symmetry, has two nonequivalent protons at C-5 and two nonequivalent methyl substituents at C-1. Since *cis*-**15** is formed from the major component of the oxidation reaction of **1**, the assignment of stereochemistry to *cis*-**6** is thereby confirmed. Close spectral similarity between *cis*-**6** and the major products from the other co-oxidation reactions strongly suggests that they also possess cis stereochemistry.

The conclusion that alkylperoxy radicals of type **3** preferentially afford cis-disubstituted cyclic products is fully consistent with the behavior of closely related carbon-centered radicals,[5] and has important implications for prostanoid synthesis and biosynthesis since it is only through intermediates of cis orientation that prostaglandin endoperoxides can be constructed.

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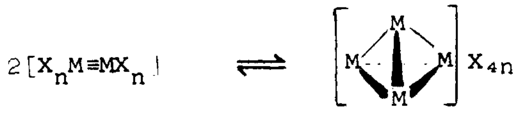
Metal-to-Metal Triple Bonds—to Cluster or Not to Cluster? Structural Characterization of Octakis(*tert*-butoxy)tetrakis(μ-fluoro)-tetramolybdenum and Octakis(*tert*-butoxy)tris(μ-fluoro)-(μ-dimethylamido)-tetramolybdenum

Sir:

We note that the chemistry of molybdenum and tungsten in the +3 oxidation state is currently dominated by compounds containing the central $(M{\equiv}M)^{6+}$ unit.[1] This is in contrast to the coordination chemistry of Cr(3+) which has a marked propensity to form octahedral complexes.[2] Furthermore, tetranuclear complexes of molybdenum and tungsten in the +3 oxidation state in which there is a central tetrahedral M_4 skeleton with delocalized M—M bonding are relatively rare.[3] Thus we have been trying to establish an equilibrium of the type expressed in (eq 1) below since it seemed plausible that,



(1)

for a given ligand X, or combinations of ligands X and Y, such an equilibrium could be established.[4] We report herein the structural characterization of two novel tetranuclear complexes of molybdenum formed by the coupling of two dinuclear species, $(M{\equiv}M)^{6+}$

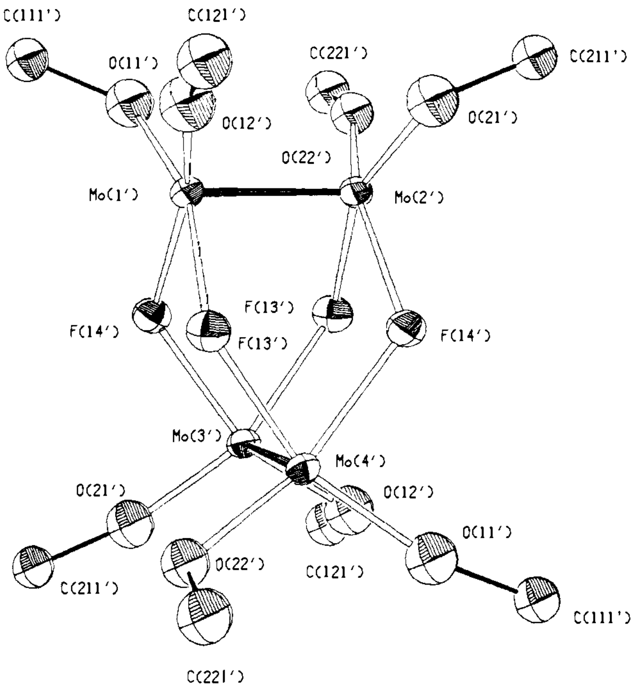


Figure 1. An ORTEP view of the central $Mo_4(\mu\text{-}F)_4(OC)_8$ skeleton of the $Mo_4(\mu\text{-}F)_4(OBu^t)_8$ molecule showing the atomic numbering scheme used in Table I. All atoms are represented by 50% thermal ellipsoids. A center of symmetry is located in the center of the molecule and the four alternate molybdenum positions have been removed for clarity.

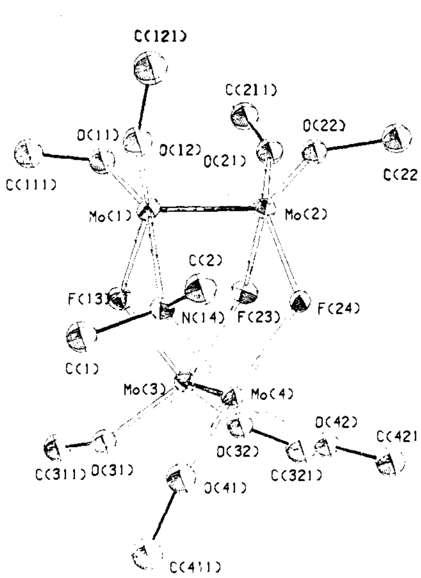


Figure 2. An ORTEP view of the central $Mo_4(\mu\text{-}F)_3(\mu\text{-}NC_2)(OC)_8$ skeleton of the $Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8$ molecule showing the atomic numbering scheme used in Table II. All atoms are represented by 50% thermal ellipsoids.

Addition of PF_3 (2 equiv) to a hydrocarbon solution of $Mo_2(OBu^t)_6$ $(M{\equiv}M)$ leads to a F- for -OBu^t exchange reaction in a similar manner to that previously reported in the preparation of $Mo_2Cl_2(NMe_2)_4$ from $Mo_2(NMe_2)_6$ and Me_3SiCl (2 equiv).[5] The resulting black, air-sensitive, hydrocarbon-soluble solid of empirical formula $MoF(OBu^t)_2$ is, however, tetranuclear unlike $Mo_2Cl_2(NMe_2)_4$ $(M{\equiv}M)$. In one preparation of this new molybdenum compound, crystals suitable for detailed X-ray work were grown from a hexane solution.

A preliminary solution of an X-ray data set collected at room temperature indicated that there were three Mo_4-containing molecules in the unit cell.[6] One molecule was disordered about the origin but refined well as $Mo_4(\mu\text{-}F)_4(OBu^t)_8$. See Figure

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Table I. Pertinent Structural Parameters for the $\mathrm{Mo_4(\mu\text{-}F)_4(OBu^t)_8}$ Molecule

Bond Distances in Ångstroms

A	B	distance	A	B	distance
Mo(1′)	Mo(2′)	2.262 (2)	Mo(3′)	Mo(4′)	2.263 (2)
Mo(1′)	Mo(3′)	3.743 (2)	Mo(3′)	F(13′)	2.121 (5)
Mo(1′)	Mo(4′)	3.730 (2)	Mo(3′)	F(14′)	2.122 (4)
Mo(1′)	F(13′)	2.056 (5)	Mo(3′)	O(12′)	1.963 (7)
Mo(1′)	F(14′)	2.101 (5)	Mo(3′)	O(21′)	1.850 (7)
Mo(1′)	O(11′)	1.968 (7)	Mo(4′)	F(13′)	2.142 (4)
Mo(1′)	O(12′)	1.882 (7)	Mo(4′)	F(14′)	2.120 (5)
Mo(2′)	Mo(3′)	3.713 (2)	Mo(4′)	O(11′)	1.914 (7)
Mo(2′)	Mo(4′)	3.700 (2)	Mo(4′)	O(22′)	1.923 (6)
Mo(2′)	F(13′)	2.101 (4)	O(11′)	C(111′)	1.459 (10)
Mo(2′)	F(14′)	2.092 (4)	O(12′)	C(121′)	1.455 (11)
Mo(2′)	O(21′)	1.992 (6)	O(21′)	C(211′)	1.411 (10)
Mo(2′)	O(22′)	1.908 (6)	O(22′)	C(221′)	1.422 (11)

Angles in Degrees

A	B	C	angle	A	B	C	angle
Mo(2′)	Mo(1′)	Mo(3′)	43.6 (1)	Mo(4′)	Mo(3′)	F(14′)	93.9 (1)
Mo(2′)	Mo(1′)	Mo(4′)	43.9 (1)	Mo(4′)	Mo(3′)	O(12′)	100.4 (2)
Mo(2′)	Mo(1′)	F(13′)	92.5 (1)	Mo(4′)	Mo(3′)	O(21′)	104.8 (2)
Mo(2′)	Mo(1′)	F(14′)	91.8 (1)	F(13′)	Mo(3′)	F(14′)	72.9 (2)
Mo(2′)	Mo(1′)	O(11′)	99.6 (2)	F(13′)	Mo(3′)	O(12′)	84.4 (2)
Mo(2′)	Mo(1′)	O(12′)	104.2 (2)	F(13′)	Mo(3′)	O(21′)	156.3 (2)
Mo(3′)	Mo(1′)	Mo(4′)	87.5 (1)	F(14′)	Mo(3′)	O(12′)	153.8 (2)
Mo(3′)	Mo(1′)	F(13′)	69.1 (1)	F(14′)	Mo(3′)	O(21′)	90.2 (2)
Mo(3′)	Mo(1′)	F(14′)	118.4 (1)	O(12′)	Mo(3′)	O(21′)	107.0 (3)
Mo(3′)	Mo(1′)	O(11′)	130.5 (2)	Mo(1′)	Mo(2′)	Mo(4′)	89.5 (1)
Mo(3′)	Mo(1′)	O(12′)	67.5 (2)	Mo(1′)	Mo(4′)	Mo(3′)	46.1 (1)
Mo(4′)	Mo(1′)	F(13′)	118.4 (1)	Mo(1′)	Mo(4′)	F(13′)	116.2 (1)
Mo(4′)	Mo(1′)	F(14′)	67.7 (1)	Mo(1′)	Mo(4′)	F(14′)	66.5 (1)
Mo(4′)	Mo(1′)	O(11′)	63.3 (2)	Mo(1′)	Mo(4′)	O(11′)	66.7 (2)
Mo(4′)	Mo(1′)	O(12′)	134.6 (2)	Mo(1′)	Mo(4′)	O(22′)	138.7 (2)
F(13′)	Mo(1′)	F(14′)	75.2 (2)	Mo(2′)	Mo(4′)	Mo(3′)	43.6 (1)
F(13′)	Mo(1′)	O(11′)	159.4 (2)	Mo(2′)	Mo(4′)	F(13′)	66.9 (1)
F(13′)	Mo(1′)	O(12′)	88.3 (2)	Mo(2′)	Mo(4′)	F(14′)	115.6 (1)
F(14′)	Mo(1′)	O(11′)	87.8 (2)	Mo(2′)	Mo(4′)	O(11′)	136.4 (2)
F(14′)	Mo(1′)	O(12′)	157.6 (2)	Mo(2′)	Mo(4′)	O(22′)	65.3 (2)
O(11′)	Mo(1′)	O(12′)	104.5 (3)	Mo(3′)	Mo(4′)	F(13′)	93.4 (1)
Mo(1′)	Mo(2′)	Mo(3′)	46.2 (1)	Mo(3′)	Mo(4′)	F(14′)	94.3 (1)
Mo(1′)	Mo(2′)	Mo(4′)	46.5 (1)	Mo(3′)	Mo(4′)	O(11′)	102.8 (2)
Mo(1′)	Mo(2′)	F(13′)	95.2 (1)	Mo(3′)	Mo(4′)	O(22′)	101.1 (2)
Mo(1′)	Mo(2′)	F(14′)	94.6 (1)	F(13′)	Mo(4′)	F(14′)	72.5 (2)
Mo(1′)	Mo(2′)	O(21′)	99.8 (2)	F(13′)	Mo(4′)	O(11′)	156.1 (2)
Mo(1′)	Mo(2′)	O(22′)	106.0 (2)	F(13′)	Mo(4′)	O(22)	84.7 (2)
Mo(3′)	Mo(2′)	Mo(4′)	92.6 (1)	F(14′)	Mo(4′)	O(11′)	88.7 (2)
Mo(3′)	Mo(2′)	F(13′)	121.6 (1)	F(14′)	Mo(4′)	O(22′)	153.2 (2)
Mo(3′)	Mo(2′)	F(14′)	69.3 (1)	O(11′)	Mo(4′)	O(22′)	108.8 (3)
Mo(3′)	Mo(2′)	O(21′)	61.4 (2)	Mo(1′)	F(13′)	Mo(2′)	105.4 (2)
Mo(3′)	Mo(2′)	O(22′)	137.8 (2)	Mo(1′)	F(13′)	Mo(3′)	46.0 (1)
Mo(4′)	Mo(2′)	F(13′)	69.7 (1)	Mo(1′)	F(13′)	Mo(4′)	125.3 (2)
Mo(4′)	Mo(2′)	F(14′)	121.5 (1)	Mo(2′)	F(13′)	Mo(3′)	123.2 (2)
Mo(4′)	Mo(2′)	O(21′)	132.8 (2)	Mo(2′)	F(13′)	Mo(4′)	43.4 (1)
Mo(4′)	Mo(2′)	O(22′)	6.3 (2)	Mo(3′)	F(13′)	Mo(4′)	106.4 (2)
F(13′)	Mo(2′)	F(14′)	74.4 (2)	Mo(1′)	F(14′)	Mo(2′)	104.1 (2)
F(13′)	Mo(2′)	O(21′)	157.2 (2)	Mo(1′)	F(14′)	Mo(3′)	124.9 (2)
F(13′)	Mo(2′)	O(22′)	86.2 (2)	Mo(1′)	F(14′)	Mo(4′)	45.8 (1)
F(14′)	Mo(2′)	O(21′)	87.3 (2)	Mo(2′)	F(14′)	Mo(3′)	43.5 (1)
F(14′)	Mo(2′)	O(22′)	153.0 (2)	Mo(2′)	F(14′)	Mo(4′)	122.9 (2)
O(21′)	Mo(2′)	O(22′)	105.8 (3)	Mo(3′)	F(14′)	Mo(4′)	107.2 (2)
Mo(1′)	Mo(3′)	Mo(2′)	90.2 (1)	Mo(1′)	O(11′)	Mo(4′)	50.0 (2)
Mo(1′)	Mo(3′)	Mo(4′)	46.4 (1)	Mo(1′)	O(11′)	C(111′)	118.5 (5)
Mo(1′)	Mo(3′)	F(13′)	64.9 (1)	Mo(4′)	O(11′)	C(111′)	165.7 (5)
Mo(1′)	Mo(3′)	F(14′)	116.5 (1)	Mo(1′)	O(12′)	Mo(3′)	50.2 (2)
Mo(1′)	Mo(3′)	O(12′)	62.3 (2)	Mo(1′)	O(12′)	C(121′)	161.2 (6)
Mo(1′)	Mo(3′)	O(21′)	138.7 (2)	Mo(3′)	O(12′)	C(121′)	116.6 (5)
Mo(2′)	Mo(3′)	Mo(4′)	43.9 (1)	Mo(2′)	O(21′)	Mo(3′)	47.8 (2)
Mo(2′)	Mo(3′)	F(13′)	115.2 (1)	Mo(2′)	O(21′)	C(211′)	118.1 (5)
Mo(2′)	Mo(3′)	F(14′)	67.3 (1)	Mo(3′)	O(21′)	C(211′)	163.8 (6)
Mo(2′)	Mo(3′)	O(12′)	136.6 (2)	Mo(2′)	O(22′)	Mo(4′)	48.4 (2)
Mo(2′)	Mo(3′)	O(21′)	70.9 (2)	Mo(2′)	O(22′)	C(211′)	157.5 (6)
Mo(4′)	Mo(3′)	F(13′)	93.0 (1)	Mo(4′)	O(22′)	C(221′)	114.3 (5)

Table II. Pertinent Structural Parameters for the $\mathrm{Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8}$ Molecule

Bond Distances in Ångstroms

A	B	distance	A	B	distance
Mo(1)	Mo(2)	2.257 (2)	Mo(4)	O(41)	1.876 (5)
Mo(1)	N(14)	2.224 (6)	Mo(4)	O(42)	1.946 (5)
Mo(1)	F(13)	2.139 (4)	N(14)	C(1)	1.520 (10)
Mo(1)	O(11)	1.941 (5)	N(14)	C(2)	1.531 (10)
Mo(2)	O(12)	1.881 (5)	O(11)	C(111)	1.445 (10)
Mo(1)	F(23)	2.109 (4)	O(12)	C(121)	1.444 (10)
Mo(2)	F(24)	2.090 (4)	O(21)	C(211)	1.441 (9)
Mo(2)	O(21)	1.869 (5)	O(22)	C(221)	1.494 (9)
Mo(2)	O(22)	1.920 (5)	O(31)	C(311)	1.455 (9)
Mo(3)	Mo(4)	2.261 (1)	O(32)	C(321)	1.440 (10)
Mo(3)	F(13)	2.087 (4)	O(41)	C(411)	1.446 (10)
Mo(3)	F(23)	2.114 (4)	O(42)	C(421)	1.476 (9)
Mo(3)	O(31)	1.922 (5)	Mo(1)	Mo(3)	3.718 (1)
Mo(3)	O(32)	1.867 (5)	Mo(1)	Mo(4)	3.788 (1)
Mo(4)	N(14)	2.208 (6)	Mo(2)	Mo(3)	3.742 (1)
Mo(4)	F(24)	2.130 (4)	Mo(2)	Mo(4)	3.719 (1)

Angles in Degrees

A	B	C	angle	A	B	C	angle
Mo(2)	Mo(1)	N(14)	94.4 (2)	O(31)	Mo(3)	O(32)	103.3 (2)
Mo(2)	Mo(1)	F(13)	95.0 (1)	Mo(3)	Mo(4)	N(14)	94.1 (2)
Mo(2)	Mo(1)	O(11)	103.0 (2)	Mo(3)	Mo(4)	F(24)	94.7 (2)
Mo(2)	Mo(1)	O(12)	108.7 (2)	Mo(3)	Mo(4)	O(41)	108.7 (2)
N(14)	Mo(1)	F(13)	74.8 (2)	Mo(3)	Mo(4)	O(42)	102.4 (2)
N(14)	Mo(1)	O(11)	152.2 (2)	N(14)	Mo(4)	F(24)	75.6 (2)
N(14)	Mo(1)	O(12)	93.3 (2)	N(14)	Mo(4)	O(41)	94.6 (2)
F(13)	Mo(1)	O(11)	82.2 (2)	N(14)	Mo(4)	O(42)	152.9 (2)
F(13)	Mo(1)	O(12)	154.3 (2)	F(24)	Mo(4)	O(41)	155.3 (2)
O(11)	Mo(1)	O(12)	101.3 (2)	F(24)	Mo(4)	O(42)	81.6 (2)
Mo(1)	Mo(2)	F(23)	92.2 (1)	O(41)	Mo(4)	O(42)	100.3 (2)
Mo(1)	Mo(2)	F(24)	96.3 (1)	Mo(1)	N(14)	Mo(4)	117.5 (3)
Mo(1)	Mo(2)	O(21)	109.8 (2)	Mo(1)	N(14)	C(1)	105.4 (4)
Mo(1)	Mo(2)	O(22)	100.7 (2)	Mo(1)	N(14)	C(2)	111.6 (4)
F(23)	Mo(2)	F(24)	73.9 (2)	Mo(4)	N(14)	C(1)	111.9 (4)
F(23)	Mo(2)	O(21)	89.8 (2)	Mo(4)	N(14)	C(2)	104.0 (4)
F(23)	Mo(2)	O(22)	157.7 (2)	C(1)	N(14)	C(2)	106.0 (6)
F(24)	Mo(2)	O(21)	149.9 (2)	Mo(1)	F(13)	Mo(3)	123.3 (2)
F(24)	Mo(2)	O(22)	86.5 (2)	Mo(2)	F(23)	Mo(3)	124.7 (2)
O(21)	Mo(2)	O(22)	102.6 (2)	Mo(2)	F(24)	Mo(4)	123.6 (2)
Mo(4)	Mo(3)	F(13)	96.3 (1)	Mo(1)	O(11)	C(111)	126.2 (5)
Mo(4)	Mo(3)	F(23)	92.4 (1)	Mo(1)	O(12)	C(121)	153.3 (5)
Mo(4)	Mo(3)	O(31)	100.5 (2)	Mo(2)	O(21)	C(211)	156.9 (5)
Mo(4)	Mo(3)	O(32)	109.6 (2)	Mo(2)	O(22)	C(221)	121.8 (4)
F(13)	Mo(3)	F(23)	73.9 (2)	Mo(3)	O(31)	C(311)	124.5 (4)
F(13)	Mo(3)	O(31)	87.8 (2)	Mo(3)	O(32)	C(321)	156.2 (5)
F(13)	Mo(3)	O(32)	149.1 (2)	Mo(4)	O(41)	C(411)	153.7 (5)
F(23)	Mo(3)	O(31)	158.6 (2)	Mo(4)	O(42)	C(421)	125.0 (4)
F(23)	Mo(3)	O(32)	88.0 (2)				

1. The other two molecules which are related by a center of inversion did not refine well as $\mathrm{Mo_4(\mu\text{-}F)_4(OBu^t)_8}$: one of the bridges did not refine as a fluorine atom. Consequently another crystal was examined and a more extensive data set was collected at −145 °C.[7] Refinement using the new data proceeded smoothly with the disordered $\mathrm{Mo_4(\mu\text{-}F)_4(OBu^t)_8}$ molecule yielding the bond distances and angles given in Table I. The refinement of the other two symmetry related $\mathrm{Mo_4}$-containing molecules indicated that the unique bridging group was a dimethylamido group. The unit cell thus contains one molecule of $\mathrm{Mo_4(\mu\text{-}F)_4(OBu^t)_8}$ and two molecules of $\mathrm{Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8}$. The unexpected presence of the dimethylamido group was subsequently supported by elemental analysis on the specific crystalline sample. We attribute the presence of the dimethylamido group to incomplete alcoholysis in the preparation[8] of the sample of $\mathrm{Mo_2(OBu^t)_6}$ used in the reaction from which crystals were obtained. Pertinent bond distances and angles for $\mathrm{Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8}$ are given in Table II and an ORTEP view of the molecule is shown in Figure 2.

$\mathrm{Mo_4(\mu\text{-}F)_4(OBu^t)_8}$ and $\mathrm{Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8}$ both contain a bisphenoid of molybdenum atoms. There are two short Mo-to-Mo distances, 2.26 Å (averaged), corresponding to localized Mo-to-Mo triple bonds and four long, nonbonding, Mo-to-Mo distances, 3.75 Å (averaged). The local geometry of each $\mathrm{Mo_2F_4O_4}$ unit (M≡M) compares very closely with that observed for the $\mathrm{Mo_2O_4O_4'}$ unit in $\mathrm{Mo_2(OBu^t)_4(O_2CO\text{-}Bu^t)_2}$ (M≡M).[9] The presence of the bridging $\mathrm{NMe_2}$ ligand in $\mathrm{Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu^t)_8}$ produces a minimal perturbation of the $\mathrm{Mo_4}$ unit. The more acute Mo–N–Mo angle of 115° relative to the Mo–F–Mo angle of 125° (averaged) is complemented by the longer Mo–N distance, 2.21 Å (averaged), relative to the Mo–F distance, 2.12 Å (averaged).

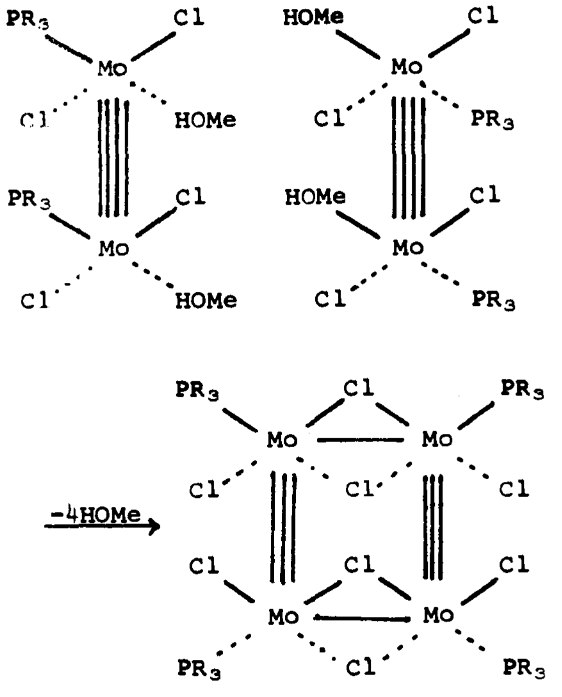
This work shows that replacement of an $\mathrm{OBu^t}$ group by the smaller[10] and more electronegative fluoride ligand promotes a Lewis base association reaction which in this case is the formation of metal-ligand-metal bridges. The striking structural feature seen in both molecules is that the Mo-to-Mo triple bonds are maintained; indeed it seems that the Mo-to-Mo triple bonds are purposefully held apart by the bridging groups. The choice of bridging groups is established F > $\mathrm{NMe_2}$ > OBu^t which is not what we would have anticipated in view of the well known ability of alkoxy groups to bridge two or three metal atoms with quite flexible M-O-M angles.[11]

We have no way of knowing at this time whether the tetranuclear complexes that we have isolated are kinetically or thermodynamically favored. However, we find it hard to believe that the tetranuclear complexes reported here are isolated under kinetic control, i.e., are thermodynamically unstable with respect to a tetrahedral $\mathrm{Mo_4}$-cluster compound having delocalized M—M bonding, for the following reasons. (1) $\mathrm{Mo_2(OR)_6}$ compounds (R = Bu^t and Pr^i) are exceedingly reactive (low kinetic barrier to reaction) toward Lewis base association reactions and reactions with unsaturated organic molecules such as CO, NO, acetylenes, allenes, and RCN compounds.[12] (2) The crystal structure of $[\mathrm{Al(OPr}^i)_3]_4$ and the electronic spectrum of $[\mathrm{Cr(OPr}^i)_3]_x$ show that the much smaller (relative to $\mathrm{Mo^{3+}}$) $\mathrm{Cr^{3+}}$ and $\mathrm{Al^{3+}}$ ions are capable of accommodating six isopropoxy ligands;[11] yet $(\mathrm{Pr}^i\mathrm{O})_3\mathrm{Mo{\equiv}Mo(OPr}^i)_3$ appears indefinitely stable with respect to oligomerization even at ~100 °C both in the solid state and in refluxing toluene.

At this point we return to the question raised in the title:[13] what factors will favor dinuclear compounds containing M—M bonds of multiple order compared with cluster compounds of the same empirical formula in which metal-metal bonding is delocalized? Since at present there are no thermochemical data available, the answers must be speculative but the question is still worthy of general consideration.

We note, for example, that molybdenum in oxidation state +2 and with chloride ligands can exist either as an octahedral $\mathrm{Mo_6}$ cluster with delocalized M—M bonding[14] or as a dinuclear anion $\mathrm{Mo_2Cl_8^{4-}}$ which contains a Mo-to-Mo quadruple bond.[15]

The only known coupling of two dinuclear compounds ($\mathrm{Mo{\equiv}Mo}$) to give a rectangular $\mathrm{Mo_4}$ cluster was recently reported by McCarley et al.[16] and is shown in eq 2. Here the Mo-to-Mo distances are 2.211 (3) and 2.901 (2) Å which may be reasonably taken to represent Mo-to-Mo triple and single bonds, respectively.[17] One notes here the δ-type d orbitals of the $\mathrm{Mo_2Cl_4(PR_3)_2(HOMe)_2}$ molecule are available to form four new cluster molecular orbitals: two are easy to picture and order in energy, namely the totally bonding, ψ_1, and totally antibonding molecular orbital, ψ_4. The other two are molecular orbitals which are (i) σ bonding between the Mo atoms which have chloride bridges and antibonding, δ*, between the nonbridged Mo atoms, ψ_2, and (ii) bonding between the unbridged Mo atoms (δ bonding) and antibonding, σ*, between the chloride bridged Mo atoms. There are only four electrons and apparently the cluster has the $\psi_1{}^2\psi_2{}^2$ ground-state electronic configuration since the short Mo–Mo distance, 2.211 (3) Å, is close to those distances in $\mathrm{Mo_2(OSiMe_3)_6(HNMe_2)_2}$ and $\mathrm{Mo_2(OBu}^t)_4(\mathrm{O_2COBu}^t)_2$ (2.241 (1) Å) (both of which contain Mo-to-Mo triple bonds of configuration $\sigma^2\pi^4$) and is considerably longer than the Mo-to-Mo quadruple bond distance in $\mathrm{Mo_2Cl_4(PR_3)_2(HOMe)_2}$,[16] 2.143 (1) Å.



(2)

Evidently, in the $\mathrm{Mo_4(\mu\text{-}F)_4(OBu}^t)_8$ and $\mathrm{Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(OBu}^t)_8$ molecules, the Mo-to-Mo triple bonds remain discrete. The choice of bridging ligands F > $\mathrm{NMe_2}$ > OBu^t may be a result of the π-donor properties of ligands which are likely to be in the inverse order.[18]

Currently we are extending our synthetic work to prepare compounds of the form $\mathrm{Mo_2X_2(NMe_2)_4}$ and $\mathrm{Mo_2X_2(OR)_4}$ to include X = H, SR, and $\mathrm{PR_2}$ with the hope of gaining further insight into the generalized reaction 1.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Marshal H. Wrubel Computing Center, and the tax payers of the State of Indiana for financial support of this work.

References and Notes

(1) For recent reviews of compounds containing M—M triple bonds (M = Mo, W), see (a) M. H. Chisholm, and F. A. Cotton, *Acc. Chem. Res.*, **11**, 356 (1978); (b) M. H. Chisholm, *Trans. Met. Chem.*, **3**, 321 (1978).

(2) See F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, Section 25-C-4, p 830. "There are literally thousands of chromium(III) complexes which, with a few exceptions, are all hexacoordinate."

(3) The $\mathrm{Mo_4S_4X_4}$ compounds (X = Cl, Br, I) contain a central $\mathrm{Mo_4S_4}$ cube, a tetrahedral $\mathrm{Mo_4}$ unit with Mo–Mo distances of 2.80 Å . See C. Perrin R. Chevrel, and M. Sergent, *C.R. Hebd. Seances Acad. Sci. Ser. C*, **280**, 949 (1975).

(4) M. H. Chisholm, M. W. Extine, R. L. Kelly, W. C. Mills, C. A. Murillo, L. A. Rankel, and W. W. Reichert, *Inorg. Çhem.* **17**, 1673 (1978).

(5) M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo *Inorg. Chem.* **16,** 2407 (1977). The mechanistic details of the $\mathrm{PF_3}$-induced exchange reaction are not yet understood. Further work on this reaction and reactions leading to compounds of empirical formula $\mathrm{Mo(OBu}^t)_2\mathrm{X}$ where X = Cl, Br, and I are also in progress by Mr. J. Garman.

(6) This data set was collected by the Molecular Structure Corporation, College Station, Texas 77843.

(7) Crystal data were collected at −145 °C using a gaseous nitrogen cold stream and locally constructed goniostat system: triclinic, space group $P1$ with a = 13.453 (4), b = 16.746 (6), c = 17.736 (2) Å; α = 101.65 (3), β = 108.26 (3), γ = 99.21 (3)°; Z = 1.5; d_{calcd} = 1.445 g/cm^3. Of the 12 761 unique structure amplitudes, the 11 566 which have $I \geq 2.33\ \sigma(I)$ were used in the full-matrix refinement. Final residuals are $R(F)$ = 0.070 and $R_w(F)$ = 0.104.

(8) We have found that the reaction $\mathrm{Mo_2(NMe_2)_6 + 6Bu^{\mathit{t}}OH \rightarrow Mo_2(OBu^{\mathit{t}})_6 + 6HNMe_2}$ proceeds slowly. In order to achieve complete alcoholysis in a short period of time, a large excess of $\mathrm{Bu}^t\mathrm{OH}$ should be used. M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, **16**, 1801 (1977).

(9) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100,** 3354 (1978).

(10) It has already been demonstrated that decreasing the steric bulk of the alkoxy group promotes Lewis base association and the Lewis base adduct $\mathrm{Mo_2(OSiMe_3)_6(HNMe_2)_2}$ ($\mathrm{M{\equiv}M}$) has been structurally characterized: M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100,** 153 (1978).

(11) For a general review of metal alkoxides, see D. C. Bradley, R. C. Mehrotra, and D. P. Gaur in "Metal Alkoxides", Academic, New York, 1978. Specifically in the chemistry of molybdenum we have recently found RO ligands spanning molybdenum atoms which are 2.5 Å apart as in $\mathrm{Mo_2(OBu}^t)_6\mathrm{CO}$ (M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, **100,** 2256 (1978)) and 3.335 Å apart as in $\mathrm{Mo_2(OPr}^i)_6\mathrm{(NO)_2}$ (M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *ibid.*, **100,** 3354 (1978)).

(12) See M. H. Chisholm et al., references quoted in ref 11 above, and M. H. Chisholm and R. L. Kelly, *Inorg. Chem.*, **18**, 2321 (1979).

(13) One of the referees suggested that, in view of the title, this article should preferentially be published in the April 21st issue of *J. Am. Chem. Soc.* Obviously this referee has both a sense of humor and is well advanced in Stephen Potter's "Game of One Upmanship".

(14) The cluster structure of MoCl$_2$ may be expressed as (Mo$_6$Cl$_8$)Cl$_2$Cl$_{4/2}$ where eight Cl atoms occupy faces of the octahedral Mo$_6$ moiety, two Cl atoms are terminally bonded to Mo atoms, and four Cl atoms are bridged to neighboring Mo$_6$ units: H. Schäfer, H.-G. v. Schnering, J. Tillack, F. Kuhnan, H. Wöhrle, and H. Bauman, Z. Anorg. Allgem. *Chem.*, **353**, 281 (1967).

(15) F. A. Cotton, *Acc. Chem. Res.*, **11**, 225 (1978).

(16) R. N. McGinnis, T. R. Ryan, and R. E. McCarley, *J. Am. Chem. Soc.*, **100**, 7900 (1978).

(17) (a) For a recent listing of Mo≡Mo distances see ref 1b. (b) For a review of Mo—Mo single-bond distances which vary greatly depending upon the oxidation of molybdenum and the presence or nature of groups which directly bridge the two metal atoms, see F. A. Cotton, *J. Less Common Met.*, **54**, 3 (1977).

(18) This point was emphasized by one of the referees.

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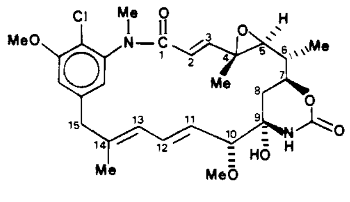
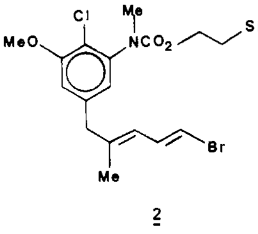
Total Synthesis of (±)-Maysine[†][1]

Sir:

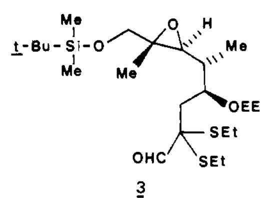
We report herein the first total synthesis of a natural maytansinoid, maysine (**1**), originally isolated and characterized by Kupchan.[1] Recently, methodology was described[2,3] which led to the total synthesis of (±)-*N*-methylmaysenine, a related member of this complex family of macrocycles. The route to **1** is based on the key intermediate **2**[3] and the highly functionalized and stereochemically pure moiety **3** which were coupled and elaborated to the target product.



(±)-**1**



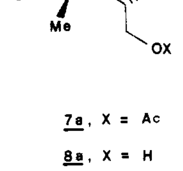
2



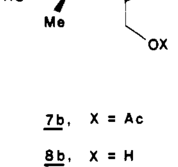
3

The preparation of **3** in multigram quantities originated with the known aldehyde **4**[3] which was reduced (NaBH$_4$, EtOH, 25 °C) to the allylic alcohol **5** and then protected as the silyl ether **6**.

4, Y = CHO
5, Y = CH$_2$OH
6, Y = CH$_2$OR
(R = t-BuMe$_2$Si)

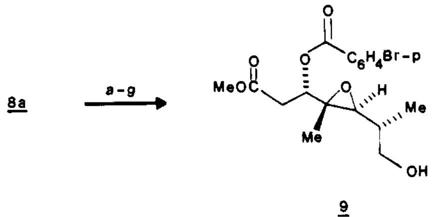


7a, X = Ac
8a, X = H



7b, X = Ac
8b, X = H

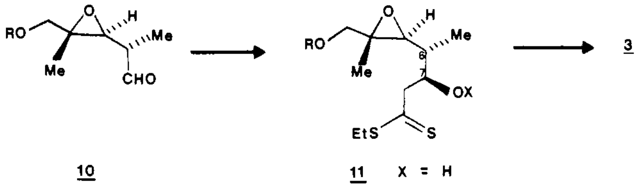
Various epoxidation procedures leading to **7** were attempted, but all gave unsatisfactory mixtures of **7a**–**7b**.[4] Finally, *m*-chloroperbenzoic acid in CH$_2$Cl$_2$ at 0 °C gave a 53:47 mixture of **7a**–**7b**, which could be readily separated after conversion (MeMgCl, 2.0 equiv, THF, 0 °C) into the corresponding alcohols **8a**–**8b**.[5] Structure proof for **8a** as the correct precursor to maysine was accomplished by correlation to the epoxy ester **9** whose stereochemistry was established by X-ray techniques several years ago.[6] By using the series of reactions a–g, **9** was prepared from **8a** which proved to be identical in all respects with the X-ray sample. Thus, the important intermediate **8a** is readily prepared in 25% overall yield from the simple α,β-unsaturated aldehyde **4**, in spite of poor selectivity in the epoxidation step.



9

(a) Ethyl vinyl ether, TsOH, Et$_2$O; (b) Bu$_4$NF, CH$_3$CN; (c) (COCl)$_2$, Me$_2$SO, Et$_3$N; (d) CH$_3$CO$_2$Me, LDA, −78 °C, THF; (e) *p*-BrC$_6$H$_4$COCl, pyridine; (f) pyridinium tosylate, MeOH; (g) separation on Waters HPLC-244, 15% THF-hexane gave pure β-acyloxy esters.

Oxidation via Collins reagent converted **8a** into the aldehyde **10** which was then treated with ethyl lithiodithioacetate (−78 °C, THF, 6 h) and quenched (1 equiv of HOAc, −78 °C) to provide the β-hydroxy dithioester **11** as a 3:1 mixture of diastereomers. Separation on medium-pressure liquid chromatography[7] (10% acetone-hexane) gave the major isomer which was shown to possess the erythro configuration at C-6,C-7 by NMR.[8]



10

11 X = H
12 X = EE

After masking the C-7 alcohol as the ethoxyethyl group (EE; ethyl vinyl ether, *p*-TsOH·H$_2$O, 25 °C, 1 h), it was treated with 3.0 equiv of ethylmagnesium iodide (−45 °C, THF, 2 h)[3] and then with 4.0 equiv of 2-(*N*-methyl-*N*-formyl)aminopyridine[3] to form the α-formyl dithioacetal **3**.[9] The overall yield of the major maysine fragment **3** was 6.9% (from **4**).

Coupling of major fragments **2** and **3** was accomplished by transforming the diene bromide **2** into its lithium derivative (2.0 equiv of *t*-BuLi, −120 to −90 °C, THF-Et$_2$O-pentane (4:1:1)), followed by addition of **3** (1.0 equiv, −120 to −60 °C, 30 min), which furnished the carbinol and subsequently the methyl ether **13** (NaH, THF, 15 equiv of CH$_3$I, 0–25 °C, 2 h, 70% yield for the two steps).[10] Removal of both silyl protecting groups to **14** took place quantitatively when **13** was treated with 7.0 equiv of tetrabutylammonium fluoride in THF for 4 h (Scheme I). The primary alcohol **14** was oxidized in 70.5% yield to the aldehyde **15** (NMR (CDCl$_3$) δ 8.84 (br s, 1)) using 1,1′-(azodicarbonyl)dipiperidine and *tert*-butoxymagnesium bromide.[11] Treatment of the aldehyde with the phosphonoacetyl chloride in pyridine gave the phosphonoamide **16** in 75% yield (IR (film) 1725, 1663 cm^{-1}; NMR (CDCl$_3$) δ 8.84 (s, 1), 2.71 (d, 2, J = 22 Hz)). At this point, the latter intermediate was properly equipped for ring closure. As already reported[3] for *N*-methylmaysenine, the Wadsworth-Emmons olefination was again attempted (1.0 equiv of KO-*t*-Bu, THF

[†] Dedicated to the memory of Professor Robert Burns Woodward.

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