Organic Chemistry of Dinitrogen and Related Ligands. Part 6.[1] Crystal and Molecular Structure of $[WBr(dppe)_2\{N_2CN(Me)CH_2CH_2NMe\}]$-$[PF_6]$ (dppe = $Ph_2PCH_2CH_2PPh_2$),† a Complex in which Fluxional Behaviour results from Steric Destabilisation of the Ground State

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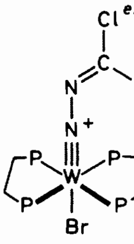
Diaminodiazomethane complexes $[WBr(dppe)_2\{NN{=}C(NHR)_2\}]^+$, which are obtained by reactions of the cationic dichlorodiazomethane complex $[WBr(dppe)_2(NN{=}CCl_2)]^+$ with primary amines, are rigid on the n.m.r. time-scale at 30 °C because of restricted rotation ($\Delta G^\ddagger > 57$ kJ mol^{-1}) about the formal carbon–nitrogen double bond. In contrast, the cyclic analogues $[WBr(dppe)_2\{NN{=}CN(R)(CH_2)_nNR\}]^+$ (R = Me or Et, n = 2 or 3) which are prepared by the action of di-secondary amines on the dichlorodiazomethane complex, are fluxional under the same conditions ($\Delta G^\ddagger = 40$ kJ mol^{-1}) with rapid rotation about the $C{=}N_2$ bond. A single-crystal *X*-ray study of $[WBr(dppe)_2\{NN{=}CN(Me)CH_2CH_2NMe\}][PF_6]$ reveals extreme steric strain due to interligand repulsions involving one of the N-methyl groups, implying that the much-reduced rotational barrier in this type of complex results from a greatly heightened ground-state energy. The complex crystallises in the triclinic space group $P\bar{1}$, with unit-cell parameters a = 12.546(3), b = 14.332(3), c = 17.174(3) Å, α = 74.07(1), β = 76.79(2), γ = 87.05(2)°, and Z = 2. The structure was solved by the heavy-atom method and refined to R = 0.047 for 5 502 independent observed reflections.

Ligating dichlorodiazomethane, in the dinitrogen-derived tungsten complex $[WBr(dppe)_2(NN{=}CCl_2)]^+$ (1) [dppe = 1,2-bis(diphenylphosphino)ethane], has proved a versatile source of novel organodinitrogen ligands, since one or both chlorine atoms are readily replaced by a wide range of nucleophiles.[2] The nature of the substituted complex is determined by both electronic and steric factors, so that although primary amines NH_2R yield disubstituted derivatives $[WBr(dppe)_2\{NN{=}C(NHR)_2\}]^+$ (2), the somewhat bulkier secondary amines NHR_2 afford only *exo*-monosubstituted complexes (3). This is consistent with crystallographic evidence[3] that *endo*-substituents in analogous compounds lie in a sterically crowded position between two phenyl rings of a diphosphine ligand.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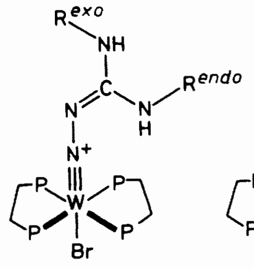
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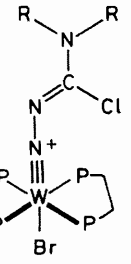
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Where cyclisation is possible however, di-secondary amines, $RNH(CH_2)_nNHR$ (R = Me or Et throughout, n = 2 or 3), *do* yield disubstituted products (4), the ^1H n.m.r. spectra of which, at ambient temperature (30 °C) display a curious equivalence of the alkyl groups R. In contrast, the acyclic compound (2; R = Me), derived from methylamine, shows two quite distinct singlet resonances (3 H each), assigned to the *exo*- and *endo*-methyl groups, at δ 2.76 and 1.12 p.p.m. respectively. In view of this difference, one of us has suggested[2] that the greater steric congestion of the cyclic structure (4) (where the *endo* N-alkyl group is forced towards the plane of the phosphine ligands) may result in a rotation of 90° about the formal $C{=}N_2$ double bond to reduce the steric strain. This would lead to equivalence of the R groups, and the resulting (static) amidiniodiazenido structure (5) is electronically quite feasible. An alternative explanation is that rapid rotation about the formal $C{=}N_2$ double bond occurs in the ligands derived from disecondary amines but not in those derived from primary amines. In order to resolve this question we have carried out a single-crystal *X*-ray study of $[WBr(dppe)_2\{N_2CN(Me)CH_2CH_2NMe\}][PF_6]$ and low-temperature ^1H n.m.r. studies of this compound and its unsubstituted analogue, $[WBr(dppe)_2(N_2CNHCH_2CH_2NH)][PF_6]$.

Results and Discussion

The *X*-ray structure of the title compound (Figures 1 and 2; Tables 1, 2, and 3) reveals that, in the solid state, the organonitrogen ligand adopts the 'planar' diaminodiazomethane conformation (4) rather than the 'twisted' amidiniodiazenido form (5). There is however much evidence of extreme steric strain within the complex, notably in the 17° deviation from linearity at N(1) (this deviation is typically[1,2] no more than 10°), in the non-coplanarity of W, N(1), N(2), and C(53) which results in a torsion angle of −166° about the N(1)–N(2) bond, in the wide variation in bond angles at C(53) (118, 131, 111°), in the partial pyramidalisation of N(3) whereby C(56) lies 20° or 0.64 Å out of the least-squares plane formed by N(2), N(3), N(4), and C(53), and finally in the 'skewed'

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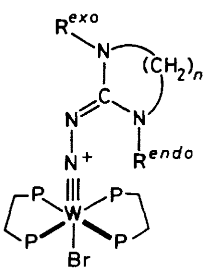
† *trans*-Bis[1,2-bis(diphenylphosphino)ethane]bromo(2-diazo-1,3-dimethyl-1,3-diazacyclopentane-N^β)tungsten hexafluorophosphate.

Supplementary data available (No. SUP 23952, 39 pp.): H-atom co-ordinates, thermal parameters, structure factors, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 398(1)	1 777(1)	1 879(1)	C(35)	3 702(10)	−1 848(8)	1 715(7)
Br(1)	3 341(1)	1 071(1)	645(1)	C(36)	2 956(10)	−2 564(8)	1 851(7)
P(1)	2 967(2)	3 386(2)	822(1)	C(37)	1 919(10)	−2 509(7)	2 293(7)
P(2)	4 333(2)	1 905(2)	2 014(1)	C(38)	1 608(8)	−1 711(6)	2 593(5)
P(3)	1 976(2)	99(1)	2 841(1)	C(39)	461(7)	59(6)	3 174(5)
P(4)	512(2)	1 503(1)	1 669(1)	C(40)	−45(7)	343(5)	2 426(5)
C(1)	3 149(7)	3 496(6)	−285(5)	C(41)	116(7)	1 372(5)	737(5)
C(2)	2 229(8)	3 518(7)	−585(6)	C(42)	864(8)	1 437(6)	−8(5)
C(3)	2 294(9)	3 580(7)	−1 420(6)	C(43)	521(9)	1 354(7)	−687(6)
C(4)	3 287(11)	3 659(8)	−1 965(7)	C(44)	−538(10)	1 171(7)	−633(7)
C(5)	4 217(10)	3 676(8)	−1 680(6)	C(45)	−1 295(10)	1 083(7)	90(6)
C(6)	4 157(9)	3 596(8)	−831(6)	C(46)	−971(8)	1 179(6)	762(6)
C(7)	2 210(7)	4 490(5)	886(5)	C(47)	−504(7)	2 394(5)	1 950(5)
C(8)	2 648(8)	5 386(6)	367(6)	C(48)	−739(7)	3 170(6)	1 346(6)
C(9)	2 091(9)	6 236(6)	425(6)	C(49)	−1 469(8)	3 868(7)	1 534(7)
C(10)	1 084(8)	6 194(6)	980(6)	C(50)	−1 954(8)	3 805(7)	2 343(7)
C(11)	671(8)	5 325(6)	1 481(6)	C(51)	−1 741(9)	3 034(7)	2 947(7)
C(12)	1 223(7)	4 467(6)	1 433(5)	C(52)	−1 020(8)	2 330(7)	2 768(6)
C(13)	4 335(7)	3 696(6)	922(5)	C(53)	914(7)	3 096(6)	3 656(5)
C(14)	5 036(7)	2 804(6)	1 086(5)	C(54)	841(9)	4 652(7)	3 790(6)
C(15)	4 444(7)	2 369(6)	2 865(5)	C(55)	−136(8)	4 080(6)	4 385(6)
C(16)	3 756(7)	1 982(6)	3 633(5)	C(56)	2 478(8)	4 169(7)	2 891(6)
C(17)	3 787(9)	2 282(7)	4 321(6)	C(57)	−570(9)	2 286(7)	4 833(6)
C(18)	4 550(10)	3 017(9)	4 235(7)	N(1)	1 752(5)	2 209(4)	2 745(4)
C(19)	5 243(9)	3 420(8)	3 480(7)	N(2)	1 155(6)	2 267(4)	3 462(4)
C(20)	5 192(8)	3 087(8)	2 790(6)	N(3)	1 341(6)	3 983(5)	3 296(4)
C(21)	5 285(7)	888(6)	2 090(5)	N(4)	93(6)	3 104(5)	4 306(4)
C(22)	5 519(9)	405(7)	2 834(6)	P(5)	8 430(3)	7 009(2)	3 669(2)
C(23)	6 206(11)	−402(8)	2 917(7)	F(1)	9 649(6)	6 747(6)	3 722(5)
C(24)	6 617(9)	−732(8)	2 237(7)	F(2)	8 048(7)	6 429(6)	4 609(5)
C(25)	6 390(8)	−288(7)	1 473(7)	F(3)	7 210(6)	7 269(6)	3 647(5)
C(26)	5 732(8)	536(7)	1 397(6)	F(4)	8 773(8)	7 568(7)	2 746(5)
C(27)	2 378(8)	−255(5)	3 842(5)	F(5)	8 328(8)	6 063(6)	3 415(6)
C(28)	1 847(9)	139(6)	4 492(5)	F(6)	8 548(8)	7 941(6)	3 929(6)
C(29)	2 193(10)	−101(7)	5 235(6)	O(1) *	3 222(15)	5 857(12)	5 215(11)
C(30)	3 048(10)	−709(8)	5 337(7)	O(2) *	4 746(13)	6 846(11)	3 693(10)
C(31)	3 561(10)	−1 107(9)	4 719(8)	O(3) *	4 898(17)	5 794(14)	4 063(12)
C(32)	3 230(9)	−877(8)	3 975(7)	C(58) *	3 150(20)	6 342(15)	3 975(15)
C(33)	2 337(7)	−965(6)	2 448(5)	C(59) *	3 318(26)	5 744(19)	4 602(16)
C(34)	3 390(8)	−1 037(6)	2 007(6)				

* Disordered solvent fragments, occupancy *ca.* 0.5.



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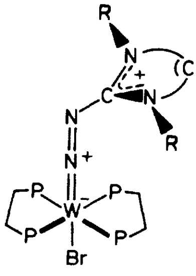

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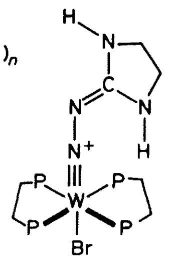


(6)

nature of the co-ordination sphere about tungsten. The phosphorus atoms P(1) and P(2), for example, do not lie orthogonal to the W–N(1) vector, but appear to be forced away from N(1) to give angles N–W–P of 99.1 and 97.0° respectively. The corresponding angles involving P(3) and P(4) are much less affected, and are in fact *narrowed* very slightly (86.2 and 88.5° respectively). It should be noted however that the partial pyramidalisation of N(3) is not accompanied by any increase in the N(3)–C(53) bond length, which does not differ significantly from that of N(4)–C(53), so that there is no apparent loss of double-bond character in the N(3)–C(53) bond.

Inspection of Figures 2 and 3, and of a space-filling molecular model (Figure 4), strongly suggests that *all* the above distortions result from severe non-bonded repulsions between the N-methyl group of C(56) and one of the chelating diphosphine ligands. This result confirms the proposal that the ability of primary but not mono-secondary amines to displace the *endo*-chlorine from (1) is essentially steric in origin, since the NHR group derived from a primary amine can adopt a conformation (2) in which the *endo*-alkyl group R is directed away from the phosphine ligand.

The existence of structure (4) in the solid state proves that, for cyclic structures of this type, the apparent equivalence of the N-alkyl groups R in the ^{1}H n.m.r. spectrum at ambient temperature is a consequence of rapid rotation about the C(53)–N(2) bond. Indeed, at −30 °C the singlet N-methyl resonance (6 H) of the title compound broadens significantly and at −60 °C disappears entirely to be replaced by a singlet (3 H) at δ 0.12. This resonance is assigned to the *endo* N-methyl group, but the signal corresponding to the *exo* N-methyl is obscured by the phosphine methylene resonance centred at δ 3.05. The coalescence temperature is estimated as −60 °C and the associated barrier to rotation, $\Delta G^‡$, is then

Table 2. Selected bond lengths (Å) with e.s.d.s in parentheses

W–Br(1)	2.611(1)	P(1)–C(1)	1.826(9)	P(4)–C(40)	1.860(7)	C(54)–N(3)	1.474(13)
W–P(1)	2.530(2)	P(1)–C(7)	1.819(8)	C(53)–N(2)	1.323(11)	C(55)–N(4)	1.450(12)
W–P(2)	2.511(2)	P(1)–C(13)	1.852(10)	C(53)–N(3)	1.331(10)	C(56)–N(3)	1.440(11)
W–P(3)	2.519(2)	P(2)–C(14)	1.824(7)	C(53)–N(4)	1.337(10)	C(57)–N(4)	1.435(11)
W–P(4)	2.539(2)	P(3)–C(39)	1.854(9)	C(54)–C(55)	1.513(13)	N(1)–N(2)	1.309(9)
W–N(1)	1.776(7)						

Table 3. Selected valence angles (°) with e.s.d.s in parentheses

Br(1)–W–P(1)	83.2(1)	P(2)–W–P(4)	173.9(1)	W–P(2)–C(14)	107.0(3)	W–N(1)–N(2)	163.0(5)
Br(1)–W–P(2)	83.0(1)	P(3)–W–P(4)	79.9(1)	W–P(3)–C(39)	104.1(2)	C(53)–N(2)–N(1)	123.5(6)
P(1)–W–P(2)	79.9(1)	Br(1)–W–N(1)	177.7(2)	W–P(4)–C(40)	107.7(3)	C(53)–N(3)–C(54)	109.9(7)
Br(1)–W–P(3)	91.5(1)	P(1)–W–N(1)	99.1(2)	N(2)–C(53)–N(3)	130.9(7)	C(53)–N(3)–C(56)	123.5(7)
P(1)–W–P(3)	174.3(1)	P(2)–W–N(1)	97.0(2)	N(2)–C(53)–N(4)	118.4(7)	C(54)–N(3)–C(56)	115.5(8)
P(2)–W–P(3)	97.5(1)	P(3)–W–N(1)	86.2(2)	N(3)–C(53)–N(4)	110.6(8)	C(53)–N(4)–C(55)	111.5(7)
Br(1)–W–P(4)	91.4(1)	P(4)–W–N(1)	88.5(2)	C(55)–C(54)–N(3)	103.2(8)	C(53)–N(4)–C(57)	126.2(8)
P(1)–W–P(4)	102.1(1)	W–P(1)–C(13)	106.9(3)	C(54)–C(55)–N(4)	102.5(7)	C(55)–N(4)–C(57)	122.0(7)

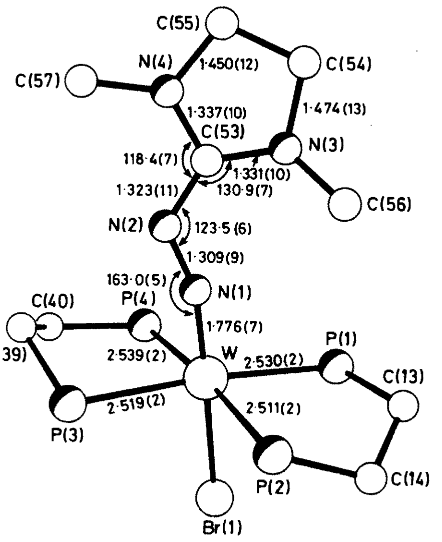


Figure 1. Structure of $[WBr(dppe)_2\{N_2\overline{CN(Me)CH_2CH_2N}Me\}]^+$ (phenyl groups omitted for clarity) showing important bond lengths and angles

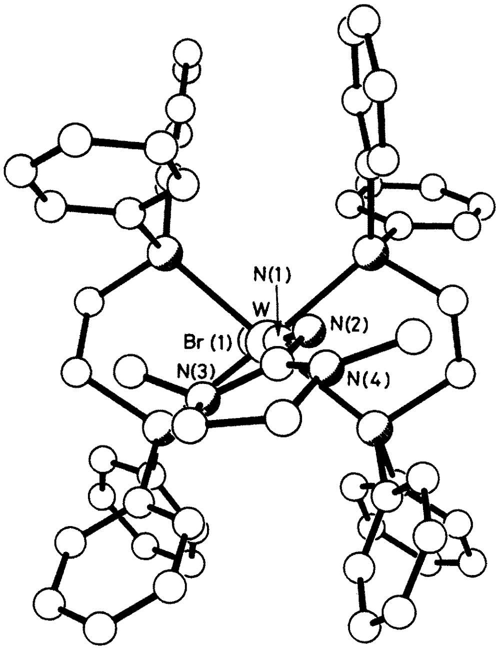


Figure 2. View of the structure along the N(1)–W–Br direction showing the distortions of the organonitrogen ligand, particularly the pyramidalisation of N(3)

40 ± 2 kJ mol^{-1}. Since the signal at δ 1.70 in the spectrum at ambient temperature represents an average of *exo* and *endo* N-methyl chemical shifts, the *exo*-protons should appear at δ 3.28, implying a difference in chemical shift of 3.16 p.p.m. between what are in fact *electronically equivalent* protons. Ring-current shielding by the phenyl groups of a dppe ligand is known[3] to produce substantial chemical shift differences between *exo* and *endo* groups R in the analogous diazoalkane complexes $[WBr(dppe)_2(NN{=}CR_2)]^+$ (R = H, Δδ = 1.44 p.p.m.; R = Me, Δδ = 1.87 p.p.m.), but the present effect (Δδ = 3.16 p.p.m.) is exceptionally large. In contrast, the difference in chemical shift between the N-methyl groups in the 'rigid' complex (2; R = Me) is only 1.66 p.p.m., in keeping with the *endo*-methyl now lying much further from the phenyl rings.

The problem of why the cyclic structure (4) allows 'free' rotation about the C(53)–N(2) bond, when the acyclic structure (2) does not, may now be resolved as follows. Electronically, the ground state for both types of complex is the planar diaminodiazomethane structure, since this permits maximum delocalisation of electron density (Scheme). Rotation about the C(53)–N(2) partial double bond will clearly raise the electronic energy to a maximum at the 90°-twisted, amidiniodiazenido conformation, since π overlap between C(53) and N(2) is then reduced to zero (Figure 3, solid curve). In the acyclic, primary amine derivatives (2), the energy difference ΔE (>57 kJ mol^{-1} for R = Me) between planar and twisted forms is then sufficient to prevent rapid rotation under ambient conditions. For complexes (4), containing cyclic ligands derived from di-secondary amines, however, the extreme steric congestion in the planar conformation apparently destabilises this ground state form relative to the 90°-twisted structure (in which steric repulsions are much less severe) so that the net rotational barrier ΔE′ is reduced (Figure 3, broken curve) and rapid rotation is observed.

As a final check on this interpretation, the non-methylated

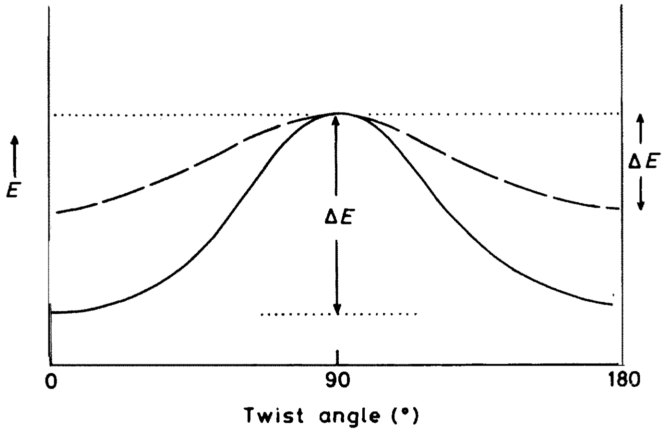
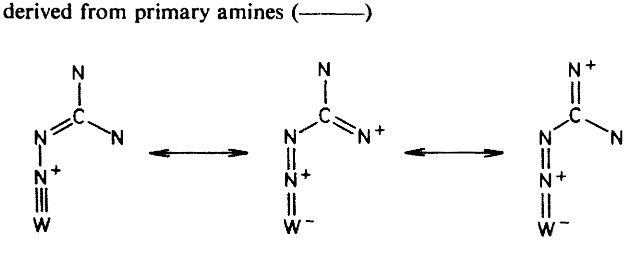


Figure 3. Variation in energy (qualitative) with rotation about the $C{=}N_2$ bond for alkyl-substituted, cyclic diaminodiazomethane ligands (— — —) and for acyclic diaminodiazomethane ligands derived from primary amines (———)



Scheme. Delocalisation of electron density within the diaminodiazomethane–tungsten moiety

analogue of the title complex, $[WBr(dppe)_2(N_2CNHCH_2CH_2NH)][PF_6]$ (6) was prepared, and its low-temperature ^1H n.m.r. behaviour investigated. Coalescence of the N-methylene resonances occurred at +5 °C, and the associated rotational barrier $\Delta G^{\ddagger}$ is then 55 ± 2 kJ mol^{-1}, which though a little lower than that of complex (2; R = Me) (which is more flexible and therefore presumably able to adopt a lower-energy ground-state conformation) is still 15 kJ mol^{-1} higher than the barrier for the title complex.

This result confirms that steric repulsions involving the *endo* N-methyl group are primarily responsible for raising the energy of the ground state and hence for lowering the barrier to rotation about the $C{=}N_2$ bond in the title complex.

Experimental

Variable-temperature ^1H n.m.r. spectra were obtained at intervals of 5 °C on a JEOL FX100 FT spectrometer, using CD_2Cl_2 as solvent. Microanalyses were by the Characterisation and Measurement Group of I.C.I., Mond Division. The complexes $[WBr(dppe)_2(N_2CCl_2)][PF_6]$ and $[WBr(dppe)_2\{N_2C(NHMe)_2\}][PF_6]$ were prepared as described previously.[2] The new complexes $[WBr(dppe)_2\{N_2CN(Me)CH_2CH_2NMe\}][PF_6]$ and $[WBr(dppe)_2(N_2CNHCH_2CH_2NH)][PF_6]$ were obtained by reaction of the dichlorodiazomethane complex (0.2 mmol) with *NN′*-dimethyl-1,2-diaminoethane (1 mmol) and 1,2-diaminoethane (1 mmol) respectively in dichloromethane (10 cm^3).

Characterisation of the Complexes.—trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(2-*diazo*-1,3-*dimethyl*-1,3-*diazacyclopentane*-N$^{\beta}$)*tungsten hexafluorophosphate.* The deep red reaction mixture was evaporated under reduced pressure, and the oily residue recrystallised from dichloromethane–diethyl ether (70% yield) to give an orange-red crystalline solid containing dichloromethane of solvation, m.p. 224 °C (decomp.) (Found: C, 49.2; H, 4.5; N, 3.6. Calc. for $[WBr(dppe)_2\{N_2CN(Me)CH_2CH_2NMe\}][PF_6]{\cdot}CH_2Cl_2$: C, 49.2; H, 4.2; N, 3.9%). Single crystals grown by slow evaporation of a dichloromethane–methanol (1 : 1) solution did not contain dichloromethane but there was evidence for a small amount of unidentified solvent in the *X*-ray crystal structure (see below). The ^1H n.m.r. spectrum at 30 °C contained resonances at δ 7.20 (m, 40 H, $P{-}C_6H_5$), 2.92 (s, br, 8 H, $P{-}CH_2$), 2.84 (s, 4 H, $N{-}CH_2$), and 1.70 p.p.m. (s, 6 H, $N{-}CH_3$).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(2-*diazo*-1,3-*diazacyclopentane*-N$^{\beta}$)*tungsten hexafluorophosphate.* The crude reaction product was recrystallised from dichloromethane–methanol (42% yield) to give an orange microcrystalline powder, m.p. 228 °C (decomp.) {Found: C, 50.8; H, 4.1; N, 4.1. Calc. for $[WBr(dppe)_2(N_2CNHCH_2CH_2NH)][PF_6]$: C, 50.7; H, 4.1; N, 4.3%}. The ^1H n.m.r. spectrum at 30 °C showed resonances at δ 7.20 (m, 40 H, $P{-}C_6H_5$), 2.92 (s, br, 8 H, $P{-}CH_2$), and 2.58 p.p.m. (sh, vbr, 4 H, $N{-}CH_2$).

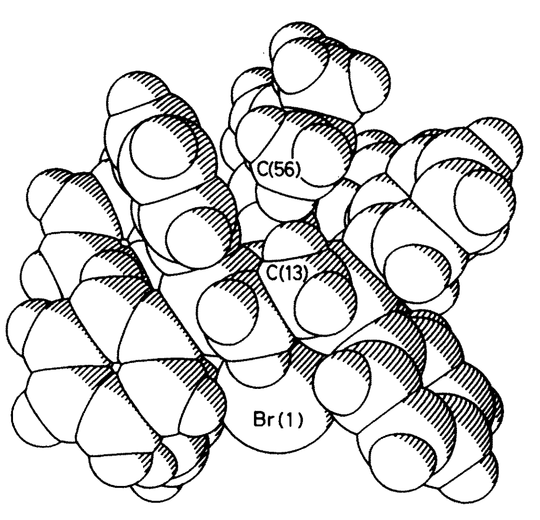


Figure 4. Space-filling molecular model of the cation $[WBr(dppe)_2\{N_2CN(Me)CH_2CH_2NMe\}]^+$

X-*Ray Crystallography.*—*Crystal data.* $[WBr(dppe)_2\{N_2CN(Me)CH_2CH_2NMe\}][PF_6]$, $M = 1\,207.9$, triclinic, space group $P\bar{1}$, $a = 12.546(3)$, $b = 14.332(3)$, $c = 17.174(3)$ Å, $\alpha = 74.07(1)$, $\beta = 76.79(2)$, $\gamma = 87.05(2)°$, $U = 2\,891$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}, $\mu(Cu\text{-}K_{\alpha}) = 65$ cm^{-1}.

Structure solution and refinement. As the crystals deteriorated slowly on standing in air, a single crystal was coated with varnish before mounting on the diffractometer. Data were measured using graphite-monochromatised Cu-K_{α} radiation ($\lambda = 1.541\,78$ Å) on a Nicolet R3m instrument. Of the 5 943 independent reflections measured ($\theta \leqslant 50°$) using the ω-scan measuring routine, 441 were classified as unobserved [$|F_o| < 3\sigma(|F_o|)$]. The data were corrected for absorption using an empirical correction based on 282 azimuthal measurements.

The structure was solved by the heavy-atom method, and the non-hydrogen atoms were refined anisotropically. The N-methyl hydrogens were clearly resolved in a ΔF map, and these groups were refined as rigid bodies. All other hydrogen atoms were placed in calculated positions and allowed to ride on their parent carbons. A ΔF map revealed small peaks due to unidentified and disordered solvent with only partial occupancy of different sites in the unit cell. Refinement was carried out using full-matrix block-cascade least squares (~100 parameter blocks) and the refinement converged to a final R value of 0.047. Computations were carried out on an Eclipse S140 computer using the SHELXTL system of programs.[4]

Fractional co-ordinates for the non-hydrogen atoms are given in Table 1, and bond lengths and angles in Tables 2 and 3 respectively.

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