Protonation of Bis[1,2-bis(diethylphosphino)ethane]bis(dinitrogen)-molybdenum and -tungsten with Fluoroboric Acid–Diethyl Ether (1/1) in Benzene; Crystal and Molecular Structure of Bis[1,2-bis(diethylphosphino)ethane]fluoro[hydrazido(2−)]tungsten Tetrafluoroborate†

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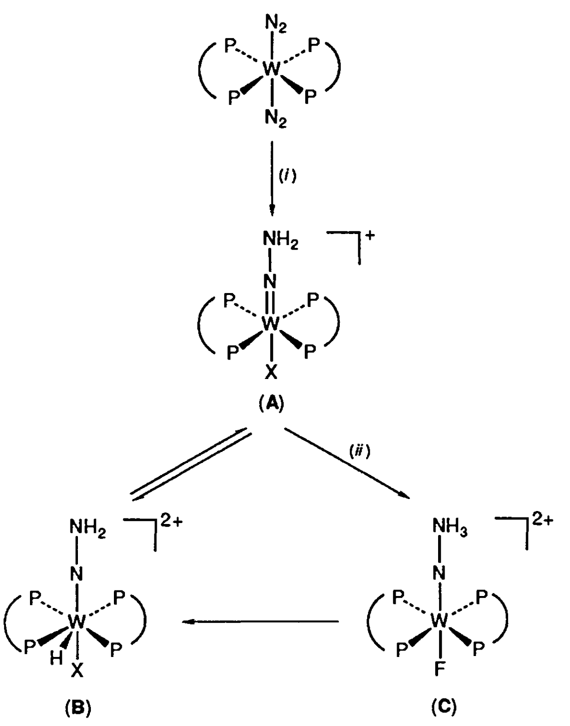
The reaction of $HBF_4{\cdot}Et_2O$ with $[W(N_2)_2(depe)_2]$ in benzene can, depending upon the conditions, give rise to $[WF(NNH_2)(depe)_2]BF_4$, $[WF(NNH_3)(depe)_2][BF_4]_2$, or $[WH(F)(NNH_2)(depe)_2][BF_4]_2$. The compounds are to some extent interconvertible. The structures have been completely elucidated using ^{31}P and ^{15}N n.m.r. spectroscopy, and the *X*-ray crystal structure of $[WF(NNH_2)(depe)_2]BF_4$ has been determined. This reveals no unusual bond distances, but an extensive system of hydrogen bonding. The parallel reaction of $[Mo(N_2)_2(depe)_2]$ yields only one product, tentatively formulated as $[Mo(BF_4)(NNH_2)(depe)_2]BF_4$. The relevance of these observations to the mechanism of the protonation of complexed dinitrogen is discussed.

We have previously shown that the reaction of $[M(N_2)_2(depe)_2]$ (M = Mo or W, depe = $Et_2PCH_2CH_2PEt_2$) with acids HX (X = Cl or Br) in tetrahydrofuran (thf) or benzene can lead to at least two nitrogen-containing products for M = W, whereas the reactions for M = Mo are solvent-dependent and in benzene lead to the complete loss of N_2.[1] The compounds completely characterized by us were $[WCl(NNH_2)(depe)_2]^+$, $[MBr(NNH_2)(depe)_2]^+$, and $[WX(H)(NNH_2)(depe)_2]^{2+}$.[1] In this paper we describe analogous reactions of $[M(N_2)_2(depe)_2]$ with HBF_4, which produce compounds homologous with those cited above as well as a completely new species.

Results

The reaction of $[Mo(N_2)_2(depe)_2]$ with $HBF_4{\cdot}Et_2O$ in benzene yields a red-brown solid however many molar equivalents of acid are used. The product analysed fairly closely for $Mo(NNH_2)(depe)_2(BF_4)_2$ (see Experimental section). The ^1H n.m.r. spectrum shows distorted ethyl resonances, phosphine bridging-methylene signals, and a signal at δ 7.11 which disappears upon addition of D_2O. We assign this last to NH_2. Similar spectra are also to be expected from $[MoF(NNH_2)(depe)_2]BF_4$, and our new complex analytically, spectrally, and conductometrically would at first sight appear to be $[Mo(BF_4)(NNH_2)(depe)_2]BF_4$. However, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at room temperature displays a singlet plus a quintet, and the singlet is not easy to account for. The quintet is consistent with splitting by four equivalent fluorides of co-ordinated BF_4^-. On cooling to −70 °C the quintet became a doublet, suggesting freezing out of the form $F_3B\text{–}F\rightarrow Mo$. However, the singlet had an intensity which varied from preparation to preparation, occasionally reaching as much as 30% of the total signal intensity, and it also increased with time, so this could be due to decomposition.

The ^{19}F n.m.r. spectrum at room temperature is a broad singlet, changing to a multiplet plus singlet at −50 °C, and a quartet of pentuplets plus a doublet at −70 °C. This is also consistent with a structure $F_3B\text{–}F\rightarrow Mo$.[2] Consistent with this and with the implied BF_4 ionic/bound exchange, the $^{11}B\text{-}\{^1H\}$ n.m.r. spectrum at room temperature is a single broad resonance. We therefore tentatively propose the formulation $[Mo(BF_4)(NNH_2)(depe)_2]BF_4$.



Scheme. (*i*) HBr, HCl, or HBF_4; (*ii*) HBF_4

In contrast, the reaction of $[W(N_2)_2(depe)_2]$ with $HBF_4{\cdot}Et_2O$ gives rise to at least three products, all unequivocally characterized, namely $[WF(NNH_2)(depe)_2]BF_4$ (**A**; X = F), $[WH(F)(NNH_2)(depe)_2][BF_4]_2$ (**B**; X = F), and $[WF(NNH_3)$-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Final atomic co-ordinates (fractional $\times 10^4$) for $[WF(NNH_2)(depe)_2]BF_4$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	7 823.9(2)	8 749.9(2)	5 000	C(4)	7 974(5)	9 896(5)	4 833(9)
C(11)	8 317(10)	8 310(9)	6 690(12)	P(4)	7 488(1)	9 281(1)	4 827(2)
C(12)	8 448(12)	8 046(13)	7 198(16)	C(41)	7 177(5)	9 224(6)	3 775(10)
C(13)	8 619(8)	8 256(7)	4 840(10)	C(42)	7 069(7)	9 621(7)	3 525(11)
C(14)	8 731(7)	7 885(9)	4 946(18)	C(43)	7 092(6)	9 234(6)	5 782(9)
P(1)	8 118(1)	8 219(1)	5 497(2)	C(44)	6 971(7)	9 605(7)	5 900(12)
C(1)	7 682(8)	7 597(7)	5 203(18)	F(5)	7 716(3)	8 783(3)	6 348(4)
C(2)	7 237(11)	7 538(10)	5 511(21)	N(6a)	7 956(4)	8 715(4)	3 845(8)
P(2)	7 083(1)	7 984(1)	4 988(2)	N(6b)	8 074(4)	8 730(4)	2 958(5)
C(21)	6 841(12)	7 728(10)	3 878(16)				
C(22)	6 760(8)	7 918(8)	3 233(10)	The disordered BF_4^- ion			
C(23)	6 586(10)	7 887(10)	5 707(21)	B(70)	9 404(5)	7 599(5)	7 466(8)
C(24)	6 510(12)	7 802(13)	6 449(14)	F(71)	9 316(5)	7 445(5)	6 642(7)
C(31)	8 934(5)	9 626(5)	6 198(8)	F(72a)[a]	9 564(7)	8 066(5)	7 566(9)
C(32)	9 322(6)	10 103(7)	6 377(10)	F(73a)[a]	9 794(9)	7 577(12)	7 771(15)
C(33)	8 914(5)	9 783(6)	4 269(8)	F(74a)[a]	9 052(7)	7 329(6)	8 018(10)
C(34)	9 198(6)	9 569(7)	4 012(11)	F(72b)[b]	9 862(8)	7 888(12)	7 644(19)
P(3)	8 533(1)	9 518(1)	5 262(2)	F(73b)[b]	9 280(12)	7 274(9)	8 156(14)
C(3)	8 340(5)	9 953(5)	5 513(9)	F(74b)[b]	9 139(32)	7 810(35)	7 451(69)

[a] Site occupancy factor 0.75. [b] Site occupancy factor 0.25.

Table 2. Selected bond dimensions (lengths in Å, angles in °) for $[WF(NNH_2)(depe)_2]BF_4$ with e.s.d.s in parentheses

(*a*) In the co-ordination sphere of tungsten			
W–P(1)	2.496(4)	W–P(3)	2.470(3)
W–P(2)	2.484(4)	W–P(4)	2.508(4)
W–F(5)	2.027(6)	W–N(6a)	1.771(12)
P(1)–W–P(2)	79.6(1)	P(2)–W–N(6a)	94.4(4)
P(1)–W–P(3)	99.9(1)	P(3)–W–P(4)	79.7(1)
P(1)–W–P(4)	168.6(1)	P(3)–W–F(5)	83.9(2)
P(1)–W–F(5)	83.8(2)	P(3)–W–N(6a)	94.5(4)
P(1)–W–N(6a)	92.4(4)	P(4)–W–F(5)	84.9(2)
P(2)–W–P(3)	171.1(1)	P(4)–W–N(6a)	98.9(4)
P(2)–W–P(4)	99.0(1)	F(5)–W–N(6a)	175.6(6)
P(2)–W–F(5)	87.3(2)		
(*b*) Torsion angles in the diphosphine ligands			
P(1)–C(1)–C(2)–P(2)	56.6(23)	P(3)–C(3)–C(4)–P(4)	54.6(12)
(*c*) In the hydrazido(2−) ligand and N–H ··· F hydrogen bonds			
N(6a)–N(6b)	1.355(13)	W–N(6a)–N(6b)	175.0(10)
N(6b) ··· F(5^{I})	2.869(11)	N(6a)–N(6b) ··· F(5^{I})	131.2(8)
N(6b) ··· F($72b^{II}$)	2.74(4)	N(6a)–N(6b) ··· F($72b^{II}$)	104.8(10)

Roman superscripts denote symmetry-related positions: I $x, 1 + x - y, z - 0.5$; II $1 - x + y, y, z - 0.5$.

$(depe)_2][BF_4]_2$ (**C**). The interconversions of these and related materials are presented in the Scheme. Some of them were described in a previous paper.[1] In addition, the ^1H and ^{31}P n.m.r. spectra of (**B**), which effectively confirm the structure as shown in the Scheme, were described along with those of the corresponding chlorides and bromides. The interconversions are conveniently followed by ^{31}P n.m.r. spectroscopy (see below).

In general, in benzene solvent the higher the amount of acid used the more likely is the hydrazidium (NNH_3^-) to be the product. However, in contrast, CH_2Cl_2 as solvent favoured the hydride–hydrazide. For n.m.r. measurements, samples were prepared *in situ* in C_6H_6 or CH_2Cl_2 using aliquots of a standard solution of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2.

The hydrazido(2−)-complex (**A**) is also conveniently prepared by addition of 2 molar equivalents of $HBF_4{\cdot}Et_2O$ to the dinitrogen complex, or by treatment of (**B**) or (**C**) with 1 molar equivalent of base. The presence of BF_4^- seems necessary for the formation of (**C**), which is apparently metastable with respect to its isomer (**B**). Reaction of (**A**; X = Br) with HBF_4 and of (**A**; X = F) with HBr yielded (**B**; X = Br or F). The formation of (**C**; X = F) is best achieved by treatment of the dinitrogen complex with an excess of $HBF_4{\cdot}Et_2O$ in benzene. In more polar solvents, such as CH_2Cl_2, the product is (**B**; X = F). Complex (**C**), once prepared and then dissolved in CH_2Cl_2, slowly yields (**B**), as does (**A**; X = F), presumably due to the traces of HCl produced by photolysis.

Complexes (**B**) and (**C**) have the same analyses, but are clearly distinguished by the ^{31}P n.m.r. spectra. We initially attempted to determine the structure of (**C**) by *X*-ray crystal-structure analysis. The crystals we prepared eventually proved to be of (**A**), whose structure we now describe. Atomic co-ordinates and selected molecular dimensions are shown in Tables 1 and 2.

The cation (Figure) is an octahedrally co-ordinated complex in which the fluoro- and hydrazido(2−)-ligands are mutually *trans*. The hydrazido(2−)-ligand is effectively linear and has normal dimensions (*cf.* Table 6 of ref. 1). Although the two hydrogen atoms of this ligand were not located in the analysis, the alignment of the NH_2 group is inferred from the positions of two neighbouring F atoms, the acceptor atoms of N–H ··· F hydrogen bonds. One of these F atoms is F(5) of the cation related by glide-plane symmetry and the cations are thus linked in chains through the crystal parallel to the *c* axis. The second hydrogen bond is to F(72b), one of the disordered atoms (with site occupancy 0.25) of the BF_4^- anion; thus only one in four cations in the crystal forms the second hydrogen bond, presumably because in this orientation the anion also comes into very close contact with a methyl group of another cation, F(74b) ··· C(12) 2.77(10) Å. Contacts from the anion in its major orientation are all at normal van der Waals distances.

The four P atoms form a shallow tetrahedral arrangement in the 'equatorial plane' and the W atom is displaced from their mean plane by 0.2 Å towards the hydrazido(2−)-ligand. The W–P and other distances (Table 2) are very similar to those in $[WBr(NNH_2)(depe)_2]Br$[1] and the depe ligands have the normal P–C–C–P *gauche* links. Some of the ethyl group atoms have large thermal parameters (which may, in fact, hide resolution of disordered groups in one or two instances). All

Table 3. Spectroscopic data for the new complexes

Complex	^{1}H N.m.r.[a] CH$_3$	PCH$_2$	NH$_2$[b]	^{31}P-{^{1}H} N.m.r.[c]	^{19}F N.m.r.[d]	I.r.[e]
$[Mo(BF_4)(NNH_2)(depe)_2]BF_4$	0.95—1.48 (br, m, 24)	1.68—2.30 (br, m, 24)	6.80—7.20 (br, s, 2)	−90.13 (qnt, J = 6), −92.65	−155.5 (s, 8), −153.8 (s, 4), −167.0 (br s, 1)	ν(NH) 3 150 ν(BF) 1 020—1 120
$[WF(NNH_2)(depe)_2]BF_4$ (**A**)	0.75—1.35 (br, m, 24)	1.40—2.35 (br, m, 24)	4.40—4.90 (br, m, 2)	−102.29, −102.69 (d, J_{PF} = 48.6, J_{WP} = 280.7, 280.7)	−150.8 (s, 4), −190.2 (t, 1)	ν(NH) 2 932 ν(BF) 1 040—1 140
$[WH(F)(NNH_2)(depe)_2][BF_4]_2$ (**B**)	1.00—1.60 (br, m, 24)	1.75—2.98 (br, m, 24)	6.84—7.04 (br, s, 2)	AA′BB′X pattern, see ref. 1	−148.7 (s, 8), −192.3 (m, 1)	ν(NH) 2 937 ν(BF) 1 040—1 140 ν(WH) 1 896
$[WF(NNH_3)(depe)_2][BF_4]_2$ (**C**)	0.88—1.45 (br, m, 24)	1.53—2.31 (br, m, 24)	6.73—7.96[f] (br, s, 3)	−103.23, −104.49 (d, $^2J_{PF}$ = 45.7, J_{WP} = 266.7, 269.3)	−155.6 (s, 8), −188.8 (m, 1)	ν(NH) 3 140 ν(BF) 1 090(br)

Abbreviations: m = multiplet, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet. [a] In CD_2Cl_2 [b] Disappeared upon addition of water. [c] In p.p.m. *vs.* trimethyl phosphite, J in Hz. [d] In p.p.m. *vs.* $CFCl_3$. [e] In cm^{-1}; KBr discs. [f] NH_3.

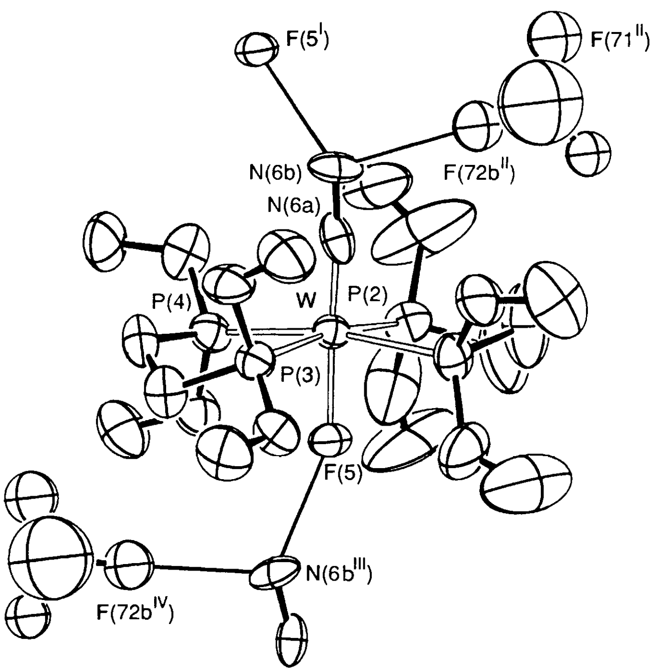

Figure. Representation of the molecular structure of $[WF(NNH_2)(depe)_2]^+$, showing the octahedral co-ordination about the tungsten and the extensive intermolecular hydrogen bonding between cations and with the BF_4^- counter ions

ethyl hydrogen atoms have been constrained to idealized staggered arrangements. However, these reservations apart, the structure of $[WF(NNH_2)(depe)_2]BF_4$ reveals no unexpected features. The hydrogen bonding between the hydrazide and the counter anion is very characteristic of this class of compound, and also, we suspect, of the hydrazidium(1−) complex (**C**), to be discussed now.

Table 3 shows the ^{1}H and ^{31}P-{^{1}H} n.m.r. and i.r. spectra of the new complexes. Complexes (**A**) and (**B**) are structurally characterized unequivocally (see above, and ref. 1) and the only query surrounds (**C**). The ^{31}P n.m.r. spectrum (doublet, due to P–F coupling) shows clearly that the compound has equivalent phosphorus atoms, so that the extra hydron must be associated with the fluoride or with the dinitrogen residue, either in the form $NHNH_2$ or NNH_3. The ^{15}N n.m.r. data (Table 4) show unequivocally that the NNH_3 configuration is adopted, since the proton-coupled spectrum shows a quartet arising from three hydrons co-ordinated to the β-nitrogen atom, whereas the only coupling evident to the other nitrogen atom is with the *trans*-fluoride.

This compound is the second example of a hydrazidium(1−) complex,[3] and the first that is stable in solution. To form it, the phosphine ligands must be strong donors, in this case depe, but in the first example PMe_3.[3] It is apparent that strong hydrogen bonding is also a requirement. It is probable that in the case of $[WCl(NNH_3)(PMe_3)_4]^+$ the lability in solution is due to the break up of the hydrogen-bonding network discernible in the *X*-ray crystal structure of the solid. In the present case, only $HBF_4{\cdot}Et_2O$ seems capable of generating the structure, which in solution slowly isomerizes to the hydride–hydrazide.

It has been proposed[4] that the hydrazidium(1−) moiety is a key intermediate in the protonation of co-ordinated dinitrogen to ammonia, although the evidence is mainly circumstantial. However, it is known that all six available electrons in an appropriate tungsten(0) dinitrogen complex can be used to reduce one dinitrogen molecule to two ammonia molecules.[5] That has been observed in complexes with monodentate phosphines, which are lost from the tungsten during the reaction. It may be possible in the present case to split the nitrogen–nitrogen bond of the hydrazidium(1−) without reduction[6] or loss of phosphine, but this is unlikely to be spontaneous because the tungsten residue is in an oxidation state and stoicheiometry which would lead to a tungsten(VI) complex of a type currently unknown: $[WF(NNH_3)(depe)_2]^{2+} \longrightarrow [WF(N)(depe)_2]^{2+} + NH_3$. However, it might be feasible to encourage nitrogen–nitrogen bond splitting by adding a suitable reagent with low hydrogen basicity but high affinity for tungsten(VI). Preliminary experiments with $NaOC_6H_4Me$-4 have not been successful.

The data in Table 4 also require some comment in terms of the reaction series $N_2 \longrightarrow NNH_2 \longrightarrow NNH_3$. The ^{31}P-{^{1}H} n.m.r. chemical shifts show no sensible changes along the series. Even the tungsten(0) complex has shifts not very different from those of the tungsten(IV) compounds. The hydride–hydrazide resonance differs significantly from those of the other three compounds and is to lower field. The ^{15}N shifts are much more informative. They move to higher field in the sequence $NNH_3 > NNH_2 > N_2$ whether one considers the α-nitrogen atoms or the β-nitrogen atoms. The values fall into the ranges already delineated by others,[7] and are to some extent diagnostic of structure. It is nevertheless remarkable that the relative high-field and low-field shifts of the two nitrogen atoms in the

Table 4. Phosphorus-31 and ^{15}N n.m.r. spectra of tungsten complexes[a] (J in Hz)

Complex	^{31}P N.m.r. (p.p.m.)	^{15}N N.m.r. (p.p.m.)
$[W(N_2)_2(depe)_2]$	s, at -104.2	-67.1, -55.8 (s, α- and β-N, respectively)[b]
$[WF(NNH_2)(depe)_2]BF_4$	d, centred at -102.49, $J_{PF} = 48.6$	-98.94, -101.37, $J_{NF} = 66$ (d) (α-N)[c] -252.52, INEPT triplet gives $J_{NH} = 80$ (β-N)
$[WHF(NNH_2)(depe)_2][BF_4]_2$	AA′BB′X, centred at -84.10, mean $J_{PF} = 29.4$[d]	-79.28, -81.96, $J_{NF} = 72$ (d) (α-N) -238.29, -241.53, -244.80, $J_{NH} = 89$ (1:2:1 t) (β-N)
$[WF(NNH_3)(depe)_2][BF_4]_2$	d, centred at -103.86, $J_{PF} = 46.9$	-158.38, -160.80, $J_{NF} = 67$ (d) (α-N) -282.70, -285.79, -288.61, -290.76, $J_{NH} = 82$ (1:4:4:1 q) (β-N)

[a] Generally in CH_2Cl_2. [b] In thf. [c] In benzene. [d] See ref. 1.

dinitrogen complex should be in the opposite sense to the relative shifts of the corresponding nitrogen atoms in the other three complexes. The β-nitrogen atom in the dinitrogen complex is likely to be the more negative of the two,[8] and it is possible that the relative positions reflect the fact that the β-nitrogen atom becomes more positive than the α-nitrogen atom upon protonation. If this is so, the trend in the α-nitrogen atom shifts is also consistent with the degree of protonation. The only exception might then be the α-nitrogen shift in the hydride–hydrazide. Of course, this complex has a geometry rather different from the octahedra of the other three molecular species, so other factors are probably also at work.

Experimental

All compounds were handled in an atmosphere of pure dry dinitrogen, and all solvents were dried as appropriate and distilled under dinitrogen before use. The compounds $Et_2PCH_2CH_2PEt_2$[9] and $[M(N_2)_2(depe)_2]$ (M = Mo or W)[10] were prepared as described elsewhere, with the method slightly modified for the synthesis of $[W(^{15}N_2)_2(depe)_2]$. Spectra were recorded using Perkin-Elmer 883 and JEOL FX9Q and 270GS spectrometers. Analyses were carried out at the AFRC Nitrogen Fixation Laboratory using a Perkin-Elmer 2400 analyser. Melting points were determined in sealed tubes using an Electrothermal apparatus and are uncorrected. Conductivities were obtained using a Portland Electronics bridge.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*][*hydrazido*(2 −)]*tetrafluoroboratomolybdenum Tetrafluoroborate.*—To $[Mo(N_2)_2(depe)_2]$ (0.58 g, 1.02 mmol) in benzene (20 cm^3) was added ethereal HBF_4 (1.65 g of nominally 54% HBF_4, 10.2 mmol). The mixture was stirred vigorously for 0.5 h, and then taken to dryness *in vacuo* leaving a purple oil. This was extracted with dichloromethane (20 cm^3). The extract was reduced to *ca.* 10 cm^3, and diethyl ether (20 cm^3) added. After 24 h, brown-red crystals were filtered off and recrystallized from dichloromethane–n-hexane. Yield 0.62 g, 85%. Molar conductance ($MeNO_2$) = 48.0 ohm^{-1} cm^2 mol^{-1}, m.p. 179–181 °C (decomp.) (Found: C, 32.6; H, 7.05; N, 3.75. $C_{20}H_{50}B_2F_8MoN_2P_4$ requires C, 33.7; H, 7.0; N, 3.95%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*fluoro*[*hydrazido*(2 −)]*hydridotungsten Bis*(*tetrafluoroborate*) (**B**; X = F).—To a solution of $[W(N_2)_2(depe)_2]$ (0.39 g, 0.59 mmol) in benzene (25 cm^3) was added ethereal HBF_4 (0.38 g of nominally 54% HBF_4, 2.35 mmol). The brown solution was stirred for 0.5 h, by which time it had turned yellow-brown. This was filtered through Celite, and the filtrate taken to dryness *in vacuo*. The residue was extracted with dichloromethane, an excess of diethyl ether added, and the solution stored at −5 °C for 15 h, yielding pale yellow crystals, 0.20 g (41%), m.p. 181–183 °C, $\Lambda_M(MeNO_2)$ = 146 ohm^{-1} cm^2 mol^{-1} (Found: C, 29.3; H, 6.0; N, 3.75. $C_{20}H_{51}B_2F_9N_2P_4W$ requires C, 29.3; H, 6.25; N, 3.40%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*fluoro*[*hydrazido*(2 −)]*tungsten Tetrafluoroborate* (**A**; X = F).—From the mother-liquor from the recrystallization above, after 2—3 weeks at −5 °C, about 0.10 g of yellow crystals was separated. These were filtered off, washed with diethyl ether, and dried *in vacuo*. Yield *ca.* 23%, m.p. 145–147 °C, Λ_M = 71 ohm^{-1} cm^2 mol^{-1} (Found: C, 33.1; H, 6.90; N, 3.80. $C_{20}H_{50}BF_5N_2P_4W$ requires C, 32.8; H, 6.90; N, 3.85%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*fluoro*[*hydrazidium*-(1 −)]*tungsten Bis*(*tetrafluoroborate*) (**C**).—To a solution of $[W(N_2)_2(depe)_2]$ (0.40 g, 0.61 mmol) in benzene (30 cm^3) was added ethereal HBF_4 (0.98 g of nominally 54% HBF_4, 6.05 mmol) and the mixture stirred for 0.5 h. The red-pink precipitate was filtered off, washed with benzene (2 × 2 cm^3), and dried *in vacuo*. The solid was recrystallized from dichloromethane–diethyl ether. Yield 0.34 g (67%), m.p. 155—157 °C (Found: C, 29.0; H, 6.10; N, 3.40. $C_{20}H_{51}B_2F_9N_2P_4W$ requires C, 29.3; H, 6.25; N, 3.40%).

Samples prepared for n.m.r. analysis only were obtained as follows.

Compound (**A**; X = F). About 40 mg of $[W(N_2)_2(depe)_2]$ were dissolved in CH_2Cl_2 (5 cm^3) and 1.5 equivalents of a stock solution of $HBF_4{\cdot}Et_2O$ (0.5 cm^3) in CH_2Cl_2 (50 cm^3) added. The solution was taken to dryness, redissolved in C_6H_6 (4 cm^3), and filtered. The filtrate (plus a trace of C_6D_6 to provide a lock) was examined spectroscopically.

Compound (**B**; X = F). About 40 mg of $[W(N_2)_2(depe)_2]$ were dissolved in CH_2Cl_2 (5 cm^3) and 3 equivalents of $HBF_4{\cdot}Et_2O$ stock solution added. After filtration, and addition of a trace of CD_2Cl_2, the filtrate was examined spectroscopically.

Compound (**C**). About 40 mg of $[W(N_2)_2(depe)_2]$ were dissolved in C_6H_6 (10 cm^3) and 6 equivalents of $HBF_4{\cdot}Et_2O$ added. The solution was stirred for 0.5 h, filtered, and the filtrate taken up in CH_2Cl_2–CD_2Cl_2, and examined spectroscopically.

These procedures were the only ones used with $[W(^{15}N_2)_2(depe)_2]$.

X-*Ray Structure Analysis of* $[WF(NNH_2)(depe)_2]BF_4$.—*Crystal data.* $C_{20}H_{50}B_5F_5N_2P_4W$, M = 732.2, rhombohedral, space group $R3c$ (no. 161) obverse hexagonal cell, $a = b$ = 32.962(8), c = 14.707(5) Å, U = 13.838 Å^3, Z = 18, D_c = 1.581 g cm^{-3}, $F(000)$ = 6 624, T = 293 K. μ(Mo-K_α) = 40.8 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0.710 69 Å.

The orange-yellow irregularly shaped crystals were air-sensitive; one, *ca.* 0.57 × 0.50 × 0.42 mm, was sealed under dry dinitrogen in a glass capillary. After photographic examination, the crystal was transferred to our Enraf-Nonius diffractometer (with monochromator) for determination of accurate cell parameters (from the goniometer settings of 25 reflections with θ *ca.* 10.5°) and measurement of diffraction intensities (to $\theta_{max.}$ = 20°). The intensity data were corrected for Lorentz-polarization effects, slight deterioration, and to ensure no negative intensities; an absorption correction was not possible as the crystal had moved in the capillary tube. A complete hemisphere of data (8 732 reflections) was recorded; equivalences (but not Friedel opposites) were merged to yield 2 861 reflections which were input into the SHELX system.[11]

The W and P atoms were located by the automated Patterson routines of SHELXS,[12] and the remaining non-hydrogen atoms were found in subsequent electron-density and difference Fourier maps. Hydrogen atoms in the depe ligands were included in idealised positions and set to ride on their bonded C atoms; the hydrazide(2−) hydrogen atoms were not located. The BF_4^- ion was found to be disordered, in *ca.* 3:1 occupancy ratio, over two orientations which have one common B–F bond. It was necessary to apply geometrical restraints, *viz.* B–F distances of 1.36(2) Å, to the disordered bonds of this ion. All non-hydrogen atoms in the cation were refined anisotropically; those in the anion were treated isotropically.

Refinement was by full-matrix least-squares methods, and at convergence $R = 0.051$, $R' = 0.037$[11] for all 2 861 reflections weighted $w = \sigma_F^{-2}$. With the same intensity data, the inverted structure (at $\bar{x}, \bar{y}, \bar{z}$) was refined to $R = 0.074$, $R' = 0.066$ and the estimated standard deviations (e.s.d.s) on all parameters were significantly poorer.

A final difference map showed several high peaks (*ca.* 2 e Å^{-3}) close to the W atom, but nothing of significance away from that region.

Scattering curves for neutral atoms, including the anomalous dispersion terms, were from ref. 13. Computer programs used in this analysis have been noted above and in Table 4 of ref. 14, and were run on the VAX 11/750 machine of the AFRC-Institute of Horticultural Research Littlehampton Laboratory (Glasshouse Crops Research Institute).

Acknowledgements

We thank the Malaysian Government and the Universiti Sains Malaysia for financial support to H. M-A. and M. A. B., respectively.

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Received 8*th December* 1989; *Paper* 9/05248H