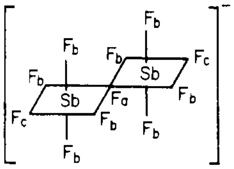
about an I(III), i.e., on going from $[ICl_2]^+[SbCl_6]^-$ to $[ICl_2]^+[SbF_6]^-$, one would have predicted that the quadrupole coupling constant would become more positive. This does not happen, and the trend, if real, is rather in the opposite sense. As the terminal I–Cl bond becomes stronger, then the I---Cl(F) bond becomes weaker so that the total electron density in the *xy* plane does not change significantly, and hence the quadrupole coupling constant remains the same.

Isomer shift changes in ^{127}I Mössbauer spectroscopy are generally quite small, and little change was expected in this series. The measured values for $[ICl_2]^+[SbF_6]^-$ and $[ICl_2]^+[SbCl_6]^-$ are the same within experimental error, and the differences for I_2Cl_6 and $K^+[ICl_4]^-\cdot H_2O$ are more likely due to errors introduced by converting data from other laboratories than to real changes in s-electron density. Perhaps this aspect should be examined more carefully.



I

^{19}F NMR. The ^{19}F NMR spectrum of a solution of I_2Cl_6/SbF_5 in SO_2ClF which ultimately produced crystals of $[ICl_2]^+[SbF_6]^-$ is shown in Figure 4. It is clear that in this solution, at low temperature, the $[Sb_2F_{11}]^-$ anion (I) predominates. The low-field multiplet observed at −89.9 ppm (all shifts relative to external $CFCl_3$) is assigned to the bridging fluorine F_a which couples to F_b with $J_{Fa-Fb} = 63$ Hz. The doublet of doublets at −111.9 ppm is due to the eight equivalent fluorines F_b. Finally a high-field quintet at −135.6 ppm is due to the two equivalent fluorines F_c such that $J_{Fc-Fb} = 105$ Hz. A partially resolved coupling of ca. 10 Hz to the bridging fluorine Fa is also observed. Two additional weak lines in the spectrum at −103.2 and −104.4 ppm are attributed to the presence of a small amount of SbF_5: the same lines are present in the ^{19}F NMR spectrum of SbF_5 in SO_2ClF. Multiplets found at ∼−70 and ∼−81 ppm are thought to be due to the presence of antimony chloride fluorides. Since no single sharp line is observed in the spectrum, this indicates that there is no appreciable quantity of $[SbF_6]^-$ present in solution. Thus it appears that, while the $[Sb_2F_{11}]^-$ anion is more stable in solution in the presence of excess SbF_5, the $[SbF_6]^-$ anion is able to stabilize the $[ICl_2]^+$ cation in the solid state. That Aubke and co-workers[7] were able to obtain a red solid analyzing as $[ICl_2]^+[Sb_2F_{11}]^-$ by pumping under vacuum on a mixture of I_2Cl_6 and excess SbF_5 remains something of a mystery. Presumably the SbF_5 initially removes a chlorine from the I_2Cl_6 to produce an antimony chloride fluoride which undergoes exchange with SbF_5 to give an $[Sb_2F_{11}]^-$ salt according to eq 1. The molecule SbF_4Cl has never been isolated

$$I_2Cl_6 + 6SbF_5 \rightarrow 2[ICl_2]^+[Sb_2F_{11}]^- + 2SbF_4Cl \quad (1)$$

but presumably rearranges to produce other antimony(V) chloride fluorides all of which are quite volatile.[25-27] The lines at ∼−70 to −80 ppm in the ^{19}F NMR spectrum are thought to be due to these species. In the SO_2ClF solution an equilibrium between $[Sb_2F_{11}]^-$, $[SbF_6]^-$, and SbF_5 (eq 2) probably exists with the equilibrium lying largely to the left-hand side.

$$[ICl_2]^+[Sb_2F_{11}]^- \rightleftharpoons [ICl_2]^+[SbF_6]^- + SbF_5 \quad (2)$$

Conclusions

Single-crystal X-ray crystallographic studies on the product of the reaction between I_2Cl_6 and excess SbF_5 in SO_2ClF solution have shown that it is the $[SbF_6]^-$ rather than the $[Sb_2F_{11}]^-$ compound that is produced. ^{19}F NMR indicates the presence of the $[Sb_2F_{11}]^-$ species in solution. The arrangement about the iodine(III) in the cation is that of a distorted square with two short terminal I–Cl bonds and two unusually short I---F bridge bonds of length 2.650 (6) Å, indicating a rather strong cation–anion interaction. ^{127}I Mössbauer spectroscopic studies of $[ICl_2]^+[SbF_6]^-$ and $[ICl_2]^+[SbCl_6]^-$ show that the bridging I---F interaction in the former compound is of comparable strength to that of the I---Cl interaction in the latter molecule.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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The Molybdenum–Molybdenum Triple Bond. 9.[1] Bis(1,3-di-*p*-tolyltriazenido)bis(dimethylamido)dimethyldimolybdenum

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1,2-$Mo_2Me_2(NMe_2)_4$ reacts in hydrocarbon solvents with 1,3-di-*p*-tolyltriazine, $C_7H_7NNNHC_7H_7$, to give the title compound as a red crystalline solid. An X-ray study shows that, in the solid state, the molecule has a crystallographically imposed C_2 axis of symmetry. The Mo≡Mo bond (2.174 (1) Å) is bridged by a cis pair of triazenido ligands which afford sufficient flexibility to allow a noneclipsed geometry. Each molybdenum atom is coordinated to three nitrogen atoms and one carbon atom which roughly lie in a plane. Pertinent bond distances are Mo–C(methyl) = 2.193 (4) Å, Mo–N(dimethylamido) = 1.948 (3) Å, and Mo–N(triazenido) = 2.157 (3) and 2.283 (3) Å, with the longer distance associated with the Mo–N bond which is trans to the Mo–CH_3 bond. These observations are compared with other findings in dimolybdenum and ditungsten chemistry (M≡M). Crystal data for $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ are $a = 21.608$ (5) Å, $b = 9.440$ (2) Å, $c = 24.076$ (6) Å, $\beta = 135.49$ (1)°, $V = 3442.5$ (1) Å^3, $Z = 4$, $d_{calcd} = 1.464$ g cm^{-3}, and space group $C2/c$.

An extensive coordination chemistry surrounds the $(M \equiv M)^{6+}$ unit for molybdenum and tungsten. The metal atoms may be coordinated to 3, 4, 5, or 6 ligand atoms, and, for a given coordination number, there appears to be a preference

Table I. Fractional Coordinates for $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	4959.8 (2)	3483.4 (3)	2023.4 (1)	13
N(2)	5432 (2)	1695 (3)	2053 (2)	19
C(3)	5315 (3)	1419 (4)	1387 (3)	27
C(4)	5802 (3)	449 (4)	2558 (3)	26
C(5)	3584 (2)	2926 (4)	963 (2)	20
N(6)	4199 (2)	5558 (3)	1628 (1)	13
N(7)	3834 (2)	5927 (3)	1856 (1)	14
N(8)	4015 (2)	5061 (3)	2384 (1)	14
C(9)	3998 (2)	6484 (3)	1050 (2)	16
C(10)	4229 (2)	6053 (4)	665 (2)	17
C(11)	4076 (2)	6925 (4)	115 (2)	20
C(12)	3680 (2)	8239 (4)	−80 (2)	20
C(13)	3449 (2)	8659 (4)	305 (2)	20
C(14)	3607 (2)	7805 (4)	864 (2)	19
C(15)	3520 (3)	9189 (5)	−676 (2)	26
C(16)	3688 (2)	5538 (3)	2699 (2)	14
C(17)	3431 (2)	4533 (3)	2920 (2)	15
C(18)	3188 (2)	4940 (4)	3298 (2)	17
C(19)	3208 (2)	6351 (3)	3471 (2)	17
C(20)	3447 (2)	7349 (4)	3226 (2)	19
C(21)	3680 (2)	6960 (4)	2846 (2)	18
C(22)	2992 (3)	6801 (4)	3917 (2)	23
H(23)	5010 (21)	2201 (38)	1027 (19)	14 (7)
H(24)	5886 (25)	1188 (37)	1566 (22)	23 (8)
H(25)	5010 (27)	594 (48)	1139 (24)	34 (9)
H(26)	5420 (24)	−359 (41)	2265 (20)	22 (7)
H(27)	6314 (25)	232 (38)	2713 (21)	23 (8)
H(28)	5880 (25)	650 (44)	3000 (23)	31 (9)
H(29)	3158 (24)	3292 (37)	919 (21)	21 (8)
H(30)	3457 (26)	3325 (43)	552 (24)	31 (9)
H(31)	3523 (24)	1991 (48)	898 (22)	27 (8)
H(32)	4466 (20)	5176 (34)	776 (18)	8 (6)
H(33)	4234 (24)	6625 (38)	−105 (22)	25 (8)
H(34)	3182 (21)	9523 (39)	185 (19)	14 (7)
H(35)	3461 (20)	8080 (35)	1114 (19)	12 (7)
H(36)	4061 (27)	9622 (42)	−442 (22)	28 (8)
H(37)	3340 (31)	8757 (50)	−1066 (29)	47 (12)
H(38)	3147 (32)	9822 (55)	−846 (28)	48 (13)
H(39)	3444 (21)	3589 (34)	2812 (19)	14 (6)
H(40)	3005 (20)	4291 (35)	3419 (18)	11 (6)
H(41)	3456 (22)	8235 (40)	3326 (20)	17 (7)
H(42)	3846 (22)	7540 (38)	2724 (20)	20 (8)
H(43)	3504 (30)	7269 (50)	4399 (28)	46 (11)
H(44)	2469 (24)	7337 (37)	3566 (21)	20 (7)
H(45)	2880 (27)	6031 (46)	4040 (24)	29 (9)

[a] The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalent. The numbers in parentheses in this and all following tables refer to the errors in the least significant digits. Estimated standard deviations greater than 29 are not statistically significant but are left "unrounded", since the tables are all produced automatically by the X-TEL interactive programs.

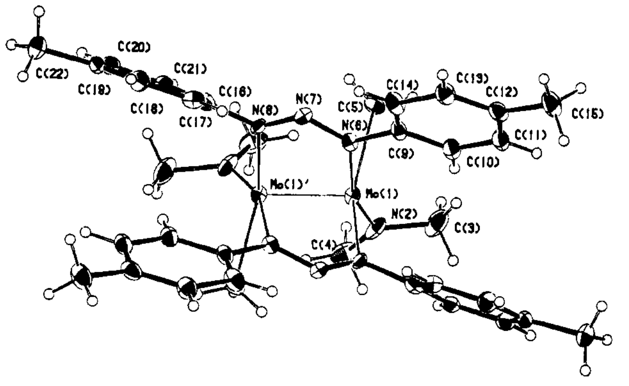

Figure 1. ORTEP view of the $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ molecule viewed down the C_2 axis of symmetry and showing the atom numbering scheme used in the tables. Atoms are represented by their thermal ellipsoids drawn at the 50% probability level.

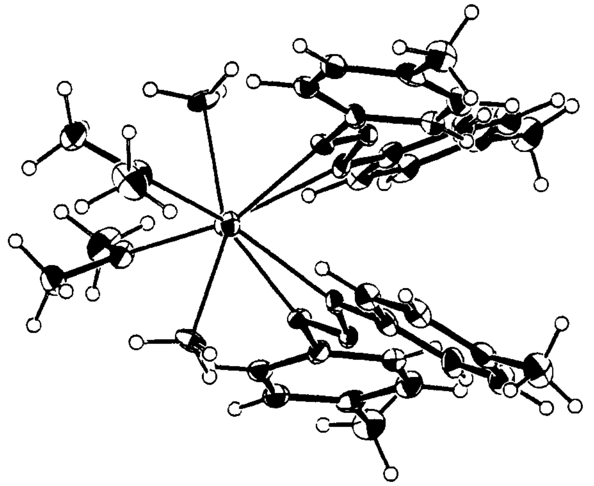

Figure 2. ORTEP view of the $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ molecule viewed down the Mo≡Mo bond.

for a specific geometry.[2] The data set is, however, still very limited, and caution must be applied against any wish to state rules for these systems. We are, however, trying to establish trends in coordination preferences and reactivity patterns. We report here the preparation and structure of $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$. The structure of the closely related compound $Mo_2(NMe_2)_4(C_7H_7N_3C_7H_7)_2$ was previously reported.[4]

Results and Discussion

Synthesis. In hydrocarbon solvents $Mo_2Me_2(NMe_2)_4$[5] and 1,3-di-*p*-tolyltriazine react upon mixing at room temperature to give red solutions from which $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ can be obtained as red crystals. Even in the presence of excess triazine, no further displacement of dimethylamido ligands occurs. The reaction shown below in eq

$$Mo_2Me_2(NMe_2)_4 + C_7H_7NNNHC_7H_7 \text{ (excess)} \rightarrow Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2 + 2HNMe_2 \quad (1)$$

$$Mo_2(C_nH_{2n+1})_2(NMe_2)_4 + ArNNNHAr \text{ (excess)} \rightarrow Mo_2(ArN_3Ar)_4 + C_nH_{2n} + C_nH_{2n+2} + 4HNMe_2 \quad (2)$$

$$Mo_2Et_2(NMe_2)_4 + CO_2 \text{ (excess)} \rightarrow Mo_2(O_2CNMe_2)_4 + CH_2{=}CH_2 + CH_3CH_3 \quad (3)$$

1 appears stoichiometric and irreversible. This contrasts with the reactions between 1,3-diaryltriazines (phenyl and *p*-tolyl) and $Mo_2R_2(NMe_2)_4$ compounds, where R = Et and *i*-Pr, which react according to eq 2.[6] Here by reductive elimination of alkene and alkane and further replacement of dimethylamido groups by triazenido ligands, the Mo-to-Mo triple bond is transformed to a quadruple bond.[7] In the related reaction between $Mo_2Et_2(NMe_2)_4$ and CO_2, which proceeds according to eq 3,[8] an intermediate, $Mo_2Et_2(NMe_2)_2(O_2CNMe_2)_2$, has been detected by ^1H NMR spectroscopic studies.[6] The structure of the $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ molecule was thus of particular interest to us.

Solid-State Structure. In the crystalline state, the compound is composed of discrete molecules of $Mo_2Me_2(NMe_2)_2$-

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Table II. Anisotropic Thermal Parameters (×10^4) for $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	197 (2)	127 (2)	198 (2)	−17 (1)	158 (1)	−20 (1)
N(2)	281 (15)	183 (14)	375 (16)	−33 (12)	273 (14)	−56 (13)
C(3)	444 (23)	266 (21)	479 (23)	−96 (20)	382 (21)	−149 (20)
C(4)	314 (20)	173 (18)	555 (26)	11 (16)	326 (20)	−42 (18)
C(5)	251 (18)	263 (20)	253 (18)	−84 (15)	184 (16)	−67 (15)
N(6)	181 (13)	157 (13)	184 (12)	−9 (11)	141 (11)	4 (11)
N(7)	198 (13)	166 (13)	195 (13)	−5 (11)	145 (12)	2 (11)
N(8)	205 (13)	161 (13)	210 (13)	26 (10)	162 (12)	38 (11)
C(9)	195 (15)	191 (15)	179 (14)	−36 (14)	124 (14)	−20 (13)
C(10)	232 (17)	209 (17)	202 (16)	21 (14)	155 (15)	10 (13)
C(11)	275 (18)	322 (19)	202 (16)	−56 (15)	187 (16)	−32 (14)
C(12)	249 (17)	278 (19)	172 (15)	−73 (14)	132 (14)	1 (14)
C(13)	282 (18)	175 (17)	263 (17)	−0 (15)	180 (16)	26 (14)
C(14)	290 (18)	227 (17)	242 (17)	−2 (14)	209 (16)	3 (14)
C(15)	397 (23)	320 (22)	267 (20)	−43 (20)	242 (19)	37 (18)
C(16)	176 (15)	202 (15)	163 (15)	25 (14)	118 (14)	10 (14)
C(17)	203 (15)	144 (15)	193 (15)	−1 (13)	135 (14)	−0 (13)
C(18)	233 (17)	218 (17)	230 (16)	−2 (13)	176 (15)	41 (13)
C(19)	209 (16)	272 (18)	200 (15)	28 (14)	154 (14)	9 (14)
C(20)	286 (18)	180 (18)	282 (18)	6 (14)	208 (16)	−29 (14)
C(21)	282 (18)	149 (16)	306 (18)	−10 (14)	230 (16)	22 (14)
C(22)	342 (21)	316 (21)	317 (20)	16 (17)	268 (19)	−19 (17)

[a] The form of the exponent is $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$.

Table III. Bond Distances (A) for the $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule[a]

A	B	dist
Mo(1)	Mo(1)′	2.174 (1)
Mo(1)	N(2)	1.948 (3)
Mo(1)	N(6)	2.283 (3)
Mo(1)′	N(8)′	2.157 (3)
Mo(1)	C(5)	2.193 (4)
N(2)	C(3)	1.457 (5)
N(2)	C(4)	1.454 (5)
N(6)	N(7)	1.290 (3)
N(6)	C(9)	1.425 (4)
N(7)	N(8)	1.314 (3)
N(8)	C(16)	1.428 (4)
C(9)	C(10)	1.391 (4)
C(9)	C(14)	1.389 (5)
C(10)	C(11)	1.383 (5)
C(11)	C(12)	1.386 (5)
C(12)	C(13)	1.389 (5)
C(12)	C(15)	1.507 (5)
C(13)	C(14)	1.385 (5)
C(16)	C(17)	1.383 (4)
C(16)	C(21)	1.392 (5)
C(17)	C(18)	1.388 (4)
C(18)	C(19)	1.387 (5)
C(19)	C(20)	1.391 (5)
C(19)	C(22)	1.505 (5)
C(20)	C(21)	1.373 (5)

[a] Bond distances to hydrogen atoms are given as supplementary material.

Table IV. Bond Angles (Deg) for the $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ Molecule[a]

A	B	C	angle
Mo(1)′	Mo(1)	N(2)	108.4 (1)
Mo(1)′	Mo(1)	N(6)	86.1 (1)
Mo(1)′	Mo(1)	N(8)′	91.7 (1)
Mo(1)′	Mo(1)	C(5)	104.5 (1)
N(2)	Mo(1)	N(6)	164.1 (1)
N(2)	Mo(1)	N(8)′	108.0 (1)
N(2)	Mo(1)	C(5)	94.3 (1)
N(6)	Mo(1)	N(8)′	77.2 (1)
N(6)	Mo(1)	C(5)	75.2 (1)
N(8)′	Mo(1)	C(5)	146.7 (1)
Mo(1)	N(2)	C(3)	116.1 (2)
Mo(1)	N(2)	C(4)	133.8 (2)
C(3)	N(2)	C(4)	109.6 (3)
Mo(1)	N(6)	N(7)	122.1 (2)
Mo(1)	N(6)	C(9)	124.1 (2)
N(7)	N(6)	C(9)	113.4 (2)
N(6)	N(7)	N(8)	113.1 (2)
Mo(1)′	N(8)	N(7)	121.8 (2)
Mo(1)′	N(8)	C(16)	122.0 (2)
N(7)	N(8)	C(16)	113.4 (2)
N(6)	C(9)	C(10)	117.9 (3)
N(6)	C(9)	C(14)	123.8 (3)
C(10)	C(9)	C(14)	118.3 (3)
C(9)	C(10)	C(11)	120.6 (3)
C(10)	C(11)	C(12)	121.8 (3)
C(11)	C(12)	C(13)	117.2 (3)
C(11)	C(12)	C(15)	121.5 (3)
C(13)	C(12)	C(15)	121.2 (3)
C(12)	C(13)	C(14)	121.7 (3)
C(9)	C(14)	C(13)	120.5 (3)
N(8)	C(16)	C(17)	118.3 (3)
N(8)	C(16)	C(21)	122.7 (3)
C(17)	C(16)	C(21)	118.8 (3)
C(16)	C(17)	C(18)	120.3 (3)
C(17)	C(18)	C(19)	121.2 (3)
C(18)	C(19)	C(20)	117.6 (3)
C(18)	C(19)	C(22)	121.8 (3)
C(20)	C(19)	C(22)	120.5 (3)
C(19)	C(20)	C(21)	121.6 (3)
C(16)	C(21)	C(20)	120.3 (3)

[a] Bond angles involving hydrogen atoms are given as supplementary material.

$(C_7H_7N_3C_7H_7)_2$. An ORTEP view of the molecule looking down the C_2 axis of symmetry and giving the atom numbering scheme used in the tables is shown in Figure 1. A view of the molecule looking down the Mo–Mo bond is shown in Figure 2. Final atomic coordinates and thermal parameters are given in Tables I and II, respectively. Complete listings of bond distances and angles are given in Tables III and IV, respectively. Pertinent torsional angles are given in Table V. Tables listing a number of least-squares planes calculated for this molecule and the deviations of atoms from these planes, together with dihedral angles between planes, are available as supplementary material.

The Mo-to-Mo distance is 2.174 (1) Å, which is crystallographically significantly shorter than that in either the parent compound[5] $Mo_2Me_2(NMe_2)_4$ (2.201 (1) Å) or the closely related compound $Mo_2(NMe_2)_4(C_7H_7N_3C_7H_7)_2$ (2.212 (1) Å).[4] Little chemical significance can be attributed to such a small variation in Mo-to-Mo distance, however, and the observed distance falls within the previously observed distances

Table V. Torsional Angles (Deg) for the $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$ Molecule

	(a) Along the Mo(1)–Mo(1)′ Bond			
N(2)	Mo(1)	Mo(1)′	C(5)′	51.66
N(2)	Mo(1)	Mo(1)′	N(6)′	125.31
N(2)	Mo(1)	Mo(1)′	N(8)	−157.67
C(5)	Mo(1)	Mo(1)′	N(6)′	−135.05
C(5)	Mo(1)	Mo(1)′	N(8)	−58.03
N(6)	Mo(1)	Mo(1)′	N(8)	15.62
N(8)′	Mo(1)	Mo(1)′	N(8)	92.64
	(b) In the Mo-Mo-Triazenido Ring			
Mo(1)′	Mo(1)	N(6)	N(7)	−18.70
Mo(1)	N(6)	N(7)	N(8)	5.76
N(6)	N(7)	N(8)	Mo(1)′	12.63
N(7)	N(8)	Mo(1)′	Mo(1)	−23.25
N(8)	Mo(1)′	Mo(1)	N(6)	15.62
Mo(1)′	Mo(1)	N(6)	C(9)	168.40
N(8)	N(7)	N(6)	C(9)	179.36
Mo(1)	Mo(1)′	N(8)	C(16)	176.94
N(6)	N(7)	N(8)	C(16)	174.03

associated with compounds containing a central $(\text{Mo}\equiv\text{Mo})^{6+}$ unit.[9] The Mo–C(methyl) and Mo–N(dimethylamido) distances are essentially identical with those found for $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$.

A comparison with the $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$ structure is interesting. In the latter, the triazenido ligands are bidentate but not bridging. The four nitrogen atoms bonded to each molybdenum atom also lie roughly within a plane, and a staggered conformation with respect to each end of the molecule is achieved by the interlocking of the Mo–NC_2 blades which are preferentially aligned along the Mo–Mo axis in order to maximize N p-to-Mo d π bonding. In the $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$ structure, the replacement of the NMe_2 ligand by the less sterically demanding Me ligand allows the triazenido ligands to act as bridging bidentate ligands without introducing an eclipsed configuration. The observed skew geometry, which is revealed in the view of the molecule shown in Figure 2 and in the torsional angles listed in Table V, is quite reconcilable with steric considerations. The only metal–ligand distances, which may reveal the influence of electronic factors, are the two Mo–N(triazenido) distances. The Mo–N distance trans to the Mo–NMe_2 bond is longer by more than 0.1 Å than that trans to the Mo–CH_3 bond. This could be attributable to a trans influence phenomenon which is typically found in square-planar platinum(II) compounds[10] and could similarly operate in dimetallic systems where metal–ligand bonding utilizes essentially sp^2d hybrid atomic orbitals, e.g., as in $(\text{Mo}\overset{4}{-}\text{Mo})^{4+}$-containing compounds.[11] However, in $(\text{Mo}\equiv\text{Mo})^{6+}$-containing compounds, the molybdenum atoms have five atomic orbitals available for forming bonds in the xy plane (s, p_x, p_y, d_{xy}, $\text{d}_{x^2-y^2}$) and can indeed form five bonds in a pentagonal plane as is seen in the structure of the $\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ molecule.[12] An inspection of the angles subtended from molybdenum to the ligating atoms in the $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$ molecule shows the trans angles N–Mo–N and C–Mo–N are 164.1 (1) and 146.7 (1)°, respectively. While the former may reasonably be called a trans angle, the latter much smaller angle of 146.7 (1)° cannot. Thus, it seems that with the availability of five molybdenum atomic orbitals, the methyl group, and triazenido nitrogen donor are not forced into mutual competition and the high trans influence which is associated with the methyl ligand[10] can be obviated.

^1H NMR data for $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$ are given in the Experimental Section and are consistent with the maintenance in solution of a structure akin to that found in the crystal.

Concluding Remarks. The present work provides an additional observation that the $(\text{Mo}\equiv\text{Mo})^{6+}$ unit will readily coordinate four ligand atoms to each molybdenum atom in a planar manner. The geometry with respect to each end of the molecule is reconcilable with steric considerations and consistent with the view that the Mo≡Mo bond, $\sigma^2\pi^4$, is cylindrical. For compounds in which the molybdenum atoms are coordinated to four ligand atoms, the overall geometry with respect to each end of the molecule may be eclipsed as is seen for $\text{Mo}_2(\text{O-}t\text{-Bu})_2(\text{O}_2\text{CO-}t\text{-Bu})_2$[13] and $\text{Mo}_2(\text{O}_2\text{P(O)OH})_4{}^{2-}$,[14] partially staggered as in $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$[15] and $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$, or fully staggered as in $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$.[4] In all of these compounds, the four ligand atoms coordinated to each molybdenum lie roughly in a square plane: coordination along the M–M axis is not found. The latter may not be favored because it would weaken the M–M σ bond. Cotton and co-workers[16] have shown this to be the case for the $(\text{Mo}\equiv\text{Mo})^{4+}$ moiety.

It is likely that $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$ and $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_2(\text{O}_2\text{CNEt}_2)_2$ compounds, which are intermediates in reactions 2 and 3, have similar ground-state geometries to that of $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$. Further studies are being directed toward characterizing the reactivity patterns of $\text{Mo}_2\text{R}_2(\text{NMe}_2)_2(\text{chelate})_2$ compounds.

Experimental Section

General procedures and the preparation of $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$ have been described.[5] Note the use of dry and oxygen-free solvents and atmospheres.

Preparation of $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_2(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$. All manipulations were carried out in a Vacuum Atmospheres Dri Box facility equipped with a p-tolyltriazine cold-storage box maintained at −30 °C.

In a typical preparation, $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$ (0.38 g, 0.95 mmol) was added to a 5-mL round-bottomed flask containing toluene (30 mL). The solution changed immediately from golden, characteristic of 1,2-$\text{Mo}_2\text{R}_2(\text{NMe}_2)_4$ compounds, to an intense red as p-tolyltriazine (0.49 g, 2.3 mmol) was added with stirring. Hexane (ca. 10 mL) was then added, and the flask was placed in the refrigeration unit of the drybox. After 4 days, the solution yielded ruby red crystals (ca. 0.4 g) which were collected and used for the X-ray crystallographic analysis. Satisfactory elemental analyses were not obtained. This situation was also found for $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_7\text{N}_3\text{C}_7\text{H}_7)_2$, and we believe results from solvent inclusion into some, but not all crystals. (In this X-ray study, no solvent molecule was present in the unit cell.)

^1H NMR data obtained in benzene-d_6 at 220 MHz at 20 °C: $\delta(\text{Mo–CH}_3)$ 1.50; $\delta(p\text{-tolyl CH}_3)$ 2.03, 2.19 (in the integral ratio 1:1); δ(NMe distal) 2.53; δ (NMe proximal) 4.13. δ values are in the ppm relative to Me_4Si.

X-ray Structural Determination. A crystal of dimensions 0.18 × 0.20 × 0.21 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off system of the diffractometer.[17] The diffractometer utilized for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator was interfaced to a TI 980 minicomputer with Slo-syn stepping motors to drive the angles. Centering was accomplished by using top/bottom–left/right slit assemblies. The minicomputer was interfaced by

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low-speed data lines to a CYBER 172-CDC 6600 multimain system where all computations were performed.

The cell dimensions obtained from 46 reflections at −170 °C with Mo Kα (λ = 0.71069 Å) were a = 21.608 (5) Å, b = 9.440 (2) Å, c = 24.076 (6) Å, β = 135.49 (1)°, V = 3442.5 (1) Å^3, Z = 4, d_{calcd} = 1.464 g cm^{-3}, and space group $C2/c$.

A total number of 6150 reflections were collected with use of standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 5 s, aperture size = 3.0 × 4.0 mm. Of the 6150 reflections collected, the number with unique amplitudes was 3050 and the number with $F > 2.33\sigma(F)$ was 2588. The limits of data collection were $5° < 2\theta < 50°$.

The structure was solved by a combination of direct and Fourier methods to give final residuals $R(F)$ = 0.0289 and $R_w(F)$ = 0.0309. The goodness of fit for the last cycle was 1.357, and the maximum Δ/σ for the last cycle was 0.65.

All of the hydrogen atoms were located and refined with use of isotropic thermal parameters. All nonhydrogen atoms were refined anisotropically.

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Registry No. $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$, 77080-92-3; $Mo_2Me_2(NMe_2)_4$, 67030-82-4.

Supplementary Material Available: A listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center,
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The Molybdenum–Molybdenum Triple Bond. 10.[1] Bis(1,3-diphenyltriazenido)- and Bis(2-oxy-6-methylpyridino)tetraisopropoxydimolybdenum

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Hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6$ (M≡M) react with each of 1,3-diphenyltriazine and 2-hydroxy-6-methylpyridine to give $Mo_2(O\text{-}i\text{-}Pr)_4(PhN_3Ph)_2$ and $Mo_2(O\text{-}i\text{-}Pr)_4(mhp)_2$, respectively. In both reactions, two isopropoxy groups are replaced by two bidentate groups which form cis bridges across the Mo≡Mo bond. The new compounds have been characterized by elemental analyses and IR and ^{1}H NMR spectroscopy; the 2-oxy-6-methylpyridino compound has been structurally characterized by a single-crystal X-ray study. Pertinent distances are Mo–Mo = 2.206 (1) Å, Mo–O (O-*i*-Pr) = 1.91 Å (average), Mo–N = 2.27 Å (average), and Mo–O (mhp) = 2.05 Å (average). Each molybdenum atom is coordinated to three oxygen atoms and a nitrogen atom, which lie roughly in a square plane. The molecule has virtual C_2 symmetry, and the two ends of the molecule avoid an eclipsed conformation by a slight twisting of the bridging groups: the average N–Mo–Mo–O torsional angle associated with the 2-oxy-6-methylpyridino ligand is 12°. These results are compared to other recent findings in the chemistry of Mo_2^{6+}-containing compounds. Crystal data for $Mo_2(O\text{-}i\text{-}Pr)_6(mhp)_2$ are a = 18.224 (8) Å, b = 15.991 (7) Å, c = 19.265 (10) Å, V = 5614 (1) Å^3, Z = 8, d_{calcd} = 1.402 g cm^{-3}, and space group $Pcab$.

Introduction

In contrast to the rather well-defined preference for six-coordinate octahedral geometries shown by chromium in its 3+ oxidation state, molybdenum(3+) and tungsten(3+) show a wide variety of coordination numbers and geometries and often form dinuclear compounds.[2] There are structurally characterized examples in which the metal atoms are coordinated to three, four, five, or six ligand atoms and to each other by metal-to-metal triple bonds.[3-5] Bioctahedra are also known and form an alternative to the structures involving unbridged M≡M bonds. These may be edge shared as in $W_2Cl_6(py)_4$[6] or face shared as in $W_2Cl_9^{3-}$.[7,8] As part of our continuing program in dinuclear transition-metal chemistry, we now report the syntheses and characterizations of two new Mo_2^{6+}-containing compounds.

Results and Discussions

Syntheses. Addition of 1,3-diphenyltriazine and 2-hydroxy-6-methylpyridine (2 equiv) to hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6$ (M≡M)[9] leads to the formation of $Mo_2(O\text{-}i\text{-}Pr)_4(PhN_3Ph)_2$ and $Mo_2(O\text{-}i\text{-}Pr)_4(mhp)_2$, respectively, with the elimination of 2 equiv of isopropyl alcohol (mhp is used, hereafter, as an abbreviation for the anion derived from deprotonation of 2-hydroxy-6-methylpyridine). The reaction appears quantitative and irreversible.

Properties. Both compounds are red, air-sensitive, crystalline solids. They are appreciably soluble in aromatic hydrocarbon solvents, but noticeably less soluble in alkanes. Infrared data, ^{1}H NMR data, and elemental analyses are given in the Experimental Section.

Solid-State Structure of $Mo_2(O\text{-}i\text{-}Pr)_4(mhp)_2$. Final atomic positional parameters are given in Table I, anisotropic thermal parameters are given in Table II, and bond distances and angles are given in Tables III and IV, respectively. An ORTEP view of the molecule, giving the atom numbering scheme used in the tables, is shown in Figure 1; a view of the molecule down the Mo–Mo axis is shown in Figure 2. Torsional angles for

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