^1H NMR (acetone-d_6) δ 5.95 (s, 1 H, =CH), 3.55 (m, 1 H, CH_3CH), 1.15 (d, 3 H, J = 6 Hz, CH_3); ^{13}C NMR (acetone-d_6) δ 126.8 (=CH), 75.0 (CH_3CH), 17.1 (CH_3).

Structure Determination of 2a. Single crystals were grown by slow diffusion from methylene chloride/diethyl ether. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of good quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[27] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.[28] All computational work was carried out on a VAX 8600 computer using the Enraf-Nonius SDP software package. Details of the structure analysis, in outline form, are presented in Table I. Atomic coordinates for all non-hydrogen atoms appear in Table II.

Structure Determination of 4c. Single crystals were grown by slow diffusion from petroleum ether/diethyl ether. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of excellent quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[27] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.[28] All computational work was carried out on a NOVA 1200 computer using the Syntex XTL package. Details of the structure analysis, in outline form, are presented in Table V. Atomic coordinates for all non-hydrogen atoms appear in Table VI.

Acknowledgment. This work was supported by the National Institutes of Health (GM 16395), which is gratefully acknowledged.

Registry No. **1**, 78251-23-7; **2a**, 110725-92-3; **2b**, 110772-33-3; **4a**, 101224-97-9; **4b**, 101224-98-0; **4c**, 101225-00-7; **4d**, 110903-56-5; **4e**, 101225-01-8; **5a**, 101224-92-4; **5b**, 101224-93-5; **5c**, 101224-95-7; **5d**, 110903-57-6; **5f**, 110903-58-7; **6**, 110903-60-1; **7**, 111002-62-1; **8**, 110903-62-3; **9**, 111002-55-2; **12**, 108857-47-2; **13a**, 110903-64-5; **13b**, 111002-59-6; **14a**, 111002-57-4; **14b**, 111002-58-5; **15**, 110903-65-6; **16**, 111002-60-9; **18**, 110903-61-2; **19**, 110903-67-8; **21**, 110903-68-9; $NaBH_3CN$, 25895-60-7; LiMeCuCN, 41753-78-0; Et_4NCN, 13435-20-6; PhMgBr, 100-58-3; CH_2=CHMgBr, 1826-67-1; $PhCH_2SNa$, 3492-64-6; Fp(isobutylene) tetrafluoroborate, 41707-16-8; *cis*-dimethoxyethene, 7062-96-6; Fp(acetone-d_6) tetrafluoroborate, 110903-69-0; ethylene glycol, 107-21-1; (*R*,*R*)-2,3-butanediol, 24347-58-8; 1,2-propanediol, 57-55-6; 2,3-dihydrodioxin, 543-75-9; (2*R*,3*R*)-*trans*-2,3-dimethyl-2,3-dihydrodioxin, 110874-64-1.

Supplementary Material Available: Tables SI through SIV, listing thermal parameters and atomic coordinates for hydrogen atoms for each structure (4 pages); tables of observed and calculated structure factors for each structure (15 pages). Ordering information is given on any current masthead page.

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Organogermanium and Organotin Amido Derivatives of Carbon Suboxide. Crystal and Molecular Structure of $(Me_3M)_2C(CONMe_2)_2$ (M = Ge, Sn)

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Received May 26, 1987

The compounds $(Me_3Ge)_2C(CONMe_2)_2$ (A) and $(Me_3Sn)_2C(CONMe_2)_2$ (B) have been synthesized. They are isomorphous and crystallize in the orthorhombic space group $P2_12_12_1$ with a = 14.437 (4) Å, b = 13.243 (4) Å, and c = 9.826 (3) Å for A and a = 14.706 (4) Å, b = 13.420 (4) Å, and c = 9.920 (3) Å for B, respectively. The coordination geometry about Ge and Sn is almost undistorted tetrahedral. However two short intramolecular contact distances Ge···O and Sn···O of 2.89, 2.92 Å and 2.95, 2.97 Å, respectively, are found. Structural considerations as well as NMR spectra exclude the possibility that any bond interaction exists between metal and oxygen atoms. The shift of CO stretching bands to unusually low frequencies is explained in terms of electron withdrawal due to the presence of the metals.

Introduction

Recently two of us started a systematic study of molecular structures of compounds of the type R_2MX_2 (X = Ge, Sn)[1,2] in order to elucidate the much discussed problem of the coordination number attributed to M when X is a halogen.[3-7] The same problem seems to be more in dispute

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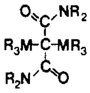
in complexes of the type R_3MX when X contains oxygen atoms (such as $-O-CO-CR_3$[8-12]), which sometimes are and sometimes are not interpreted as be bonded to M.

We can also find examples of structures in which M···O distances ranging from 2.3 to 3.7 Å are indifferently assumed as bond or weak bond distances, disregarding the geometrical parameters about M[10,13,14] The controversy is worse for compounds of the type $[(R_2SnX)O(R_2SnY)]_2$, referred to as tetraorganostannoxanes where X and Y are two equal or two different mono- or bidentate ligands.[15-19]

For a deeper investigation of this subject we synthesized a molecule designed to show unambiguous structural features. Complexes of the type



seemed be well-suited for this study. Such an overcrowded molecule was expected to assume a conformation with relatively short M···O intramolecular contact distances. If such distances are bonding or weakly bonding distances, the geometry about M should be trigonal-bipyramidal or very distorted tetrahedral, in order to relieve internal conformational strain arising from a large number of intramolecular short contacts.

Here we report the synthesis, the physicochemical characterization, and the crystal and molecular structures of $(Me_3Ge)_2C(CONMe_2)_2$ (A) and $(Me_3Sn)_2C(CONMe_2)_2$ (B).

A preliminary note on the synthesis and characterization of B already appeared.[20] As emphasized there, it was also possible to obtain the monometal derivatives of C_3O_2, $[(Me_3Ge)(CONMe_2)]C{=}C{=}O$ (C), and $[(Me_3Sn)(CONMe_2)]C{=}C{=}O$ (D). They present typical IR and ^1H NMR spectral patterns but were identified only in solution and not further purified or characterized.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of argon in oven-dried glassware. Solvents were purified, dried, and distilled before use. Carbon suboxide was prepared by reacting malonic acid with P_4O_{10} and purified by trap-to-trap distillation. Me_3GeBr was purchased from Aldrich Chemie and used without further purification. Me_3GeNMe_2 and Me_3SnNMe_2 were prepared by reported methods.[21,22]

Table I. Crystal Data and Details of Intensity Data and Structure Refinement of A and B

	A (M = Ge)	B (M = Sn)
formula	$C_{13}H_{30}N_2O_2M_2$	
mol wt	391.58	483.78
space group	$P2_12_12_1$	
cell const		
a, Å	14.437 (4)	14.706 (4)
b, Å	13.243 (4)	13.420 (4)
c, Å	9.826 (3)	9.920 (3)
cell vol., Å^3	1878.6 (3)	1957.8 (2)
Z	4	
D(calcd), g cm^{-3}	1.384	1.641
radiatn	Mo Kα (0.7107 Å)	
T, K	291	
cryst dimens, mm	0.4 × 0.3 × 0.3	0.7 × 0.5 × 0.5
μ, cm^{-1}	31.58	25.62
2θ range, deg	45	
decay of std reflctns, %	+3	+8
reflctns collected	2592	1679
reflctns with $I > 2\sigma(I)$	1437	1126
R int	0.010	0.016
R	0.047	0.096
R_w	0.046	0.092

Infrared spectra were obtained on a Perkin-Elmer 597 spectrophotometer. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a JEOL FX 90 Q instrument.

Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

Synthesis of $(Me_3Ge)_2C(CONMe_2)_2$ (A). Me_3GeNMe_2 (0.57 g, 3.6 mmol), dissolved in 5 mL of *n*-hexane, was added, at −78 °C, to an *n*-hexane solution of C_3O_2 (1.8 mmol in 25 mL). The resulting light yellow solution was allowed to reach room temperature and then was stirred for 20 min. On standing for 12 h at −30 °C, white crystals formed. A second crop of crystals was obtained by concentrating the mother liquors and freezing the residue at −30 °C (total yield 0.3 g, 43%). The product was recrystallized from boiling *n*-hexane, giving crystals suitable for X-ray analysis.

A: IR (*n*-hexane) $\nu(CO)$ 1590 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 28 °C) δ 2.90 (s) + 2.83 (s) (12 H, CH_3N), 0.33 (18 H, s, CH_3Ge). Anal. Calcd for $Ge_2C_{13}H_{30}O_2N_2$: C, 39.88; H, 7.67; N, 7.16. Found: C, 39.61; H, 7.75; N, 7.06.

Synthesis of $(Me_3Sn)_2C(CONMe_2)_2$ (B). Me_3SnNMe_2 (0.83 g, 4 mmol) was dissolved in 10 mL of *n*-hexane. At room temperature, 2 mmol of C_3O_2 was added under vigorous stirring. After 30 min the solution was cooled to 0 °C, and colorless crystals were obtained (0.5 g, 52%). The compound was recrystallized from boiling *n*-hexane, giving crystals suitable for X-ray analysis.

B: IR (*n*-hexane) $\nu(CO)$ 1580 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 10 °C) δ 2.90 (s) + 2.87 (s) (12 H, CH_3N), 0.19 (18 H, s, $J(^{119}Sn-^1H)$ = 52 Hz, CH_3Sn); ^{13}C NMR ($CDCl_3$, 28 °C) δ 173.0 (CO), 38.42, +36.36 (CH_3N), −4.7 ($J(^{119}Sn-^{13}C)$ = 352 Hz, CH_3Sn); ^{119}Sn NMR ($CDCl_3$, 28 °C) δ 5.5. Anal. Calcd for $Sn_2C_{13}H_{30}O_2N_2$: C, 32.27; H, 6.21; N, 5.79. Found: C, 32.13; H, 6.31; N, 5.72.

Synthesis of $[(Me_3Ge)(CONMe_2)]C{=}C{=}O$ (C). Me_3GeNMe_2 (0.71 g, 4.4 mmol) was dissolved in 15 mL of *n*-hexane. At −78 °C, 5 mmol of C_3O_2 was added with vigorous stirring. The solution became yellow and a red solid formed. The suspension was allowed to reach room temperature, and the solid was filtered and identified as C_3O_2 polymer. The solvent was evaporated from the solution, and the remaining oil was shown to be a mixture of C with some traces of A. Every attempt at purification caused decomposition of C. Although impure, C showed significant IR absorptions at 2100 (ν(CCO)) and 1635 cm^{-1} (ν(CO)) and ^1H NMR signals at δ 2.93 (6 H, br s, CH_3N) and 0.38 (9 H, s, CH_3Ge).

Synthesis of $[(Me_3Sn)(CONMe_2)]C{=}C{=}O$ (D). Me_3SnNMe_2 (0.62 g, 3 mmol) was dissolved in 10 mL of *n*-hexane. At room temperature, 3.5 mmol of C_3O_2, dissolved in 15 mL of *n*-hexane, was added. A red solid precipitated, and the solution became yellow. The solid was filtered and identified to be C_3O_2

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Table II. Fractional Atomic Coordinates with the Estimated Standard Deviations

$C_{13}H_{30}N_2O_2Ge_2$ (A)				$C_{13}H_{30}N_2O_2Sn_2$ (B)			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ge(1)	0.5029 (1)	0.6307 (1)	0.6414 (2)	Sn(1)	0.5025 (1)	0.6310 (2)	0.6518 (2)
Ge(2)	0.3884 (1)	0.5183 (1)	0.3953 (2)	Sn(2)	0.3854 (2)	0.5190 (2)	0.3910 (2)
O(1)	0.5576 (8)	0.4211 (8)	0.6306 (12)	O(1)	0.5585 (11)	0.4207 (15)	0.6294 (27)
O(2)	0.5188 (8)	0.6666 (8)	0.2879 (11)	O(2)	0.5184 (18)	0.6649 (18)	0.2884 (23)
N(1)	0.5906 (8)	0.3823 (8)	0.4142 (12)	N(1)	0.5918 (15)	0.3817 (15)	0.4153 (29)
N(2)	0.6609 (8)	0.6199 (10)	0.3637 (14)	N(2)	0.6614 (21)	0.6203 (17)	0.3644 (25)
C(1)	0.518 (1)	0.548 (1)	0.467 (1)	C(1)	0.519 (2)	0.550 (2)	0.467 (2)
C(2)	0.557 (1)	0.447 (1)	0.511 (2)	C(2)	0.558 (2)	0.445 (2)	0.510 (2)
C(3)	0.600 (1)	0.402 (1)	0.268 (2)	C(3)	0.600 (2)	0.403 (2)	0.268 (3)
C(4)	0.625 (2)	0.282 (1)	0.459 (2)	C(4)	0.625 (3)	0.282 (2)	0.460 (3)
C(5)	0.576 (1)	0.616 (1)	0.367 (2)	C(5)	0.567 (2)	0.615 (2)	0.367 (3)
C(6)	0.703 (1)	0.676 (2)	0.255 (2)	C(6)	0.703 (3)	0.677 (3)	0.255 (3)
C(7)	0.726 (1)	0.573 (1)	0.457 (2)	C(7)	0.725 (2)	0.573 (2)	0.457 (3)
C(8)	0.401 (2)	0.578 (2)	0.756 (2)	C(8)	0.392 (2)	0.570 (2)	0.769 (3)
C(9)	0.616 (2)	0.635 (2)	0.757 (2)	C(9)	0.625 (2)	0.635 (2)	0.769 (3)
C(10)	0.482 (1)	0.772 (1)	0.585 (2)	C(10)	0.470 (2)	0.781 (2)	0.590 (4)
C(11)	0.387 (2)	0.483 (2)	0.201 (2)	C(11)	0.395 (3)	0.483 (2)	0.180 (3)
C(12)	0.301 (1)	0.633 (1)	0.422 (2)	C(12)	0.298 (2)	0.647 (2)	0.405 (4)
C(13)	0.339 (1)	0.400 (1)	0.493 (2)	C(13)	0.326 (2)	0.399 (3)	0.500 (3)

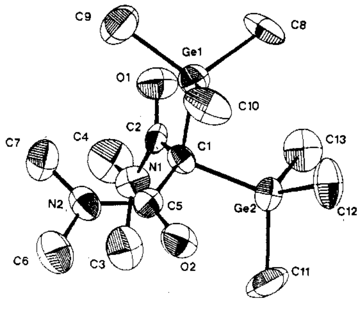
polymer. When the solution was concentrated, colorless crystals of B were obtained. The viscous residual oil, which we could not be purified further, showed IR absorptions at 2082 (ν(CCO)) and 1630 cm^{-1} (ν(CO)).

Synthesis of $H_2C(CONMe_2)_2$ (E). Me_2NH (0.54 g, 12 mmol) was dissolved in 50 mL of *n*-hexane at −30 °C, and with vigorous stirring, 5.5 mmol of C_3O_2 was added. After 20 min the solution was allowed to reach room temperature, and the solvent was evaporated under vacuum. The residual colorless, viscous oil was distilled, giving 0.50 g of E (80%). The compound was compared with an authentic sample,[23] giving the same IR and ^1H NMR spectra.

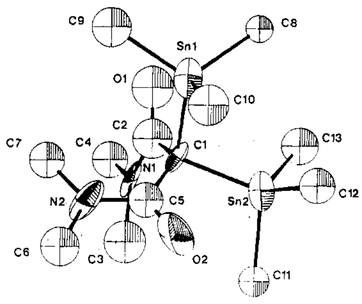
E: IR (film) ν(CO) 1670 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 28 °C) δ 3.51 (s, 2 H, CH_2), 3.08 (s) + 2.95 (s) (12 H, CH_3).

Collection of X-ray Diffraction Data for A and B. White crystals of A and B of approximate dimensions 0.4 × 0.3 × 0.3 mm and 0.7 × 0.5 × 0.5 mm, respectively, were sealed in Lindeman capillaries under argon atmosphere. They were mounted on a Philips PW 1100 computer-controlled four-circle diffractometer with graphite monochromator. Standard centering and autoindexing procedures[24] indicated a primitive orthorhombic lattice, space group $P2_12_12_1$, for both A and B. The orientation matrix and accurate unit cell dimensions were determined from a least-squares fit of 25 symmetry-related reflections. Both A and B undergo decomposition, which is particularly pronounced for B, for which three crystals were used during the data collection. All operations were carried out by the previously described techniques of our laboratory. Details appear in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption, owing to the relatively low μ values. The data were scaled to give 1437 independent F_{hkl} values for A and 1126 for B with $I > 2\sigma(I)$.

Solution and Refinement of the Structures. The position of Ge and Sn were determined from three-dimensional Patterson syntheses. The light atoms were located from subsequent Fourier maps. The hydrogen atoms were located from the final difference Fourier syntheses only for A. They were included in the calculations but not refined. Anisotropic thermal parameters were used for all the non-hydrogen atoms in A and for all atoms except hydrogens and methyl carbon atoms in B. Blocked-cascade least-squares refinements were used; they converged to the conventional *R* index of 0.047 for A and 0.096 for B. The weighting scheme used in the final calculations was of the form $w^{-1} = a_j|F_o|^j$. The a_j parameters were calculated by using the program PESO.[25] Scattering factors for the atoms were taken from Cromer and Waber;[26] the scattering factors for Ge and Sn were corrected for the real and imaginary parts of anomalous dispersion using Cromer's values.[27] All computations were carried out on a Cyber 76 computer using the programs in ref 28. The final positional parameters of the non-hydrogen atoms are listed in Table II, the labeling scheme being shown in Figure 1.[29]



$(Me_3Ge)_2C(CONMe_2)_2$ A



$(Me_3Sn)_2C(CONMe_2)_2$ B

Figure 1. ORTEP diagram showing the labeling of non-hydrogen atoms and the molecular structures of A and B as viewed down the *b* axis.

Results and Discussion

The crystals of A and B are isomorphous; the unit-cell dimensions of the tin derivative are only 1–2% larger. Due to the above described experimental difficulties, structural parameters for the tin derivative were refined only to the conventional *R* value, 0.096; however, comments on the

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[29] Data listed refer to the left-hand enantiomer for both A and B; the *R* residual for the right-hand enantiomer were only slightly and probably not significantly higher.

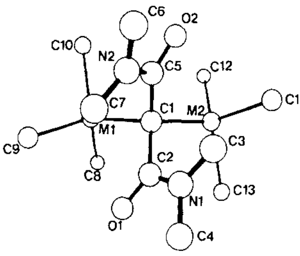

Figure 2. Molecular structure of A and/or B as viewed in a suitable projection showing the pseudo twofold axis passing through C(1).

structural results apply equally to A and B. We will hereafter refer to the better refined structure of the germanium derivative A (R = 0.047) except for a few instances in which parameters for A and B have remarkably different values. The relevant geometrical parameters for A and B are shown in Table III.

The molecule is characterized by a pseudo twofold symmetry; the twofold axis 2 passes through C(1) and bisects the angles C(2)–C(1)–C(5) and Ge(1)–C(1)–Ge(2) (Figure 2). The groups $GeMe_3$ are rotated ~20° from a staggered conformation; the geometry about the metal can be assumed (within the standard deviations) to be undistorted tetrahedral (see Table III); slight distortions have no explanation except for experimental error or packing.

The amide groups are almost planar; the torsion angles about the amide bonds C–N range from 3 to 7°, as normally found in free amides[30,31] or in open peptides.[32] The C—N amide bond lengths with an average value of 1.36 Å (1.37 Å for the tin complex) and the C=O bond lengths with an average value of 1.23 Å (1.24 Å for the tin complex) are quite noticeable, considering the absence of nonplanar distortions.[33] This feature will be further discussed below.

The amide groups are symmetrically oriented in such a way as to minimize the intramolecular nonbonded interactions. The resulting conformation shows relatively short contact distances between amide groups—N(1)–C(7) = 3.21 Å, N(2–)–C(3) = 3.16 Å, and C(3)–C(7) = 3.47 Å—and between amide groups and $GeMe_3$ groups—C(7)–C(9) = 3.44 Å, C(3)–C(11) = 3.32 Å, C(10)–C(12) = 3.57 Å, C(11)–O(2) = 3.20 Å, and C(9)–O(1) = 3.21 Å. Nonetheless a change in orientation of the amide groups would lead to shorter contact distances on either side; the conformation observed in the crystal is likely that of minimum internal energy. A consequence of this conformation is two symmetrical and relatively short contact distances between the metal and oxygen atoms with an average value for Ge–O of 2.90 Å (Sn–O = 2.96 Å). These short distances give rise to the question of whether the oxygen atoms are coordinated to the metal.

The almost undistorted tetrahedral coordination suggests the absence of M–O coordination. In contrast, the amidic CO stretching in the IR spectra shifted toward low frequencies (Ge, 1590 cm^{-1}; Sn, 1580 cm^{-1}) might be an indication that the amide groups are involved in some coordinative interaction with the metals.[20]

However, we note that (a) there are many examples of similar structures with metal–oxygen distances ranging from 2.3 to 3.2 Å and assumed to be bonding or weak bonding distances where the ν(CO) values are quite normal[4-9] (it is also notable that in the same examples the

Table III. Selected Geometrical Parameters for A and B

	Ge	Sn		Ge	Sn		Ge	Sn		Ge	Sn
					Bond Lengths (Å)						
M(1)–C(1)	2.05 (1)	2.15 (2)	M(2)–C(1)	2.04 (1)	2.14 (2)	C(2)–O(1)	1.23 (1)	1.23 (2)	C(5)–O(2)	1.24 (1)	1.25 (2)
M(1)–C(8)	1.98 (2)	2.16 (2)	M(2)–C(11)	1.96 (1)	2.15 (2)	C(2)–N(1)	1.36 (1)	1.36 (2)	C(5)–N(2)	1.36 (1)	1.39 (3)
M(1)–C(9)	1.99 (1)	2.15 (2)	M(2)–C(12)	1.99 (2)	2.15 (2)	N(1)–C(3)	1.46 (1)	1.49 (3)	N(2)–C(6)	1.44 (2)	1.46 (3)
M(1)–C(10)	1.97 (1)	2.16 (2)	M(2)–C(13)	1.97 (1)	2.11 (2)	N(1)–C(4)	1.48 (2)	1.49 (3)	N(2)–C(7)	1.45 (2)	1.46 (3)
C(1)–C(2)	1.52 (2)	1.58 (3)	C(1)–C(5)	1.50 (2)	1.50 (3)						
					Intramolecular Nonbonded Distances (Å)						
N(1)···C(7)	3.21	3.26	N(2)···C(3)	3.16	3.20	C(9)···O(1)	3.21	3.34	C(11)···O(2)	3.20	3.25
C(3)···C(7)	3.43	3.48	C(3)···C(11)	3.32	3.31	C(13)···O(1)	3.44	3.67	C(12)···O(2)	3.44	3.45
C(7)···C(9)	3.44	3.52	C(10)···C(12)	3.57	3.61	M(1)···O(1)	2.89	2.95	M(2)···O(2)	2.92	2.97
C(8)···O(1)	3.32	3.46	C(10)···O(2)	3.28	3.43						
					Bond Angles (deg)						
C(1)–M(1)–C(8)	112 (1)	111 (2)	C(1)–M(2)–C(11)	113 (1)	109 (2)	M(1)–C(1)–M(2)	107 (0)	107 (2)	C(2)–C(1)–C(5)	123 (1)	122 (2)
C(1)–M(1)–C(9)	114 (1)	112 (2)	C(1)–M(2)–C(12)	113 (1)	112 (2)	C(1)–C(2)–N(1)	119 (2)	120 (3)	C(1)–C(5)–N(2)	120 (2)	121 (3)
C(1)–M(1)–C(10)	106 (1)	105 (3)	C(1)–M(2)–C(13)	108 (0)	111 (2)	C(1)–C(2)–O(1)	121 (1)	121 (2)	C(1)–C(5)–O(2)	118 (2)	117 (3)
C(8)–M(1)–C(9)	107 (1)	111 (3)	C(11)–M(2)–C(12)	107 (1)	106 (2)	O(1)–C(2)–N(1)	120 (2)	120 (3)	O(2)–C(5)–N(2)	121 (2)	121 (3)
C(8)–M(1)–C(10)	112 (1)	110 (2)	C(11)–M(2)–C(13)	106 (1)	110 (2)	C(2)–N(1)–C(3)	127 (2)	126 (3)	C(5)–N(2)–C(6)	118 (2)	117 (3)
C(9)–M(1)–C(10)	105 (1)	109 (3)	C(12)–M(2)–C(13)	108 (1)	109 (3)	C(2)–N(1)–C(4)	118 (2)	118 (3)	C(5)–N(2)–C(7)	128 (2)	127 (3)
M(1)–C(1)–C(5)	106 (1)	109 (3)	M(2)–C(1)–C(2)	105 (1)	105 (3)	C(3)–N(1)–C(4)	115 (2)	116 (3)	C(6)–N(2)–C(7)	115 (2)	116 (3)
M(1)–C(1)–C(2)	106 (1)	105 (2)	M(2)–C(1)–C(5)	106 (1)	108 (2)						
					Torsion Angles (deg)						
C(9)–M(1)–C(1)–M(2)	|163|	|159|	C(11)–M(2)–C(1)–M(1)	|160|	|162|	C(1)–C(2)–N(1)–C(4)	|178|	|178|	C(1)–C(5)–N(2)–C(6)	|173|	|174|
C(5)–C(1)–C(2)–O(1)	|135|	|135|	C(2)–C(1)–C(5)–O(2)	|145|	|146|	C(1)–C(2)–N(1)–C(3)	|4|	|2|	C(1)–C(5)–N(2)–C(7)	|6|	|4|

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geometrical distorsions about the metal from tetrahedral values are often very large (e.g., bond angles of 90–95° or 118–120°)[13,14]); (b) a trend toward lower frequences has been considered absolutely unexceptional for the stretching band of any double bond in position with respect to metals of group IV[34] (14[38]); (c) the above reported geometrical parameters of the amide groups probably indicate that strong electron withdrawal takes place due to the metal atom. The normal ν(CO) values observed in similar cases [$H_2C(CONMe_2)_2$ (1670 cm^{-1}) or $BrHC(CONMe_2)_2$ (1665 cm^{-1})[23]] seem to prove that the central carbon atom plays no role in such effect, which, in our opinion, is due to the metals, with increasing effect in the predictable order Ge < Sn.

Such phenomenon gives an alternative and more reliable explanation of the observed ν(CO) values shifted toward lower frequences in the reverse order. A similar effect for tin has already been observed and widely discussed.[35,36] The ^{1}H NMR spectrum of A and the ^{1}H and ^{13}C NMR spectra of B substantiate these arguments. The ^{1}H NMR spectra show the equivalence of the hydrogen atoms of methyl groups bonded to the metals. This equivalence is also confirmed by the signal (−4.7 ppm) assigned to the methyl carbon atoms bonded to Sn (^{13}C NMR spectrum of B). Moreover, this spectrum shows $J(^{119}Sn-^{13}C)$ of 352 Hz, which has been assumed as a proper value for a tetracoordinated tin atom.[37] The relatively low coalescence temperatures of ^{1}H NMR NMe_2 doublet of A and B (~50 and ~20 °C, respectively), compared with $H_2C(CONMe_2)_2$ (>70 °C), are in agreement with a marked σ character of the bonds C(1)–N(1) and C(5)–N(2).

These data are consistent with tetrahedral, four coordination about the metal in both these compounds. They exclude, or at least severely question, the possibility of pentacoordination. The same coordination is retained also in solution. Thus the many structural examples showing only slightly distorted tetrahedral geometry,[9,10,13] and with M···O distances from 2.8 Å to higher values, assumed as bonding distances, should be reexamined.

Acknowledgment. This work was supported by Ministero della Pubblica Istruzione (Roma). We are very indebted to Prof. G. Tagliavini for helpful suggestions and discussions and to Prof. B. Longato for execution of NMR spectra. We thank Mr. G. Ravazzolo for technical assistance.

Registry No. A, 110698-77-6; B, 108202-42-2; C, 110698-78-7; D, 108202-43-3; E, 7313-22-6; Me_3GeNMe_2, 13361-67-6; Me_3SnNMe_2, 993-50-0; C_3O_2, 504-64-3.

Supplementary Material Available: Tables of hydrogen positional parameters and thermal parameters (4 pages); lists of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page. Supplementary material is also available from the authors upon request.

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Transition-Metal Trihalomethyl Complexes as Cluster-Building Reagents: Preparation and X-ray Crystal Structure of $[PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)]$

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Received June 16, 1987

A new mixed-metal ketenylidene complex, $[PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)]$ (1) (PPN$^+$ = bis(triphenylphosphine)nitrogen(1+)), has been prepared from trihalomethyl manganese complexes, $Mn(CO)_5(CX_3)$ (X = Cl or Br), in combination with $[PPN][Co(CO)_4]$. Attempts to extend this technique to other trihalomethyl complexes and metal carbonyl anions did not yield any new cluster products. Instead, these reactions were characterized by electron-transfer chemistry, which resulted in oxidation of the anions. Crystal data for 1: triclinic space group $P\bar{1}$; a = 14.859 (4) Å, b = 9.209 (1) Å, c = 16.701 (3) Å, α = 90.08 (2)°, β = 102.79 (2)°, γ = 89.99 (2)°; Z = 2. Protonation of 1 leads to the new mixed-metal methylidyne $MnCo_2(CO)_{10}(\mu_3\text{-}CH)$ (2).

Introduction

Transition-metal trihalomethyl complexes (X = Cl, Br) were rare until recently when a novel route to their preparation was discovered.[1] The facile halogen-exchange reaction between trifluoromethyl transition-metal complexes and boron trihalides affords the corresponding trihalomethyl complexes (X = Cl, Br) conveniently and in high yield (eq 1). The carbon atom in these complexes

$$M{-}CF_3 + BX_3 \rightarrow M{-}CX_3 + BF_3 \qquad (1)$$

acts as an electrophile, reacting with nucleophiles (H–NU) to give C–X bond cleavage and C–Nu bond formation (eq 2). The iron complex $CpFe(CO)_2(CCl_3)$, for example, reacts better with water, ammonia, primary amines, and thiols, transforming the CX_3 ligand to –CO, –CN, –CNR,

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