Preparation and Characterization of a Series of Novel Mono(metallo)stibanes [M]Sb(CF_3)$_2$[†]

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Isolable mono(metallo)stibanes of the type [M]Sb(CF_3)$_2$ ([M] = $(CO)_5Mn$ (**3a**), $(CO)_5Re$ (**3b**), $Cp(CO)_3Cr$ (**3c**), $Cp(CO)_3Mo$ (**3d**), $C_5Me_5(CO)_3W$ (**3e**)) are formed quantitatively by reactions of $Sb(CF_3)_3$ (**1**) with the corresponding hydride complexes [M]H (**2**) with elimination of trifluoromethane. Structural analyses of the derivatives **3a** and **3e** by X-ray diffraction show a considerable shortening of the M−Sb bonds in comparison with the sum of the single bond radii. In the crystal lattice of **3a** a significant intermolecular Sb···Sb interaction of pairs of molecules is observed.

Introduction

Transition metal substituted arsanes and stibanes of the type [M]ER_2 (E = As, Sb) are possible precursors for the synthesis of oligonuclear complexes[1−3] or of highly reactive species with M−E double bonds.[4,5] In this rewarding area of research, so far, quite a number of arsenic compounds are known, but representatives containing antimony are still very rare. This is particularly true for trifluoromethyl antimony derivatives. So metalloarsanes such as [$Cp(CO)_3MAs(CF_3)_2$] (M = Cr, Mo, W) have been prepared by metathesis from [$Cp(CO)_3Mo$]$_2$ and $As_2(CF_3)_4$ [6] or by cleavage of the diarsane with $Cp(CO)_3MH$,[7] while no certain evidence could be presented for a [M]Sb(CF_3)$_2$ compound.

Based on analogies to the chemistry of arsenic Cullen et al.[8] postulated the formation of the complex [$Cp(CO)_2Fe{-}Sb(CF_3)_2$] in the reaction of the distibane $Sb_2(CF_3)_4$ with the binuclear compound [$Cp(CO)_2Fe$]$_2$, but they were unable to isolate and characterize the expected product. They attributed this result to the instability of the antimony compound. However, their conclusion was questioned for two reasons:

(i) The related metallostibanes [$Cp(CO)_3MSbMe_2$] (M = Cr, Mo, W) are stable and can be prepared in pure form without problems.[9]

(ii) On the basis of literature information the tendency to form binuclear complexes from [M]ER_2 precursors decreases from As to Sb and CH_3 to CF_3, respectively, due to the declining basicity of the ER_2 group.

Despite this critical resonance, the reasons for unsuccessful attempts to prepare metallo(trifluoromethyl)stibanes remained obscure for several decades.

In connection with our investigations of fluorine containing arsaalkenes[10,11] we recently explored an effective synthetic route[12] to trimethylstannylbis(trifluoromethyl)arsane, a particularly useful precursor for the preparation of perfluoro-2-arsapropene,[10] by As−C bond cleavage of $As(CF_3)_3$ with trimethylstannane Me_3SnH.

$$As(CF_3)_3 + Me_3SnH \rightarrow Me_3SnAs(CF_3)_2 + HCF_3$$

This result encouraged us to study the reactivity of $Sb(CF_3)_3$ with transition metal hydride derivatives [M]H aimed at the preparation of the title compounds.

Results and Discussion

Synthesis and Characterization of the Mono(metallo)stibanes 3a−e. The reactions of $Sb(CF_3)_3$ (**1**) with the hydride derivatives **2a−e** in chloroform or toluene solution at 0−20 °C yield the corresponding metallostibanes **3a−e** and trifluoromethane almost quantitatively within 7−11 h (Scheme 1).

3a−e are light-, air-, and moisture-sensitive compounds, but can be isolated under suitable precautions. Derivatives **3c−e** are less stable and undergo slow decomposition even at room temperature. Composition and constitution of the new complexes are determined by NMR spectroscopic investigations (^1H, ^{19}F, ^{13}C) as well as by X-ray diffraction analyses on single crystals of **3a** and **3e**. In addition, IR and mass spectra were recorded for the relatively stable derivatives **3a**, **3b**, and **3e**.

[†] Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

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Scheme 1

$$\underset{\mathbf{1}}{Sb(CF_3)_3} + \underset{\mathbf{2a-2e}}{[M]\text{–}H} \rightarrow \underset{\mathbf{3a-3e}}{[M]\text{–}Sb(CF_3)_2} + \underset{\mathbf{4}}{HCF_3}$$

[M] = $(CO)_5Mn$ (**a**), $(CO)_5Re$ (**b**), $Cp(CO)_3Cr$ (**c**), $Cp(CO)_3Mo$ (**d**), $C_5Me_5(CO)_3W$ (**e**)

The ^{19}F resonances of **3a**−**e** are observed at low field between −33.4 (**3b**) and −34.9 (**3d**). They are particularly useful in controlling the course of the syntheses. The ^{13}C NMR signals of the trifluoromethyl groups appear as quartet of quartets with typical coupling constants $^1J(C, F) \approx 365$ Hz and $^4J(C, F) \approx 4.8$ Hz. The CO valence frequencies of **3a** and **3b** very well correspond to the known data of the homologous compounds $[(CO)_5ME(CF_3)_2]$ (M = Mn, Re; E = P, As).[13] The mass spectra of **3a**, **3b**, and **3e** show the molecular peaks M^+ with high intensity (in case of **3a** M^+ is the basis peak). As expected for metal carbonyl derivatives an important fragmentation pattern results from the stepwise elimination of the CO ligands.

The reactions according to Scheme 1 were found to be selective since no further substitution of CF_3 groups in **3a**−**e** occurs when the hydride complexes are applied in large excess. It is noteworthy that the synthetic route described above is only suited for trifluoromethyl antimony compounds; similar cleavage reactions of the arsane $As(CF_3)_3$ with transition metal hydride derivatives [M]H do not occur even under forced conditions at higher temperatures. In comparison with the analogous methyl substituted compounds $[Cp(CO)_3M\text{-}SbMe_2]$ (M = Cr, Mo, W)[9] the CF_3 derivatives **3c**−**e** are of lower stability. This is probably due to the special properties of trifluoromethyl antimony compounds (tendency to CF_2 elimination) and not to the basicity of the systems.

X-ray Structural Analyses of 3a and 3e. The first X-ray diffraction study of a mono(metallo)stibane of the type L_nMSbR_2 (R = alkyl, aryl) was published in 1997 for the niobocen derivative $[Cp_2(H)_2NbSbPh_2]$.[15] This is due to the fact that up to now only few representatives are known.[3,14] With the structures of **3a** and **3e** we here present two further examples. In Figure 1 and Figure 2 the molecular structures of **3a** and **3e** are given together with a selection of bond lengths and bond angles. The geometry at the Sb atom in **3a** or **3e** is a distorted trigonal pyramid. In both structures the M−Sb distances [2.663(1) Å for **3a**, 2.805(2) Å for **3e**] are significantly shorter than the sum of the covalent radii of Sb (1.41 Å)[16] and Mn (1.45 Å, derived from the Mn−Mn bond length in $Mn_2(CO)_{10}$ [17]) or W (1.61 Å, deduced from the structure of $[Cp(CO)_3W]_2$ [18]). On the other hand the Sb−C bonds of **3a** and **3e** with average values of 2.225 Å are somewhat longer than the sum of covalent radii of antimony and sp^3-hybridized carbon (2.18 Å).

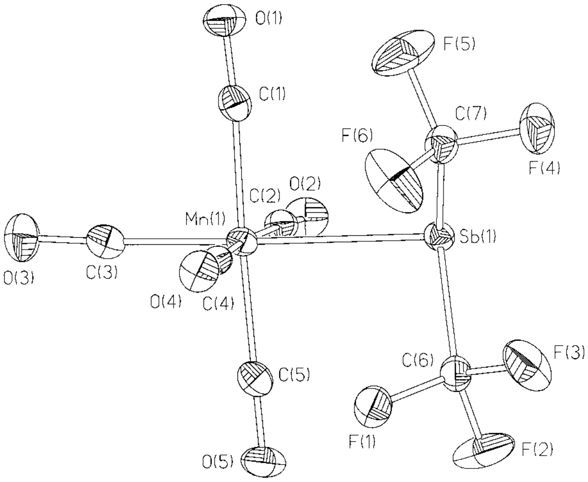

Figure 1. Molecular structure of **3a**. Selected bond lengths [Å] and angles [deg]: Mn1−Sb1, 2.6630(12); Mn1−C1, 1.874(3); Mn1−C2, 1.868(3); Mn1−C3, 1.844(3); Mn1−C4, 1.858(3); Mn1−C5, 1.867(3); Sb1−C6, 2.227(3); Sb1−C7, 2.220(3); C1−Mn1−Sb1, 89.76(9); C2−Mn1−Sb1, 85.63(9); C3−Mn1−Sb1, 177.97(8); C4−Mn1−Sb1, 88.86(9); C5−Mn1−Sb1, 87.89(9); C6−Sb1−Mn1, 100.86(8); C7−Sb1−Mn1, 101.63(8); C6−Sb1−C7, 89.87(11).

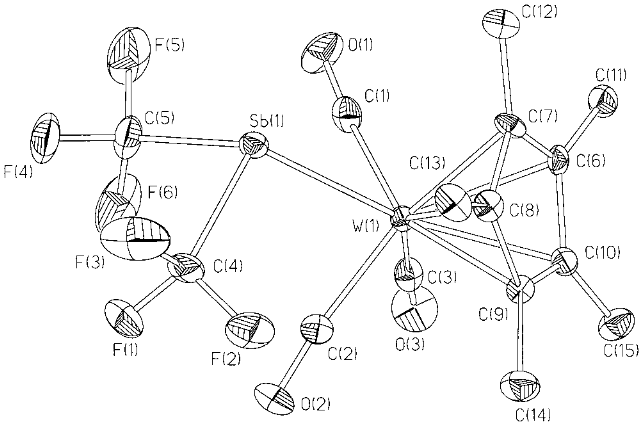

Figure 2. Molecular structure of **3e**. Selected bond lengths [Å] and angles [deg]: W1−Sb1, 2.8058(7); W1−C1, 2.004(8); W1−C2, 1.978(8); W1−C3, 1.993(8); Sb1−C4, 2.230(8); Sb1−C5, 2.220(9); C1−W1−Sb1, 75.8(2); C2−W1−Sb1, 78.3(2); C3−W1−Sb1, 133.7(2); C4−Sb1−W1, 106.5(2); C5−Sb1−W1, 105.1(2); C4−Sb1−C5, 89.1(4).

The M−Sb bond shortening[19] together with the widening of Sb−C bonds can be attributed to important back-bonding by overlap of filled M d-orbitals with empty σ^* MOs of the $Sb(CF_3)_2$ fragment.[20]

In the crystal lattice of **3a** the molecules are arranged in pairs by intermolecular interactions (Figure 3). The Sb···Sb distance in the pairs amounts to 4.036 Å and thus is shorter than the sum of van der Waals radii (4.40 Å).[21] Similar Sb···Sb distances have been detected also in structures of organostibanes such as Me_4Sb_2 (3.68

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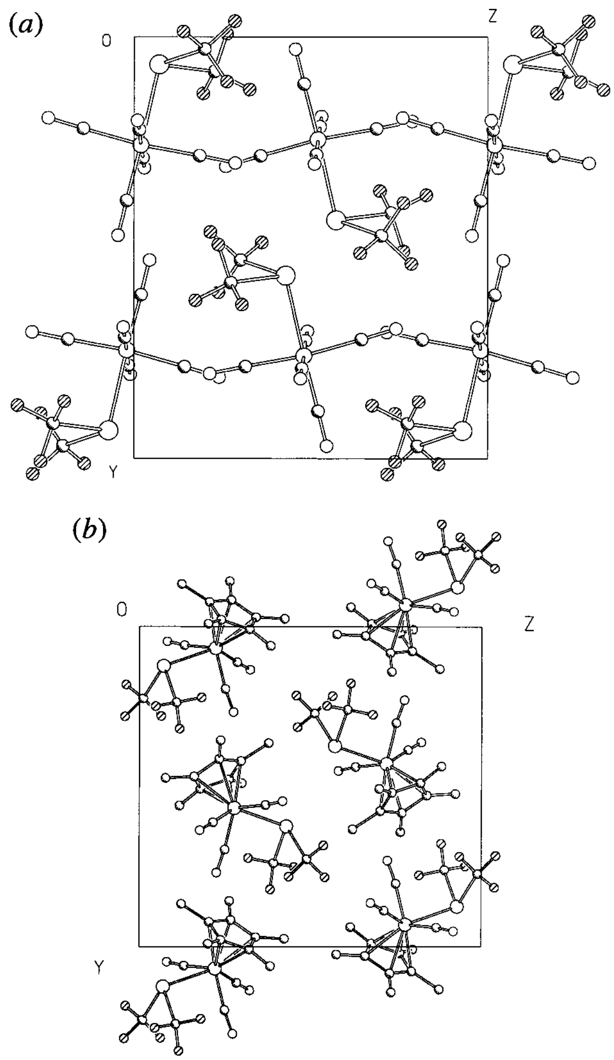

Figure 3. (a) Unit cell of [(CO)$_5$MnSb(CF$_3$)$_2$] (**3a)** and (b) unit cell of [C$_5$Me$_5$(CO)$_3$WSb(CF$_3$)$_2$] (**3e)**. Projection onto the *yz* plane.

Å)[22] and (Me$_3$Si)$_4$Sb$_2$ (3.99 Å)[23] or the complex [C$_5$H$_5$(CO)$_2$-MoSb$_3$] (3.839–4.271 Å).[24]

In the tungsten compound **3e** due to the bulky C$_5$Me$_5$ ligand the intermolecular Sb···Sb distance is enlarged to 4.971 Å and clearly beyond the sum of van der Waals radii. Therefore, in the crystal lattice this compound has to be described as essentially monomeric.

Experimental Section

All experiments were carried out using a standard vacuum line (or under argon). Reaction vessels were either Schlenk flasks or ampules with several break seals and an NMR tube. Solvents and deuterated compounds for NMR measurements were carefully dried and degassed. NMR: Bruker AC 200 (200.13 MHz, ^{1}H, standard: TMS; 188.31 MHz, ^{19}F, standard: CCl$_3$F; 50.32 MHz, ^{13}C, standard: TMS). MS: Model CH5 MAT-Finnigan. IR: Nicolet Impact 400, Bruker IFS 48. The transition metal hydride complexes **2a**,[25a] **2b**,[25b] **2c**,[25c] **2d**,[25c] and **2e**[25d] were prepared according to the literature.

The preparation of tris(trifluoromethyl)stibane **1** by reaction of Cd(CF$_3$)$_2$·2CH$_3$CN with SbCl$_3$ was only successful after a careful modification of the literature method.[26]

Modified Synthesis of Sb(CF$_3$)$_3$ (1). A 4.26 g (25 mmol) amount of CdEt$_2$ and 2.05 g (50 mmol) of CH$_3$CN are placed in a 500 mL Schlenk bulb by vacuum condensation and thoroughly mixed. The solution is cooled at −196 °C before 15.7 g (80 mmol) of CF$_3$I is introduced by condensation. After thawing the bulb is filled with argon at −60 to −50 °C and then transferred to a −23 °C bath (*not to a −35 °C bath as suggested in the literature*[26a]). When the mixture is stirred at −23 °C a strongly exothermic reaction starts immediately, indicated by solidification, and results in the formation a white solid. The reaction is complete within 1−2 min (*not after 2 days as reported* [26a]). After removal of the iodoethane formed and the CF$_3$I excess in vacuo Cd(CF$_3$)$_2$·2CH$_3$CN is obtained as a white powder in quantitative yield and applied to the synthesis of Sb(CF$_3$)$_3$ (**1**).

A 2.28 g (10 mmol) amount of SbCl$_3$ is placed in a 50 mL Schlenk vessel and dried at room temperature by pumping of trace amounts of water. Then 5.0 g (15 mmol) Cd(CF$_3$)$_2$·2CH$_3$CN is added under an argon atmosphere, the vessel is evacuated, and 5 mL of acetonitrile is brought in by vacuum condensation. The mixture is stirred at 20 °C for 4 h. A white precipitate of CdCl$_2$ indicates the start of the substitution of Cl for CF$_3$. After completion the volatile components are removed under mild heating in vacuo. The resulting solution of Sb(CF$_3$)$_3$ in acetonitrile is cooled at −55 °C in order to slowly remove the solvent by condensation to a −196 °C trap. Tris(trifluoromethyl)stibane is obtained as residue in form of a clear, colorless liquid. The ^{19}F and ^{13}C NMR spectra as well as the mass spectroscopic data are in good agreement with the literature data.[26b] Yield: 2.96 g (90%).

General Procedure for the Synthesis of the Mono(metallo)stibanes 3a−e. A 1 mmol amount of the corresponding hydride complex **2a**−**e** is placed in an ampule with a side-fixed NMR tube together with 2 mL of a solvent (for **2a**, **2b**, chloroform; for **2c**−**e**, toluene) and well mixed. To this solution an equimolar amount of Sb(CF$_3$)$_3$ is added by vacuum condensation. After mixing at −10 °C with continuous stirring the mixture is slowly heated to 20 °C while being kept in the dark. Except for the rhenium complex **2b** all other hydride precursors react with Sb(CF$_3$)$_3$ with a color change of the reaction mixture (**2a**: colorless to orange; **2c**−**e**, light yellow to deep yellow). In case of **2b** the product precipitates as a white solid during the reaction. ^{19}F NMR control measurements prove the reactions to be complete at room temperature after 5−6 h. HCF$_3$ and the solvent are removed in vacuo to give the complexes **3a**−**e** in spectroscopically pure form. Yield: 95% (**3a**), 99% (**3b**), 85% (**3c**), 94% (**3d**), 96% (**3e**).

Bis(trifluoromethyl)[(pentacarbonyl)manganeso]stibane (3a). ^{19}F NMR (CDCl$_3$, 25 °C): δ −33.1 (s). − ^{13}C NMR (CDCl$_3$, 25 °C): δ 120.8 [qq, ^1J(F,C) = 364.9 Hz, ^4J(F,C) = 4.7 Hz, CF$_3$], 210 [s, br, CO]. IR [ν(CO), toluene]: 2116 (w), 2060 (w), 2030 (vs), 2020 (s) cm^{-1}. MS (EI, 70 eV, selected, relative to ^{121}Sb); *m/z* (%): 454 (100) [M$^+$], 435 (2) [M$^+$ − F], 385 (3) [M$^+$ − CF$_3$], 342 (3) [M$^+$ − 4CO], 314 (10) [M$^+$ − 5CO], 195 (68) [(CO)$_5$Mn$^+$], 178 (10) [MnSb$^+$].

Bis(trifluoromethyl)[(pentacarbonyl)rhenio]stibane (3b). ^{19}F NMR (CDCl$_3$, 25 °C): δ −32.3 (s). ^{13}C NMR (CDCl$_3$): δ 119.5 [qq, ^1J(F,C) = 363.4 Hz, ^4J(F,C) = 4.7 Hz, CF$_3$], 205 [s, br, CO]. IR [ν(CO), toluene]: 2135 (w), 2070 (w), 2033 (vs),

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2016 (s) cm^{-1}. MS (EI, 70 eV, selected, relative to ^{121}Sb, ^{187}Re); *m*/*z* (%): 586 (61) [M^+], 536 (10) [$M^+ - CF_2$], 517 (23) [$M^+ - CF_3$], 467 (28) [$M^+ - C_2F_5$], 439 (28) [$M^+ - C_2F_5 - CO$], 411 (26) [$M^+ - C_2F_5 - 2CO$], 383 (79) [$M^+ - C_2F_5 - 3CO$], 364 (23) [$(CO)_2ReSb^+$], 355 (42) [$(CO)ReSbF^+$], 336 (27) [$(CO)ReSb^+$], 327 (92) [$(CO)_5Re^+$], 308 (56) [$ReSb^+$], 187 (20) [Re^+], 121 (19) [Sb^+], 69 (16) [CF_3^+], 28 (100) [CO^+].

Bis(trifluoromethyl)[(tricarbonyl-η^5-cyclopentadienyl)chromio]stibane (3c). ^1H NMR ($CDCl_3$, 25 °C): δ 5.0 (s, Cp). ^{19}F NMR ($CDCl_3$, 25 °C): δ −34.4 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 87.6 (s, Cp), 121.9 [qq, $^1J(F,C) = 367.0$ Hz, $^4J(F,C) = 4.8$ Hz, CF_3], 227 [s, br, CO].

Bis(trifluoromethyl)[(tricarbonyl-η^5-cyclopentadienyl)molybdeno]stibane (3d). ^1H NMR ($CDCl_3$, 25 °C): δ 5.3 (s, Cp). ^{19}F NMR ($CDCl_3$, 25 °C): δ −34.9 (s). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 89.0 (s, Cp), 119.2 [qq, $^1J(F,C) = 366.7$ Hz, $^4J(F,C) = 4.7$ Hz, CF_3], 215 [s, CO].

Bis(trifluoromethyl)[(tricarbonyl-η^5-pentamethylcyclopentadienyl)tungsteno]stibane (3e). ^1H NMR ($CDCl_3$, 25 °C): δ 2.1 (s, CH_3). ^{19}F NMR ($CDCl_3$, 25 °C): δ −33.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 10.5 (s, CH_3), 103.5 (s, aromatic C), 119.1 [qq, $^1J(F,C) = 366.4$ Hz, $^4J(F,C) = 4.7$ Hz, CF_3], 220.7 [s, CO]. MS (EI, 70 eV, selected, relative to ^{121}Sb, ^{184}W); *m*/*z* (%): 662 (66) [M^+], 593 (32) [$M^+ - CF_3$], 543 (100) [$M^+ - C_2F_5$], 487 (59) [$M^+ - C_2F_5 - 2CO$], 459 (74) [$M^+ - C_2F_5 - 3CO$], 403 (48) [$M^+ - Sb(CF_3)_2$], 190 (40) [CF_3Sb^+], 121 (69) [Sb^+], 119 (34) [$C_2F_5^+$], 69 (36) [CF_3^+], [CO^+].

Crystal Structure Determination of 3a and 3e. X-ray data of **3a** and **3e** were collected with a Syntex $P2_1$ diffractometer by using Mo Kα radiation and $\theta/2\theta$ scan technique. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL-93[27]). Crystallographic data are given in Table 1.

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Table 1. Crystallographic Data and Parameters of the Crystal Structure Determinations

compound	**3a**	**3e**
empirical formula	$C_7F_6MnO_5Sb$	$C_{15}H_{15}F_6O_3SbW$
fw	454.76	662.87
cryst size [mm]	0.27 × 0.25 × 0.08	0.27 × 0.25 × 0.08
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a [Å]	8.335(3)	8.2090(10)
b [Å]	13.309(6)	14.588(3)
c [Å]	11.102(5)	15.559(3)
β [deg]	97.08	93.29
V [$Å^3$]	1222.2(9)	1860.2(6)
Z	4	4
ρ_{calcd} [$g\cdot cm^{-3}$]	2.472	2.367
μ [mm^{-1}]	3.336	7.700
$F(000)$	848	1232
temperature [K]	150	150
$2\theta_{max}$ [deg]	54.11	54.11
index ranges	$0 \le h \le 10$ $0 \le k \le 17$ $-14 \le l \le 14$	$0 \le h \le 10$ $0 \le k \le 18$ $-19 \le l \le 19$
transmission (min/max)	0.555/ 0.854	0.970/ 0.370
no. of reflns measd	2482	4049
no. of indep rflns with $I > 2\sigma(I)$	2168	3357
no. of parameters	181	235
R1	0.0198	0.0402
wR2	0.0488	0.1002
GooF on F^2	1.023	1.051
resid. electron density [e $Å^{-3}$]	+0.657/ −0.401	+4.454/ −3.860

Supporting Information Available: Tables giving atomic coordinates, thermal parameters, and bond distances and angles for **3a** and **3e** (14 pages). Ordering information is given on any current masthead page.

OM9807452

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