ously been observed in the SIMS spectra of amides.[36] It should not be forgotten, however, that the predominant fragmentations of the C_2A^+ ion yield Ag^+, Ag_2^+, and Ag_2H^+, which are *not* C-C bond scissions. It may be possible to account for Ag_2^+ ion formation via Scheme I, which is illustrated for silver propionate and which is based on MS/MS data.

The Ag_2H^+ ion does not arise in a sequential manner as indicated by the absence of the fragmentation routes marked with an "X". This suggests a direct route from $(Ag_2O_2CC_2H_5)^+$ to Ag_2H^+ via loss of $CH_2{=}CHCOOH$. This is consistent with the results of the overall study, which show little or no Ag_2H^+ in the spectra of silver acetate (necessitating loss of an epoxidate) and silver benzoate (loss of a destabilized aromatic ring) but relatively abundant Ag_2H^+ ions for silver butyrate (loss of $CH_3CH{=}CHCOOH$ or an isomer).[24]

An unexpected result in this study were the implications for small silver cluster ion structures. The species encountered here are simple prototypes of metal cluster complexes and as such are of particular importance. Reference has been made to the inability of Ag_2H^+ to yield Ag_2^+ as evidence for lack of a metal-metal bond in the former. Also, since $Ag_2H_2^+$ does not form Ag_2^+, the lack of a metal-metal bond would seem to be indicated here, too. Two linear structures may be imagined ($AgHAgH^+$ or $AgHHAg^+$) as well as a four-membered cyclic structure. Since this ion dissociates readily to form Ag_2H^+, the second linear structure is less likely than the former. The structure and energetics of the Ag_2H^+ ion have been studied with use of computational methods,[37] which show it to be hydrogen bonded. Other Ag_2X^+ ions that appear to contain Ag-Ag bonds are $Ag_2CH_3^+$ and $Ag_2C_6H_5^+$; daughter spectra of these ions show both Ag^+ and Ag_2^+. In the case of $Ag_2CH_3^+$, the daughter spectra are very simple, with Ag^+ and Ag_2^+ being present in 100% and 30% relative abundance, together with a trace of $AgCH_3^+$.

Conclusions

Both secondary ion and electron ionization mass spectra of the silver salts of organic acids contain ions that result from cleavage of a C-C bond, in analogy with the Hünsdiecker reaction in solution. In contrast to the proposed involvement of halogen in the condensed-phase reaction, studies of the MS/MS spectra of cluster ions containing several silver atoms confirm the unimolecular cleavage of these bonds. Formation of side products corresponding to free-radical dissociations is observed, and this is particularly evident in the case of silver benzoate. EI produces ions similar to those observed in SIMS, since both yield the cation/salt complex C_2A^+, although apparently from different precursors. In addition to fragmentation processes involving the C-C bond scission, metal-metal bond formation, as in Ag_2O^+, $Ag_2CH_3^+$, and $Ag_2C_6H_5^+$, is a noteworthy feature of the ion chemistry of silver carboxylic acid salts.

Acknowledgment. SIMS studies are supported by the National Science Foundation (Grant. No. CHE81-14410) and the MRL Program (Grant No. DMR80-20249).

Registry No. Silver acetate, 563-63-3; silver propionate, 5489-14-5; silver benzoate, 532-31-0.

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Contribution from the Department of Chemistry
and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

The Molybdenum-Molybdenum Triple Bond. 15.[1] Compounds with Chains of Metal Atoms Having M-M Single and Triple Bonds: $M_2(M'(M'Me_3)_3)_2(NMe_2)_4$ (M≡M) Where M = Mo and W and M' = Si and Sn

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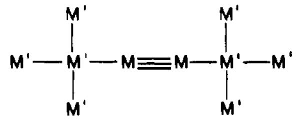
Metathetic reactions involving $M_2Cl_2(NMe_2)_4$ and $(THF)_3LiM'(M'Me_3)_3$, where M = Mo and W and M' = Si and Sn, carried out at room temperature in hydrocarbon solvents yield yellow-orange crystalline compounds $M_2(M'(M'Me_3)_3)_2(NMe_2)_4$. These compounds have a branched 10 metal atom chain with M'—M' and M—M' single bonds and a central M≡M bond. The compounds have been characterized by infrared, NMR, and mass spectroscopy and, for M = Mo and M' = Si and Sn, by single-crystal X-ray crystallography. They are members of a series of compounds of formula $1,2\text{-}M_2X_2(NMe_2)_4$, which adopt the anti-ethane-like geometry in both the solid state and solution. There are unprecedentedly high barriers to rotation about the M-N bond estimated at ca. 16 kcal mol^{-1} (M' = Sn) and >19 kcal mol^{-1} (M' = Si), reflecting the severe steric crowding at the metal centers M (Mo and W). Pertinent averaged bond distances (Å) and angles (deg): for I (M = Mo, M' = Si), Mo-Mo = 2.216 (1), Mo-Si = 2.670 (2), Mo-N = 1.95 (1), Si-Si = 2.38 (1), Mo-Mo-Si = 106.9 (1), Mo-Mo-N = 105 (1); for II (M = Mo, M' = Sn), Mo-Mo = 2.201 (2), Mo-Sn = 2.77 (1), Sn-Sn = 2.77 (1), Mo-N = 1.95 (2), Mo-Mo-Sn = 100.7 (2), Mo-Mo-N = 105 (2). Crystal data for I at -165 °C: $a = 9.400$ (3) Å, $b = 9.949$ (4) Å, $c = 13.304$ (6) Å, $\alpha = 83.24$ (3)°, $\beta = 97.81$ (2)°, $\gamma = 69.80$ (2)°, $Z = 1$, $d_{calcd} = 1.259$ g cm^{-3}, space group $P\bar{1}$. Crystal data for II at -162 °C: $a = 14.600$ (4) Å, $b = 31.737$ (13) Å, $c = 13.545$ (4) Å, $Z = 4$, $d_{calcd} = 1.876$ g cm^{-3}, space group $Pbn2_1$.

Introduction

As part of our continuing studies of the chemistry associated with compounds containing a central $(M{\equiv}M)^{6+}$ unit (M = Mo, W), we describe here the preparation and characterization of compounds containing the metal atom connectivity shown below. These are the first examples of compounds containing chains of metal atoms incorporating a multiple metal-metal bond.[2]



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[1] Part 14: Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 754.

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	4973.4 (3)	445.1 (3)	725.4 (2)	9
Si(2)	6829 (1)	−1718 (1)	2230 (1)	11
Si(3)	8076 (1)	−608 (1)	3347 (1)	15
Si(4)	5547 (1)	−2789 (1)	3323 (1)	13
Si(5)	8893 (1)	−3776 (1)	2002 (1)	14
C(6)	9619 (4)	−1915 (4)	4422 (3)	24
C(7)	6647 (4)	701 (4)	3976 (3)	22
C(8)	9093 (4)	401 (4)	2614 (3)	20
C(9)	5340 (4)	−4499 (4)	2957 (3)	22
C(10)	6571 (4)	−3324 (4)	4710 (3)	21
C(11)	3539 (4)	−1519 (4)	3316 (3)	19
C(12)	9510 (4)	−5310 (4)	3132 (3)	23
C(13)	10733 (4)	−3441 (4)	1905 (3)	22
C(14)	8285 (4)	−4487 (4)	830 (3)	19
N(15)	5789 (3)	1986 (3)	497 (2)	13
C(16)	6326 (5)	2563 (4)	−372 (3)	22
C(17)	5545 (4)	2993 (4)	1228 (3)	18
N(18)	2846 (3)	962 (3)	941 (2)	14
C(19)	2468 (4)	1785 (4)	1780 (3)	19
C(20)	1435 (4)	913 (4)	357 (3)	20

In the present case, M′ = Si and Sn. In a subsequent paper we shall describe compounds where M′ is a transition metal. A preliminary report of this work has appeared.[3]

Results and Discussion

Syntheses. The general procedure employed the metathetic reaction shown in eq 1. The reactions were carried out in hexane or toluene. Crystals of the $M_2(M'(M'Me_3)_3)_2(NMe_2)_4$

$$M_2Cl_2(NMe_2)_4 + 2(THF)_3LiM'(M'Me_3)_3 \rightarrow M_2(M'(M'Me_3)_3)_2(NMe_2)_4 + 2LiCl \quad (1)$$

$$M = Mo, W; M' = Si, Sn$$

compounds were obtained from the filtrate at −15 °C. The isolated crystalline yields ranged from 51% for M = W and M′ = Sn to 23% for M = Mo and M′ = Si. The lower yields of the silicon-containing compounds probably reflect the greater steric crowding associated with the substitution step. Once formed, the silicon-containing compounds are kinetically more inert than their tin analogues.

The choice of the $(THF)_3LiM'(M'Me_3)_3$ compounds was made because they are soluble in hydrocarbon solvents. The commonly employed compounds $LiM'Me_3$ are only stable in solvents such as THF and Et_2O. These solvents react with $M_2Cl_2(NMe_2)_4$ slowly, and metathetic reactions involving $M_2Cl_2(NMe_2)_4$ compounds are preferentially carried out in inert hydrocarbon solvents such as hexane or toluene.

The new compounds are yellow or orange, diamagnetic, crystalline compounds. They are thermally stable at room temperature and may be stored indefinitely in sealed vials under nitrogen or in vacuo. They do not sublime when heated in vacuo and decompose above +120 °C. The silicon-containing compounds are sufficiently volatile to yield a low-intensity molecular ion corresponding to $M_2(Si(SiMe_3)_3)_2(NMe_2)_4^+$ by use of the method of direct insertion and electron impact. The ion of highest mass seen under comparable conditions for the tin compounds was $M_2(Sn(SnMe_3)_3)(NMe_2)_4^+$. In contrast to the tin compounds, the silicon-containing compounds in the crystalline state can be handled in the air. This is unprecedented for $M_2X_2(NMe_2)_4$ compounds, where X = Cl,[4] alkyl,[5] aryl,[6] OR, and SR,[7] which all rapidly, if not violently, react with air. Presumably in $M_2(Si(SiMe_3)_3)_2(NMe_2)_4$ compounds the steric crowding is so great that the M_2 center is shielded from even small molecules like H_2O, CO_2, and O_2.

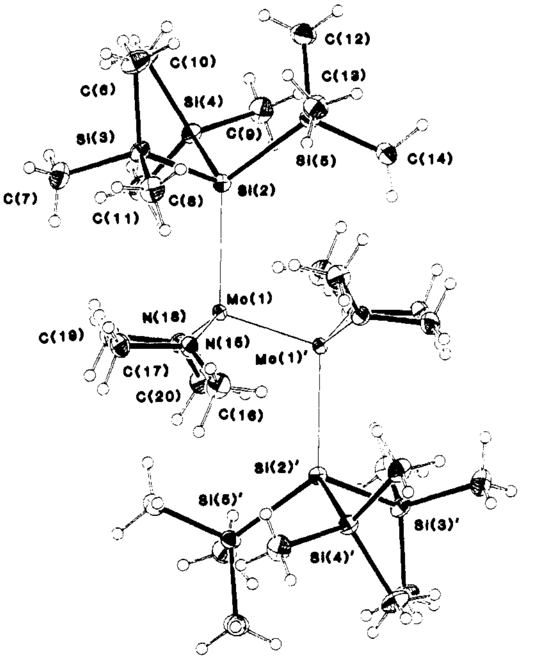

Figure 1. ORTEP view of the $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ molecule giving the atom number scheme used in the tables.

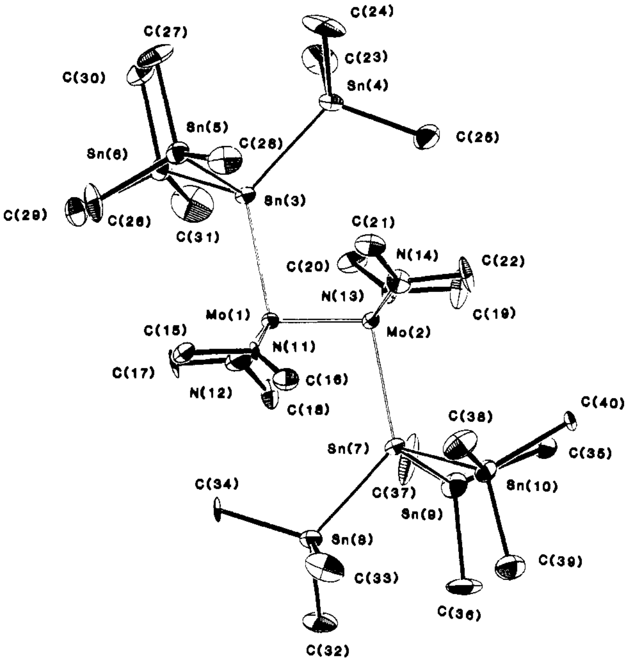

Figure 2. ORTEP view of the $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ molecule giving the atom number scheme used in the tables.

Solid-State and Molecular Structures. Crystals of $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ (I) were grown from THF solutions.

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Table II. Fractional Coordinates and Isotropic Thermal Parameters Parameters for $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4 \cdot 2C_7H_8$[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	7253 (1)	6158 (1)	3966 (5)	13
Mo(2)	7296 (1)	6355 (1)	2409 (2)	12
Sn(3)	7561 (1)	5296.1 (4)	3771 (2)	14
Sn(4)	7492 (1)	4849.5 (4)	2011 (2)	18
Sn(5)	6265 (1)	4869.9 (4)	4886 (2)	19
Sn(6)	9144 (1)	5027.8 (5)	4719 (2)	25
Sn(7)	7114 (1)	7221.3 (4)	2612 (2)	15
Sn(8)	7054 (1)	7658.8 (4)	4379 (2)	18
Sn(9)	8495 (1)	7647.5 (4)	1617 (2)	20
Sn(10)	5633 (1)	7535.0 (4)	1563 (2)	20
N(11)	6035 (10)	6279 (5)	4420 (14)	18
N(12)	8387 (11)	6387 (5)	4554 (12)	17
N(13)	8538 (13)	6242 (5)	1915 (15)	31
N(14)	6176 (10)	6117 (5)	1868 (11)	11
C(15)	5871 (15)	6181 (8)	5494 (15)	26
C(16)	5271 (13)	6524 (7)	4048 (18)	23
C(17)	8488 (15)	6273 (9)	5671 (18)	32
C(18)	9081 (15)	6699 (6)	4217 (18)	25
C(19)	8669 (16)	6352 (7)	898 (15)	25
C(20)	9330 (14)	6005 (7)	2325 (15)	22
C(21)	5491 (15)	5821 (6)	2120 (18)	24
C(22)	6041 (18)	6236 (6)	747 (16)	28
C(23)	8496 (15)	4349 (7)	1889 (20)	32
C(24)	6171 (14)	4549 (8)	1906 (21)	36
C(25)	7690 (17)	5242 (7)	729 (16)	26
C(26)	6347 (16)	5039 (6)	6456 (15)	23
C(27)	6446 (16)	4199 (7)	4825 (20)	32
C(28)	4879 (16)	5006 (8)	4424 (22)	35
C(29)	9116 (19)	5093 (7)	6322 (17)	34
C(30)	9416 (23)	4359 (7)	4426 (23)	52
C(31)	10379 (16)	5371 (10)	4307 (20)	47
C(32)	8272 (17)	8039 (8)	4581 (21)	38
C(33)	5891 (18)	8098 (8)	4483 (24)	47
C(34)	6979 (19)	7236 (7)	5688 (19)	34
C(35)	8507 (16)	7538 (7)	95 (18)	29
C(36)	8442 (17)	8320 (7)	1758 (20)	34
C(37)	9835 (17)	7448 (9)	2120 (26)	50
C(38)	4329 (14)	7309 (7)	2082 (21)	32
C(39)	5669 (16)	8222 (6)	1689 (23)	35
C(40)	5734 (16)	7383 (9)	25 (17)	33
C(41)	2834 (21)	3345 (9)	3199 (18)	42
C(42)	1918 (21)	3372 (9)	3208 (17)	39
C(43)	1460 (19)	3731 (11)	3319 (19)	40
C(44)	3076 (21)	−886 (9)	3363 (16)	42
C(45)	2095 (18)	−879 (8)	3294 (20)	34
C(46)	3364 (16)	3731 (10)	3186 (20)	37
C(47)	4392 (20)	3710 (15)	3107 (22)	68
C(48)	2517 (25)	976 (13)	2612 (33)	68 (10)
C(49)	2181 (31)	705 (15)	3614 (39)	36 (9)
C(50)	2264 (35)	864 (17)	4363 (45)	103 (14)
C(51)	2740 (46)	1337 (23)	4322 (57)	55 (15)
C(52)	2871 (37)	1529 (19)	3634 (52)	107 (15)
C(53)	2834 (30)	1324 (14)	2722 (35)	30 (10)
C(54)	3258 (40)	1673 (19)	2197 (49)	115 (16)
C(55)	3029 (41)	1358 (20)	1740 (49)	48 (14)
C(56)	3207 (43)	1769 (21)	3193 (52)	55 (13)
C(57)	2452 (34)	1097 (16)	3451 (38)	31 (10)

[a] Carbons C(41)–C(57) are solvent, one molecule of which was disordered.

Table III. Selected Bond Distances (Å) and Angles (deg) for the $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ Molecule

A	B	dist	A	B	dist
Mo(1)′	Mo(1)	2.216 (1)	Si(4)	C(9)	1.888 (4)
Mo(1)	Si(2)	2.670 (2)	Si(4)	C(10)	1.883 (4)
Mo(1)	N(15)	1.948 (3)	Si(4)	C(11)	1.872 (4)
Mo(1)	N(18)	1.956 (3)	Si(5)	C(12)	1.880 (4)
Si(2)	Si(3)	2.368 (2)	Si(5)	C(13)	1.889 (4)
Si(2)	Si(4)	2.388 (1)	Si(5)	C(14)	1.885 (4)
Si(2)	Si(5)	2.368 (2)	N(15)	C(16)	1.457 (4)
Si(3)	C(6)	1.880 (4)	N(15)	C(17)	1.462 (4)
Si(3)	C(7)	1.886 (4)	N(18)	C(19)	1.471 (4)
Si(3)	C(8)	1.886 (4)	N(18)	C(20)	1.462 (4)

A	B	C	angle	A	B	C	angle
Mo(1)′	Mo(1)	Si(2)	106.9 (0)	Mo(1)	Si(2)	Si(5)	125.2 (1)
Mo(1)′	Mo(1)	N(15)	104.1 (1)	Si(3)	Si(2)	Si(4)	103.4 (1)
Mo(1)′	Mo(1)	N(18)	105.5 (1)	Si(3)	Si(2)	Si(5)	103.1 (1)
Si(2)	Mo(1)	N(15)	111.6 (1)	Si(4)	Si(2)	Si(5)	102.3 (1)
Si(2)	Mo(1)	N(18)	109.0 (1)	Mo(1)	N(15)	C(16)	133.4 (2)
N(15)	Mo(1)	N(18)	118.8 (1)	Mo(1)	N(15)	C(17)	115.8 (2)
Mo(1)	Si(2)	Si(3)	105.1 (1)	Mo(1)	N(18)	C(19)	115.4 (2)
Mo(1)	Si(2)	Si(4)	115.3 (1)	Mo(1)	N(18)	C(20)	134.2 (2)

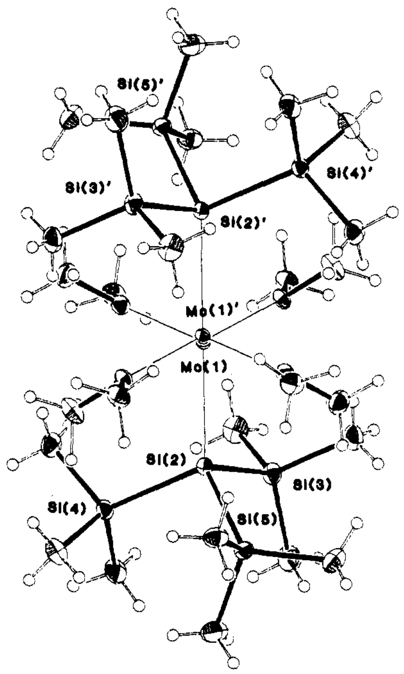

Figure 3. ORTEP view of the $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ molecule down the Mo–Mo bond.

$Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ (**II**) was crystallized from toluene, and the crystals contained solvent molecules. Fractional coordinates for I and II are given in Tables I and II, respectively. Selected bond distances and angles for I and II are given in Tables III and IV, and ORTEP views are shown in Figures 1 and 2, respectively.

In both I and II, the Mo–Mo distances are typical of what has been seen before for Mo≡Mo bonds in compounds of formula 1,2-$Mo_2X_2(NMe_2)_4$; cf. 2.211 (2) and 2.217 (2) Å (X = NMe_2),[8] 2.201 (1) (X = Me) Å,;[9] 2.200 (2) and 2.202 (2) Å (X = Cl),[4] 2.217 (1) Å (X = S-*t*-Bu),[7] 2.196 (1) Å (X = *p*-tolyl),[6] and 2.200 (1) Å (X = benzyl).[6] Similarly the Mo–N distances, 1.95 Å (averaged), and the proximal (135°) and distal (116°) Mo–N–C angles are comparable to those seen in the aforementioned group of 1,2-$Mo_2X_2(NMe_2)_4$ compounds.

II has virtual C_{2h} symmetry with six metal atoms, Sn(4), Sn(3), Mo(1), Mo(2), Sn(7), and Sn(8), lying in a plane. I has a rigorous, crystallographically imposed center of inversion. However, the Mo_2Si_8 skeleton is twisted such that the angle between the plane containing Mo(1), Si(2), and Si(5) and that containing Mo(1)′, Si(2)′, and Si(5)′ is 30°. This twisting is seen in the view of the $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ molecule shown in Figure 3.

In II, these are $SnMe_3$ groups that lie across the M≡M bond causing the N–Mo–N angles to be enlarged, 125°,

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Table IV. Selected Bond Distances (Å) and Angles (deg) for the $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ Molecule

A	B	dist
Sn(3)	Sn(4)	2.775 (2)
Sn(3)	Sn(5)	2.774 (2)
Sn(3)	Sn(6)	2.779 (2)
Sn(3)	Mo(1)	2.783 (2)
Sn(4)	C(23)	2.167 (19)
Sn(4)	C(24)	2.158 (21)
Sn(4)	C(25)	2.157 (21)
Sn(5)	C(26)	2.196 (20)
Sn(5)	C(27)	2.146 (22)
Sn(5)	C(28)	2.160 (23)
Sn(6)	C(29)	2.180 (24)
Sn(6)	C(30)	2.194 (23)
Sn(6)	C(31)	2.179 (24)
Sn(7)	Sn(8)	2.768 (2)
Sn(7)	Sn(9)	2.777 (2)
Sn(7)	Sn(10)	2.772 (2)
Sn(7)	Mo(2)	2.774 (2)
Sn(8)	C(32)	2.166 (20)
Sn(8)	C(33)	2.203 (21)
Sn(8)	C(34)	2.226 (25)
Sn(9)	C(35)	2.091 (24)
Sn(9)	C(36)	2.144 (22)
Sn(9)	C(37)	2.166 (25)
Sn(10)	C(38)	2.153 (23)
Sn(10)	C(39)	2.189 (21)
Sn(10)	C(40)	2.143 (23)
Mo(1)	Mo(2)	2.201 (2)
Mo(1)	N(11)	1.921 (15)
Mo(1)	N(12)	1.977 (16)
Mo(2)	N(13)	1.966 (18)
Mo(2)	N(14)	1.946 (15)
N	C	1.48 (3) (av)

A	B	C	angle
Sn(4)	Sn(3)	Sn(5)	101.2 (1)
Sn(4)	Sn(3)	Sn(6)	105.7 (1)
Sn(4)	Sn(3)	Mo(1)	125.3 (1)
Sn(5)	Sn(3)	Sn(6)	99.6 (1)
Sn(5)	Sn(3)	Mo(1)	108.5 (1)
Sn(6)	Sn(3)	Mo(1)	113.0 (1)
Sn(8)	Sn(7)	Sn(9)	101.4 (1)
Sn(8)	Sn(7)	Sn(10)	103.8 (1)
Sn(8)	Sn(7)	Mo(2)	125.8 (1)
Sn(9)	Sn(7)	Sn(10)	98.2 (1)
Sn(9)	Sn(7)	Mo(2)	111.4 (1)
Sn(10)	Sn(7)	Mo(2)	112.3 (1)
Sn(3)	Mo(1)	Mo(2)	100.6 (10)
Sn(3)	Mo(1)	N(11)	112.2 (5)
Sn(3)	Mo(1)	N(12)	105.4 (5)
Mo(2)	Mo(1)	N(11)	106.0 (5)
Mo(2)	Mo(1)	N(12)	104.9 (5)
N(11)	Mo(1)	N(12)	124.9 (7)
Sn(7)	Mo(2)	Mo(1)	100.7 (1)
Sn(7)	Mo(2)	N(13)	107.7 (4)
Sn(7)	Mo(2)	N(14)	110.1 (4)
Mo(1)	Mo(2)	N(13)	107.5 (6)
Mo(1)	Mo(2)	N(14)	103.0 (4)
N(13)	Mo(2)	N(14)	125.1 (7)
Mo(1)	N(11)	C(15)	114.5 (14)
Mo(1)	N(11)	C(16)	135.2 (15)
Mo(1)	N(12)	C(17)	112.6 (13)
Mo(1)	N(12)	C(18)	133.7 (14)
Mo(2)	N(13)	C(19)	113.9 (15)
Mo(2)	N(13)	C(20)	133.1 (15)
Mo(2)	N(14)	C(21)	139.7 (14)
Mo(2)	N(14)	C(22)	112.0 (13)

relative to 118° in I and 114.6 ± 6° in $Mo_2(NMe_3)_6$. This also has the effect of reducing the N-Mo-Mo-N dihedral angles from the idealized staggered value of 60° as is apparent from the view down the Mo-Mo bond shown in Figure 3. Also the Mo-Sn-Sn and Mo-Si-Si angles associated with the $M'Me_3$ groups that lie across the Mo-Mo bond are enlarged to 125°. The Si-Si-Si and Sn-Sn-Sn angles are all smaller than the tetrahedral angle.

Table V. ^{119}Sn Chemical Shifts of Some $XSn(SnMe_3)_3$ Compounds[a]

compd	$\delta(Sn^a)$	$\delta(Sn^b)$	ref
$RLi(THF)_3$	−104 to −107.1	−1031 to −1042	*b*
$RFeCpP(OPh)_3$	−103 (0.5)	−401 (0.5)	*b*
$Mo_2R_2(NMe_2)_4$	−68.0	−646.4	this work
$W_2R_2(NMe_2)_4$	−54.8	−574.4	this work
$RSnMe_3$	−80	−806	*c*
RMe	−89.5	−489.7	*d*
REt	−89.3	−440.9	*d*
R-*n*-Bu	−90.3	−459.9	*d*
R-*i*-Bu	−90.8	−480.4	*d*
R-*n*-C_5H_{11}	−90.1	−460.5	*d*
RPh	−83.2	−434.2	*d*

[a] All chemical shifts are in ppm relative to Me_4Sn; R = $Sn^b(Sn^aMe_3)_3$. [b] Kennedy, J. D.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* 1976, 1219. [c] Smith, P. J.; Tupcianskas, A. P. *Annu. Rep. NMR Spectrosc.* 1978, *8*, 361. [d] Mitchell, T. N.; el-Behairy, M. *J. Organomet. Chem.* 1977, *141*, 43.

Finally, it should be noted that the Si-Si distances, 2.37(1), Å (averaged), and the Sn-Sn distances, 2.77(1) Å (averaged), are as expected; cf. Si-Si = 2.361 (3) Å in $Si(SiMe_3)_4$[10] and Sn-Sn = 2.77 (1) Å (averaged) for $(SnPh_2)_6$.[11] A covalent radius for Mo to a pure σ-donor ligand in compounds of formula 1,2-$Mo_2X_2(NMe_2)_4$ has been estimated as 1.40 Å.[7] This value plus half of either the averaged Si-Si or Sn-Sn distance above yields 2.585 and 2.78 Å for predicted Mo-Si and Mo-Sn bond distances, respectively. The observed and predicted Mo-Sn distances agree well, but the observed Mo-Si distance is longer by 0.1 Å than the predicted value. We attribute this lengthening to steric crowding.

NMR Studies. At room temperature, the NMR spectra of $M_2(M'(M'Me_3)_3)_2(NMe_2)_4$ compounds show three singlets in the intensity ratio 9:2:2. These signals can be easily assigned to the methyl groups attached to M′ and the distal and the proximal methyl groups on the dimethylamide ligands. Only the anti rotamer is present in solution. Also, three sets of satellites are observed in the neighborhood of the $SnMe_3$ signal with coupling constants 45.4, 43.6, and 9.4 Hz for M = Mo and 45.6, 44.0, and 9.8 Hz for M = W. They can be assigned as $J(^{119}Sn\text{-}C\text{-}H)$, $J(^{117}Sn\text{-}C\text{-}H)$, and $J(^{119,117}Sn\text{-}Sn\text{-}C\text{-}H)$ for each respective set of satellites. The magnitude of $J(^{119}Sn\text{-}C\text{-}H)$ suggests that the Sn-C bonds of these complexes are essentially sp^3 hybridized.[12] Upon heating, the two NMe signals start to broaden and then they merge into the baseline at the coalescence temperature of +90 ± 5 °C for $M_2(Sn(SnMe_3)_3)_2(NMe_2)_4$. The activation energies for the rotation about M-N bonds are calculated as 16.4 ± 0.5 and 16.8 ± 0.5 kcal mol^{-1} for the molybdenum and the tungsten compounds, respectively. The $M_2(Si(SiMe_3)_3)_2(NMe_2)_4$ analogues show similar coalescence behavior; however, the T_c's were not recorded because they are beyond the boiling point of toluene-d_8. It is reasonable to estimate that the coalescence temperatures are between +130 and +140 °C, and therefore, a significantly higher activation energy for the rotation about M-N bonds, roughly 19 kcal mol^{-1}, can be calculated for the $M_2(Si(SiMe_3)_3)_2(NMe_2)_4$ compounds. Rotation about M-M′ and M′-M′ bonds is evidently rapid on the NMR time scale since only single methyl resonances are seen for the $SnMe_3$ groups even at −85 °C.

For $M_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ compounds, there are two types of tin atoms, one being bonded to three methyl groups, Sn^a, and the other to three trimethylstannyl groups, Sn^b, and two singlets are observed in the ^{119}Sn NMR spectra of Mo_2-

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(10) Bartell, L. S.; Chippard, F. B., Jr.; Boates, T. L. *Inorg. Chem.* **1970**, *9*, 2436.

(11) Olson, D. H.; Rundle, R. E. *Inorg. Chem.* **1963**, *2*, 1310.

(12) Holmes, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 3903.

$(Sn(SnMe_3)_3)_2(NMe_2)_4$ and $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$. Both signals are upfield relative to tetramethyltin, –68.0 ppm (Sn^a) and –646.4 ppm (Sn^b) for the molybdenum compound and –54.8 ppm (Sn^a) and –574.4 ppm (Sn^b) for the tungsten compound. These numbers are within the range of the chemical shifts of other $RSn(SnMe_3)_3$ compounds previously studied. See Table V. In addition to the main signals observed for Sn^a and Sn^b, several sets of satellites were also observed. However, no definite assignments have been made since it is difficult to separate couplings arising from ^{13}C, ^{x}Sn (x = 119, 117), and ^{183}W.

Concluding Remarks

From the relative ease of preparation and the stability of the compounds described herein, preparations of other M′—M≡M—M′-containing compounds can be anticipated. The structural characterizations of I and II reveal that the central $Mo_2(NMe_2)_4$ unit is little perturbed by the presence of two $M'(M'Me_3)_3$ units. The Mo–Mo and Mo–N distances are essentially identical with those seen previously in 1,2-$Mo_2X_2(NMe_2)_4$ compounds. The barriers to rotation about the Mo–N bonds are higher in the present compounds than have been previously noted. Normally restricted rotation arises because of electronic factors: Me_2N–Mo π-bonding.[6] There is no reason to believe that it is unusually perturbed in the Sn- and Si-substituted compounds, and we suggest that steric crowding in the present cases (Si > Sn) results in the anomalously high rotational barriers. The steric crowding, which is greater in the silicon-containing compounds, results in a lengthening of the Mo–Si bonds by 0.1 Å from that which otherwise would be expected. Steric crowding is responsible for the kinetic inertness toward decomposition in air. The presence of only the anti rotamer in solution is also understandable in terms of steric considerations. A molecular model indicates that a gauche rotamer would lead to an unacceptable amount of $M'Me_3$–$M'Me_3$ interaction across the M–M bond.

Experimental Section

General Procedures. Dry and oxygen-free atmosphere and solvents were used throughout.

^1H NMR spectra were recorded by using either a Varian HR-220 or a Nicolet 360 spectrometer equipped with variable-temperature accessories. ^{119}Sn NMR spectra were obtained from a Nicolet NT360 spectrometer with proton decoupling. Infrared spectra were recorded from Nujol mulls between CsI plates with the use of a Perkin-Elmer 283 spectrometer. Mass spectra were obtained on a Varian MS-902 by the method of direct insertion, courtesy of Dr. Peter Cook, Queen Mary College, London.

Chemicals. $Mo_2Cl_2(NMe_2)_4$ and $W_2Cl_2(NMe_2)_4$ were prepared according to the published procedures.[4] $(THF)_3LiSn(SnMe_3)_3$ and $(THF)_3LiSi(SiMe_3)_3$ were synthesized according to the literature routes.[13,14]

Preparation of $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$. $(THF)_3LiSn(SnMe_3)_3$ (1.05 g, 1.26 mmol) dissolved in hexane (20 mL) was added to $Mo_2Cl_2(NMe_2)_4$ (0.277 g, 0.631 mmol) suspended in hexane (20 mL). Upon addition, the mixture turned orange with the formation of an orange precipitate. After it was stirred for 1 h at room temperature, the solution was filtered. Then, the orange solids were collected and washed with hexane (10 mL, five times) until all the orange solids were extracted into the filtrate. The solution was then placed in a refrigerator at –15 °C, and the orange crystals that formed over a period of 12 h were collected by filtration and dried in vacuo (0.45 g, 44% based on Mo).

IR data in the region 1500–200 cm^{-1}: 1417 m, 1410 m, 1390 m, 1260 w, 1238 m, 1183 w, 1180 w, 1175 m, 1166 mw, 1141 m, 1090 w, br, 1065 w, 1033 m, 1015 w, br, 950 s, 937 s, 755 s, br, 568 m, 518 s, 500 s, 350 m.

Table VI. Crystal Data Summary[a]

	I	II
empirical formula	$Mo_2C_{26}H_{78}N_4Si_8$	$Mo_2C_{26}H_{78}N_4Sn_8\cdot 2C_7H_8$
color	yellow orange	light yellow
cryst dimens, mm	0.20 × 0.25 × 0.25	0.14 × 0.14 × 0.10
space group	$P\bar{1}$	$Pbn2_1$
temp, °C	–165	–162
a, Å	9.400 (3)	14.600 (4)
b, Å	9.949 (4)	31.737 (13)
c, Å	13.304 (6)	13.545 (4)
α, deg	83.24 (3)	
β, deg	97.81 (2)	
γ, deg	69.80 (2)	
Z, molecules/cell	1	4
V, Å^3	1138.60	6276.21
d_{calcd}, g/cm^3	1.259	1.876
wavelength, Å	0.710 69	0.710 69
mol wt	863.50	1772.61
linear abs coeff, cm^{-1}	7.652	35.434
detector to sample dist, cm	22.5	22.5
sample to source dist, cm	23.5	23.5
av Ω scan width at half-height, deg	0.25	0.25
scan speed, deg/min	4.0	4.0
scan width, deg (+dispersion)	2.0	2.0
individual bkgd, s	10	5
aperture aize, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflcns collcd	3138	4783
no. of unique intensities	2992	4330
no. of reflcns with $F > 3.00\sigma(F)$	2768	4105
$R(F)$	0.026	0.046
$R_w(F)$	0.030	0.049
goodness of fit for the last cycle	0.926	1.482
max Δ/σ for last cycle	0.05	0.05

[a] I is $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$ and II is $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4\cdot 2C_7H_8$.

^1H NMR data recorded at 220 MHz in toluene-d_8 at +16 °C (all chemical shifts in ppm relative to Me_4Si): NMe proximal, 3.96 (s, 12 H); NMe distal, 2.50 (s, 12 H); $SnMe_3$, 0.38 (s, 54 H); $J(^{119}Sn{-}C{-}H)$ = 45.4, $J(^{117}Sn{-}C{-}H)$ = 43.6, $J(^{117,119}Sn{-}Sn{-}C{-}H)$ = 9.4 Hz.

^{119}Sn NMR data recorded at 134 MHz in toluene-d_8 at +20 °C (all chemical shifts in ppm relative to Me_4Sn): $SnMe_3$, –68.0; Sn*Sn*Me_3, –646.4.

Preparation of $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$. To $W_2Cl_2(NMe_2)_4$ (0.652 g, 1.05 mmol) suspended in toluene (20 mL) was added $(THF)_3LiSn(SnMe_3)_3$ (1.77 g, 2.12 mmol) dissolved in toluene (20 mL). The color of the mixture turned dark red, and dark orange solids precipitated immediately. After 1 h of stirring, the mixture was filtered and the solids were washed with toluene (30 mL). Then, the solution was stored at –15 °C overnight. Dark orange crystals were collected and dried (0.95 g, 51% based on W).

IR data in the region 1500–200 cm^{-1}: 1420 ms, 1414 ms, 1393 m, 1262 m, 1245 m, 1186 m, 1182 m, sh, 1176 ms, 1169 m, sh, 1162 w, sh, 1143 ms, 1118 mw, 1093 w, br, 1070 mw, 1035 ms, 1020 w, br, 951 vs, 937 vs, 755 vs, br, 560 mw, br, 517 s, 500 s, 350 m, 318 w, 245 w, br, 226 w, br.

^1H NMR data recorded at 220 MHz in toluene-d_8 at +16 °C (all chemical shifts in ppm relative to Me_4Si): NMe proximal, 4.00 (s, 12 H); NMe distal, 2.38 (s, 12 H); $SnMe_3$, 0.40 (s, 54 H); $J(^{119}Sn{-}C{-}H)$ = 45.6, $J(^{117}Sn{-}C{-}H)$ = 44.0, $J(^{117,119}Sn{-}Sn{-}C{-}H)$ = 9.8 Hz.

^{119}Sn NMR data recorded at 134 MHz in toluene-d_8 at +20 °C (all chemical shifts in ppm relative to Me_4Sn): $SnMe_3$, –54.8; *Sn*SnMe_3, –574.4.

Preparation of $Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$. After $Mo_2Cl_2(NMe_2)_4$ (0.910 g, 2.07 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (1.90 g, 4.04 mmol) were placed into a flask in the drybox, hexane (20 mL) was added. The mixture was stirred for 1 h at room temperature. Then, it was

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(14) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem* .**1982**, *225*, 1.

filtered and the solids were washed with hexane (20 mL). Yellow crystals precipitated while the solution was concentrated. The crystals were separated and dried (0.395 g, 22.8% based on Mo).

IR data in the region 1500–200 cm^{-1}: 1419 mw, 1411 mw, 1393 m, 1296 w, br, 1255 ms, 1239 s, 1144 m, 1095 m, br, 1038 ms, 1020 m, br, 953 s, 938 s, 835 vs, br, 730 mw, br, 679 ms, 625 m, 619 ms, 570 mw, br, 470 w, br, 430 w, 418 w, 392 w, 360 w, br, 345 w, 335 w, 330 w, 319 w, 310 w, 294 w, 285 w, 270 w, 265 w, br, 230 w, br.

^1H NMR data recorded at 220 MHz in toluene-d_8 at +16 °C (all chemical shifts in ppm relative to Me_4Si): NMe proximal, 4.14 (s, 12 H); NMe distal, 2.56 (s, 12 H); $SiMe_3$, 0.35 (s, 54 H).

Preparation of $W_2(Si(SiMe_3)_3)_2(NMe_2)_4$. To $(THF)_3LiSi(SiMe_3)_3$ (0.55 g, 1.01 mmol) and $W_2Cl_2(NMe_2)_4$ (0.315 g, 0.512 mmol), which were placed into a flask in the drybox, was added hexane (20 mL). The mixture was stirred for 5 min, while yellow solids precipitated. The mixture was filtered and washed with hexane (20 mL). After workup, orange crystals were collected from the solution (0.131 g, 25.3% based on W).

IR data in the region 1500–200 cm^{-1}: 1418 mw, 1410 mw, 1391 m, 1295 w, br, 1253 ms, 1242 s, 1236 s, 1140 m, 1090 m, br, 1035 ms, 1018 m, br, 950 s, 935 s, 830 vs, br, 728 mw, br, 674 ms, 621 ms, 614 ms, 550 mw, br, 465 mw, br, 430 w, 415 w, 390 w, 355 w, br, 326 w, 316 w, 305 w, 290 w, 225 w, br.

^1H NMR data recorded at 220 MHz in toluene-d_8 at +16 °C (all chemical shifts in ppm relative to Me_4Si): NMe proximal, 4.17 (s, 12 H); NMe distal, 2.41 (s, 12 H); $SiMe_3$, 0.36 (s, 54 H).

Structural Determinations. General procedures and a listing of programs used have been reported.[15] Crystal data are summarized in Table VI.

$Mo_2(Si(SiMe_3)_3)_2(NMe_2)_4$. A suitable small sample was selected and transferred to the goniostat where it was cooled to −165 °C and characterized in the usual manner. The crystal was triclinic, space group $P\bar{1}$.

The data collection was carried out at −165 °C, by using a scan speed of 4°/min and background times of 10 s at either end of the scan width of 1.8° + dispersion. Data in the range $6° < 2\theta < 45$ were collected; a total of 3138 reflections were reduced to a unique set of 2992.

The molecule has a crystallographic center of symmetry, imposed by the space group. The Mo atom was located from a Patterson function, and the remaining atoms were readily located in a difference Fourier map. All non-hydrogen atoms were refined by full-matrix least squares by using anisotropic thermal parameters; the hydrogen atoms were located in a difference map and refined by using isotropic thermal parameters. A total of 1586 reflections having $F > 3\sigma(F)$ were used during the refinements. A total of 337 parameters were refined in a cyclical manner.

$Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$. Initial examination of the crystals indicated that they lost solvent, so the sample used in the study was cleaved while still in the crystallization liquid and transferred rapidly to the goniostat where it was cooled to −162 °C. Optical examination of the mounted crystal indicated a slight split at one end, but careful examination of Ω and 2θ scans indicated no splitting.

Examination of a limited hemisphere of reciprocal space yielded diffraction maxima that could be assigned an orthorhombic space group.

Examination of the four reflections chosen as standards indicated an abrupt drop in intensities approximately halfway through the data collection. When the crystal was examined, it was discovered that the fragment of the crystal where the original fracture was seen had indeed fallen off. Since the standards dropped by nearly identical percentages, a simple scaling function was applied.

The structure was solved by direct methods (MULTAN78) and refined by full-matrix least squares. Two toluene molecules of solvation were located, one well-behaved and the other disordered. All atoms with the exception of the disordered solvent were allowed to vary anisotropically. A difference Fourier at this stage consisted of numerous peaks of density 0.4–0.9 e/Å^3, with no clear indication of hydrogen atoms. The refinement was thus concluded.

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Registry No. I, 92456-19-4; II, 92456-18-3; $W_2(Si(SiMe_3)_3)_2(NMe_2)_4$, 84521-35-7; $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$, 84521-34-6; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $(THF)_3LiSi(SiMe_3)_3$, 81859-95-2; $(THF)_3LiSn(SnMe_3)_3$, 60552-34-3; Sn, 7440-31-5; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Complete listings of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles, VERSORT drawings, and listings of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page. The complete structural reports are available, in microfiche form only, from the Indiana University Library at \$2.50 per report. For compounds I and II request MSC Report Nos. 83036 and 82068, respectively.

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(15) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpartrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.