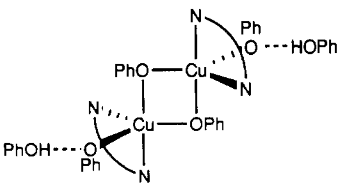

VI

occurs between coordinated phenoxide and lattice phenol. Co(Salen)(py)(OMe)·MeOH involves hydrogen bonding from the lattice methanol hydrogen to the coordinated methoxide.[35,36]

Summary and Generalizations. This discussion of hydrogen bonding can also be generalized. The phenomenon is most fundamentally one in which an anionic $M_2(OR)_2^-$ moiety behaves as a bidentate group toward *any electrophile*. In addition to H^+, the electrophile could be an alkali-metal cation, Tl^+, Cu^+, or even more highly charged metals: $CuCl^+$, HgX^+, etc. Compounds of this type (alternatively called intimate ion pairs) have been structurally characterized: $(diglyme)NaW_2H(O^iPr)_8$,[37] $KU_2(O^tBu)_9$.[38] This generalization also incorporates those cases where a monometallic unit binds cationic electrophiles: $(ROH)Li(\mu\text{-}OR)_2Fe(OR)_2$ with $R = CH^tBu_2$.[39] An extensive network of hydrogen bonding is also observed between the terminal alkoxo groups and the methanol that solvates the cation ($M = Mg^{2+}$, Na^+) in compounds such as $[M(MeOH)_6]_n[Nb_2(OMe)_9]$.[40]

Moving beyond alkoxide chemistry to isoelectronic species, strong amido–ammine hydrogen bonding has been reported between groups positioned on adjacent metals in a Pt(IV)/Pt(IV) dinuclear complex.[41]

The pattern that emerges from the existing body of compounds is that hydrogen bonding will occur when M–OR and M–O(H)R vectors lie approximately parallel to one another.[42] Since examples are known with a metal–metal separation as large as 3.8 Å, it is clear that a metal–metal bond is not required. $M(OR)_3$ compounds (e.g., M = Mo, W, Y, ...) must aggregate in order to achieve a (preferred) coordination number of 6, and the available degrees of aggregation and associated polyhedra still demand additional neutral ligands. Alcohol is a reactant which is frequently available, as a result of the synthetic procedure, as a solvent when alkoxides are used in material science[43] or in catalysis;[36] it may also be generated by undesirable hydrolysis. Although alkoxides display a limited affinity for binding Lewis bases,[44] alcohol has the advantage over conventional bases of 3–15 kcal/mol from the hydrogen bond; numerous alkoxide–alcohol adducts have been reported and hydrogen bonding must be anticipated. The initial coordination of alcohol may play a critical role for many reactions.[34] More generally, the electron density of the alkoxide oxygen atom might act as an additional "anchor" directed to a four-centered transition state in reactions involving compounds bearing an OH or NH functionality. At the same time, volatile alcohols can be inadvertently removed in subsequent workup, with the result that physical and spectroscopic properties may appear variable as the material is altered from $[M_a(OR)_b(ROH)_c]_m$ to $[M_a(OR)_b]_{m'}$. This is a problem that can plague the discovery and characterization of new binary metal alkoxides.

Acknowledgment. We thank the U.S. Department of Energy and the Commissariat à l'Energie Atomique for financial support and Scott Horn for skilled technical assistance.

Supplementary Material Available: For $M_2(O^iPr)_8(^iPrOH)_2$ (M = Zr, Ce), tables of anisotropic thermal parameters, fractional coordinates and isotropic thermal parameters, and full crystallographic details (10 pages); listings of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Organometallic Chemistry of Fluorocarbon Acids. Structure of $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2\text{-}O,O]_2$, an Example of an Oxygen-Bonded $HC(SO_2CF_3)_2$ Ligand

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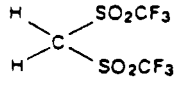
Dimeric $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2\text{-}O,O]_2$ was obtained from $(i\text{-}PrO)_3TiCl$ and $Ag[HC(SO_2CF_3)_2]$. Each titanium atom is bonded to two bridging and two terminal isopropoxy groups. Oxygen atoms, one from each sulfone fragment of the asymmetrically chelating $HC(SO_2CF_3)_2$ ligand, are also bonded to each titanium with the two Ti–O distances being 2.153 (4) and 2.264 (3) Å. Crystal data (at −155 °C): triclinic, $P\bar{1}$, $a = 10.384$ (5) Å, $b = 12.092$ (8) Å, $c = 10.338$ (6) Å, $\alpha = 101.99$ (4)°, $\beta = 119.41$ (3)°, $\gamma = 99.25$ (3)°, $Z = 1$, $R(F) = 0.045$, $R_w(F) = 0.0445$.

Introduction

We have sought to develop new organometallic chemistry based on the fluorocarbon acids **1**–**3**.[1-10] These materials exhibit a unique constellation of properties. All are volatile, crystalline solids that are readily soluble in noncoordinating solvents such as toluene



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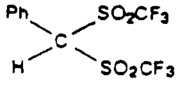

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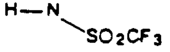

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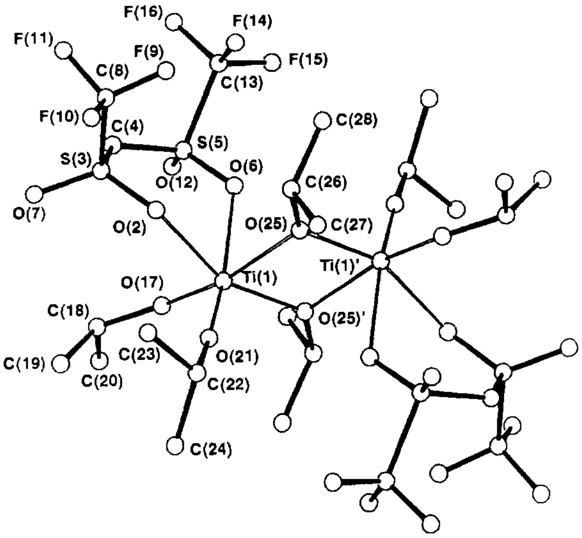

Figure 1. Molecular structure and numbering scheme for $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2]_2$.

and dichloromethane. The strong, carbon-centered acids **1** and **2** are not hygroscopic and may be easily handled in air. The acids are nonoxidizing and only two substrates have been found, $(Ph_2PC_2H_4PPh_2)_2Pt$ and $[(Ph_3P)_2Rh(CO)]_2$, whose reactions involve electron transfer.[10] The conjugate bases are, in most cases, noncoordinating. Only two examples are extant of compounds in which the $HC(SO_2CF_3)_2$ moiety is covalently bound to a transition metal.[4,7] Both involve a bond between platinum and the central, methine, carbon as in crystallographically characterized *trans*-$(Ph_3P)_2PtH[HC(SO_2CF_3)_2\text{-}C]$.[7] No compounds containing an oxygen-bonded $HC(SO_2CF_3)_2$ ligand are known, and it appeared that, if such a bonding mode were to be discovered, it would most likely be in a derivative of the electropositive group IVb metals. We describe here the characterization of a material in which such oxygen ligation occurs in an unusual way.

Synthetic Chemistry

The reaction between $(i\text{-}PrO)_3TiCl$ and $Ag[HC(SO_2CF_3)_2]$ in a mixture of dichloromethane and acetonitrile yields silver chloride and white, crystalline $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2\text{-}O,O]$ (**4**). This material does not irreversibly coordinate acetonitrile, as shown by elemental analyses and ^1H NMR spectroscopy. It is highly reactive toward water, liquefying within a few seconds upon exposure to the atmosphere. Water reactivity made suspect osmometric molecular weight determinations that indicated that the compound is a dimer. The ^1H and ^{13}C NMR spectra disclose only one type of isopropoxy group (cf. Experimental Section). The NMR parameters for the $HC(SO_2CF_3)_2$ fragment are quite similar to those of $[n\text{-}Pr_4N][HC(SO_2CF_3)_2]$, and, in particular, J_{CH} for the methine carbon atom is 185 Hz, indicative of sp^2 hybridization at carbon and of the absence of a Ti–C bond. The ^{19}F spectrum comprises a singlet at −80.0 ppm, but the width of this resonance, $w/2$ = 100 Hz at 25 °C, suggests that a dynamic process may be occurring. Limiting low-temperature NMR spectra could not be obtained; the compound precipitates from CD_2Cl_2 at <−10 °C. More polar solvents, such as CH_3CN, might displace coordinated $HC(SO_2CF_3)_2^-$ or participate in equilibrium exchange processes. Because spectroscopic data failed to lead unambiguously to a reasonable structure, an X-ray crystallographic study was performed.

Table I. Selected Bond Distances (Å) and Angles (deg)

	Distances		
Ti(1)–Ti(1)′	3.198 (3)	S(3)–C(4)	1.645 (5)
Ti(1)–O(2)	2.154 (4)	S(3)–C(8)	1.830 (6)
Ti(1)–O(6)	2.264 (3)	S(5)–O(6)	1.455 (4)
Ti(1)–O(17)	1.780 (4)	S(5)–O(12)	1.421 (4)
Ti(1)–O(21)	1.735 (3)	S(5)–C(4)	1.655 (6)
Ti(1)–O(25)′	1.927 (3)	S(5)–C(13)	1.842 (6)
Ti(1)–O(25)	2.108 (3)	F(9)–C(8)	1.319 (7)
S(3)–O(2)	1.457 (4)	C(4)–H(1)	0.74 (6)
S(3)–O(7)	1.423 (4)		
	Angles		
Ti(1)′–Ti(1)–O(2)	120.78 (11)	O(6)–Ti(1)–O(21)	163.50 (14)
Ti(1)′–Ti(1)–O(6)	80.87 (11)	O(6)–Ti(1)–O(25)	87.45 (14)
Ti(1)′–Ti(1)–O(17)	140.07 (12)	O(6)–Ti(1)–O(25)′	78.45 (13)
Ti(1)′–Ti(1)–O(21)	100.95 (14)	O(17)–Ti(1)–O(21)	101.88 (17)
Ti(1)′–Ti(1)–O(25)	39.59 (10)	O(17)–Ti(1)–O(25)	102.61 (15)
Ti(1)′–Ti(1)–O(25)′	35.64 (9)	O(17)–Ti(1)–O(25)′	164.55 (14)
O(2)–Ti(1)–O(6)	74.89 (3)	O(21)–Ti(1)–O(25)	104.49 (16)
O(2)–Ti(1)–O(17)	91.35 (15)	O(21)–Ti(1)–O(25)′	93.42 (15)
O(2)–Ti(1)–O(21)	90.42 (15)	O(25)–Ti(1)–O(25)′	75.24 (15)
O(2)–Ti(1)–O(25)	156.77 (13)	O(2)–S(3)–C(4)	112.25 (25)
O(2)–Ti(1)–O(25)′	86.35 (14)	O(6)–S(5)–C(4)	111.98 (24)
O(6)–Ti(1)–O(17)	86.20 (15)	Ti(1)–O(25)–Ti(1)′	104.76 (15)

Table II. Crystallographic Data for $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2]_2$

chem formula $C_{24}H_{44}F_{12}O_{14}S_4Ti_2$	fw 1051.46
a = 10.384 (6) Å	space group $P\bar{1}$
b = 12.092 (8) Å	T = −155 °C
c = 10.338 (7) Å	λ = 0.71069 Å
α = 101.99 (4)°	ρ_{calcd} = 1.592 g/cm^3
β = 119.41 (3)°	μ = 6.709 cm^{-1}
γ = 99.25 (3)°	$R(F)$ = 0.044
V = 1051.4 (4) Å^3	$R_w(F)$ = 0.045
Z = 1	GOF = 1.029

Description of the Structure

$Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2]_2$ crystallizes as a centrosymmetric dimer that is shown in Figure 1. Selected bond distances and angles are given in Table I. Each titanium atom has a distorted octahedral coordination geometry and is bonded to one axial and one equatorial terminal isopropoxy ligand, with d(Ti–O(17)) and d(Ti–O(21)) being 1.780 (4) and 1.735 (3) Å, respectively, and to two bidentate, bridging isopropoxy groups in which the Ti–O(25) bond distances are 1.927 (3) and 2.108 (3) Å. The tendency that bridging Ti–O bonds are longer than terminal ones is also seen in $[Ti(OEt)_4]_4$, in which d(Ti–O) involving terminal, doubly bridging, and triply bridging Ti–OEt groups is 1.77 (3), and 2.03 (3), and 2.23 (3) Å respectively.[11] Geometric constraints are likely associated with a contraction of the O(25)–Ti–O(25)′ angles in the Ti_2O_2 rhombus to 75.2 (1)° whereas the O(17)–Ti–O(21) angle, involving the terminal alkoxy ligands, is much larger, 101.9 (2)°.

Titanium also interacts with one sulfone oxygen atom on each of the SO_2 groups in the $HC(SO_2CF_3)_2$ moiety. The Ti–O bond lengths in this portion of the molecule, Ti–O(2) (equatorial) and Ti–O(6) (axial), are quite long, 2.153 (4) and 2.264 (3) Å, respectively. The O(2)–Ti–O(6) bite angle is 74.9 (1)°, and the O(6)–Ti–O(21) angle is 163.5 (1)°. Interestingly, the Ti–O(21)

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bond, which is trans to the weakly bonding sulfone O(6) atom, is significantly shorter than the Ti–O(17) bond, which is trans to a bridging isopropoxy oxygen atom.

Within the $HC(SO_2CF_3)_2$ ligand, bond distances and angles are similar to those found in ionic $[HC(SO_2CF_3)_2]^-$ derivatives.[5,6,7,9,12,13] The S(3)–C(4)–S(5) angle, 125.4 (3)°, is consistent with the sp^2 hybridization deduced from the C–H coupling constant. Although the Ti–O(2) and Ti–O(6) bond lengths are grossly inequivalent, the bonds between these oxygen atoms and sulfur, S(3)–O(2) and S(5)–O(6), are of comparable length. There is however, a pairwise relationship: a given sulfur atom has one short and one long S–O contact so that the S–O bonds to coordinated oxygen atoms are longer than those to terminal oxygen atoms. Thus, the S(3)–O(2), S(3)–O(7), S(5)–O(6), and S(5)–O(12) distances are 1.457 (4), 1.423 (4), 1.455 (4), and 1.421 (4) Å, respectively.

Discussion

An interesting feature of the structure of **4** is the way in which the $HC(SO_2CF_3)_2$ ligand is attached to titanium. The axial and equatorial Ti–O bonds differ by 0.10 Å. A more extreme situation occurs in the hexafluoroacetylacetonate complex $[(Ph_2PC_2H_4P(Ph)C_2H_4PPh_2)Pd(CF_3COCHCOCF_3)]^+$.[14] In this cation, one oxygen terminus of the $CF_3COCHCOCF_3$ ligand lies in the P_3PdO plane, in which *d*(Pd–O) is 2.110 (5) Å. The other oxygen is in an axial position with *d*(Pd–O) = 2.653 (6) Å. This bonding mode has been referred to as semichelating,[14,15] which is not an inappropriate description as well for $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2\text{-}O,O]_2$. It is probable that, in solution, the Ti–O(2) and Ti–O(6) bonds alternately lengthen and contract in a dynamic process that averages on the NMR time scale the CF_3 environments. Rationalization of the NMR data requires, in addition, a rapid interconversion between bridging and terminal isopropoxy ligands. In the context of metal alkoxide chemistry,[16] semibridging alkoxy ligands occur in $Mo_6O_{10}(i\text{-}PrO)_{12}$. In this serpentine-chain compound, unsymmetrically bridging isopropoxy ligands are situated so that 1.919 (2) and 2.88 (1) Å Mo–O bonds result.[17]

We have previously suggested that coordination of a metal to a sulfone oxygen in $[HC(SO_2CF_3)_2\text{-}O,O]^-$ could be detected by a shift in the S=O stretching frequency.[6] This idea cannot be tested by reference to the infrared spectrum of **4**. The spectrum is very complex and a definitive identification of S–O, C–F, and Ti–O stretching bands is difficult. Indeed, it is not certain that pure modes, uncomplicated by S–O and C–F vibrational coupling, exist. Until normal-coordinate analyses of suitable model compounds become available, X-ray crystallography will be the only way of positively identifying this oxygen-bonded ligand. It is to be expected, however, that such a bonding type will be prevalent when $HC(SO_2CF_3)_2^-$ is present in a molecule containing high-valency, electropositive metals.

Experimental Section

Reactions were carried out under nitrogen with use of dry, deoxygenated solvents. NMR shifts, obtained on a Varian XL-400 spectrometer, are expressed relative to internal $(CH_3)_4Si$ (^1H and ^{13}C) and $CFCl_3$ (^{19}F), with positive shifts being downfield of the reference.

$Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2]_2$. A solution of 1.16 g (3 mmol) of $Ag[HC(SO_2CF_3)_2]$[18] in 6 mL of CH_3CN was added dropwise with stirring to 3 mmol of $(i\text{-}PrO)_3TiCl$ (Aldrich) in 5 mL of CH_2Cl_2. After 1 h, the reaction mixture was filtered to remove precipitated AgCl. Toluene, 12 mL, was added and the resulting solution concentrated under reduced pressure. Filtration then afforded 1.3 g (87%) of white, crystalline **4**, which was dried under vacuum. Anal. Calcd (found): C, 28.6 (29.0); H, 4.0 (4.0); S, 12.8 (12.6); Ti, 9.5 (9.5); N, 0.0 (<0.1); mol wt 1008 (923, osmometric in $CHCl_3$). ^1H NMR (CD_2Cl_2): δ 5.05 (heptet, $^2J_{CH}$ = 6 Hz, 3 H, $(CH_3)_2C\mathit{H}O$–), 4.16 (s, 1 H, $\mathit{H}C(SO_2CF_3)_2$), 1.40 (d, 6 Hz, 18 H, $(C\mathit{H}_3)_2CHO$–). ^{13}C NMR (CD_2Cl_2): δ 119.95 (q, 323, $\mathit{C}F_3$) 48.9 (d, 185, $H\mathit{C}(SO_2CF_3)_2$), 82.92 (d, 142, O*C*H), 24.48 (q, 127, $\mathit{C}H_3$). The infrared spectrum (Nujol mull) contains strong bands at 3072, 1382, 1367, 1335, 1315, 1216, 1190, 1174, 1100, 1071, 1021, 990, 923, 858, 848, 820, 655, 611, 582, 508, 480, 470, and 447 ± 5 cm^{-1}.

X-ray Structure Determination. Crystals used for the X-ray study were obtained by slow diffusion of pentane vapor into a solution of the compound in dichloromethane. A summary of crystallographic data is given in Table II. Final values of fractional atomic coordinates are given

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $Ti_2(i\text{-}PrO)_4(\mu\text{-}i\text{-}PrO)_2[HC(SO_2CF_3)_2]_2$

atom	10^4x	10^4y	10^4z	$10B_{iso}$,[a] Å^2
Ti(1)	5496 (1)	1349 (1)	6057 (1)	13
O(2)	7026 (4)	2750 (3)	6008 (4)	15
S(3)	8487 (1)	3673 (1)	7218 (1)	17
C(4)	9594 (6)	3222 (5)	8666 (6)	19
S(5)	9297 (1)	1832 (1)	8651 (1)	17
O(6)	7841 (1)	1038 (3)	7242 (1)	16
O(7)	8460 (4)	4839 (3)	7795 (4)	28
C(8)	9341 (7)	3857 (5)	6064 (7)	30
F(9)	9377 (4)	2833 (3)	5352 (4)	37
F(10)	8513 (4)	4302 (3)	4965 (4)	44
F(11)	10786 (4)	4588 (4)	7000 (4)	50
O(12)	9701 (4)	1776 (3)	10158 (4)	24
C(13)	10725 (6)	1292 (5)	8355 (7)	25
F(14)	10454 (4)	1226 (3)	6949 (4)	34
F(15)	10668 (4)	229 (3)	8503 (4)	36
F(16)	12146 (3)	2028 (3)	9444 (4)	33
O(17)	6056 (4)	2196 (3)	7981 (4)	19
C(18)	6359 (13)	3230 (6)	9167 (9)	50
C(19)	5467 (16)	4008 (10)	8515 (11)	60
C(20)	6289 (11)	2927 (7)	10450 (9)	39
O(21)	3912 (4)	1770 (3)	4875 (4)	18
C(22)	2767 (6)	2162 (5)	3732 (6)	22
C(23)	3582 (9)	3199 (6)	3546 (9)	32
C(24)	1677 (8)	2424 (7)	4232 (8)	31
O(25)	4604 (4)	−243 (3)	5879 (3)	14
C(26)	4279 (6)	−641 (5)	6962 (6)	16
C(27)	5751 (7)	−357 (6)	8529 (6)	21
C(28)	3079 (7)	−125 (6)	7037 (7)	21
atom	10^3x	10^3y	10^3z	$10B_{iso}$,[a] Å^2
H(1)	1017 (7)	367 (5)	945 (7)	9 (13)
H(2)	759 (9)	388 (7)	972 (9)	161 (22)
H(3)	582 (9)	474 (8)	936 (10)	38 (22)
H(4)	542 (9)	418 (7)	763 (11)	10 (23)
H(5)	437 (10)	341 (8)	814 (10)	124 (30)
H(6)	542 (8)	241 (6)	1021 (8)	73 (18)
H(7)	695 (8)	251 (6)	1080 (8)	29 (19)
H(8)	656 (8)	357 (6)	1122 (8)	24 (17)
H(9)	222 (7)	152 (5)	288 (7)	15 (13)
H(10)	419 (8)	382 (6)	445 (8)	32 (16)
H(11)	425 (8)	305 (6)	318 (7)	47 (17)
H(12)	289 (8)	342 (5)	272 (8)	42 (15)
H(13)	233 (7)	310 (6)	523 (8)	48 (16)
H(14)	85 (8)	260 (5)	341 (8)	46 (15)
H(15)	129 (7)	179 (6)	447 (7)	35 (17)
H(16)	382 (6)	−147 (5)	644 (6)	7 (12)
H(17)	550 (6)	−68 (5)	916 (7)	9 (13)
H(18)	650 (7)	−68 (5)	846 (6)	20 (13)
H(19)	625 (7)	45 (6)	898 (7)	14 (13)
H(20)	351 (7)	75 (6)	755 (7)	22 (13)
H(21)	219 (7)	−34 (5)	601 (7)	19 (13)
H(22)	272 (6)	−43 (5)	759 (7)	20 (13)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula of: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

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in Table III. Additional experimental details are given in the supplementary material, along with tables of anisotropic thermal parameters, bond distances and angles, and observed and calculated structure factors.

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Supplementary Material Available: Tables of crystallographic data and refinement parameters, anisotropic thermal parameters, and bond distances and angles (7 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Oxidative Decarbonylation of Dimanganese Decacarbonyl by Polyselenide Anions: Molecular Structure of $[(C_6H_5)_4P]_2[Mn_2(Se_2)_2(CO)_6]\cdot C_4H_{10}O$, $[(C_6H_5)_4P]_2[Mn_2(Se_4)_2(CO)_6]$, and $[(C_6H_5)_4P]_2[Mn(Se_4)_2]$

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A series of three manganese polyselenide anions has been isolated and characterized. They are all derived from the reaction of $Mn_2(CO)_{10}$ and polyselenide anions in DMF solution. The reaction of $Mn_2(CO)_{10}$ with 1 equiv of K_2Se_3 in DMF generates $[Mn_2(Se_2)_2(CO)_6]^{2-}$ (Ia). Reaction of $Mn_2(CO)_{10}$ with 2 equiv of K_2Se_3 produces $[Mn_2(Se_4)_2(CO)_6]^{2-}$ (IIa), which can also be obtained by reaction of Ia with red selenium. Thermolysis of IIa in DMF leads to $[Mn(Se_4)_2]^{2-}$ (IIIa), which is the final product of oxidative decarbonylation. Thermolysis of Ia does not appear to lead to IIIa, suggesting that IIa is a necessary intermediate in the oxidative decarbonylation reaction. All three products have been structurally characterized as their $[(C_6H_5)_4P]^+$ salts (I–III). Structural data are as follows. For I: formula = $[(C_6H_5)_4P]_2[Mn_2(Se_2)_2(CO)_6]\cdot C_4H_{10}O$, space group $P\bar{1}$, $Z = 1$, $a = 11.120$ (6) Å, = 11.319 (5) Å, $c = 13.062$ (7) Å, $\alpha = 114.90$ (4)°, $\beta = 107.64$ (4)°, $\gamma = 90.57$ (4)°, $V = 1403$ (1) Å^3, $R(F_o) = 0.0688$, $R_w(F_o) = 0.0684$. For II: formula = $[(C_6H_5)_4P]_2[Mn_2(Se_4)_2(CO)_6]$, space group $P2_1/n$, $Z = 2$, $a = 12.022$ (5) Å, $b = 14.542$ (7) Å, $c = 16.251$ (8) Å, $\beta = 98.46$ (4)°, $V = 2810$ (1) Å^3, $R(F_o) = 0.0554$, $R_w(F_o) = 0.0580$. For III: formula = $[C_6H_5)_4P]_2[Mn(Se_4)_2]$, space group $P2_1$, $Z = 4$, $a = 10.048$ (3) Å, $b = 13.394$ (4) Å, $c = 33.969$ (11) Å, $\beta = 92.11$ (2)°, $V = 4756$ (1) Å^3, $R(F_o) = 0.0624$, $R_w(F_o) = 0.0613$. Both carbonyl containing anions, Ia and IIa, consist of two manganese tricarbonyl fragments chelated by a Se_n^{2-} chain ($n = 2, 4$). One of the terminal selenium atoms on each manganese also bridges to the second metal center, completing its 18-electron count. Thus each metal center is pseudooctahedrally coordinated by three Se atoms and three carbonyl ligands. The monomer IIIa has two Se_4^{2-} chains chelating to a manganese(II) center in a tetrahedral fashion.

Introduction

We have recently reported a series of reactions involving transition-metal carbonyls with polychalcogenides in polar aprotic solvents.[1-3] It turns out that the group 6 metal carbonyls undergo a remarkably diverse series of reactions with polychalcogenides. These reactions range from simple substitution with polytellurides[1] to oxidative decarbonylation of the metal center to form molybdenum and tungsten sulfides and selenides[2] and to oxidation of coordinated carbon monoxide to form chromium(III) trisdithiocarbonate.[3]

However, there has been very little work previously reported on the sulfides[4] and selenides[5] of group 7 metals. In general they do not enjoy the popularity of their group 6 neighbors. In fact, the only molecular binary sulfide of manganese reported to data is MnS_{11}^{2-}, which contains a disordered tetrahedron of two polysulfide rings coordinated to the metal center.[4f] The tetrathiorhenate ReS_4^-, has been prepared, along with several of its complexes,[6] as well as ReS_9^- [6b,7] and $Re_4S_{22}^{4-}$.[8] In addition, there have been several group 7 complexes reported that contain either selenide or diselenide as a ligand.[9] However, the area is very underdeveloped.

Recently, we reported the formation of $[Re_2(Se_4)_2(CO)_6]^{2-}$ from $Re_2(CO)_{10}$ and polyselenide anions in DMF solution.[10] In this paper, we describe the results of the investigation of the corresponding reactions of $Mn_2(CO)_{10}$ with polyselenide solution. We report the structure of a completely decarbonylated product $[Mn(Se_4)_2]^{2-}$, as well as the isolation and characterization of two possible precursors. Also, we provide more mechanistic information about the oxidative decarbonylation reaction.

Experimental Section

General Information. The compounds investigated in this report are air-sensitive, as is typical for d-block metal carbonyl anions. Thus, all reactions were performed in dried, degassed solvents under a purified argon atmosphere by using standard Schlenk techniques. All solids were stored and handled in an argon-filled glovebox. The selenide reagent, K_2Se_3, was prepared by a previously reported procedure,[2] and all other reagents are commercially available and were used as received. Solvents were Aldrich Gold Label grade and stored over activated sieves and degassed. IR spectra were obtained as Nujol mulls between KBr plates or polyethylene bags, and analytical data were otained from Atlantic Microlabs, Atlanta, GA.

Preparation of $[(C_6H_5)_4P]_2[Mn_2(Se_2)_2(CO)_6]\cdot C_4H_{10}O$ (I). In a typical reaction, 0.25 g (0.79 mmol) of K_2Se_3, 0.30 g (0.76 mmol) of Mn_2CO_{10}, and 0.66 g (1.58 mmol) of $(C_6H_5)_4PBr$ were dissolved in 5 mL of DMF, and stirred at room temperature for 15 min. The red solution was then

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