there is a close contact of 2.656 (5) Å between C(21) and H(432). Similar limiting intramolecular C···H contacts of ca. 2.6 Å occur in $[MoL_4L'I]I$ and $[MoL_4L'I](PF_6)$ between methyl hydrogen atoms of the "coupled" ligand and the C≡N moieties of the four *t*-BuNC ligands forming the capped face. The difference between the present compound and the CTP complexes lies in the angles between the capping ligand and the four ligands of the capped face (vide supra). In the CTP complexes, these four angles in each complex are close to 80°. In the present compound, the similar angle involving ligands 3 and 3′, angle C(11)–Mo–C(31), opens up to 87.9° and that involving ligands 2 and 2′, angle C(11)–Mo–C(21), closes to ca. 75.2°. The implications in the present compound are that if this 75° angle could close up further (i.e., ligands 2 and 2′ move closer to the cyanide ligand), the four ligands 3, 3′, 2, and 2′ could rotate such that 2 and 2′ were now in the plane of the coupled ligand and the stereochemistry would be pentagonal bipyramidal (stereochemistry B).

Intramolecular repulsions, due to bulky $P(OMe)_3$ groups, were invoked to rationalize the deviation of the recently determined structure[25] of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(P(OMe)_3)_2]$ from a regular pentagonal bipyramid (Table IV). The reason why the present compound does not have the less hindered capped trigonal-prismatic geometry adopted by the other $[MoL_4L'X]^+$ cations is not clear but obviously may be electronic in origin.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant NSF CHE79-12436.

Registry No. $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$, 78963-11-8; $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)](PF_6)$, 78891-51-7; $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$, 41982-05-2.

Supplementary Material Available: Tables S1–S3 reporting respectively final observed and calculated structure factors, hydrogen atom positional parameters, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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Contribution from the Corporate Laboratory, Imperial Chemical Industries Ltd., Runcorn, Cheshire, England WA7 4QE, and the Department of Chemistry, The Polytechnic of North London, London, England N7 8DB

Synthesis and X-ray Crystal Structure of $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot{}^1/_3CH_2Cl_2$: A Complex Containing the Bridging Formazanido(3–) Ligand[1]

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The reaction between $CHFBr_2$ and the dinitrogen-derived hydrazido(2–) complex $[WBr(dppe)_2N_2H_2]^+Br^-$, in the presence of $[Ph_2I]^+Br^-$ and aqueous base, yields a cationic, binuclear complex $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$. This complex has been isolated as its bromide, hexafluorophosphate, and Reineckate salts, and a single-crystal X-ray study of the latter confirms that the cation contains a formazanido(3–) ligand, $[N_2CHN_2]^{3-}$, bridging two tungsten atoms in a seven-atom chain. Crystals of $[[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot{}^1/_3CH_2Cl_2]$ are monoclinic, space group $P2_1/n$, with $Z = 4$, a = 19.089 (3) Å, b = 44.263 (4) Å, c = 13.807 (2) Å, β = 104.4 (1)°, and V = 11299.5 Å^3. The structure was refined by blocked full-matrix least squares, with the phenyl rings treated as rigid bodies, to a final R value of 0.082 and R_w of 0.083 for the 5918 unique observed reflections [$I > 3\sigma(I)$].

Introduction

It has recently been shown that reactions of the dinitrogen-derived hydrazido(2–) complex $[WBr(dppe)_2N_2H_2]^+Br^-$ with organic solvents, in the presence of diphenyliodonium bromide and aqueous base, often lead to products in which solvent-drived radicals have added to the nitrogen-containing ligand. Such products include the formyldiazenido complex $[WBr(dppe)_2N_2CHO]$ (from CH_2Cl_2 or $CHBr_3$)[3] and the cationic dichlorodiazomethane complex $[WBr(dppe)_2(N_2CCl_2)]^+$ (from $CHCl_3$ or $CBrCl_3$)[4], which are thought to arise by the sequence of ionic and radical reactions typified in Scheme I.

We now report that when the above reaction is carried out using dibromofluoromethane as the organic phase, small amounts of $[WBr(dppe)_2N_2CHO]$ are again formed, but the major product is the bromide salt of a complex cation which we have characterized spectroscopically and crystallographically as a binuclear species containing the bridging formazanido(3–) ligand $[\mu\text{-}N_2CHN_2]^{3-}$. Part of this work has been described in a preliminary communication.[5]

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer PE197 spectrometer, and ^1H and ^{31}P NMR spectra were recorded on a JEOL XL100 FT instrument. Fluorodibromomethane was purchased from Fluorochem Ltd., and diphenyliodonium bromide from Lancaster Synthesis Ltd. The hydrazido(2–) complex[6] $[WBr(dppe)_2N_2H_2]^+Br^-$ was prepared by protonation of $[W(dppe)_2(N_2)_2]$ with aqueous hydrobromic acid in dichloromethane.[3] Unless otherwise specified, no special precautions were taken to exclude atmospheric oxygen or moisture.

Preparation of $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+Br^-\cdot 3CH_2Cl_2$. The hydrazido(2–) complex $[WBr(dppe)_2N_2H_2]^+Br^-$ (2.00 g, 1.71 mmol) and diphenyliodonium bromide (0.70 g, 1.93 mmol) were suspended in $CHFBr_2$ (25 cm^3) and degassed aqueous potassium carbonate (20 cm^3 of a 5% solution) was added. The mixture was stirred vigorously under nitrogen for 45 min and then treated with diethyl ether (200 cm^3). The resulting dark olive green precipitate was filtered off, washed

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(1) dppe = 1,2-bis(diphenylphospino)ethane.

(2) (a) ICI Corporate Laboratory. (b) The Polytechnic of North London.

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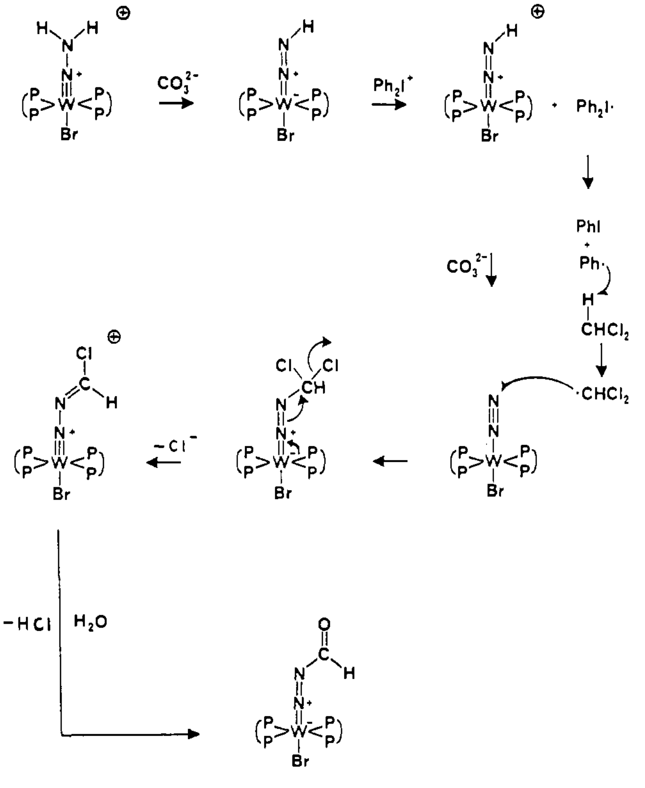

Scheme I. Formation of $[WBr(dppe)_2N_2CHO]$ from $[WBr(dppe)_2N_2H_2]^+Br^-$ and CH_2Cl_2

with water (200 cm^3) and diethyl ether (100 cm^3), and dried under vacuum.

The filtrate was extracted with a further 100 cm^3 of diethyl ether, and the organic layer was then separated, dried over sodium sulfate, and filtered. Evaporation to ca. 50 cm^3, followed by slow addition of hexane (100 cm^3), gave $[WBr(dppe)_2N_2CHO]$ (0.23 g, 12%) as an orange crystalline solid, identified by its melting point and IR spectrum.[3]

The original olive green precipitate was taken up in dichloromethane, and the deep brown solution was filtered and treated with diethyl ether (100 cm^3). After 48 h, dark brown crystals (green by reflected light) had formed, and these were filtered off, washed with diethyl ether, and dried under vacuum. The yield was 0.85 g, 39%; mp 244 °C. Anal. Calcd for $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+Br^-\cdot 3CH_2Cl_2$: C, 51.3; H, 4.1; N, 2.2. Found: C, 51.4; H, 3.3; N, 2.0. The ^1H NMR spectrum (CD_2Cl_2 solution; δ 0 for Me_4Si) showed resonances at δ 2.81 (s, 8 H, CH_2), 1.79 (s, 8 H, CH_2), 7.69, 7.39, 7.15, 6.95, and 6.65 (complex m, 80 H, PPh_2), δ 8.22 (s, 1 H, $CH(N_2)_2$).

The *hexafluorophosphate* salt $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[PF_6]^-$ was obtained on addition of NH_4PF_6 in methanol to a methanol solution of the corresponding bromide salt and was filtered off, dried, and recrystallized from dichloromethane–methanol. The ^{31}P NMR spectrum of this compound (CD_2Cl_2 solution; δ 0 for external H_3PO_4) showed resonances at δ −144.6 (septet, 1 P, $J(^{19}F-^{31}P)$ = 7100 Hz, PF_6^-) and at −35.4 (singlet with ^{183}W satellites, 8 P, $J(^{183}W-^{31}P)$ = 282 Hz, $[W_2(dppe)_4]$.

The *Reineckate* salt $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-$ was similarly precipitated from methanol by addition of $NH_4^+[Cr(NH_3)_2(NCS)_4]^-$ to a solution of the bromide salt and was recrystallized from dichloromethane–methanol; mp 248 °C. An analytical sample contained 2 molar equiv of dichloromethane. Anal. Calcd for $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot 2CH_2Cl_2$: C, 49.8; H, 3.8; N, 5.2. Found: C, 50.2; H, 3.8; N, 5.2. Single crystals of the Reineckate salt, suitable for x- ray analysis, were grown by slow evaporation of a dichloromethane–methanol solution and, unlike the analytical sample, contained only $^1/_3$ molar equiv of dichloromethane of crystallization.

X-ray Crystallography. Crystal data for $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot{}^1/_3CH_2Cl_2$: $C_{109}H_{103}Br_2CrN_{10}P_8S_4W_2\cdot{}^1/_3CH_2Cl_2$; M_r 2534.8; monoclinic; space group $P2_1/n$; a = 19.089 (3), b = 44.263 (4), c = 13.807 (2) Å; β = 104.4 (1)°; V = 11299.5 Å^3; T = 22 °C; d(calcd) = 1.489 g cm^{-3}; Z = 4; μ(Mo Kα) = 28.9 cm^{-1}. The centric space group was assumed from systematic absences and subsequently confirmed by the satisfactory refinement of the structure. Data were collected on a crystal of dimensions 0.12 × 0.15 × 0.10 mm with use of a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The θ–2θ scan mode was used, and reflections with $3.0 < \theta < 22.5°$ in one quadrant were examined. The method of data collection was similar to that previously described.[7] Three standard reflections were measured evry 2 h during collection and showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements with use of a program written for the PW 1100 diffractometer. The variance of intensity I was calcualted as $[(\sigma_c(I))^2 + (0.04I)^2]^{1/2}$, where $\sigma_c(I)$ is the variance due to counting statistics and the term in I^2 was introduced to allow for other sources of error. I and $\sigma(I)$ were corrected for Lorentz and polarization factors, and absorption corrections were not applied. Reflections for $I < 3\sigma(I)$ were rejected, and equivalents were averaged to give 5918 unique reflections.

Structure Solution and Refinement. The two tungsten atoms were located from a Patterson map. Subsequent Fourier synthesis revealed the positions of all nonhydrogen atoms. Refinement with isotropic thermal parameters for all nonhydrogen atoms, and with the phenyl rings treated as rigid bodies with C–C = 1.395 Å and C–C–C = 120°, converged to R = 0.101. Refinement of the site occupation factor for the dichloromethane molecule converged to 0.362, and this group was included in the subsequent refinement at an occupancy of $^1/_3$. The final cycles of refinement included anisotropic thermal parameters for the W and Br atoms. Hydrogen atoms were not included in the structure. The final R was 0.082 and R_w = 0.083 [$R_w = \sum||F_o| - |F_c||w^{1/2}/\sum w^{1/2}|F_o|$ and weights (w) were assigned to reflections as $w = (\sigma(F_o))^{-2}$]; maximum shift = 0.022σ and average shift = 0.012σ. Major computations were performed with the SHELX 76 program.[8] Scattering factors and anomalous dispersion corrections were taken from ref 9 and 10. Final atomic and thermal parameters are shown in Table I.

Results and Discussion

The reaction between $[WBr(dppe)_2N_2H_2]^+Br^-$ and $[Ph_2I]^+Br^-$, in a rapidly stirred mixture of $CHFBr_2$ and 5% (w/w) aqueous potassium carbonate, gave an intensely yellow-brown organic phase from which the known orange complex $[WBr(dppe)_2N_2CHO]^3$ (~10%) and a new olive green compound (~40%) could be crystallized. The latter proved to be the bromide salt of a cationic tungsten complex, which was also obtained as its hexafluorophosphate and Reineckate salts by metathetical reactions in methanol.

Integrated ^{31}P NMR spectra of the hexafluorophosphate salt showed that, for every PF_6^- ion, the cation contained eight equivalent phosphorus atoms assignable to dppe ligands bound to tungsten [$J(^{183}W-^{31}P)$ = 282 Hz]. This result strongly suggested the presence of a monocation containing two $[WBr(dppe)_2]$ units. IR spectra of all three salts of this cation showed absorptions at 1450 and 1325 cm^{-1}, assigned to $\nu(\mathrm{C\overset{\cdots}{-}N})$ and $\nu(\mathrm{N\overset{\cdots}{-}N})$ modes, respectively, and the intense yellow-brown color of the cation in solution was found to be due to a broad visible absorption band centered at 475 nm (ϵ 5.5 × 10^4).

The monocation was protonated to a green dication (λ_{max} = 390 nm, ϵ 3.7 × 10^4) by trifluoroacetic acid in dichloromethane, but the added proton was readily lost on contact with weak bases such as acetone or diethyl ether, and pure salts of the dication were not isolated. in solution, however, the dication showed a single strong IR absorption at 1560 cm^{-1}, which we assign to the stretching vibration of a C=N double bond.

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Table I. Refined Atomic Positional and Thermal Parameters (A^2) ($\times 10^3$) for $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]\,[Cr(NH_3)_2(NCS)_4]\cdot{}^1/_3CH_2Cl_2$[a]

atom	x	y	z	U_{iso}, A^2	atom	x	y	z	U_{iso}, A^2
(i) Complex Cation									
W(1)	0.2772 (1)	0.5443 (1)	0.2544 (1)	*b*	C(141)	0.3441 (13)	0.5849 (7)	0.0587 (14)	49 (10)
Br(1)	0.2155 (2)	0.4936 (1)	0.1814 (3)	*b*	C(142)	0.3631	0.5808	−0.0317	126 (19
P(11)	0.3964 (4)	0.5151 (2)	0.2683 (6)	41 (2)	C(143)	0.4284	0.5922	−0.0440	140 (20)
P(12)	0.2851 (4)	0.5145 (2)	0.4131 (6)	42 (2)	C(144)	0.4748	0.6078	0.0340	66 (12)
P(13)	0.1559 (4)	0.5687 (2)	0.2279 (6)	39 (2)	C(145)	0.4558	0.6120	0.1243	85 (15)
P(14)	0.2612 (4)	0.5666 (2)	0.0839 (7)	52 (2)	C(146)	0.3905	0.6006	0.1366	134 (19)
C(11)	0.4178 (14)	0.4922 (6)	0.3853 (21)	46 (8)	C(147)	0.2169 (15)	0.5456 (7)	−0.0330 (18)	81 (13)
C(12)	0.3475 (14)	0.4803 (7)	0.4130 (22)	54 (9)	C(148)	0.2433	0.5163	−0.0363	59 (12)
C(13)	0.1610 (15)	0.6034 (7)	0.1598 (23)	54 (9)	C(149)	0.2264	0.5002	−0.1258	92 (15)
C(14)	0.1943 (19)	0.6013 (9)	0.0726 (30)	103 (13)	C(1410)	0.1832	0.5133	−0.2120	91 (15)
N(11)	0.3107 (11)	0.5776 (5)	0.3061 (18)	49 (7)	C(1411)	0.1568	0.5425	−0.2087	69 (12)
N(12)	0.3509 (12)	0.6000 (6)	0.3715 (18)	54 (7)	C(1412)	0.1737	0.5587	−0.1192	87 (15)
C	0.3282 (13)	0.6275 (6)	0.3679 (20)	38 (7)	C(211)	0.4425 (15)	0.7683 (6)	0.3506 (24)	68 (12)
W(2)	0.3206 (1)	0.7140 (1)	0.4484 (1)	*b*	C(212)	0.4820	0.7931	0.3973	99 (15)
Br(2)	0.2958 (2)	0.7714 (1)	0.4642 (3)	*b*	C(213)	0.4887	0.8188	0.3418	90 (14)
P(21)	0.4407 (4)	0.7336 (2)	0.4249 (7)	51 (2)	C(214)	0.4560	0.8197	0.2395	74 (12)
P(22)	0.3871 (4)	0.7243 (2)	0.6290 (7)	50 (2)	C(215)	0.4166	0.7949	0.1928	103 (15)
P(23)	0.2381 (4)	0.7137 (2)	0.2751 (6)	45 (2)	C(216)	0.4099	0.7692	0.2484	88 (15)
P(24)	0.2047 (4)	0.6962 (2)	0.4854 (6)	44 (2)	C(217)	0.5053 (12)	0.7087 (6)	0.3828 (22)	61 (11)
C(21)	0.5016 (15)	0.7402 (7)	0.5574 (23)	53 (9)	C(218)	0.5447	0.7176	0.3151	109 (16)
C(22)	0.4614 (15)	0.7509 (7)	0.6327 (24)	62 (9)	C(219)	0.5932	0.6976	0.2885	104 (17)
C(23)	0.1510 (15)	0.6930 (7)	0.2791 (24)	60 (9)	C(2110)	0.6022	0.6686	0.3296	80 (13)
C(24)	0.1640 (13)	0.6732 (6)	0.3743 (21)	41 (8)	C(2111)	0.5627	0.6597	0.3973	93 (15)
N(21)	0.3390 (10)	0.6773 (5)	0.4360 (15)	31 (5)	C(2112)	0.5143	0.6798	0.4239	83 (14)
N(22)	0.3628 (12)	0.6490 (6)	0.4336 (18)	55 (7)	C(221)	0.3401 (15)	0.7426 (6)	0.7134 (22)	50 (11)
C(111)	0.4842 (11)	0.5328 (7)	0.2867 (20)	51 (11)	C(222)	0.3021	0.7249	0.7667	60 (11)
C(112)	0.5436	0.5171	0.2702	74 (13)	C(223)	0.2643	0.7386	0.8294	126 (20)
C(113)	0.6104	0.5315	0.2847	80 (13)	C(224)	0.2645	0.7700	0.8387	104 (16)
C(114)	0.6179	0.5616	0.3158	83 (14)	C(225)	0.3025	0.7877	0.7854	119 (18)
C(115)	0.5585	0.5773	0.3322	118 (18)	C(226)	0.3403	0.7740	0.7227	86 (14)
C(116)	0.4917	0.5629	0.3177	98 (15)	C(227)	0.4368 (12)	0.6925 (5)	0.7065 (23)	49 (10)
C(117)	0.3989 (10)	0.4878 (5)	0.1694 (15)	26 (8)	C(228)	0.4607	0.6963	0.8097	87 (14)
C(118)	0.3816	0.4574	0.1753	46 (9)	C(229)	0.5029	0.6740	0.8680	81 (14)
C(119)	0.3809	0.4381	0.0950	87 (4)	C(2210)	0.5211	0.6480	0.8230	78 (13)
C(1110)	0.3974	0.4493	0.0089	74 (13)	C(2211)	0.4972	0.6442	0.7197	59 (11)
C(1111)	0.4147	0.4798	0.0030	77 (13)	C(2212)	0.4550	0.6665	0.6615	53 (10)
C(1112)	0.4154	0.4990	0.0833	45 (10)	C(231)	0.2056 (12)	0.7509 (4)	0.2225 (19)	44 (10)
C(121)	0.2062 (11)	0.4957 (7)	0.4356 (18)	44 (10)	C(232)	0.2274	0.7626	0.1407	64 (12)
C(122)	0.1531	0.5129	0.4632	59 (11)	C(233)	0.2041	0.7912	0.1038	82 (13)
C(123)	0.0933	0.4987	0.4843	124 (18)	C(234)	0.1592	0.8081	0.1487	62 (11)
C(124)	0.0866	0.4673	0.4777	148 (21)	C(235)	0.1375	0.7965	0.2305	61 (11)
C(125)	0.1397	0.4501	0.4501	166 (23)	C(236)	0.1607	0.7679	0.2674	66 (12)
C(126)	0.1995	0.4643	0.4290	128 (18)	C(237)	0.2666 (15)	0.6957 (6)	0.1742 (17)	51 (10)
C(127)	0.3281 (9)	0.5351 (6)	0.5318 (14)	50 (11)	C(238)	0.2166	0.6895	0.0840	69 (12)
C(128)	0.3043	0.5325	0.6192	58 (11)	C(239)	0.2403	0.6783	0.0030	104 (16)
C(129)	0.3429	0.5464	0.7069	100 (15)	C(2310)	0.3138	0.6735	0.0123	101 (16)
C(1210)	0.4053	0.5629	0.7073	100 (16)	C(2311)	0.3638	0.6797	0.1024	113 (18)
C(1211)	0.4290	0.5655	0.6200	63 (12)	C(2312)	0.3402	0.6909	0.1834	80 (13)
C(1212)	0.3904	0.5516	0.5322	71 (13)	C(241)	0.1312 (13)	0.7218 (6)	0.4935 (22)	83 (14)
C(131)	0.0762 (14)	0.5473 (7)	0.1554 (15)	70 (13)	C(242)	0.0597	0.7130	0.4534	72 (12)
C(132)	0.0525	0.5229	0.2027	84 (14)	C(243)	0.0031	0.7307	0.4694	75 (12)
C(133)	−0.0118	0.5082	0.1569	73 (12)	C(244)	0.0182	0.7572	0.5254	83 (14)
C(134)	−0.0525	0.5179	0.0637	78 (13)	C(245)	0.0897	0.7660	0.5655	98 (15)
C(135)	−0.0289	0.5423	0.0164	104 (16)	C(246)	0.1462	0.7483	0.5496	92 (15)
C(136)	0.0355	0.5570	0.0622	70 (12)	C(247)	0.2100 (13)	0.6714 (5)	0.5941 (15)	36 (9)
C(137)	0.1278 (14)	0.5837 (5)	0.3372 (15)	42 (9)	C(248)	0.1556	0.6698	0.6451	62 (12)
C(138)	0.1772	0.5868	0.4298	51 (10)	C(249)	0.1638	0.6509	0.7281	73 (13)
C(139)	0.1537	0.5964	0.5127	54 (11)	C(2410)	0.2264	0.6336	0.7600	65 (12)
C(1310)	0.0808	0.6029	0.5029	133 (21)	C(2411)	0.2808	0.6352	0.7090	62 (11)
C(1311)	0.0313	0.5997	0.4103	103 (16)	C(2412)	0.2727	0.6541	0.6260	58 (11)
C(1312)	0.0548	0.5901	0.3274	102 (15)					
(ii) Complex Anion									
Cr	0.6934 (3)	0.1208 (1)	0.6047 (4)	63 (1)	N(4)	0.6209 (18)	0.1079 (7)	0.6756 (25)	100 (11)
S(1)	0.5133 (6)	0.1608 (3)	0.3395 (9)	113 (4)	N(5)	0.6945 (12)	0.0768 (5)	0.5433 (19)	62 (7)
S(2)	0.8457 (6)	0.1472 (3)	0.3979 (10)	116 (4)	N(6)	0.6942 (12)	0.1638 (6)	0.6652 (19)	68 (8)
S(3)	0.8714 (6)	0.0984 (3)	0.9043 (9)	113 (4)	C(1)	0.5741 (17)	0.1451 (8)	0.4350 (26)	66 (10)
S(4)	0.4954 (8)	0.0961 (4)	0.7354 (12)	160 (5)	C(2)	0.7970 (17)	0.1388 (8)	0.4809 (27)	67 (10)
N(1)	0.6153 (13)	0.1326 (6)	0.4869 (20)	64 (18)	C(3)	0.8115 (16)	0.1038 (7)	0.7955 (26)	57 (9)
N(2)	0.7664 (14)	0.1337 (6)	0.5372 (21)	71 (9)	C(4)	0.5744 (24)	0.1031 (10)	0.6935 (34)	116 (16)
N(3)	0.7701 (14)	0.1091 (6)	0.7214 (22)	75 (9)					
(iii) Dichloromethane Solvate									
C(7)	0.6824 (42)	0.1146 (20)	0.2434 (66)	34 (26)	Cl(72)	0.6638 (14)	0.0812 (7)	0.2694 (23)	88 (9)
Cl(71)	0.6892 (14)	0.1232 (6)	0.1321 (21)	75 (8)					

Table I (*Continued*)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	28 (1)	35 (1)	36 (1)	−1 (1)	4 (1)	−1 (1)
W(2)	31 (1)	39 (1)	35 (1)	−1 (1)	3 (1)	−2 (1)
Br(1)	47 (2)	56 (2)	68 (3)	−5 (2)	7 (2)	−12 (2)
Br(2)	55 (2)	59 (2)	53 (3)	4 (2)	2 (2)	1 (2)

[a] The standard deviation of the least significant digit is included in parentheses in this and subsequent tables. [b] Anisotropic thermal parameters (×10³, Å²) are given in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

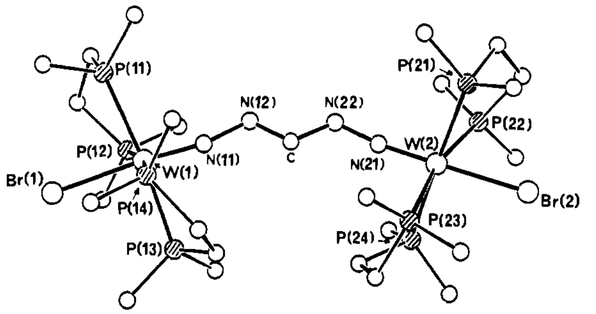

Figure 1. Structure of the $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$ cation (phenyl groups omitted).

Table II. Selected Bond Distances (Å) of the $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$ Cation

W(1)-Br(1)	2.618 (3)	W(2)-Br(2)	2.607 (4)
W(1)-P(11)	2.583 (8)	W(2)-P(21)	2.547 (9)
W(1)-P(12)	2.531 (9)	W(2)-P(22)	2.544 (8)
W(1)-P(13)	2.498 (7)	W(2)-P(23)	2.516 (7)
W(1)-P(14)	2.500 (9)	W(2)-P(24)	2.517 (8)
W(1)-N(11)	1.690 (23)	W(2)-N(21)	1.677 (21)
N(11)-N(12)	1.43 (3)	N(21)-N(22)	1.34 (3)
N(12)-C	1.29 (4)	N(22)-C	1.37 (4)

Table III. Selected Bond Angles (Deg) of the $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$ Cation

Br(1)-W(1)-P(11)	84.5 (2)	Br(2)-W(2)-P(21)	82.3 (2)
Br(1)-W(1)-P(12)	79.0 (2)	Br(2)-W(2)-P(22)	78.4 (2)
Br(1)-W(1)-P(13)	90.1 (2)	Br(2)-W(2)-P(23)	90.0 (2)
Br(1)-W(1)-P(14)	92.1 (2)	Br(2)-W(2)-P(24)	96.8 (2)
Br(1)-W(1)-N(11)	174.9 (8)	Br(2)-W(2)-N(21)	177.8 (7)
P(11)-W(1)-P(12)	79.2 (3)	P(21)-W(2)-P(22)	79.5 (3)
P(11)-W(1)-P(13)	174.2 (3)	P(21)-W(2)-P(23)	104.6 (3)
P(11)-W(1)-P(14)	99.5 (3)	P(21)-W(2)-P(24)	175.4 (3)
P(11)-W(1)-N(11)	99.8 (8)	P(21)-W(2)-N(21)	95.7 (7)
P(12)-W(1)-P(13)	101.9 (3)	P(22)-W(2)-P(23)	167.2 (3)
P(12)-W(1)-P(14)	171.1 (3)	P(22)-W(2)-P(24)	96.1 (3)
P(12)-W(1)-N(11)	98.9 (8)	P(22)-W(2)-N(21)	102.0 (7)
P(13)-W(1)-P(14)	78.5 (2)	P(23)-W(2)-P(24)	79.5 (3)
P(13)-W(1)-N(11)	85.7 (8)	P(23)-W(2)-N(21)	89.8 (7)
P(14)-W(1)-N(11)	90.0 (8)	P(24)-W(2)-N(21)	86.4 (7)
W(1)-N(11)-N(12)	163 (2)	W(2)-N(21)-N(22)	172 (2)
N(11)-N(12)-C	121 (2)	N(21)-N(22)-C	124 (2)
N(12)-C-N(22)	122 (2)		

On the basis of these results, the monocation was provisionally formulated as a binuclear species in which two $[WBr(dppe)_2N_2]$ units are linked at their terminal nitrogen atoms by a CH group derived from $CHFBr_2$; a single-crystal X-ray study of the Reineckate salt has confirmed this proposal.

The structure of the $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$ cation, shown in Figure 1 (phenyl groups omitted), reveals an essentially planar $[WN_2CN_2W]$ bridge system with maximum deviation from the least-squares plane of 0.091 Å (Table IV). Bond angles at the central NCN fragment indicate sp² hybridization; 120, 124° at N and 122° at C. A more detailed view of the environment of W(1) is shown in Figure 2, and selected bond lengths and angles are given in Tables II and III, respectively. In spite of the weakly diffracting nature of the crystal used, with 139 nonhydrogen atoms to 5918 unique observed data, significant bond differences can be observed between this and related structures. As an example of the accuracy of the found atomic positions, seven published structures containing the dppe ligand coordinated to tungsten[4,11-14] show a mean W-P bond distance of 2.530 Å (range 2.493 (2)-2.59 (1) Å, and in the present cation the mean W-P distance is 2.530 Å (range 2.498 (8)-2.583 (8) Å. However, the mean W-N distance found here of 1.683 Å is ca. 0.08 Å shorter than the reported W-N distances in related compounds (mean, 1.762 Å; range, 1.75 (2)-1.783 (5) Å).[4,11-14] This bond shortening is accompanied by a lengthening of the W-Br distances to a mean of 2.613 Å compared to a mean value of 2.583 Å (range 2.569-2.609 Å) observed previously for five related tungsten complexes.[4,12,13] The coordination environ-

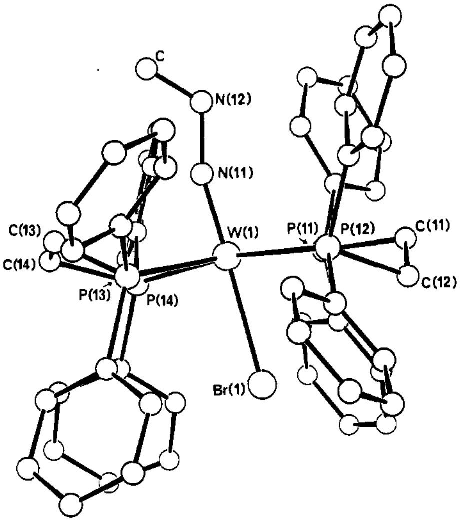

Figure 2. Coordination environment of W(1).

Table IV. Least-Squares Planes for $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$ Cation in the Form $pX + qY + rZ = s$ in Orthogonal Space with Deviations from Planes (Å) in Square Brackets[a]

Plane 1: W(1), P(11), P(12), P(13), P(14)
$p = 0.4746$, $q = 0.7991$, $r = 0.3689$, $s = 22.3700$
[W(1) 0.127, P(11) 0.003, P(12) −0.066,
P(13) 0.002, P(14) −0.067]

Plane 2: W(2), P(21), P(22), P(23), P(24)
$p = 0.3109$, $q = 0.9452$, $r = 0.0991$, $s = 28.6121$
[W(2) −0.121, P(21) −0.079, P(22) 0.147,
P(23), 0.144, P(24) −0.090]

Plane 3: W(1), N(11), N(12), C, W(2), N(21), N(22)
$p = 0.4113$, $q = -0.2550$, $r = 0.8751$, $s = -6.4061$
[W(1) 0.076, N(11) −0.068, N(12) −0.005, C −0.091,
W(2) −0.006, N(21) 0.042, N(22) 0.052, Br(1) 0.492,
Br(2) −0.173]

[a] Angles between least-squares planes: 1,2 = 50°; 1,3 = 94°; 2,3 = 92°.

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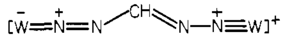
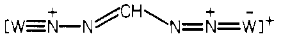
ments of the two tungsten atoms in the present structure are identical within experimental error.

In our preliminary description of the structure,[5] we suggested that the bridging ligand could be formally considered as a triply deprotonated derivative of formazan ($NH_2N{=}C{-}HN{=}NH$), and the two equivalent canonical forms i and ii


i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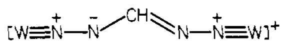
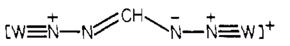
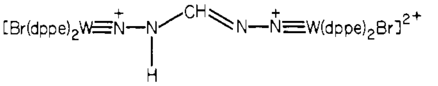

iii


iv

were therefore ascribed to the cation. Taken together, forms i and ii suggest an order of 2.5 for the tungsten–nitrogen bonds, but in view of the very short W–N distances involved, it seems necessary to invoke two further canonical forms, iii and iv, in which full triple bonds link tungsten and nitrogen.

Moreover, with use of literature values of C—N = 1.470 Å,[15] C=N = 1.255 Å,[15] N—N = 1.418 Å,[16] N=N = 1.240 Å[17], and by application of applying Pauling's equation[18] $r = r_1 - (r_1 - r_2)[3b/(2b + 1)]$, the double-bond character b within the N_2CN_2 fragment of the complex cation can be determined. In fact, a total of only 1.04 double bonds is present in this fragment, and even when the N–N distance in hydrazine itself [1.449 (4) Å][19] is used as the single-bond distance, a total of only 1.15 double bonds is calculated for the bridging ligand. The latter could thus also be regarded as a quintuply deprotonated derivative of methanehydrazonic hydrazide ($NH_2N{-}HCH{=}NNH_2$), since forms iii and iv are obviously major contributors to the structure, but for the sake of consistency and simplicity, we shall continue to refer to the bridging moiety as a formazanido(3–) ligand.

Although, in the present structure, this ligand appears only very approximately symmetrical about the central carbon atom, it seems unlikely a priori that the observed differences in N–N and C–N bond distances (Table II) represent significant departures from the symmetrical, delocalized structure implied by canonical forms i–iv. Certainly the IR spectrum shows no evidence for a full carbon–nitrogen double bond, although on protonation to the dication a strong $\nu(C{=}N)$ band appears at 1560 cm^{-1}. Clearly, protonation "fixes" the structure in a more localized form, and the relatively high electron density placed on nitogen by canonical forms iii and iv strongly suggests structure v for the dication.


v

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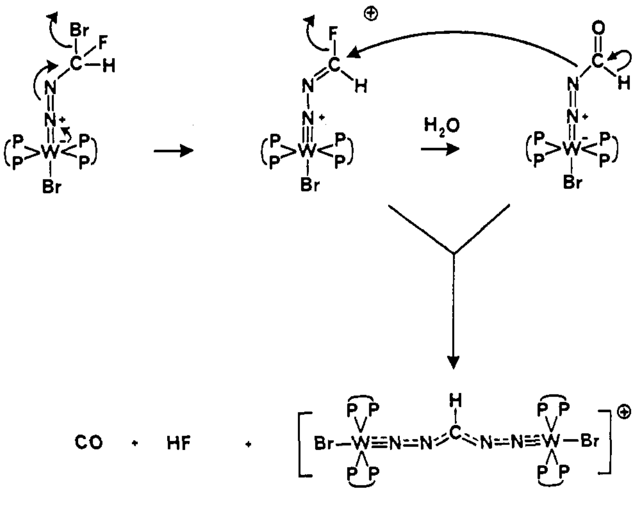
Scheme II. Proposed Mechanism of Formation of the $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$ Cation



The mechanism previously proposed[3] for generation of the formyldiazenido complex [WBr(dppe)$_2$N$_2$CHO] (Scheme I) may be extended to accommodate the present results. Since the susceptibility of a C–X bond to abstraction of X by the phenyl radical decreases in the order[20] C–X = C–I > C–Br > C–H > C–Cl > C–F, it seems certain that Ph will abstract bromine from $CHFBr_2$, giving the ·CHFBr radical and thus a fluorobromomethyldiazenido complex. Ionization of this species (Scheme II) would release bromide ion to give a complex of fluorodiazomethane which can hydrolyze to [WBr(dppe)$_2$N$_2$CHO]. The latter is indeed isolated from the reaction in low yield but, as shown in Scheme II, it can also react with its own precursor $[WBr(dppe)_2N_2CHF]^+$ to give the binuclear cation by loss of a proton and carbon monoxide. A precedent for this may be found in the reaction of Me_2NCHO with $Me_2N{=}CHCl^+$, which is known to afford the symmetrical, delocalized, tetramethylformamidinium ion by decarbonylation and loss of HCl (eq 1).[21]

$$Me_2NCHO + [Me_2N{=}CHCl]^+ \rightarrow [Me_2N{\cdots}CH{\cdots}NMe_2]^+ + CO + HCl \quad (1)$$

Acknowledgment. We wish to thank Dr. W. Hewertson and Dr. R. A. Head for valuable discussions.

Registry No. $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot{}^1/_3CH_2Cl_2$, 79199-39-6; $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+Br^-$, 77983-52-9; $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+PF_6^-$, 77983-53-0; WBr(dppe)$_2N_2$CHO, 77945-95-0; $[WBr(dppe)_2N_2H_2]^+Br^-$, 73460-77-2; $CHFBr_2$, 1868-53-7.

Supplementary Material Available: Bond distances and angles within the dppe ligands and the complex anion (Tables IIs and IIIs, respectively) and listings of structure factors for the X-ray structure determination (36 pages).

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