Diazoalkane Complexes of Tungsten. Crystal Structures of $[WBr(N{-}N{=}CHCH_2CH_2CH_2OH)(dppe)_2][PF_6]{\cdot}0.5EtOH$ (1) and $[WBr(N{-}N{=}CMe_2)(dppe)_2]Br{\cdot}0.5MeOH$ (2) †

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The *X*-ray crystal-structure determinations of the title complexes are described. Crystals of (1) are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 17.43(1), b = 17.28(1), c = 19.00(1) Å, β = 100.85(2)°, and Z = 4, and the structure has been refined to R = 0.064 based on 4 168 counter reflections. Crystals of (2) are monoclinic, space group $P2_1/c$, with a = 11.745(2), b = 22.638(2), c = 21.029(3) Å, β = 111.2(2)°, and Z = 4, and the structure has been refined to R = 0.060 based on 6 402 counter reflections. Complex (1) was previously thought to be $[WBr(\overline{N{-}N{=}CHCH_2CH_2CH_2})(dppe)_2][PF_6]$ [dppe = 1,2-bis(diphenylphosphino)ethane]. Unusual n.m.r. parameters and difficulties in the preparation of diazoalkane complexes where both groups are larger than methyl are explained.

REACTIONS of co-ordinated dinitrogen to form nitrogen–carbon bonds are well known with both diazenido- (–N=N–R) and hydrazido(2–)-[=N–N(H)R] complexes being obtained for Mo,[1,2] W,[1] and Re [1] (R = alkyl, azyl, or aroyl). Recently a new class of compound containing the diazoalkane grouping (=N–N=CRR′) has been synthesised.[3–5] Thus, treatment of $[M(N_2)_2(dppe)_2]$ (M = Mo or W) with methyl bromide in tetrahydrofuran (thf) affords, after protonation of the product, $[MBr\{{=}N{-}N{=}CH(CH_2)_3OH\}(dppe)_2]Br$ which were the first diazoalkane complexes prepared. These materials were originally considered to contain the tetrahydropyridazido-ligand $(\overline{{-}N{-}N{=}CH{-}CH_2{-}CH_2{-}CH_2})$;[6] this present work has revealed their true identity. More general routes to these new complexes containing simple alkyl groups have now been developed and include the reaction of $[M(N_2)_2(dppe)_2]$ (M = Mo or W) with *gem* dibromides [3] and by the condensation of $[MBr(N{-}NH_2)(dppe)_2]Br$ with aldehydes and ketones.[4,7] While the former route is preferred as having a higher yield and fewer steps, the latter has been extended to complexes containing monotertiary phosphines [8] which have proved unattainable by the former route.

These new complexes have an interesting chemistry which is different from either the closely related alkyldiazenido- or alkylhydrazido(2–)-compounds. However the preparation of diazoalkane complexes $[MBr(N{-}N{=}CRR')(dppe)_2]^+$ where both alkyl groups are larger than methyl has proved impossible. This present study has been carried out to explain these observations and to characterise the material obtained from methylations of co-ordinated dinitrogen in thf solution. We now report the full details of the single-crystal *X*-ray structure analyses of $[WBr(N{-}N{=}CHCH_2CH_2CH_2OH)(dppe)_2][PF_6]{\cdot}0.5EtOH$ (1) and $[WBr(N{-}N{=}CMe_2)(dppe)_2]Br{\cdot}0.5MeOH$ (2) for which preliminary accounts have been published.[9,10]

EXPERIMENTAL

Synthesis of $[WBr\{N{-}N{=}CH(CH_2)_3OH\}(dppe)_2][PF_6]{\cdot}0.5EtOH$ (1).—Methyl bromide (0.106 g, 1.1 mmol) was condensed into a flask containing $[W(N_2)_2(dppe)_2]$ (1.12 g, 1.1 mmol) and thf (180 cm^3) at –196 °C. After warming to room temperature the mixture was stirred overnight under irradiation from two tungsten-filament light bulbs each 30 cm away from the vessel. The solvent was reduced to one third volume and addition of HBr (0.090 g, 1.1 mmol) followed by vigorous stirring at room temperature resulted in the precipitation of a light grey solid The precipitate was filtered of, washed with thf (5 cm^3), and dried *in vacuo* to give $[WBr\{N{-}N{=}CH(CH_2)_3OH\}(dppe)_2]Br$ (0.775 g, 62%).

A solution of the above product (0.398 g) in ethanol (20 cm^3) was treated with $Ag[PF_6]$ (0.088 g, 0.36 mmol) which resulted in the rapid precipitation of silver bromide. The mixture was filtered and addition of diethyl ether and hexane to the green solution gave green crystals of the product (0.364 g, 96%) (Found: C, 51.65; H, 4.55; N, 2.20. $C_{57}H_{59}BrF_6N_2O_{1.5}P_5W$ requires C, 52.15; H, 4.55; N, 2.15%).

Synthesis of $[WBr(N{-}N{=}CMe_2)(dppe)_2]Br{\cdot}0.5MeOH$ (2).—A solution of $[W(N_2)_2(dppe)_2]$ (1.240 g, 1.2 mmol) and CBr_2Me_2 (0.505 g, 2.5 mmol) in benzene (200 cm^3) was stirred at room temperature for 15 h with irradiation from two tungsten-filament light bulbs each 30 cm away from the vessel. The resulting light brown precipitate was filtered off, washed with benzene and pentane, and reduced to dryness. Recrystallisation from methanol–diethyl ether–hexane afforded dark brown crystals of the product (1.233 g, 85%) (Found: C, 54.25; H, 4.70; Br, 13.0; N, 2.45. $C_{55.5}H_{56}Br_2N_2O_{0.5}P_4W$ requires C, 54.35; H, 4.60; Br, 13.0; N, 2.30%).

X-*Ray Structure Determinations*.—*Crystal data.* (1) $C_{56}H_{56}BrF_6N_2OP_5W{\cdot}0.5C_2H_6O$, M = 1 328.9, Monoclinic, a = 17.43 (1), b = 17.28(1), c = 19.00(1) Å, β = 100.85(2)°, Z = 4, D_c = 1.55, D_m = 1.52 g cm^{-3}, U = 5 620.3 Å^3, $F(000)$ = 2 660, Mo-K_α radiation, μ = 31.4 cm^{-1}. Space group $P2_1/n$ from systematic absences of $0k0$ for k odd and $h0l$ for $(h + l)$ odd.

A crystal of irregular shape *ca.* 0.4 × 0.6 × 0.1 mm was used for data collection on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell parameters were derived from setting angles for 12 reflections. Intensities for

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† Bis[1,2-bis(diphenylphosphino)ethane]bromo-4-diazobutanoltungsten hexafluorophosphate–ethanol (2/1) and bis[1,2-bis(diphenylphosphino)ethane]bromo-1-diazo-1-methylethanetungsten bromide–methanol (2/1).

$hk\pm l$ reflections with $2 < \theta < 20°$ were collected by an ω—2θ step scan using Mo-K_α radiation with a graphite-crystal monochromator. Each reflection was measured over 80 steps of 0.01° and 0.5 s with background counts of 20 s at each end of the scan. The intensities of three standard reflections measured after every 100 reflections showed no significant variation. The 5 929 reflections measured were corrected for Lorentz and polarisation effects but not for absorption, and after averaging equivalent data 4 168 unique reflections with $I > 3\sigma(I)$ based on counting statistics were used for the structure analysis.

The positions of the non-hydrogen atoms were derived by the usual heavy-atom procedures and refined by large block-matrix least squares. A difference map revealed a molecule of ethanol solvent which was included with an occupancy of 0.5. The W, Br, P, and F atoms were refined anisotropically as were the C and O atoms of the diazobutanol and solvent moieties. Hydrogen atoms were included at calculated positions (C–H 1.08 Å) when defined by the geometry of the molecule and held fixed with a common isotropic temperature factor of $U = 0.038$ Å^2. Continued least-squares refinement with unit weights converged at $R = 0.064$, $R' = 0.075$, with a maximum shift-to-error of 0.4. A final difference map was everywhere <0.5 e Å^{-3}.

Crystal data. (2) $C_{55}H_{54}Br_2N_2P_4W\cdot0.5CH_4O$, $M = 1\,226.8$, Monoclinic, $a = 11.745(2)$, $b = 22.638(2)$, $c = 21.029(3)$ Å, $\beta = 111.20(2)°$, $U = 5\,212.9$ Å^3, $Z = 4$, $D_c = 1.56$, $D_m = 1.49$ g cm^{-3}, $F(000) = 2\,444$, Mo-K_α radiation, $\mu = 41.4$ cm^{-1}. Space group $P2_1/c$ from systematic absences of $0k0$ for k odd and $h0l$ for l odd.

A crystal of irregular outline *ca.* 0.6 × 0.7 × 1.0 mm was used for the structure determination. The details of the data collection, between $2 < \theta < 25°$, and processing were as for (1) unless otherwise stated. Of 9 493 reflections measured, 6 402 unique reflections with $I > 3\sigma(I)$ were used in the structure analysis.

The structure was solved by routine heavy-atom methods and refined by large block least squares with anisotropic temperature factors for the W, Br, and P atoms and for the C and N atoms of the diazopropane moiety. The phenyl rings were refined as rigid groups of idealised geometry (C–C 1.395 Å). A difference map revealed a molecule of methanol solvent which was included with an occupancy of 0.5. Those hydrogen atoms defined by the geometry of the molecule were included at calculated positions and held fixed with a common isotropic temperature factor of $U = 0.028$ Å^2. Continued least-squares refinement with unit weights converged at $R = 0.060$, $R' = 0.069$, with a maximum shift-to-error of 0.4. A final difference map was everywhere <0.5 e Å^{-3}.

Several attempts have been made to apply absorption corrections to both these structures, however, presumably due to difficulties in defining the crystal boundaries, the results always gave higher residuals than before the correction, and it was finally decided to omit the correction. For both structure analyses the *X*-ray program system [11] was used with scattering factors and dispersion corrections taken from ref. 12. The final atom co-ordinates are listed in Tables 1 and 2. Tables of hydrogen-atom co-ordinates, thermal vibration parameters, and final structure factors have been deposited as Supplementary Publication No. 22723 (51 pp.).*

Table 1 Final atomic co-ordinates (× 10^4) for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	9 711.7(4)	1 817.6(4)	2 035.3(4)
Br	9 831(1)	0 567(1)	1 331(1)
P(1)	10 925(3)	2 372(3)	1 693(3)
P(2)	10 742(3)	1 272(3)	3 030(3)
P(3)	8 773(3)	2 180(3)	0 904(3)
P(4)	8 460(3)	1 253(3)	2 311(3)
P(5)	4 940(3)	1 431(3)	2 019(3)
F(1)	5 308(10)	2 187(8)	2 368(12)
F(2)	4 582(10)	1 856(13)	1 327(10)
F(3)	4 181(9)	1 577(11)	2 330(10)
F(4)	5 702(9)	1 274(11)	1 731(11)
F(5)	5 291(10)	1 023(12)	2 716(11)
F(6)	4 559(9)	0 689(9)	1 667(12)
N(1)	9 635(8)	2 654(8)	2 557(7)
N(2)	9 665(8)	3 304(9)	2 924(8)
O(1) *	8 912(18)	4 951(18)	5 246(19)
O(1′) *	9 404(25)	5 481(24)	4 528(21)
C(1)	8 998(13)	3 591(11)	3 010(12)
C(2)	9 014(15)	4 337(12)	3 422(15)
C(3)	8 990(14)	4 246(13)	4 163(14)
C(4)	8 859(18)	4 994(16)	4 568(16)
C(5)	10 913(9)	3 355(10)	1 311(9)
C(6)	10 953(11)	3 470(11)	629(10)
C(7)	10 940(13)	4 223(14)	338(12)
C(8)	10 866(13)	4 828(14)	789(12)
C(9)	10 814(13)	4 736(14)	1 466(12)
C(10)	10 822(12)	3 973(12)	1 766(11)
C(11)	11 438(10)	1 828(11)	1 094(9)
C(12)	11 041(10)	1 535(10)	479(9)
C(13)	11 383(12)	1 129(12)	4(10)
C(14)	12 193(13)	1 053(13)	166(12)
C(15)	12 613(12)	1 344(13)	779(11)
C(16)	12 257(11)	1 749(12)	1 251(10)
C(17)	11 600(11)	2 459(11)	2 537(10)
C(18)	10 623(10)	1 541(10)	3 913(9)
C(19)	10 773(12)	2 295(12)	4 190(11)
C(20)	10 659(12)	2 503(13)	4 863(11)
C(21)	10 364(14)	1 978(14)	5 272(12)
C(22)	10 194(14)	1 256(14)	5 023(13)
C(23)	10 329(12)	1 041(12)	4 358(11)
C(24)	10 976(11)	249(11)	3 157(10)
C(25)	11 730(13)	21(13)	3 468(12)
C(26)	11 916(15)	−784(16)	3 640(14)
C(27)	11 305(14)	−1 303(14)	3 467(12)
C(28)	10 561(12)	−1 098(13)	3 139(11)
C(29)	10 398(11)	−302(11)	2 984(10)
C(30)	11 698(10)	1 710(10)	2 953(9)
C(31)	9 012(10)	2 089(10)	45(9)
C(32)	9 001(11)	1 403(11)	−336(10)
C(33)	9 195(13)	1 371(14)	−999(12)
C(34)	9 458(15)	2 001(16)	−1 306(14)
C(35)	9 486(15)	2 708(15)	−946(14)
C(36)	9 281(12)	2 738(12)	−287(11)
C(37)	8 369(10)	3 179(11)	855(9)
C(38)	7 684(11)	3 324(12)	373(10)
C(39)	7 407(13)	4 086(13)	280(12)
C(40)	7 833(12)	4 662(13)	674(11)
C(41)	8 508(12)	4 535(12)	1 144(11)
C(42)	8 786(11)	3 761(11)	1 231(10)
C(43)	7 912(10)	1 547(10)	858(9)
C(44)	8 097(10)	1 604(10)	3 107(9)
C(45)	7 287(10)	1 535(10)	3 111(9)
C(46)	7 020(12)	1 791(12)	3 711(11)
C(47)	7 502(12)	2 064(12)	4 273(11)
C(48)	8 290(12)	2 119(12)	4 289(11)
C(49)	8 564(10)	1 910(11)	3 678(9)
C(50)	8 344(9)	187(10)	2 402(9)
C(51)	8 436(11)	−112(11)	3 064(10)
C(52)	8 402(13)	−953(13)	3 144(12)
C(53)	8 297(12)	−1 388(12)	2 551(11)
C(54)	8 206(12)	−1 088(12)	1 897(11)
C(55)	8 239(11)	−273(11)	1 799(10)
C(56)	7 670(10)	1 513(10)	1 565(9)
C(57)	12 568(23)	4 594(25)	2 889(21)
C(58)	12 087(35)	4 423(33)	3 526(31)
O(2)	11 847(16)	4 010(14)	3 973(13)

* These atoms were included with an occupancy of 0.5.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

RESULTS AND DISCUSSION

The molecular conformations and atom-numbering schemes for (1) and (2) are shown in Figures 1 and 2, and selected bond lengths and angles are listed in Tables 3 and 4. Both structures have similar co-ordination around the tungsten atom with a meridional plane of four phosphorus atoms. The mean W–P distances of 2.526 (8) Å (1) and 2.533(15) Å (2) are similar to those found in related alkylhydrazido(2–) complexes of both tungsten [13] and molybdenum.[14,15] The tungsten atom is situated slightly above the plane of the phosphorus atoms and away from the bromine atom. This has also been noted in complexes of molybdenum.[16] In both cases the W–N bond is short indicating some multiple character in these bonds. Comparison of selected bond lengths and angles in related molecules is made in Table 5. There appears to be little significant change in metal–nitrogen bond distances with change of metal and ligands.[17]

TABLE 2

Final atomic co-ordinates (× 10^4) for (2) with estimated standard deviations in parentheses. For atoms refined in rigid groups the estimated standard deviation of the group is shown for the first atom of the group

Atom	*x*	*y*	*z*
W	2 849.9(4)	2 568.6(2)	–136.6(2)
Br(1)	7 268.6(16)	1 242.6(7)	2 710.7(9)
Br(2)	2 015.5(11)	2 589.2(5)	844.4(6)
P(1)	3 607(3)	1 525(1)	210(2)
P(2)	684(3)	2 336(1)	–875(2)
P(3)	4 967(3)	2 767(1)	737(2)
P(4)	1 960(3)	3 607(1)	–394(2)
N(1)	3 403(8)	2 554(4)	–792(5)
N(2)	3 975(9)	2 489(4)	–1 244(5)
C(1)	3 631(12)	2 748(6)	–1 830(7)
C(2)	4 433(17)	2 669(8)	–2 229(8)
C(3)	2 546(14)	3 132(6)	–2 114(7)
C(4)	5 274(12)	1 558(6)	555(7)
C(5)	5 720(12)	2 050(6)	1 086(7)
C(6)	–260(10)	2 986(5)	–895(6)
C(7)	376(10)	3 542(5)	–1 007(6)
C(8)	1 776(5)	4 099(2)	257(2)
C(9)	2 642	4 541	551
C(10)	2 509	4 911	1 052
C(11)	1 510	4 840	1 259
C(12)	644	4 399	965
C(13)	777	4 028	464
C(14)	2 630(5)	4 116(3)	–832(2)
C(15)	3 852	4 053	–771
C(16)	4 376	4 461	–1 084
C(17)	3 678	4 932	–1 458
C(18)	2 456	4 994	–1 519
C(19)	1 932	4 586	–1 206
C(20)	–208(6)	1 752(3)	–676(2)
C(21)	–304	1 201	–995
C(22)	–987	749	–850
C(23)	–1 574	848	–387
C(24)	–1 478	1 398	–68
C(25)	–795	1 850	–213
C(26)	472(5)	2 195(3)	–1 762(2)
C(27)	–454	2 469	–2 302
C(28)	–587	2 342	–2 976
C(29)	205	1 942	–3 111
C(30)	1 130	1 668	–2 572
C(31)	1 264	1 794	–1 897
C(32)	3 198(5)	1 160(2)	868(2)
C(33)	1 959	1 116	778
C(34)	1 609	824	1 265
C(35)	2 498	578	1 843
C(36)	3 737	622	1 934
C(37)	4 087	913	1 447
C(38)	3 340(6)	945(3)	–425(2)
C(39)	4 006	975	–949
C(40)	3 829	544	–1 365
C(41)	2 993	85	–1 434
C(42)	2 331	56	–1 000
C(43)	2 504	486	–495
C(44)	6 025(5)	3 101(3)	377(2)
C(45)	6 283	2 793	–132
C(46)	6 995	3 057	–463
C(47)	7 448	3 629	–284
C(48)	7 189	3 938	225
C(49)	6 478	3 674	555
C(50)	5 291(6)	3 187(3)	1 522(2)
C(51)	6 437	3 128	2 043
C(52)	6 723	3 467	2 638
C(53)	5 864	3 863	2 710
C(54)	4 718	3 922	2 189
C(55)	4 432	3 583	1 594

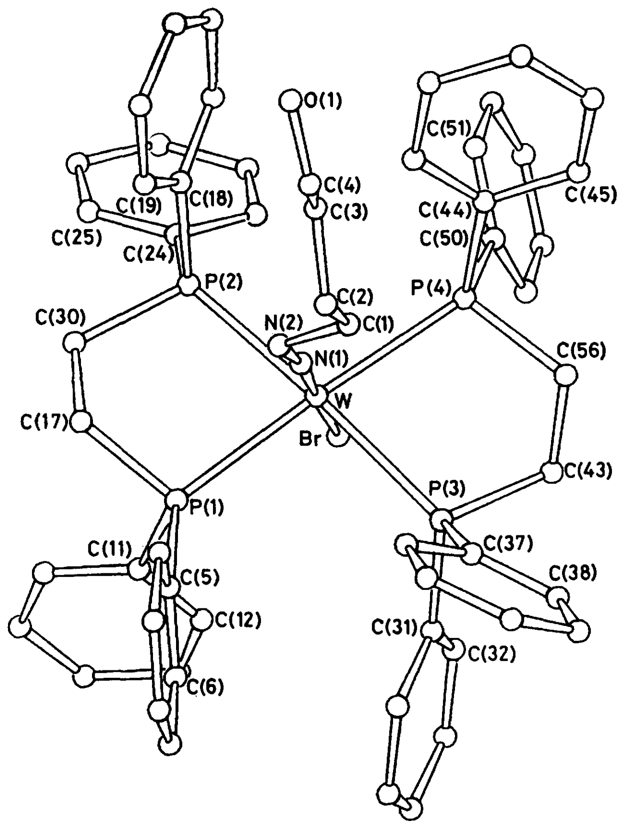

FIGURE 1 The molecular structure of [WBr(N–N=CHCH$_2$CH$_2$CH$_2$OH)(dppe)$_2$]$^+$. Carbon atoms in phenyl rings are labelled sequentially

The W–N–N bond angles in (1) and (2) are essentially linear indicating that the diazoalkane groups are four-electron ligands and that the metal is formally in the IV oxidation state. This is in agreement with the ^{31}P n.m.r. spectra of (1) and (2) where the magnitude of ^{1}J(WP) is 276 Hz and similar to closely related hydrazido-(2–)-complexes, while in the analogous tungsten(II) alkyldiazenido-complexes ^{1}J(WP) increases as expected to 295 Hz.[18] The N–N bond length again is evidence of multiple bonding and indicates that of the possible canonical forms shown below a greater contribution comes from c. In complexes (1) and (2) the N–C bond lengths are consistent with a bond order of two and that for (1) is identical to the value found for acetoxime,[19] $Me_2C{=}NOH$.

$$[\mathrm{Br(dppe)_2}\overset{+}{\mathrm{W}}{=}\mathrm{N{-}N{=}CRR'}] \longleftrightarrow$$
a

$$[\mathrm{Br(dppe)_2W}{\equiv}\overset{+}{\mathrm{N}}\mathrm{{-}N{=}CRR'}] \longleftrightarrow$$
b

$$[\mathrm{Br(dppe)_2}\overset{-}{\mathrm{W}}{=}\overset{+}{\mathrm{N}}{=}\overset{+}{\mathrm{N}}{=}\overset{\bullet}{\mathrm{C}}\mathrm{RR'}] \longleftrightarrow$$
c

$$[\mathrm{Br\ (dppe)_2}\overset{+}{\mathrm{W}}{=}\mathrm{N}{-}\overset{+}{\mathrm{N}}{\equiv}\overset{-}{\mathrm{C}}\mathrm{RR'}]$$
d

The cation of complex (1) was previously characterised as $[\mathrm{WBr}(\overline{\mathrm{N{-}N{=}CHCH_2CH_2CH_2}})(\mathrm{dppe})_2]^+$ on the basis of ^1H n.m.r., analytical, and i.r. data.[6] The structure of (1) indicates that the carbon chain is not bonded to the nitrogen atom as had previously been expected but that it is directed away from the nitrogen atoms and is terminated by a hydroxyl group. The oxygen atom was not recognised in the initial structural assignment. However the i.r. and ^1H n.m.r. spectra on which that assignment was made are in fact consistent with the presence of the diazobutanol group found in (1). The i.r. band at 3 265 cm^{-1} previously thought to be due to ν(N–H) is in fact due to ν(O–H) and while the position of the band is at lower frequency than expected this is probably due to the presence of hydrogen bonding to the anionic group. This idea is supported by the crystal structure where the hydroxyl oxygen atom is disordered between two positions O(1) and O(1′) in approximately equal proportion and both positions have close contacts with the fluorine atoms of two symmetry-related hexafluorophosphate anions, O(1)–F(6) 2.9 Å and O(1′)–F(4) 2.73 Å, presumably indicating hydrogen bonding (see Figure 3).

TABLE 3

Selected interatomic distances and angles for (1)

(a) Distances (Å)

W–Br	2.569(2)	C(3)–C(4)	1.54(4)
W–P(1)	2.516(5)	C(4)–O(1)	1.28(5)
W–P(2)	2.532(5)	C(4)–O(1)	1.28(5)
W–P(3)	2.523(5)	P(5)–F(1)	1.55(2)
W–P(4)	2.533(5)	P(5)–F(1)	1.53(2)
W–N(1)	1.772(13)	P(5)–F(3)	1.57(2)
N(1)–N(2)	1.32(2)	P(5)–F(4)	1.55(2)
N(2)–C(1)	1.30(3)	P(5)–F(5)	1.52(2)
C(1)–C(2)	1.51(3)	P(5)–F(6)	1.54(2)
C(2)–C(3)	1.43(4)	P(1)–C(5)	1.85(2)
P(4)–C(44)	1.85(2)	P(1)–C(11)	1.83(2)
P(4)–C(50)	1.86(2)	P(1)–C(17)	1.81(2)
P(4)–C(56)	1.84(2)	P(2)–C(18)	1.79(2)
F(4) · · · O(1^{I})	2.73(5)	P(2)–C(24)	1.82(2)
F(6) · · · O(1^{II})	2.94(4)	P(2)–C(30)	1.86(2)
Phenyl ring C–$C_{max.}$	1.46(3)	P(3)–C(37)	1.86(2)
Phenyl ring C–$C_{min.}$	1.32(3)	P(3)–C(31)	1.77(2)
Phenyl ring C–$C_{av.}$	1.38(3)	P(3)–C(43)	1.85(2)

(b) Angles (°)

Br–W–N(1)	177.3(4)	N(1)–W–P(2)	90.2(4)
Br–W–P(1)	91.8(1)	N(1)–W–P(3)	99.7(4)
Br–W–P(2)	87.6(1)	N(1)–W–P(4)	92.3(5)
Br–W–P(3)	82.5(1)	W–N(1)–N(2)	172.6(12)
Br–W–P(4)	86.6(1)	N(1)–N(2)–C(1)	116.2(15)
P(1)–W–P(2)	79.8(2)	N(2)–C(1)–C(2)	117.5(19)
P(1)–W–P(4)	177.0(2)	C(1)–C(2)–C(3)	114.8(20)
P(2)–W–P(3)	169.6(2)	C(2)–C(3)–C(4)	115.8(20)
P(2)–W–P(4)	102.7(2)	C(3)–C(4)–O(1)	117.7(26)
P(3)–W–P(4)	80.0(2)	C(3)–C(4)–O(1′)	109.9(31)
N(1)–W–P(1)	89.4(5)		

Roman numeral superscripts refer to symmetry elements: I $1.5 - x, 0.5 + y, 0.5 - z$; II $0.5 + x, 0.5 - y, 0.5 + z$.

TABLE 4

Selected interatomic distances and angles for (2)

(a) Distances (Å)

W–Br(2)	2.585(2)	C(1)–C(2)	1.482(27)
W–P(1)	2.536(3)	C(1)–C(3)	1.478(19)
W–P(2)	2.508(3)	P(1)–C(4)	1.825(14)
W–P(3)	2.538(3)	P(1)–C(32)	1.821(4)
W–P(4)	2.549(3)	P(1)–C(38)	1.818(3)
W–N(1)	1.724(12)	P(2)–C(6)	1.832(12)
N(1)–N(2)	1.355(18)	P(2)–C(20)	1.827(3)
N(2)–C(1)	1.290(17)	P(2)–C(26)	1.820(3)
P(3)–C(5)	1.867(13)	P(4)–C(7)	1.845(10)
P(3)–C(44)	1.835(4)	P(4)–C(8)	1.837(3)
P(3)–C(50)	1.821(3)	P(4)–C(14)	1.822(3)
C(4)–C(5)	1.529(19)	C(6)–C(7)	1.525(17)

(b) Angles (°)

Br(2)–W–N(1)	179.9(3)	P(2)–W–P(3)	172.8(1)
Br(2)–W–P(1)	89.0(1)	P(2)–W–P(4)	79.5(1)
Br(2)–W–P(2)	84.6(1)	P(3)–W–P(4)	102.0(1)
Br(2)–W–P(3)	88.5(1)	W–N(1)–N(2)	171.3(7)
Br(2)–W–P(4)	84.7(1)	N(1)–N(2)–C(1)	123.9(11)
P(1)–W–P(2)	98.9(1)	N(2)–C(1)–C(2)	116.3(12)
P(1)–W–P(3)	78.9(1)	N(2)–C(1)–C(3)	125.4(15)
P(1)–W–P(4)	173.6(1)	C(2)–C(1)–C(3)	118.2(13)

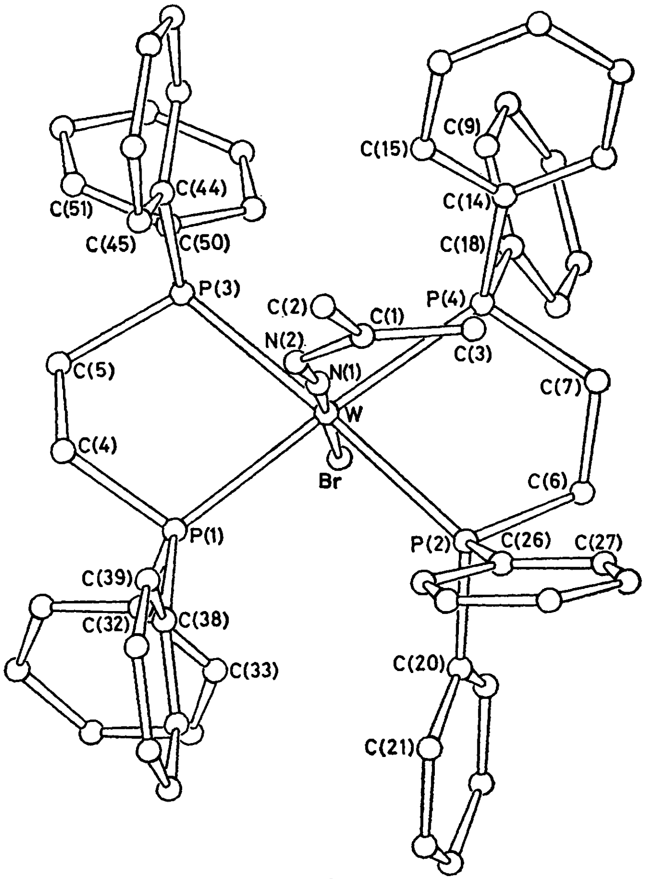

FIGURE 2 The molecular structure of $[\mathrm{WBr(N{-}N{=}CMe_2)(dppe)_2}]^+$

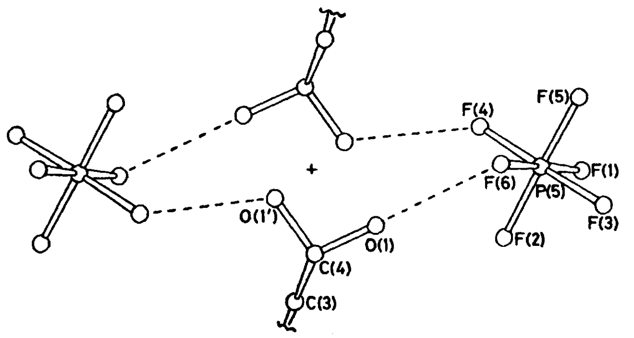

FIGURE 3 The probable hydrogen bonding surrounding an inversion centre in crystals of $[WBr(N{-}N{=}CHCH_2CH_2CH_2OH)(dppe)_2][PF_6]$. The two alternative sites for the hydroxyl oxygen atoms are shown

An interesting feature of these new diazoalkane complexes is their unusual n.m.r. spectra. When two similar groups are bonded to the diazoalkane carbon atom their ^1H and ^{13}C n.m.r. chemical shifts are quite dissimilar.[3] A typical example is that of (2) where the two methyl groups give rise to single lines at τ 8.87 (^{13}C n.m.r., 24.9 p.p.m.) and 10.75 (^{13}C n.m.r., 20.3 p.p.m.). While a difference in chemical shift may be expected owing to the presence of the asymmetry around the unique diazoalkane carbon atom,* the observed shift difference is far too great to be explained this way. The structure determination of (2) was carried out to explain these observations and the result is shown in Figure 2. The N–N bond is slightly longer than that found for (1) while the N–C bond is slightly shorter. The two methyl groups occupy quite different sites. One is virtually collinear with the Br, W, and N atoms and is positioned in the space between the phenyl rings of the two dppe ligands. The closest phenyl ring has C · · · C contacts in the range 3.95—5.91 Å. On the other hand the other methyl group is held in a sandwiched position between two phenyl rings of the same dppe ligand. Distances to one ring (3.5, 3.7, 3.9, 3.9, 3.7, and 3.5 Å) indicate that it occupies an almost axial position while approaching one edge of the other ring (3.4, 3.3, 3.9, 4.4, 4.4, and 4.0 Å). This position in the field generated by the ring currents of the two phenyl rings accounts for the unusual chemical shift of one methyl group and this group is considered to give rise to the lines at τ 10.75 (^{13}C n.m.r., 20.3 p.p.m.).

TABLE 5

Comparison of bond lengths(Å) and angles(°) in diazoalkane and hydrazido(2—)-complexes

Complex	M–N	N–N	M–N–N	Reference
$[WBr\{NNCH(CH_2)_3OH\}(dppe)_2]^+$	1.772(13)	1.317(20)	172.6(12)	This work
$[WBr(NNCMe_2)(dppe)_2]^+$	1.724(12)	1.355(18)	171.3(7)	This work
$[WBr(NNHCH_3)(dppe)_2]^+$	1.768(14)	1.32(2)	174(1)	13
$[MoI(NNHC_8H_{17})(dppe)_2]^+$	1.801(11)	1.259(4)	174(1)	15
$[MoF(NNH_2)(dppe)_2]^+$	1.762(12)	1.333(24)	176.4(13)	16
$[Mo(NNEtPh)\{S_2CN(CH_2)_5\}_3]^+$	1.715(16)	1.37(2)	170(2)	13
$[ReCl_2(NH_3)(NNHPh)(PMe_2Ph)_2]^+$	1.75(1)	1.28(2)	172(1)	*a*
$[WF\{NNC(CH_3)CH_2COCH_3\}(dppe)_2]^+$	1.770(17)	1.317(25)	173.8(15)	21
$[MoCl(NNCOC_6H_5)(dppe)_2]^+$	1.813(7)	1.255(10)	172.1(6)	22
$[WCl(NNH_2)(dppe)_2]^+$	1.73(1)	1.37(2)	171(1)	*b*

[a] R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Doublas, A. R. Golbraith, and B. L. Shaw, *J. Amer. Chem. Soc.*, 1974, **96**, 260.
[b] G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 259.

Complexes containing two groups larger than methyl bonded to the unique carbon atom have not been synthesised when dppe ligands are present, while a similar restriction has not been encountered when monotertiary phosphine ligands are incorporated. For example no reaction occurs between $[WBr(N{-}NH_2)(dppe)_2]Br$ and CEt_2O even after several days while the condensation with $[WBr_2(N{-}NH_2)(PMe_2Ph)_3]$ is complete within 0.5 h to afford $[WBr_2(N{-}N{=}CEt_2)(PMe_2Ph)_3]$. In an attempt to explain why the former reaction does not occur the positions of the two ethyl groups have now been extrapolated from the positions obtained for complex (2). We find that the group sandwiched between the phenyl rings has very close contacts with one of the rings. For the three possible positions calculated for the terminal carbon atom of this ethyl group, assuming a staggered conformation at the C–C bond, the minimum contact distances to the phenyl rings are 2.1, 2.0, and 1.4 Å, representing an impossibly high steric strain. It is also noticeable that in (1) the conformation of the diazobutanol group is related to that in (2) with the bulky group occupying the C(2) position and not the hindered C(3) position.

Figures 1 and 2 illustrate the very close similarity in conformation of the dppe ligands in the two molecules, the only noticeable difference being a small relative rotation of the phenyl ring at C(26) in $[WBr(NNCMe_2)(dppe)_2]^+$, presumably to accommodate the C(3) methyl group. This similarity suggested that the conformations were decided by intramolecular constraints alone and prompted us to examine the structures of related dinitrogen and diazenido-complexes of Mo and W with dppe ligands to see if the same conformations are observed there.

Complexes (1) and (2) both have the methylene groups of the dppe ligands related by a two-fold axis perpendicular to the plane through the W atom, whilst the phenyl rings are approximately related by an inversion centre at W. The complex $[W(N_2)_2(dppe)_2]$ [20] has both the methylene groups and the phenyl rings related by an exact inversion centre at W and shows little similarity to (1) and (2). The complex cation $[MoF(NNH_2)(dppe)_2]^+$ [16]

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* The ^1H n.m.r. spectrum of $[WBr_2(NNCMe_2)(PMe_2Ph)_3]$ shows two CH_3 resonances at τ 8.59 and 8.75 (P. C. Bevan, personal communication).

has both the methylene groups and the phenyl rings related by a two-fold rotation axis through Mo whereas $[WBr(NNHMe)(dppe)_2]^+$ [13] has the methylene groups related by a two-fold axis through W and the phenyl rings not related by symmetry at all. The crystal structures of $[WF\{NNCH_2CHMeC(O)Me\}(dppe)_2]$ [21] and $[MoCl\{NNC(O)Ph\}(dppe)_2]$ [22] show both molecules to have the methylene groups related by a two-fold rotation axis and the phenyl groups arranged in a similar way to (1) and (2) although small differences in the angles of rotation about the P–C(phenyl) bonds were apparent. We conclude that there is no one conformation of lowest energy in this type of complex and that both the nature of the substituents on the nitrogen atoms and packing forces influence the conformation adopted.

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