to one triplet (δ 0.93) and one quartet (δ 3.00) at 100 °C. The aromatic protons behave similarly and exhibit a typical A_2X signal (δ 6.91, 7.07) at 100 °C.

Crystallographic Analysis of 3. The crystals are orthorhombic with a = 9.787 (2) Å, b = 18.694 (3) Å, c = 19.289 (2) Å, U = 3529 Å^3, space group $Pcnb$, Z = 4, and D_{calcd} = 1.11 g cm^{-3}.[11] In view of the air and moisture sensitivity of 3, a small single crystal surrounded by a small drop of mother liquor was sealed under argon in a Lindemann glass capillary tube. Data were measured on a Nicolet R3m diffractometer ($\theta \leq 50°$) with graphite-monochromated Cu Kα radiation and the ω scan measuring routine. The structure was solved by direct methods and refined anisotropically to a current R = 0.072 and R_w = 0.087[12] for 1575 independently observed reflections. Despite large thermal vibrations (or disorder) for the ethyl groups (and the consequent high R value), the definition of the Si=Si bond is good and of acceptable accuracy. The maximum residual electron density was 0.3 e Å^{-3} around the ethyl group and 0.14 e Å^{-3} in the region of the silicon atom.

The analysis shows (Figure 1) that there is a crystallographic twofold axis which bisects the Si=Si bond. Each silicon atom and the three atoms directly attached to it are coplanar with a C–Si–C angle of 117.6 (2)° and C–Si–Si′ angles of 117.6 (2)° and 124.8 (2)°. The Si=Si′ bond length is 2.140 (3) Å, and the Si–C bonds are 1.886 (4) and 1.878(4) Å, respectively. It is interesting to note that the presence of the silicon–silicon double bond does not result in any shortening of the silicon–aryl bond. All four Si–Ar bonds are not coplanar; the dihedral angle between the C–Si–C and C′–Si′–C′ planes is 10°. The planes of the phenyl rings are rotated by 62° and 64° from the C–Si–Si′ plane, respectively. This rotation and the twisting of the Si=Si bond are obviously brought about to minimize possible steric congestion due to the ethyl groups attached on the phenyl rings. The structure as a whole is loosely packed with short intermolecular contacts.

In recent years an extensive theoretical investigation of the Si_2H_4 potential surface has been performed. Although calculations at various levels lead to different results as to the relative stability of the silylsilylene and disilene ground states,[13] the former (in the singlet state) is 2–3 kcal/mol more stable than the latter (in the singlet state) at HF/6-31G level.[13a] Correlation energy corrections reverse this order, however. It appears that trans-bent disilene (C_{2h}) lies very slightly lower in energy than planar disilene (D_{2h}), but this C_{2h} conformation resides in a region of rather flat potential energy surface. The Si=Si bond distance is predicted to be between 2.13 and 2.17 Å.[13a] With the crystal structure of 3 described above a significant step has now been taken in solving this intriguing problem experimentally.[14]

Acknowledgment. We thank the National Science Foundation and Yoshitomi Pharmaceutical Industries, Ltd. Japan, for financial support. High-resolution mass spectra were provided by the facility supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann), from the Biotechnology Resources Branch, Division of Research Resources.

Registry No. 3, 88245-20-9; 4, 88245-21-0; 5, 88245-22-1.

Supplementary Material Available: Experimental details including the synthesis of 5 and detailed information of the X-ray crystal analysis of 3 (16 pages). Ordering information is given on any current masthead page.

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[11] The unit cell dimensions from least squares for 18 reflections centered on the diffractometer with Cu Kα radiation (θ between 20 and 40°). Positive and negative (hkl) values were used.

[12] Four reflections which had $|F_0| > |F_c|$ were suspected of being affected by extinction and were removed.

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$[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$: A 12-Membered Organometallic Ring System Held Together by Ti–O–C–Mo Bridges

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Received August 16, 1983

Summary: The reaction between $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_4CH_3)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_4CH_3)$ in toluene at room temperature leads to the formation of $[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$, **2a**. Complex **2a** was found to crystallize in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions a = 13.510 (4) Å, b = 10.951 (2) Å, c = 13.361 (3) Å, β = 114.66 (2)°, V = 1797 (1) Å^3, and d_{calcd} = 1.616 g cm^{-3}. The core of **2a** consists of an unusual 12-membered ring: Ti–O–C–Mo–C–O–Ti–O–C–Mo–C–O. Each titanium atom is further bound by two η^5-C_5H_5 ligands while each molybdenum is further bound by one terminal carbonyl and one η^5-$C_5H_4CH_3$ ligand. Complex **2a** reacts with the donor tetrahydrofuran to form the known complex $(C_5H_5)_2Ti(THF)OCMo(CO)_2(C_5H_4CH_3)$, **1a**.

In recent years, a considerable effort has been directed toward the synthesis of early transition metal/later transition metal combination complexes with much of that effort focused on complexes of titanium, zirconium, and hafnium.[1] We became interested in building up complexes of the early transition elements by the reaction of a lower valent group 4B complex with metal dimers possessing metal–metal unsaturation. In a previous communication,[2] we reported on the synthesis and molecular structure of the Ti(III) complex $(C_5H_5)_2Ti(THF)OCMo(CO)_2(C_5H_5)$,

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[1] See: Casey, C. P; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665 and references therein.

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0276-7333/84/2303-0334$01.50/0

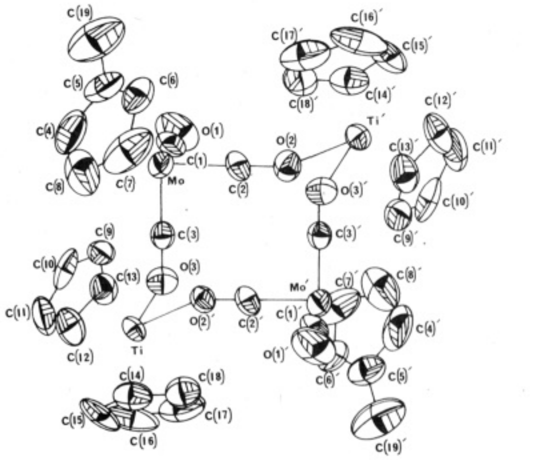

Figure 1. Molecular structure of $[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$. Atoms labeled with and without a prime are related by the crystallographic inversion center.

1, in which the Ti and Mo atoms are held together by a Ti–O–C–Mo bridge. 1 was formed in the reaction between $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ in a tetrahydrofuran (THF) solution (eq 1). When the above

$$(C_5H_5)_2Ti(CO)_2 + (C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5) \xrightarrow{THF} (C_5H_5)_2Ti(THF)OCMo(CO)_2(C_5H_5) \quad (1)$$

reaction is carried out in the noncoordinating solvent, toluene, a more unusual complex, **2**, is formed. In the present communication we now report on the synthesis, structure, and chemistry of **2**.

When $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ are stirred together in toluene solution at room temperature, a green microcrystalline solid, **2**, precipitates from solution.[3] Complex **2** possesses only a very slight solubility in toluene and appears to react with halogenated solvents.[4] **2** is quite air and moisture sensitive, and, although we have been unable to obtain satisfactory C and H analysis, Ti and Mo analyses suggest the general formula $[(C_6H_5)_2Ti{\cdot}(C_5H_5)Mo(CO)_3]_x$.[5] The infrared spectrum of **2** taken as a Nujol mull displays ν(CO) at 1920, 1755, and 1710 cm^{-1}. The lack of solubility in other solvents prevented its adequate characterization.

In order to obtain a complex analogous to **2** with increased toluene solubility, $(C_5H_5)_2Ti(CO)_2$ was allowed to react with $(C_5H_4CH_3)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_4CH_3)$. A product, **2a**, was isolated identical with **2** in all respects with the exception that **2a** possesses appreciable toluene solubility.[6] Complex **2a** could be recrystallized from toluene/hexane to yield crystals which analyze for the empirical formula $[(C_5H_5)_2Ti{\cdot}(C_5H_4CH_3)Mo(CO)_3]_x$.[7] The Ti–O–C–Mo bond in **1** displays ν(CO) at 1650 cm^{-1} while the lowest energy CO stretch in **2** and **2a** is at 1710 cm^{-1}, some 60 cm^{-1} higher energy. In order to determine the nature of the bonding in these complexes, we undertook a single-crystal X-ray diffraction study of **2a**.[8]

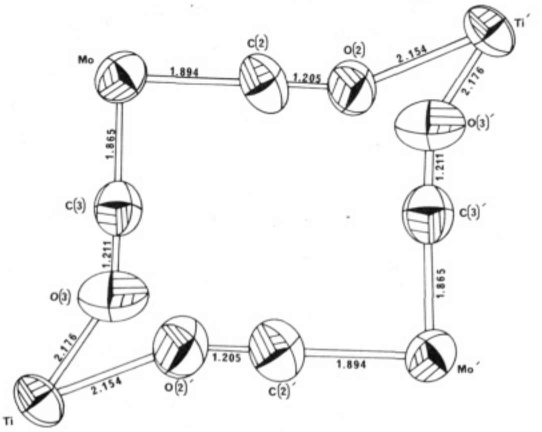

Figure 2. Core atom portion of the molecular structure of $[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$. Other bond lengths (Å) of interest are as follows: Mo–C(1) (Mo′–C(1)′) = 1.915 (14); C(1)–O(1) (C(1)–O(1)′) = 1.180 (5). Bond angles (deg) of interest are as follows: O(2)′–Ti–O(3) (O(2)–Ti′–O(3)′) = 78.72; Ti–O(2)′–C(2)′ (Ti′–O(2)–C(2)) = 141.18; Ti–O(3)–C(3) (Ti′–O(3)′–C(3)′) = 143.38; Mo–C(2)–O(2) (Mo′–C(2)′–O(2)′) = 177.08; Mo–C(3)–O(3) (Mo′–C(3)′–O(3)′) = 178.48; Mo–C(1)–O(1) (Mo′–C(1)′–O(1)′) = 178.95.

The structure of **2a** is shown in Figure 1, and it can be seen that in the general formula $[(C_5H_5)_2Ti{\cdot}(C_5H_4CH_3)Mo(CO)_3]_x$, $x = 2$. The Ti and Mo atoms in the complex are held together by μ,η^2-bridging carbonyls of the form Ti–O–C–Mo, which have been observed by us[2] and others[9] in a variety of compounds. What is unusual is that the formally Ti(III) centers are bound to the oxygens of two carbonyl ligands forming a central core of a 12-membered ring: $\overline{\text{Ti-O-C-Mo-C-O-Ti-O-C-Mo-C-O}}$. Each titanium atom is further bound to two η^5-(C_5H_5) rings while each molybdenum atom is further bound to one η^5-$(C_5H_4CH_3)$ ring as well as one terminal carbonyl. Figure 2 is a close-up view of this core atom portion of **2a** showing the numbering scheme and bond lengths. Additional bond lengths and angles may be found in the supplementary material. As we,[2] and others,[9] have shown, the consequence of coordination of the oxygen of a terminal metal carbonyl to a second metal is the lengthening of the C–O bond and a shortening of the M–C bond of that carbonyl. In **2a**, there are two different types of Ti–O–C–Mo bridges: the C(2)′–O(2)′ and C(2)–O(2) distances are 1.205 (9) Å and the C(3)′–O(3)′ and C(3)–O(3) distances are 1.211 (10) Å, compared with the purely terminal C(1)–O(1) and C(1)′–O(1)′ distances of 1.180 (5) Å. Concomitantly, the Mo–C(2)

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[3] In a nitrogen glovebox, $(C_5H_5)_2Ti(CO)_2$ (3.0 g, 12.8 mmol) and $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ (6.3 g, 12.8 mmol) were dissolved in 100 mL of toluene and stirred at room temperature for 18 h. At the end of that time the reaction mixture consisted of a green precipitate in a red-brown solution. The mixture was filtered and the precipitate washed with toluene until the washings were colorless. The yield of **2** was 5.0 g (5.9 mmol, 92% yield based on Ti).

[4] On dissolving **2** in CH_2Cl_2, the green color turns to red in a matter of minutes. The infrared spectrum of this red solution is that of $(C_5H_5)Mo(CO)_3$–$Mo(CO)_3(C_5H_5)$.

[5] Calcd for $C_{18}H_{15}OMoTi$: Mo, 22.67; Ti, 11.31. Found: Mo, 21.64; Ti, 10.78.

[6] In a nitrogen glovebox, $(C_5H_5)_2Ti(CO)_2$ (2.0 g, 8.6 mmol) and $(C_5H_4CH_3)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_4CH_3)$ (3.98 g, 8.6 mmol) were dissolved in a mixture of 100 mL of hexane and 100 mL of toluene for 18 h. At the end of that time, a green microcrystalline solid was present. These were filtered, washed with hexane, and dried to yield 2.90 g (3.3 mmol, 72% yield) of **2a**.

[7] Calcd for $C_{18}H_{17}O_3MoTi$: C, 52.19; H, 3.93; Mo, 21.94; Ti, 10.96. Found: C, 51.11; H, 4.13; Mo, 21.30; Ti, 10.87.

[8] Crystals of **2** suitable for X-ray diffraction were crystallized in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions $a = 13.510$ (4) Å, $b = 10.951$ (2) Å, $c = 13.361$ (3) Å, $\beta = 114.66$ (2)°, $V = 1797$ (1) Å^3, and $d_{calcd} = 1.616$ g cm^3. The data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. A total of 3672 independent reflections were collected for $0.0° < \theta < 25.0°$ using two crystals in sequence since the crystals decomposed during data collection. Of the total, 1546 were considered to be observed with $(F_o)^2 > 2\sigma(F_o)^2$; $R_1 = 0.068$ and $R_2 = 0.064$.

[9] For transition-metal and lanthanide-metal complexes, see: (a) Hamilton, D. M., Jr.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255. (b) Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 365. (c) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985. (d) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 772. (e) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *Ibid.* **1982**, *104*, 6360.

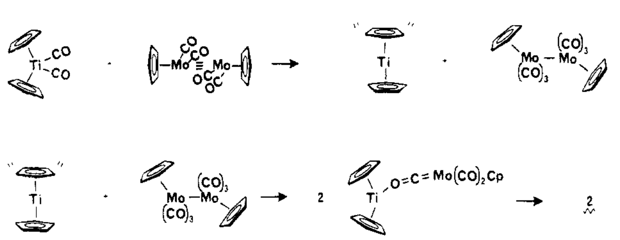

Figure 3. Possible mechanism for the formation of **2**.

and Mo′–C(2)′ distances of 1.894 (9) Å and the Mo–C(3) and Mo′–C(3)′ distances of 1.865 (9) Å are significantly shortened when compared with the Mo–C(1) and Mo′–C(1)′ distances of 1.915 (14) Å.

To our knowledge, the only other organometallic complex of this type is the Al/W complex $[(CH_3)_2AlOCW(CO)_2(C_5H_5)]_2$, **3**.[10] However, there are some intriguing structural differences between the 12-membered ring in $[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$ vs. the ring in $[(CH_3)_2AlOCW(CO)_2(C_5H_5)]_2$. In **2a** both Ti–O–C angles average 142°. While **3** shows one Al–O–C angle of 149° with the second unique Al–O–C bond being nearly linear with an angle of 176°. Norton and co-workers[9e] have discussed in some length the nature of the Zr–O–C–Mo bond in $[(C_5H_5)_2(CH_3C(O))]ZrOCMo(CO)_2(C_5H_5)$ and M–O–C–M′ bonds in general. Complex **2** is an interesting addition to the field in that in other examples of $M{-}O{-}C{-}Mo(CO)_2(C_5H_5)$ complexes,[1,9] the infrared stretching frequency of the bridging carbonyl is found between 1650 and 1500 cm^{-1} while those in a **2** are found above 1700 cm^{-1}. Yet, the C–O bond distance in the bridging carbonyls are as long or longer than those of other structurally characterized M–O–C–Mo bridges.[9] The nature of the bonding in these complexes as regards the M–O–C–M′ interaction warrants further consideration before any conclusions may be made. A very subtle interplay between steric and electronic requirements is responsible for the varying M–O–C–M′ angles seen in the complexes known to date. At present, we prefer the bonding scheme $\mathrm{Ti{-}O{=}C{=}Mo{\equiv}C{-}O{-}Ti{-}O{=}C{=}Mo{\equiv}C{-}O}$ to describe crudely the major contributions to the valence bond picture of the core structure of **2a**.

A material with general formula $(C_5H_5)_2Ti{\cdot}(C_5H_5)Mo(CO)_3$ was previously claimed by Lappert and Sanger from the reaction between $[(C_5H_5)_2TiNMe_2]_2$ and $(C_5H_5)Mo(CO)_3H$.[11] The infrared reported shows $\nu(CO)$ at 1956, 1928, and 1903 cm^{-1}. Although the reaction may have initially yielded **2** as the product, the reported color (red-brown) and the infrared clearly indicate that what is reported is $[(C_5H_5)Mo(CO)_3]_2$. In our experience, **2** is extremely air sensitive, turning red within seconds after exposure to air with formation of $[(C_5H_5)Mo(CO)_3]_2$ as the only carbonyl-containing product. We can only conclude that the material examined by Lappert and Sanger had been exposed to air.

As we proposed earlier, the $(C_5H_5)_2Ti(CO)_2$ reacts with $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ in a slow step to yield some form of titanocene, "$(C_5H_5)_2Ti$", and $(C_5H_5)Mo(CO)_3{-}Mo(CO)_3(C_5H_5)$ (see Figure 3). These then react in a fast second step to form the observed product. Indeed, we have found that metastable titanocene, "$[(C_5H_5)_2Ti]_2$", formed by the procedure of Bercaw et al., reacts instantaneously with $(C_5H_5)Mo(CO)_3{-}Mo(CO)_3(C_5H_5)$ to form **2** in high yield.[12] In a similar type of reaction, Berry and Bercaw found that $[(C_5Me_5)_2ZrN_2]_2N_2$ reacted with $(C_5H_5)Mo(CO)_3{-}Mo(CO)_3(C_5H_5)$ to form the Zr(IV) complex $(C_5Me_5)_2Zr[OCMo(CO)_2(C_5H_5)]_2$.[14] That $[(C_5H_5)_2TiOCMo(CO)_2(C_5H_5)]_2$ is formed in the present chemistry speaks for the accessibility and relative stability of the Ti(III) oxidation state. In fact, a reaction between $(C_5H_5)_2Zr(CO)_2$ and $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ yields a product which has been only poorly characterized but which seems to be the unsubstituted analogue to the compound reported by Berry and Bercaw, i.e., $(C_5H_5)_2Zr[OCMo(CO)_2(C_5H_5)]_2$.[14] Moreover, when $(C_5H_5)_2Ti(CO)_2$ is replaced by $(C_5Me_5)_2Ti(CO)_2$, in a very slow reaction the Ti(IV) complex $(C_5Me_5)_2Ti[OCMo(CO)_2(C_5H_5)]_2$,[15] also analagous to the zirconium complex reported by Bercaw et al., is isolated in high yield. Here it would seem that the permethyl substitution of the bis(cyclopentadienyl)titanium center favors the complete oxidation to the Ti(IV) product, although the reaction is slowed down considerably.

Compound **2** dissolves in THF with cleavage of the dimeric structure to yield the previously reported **1**, $Cp_2Ti(THF)OCMo(CO)_2Cp$ (eq 2). This cleavage appears to be general for a number of Lewis bases yielding a wide range of complexes which we will discuss in a future report.

$$[(C_5H_5)_2TiOCMo(CO)_2(C_5H_5)]_2 + 2THF \rightarrow 2(C_5H_5)_2Ti(THF)OCMo(CO)_2(C_5H_5) \quad (2)$$

We were most interested in the reactivity of **2** with molecular hydrogen and in determining if the Ti–O–C–Mo carbonyls could be reduced. Complex **2** reacts with molecular hydrogen at room temperature to form $[(C_5H_5)_2TiH]_x$ and $(C_5H_5)Mo(CO)_3H$, a reaction which is reversed upon removal of the H_2 (eq 3). To the extent

$$[(C_5H_5)_2TiOCMo(CO)_2(C_5H_5)]_2 \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} 2[(C_5H_5)_2TiH]_x + 2(C_5H_5)Mo(CO)_3H \quad (3)$$

that **2** appears to be a complex of $(C_5H_5)Mo(CO)_3^-$ with $(C_5H_5)_2Ti^+$, this reaction could be considered the heterolytic cleavage of dihydrogen. We have observed no evidence for the reduction of a carbonyl ligand. As with the chemistry reported for **1**,[2] other attempts to functionalize the μ,η^2-CO ligand failed. Thus, it appears that the structural activation observed in these systems does not translate into chemical activation.

Our work is continuing on the reactivity of early transition-metal complexes with unsaturated metal dimers and are currently examining ways of directing the molecules to metal–metal bond formation rather than M–O–C–M′ bridge formation.

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(10) Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499.

(11) Lappert, M. F.; Sanger, A. R. *J. Chem. Soc. A* **1971**, 1314.

(12) In a nitrogen glovebox, $[(C_5H_5)_2TiH]_x$ (0.5 g, 2.8 mmol) was stirred in toluene for 1 h to yield a solution of $[(C_5H_5)_2Ti]_2$.[13] To this solution was added $(C_5H_5)Mo(CO)_3{-}Mo(CO)_3(C_5H_5)$ (0.67 g, 1.4 mmol) and within minutes a green precipitate formed. This was filtered, washed with toluene, and dried to yield 0.90 g (1.1 mmol, 79% yield) of **2**.

(13) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(14) Berry, D. H.; Bercaw, J. E.; Vircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4713.

(15) In a nitrogen glovebox, $(C_5H_5)_2Zr(CO)_2$ (1.0 g, 3.6 mmol) and $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ (1.56 g, 3.6 mmol) were dissolved in 100 mL of toluene and stirred at room temperature for 18 h. At the end of that time a rust colored precipitate had formed which was washed, filtered, and dried to yield 1.22 g of a red-brown powder (IR (Nujol mull, CO region) $\nu(CO)$ 1920 (s, vbr), 1850 (s, vbr), 1560 (s, vbr) cm^{-1}).

(16) In a nitrogen glovebox, $[C_5(CH_3)_5]_2Ti(CO)_2$ (0.5 g, 1.34 mmol) and $(C_5H_5)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_5)$ (0.58 g, 1.34 mmol) were stirred at room temperature in 50 mL of toluene. Infrared monitoring of the reaction indicated the disappearance of starting material only 5 days after reaction at room temperature. The toluene was removed to yield a dark red solid that was washed with hexane to yield 0.79 g (0.93 mmol, 70% yield) of $[(C_5(CH_3)_5]_2Ti[OCMo(CO)_2C_5H_5]_2$: IR (Nujol mull) $\nu(CO)$ 1925 (s), 1835 (s), 1610 (s) cm^{-1}. Calcd for $C_{36}H_{40}O_6TiMo_2$: C, 53.47; H, 5.00; Ti, 5.92; Mo, 23.73. Found: C, 54.19; H, 5.46; Ti, 6.10; Mo, 23.82.

Supplementary Material Available: Details of the X-ray diffraction experiment, complete listings of bond lengths and bond angles, table of positional and thermal parameters, listings of F_o and F_c, and general temperature factor expressions for complex **2a** (25 pages). Ordering information is given on any current masthead page.

The Structure of Tetramethyldistibine

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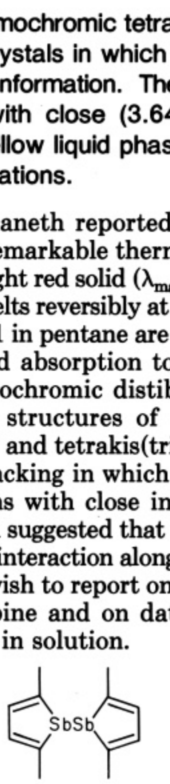
Received November 28, 1983

Summary: The thermochromic tetramethyldistibine forms orthorhombic red crystals in which the molecules adopt a staggered trans conformation. The antimony atoms are aligned in chains with close (3.645 Å) intermolecular contacts. In the yellow liquid phase the distibine populates other conformations.

Fifty years ago Paneth reported that tetramethyldistibine (**1**) showed remarkable thermochromic behavior.[1] The distibine is a bright red solid (λ_{max} = 530 nm by diffuse reflectance) which melts reversibly at 17 °C to a pale yellow liquid. Solutions of **1** in pentane are also pale yellow (λ_{max} < 220 nm, weak end absorption to 450 nm). Recently several other thermochromic distibines have been prepared.[2–7] Crystal structures of two of them, tetramethylbistibolyl (**2**)[2] and tetrakis(trimethylsilyl)distibine (**3**),[3] show similar packing in which the antimony atoms are aligned in chains with close intermolecular Sb···Sb contacts. It has been suggested that the solid-phase colors are due to electronic interaction along these Sb–Sb···Sb–Sb chains.[2,8] We now wish to report on the crystal structure of tetramethyldistibine and on data which bear on its molecular structure in solution.

Me_4Sb_2

1



2

$(Me_3Si)_4Sb_2$

3

A 0.050 × 0.080 × 0.080 mm crystal grown from cooled liquid sealed in a thin walled capillary was used for data collection. The crystal was cooled to −160 °C and characterized by a reciprocal lattice search technique.[9] The space group and cell data are as follows: orthorhombic, space group *Pmnb* with a = 11.314 (6) Å, b = 11.507 (6) Å, c = 6.507 (2) Å, V = 847.1 Å^3, d = 2.381 g/cm^3, and Z = 4. A total of 1769 independent reflections with 6° < 2θ (Mo K$\bar{\alpha}$) < 45° were collected by using a Picker four-circle goniostat equipped with a Furnas Monochromator (HOG crystal) and Picker X-ray ϕ generator interfaced to a TI980 minicomputer. The data were reduced by procedures previously described, and the structure was solved by inspection of a Patterson synthesis.[10] Hydrogen atoms were included in the final refinement as fixed atom contributors. Final residuals were as follows: $R(F)$ = 0.059 and $R_w(F)$ = 0.070.[11]

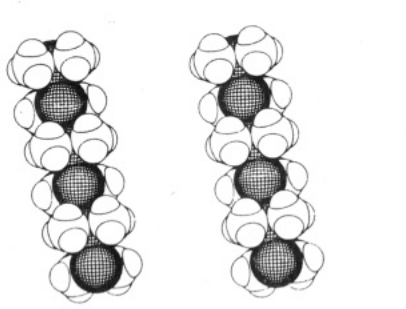


Figure 1. Crystal packing drawing of the solid-state structure of tetramethyldisitibine. Six molecules are illustrated in two chains. The bond distances are as follows: Sb–Sb = 2.862 (2), 3.645 (1) Å; mean SbC = 2.15 (2) Å. The bond angles are as follows: mean SbSbC = 93.6 (6)°; mean CSbC = 93.5 (15)°.

The crystal packing structure of tetramethyldistibine is illustrated in Figure 1. The SbSb and SbC bond lengths and the bond angles about the Sb atoms are very similar to those reported for **2**,[2] **3**,[3] and tetraphenyldistibine (**4**).[12] All four distibines adopt a staggered trans conformation about the Sb–Sb axis.

However, tetramethyldistibine must adopt a different molecular structure in the liquid phase and in solution. The Raman spectrum of the solid shows an intense band at 179 cm^{-1} assigned to the trans Sb–Sb stretch, while the liquid has two Sb–Sb bands (175 and 143 cm^{-1}), indicating population of a second (probably gauche) conformer.[13] The C NMR of **1** in solution has a resonance at δ (C_4D_8O) −10.6, while in the solid it is shifted to δ −6.4.[14] Tetramethyldistibine shows a dipole moment of 0.95 ± 0.04 D in benzene. Since the symmetrical trans conformation can have no dipole moment, a significant fraction of the tetramethyldistibine molecules must adopt another conformation.

It is particularly interesting to note that the crystal packing structure of **1** is nearly identical with that of **2**. The chains of Sb atoms are completely colinear with alternating intramolecular and short "intermolecular" separations. The intermolecular Sb···Sb separations at 3.645 (2) Å for **1** and 3.625 (1) Å for **2** are only about 25% longer than the intramolecular bond length. In the more sterically congested tetrakis(trimethylsilyl)distibine (**3**), the chains of Sb atoms are not linear and the Sb···Sb separation is greater at 3.99 Å.

The antimony atoms of distibines use primarily p orbitals for bonding since the bond angles about antimony

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[11] $R(F) = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

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[14] The solid C NMR spectrum was recorded by the Colorado State University Regional NMR Center funded by the National Science Foundation Grant No. CHE 78-18581.

0276-7333/84/2303-0337$01.50/0