Crystal and Molecular Structure of (Di-*tert*-butylstannylene)pyridinopentacarbonylchromium[1]

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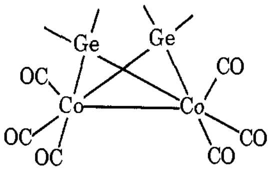
Abstract: The structure of $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot C_5H_5N$, the pyridine adduct of (di-*tert*-butylstannylene)chromium pentacarbonyl, has been determined by standard X-ray crystallographic methods. The compound crystallizes in the monoclinic space group $P2_1/n$, $Z = 4$, with unit cell dimensions $a = 8.466$ (2), $b = 28.149$ (5), $c = 9.223$ (2) Å, $\beta = 96.89$ (2)°. The intensity data were measured with an automated counter-diffractometer using Mo Kα radiation. The structure was refined using a full-matrix least-squares technique to give final values for R_1 and R_2 of 0.068 and 0.060, respectively. The molecular structure contains a $Cr(CO)_5$ group with virtual C_{4v} symmetry. The $(t\text{-}C_4H_9)_2Sn$ group is bonded to Cr (Sn–Cr, 2.654 (3) Å), and the pyridine is coordinated to the Sn atom (Sn–N, 2.29 (1) Å). The Sn–C bonds are relatively long (2.24 (1), 2.25 (1) Å). The C–Sn–C and two C–Sn–Cr angles are 109, 120, and 121°; the N–Sn–Cr and two N–Sn–C angles are 108, 100, and 94°. Thus the arrangement is intermediate between a planar $SnCrC_2$ group with pyridine approaching perpendicularly and a tetrahedral $SnCr_2N$ group. The compound is not a simple stannylene complex. Instead, the presence of the coordinated pyridine molecule allows the tin atom to achieve a coordination number of four and a valence shell octet of electrons.

Marks[2a] has attempted to prepare germylene and stannylene analogs of the well known complexes of the type $(RR'C)M(CO)_5$ (M = Cr, Mo, W).[2b] He found that the substances which could be isolated invariably contained 1 mol of a donor solvent, *e.g.*, $(OC)_5Cr\ Sn(t\text{-}C_4H_9)_2 \cdot L$, where L = THF or pyridine.

Our interest in these compounds arose in connection with the fluxional character of molecules such as $(OC)_3Co(\mu\text{-}GeMe_2)_2Co(CO)_3$, **1**, previously studied.[3]



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In order to account for the temperature dependence of the proton nmr spectrum of **1**, a rearrangement process in which the bridging role of the $GeMe_2$ groups is retained throughout was proposed. The alternative of having the bridges open up, as in the case of CO-bridged molecules,[4,5] was explicitly examined but considered less likely on the ground that germylene ($M = GeR_2$) or analogous silylene or stannylene intermediates would probably be too unstable to provide a pathway of sufficiently low energy.

It is obvious that if stable molecules containing $M = GeR_2$ or $M = SnR_2$ groups actually exist, preference for a bridge-preserving as against a bridge-opening pathway of rearrangement in $(OC)_3Co(\mu\text{-}GeMe_2)_2Co(CO)_3$, becomes much less defensible. It therefore appeared quite important to ascertain with certainty the structural nature of Marks' compounds by X-ray crystallographic investigation of a representative example. The consistent presence of the donor molecules raised the obvious possibility that these donors play an intimate role in stabilizing the compounds, and that simple $M = GeR_2$ or $M = SnR_2$ groups might not be present.

Through the cooperation of Professor Marks we obtained a crystalline sample of the compound $(OC)_5CrSn(t\text{-}C_4H_9)_2 \cdot C_5H_5N$. This compound was recommended as being one of the most stable, but otherwise entirely representative, examples of the group of compounds he had prepared and studied.

Experimental Section

Pale yellow, well-formed crystals of $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot C_5H_5N$, a pyridine adduct of (di-*tert*-butylstannylene)pentacarbonylchromium, were used as supplied by Professor T. J. Marks.

Crystallographic Data. $SnCrO_5NC_{18}H_{23}$, formula weight 504.1, is monoclinic with $a = 8.466$ (2), $b = 28.149$ (5), $c = 9.223$ (2) Å; $\beta = 96.89$ (2)°; $V = 2182$ Å^3; $Z = 4$; $d_{\text{calcd}} = 1.53$ g cm^{-3}; μ(Mo Kα) 16.92 cm^{-1}. The observed extinctions $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ uniquely indicate the centrosymmetric space group C^5_{2h}-$P2_1/n$. Unit cell dimensions and their estimated standard deviations were obtained at room temperature (24 ± 2°) with Mo Kα radiation (λ 0.7107 Å) using the least-squares procedure described previously.[6] Diffraction data were obtained from a crystal with boundary faces defined by the forms {110}, {010}, and {001}. Crystal dimensions normal to these faces were 0.37, 0.41, 0.11, and 0.32 mm, respectively. A check of the crystal mosaicity, expressed as the width (in degrees) at half-height of strong low-angle reflections recorded with open-counter ω scans, gave acceptably low values, in the range 0.15–0.18°.

Data were collected in the range $0 < 2\theta \leqslant 40°$ using Mo Kα radiation. The θ–2θ scan technique was used with a variable scan rate from 2.0 to 24.0°/min with a symmetric scan range from 2θ(Mo Kα_1) − 0.8° to 2θ(Mo Kα_2) + 0.8°. The scan rate used was chosen by sampling the peak intensity. Stationary crystal–stationary counter background counts were measured at both ends of the 2θ scan range, with the total background counting time equal to one-half of the scan time. The intensities of four standard reflections were monitored periodically during the course of data collection, and no appreciable loss of intensity was observed.

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(1) This investigation was supported by The Robert A. Welch Foundation (Grant No. A494). This generous support is gratefully acknowledged.

(2) (a) T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 7090 (1971); (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972); F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 486 (1972).

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(4) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, **11**, 671 (1972).

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Table II. Positional[a] and Thermal Parameters[b] for $Sn(C_4H_9)_2(NC_5H_5)Cr(CO)_5$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	0.1609 (1)	0.14578 (4)	−0.2396 (1)	0.0125 (2)	0.00116 (2)	0.0080 (1)	−0.00031 (7)	0.0006 (1)	0.00022 (5)
Cr	0.1360 (3)	0.1001 (1)	0.0084 (2)	0.0152 (5)	0.00136 (4)	0.0083 (3)	0.0000 (1)	0.0009 (3)	0.0004 (1)
O(1)	0.222 (2)	0.0076 (6)	−0.126 (2)	0.039 (3)	0.0017 (3)	0.019 (2)	0.008 (8)	0.005 (2)	−0.0010 (6)
O(2)	0.124 (2)	0.0423 (5)	0.279 (1)	0.030 (3)	0.0025 (3)	0.014 (2)	0.0001 (8)	0.004 (2)	0.0027 (6)
O(3)	0.042 (2)	0.1874 (6)	0.169 (2)	0.038 (4)	0.0018 (3)	0.018 (2)	0.0012 (8)	0.009 (2)	0.0000 (6)
O(4)	0.483 (2)	0.1230 (6)	0.100 (2)	0.018 (3)	0.0030 (8)	0.021 (2)	−0.0009 (8)	−0.003 (2)	0.0000 (6)
O(5)	−0.217 (2)	0.0850 (7)	−0.087 (2)	0.017 (3)	0.0043 (5)	0.027 (3)	−0.002 (1)	0.004 (2)	0.0021 (9)
N	−0.021 (2)	0.1137 (5)	−0.416 (1)	0.014 (2)	0.0015 (3)	0.012 (2)	−0.0002 (7)	0.002 (2)	0.0008 (5)
C(1)	0.192 (2)	0.0451 (9)	−0.076 (2)	0.020 (4)	0.0022 (4)	0.009 (2)	−0.002 (1)	0.003 (2)	−0.0007 (8)
C(2)	0.126 (2)	0.0652 (7)	0.172 (2)	0.015 (3)	0.0020 (4)	0.014 (3)	0.0000 (9)	0.005 (2)	−0.0011 (8)
C(3)	0.081 (2)	0.1540 (8)	0.104 (2)	0.022 (4)	0.0014 (4)	0.015 (3)	−0.000 (1)	0.005 (2)	0.0013 (8)
C(4)	0.351 (3)	0.1152 (7)	0.063 (2)	0.019 (4)	0.0015 (3)	0.015 (3)	−0.006 (1)	0.001 (3)	0.0007 (7)
C(5)	−0.083 (3)	0.0900 (8)	−0.053 (2)	0.022 (5)	0.0027 (5)	0.012 (3)	−0.002 (1)	0.006 (3)	0.0011 (8)
C(6)	0.089 (2)	0.2227 (6)	−0.261 (2)	0.025 (4)	0.0010 (3)	0.012 (2)	0.0007 (8)	−0.001 (2)	−0.0005 (6)
C(7)	0.367 (2)	0.1325 (6)	−0.365 (2)	0.012 (3)	0.0016 (4)	0.019 (3)	−0.0015 (8)	0.004 (2)	−0.0011 (7)
C(11)	−0.087 (2)	0.1391 (7)	−0.535 (2)	0.013 (3)	0.0016 (3)	0.010 (2)	0.0005 (9)	−0.001 (2)	0.0001 (7)
C(12)	−0.199 (2)	0.1200 (7)	−0.643 (2)	0.011 (3)	0.0018 (3)	0.013 (2)	0.0006 (8)	−0.002 (2)	−0.0003 (7)
C(13)	−0.246 (2)	0.0734 (8)	−0.627 (2)	0.016 (3)	0.0019 (4)	0.012 (2)	0.001 (1)	−0.001 (2)	0.0002 (8)
C(14)	−0.180 (2)	0.0470 (7)	−0.511 (2)	0.015 (3)	0.0016 (3)	0.017 (3)	0.000 (1)	0.003 (3)	−0.0003 (8)
C(15)	−0.069 (2)	0.0679 (7)	−0.405 (2)	0.014 (3)	0.0013 (3)	0.017 (3)	−0.0023 (8)	−0.004 (2)	−0.0018 (7)
C(61)	−0.089 (2)	0.2272 (7)	−0.242 (2)	0.017 (4)	0.0014 (3)	0.020 (3)	0.0022 (8)	0.001 (3)	−0.0000 (7)
C(62)	0.190 (3)	0.2469 (8)	−0.133 (2)	0.033 (5)	0.0023 (4)	0.011 (3)	−0.002 (1)	−0.005 (3)	−0.0021 (8)
C(63)	0.127 (3)	0.2497 (7)	−0.399 (2)	0.029 (4)	0.0014 (3)	0.013 (3)	−0.002 (1)	−0.000 (3)	0.0013 (7)
C(71)	0.331 (3)	0.145 (1)	−0.527 (2)	0.027 (4)	0.0032 (4)	0.006 (2)	−0.001 (1)	0.004 (2)	0.0006 (9)
C(72)	0.417 (3)	0.0814 (9)	−0.340 (2)	0.024 (4)	0.0022 (4)	0.020 (3)	−0.000 (1)	0.012 (3)	−0.0007 (9)
C(73)	0.505 (3)	0.166 (1)	−0.292 (3)	0.016 (4)	0.0032 (4)	0.027 (4)	−0.000 (1)	0.002 (3)	−0.001 (1)

[a] Figures in parentheses are estimated standard deviations in the last significant digit. [b] The temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The intensities of 2274 independent reflections were recorded in this way, of which 1618 had intensities greater than their estimated standard deviations, $\sigma(I)$, after Lorentz and polarization corrections were applied to the data. Here $\sigma(I)$ is calculated from the expression

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the scan count, R is the ratio of scan time to total background counting time, B is the total background count and p is a factor introduced to avoid overweighting strong reflections;[7] a value of 0.05 for p was used.

An absorption correction[8] was applied using Gaussian integration and transmission factors ranged from 0.587 to 0.831.

Structure Solution and Refinement. The structure was solved using conventional Patterson techniques; the positions of the metal atoms were determined from examination of the appropriate Harker line and section. Preliminary least-squares refinement of the positional and isotropic thermal parameters for the two metal atoms gave values for the agreement factors R_1 and R_2 of 0.220 and 0.237, respectively. All structure factor calculations and least-squares refinements were based on F and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The conventional R factor, R_1, and the weighted R factor, R_2, are defined as

$$R_1 = \frac{\Sigma\,||F_o| - |F_c||}{\Sigma\,|F_o|}$$

$$R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w\,|F_o|^2}\right]^{1/2}$$

The atomic scattering factors were taken from the tabulations of Cromer and Mann.[9] The effects of anomalous dispersion for Cr and Sn were allowed for with corrections made to F_c.[10]

Subsequent difference Fourier syntheses, followed by least-squares refinements revealed all of the nonhydrogen atoms. Least-squares refinement converged for the anisotropic model with values for R_1 and R_2 of 0.068 and 0.060, respectively. A final difference Fourier synthesis revealed no peaks which could be attributed to hydrogen atoms. As the majority of hydrogen atoms in this molecule were in methyl groups, no attempt was made to include these atoms in the model. Shifts in the last cycle of least-squares refinement were all significantly less than their estimated standard deviations. The error in an observation of unit weight is 1.33.

A listing of observed and calculated structure factor amplitudes for those data included in the refinement is given in Table I.[11] The final positional and thermal parameters are listed in Table II, and root-mean-square amplitudes of vibration are given in Table III.[11]

Results

The bonding distances and angles obtained after the final cycle of least-squares refinement are given in Tables IV and V, respectively. A view of the entire structure, showing the atom numbering scheme, is presented in Figure 1, while the bonding distances and angles around the tin atom are set out in a convenient form in Figure 2.

The crystal structure consists of discrete symmetry related units, $(t\text{-}C_4H_9)_2(C_5H_5N)SnCr(CO)_5$, packed with normal nonbonded contacts, none of which is shorter than 3.26 Å. The molecular unit possesses no crystallographically imposed symmetry.

Interest in the molecular dimensions of this compound

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(7) P. W. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(8) The following computer programs written for the IBM 360 were used; DATARED, a data reduction program by Frenz; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; JIMDAP, a version of Zalkin's FORDAP Fourier program modified by Ibers; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program; SADIAN, a program for calculating atomic distances and angles by Baur; RSCAN, a structure factor analysis program by Doedens; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

(9) "International Tables for X-ray Crystallography," Vol. IV, in preparation.

(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(11) Tables I and III will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4529. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

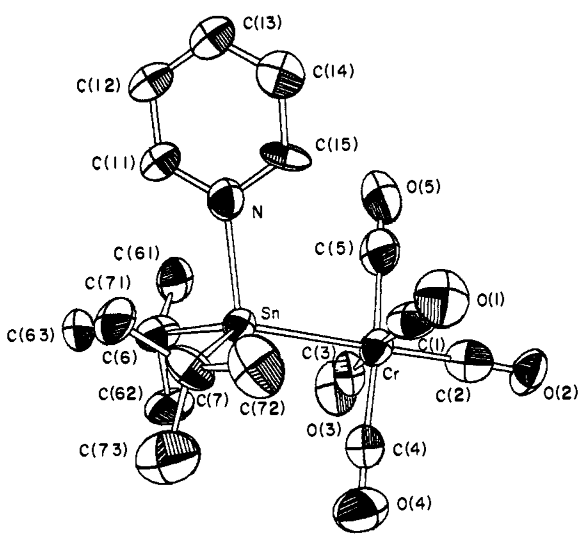

Figure 1. An ORTEP drawing of the molecular structure. Atoms are represented by their thermal ellipsoids drawn to enclose 50% of their electron density.

Table IV. Bond Distances (Å) for $Sn(C_4H_9)_2(NC_5H_5)Cr(CO)_5$

Sn–Cr	2.654 (3)	N–C(11)	1.37 (2)
		N–C(15)	1.36 (2)
Sn–N	2.29 (1)		
		C(11)–C(12)	1.40 (2)
Sn–C(6)	2.25 (2)	C(12)–C(13)	1.38 (2)
Sn–C(7)	2.24 (2)	C(13)–C(14)	1.37 (2)
		C(14)–C(15)	1.40 (2)
Cr–C(1)	1.82 (2)	C(1)–O(1)	1.19 (2)
Cr–C(2)	1.81 (2)	C(2)–O(2)	1.18 (2)
Cr–C(3)	1.84 (2)	C(3)–O(3)	1.18 (2)
Cr–C(4)	1.88 (2)	C(4)–O(4)	1.15 (2)
Cr–C(5)	1.89 (2)	C(5)–O(5)	1.15 (2)
C(6)–C(61)	1.54 (3)	C(7)–C(71)	1.53 (2)
C(6)–C(62)	1.54 (2)	C(7)–C(72)	1.51 (3)
C(6)–C(63)	1.53 (2)	C(7)–C(73)	1.58 (3)

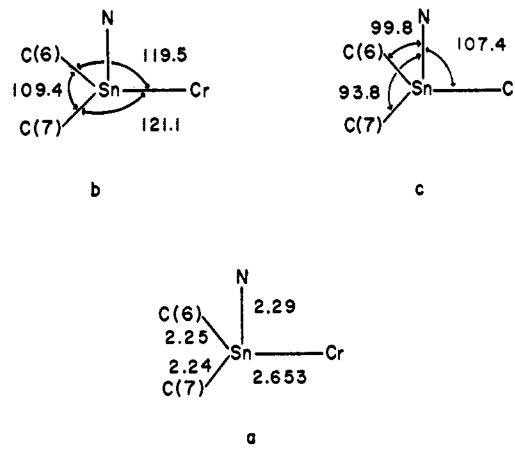

Figure 2. Distances (a) and angles (b, c) about the tin atom.

Table V. Bond Angles (deg) for $Sn(C_4H_9)_2(NC_5H_5)Cr(CO)_5$

Cr–Sn–N	107.8 (3)	N–Sn–C(6)	99.6 (6)
		N–Sn–C(7)	93.8 (5)
Cr–Sn–C(6)	119.6 (4)	C(6)–Sn–C(4)	109.5 (7)
Cr–Sn–C(7)	120.8 (5)		
		C(1)–Cr–C(3)	176.9 (8)
		C(4)–Cr–C(5)	175.3 (9)
Sn–N–C(11)	123 (1)		
Sn–N–C(15)	120 (1)	C(1)–Cr–C(2)	86.4 (8)
C(11)–N–C(15)	117 (1)	C(1)–Cr–C(4)	90.8 (8)
		C(1)–Cr–C(5)	92.1 (9)
Sn–Cr–C(2)	175.9 (6)	C(2)–Cr–C(3)	90.5 (8)
		C(2)–Cr–C(4)	92.5 (8)
Sn–Cr–C(1)	89.5 (6)	C(2)–Cr–C(5)	91.4 (8)
Sn–Cr–C(3)	93.6 (5)	C(3)–Cr–C(4)	88.8 (8)
Sn–Cr–C(4)	86.9 (5)	C(3)–Cr–C(5)	88.5 (9)
Sn–Cr–C(5)	89.5 (5)		
Cr–C(1)–O(1)	178 (1)	N–C(11)–C(12)	123 (2)
Cr–C(2)–O(2)	178 (1)	N–C(15)–C(14)	122 (2)
Cr–C(3)–O(3)	177 (1)		
Cr–C(4)–O(4)	177 (1)		
Cr–C(5)–O(5)	177 (1)	C(11)–C(12)–C(13)	118 (2)
		C(12)–C(13)–C(14)	120 (2)
Sn–C(6)–C(61)	109 (1)	C(61)–C(6)–C(62)	110 (1)
Sn–C(6)–C(62)	104 (1)	C(61)–C(6)–C(63)	110 (1)
Sn–C(6)–C(63)	118 (1)	C(62)–C(6)–C(63)	105 (1)
Sn–C(7)–C(71)	113 (1)	C(71)–C(7)–C(72)	113 (1)
Sn–C(7)–C(72)	107 (1)	C(71)–C(7)–C(73)	110 (1)
Sn–C(7)–C(73)	105 (1)	C(72)–C(7)–C(73)	108 (1)

was centered on the coordination sphere of the tin atom. The dimensions found, as shown in Figure 2, are significantly different from those found in most other organotin compounds coordinated to transition metals. The Sn–C distances are unusually long at 2.24 and 2.25 Å when compared to distances found in compounds such as $(CH_3)_3SnMn(CO)_5$[12] ($Sn\text{–}C_{av} = 2.13$ Å) and $(C_6H_5)_3SnMn(CO)_5$[13] ($Sn\text{–}C_{av} = 2.15$ Å). Some lengthening of the Sn–C bond might be expected on going from methyl to *tert*-butyl, but it seems unlikely to account for the total increase in length found for this compound. Whether this distance is representative for these stannylene complexes can only be determined by further structural studies on other members of this class of compounds. The length of the Sn–N bond at 2.29 Å appears to be normal when compared to such structures as *cis*-$SnCl_4 \cdot 2NCCH_3$[14] (Sn–N, 2.33 and 2.34 Å) and $[Me_2SnCl \cdot terpy][Me_2SnCl_3]$[15] (Sn–N, 2.29, 2.33, and 2.41 Å). The distance found in this structure is, if anything, a little shorter, but it would be unwise to draw any conclusions from the data now available.

The bonding angles around the tin atom, however, do provide some insight into the mode of bonding in this compound. The Cr–Sn–C angles (119 and 121°) and the C–Sn–C angle of 109° indicate that the p character of the Sn–C bonds has been increased only a small amount relative to a pure "carbenoid" type structure, not involving the donor ligand. This is reflected in the small deviations from planarity of the atoms C(6), C(7), Sn, and Cr. The Sn atom is only 0.44 Å above a plane defined by the three atoms Cr, C(6), and C(7).

Concluding Remarks. While this study reveals the precise structure of what is presumably a representative compound in the group prepared by Marks, this knowledge itself raises a further question. Would a truly three-connected germylene or stannylene molecule, $RR'M\text{–}Cr(CO)_5$, be obtainable if either of the R or R′ groups were an alkoxy, amino, or other group with a lone pair potentially available for dative π bonding to M? It must be remembered that *all* known carbenoid complexes have at least one such group on the carbenoid carbon atom, and structural and other physical data

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(12) R. F. Bryan, *J. Chem. Soc. A*, 696 (1968).

(13) H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967).

(14) M. Webster and H. E. Blayden, *J. Chem. Soc. A*, 2443 (1969).

(15) F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968).

show that π-electron density from these groups is critical to the stability of the compounds.[2b]

A second important implication of this study, in conjunction with the chemical studies of Marks, pertains to the rearrangement pathway for the $(OC)_3Co(GeR_2)_2Co(CO)_3$ type molecules. Adams and Cotton[3] examined two possible pathways in the case of the $(CH_3)_2$ Ge-bridged molecule: (1) polytopal rearrangements about each cobalt atom with continuous retention of the bridges, and (2) bridge opening to an intermediate (or transition state) having a dimethylgermylene, $(CH_3)_2Ge$, group on each cobalt atom, followed by reclosing of the bridges. They expressed a preference for the first of these, one reason for which was the lack of any precedent for dialkylgermylene metal moieties. Subsequently, Muetterties has expressed the opinion that pathway 2 is more probable.[16] While definitive evidence is still lacking (although efforts are being made in this laboratory by R. D. Adams to obtain such evidence), our present findings militate against pathway 2. It appears that terminal $R_2Ge{=}$ and $R_2Sn{=}$ ligands are not stable as such, but only when rendered four-coordinate by the intervention of a donor molecule L, such as THF or pyridine, to give $R_2Ge(L)$– and $R_2Sn(L)$– ligands.

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(16) E. L. Muetterties, *MTP Int. Rev. Sci., Inorg. Ser. 1*, **9**, 77 (1972).

Location of the Hydrogen Atoms in $H_3Mn_3(CO)_{12}$. A Crystal Structure Determination

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Abstract: Difference Fourier techniques have been successfully applied to locate the hydrogen atoms in the metal cluster complex $H_3Mn_3(CO)_{12}$. The hydrogen atom positions are most clearly revealed when only low-angle data ($0 < \sin\theta/\lambda < 0.33$ Å^{-1}) are used to calculate the difference maps. The hydrogen atom parameters were successfully refined by least-squares methods. The molecular structure of $H_3Mn_3(CO)_{12}$ consists of an equilateral array of manganese atoms, each with four terminal carbonyl groups. The hydrogen atoms lie in the equatorial Mn_3 plane in symmetrically bridging positions. They are displaced from the centers of the Mn–Mn bonds by about 0.7 Å and are coplanar with the Mn_3 plane by within ±0.2 Å. Average distances and angles are Mn–Mn, 3.111 (2) Å; Mn–H, 1.72 (3) Å; Mn–H–Mn, 131 (7)°; H–Mn–H, 108 (6)°. Crystallographic data: unit cell triclinic; space group $P\bar{1}$; $a = 8.22$ (1), $b = 14.86$ (2), $c = 8.99$ (1) Å; $\alpha = 105.2$ (1), $\beta = 118.5$ (1), $\gamma = 96.9$ (1)°; final R factor = 5.8% for 1537 reflections.

The location of hydrogen atoms in metal cluster complexes remains one of the more difficult tasks for the structural chemist today. The problems normally encountered in trying to find a hydrogen atom bonded to a metal atom are compounded when that hydrogen atom is simultaneously attached to two or more metal atoms, a situation which often exists in metal cluster hydrides. We wish to report here the structure determination of $H_3Mn_3(CO)_{12}$. This, we believe, is the first time that the locations of bridging hydrogen atoms in a metal cluster compound[2] have been definitively established.

$H_3Mn_3(CO)_{12}$ was first prepared by Kaesz and coworkers in 1964.[3] The method used was the treatment of $Mn_2(CO)_{10}$ with $NaBH_4$, followed by acidification. An improved synthesis was later developed by Lewis and coworkers in which concentrated aqueous KOH was used in place of $NaBH_4$.[4] In their original paper Kaesz and coworkers assigned to $H_3Mn_3(CO)_{12}$ a D_{3h} structure in which the H atoms occupied symmetrically bridging positions in the Mn_3 plane. This conclusion was reached primarily on the basis of the compound's infrared spectrum,[5] which was very similar to that of the known $Os_3(CO)_{12}$.[6] Subsequent investigations provided further support for the D_{3h} model: the presence of a single nmr signal at τ 24.0 indicated the equivalence of all H atoms in the molecule[7a] and mass spectral work confirmed the total number of H atoms to be three.[4,7b]

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(1) (a) New College; (b) University of Southern California.

(2) Metal cluster compounds are defined as "Groups of three or more metal atoms in which each is bound to all, or most, of the others." F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 656.

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