry, with the symmetry axis passing through the virtually linear *trans*-W–N–N systems. The packing of the four bulky phosphine groups in the equatorial plane of the complex is very regular, with the close contacts between one pair of adjacent groups repeated between all pairs. Typical interligand interactions are: (*i*) the plane of P(1), C(17), C(18), and C(19) lies *ca.* parallel to, and *ca.* 3.4 Å from, the phenyl ring plane C(41)—C(46), (*ii*) an H atom on C(17) points towards the centre of the ring C(41)—C(46), and (*iii*) an H atom of C(19) lies close to C(41), C(42), and C(48).

The extent of the steric interactions between the phosphine ligands is reflected in the W–P bond lengths, which, at 2.482(2)—2.498(2) Å, are at the longer end of the range for such bonds, and also in the way the four phosphorus atoms form a shallow tetrahedron in the equatorial 'plane' (Figure 4); each phosphorus atom is *ca.* 0.32 Å from their mean plane. This arrangement has been noted in other tetrakis(phosphine) complexes, *e.g.* *trans*-$[Mo(N_2)_2(PMePh_2)_4]\cdot C_6H_6$.[10]

The two dinitrogen ligands are very similar, with dimensions

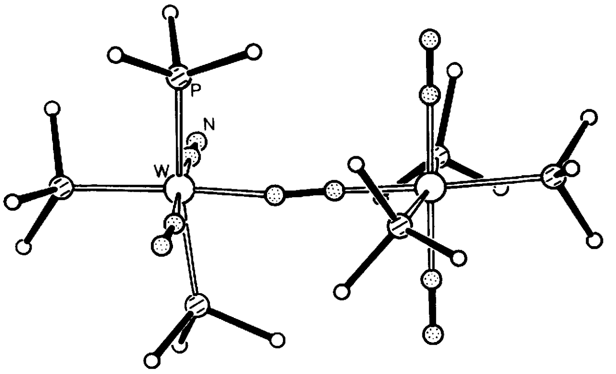

Figure 2. The core of a molecule of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1a**)

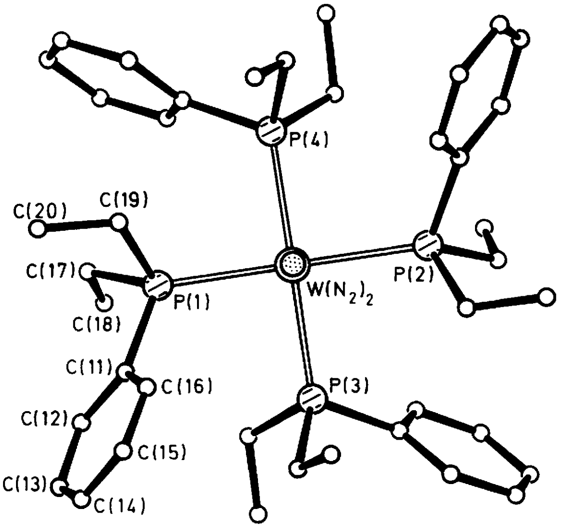

Figure 3. A molecule of *trans*-$[W(N_2)_2(PEt_2Ph)_4]$ (**2a**) projected onto the mean-plane of the four P atoms. The atoms of the phosphine ligands of P(*n*) are labelled as related by pseudo-symmetry to those of P(1)

Table 2. Selected bond lengths (Å) and angles (°) for *trans*-$[W(N_2)_2(PEt_2Ph)_4]\cdot$thf (**2a**) and $[W(\eta^6\text{-}C_6H_5PPr^n{}_2)(N_2)(PPr^n{}_2Ph)_2]$ (**3b**), with e.s.d.s in parentheses

(*a*) Complex (**2a**)			
W–P(1)	2.482(2)	P(1)–W–P(2)	165.5(1)
W–P(2)	2.492(2)	P(1)–W–P(3)	90.5(2)
W–P(3)	2.495(2)	P(2)–W–P(3)	91.1(1)
W–P(4)	2.498(2)	P(1)–W–P(4)	90.9(1)
W–N(5)	1.986(6)	P(2)–W–P(4)	91.3(1)
W–N(6)	1.994(6)	P(3)–W–P(4)	164.8(1)
		P(1)–W–N(5)	82.8(1)
N(5)–N(51)	1.146(7)	P(2)–W–N(5)	82.8(2)
N(6)–N(61)	1.139(7)	P(3)–W–N(5)	97.7(2)
		P(4)–W–N(5)	97.5(2)
		P(1)–W–N(6)	97.3(2)
		P(2)–W–N(6)	97.1(2)
		P(3)–W–N(6)	83.1(1)
		P(4)–W–N(6)	81.7(1)
		P(5)–W–N(6)	179.2(2)
		W–N(5)–N(51)	179.3(5)
		W–N(6)–N(61)	179.5(5)
(*b*) Complex (**3b**)			
W–N(1)	1.980(8)	N(1)–W–P(2)	87.5(2)
W–P(2)	2.440(2)	N(1)–W–P(3)	84.6(2)
W–P(3)	2.455(2)	P(2)–W–P(3)	92.4(1)
W–C(41)	2.303(8)		
W–C(42)	2.261(8)	W–N(1)–N(11)	175.4(8)
W–C(43)	2.292(10)		
W–C(44)	2.257(9)		
W–C(45)	2.282(9)		
W–C(46)	2.233(8)		
N(1)–N(11)	1.126(10)		

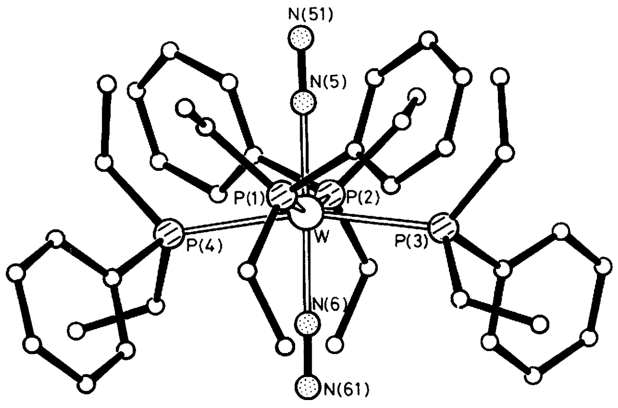

Figure 4. A molecule of (**2a**), showing the shallow tetrahedron of P atoms about the W atom

[Table 2(*a*)] which are similar to those in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$.[11] The W–N bond lengths in (**2a**) are closer to that of the N_2 ligand in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ which is not enclosed by the phenyl rings of neighbouring phosphine groups.[11] Both N–N bonds in (**2a**) appear marginally longer than in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$: this may result from the differences in intermolecular interactions of which there are fewer short contacts in the *trans* complex.

The packing of molecules in this crystal is not particularly tight, indeed a molecule of the solvent, thf, appears to lie within a lot of space in one of two distinct 'planes'; within each plane, there does not seem to be a unique orientation and we cannot identify the O-atom location distinct from those of the C atoms.

The third type of compound to be formed, $[W(\eta^6\text{-}C_6H_5PR_2)(N_2)(PR_2Ph)_2]$ (**3**), appears in highest yield when the pressure of dinitrogen over the system is relatively low. Thus, for example, the pressure of $^{15}N_2$ used to prepare the ^{15}N-labelled compounds (Figure 1) was *ca.* 0.8 atm and $[W(\eta^6\text{-}C_6H_5PPr^n{}_2)(N_2)(PPr^n{}_2Ph)]$ (**3b**) was isolated (15% yield) by initially running the normal preparation under dinitrogen at *ca.* 0.8 atm and then working the solution up under argon. Compounds (**3**) are the first examples of dinitrogen complexes of tungsten with arene ligands, although analogues of molybdenum have been known for some time.[12] Diagnostic of the $\eta^6\text{-}C_6H_5PR_2$ ligand in (**3**) is the high-field ^{31}P resonance of the unco-ordinated PR_2 group which is, as expected, close to the resonance of the free phosphine[13] (Table 1). Similarly the aromatic protons have resonances typical of a π-aryl group[13] (Table 1) and other spectroscopic data are as expected (Table 1).

Treatment of (**3**) with HCl in thf leads to the formation of an unstable purple solution which probably contains a protonated complex, but which rapidly evolves dinitrogen (1 mol/W).

The *X*-ray structure of (**3b**) shown in Figure 5 confirms that one of the phosphine ligands co-ordinates as an η^6-arene ligand through its phenyl group. The six C atoms of the ring are

Table 3. Crystal data

Complex	$[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1a**)	$[W(N_2)_2(PEt_2Ph)_4]\cdot$thf (**2a**)	$[W(\eta^6\text{-}C_6H_5PPr^n{}_2)(N_2)(PPr^n{}_2Ph)_2]$ (**3b**)
Formula	$C_{60}H_{90}N_{10}P_6W_2$	$C_{44}H_{68}N_4OP_4W$	$C_{36}H_{57}N_2P_3W$
M	1 505.0	976.8	794.6
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (equivalent to no. 14)
a/Å	19.08(1)	10.689(3)	9.302(1)
b/Å	14.79(2)	16.624(5)	15.357(2)
c/Å	25.32(2)	14.508(4)	26.632(3)
α/°	90	98.28(3)	90
β/°	110.1(1)	98.73(3)	95.71(1)
γ/°	90	108.45(3)	90
U/Å^3	6 711	2 365.7	3 785.8
Z	4	2	4
D_c/g cm^{-3}	1.49	1.371	1.394
F(000)	3 032	1 004	1 624
μ(Mo-K_α)/cm^{-1}	36.8	26.6	32.7
λ(Mo-K_α)/Å	0.710 69	0.710 69	0.710 69
Crystal size/mm	*ca.* 0.20 × 0.25 × 0.02	0.21 × 0.17 × 0.14	0.30 × 0.10 × 0.10

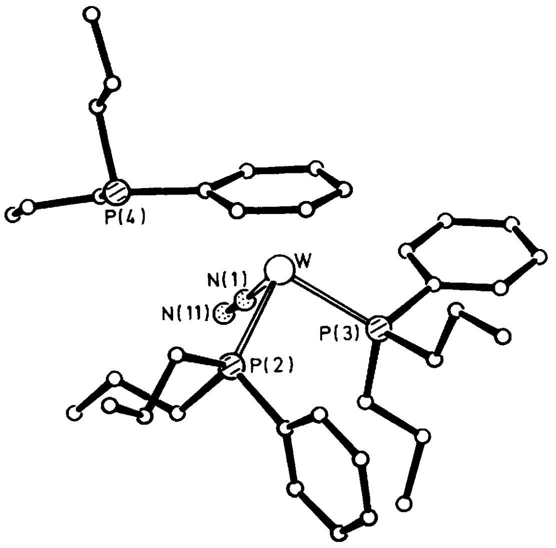

Figure 5. A molecule of $[W(\eta^6\text{-}C_6H_5PPr^n{}_2)(N_2)(PPr^n{}_2Ph)_2]$ (**3b**)

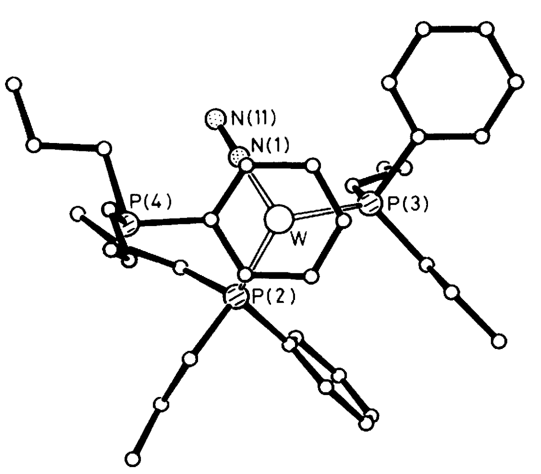

Figure 6. The projection of a molecule of (**3b**) onto the plane of the ring of the π-arene ligand

ca. equidistant from the W atom, 2.233(8)—2.303(8) Å, similarly to those of the closely-related complex $[Mo(PMe_2Ph)_3(\eta^6\text{-}C_6H_5PMe_2)]$[14] [where the range of Mo–C is 2.25(2)—2.30(2) Å] and of a π-mesitylene Mo complex[15] [where the range is 2.243(4)—2.309(4) Å]. The C atoms form a good plane [maximum deviation of any atom is 0.021(12) Å] from which the W atom is displaced 1.78 Å; P(4) is 0.036(12) Å away from the mean plane on the opposite side from the metal, exactly as found in $[Mo(PMe_2Ph)_3(\eta^6\text{-}C_6H_5PMe_2)]$.[14] The P atom of the arene ligand is not involved in metal co-ordination. The two other phosphine ligands are bonded to the W atom through the P atoms, and form two of the legs of the 'three-legged piano-stool' co-ordination arrangement about the W atom. The third leg is occupied by the linear dinitrogen ligand whose dimensions are the same as those in complex (**2a**) [Table 2(*b*)].

The ligating phenyl ring is orientated such that, in projection on to the plane of the ring (Figure 6), the dinitrogen and one phosphine ligand lie directly under the *ortho* C atoms of the phenyl ring, and the phosphine group of P(3) is distorted slightly from under the *para* position by phosphine–phosphine interactions. Hence P(4), of the π-arene ligand, is in the least sterically inhibited position.

The interactions between the phosphine ligands of P(2) and P(3) are similar to those described for complex (**2a**). The W–P distances, 2.440(2) and 2.455(2) Å, however, suggest that there is no extensive overcrowding in this complex. All the n-propyl groups have extended *trans* conformations and intermolecular contacts are all at van der Waals distances.

Conclusions

Undoubtedly the steric size of the phosphines used in the synthesis of the dinitrogen complexes described herein is a dominant factor in causing the varied nature of the products.

The crystal structure of the 'normal' complex, *trans*-$[W(N_2)_2(PEt_2Ph)_4]$ (**2a**) shows that steric pressure within the molecule causes some distortion of the phosphine plane and it might be expected that a phosphine could be easily displaced by another ligand, as has been observed for pyridine in *trans*-$[M(N_2)_2(PMePh_2)_4]$ (M = Mo[16] or W[17]) and for dinitrogen in *trans*-$[Mo(N_2)_2(PPr^n{}_2Ph)_4]$.[18]

Thus compound (**1**) can be considered as being derived from

Table 4. Details of diffractometer measurements, data processing, and structure analysis[a]

	Complex		
	(1a)	**(2a)**	**(3b)**
(*i*) Diffractometer measurements			
Scan type	ω—2θ	ω—θ	ω—θ
ω scan angle parameter DOM[b]/°	0.8	0.5	0.6
Range of ω scan speeds, as $20/n$ ° min^{-1}: n =	12	5—25[c]	5—33[c]
Max. time allowed for scans/s	—	60	90
θ range/°	1.5—15 (not quite complete)	1.2—20	1.25—20
θ range for absorption measurements/°	—	2.6—9.5	4.4—15.4
Weighting scheme: w =	k, constant	σ_F^{-2}	σ_F^{-2}
(*ii*) Data reduction			
Corrections for Lorentz-polarisation effects[d]	Yes	Yes	Yes
Corrections for deterioration[d]	Yes	Yes	Yes
No. of intensity monitoring reflections	1	2	2
Measured after exposure time/s	7 200	10 000	10 000
Overall deterioration/%	40	12	17
Absorption[e]	No	Yes	Yes
Negative intensities (by Bayesian methods)[f]	No	Yes	No
No. of unique reflections	2 567	4 402	3 515
No. of observed reflections ($I > 2\sigma_I$)	1 029	3 622	2 704
(*iii*) Refinement (by full-matrix least-squares methods)[g,h]			
Thermal parameters			
anisotropic	W atoms	W,P,N,	W,P
isotropic	P,N,C atoms	C	N,C
Treatment of H atoms[i]			
methylene groups	—	riding	riding
methyl groups	—	in rigid CH_3 groups, with independent $U_{iso.}$	
phenyl groups	—	riding	riding
Final R	0.154	0.039	0.044
R'	0.154	0.034	0.036
No. of reflections in refinement	1 029	4 399[j]	3 067
with $F > n\sigma_F$: n =	4	0	1

[a] Principal programs used are as listed in the following footnotes; others used, on a Prime 550 computer, include: GEOM, program for molecular dimensions and tables (J. D. Owen, Rothamsted Experimental Station, Harpenden, Herts., 1981); ORTEP, program for diagrams (C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A., revised 1971). [b] The ω peak-scan angle width, P, is DOM + 0.35 tan θ; the total ω scan angle is $\frac{3}{2}$ P to allow for measurements of background each side of the peak. [c] After a prescan at the fastest speed (n = 5), each reflection was remeasured at a slower speed to try to maintain a constant value of 0.02 for σ_I/I for all reflections. [d] CAD4 processing program (M. B. Hursthouse, Queen Mary College, London, 1976). [e] EMPABS, a program to apply semi-empirical absorption correction (G. M. Sheldrick, A. G. Orpen, B. E. Reichert, and P. R. Raithby, Abstracts, 4th European Crystallographic Meeting, Oxford, 1977, p. 147). [f] BAYES, a program to ensure no negative intensity values (J. D. Owen, Rothamsted Experimental Station, Harpenden, Herts.; adapted from S. French and K. Wilson, *Acta Crystallogr., Sect. A*, 1978, **34**, 517). [g] SHELX, program for structure determination (G. M. Sheldrick, University of Cambridge, 1976). [h] In each refinement, scattering factors were calculated from the analytical curves of page 99 of 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, with real and imaginary dispersion corrections from page 149. [i] Some H atoms were observed in difference Fourier syntheses of (**2a**) and (**3b**). All H atoms were included in calculated, idealised positions in these analyses; in the methyl groups, H atoms were calculated initially in staggered conformations. [j] Three reflections at low θ angle, strongly affected by extinction, have been omitted.

(**2**) by displacement of phosphine by (bridging) dinitrogen under normal or high dinitrogen pressure. When the dinitrogen pressure is low, however, loss of a phosphine would lead to coordinative unsaturation, which is avoided by one phosphine changing its ligation to the η^6-$C_6H_5PR_2$ mode, to give compounds (**3**).

We do not wish to imply at this stage that (**1**), (**2**), and (**3**) are interconvertible, although experiments are planned to test this possibility.

The formation of only hydrazine and no ammonia from compound (**1**), under the conditions used, is unexpected and further study of the mechanism of these reactions is clearly necessary.

Experimental

Preparation and manipulation of air-sensitive materials and purification of solvents followed established procedures.[1,2,6] I.r. spectra were recorded with Unicam SP3-200 or SP2000 instruments and n.m.r. spectra with JEOL FX90Q or Bruker WH360 instruments. Compounds $[WCl_4(PR_2Ph)_2]$ (R = Et or Pr^n) were prepared as previously described.[19]

Preparation of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1a**).—$[WCl_4(PEt_2Ph)_2]$ (3.8 g, 5.8 mmol), PEt_2Ph (1.9 g, 11.4 mmol), and Mg (~3 g) were stirred together in thf under N_2 keeping the temperature at 18 °C by means of a water-bath. The absorption of N_2 was monitored by means of a manometer and when this

Table 5. Final fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for (**1a**)

Atom	x	y	z	Atom	x	y	z
W(1)	2 177(5)	−722(8)	2 619(3)	N(15)	1 993(82)	−1 798(69)	3 028(55)
W(2)	2 559(5)	1 420(7)	4 339(3)	N(151)	1 828(75)	−2 432(65)	3 259(51)
N(1)	2 278(71)	182(68)	3 233(40)	P(21)	2 846(33)	2 408(48)	5 228(25)
N(2)	2 321(67)	501(85)	3 692(34)	C(210)	3 138(76)	1 678(92)	5 857(49)
P(11)	783(28)	−294(39)	2 326(20)	C(211)	3 655(121)	2 276(160)	6 335(83)
C(110)	−69(62)	−972(93)	2 190(57)	C(212)	1 962(54)	2 617(129)	5 345(61)
C(112)	563(81)	652(101)	2 712(69)	C(214)	3 426(95)	3 380(97)	5 211(53)
C(113)	−276(78)	641(136)	2 616(60)	C(215)	4 186(95)	3 292(97)	5 299(53)
C(114)	482(75)	275(110)	1 652(36)	C(216)	4 640(95)	4 058(97)	5 399(53)
C(115)	677(75)	1 147(110)	1 544(36)	C(217)	4 335(95)	4 911(97)	5 412(53)
C(116)	351(75)	1 525(110)	1 011(36)	C(218)	3 575(95)	4 998(97)	5 325(53)
C(117)	−170(75)	1 031(110)	585(36)	C(219)	3 121(95)	4 233(97)	5 224(53)
C(118)	−365(75)	159(110)	693(36)	P(22)	2 790(27)	2 627(38)	3 712(19)
C(119)	−39(75)	−219(110)	1 226(36)	C(220)	2 072(92)	2 604(183)	3 016(51)
P(12)	2 045(29)	−1 704(42)	1 807(21)	C(221)	1 764(112)	3 035(153)	2 425(67)
C(120)	1 136(51)	−2 116(104)	1 381(53)	C(222)	3 658(69)	2 435(168)	3 565(83)
C(121)	1 080(90)	−2 901(104)	966(62)	C(224)	2 827(74)	3 846(45)	3 873(43)
C(124)	2 626(141)	−2 649(116)	2 168(102)	C(225)	3 312(74)	4 570(45)	3 918(43)
C(125)	2 396(141)	−3 407(116)	2 393(102)	C(226)	3 082(74)	5 448(45)	3 974(43)
C(126)	2 745(141)	−4 239(116)	2 400(102)	C(227)	2 366(74)	5 603(45)	3 985(43)
C(127)	3 322(141)	−4 312(116)	2 182(102)	C(228)	1 880(74)	4 878(45)	3 940(43)
C(128)	3 551(141)	−3 553(116)	1 957(102)	C(229)	2 111(74)	4 000(45)	3 884(43)
C(129)	3 203(141)	−2 722(116)	1 950(102)	P(23)	2 201(36)	38(56)	4 773(27)
P(13)	3 574(33)	−939(46)	3 002(23)	C(230)	1 460(103)	−644(146)	4 300(84)
C(130)	3 861(84)	−2 025(70)	3 347(52)	C(231)	1 549(110)	−1 583(171)	4 583(77)
C(131)	3 975(96)	−2 072(141)	3 974(54)	C(232)	3 072(62)	−402(115)	5 272(51)
C(132)	4 085(68)	−173(94)	3 563(51)	C(234)	1 598(96)	85(140)	5 208(72)
C(133)	4 940(67)	−134(127)	3 850(59)	C(235)	1 814(96)	−236(140)	5 759(72)
C(134)	4 104(64)	−866(121)	2 517(44)	C(236)	1 493(96)	122(140)	6 133(72)
C(135)	4 527(64)	−1 546(121)	2 389(44)	C(237)	955(96)	800(140)	5 955(72)
C(136)	4 955(64)	−1 353(121)	2 053(44)	C(238)	738(96)	1 121(140)	5 404(72)
C(137)	4 960(64)	−481(121)	1 845(44)	C(239)	1 059(96)	763(140)	5 030(72)
C(138)	4 537(64)	199(121)	1 973(44)	N(24)	1 509(34)	1 786(99)	3 993(44)
C(139)	4 110(64)	7(121)	2 309(44)	N(241)	855(41)	1 972(97)	3 800(47)
N(14)	2 336(68)	404(55)	2 240(49)	N(25)	3 616(35)	1 055(94)	4 689(45)
N(141)	2 405(84)	1 005(77)	1 942(54)	N(251)	4 274(39)	913(117)	4 887(52)

had ceased (~3 h) the deep red solution was stirred for a further 30 min, then filtered and the solvent removed under reduced pressure at 20 °C. The dark red, sticky residue was extracted with Et_2O (3 × 50 cm^3) and the insoluble material discarded. The Et_2O solution was taken to dryness under reduced pressure, the residue dissolved in thf (20 cm^3), then MeOH (100 cm^3) added and the solution kept at 0 °C for 48 h to give *deep red plate crystals* of (**1a**) (0.5 g, 10%).

The analogue $[\{W(N_2)_2(PPr^n_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1b**) was prepared by the same technique in moderate yield $\{[WCl_4(PPr^n_2Ph)_2]$, 1.0 g; PPr^n_2Ph, 0.54 g; yield 0.2 g, 15%$\}$.

trans-*Tetrakis(diethylphenylphosphine)bis(dinitrogen)tungsten*(0), *trans*-$[W(N_2)_2(PEt_2Ph)_4]$ (**2a**).—The mother-liquor from the preparation of (**1a**) was concentrated to 20 cm^3 under reduced pressure to give *red microcrystals* of (**2a**) which were recrystallised from thf–MeOH (1:2) (1.0 g, 20%).

Compound *trans*-$[W(N_2)_2(PPr^n_2Ph)_4]$ (**2b**) was identified in solution and in the crude solid by its spectroscopic properties but was not purified (Table 1).

Dinitrogen[η^6-*(di-*n*-propylphosphino)benzene*]*bis(phenyldi-*n*-propylphosphine)tungsten*(0), $[W(\eta^6\text{-}C_6H_5PPr^n_2)_2(N_2)(PPr^n_2Ph)_2]$ (**3b**).—The mother-liquor from a preparation of (**1b**) run as above, but under a static pressure of slightly less than 1 atm of N_2, was concentrated under reduced pressure to 20 cm^3 and then kept at −20 °C for 48 h under argon. The product (**3b**) separated as *deep orange prisms* (0.2 g, 15%) which were suitable for *X*-ray crystallography.

Compound $[W(\eta^6\text{-}C_6H_5PEt_2)_2(N_2)(PEt_2Ph)_2]$ (**3a**) was identified by its spectroscopic properties in solution (Table 1) and was not isolated in a pure state (Table 1).

Reactions of Dinitrogen Complexes with Anhydrous Acids.—$[\{W(N_2)_2(PR_2Ph)_3\}_2(\mu\text{-}N_2)]$ (**1**, R = Et *or* Pr^n). Thf (25 cm^3) and anhydrous HCl (2.0 mmol) were distilled at −196 °C on to (**1**) (2.4 × 10^{-2} mmol). The flask was allowed to warm and the mixture stirred at 20 °C for 24 h to give a very pale yellow solution. Dinitrogen [2.05 mol/W (R = Et); 2.1 mol/W (R = Pr^n)] was evolved. The solvent was then removed under reduced pressure and the hydrazine produced determined (*p*-dimethylaminobenzaldehyde) after base distillation under argon into 0.1 N H_2SO_4;[2] yield, 0.21 N_2H_4 mol/W atom (R = Et or Pr^n). No ammonia was produced.

trans-$[W(N_2)_2(PEt_2Ph)_4]$ (**2a**). Complex (**2a**) (*ca.* 50 mg) was treated with H_2SO_4 (10 mol/W) in MeOH (30 cm^3) in a vacuum as previously described[2] to give NH_3 (1.8 mol/W) and N_2 (1.0 mol/W).

$[W(\eta^6\text{-}C_6H_5PPr^n_2)(N_2)(PPr^n_2Ph)_2]$ (**3b**). Complex (**3b**) was treated with anhydrous HCl in a similar fashion to (**1**, R = Et or Pr^n) to give an initially purple solution which evolved N_2 (1.0 mol/W) and finally gave a pale yellow solution together with a purple precipitate which was not investigated.

Table 6. Final fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for (**2a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.1(3)	2 517.4(2)	2 450.0(2)	C(31)	2 794(6)	4 478(4)	2 224(4)
P(1)	518(2)	1 878(1)	3 841(1)	C(32)	2 928(7)	5 346(4)	2 346(5)
C(11)	1 465(7)	2 608(4)	5 007(5)	C(33)	3 418(7)	5 831(5)	1 684(5)
C(12)	2 719(7)	2 638(5)	5 459(5)	C(34)	3 781(8)	5 471(5)	923(6)
C(13)	3 375(9)	3 210(5)	6 335(6)	C(35)	3 673(7)	4 628(5)	792(5)
C(14)	2 788(9)	3 730(6)	6 730(6)	C(36)	3 165(7)	4 128(4)	1 436(5)
C(15)	1 559(9)	3 715(5)	6 324(6)	C(37)	2 482(7)	4 592(4)	4 164(5)
C(16)	901(8)	3 159(5)	5 438(5)	C(38)	1 403(8)	4 972(6)	4 331(6)
C(17)	1 262(7)	1 011(5)	3 807(5)	C(39)	3 599(6)	3 423(4)	3 328(5)
C(18)	2 462(8)	1 110(6)	3 332(6)	C(40)	5 021(8)	4 085(5)	3 576(7)
C(19)	−1 040(7)	1 324(5)	4 243(5)	P(4)	−1 765(2)	1 107(1)	1 598(1)
C(20)	−907(9)	919(6)	5 104(6)	C(41)	−1 530(6)	88(4)	1 834(5)
P(2)	−865(2)	3 298(1)	1 306(1)	C(42)	−2 378(7)	−464(4)	2 303(5)
C(21)	−2 690(6)	2 876(4)	753(4)	C(43)	−2 145(8)	−1 205(5)	2 492(5)
C(22)	−3 191(7)	2 539(4)	−212(5)	C(44)	−1 094(8)	−1 400(5)	2 220(5)
C(23)	−4 587(7)	2 206(5)	−575(5)	C(45)	−258(8)	−871(5)	1 749(5)
C(24)	−5 459(8)	2 210(5)	4(5)	C(46)	−492(7)	−131(4)	1 564(5)
C(25)	−5 000(8)	2 534(5)	954(5)	C(47)	−3 589(7)	855(5)	1 533(5)
C(26)	−3 619(7)	2 866(4)	1 333(5)	C(48)	−4 048(8)	1 091(5)	2 454(5)
C(27)	−103(7)	3 607(4)	295(4)	C(49)	−1 779(7)	920(4)	310(4)
C(28)	230(8)	2 941(5)	−349(5)	C(50)	−2 710(8)	59(5)	−320(6)
C(29)	−765(7)	4 386(4)	1 915(5)	N(5)	−1 122(6)	2 936(3)	3 238(4)
C(30)	−1 401(8)	4 909(5)	1 346(6)	N(51)	−1 781(6)	3 175(4)	3 684(4)
P(3)	2 139(2)	3 780(1)	3 051(1)	N(6)	1 104(5)	2 083(3)	1 649(4)
				N(61)	1 729(6)	1 837(4)	1 185(5)
Solvent molecules*							
C(1)	7 515(49)	2 173(28)	6 974(45)	C(6)	7 524(34)	2 488(22)	6 430(24)
C(2)	6 631(50)	2 369(28)	6 205(36)	C(7)	7 079(52)	1 972(36)	7 154(34)
C(3)	5 767(56)	1 545(32)	5 523(31)	C(8)	5 714(43)	1 432(27)	6 813(30)
C(4)	5 578(33)	964(20)	6 202(27)	C(9)	5 335(43)	1 427(28)	5 845(35)
C(5)	6 645(35)	1 296(21)	7 008(22)	C(10)	6 393(36)	2 230(26)	5 640(27)

* Each atom was given a fixed site-occupying factor of 0.5, and refined with the C atom scattering curve; C–C bond lengths were constrained to 1.47(4) Å.

Table 7. Final fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for (**3b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	4 772.5(4)	2 679.7(2)	3 280.3(1)	C(35)	4 489(13)	3 754(7)	1 118(5)
N(1)	6 800(9)	3 090(5)	3 342(3)	C(36)	4 022(13)	3 918(7)	1 597(4)
N(11)	7 980(10)	3 268(5)	3 370(3)	C(371)	2 554(10)	4 358(6)	2 557(3)
P(2)	4 393(3)	3 631(1)	3 988.9(9)	C(381)	1 310(10)	3 722(6)	2 438(4)
C(21)	3 156(10)	4 568(5)	3 888(3)	C(391)	−141(12)	4 144(7)	2 335(4)
C(22)	1 693(11)	4 420(7)	3 792(3)	C(372)	5 468(10)	4 843(5)	2 801(3)
C(23)	717(13)	5 094(7)	3 712(4)	C(382)	5 417(12)	5 564(6)	2 419(4)
C(24)	1 220(14)	5 919(8)	3 718(4)	C(392)	6 152(15)	6 394(8)	2 638(5)
C(25)	2 610(13)	6 101(7)	3 796(4)	P(4)	6 074(3)	1 015(2)	4 242.3(9)
C(26)	3 643(12)	5 431(6)	3 889(3)	C(41)	5 070(9)	1 326(5)	3 648(3)
C(271)	3 607(10)	3 143(6)	4 535(3)	C(42)	3 621(9)	1 602(5)	3 658(3)
C(281)	3 462(12)	3 757(6)	4 984(4)	C(43)	2 730(11)	1 836(6)	3 213(3)
C(291)	2 604(13)	3 365(8)	5 379(4)	C(44)	3 336(10)	1 828(6)	2 753(3)
C(272)	6 052(10)	4 129(6)	4 308(3)	C(45)	4 735(11)	1 554(6)	2 719(4)
C(282)	7 038(12)	3 474(7)	4 593(4)	C(46)	5 607(10)	1 337(5)	3 171(3)
C(292)	8 493(14)	3 856(9)	4 795(6)	C(471)	5 985(10)	−187(6)	4 200(4)
P(3)	4 350(3)	3 871(1)	2 668.7(9)	C(481)	4 512(11)	−548(6)	4 238(4)
C(31)	4 805(10)	3 621(6)	2 027(3)	C(491)	4 463(16)	−1 544(7)	4 238(5)
C(32)	6 059(11)	3 179(6)	1 975(4)	C(472)	7 961(10)	1 167(6)	4 105(3)
C(33)	6 514(12)	3 027(7)	1 500(4)	C(482)	9 014(12)	1 049(7)	4 580(4)
C(34)	5 732(12)	3 319(6)	1 076(4)	C(492)	10 575(15)	1 223(10)	4 486(6)

X-*Ray Crystal Structure Determinations*.—Crystals of complexes (**1a**) and (**2a**) are deep red; those of (**3b**) are deep orange. Complex (**1a**) has very thin plate crystals, (**2a**) has diamond-shaped prisms, some of which are twinned, and crystals of (**3b**) are almost square plates. Samples of each were rapidly mounted on glass fibres in air, and coated with epoxy resin. After preliminary photographic examination for space-group determination and for quality, the crystals were mounted on an Enraf-Nonius CAD4 diffractometer for measurement of accurate cell parameters and diffraction intensities, with monochromated Mo-K_α radiation.

Crystal data for the three complexes are given in Table 3, and a summary of the data measurement and processing and of the structure refinement procedures is in Table 4. The structures of the complexes were all solved by the heavy-atom method.

Crystals of (**1a**) were very fragile and normally covered with fine platelets. They were rather more air-sensitive than crystals of (**2a**) or (**3b**) and their brief exposure to air was more damaging. Furthermore, they did not diffract well; several crystals were examined and more data were recorded on the diffractometer after the publication[5] of preliminary results. However, we have not been able to improve the analysis of this complex nor the accuracy of the results of that report. The refined co-ordinates of this complex, Table 5, are those used in the preliminary report.[5] In the refinement process, all phenyl groups were refined as rigid hexagons, and most bond lengths were constrained (each with $\sigma = 0.05$ Å), *viz.* P–C bonds at 1.82, N–N 1.20, W–N 2.0, and C–C in ethyl groups 1.54 Å. The W atoms were allowed to refine with anisotropic thermal parameters which always yielded 'non-positive-definite' ellipsoids; the other atoms, with isotropic thermal parameters, also have rather erratic refined parameters. Not all the β-C atoms of the ethyl groups have been identified; it is probable that some are disordered over more than one site. There appears to be much space between molecules in the crystal, and it is possible that there are solvent molecules, perhaps disordered, in this region, although none was discerned in a 'final' difference map.

We quote the full details and results of the analysis of (**1a**) for completeness and comparison with the other analyses.

In complex (**2a**), after some cycles of refinement, positions of atoms of thf solvent molecules, disordered approximately equally between two overlapping sites, were estimated from a rather blurred solvent region in a difference Fourier map. The bond distances in the solvent molecules were constrained in later cycles of refinement. It was not clear whether the O atoms of the thf molecules occupied specific sites in the crystal or whether the molecules occupy the regions roughly described by the co-ordinates of Table 6 with no preferred alignment of C and O atoms.

Complex (**3b**) refined satisfactorily to the co-ordinates listed in Table 7.

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