CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, BUCKNELL UNIVERSITY, LEWISBURG, PENNSYLVANIA 17837,
STATE UNIVERSITY OF NEW YORK AT ALBANY, ALBANY, NEW YORK 12203,
AND THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA 16802

Investigation of Some Tricarbonyl–Metal Complexes of Tin-Substituted Ligands by Nuclear Magnetic Resonance, Infrared, Laser-Raman, Tin-119m Mössbauer, and Mass Spectroscopies[1]

BY THOMAS P. POETH,[2a,c] P. G. HARRISON,[2b] THOMAS VEACH LONG, II,[2d]
BENNETT R. WILLEFORD,*[2c] AND J. J. ZUCKERMAN[2b]

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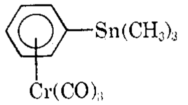
Several novel metal–carbonyl complexes of tin-containing arene ligands of the general formulas $(CH_3)_nSn(C_6H_5)_{4-n}\cdot mM(CO)_3$ (where $n = 2$ or 3, $m = 1$ or 2, and M = Cr or Mo), $[(CH_3)_3Sn]_2C_6H_4Cr(CO)_3$, and $(CH_3)_3SnCH_2C_6H_5Cr(CO)_3$ have been synthesized and studied by nmr, infrared, laser-Raman, ^{119m}Sn Mössbauer, and mass spectroscopies. Mössbauer spectra show no quadrupole splitting (QS) in any of the free ligands but small splittings in the complexes attributed to enhanced electric field gradients in the tin–phenyl bonds. Nmr spectra show the expected changes in chemical shifts on complex formation and only very small changes in $J(^{117,119}Sn–C–^1H)$ from those of the free ligands, consistent with four-coordination in solution where all the complexes are monomeric. Mass spectra indicate that all the complexes are monomeric in the gas phase; all save one show a prominent $SnCr^+$ peak. The infrared and laser-Raman spectra in the tin–methyl stretching region indicate that T_d local symmetry selection rules describe all complexes except $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$, where the ν_{sym} $(Sn–CH_3)$ band is absent in the infrared spectrum from the position in which it appears in the other compounds, indicating significant distortion from tetrahedral geometry. Of the complexes studied, the last also exhibits the largest ^{119m}Sn Mössbauer QS and nmr $J(^{117,119}Sn–C–^1H)$ values and the most intense $SnCr^+$ fragment in the mass spectrum.

There are reported in the literature a number of experimental observations on arene- and cyclopentadienyl–metal complexes which have been interpreted in terms of the overlap of filled metal orbitals with empty orbitals of substituent elements in the organic ligand. This idea was apparently first put forth by Richards and Hill,[3] who have suggested that α-ferrocenylcarbonium ions are stabilized by the direct overlap of iron orbitals with the p orbital of the α-carbon atom. Traylor[4] has presented an alternative explanation which involves the transmission of electronic effects from the metal through the complexed ring. The participation of the metal in the properties of α-metallocenylcarbonium ions has recently been reviewed.[5] Among other studies which have been interpreted in terms of these possible mechanisms are those which have been carried out on silyl-substituted ferrocenes,[6a] on (benzyl chloride)tricarbonylchromium,[6b] on π-complexed β-arylalkyl derivatives,[6c] and on *tert*-butylferrocenyl nitroxide.[6d]

A similar situation arises in the case of tin-substituted arenetricarbonyl–metal complexes where there is the possibility that the filled metal d orbitals may interact with the empty d orbitals of the tin atoms. Mössbauer spectroscopy offers a means of studying this possibility. Accordingly, a series of metal carbonyl complexes of tin-containing arene ligands (I–VI) was synthesized in an attempt to elucidate this possible interaction.



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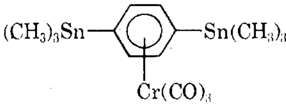

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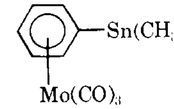

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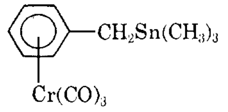

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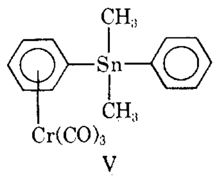

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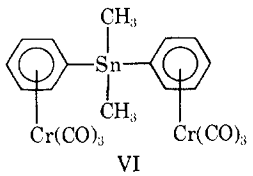

VI

Experimental Section

General Techniques.—Tin-119m Mössbauer spectra for the free ligands and the complexes were obtained on a cam-drive, constant-acceleration instrument previously described.[7] Our curve-fitting program is developed from a treatment of the least-squares solution of nonlinear equations (Taylor series expansion about estimated parameters) similar to that of Wentworth[8] and assumes that the curves are Lorentzian doublets with equal line widths. Removing the constraint on line widths does not significantly change the isomer shift (IS) or quadrupole splitting (QS) values. Mass spectra (MS) were obtained on an AEI MS-9

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[1] A preliminary account of this work was presented at the Fourth International Conference on Organometallic Chemistry, Bristol, England, July 1969. See P. G. Harrison, J. J. Zuckerman, T. V. Long, II, T. P. Poeth, and B. R. Willeford, *Inorg. Nucl. Chem. Lett.*, **6**, 627 (1970).

[2] (a) Undergraduate Research Participant, summer 1968. (b) State University of New York at Albany. (c) Bucknell University. (d) The Pennsylvania State University.

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instrument at an ionizing energy of 70 eV and a source temperature of 100°.

Infrared spectra were obtained for Nujol mulls, KBr pellets, or neat liquids on Perkin-Elmer Models 337 and 621 grating spectrometers. The carbonyl stretching region of the spectrum was also scanned for cyclohexane solutions of the complexes, and chloroform solutions of the complexes were examined in the 400–600-cm^{-1} region. Raman spectra of polycrystalline solids, liquids, and $CHCl_3$ solutions were measured with a modular instrument whose chief components are a Spex Model 1400-II monochromator spectrometer and a Spectra-Physics Model 112 He–Ne laser (exciting line at 6328 Å, 4 mW). Nmr spectra were obtained on a Varian A-60A instrument in $CDCl_3$ or CCl_4 solutions. Because of the proximity of the TMS signal to those of the Sn–CH_3 protons, residual $CHCl_3$ in the $CDCl_3$ was usually used as an internal standard (τ 2.73). In some cases, *p*-dioxane (τ 6.30 in $CHCl_3$, τ 6.40 in CCl_4) was added as an internal standard. Visible–ultraviolet spectra were recorded for cyclohexane or $CHCl_3$ solutions of the complexes in 1-cm cells on a Cary 14 spectrophotometer. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., M-H-W Laboratories, Garden City, Mich., and Alfred Bernhardt, Elbach, West Germany. Molecular weights were measured in benzene solutions on a Mechrolab Model 301A vapor pressure osmometer.

Compounds.—The complexes were synthesized by standard methods[9] using reagent grade or better materials and with great care to prevent contact with air or moisture. All recrystallizations and other work with solutions of the complexes were carried out under an atmosphere of prepurified nitrogen. Melting points are uncorrected.

Phenyltrimethyltin.—This ligand was prepared in 75% yield by the reaction of phenylmagnesium bromide and trimethyltin chloride in anhydrous diethyl ether;[10] bp 50–53° (0.2 Torr) (lit. bp 203–208° (760 Torr),[11] 76.5 (0.9 Torr)[12]). Ir (neat liquid): 2960 (m), 1425 (m), 1075 (m), 770 (s), 699 (s), 526 (s), 508 (s), and 442 cm^{-1} (s).

***p*-Bis(trimethylstannyl)benzene.**—This compound has been previously prepared by the reaction of sodium trimethyltin with *p*-dichlorobenzene.[13] The sample used in this study was prepared by the slow addition of 0.04 mol of $(CH_3)_3SnCl$ in 150 ml of anhydrous ether to 200 ml of a solution in ether of the di-Grignard reagent prepared from 0.02 mol of *p*-$C_6H_4Br_2$. The white crystals, after filtration, recrystallization from 95% ethanol, and twofold sublimation at 117° (10^{-3} Torr), melted at 122–124° (lit.[13] mp 122–124°). The yield was 20%. Ir (Nujol mull): 1093 (m), 1012 (m), 760 (s), 526 (s), 510 (s), and 466 cm^{-1} (s).

Dimethyldiphenyltin.—This compound has been previously prepared by the reaction of disodium dimethyltin with bromobenzene[11] and by the reaction of methylmagnesium bromide with diphenyltin dichloride.[14] The sample used for this study was prepared by the reaction of 0.15 mol of phenylmagnesium bromide with 0.05 mol of dimethyltin dichloride; bp 80–90° (0.05 Torr) (lit.[11] bp 127–140° (3 Torr)). Ir (neat liquid): 1300 (m), 1260 (m), 1190 (m), 1075 (s), 997 (m), 750 (s), 723 (s), 696 (s), 530 (s), 517 (s), and 446 cm^{-1} (s).

Benzyltrimethyltin.—This material was prepared both by the reaction of benzyl chloride with sodium trimethyltin[15] and also by the addition at 0° of 0.2 mol of benzyl chloride in 150 ml of tetrahydrofuran to a solution of lithium trimethyltin;[16] the mixture was stirred for 3 hr, and 100 ml of saturated aqueous ammonium chloride solution was added. The organic layer was separated, the aqueous layer was extracted several times with ether, and the combined organic layer and extracts were dried over anhydrous magnesium sulfate. After removal of the solvents, vacuum distillation gave the product in 50% yield; bp 35–36° (0.05 Torr) (lit. bp 215° dec (760 Torr)[15], 90° (9 Torr)[10]). Ir (neat liquid): 3020 (m), 2910 (m), 1595 (s), 1490 (s), 1455 (m), 1210 (s), 1096 (m), 752 (s), 694 (s), 525 (s), 507 (m), and 440 cm^{-1} (m). This compound has also been previously prepared by the reaction of trimethyltin bromide with benzylmagnesium bromide.[10]

Trimethylstannylbenzenetricarbonylchromium(0).—This complex was prepared by a method similar to that of Seyferth and Alleston.[12] *Anal.* Calcd for $C_{12}H_{14}CrO_3Sn$: C, 38.24; H, 3.74; Cr, 13.79; Sn, 31.49; mol wt 377. Found: C, 38.47; H, 3.74; Cr, 13.79; Sn, 30.79; mol wt 382 (osmometric), 377 (MS). Mp 77.5–79° (lit.[12] mp 77–77.5°). Ir (Nujol mull): 1965 (s), 1945 (s), 1895 (s), 1860 (m–s, br), 1290 (m), 1063 (m), 775 (s), 664 (s), 656 (s), 630 (s), 539 (s), 532 (s), 512 (m), and 480 cm^{-1} (m); ir (C_6H_{12}): 1975 (s) and 1905 cm^{-1} (s). Uv maxima (C_6H_{12}): 318 (ϵ 9.72 $\times$ 10^3) and 267 nm (ϵ 6.54 $\times$ 10^3).

Trimethylstannylbenzenetricarbonylmolybdenum(0).—Molybdenum hexacarbonyl (10.0 g, 38 mmol) and $(CH_3)_3SnC_6H_5$ (12.0 g, 50 mmol) were heated at reflux under N_2 for 1 hr, cooled, and filtered. The residue was sublimed at 76° and 10^{-3} Torr to remove unreacted $Mo(CO)_6$. Crude yield 75%. The residue was recrystallized three times from petroleum ether (bp 30–60°), yielding shiny yellow needles. The complex may also be purified by sublimation at 76° and 10^{-3} Torr, but the recovery is poor. This complex is very sensitive; care must be taken not to prolong the sublimation of the $Mo(CO)_6$ unduly, and storage of the purified crystals under nitrogen at 0° in the dark is advisable. *Anal.* Calcd for $C_{12}H_{14}MoO_3Sn$: C, 34.24; H, 3.35; Mo, 22.80; Sn, 28.20; mol wt 421. Found: C, 34.55; H, 3.52; Mo, 22.66; Sn, 28.32; mol wt 432 (osmometric), 421 (MS). Mp 103.5–105°. Ir (Nujol mull): 1970 (m), 1945 (s), 1900 (m), 1860 (s, br), 1290 (m), 1056 (m), 775 (s), 617 (s), 588 (s), 542 (s), 535 (s), 519 (m), 505 (s), and 455 cm^{-1} (m); ir (C_6H_{12}): 1980 (s) and 1905 cm^{-1} (s). Uv maximum (C_6H_{12}): 323 nm (ϵ 4.0 $\times$ 10^3). Cyclohexane solutions of this complex are very unstable; some decomposition was noted during uv measurements.

***p*-Bis(trimethylstannyl)benzenetricarbonylchromium(0).**—Chromium hexacarbonyl (0.4 g, 1.8 mmol), *p*-bis(trimethylstannyl)benzene (0.8 g, 2 mmol), and 10 ml of diglyme were gently refluxed for 2 hr, cooled, filtered, and chromatographed on a silica gel column (15 × 150 mm) with petroleum ether (bp 30–60°). The column effluent was evaporated to dryness under vacuum, and the residue was recrystallized three times from light petroleum ether, yielding light yellow crystals in 40% yield. The complex may also be purified by sublimation at 117° and 10^{-3} Torr. *Anal.* Calcd for $C_{15}H_{22}CrO_3Sn_2$: C, 33.38; H, 4.11; Cr, 9.63; Sn, 43.98; mol wt 540. Found: C, 33.28; H, 4.35; Cr, 9.55; Sn, 43.97; mol wt 550 (osmometric), 540 (MS). Mp 132–134°. Ir (Nujol mull): 1955 (s), 1895 (m), 1875 (m–s, sh), 1860 (s), 1313 (s), 777 (s), 661 (s), 628 (s), 532 (s), 514 (m), and 470 cm^{-1} (m); ir (C_6H_{12}): 1965 (s) and 1900 cm^{-1} (s). Uv maxima (C_6H_{12}): 321 (ϵ 1.00 $\times$ 10^4) and 270 nm (ϵ 6.62 $\times$ 10^3).

Dimethyldiphenyltintricarbonylchromium(0).—Chromium hexacarbonyl (4.0 g, 18 mmol), dimethyldiphenyltin (2.7 g, 9 mmol), and 10 ml of diglyme were refluxed for 5 hr, cooled, and filtered, and the filtrate was chromatographed on silica gel as described above. After removal of the solvents under vacuum, the yellow residue was repeatedly extracted with hot petroleum ether (bp 30–60°) until the extract was colorless. Removal of the extracting solvent gave a yellow residue which was recrystallized three times from petroleum ether. The yield of purified product was 20%. *Anal.* Calcd for $C_{17}H_{16}CrO_3Sn$: C, 46.51; H, 3.67; Cr, 11.84; Sn, 27.04; mol wt 439. Found: C, 46.70; H, 3.87; Cr, 11.84; Sn, 27.20; mol wt 449 (osmometric), 439 (MS). Mp 59.5–61°. Ir (Nujol mull): 1960 (s), 1900 (s), 1875 (m), 1860 (s), 1074 (m), 1060 (m), 725 (s), 698 (s), 664 (s),

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656 (s), 630 (s), 617 (s), 534 (s), 522 (m), 483 (m), and 443 cm^{-1} (m); ir (C_6H_{12}): 1975 (s), 1910 (s), 1880 cm^{-1} (w). Uv maxima (C_6H_{12}): 318 (ϵ 9.55 × 10^3) and 267 nm (ϵ 7.40 × 10^3); uv maxima ($CHCl_3$): 319 (ϵ 9.60 × 10^3) and 257 nm (inflection, ϵ 7.60 × 10^3).

Dimethyldiphenyltinbis(tricarbonylchromium(0)).—The residue from the petroleum ether extraction of dimethyldiphenyltintricarbonylchromium(0) was recrystallized four times from CCl_4, giving a light yellow solid in 15% yield. *Anal.* Calcd for $C_{20}H_{16}Cr_2O_6Sn$: C, 41.78; H, 2.80; Cr, 18.08, Sn, 20.64; mol wt 575. Found: C, 41.85; H, 2.94; Cr, 17.96; Sn, 20.28; mol wt 589 (osmometric), 575 (MS). Mp 146–148°. Ir (Nujol mull): 1980 (m), 1940 (s), 1880 (s), 1860 (s, br), 1292 (m), 1060 (m), 655 (s), 631 (s), 618 (m), 530 (s), and 476 cm^{-1} (m); ir (C_6H_{12}): 1975 (s), 1910 cm^{-1} (s). Uv maxima (C_6H_{12}): 318 (ϵ ~2 × 10^4) and 267 nm (ϵ ~1.6 × 10^4); uv maxima ($CHCl_3$) 318 (ϵ 2.11 × 10^4) and 258 nm (inflection, ϵ 1.61 × 10^4).

Trimethylbenzyltintricarbonylchromium(0).—Chromium hexacarbonyl (2.2 g, 10 mmol), trimethylbenzyltin (2.6 g, 10 mmol), and 10 ml of diglyme were refluxed for 30 hr, and cooled, filtered, chromatographed, and evaporated as described above. The residue was recrystallized from light petroleum ether and then sublimed three times at 130° and 10^{-3} Torr. The yield of purified product was 15%. *Anal.* Calcd for $C_{13}H_{16}CrO_3Sn$: C, 39.94; H, 4.13; Cr, 13.30; Sn, 30.36; mol wt 391. Found: C, 40.14; H, 4.25; Cr, 13.41; Sn, 30.15; mol wt 409 (osmometric), 391 (MS). Mp 146–148°. Ir (Nujol mull): 1970 (s), 1905 (m), 1875 (s), 1850 (s), 1208 (s), 1085 (s), 771 (s), 683 (m), 663 (s), 628 (s), 535 (s), 527 (s), and 510 cm^{-1} (m); ir (C_6H_{12}): 1975 (s) and 1905 cm^{-1} (s). Uv maxima (C_6H_{12}): 319 (ϵ 1.06 × 10^4) and 261 nm (ϵ 7.41 × 10^3).

Ethylbenzenetricarbonylchromium(0).—This compound is mentioned several times in the literature,[17] but its preparation and properties have not been described.[17a] Chromium hexacarbonyl (3.1 g, 14 mmol), ethylbenzene (10.6 g, 100 mmol), and 10 ml of diglyme were heated at reflux for 24 hr. The liquid was removed by vacuum distillation and the residue was recrystallized three times from hexane to give shiny yellow crystals in 40% yield. *Anal.* Calcd for $C_{11}H_{10}CrO_3$: C, 54.55; H, 4.16; Cr, 21.47; mol wt 242. Found: C, 54.27; H, 3.91; Cr, 22.11; mol wt 242 (MS). Mp 43–44.5°. Ir (Nujol mull): 1970 (s), 1950 (w), 1900 (s), 1158 (m), 817 (s), 688 (m), 664 (s), 632 (s), 536 (s), and 479 cm^{-1} (m); ir (C_6H_{12}) 1980 (s) and 1910 cm^{-1} (s). Uv maxima (C_6H_{12}): 317 (ϵ 8.42 × 10^3) and 258 nm (ϵ 6.15 × 10^3).

***tert*-Butylbenzenetricarbonylmolybdenum(0).**[17a]—Molybdenum hexacarbonyl (10.0 g, 38 mmol) and *tert*-butylbenzene (13.0 g, 100 mmol) were refluxed for 2.5 hr. The reaction must be watched carefully and stopped immediately at the first sign of decomposition to metallic molybdenum. After cooling and filtering, the unreacted $Mo(CO)_6$ was removed by sublimation at 76° and 10^{-3} Torr. The residue was recrystallized four times from petroleum ether (bp 60–115°); yield, 35%. The complex is very sensitive to heat and air. *Anal.* Calcd for $C_{13}H_{14}MoO_3$: C, 49.70; H, 4.49. Found: C, 49.37; H, 4.77. Mp (sealed tube under N_2), 109–111°. Ir (KBr disk): 1940 (s), 1850 (s), 880 (m), 798 (m), 616 (s), 588 (s), and 496 cm^{-1} (s).

Results and Discussion

The occupied orbitals of the group VI metals in these complexes are suitable with respect to energy, symmetry, and extent for overlap with the unoccupied 5d orbitals of the tin atoms. If such a direct interaction occurs to any appreciable extent, the coordination number of the tin is increased from 4 to 5. Such an increase in coordination number should result in changes in the isomer shift (IS) and quadrupole splitting (QS) in the Mössbauer spectrum, in the $J(^{117,119}Sn-C-^1H)$ values in the nmr spectrum, and in the $\nu(Sn-CH_3)$ in the infrared spectrum.

Mössbauer Spectra.—The results of the Mössbauer spectral work are summarized in Table I. Complex VI shows the largest QS value; its spectrum is shown in Figure 1. The IS for each of the free ligands is characteristic of four-coordination around the Sn atom. The value for p-$[(CH_3)_3Sn]_2C_6H_4$ shown in Table I is typical. None of the free ligands shows a discernible QS. The small QS observed for the complexes can arise from two causes: the population of tin 5d orbitals by electrons from the filled d orbitals of the group VI transition metal or an enhanced electric field gradient along the tin–phenyl σ bond. The former explanation involves (d → d)π bonding in an extention of arguments put forward by Greenwood, *et al.*,[18] based on the theory of Townes and Dailey.[19]

TABLE I

^{119m}Sn MÖSSBAUER SPECTRAL DATA[a]

Compd	IS (±0.06), mm/sec	QS (±0.06), mm/sec	QS/IS
p-$[(CH_3)_3Sn]_2C_6H_4$	1.67	0.00	. . .
$(CH_3)_3SnCH_2C_6H_5Cr(CO)_3$ (IV)	1.67	0.59	0.35
$C_6H_5(CH_3)_2SnC_6H_5Cr(CO)_3$ (V)	1.74	0.64	0.37
p-$[(CH_3)_3Sn]_2C_6H_4Cr(CO)_3$ (II)	1.69	0.72	0.43
$(CH_3)_3SnC_6H_5Cr(CO)_3$ (I)	1.67	0.72	0.43
$(CH_3)_3SnC_6H_5Mo(CO)_3$ (III)	1.43	0.84	0.59
$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$ (VI)	1.75	0.89	0.51

[a] Recorded at liquid nitrogen temperature *vs.* a $Ba^{119m}SnO_3$ source (New England Nuclear Corp.) held at ambient temperature.

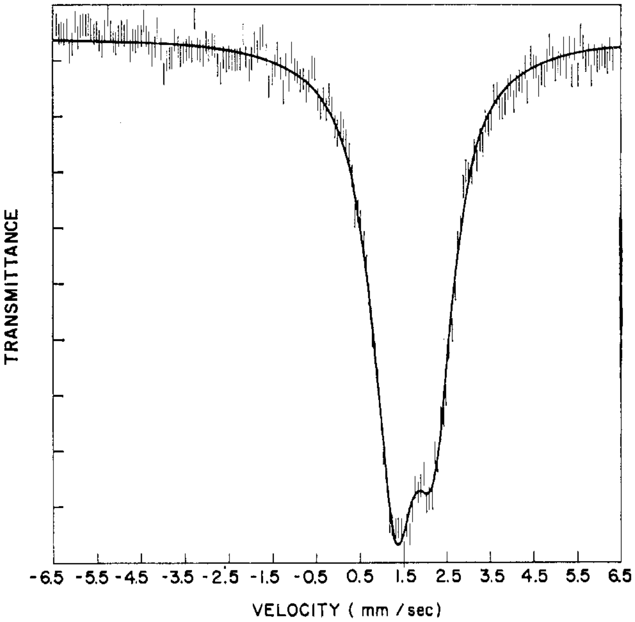

Figure 1.—The ^{119m}Sn Mössbauer spectrum of VI at 77°K *vs.* a $Ba^{119m}SnO_3$ source.

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[17a] NOTE ADDED IN PROOF.—Descriptions have recently appeared: W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. B.*, 1214 (1969); M. D. Rausch, G. A. Moser, E. J. Zaiko, and A. L. Lipman, *J. Organometal. Chem.*, **23**, 185 (1970).

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[19] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

Several investigators have now reported results which they interpret in terms of interactions in the σ framework,[20] and for the specific case of the tin–transition metal compounds containing a direct metal–metal σ bond, the Mössbauer, magnetic resonance, and structural data have been shown to fit an interpretation involving changes in the σ framework.[21] We feel that the data in Table I can also be best accommodated in the view that the small observed QS arises from σ interactions, and the decrease on going to the benzyl complex where the tin atom is separated from the phenyl group can be taken as corroboratory. The observation of $SnCr^+$ fragments discussed in the mass spectral section may be evidence to the contrary; however, if such interactions led to five-coordination about the tin atom with concomitant changes in the symmetry of the methyltin groups, these changes would be reflected in the Mössbauer QS/IS ratio. This ratio is in all the cases studied quite small. Herber, *et al.*, have suggested that QS/IS values <1.8 are associated with four-coordination at tin,[22] and subsequent work has supported the suggestion.[23]

Nmr Spectra.—The results of the analysis of the nmr spectra are given in Table II. Integration of the various signals gives proper area ratios for all compounds studied. In all cases the aromatic protons show an upfield shift of about 1.9–2.3 ppm on formation of the tricarbonylchromium complex from the ligand. This upfield shift is somewhat smaller for the molybdenum complex. In contrast, the methyl proton resonance is shifted only slightly on complexation; in most cases, the small shifts observed are to lower fields. For benzyltrimethyltin, the free ligand shows a methylene proton resonance at τ 7.60 which shifts upfield to τ 7.97 on formation of the tricarbonylchromium complex. A similar observation has been made for ethylbenzene in which a methylene proton shift from τ 7.30 to 7.58 on complexation is observed. That these changes in the chemical shifts of the methylene protons are not caused simply by the electron-withdrawing properties of the tricarbonylchromium group is indicated by a consideration of *p*-nitroethylbenzene in which the chemical shift of the methylene protons (τ 7.26) is not very different from that of ethylbenzene.

A consideration of the coupling constants of the ^{117}Sn and ^{119}Sn isotopic nuclei with the methyl protons shows a small increase of from 1.3 to 3.7 Hz on formation of the complexes from the free ligands. Although the formation of stable adducts between Lewis bases and tetraalkyltin compounds has not yet been observed, such adducts with trialkyltin halides result in an increase in J values of 9–10 Hz.[24] On this basis, it can be seen that any direct intramolecular interaction of the group VI metal with the tin atom must be quite weak. It should be noted that the largest increase in J values occurs with the $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$, which also shows the largest Mössbauer QS of the compounds studied. The monochromium complex, $C_6H_5(CH_3)_2SnC_6H_5Cr(CO)_3$, exhibits J values intermediate between those of $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$ and the free ligand.

TABLE II

NMR DATA

Compd	Chemical shifts, τ	J, Hz $^{117}Sn-C-^1H_3$	J, Hz $^{119}Sn-C-^1H_3$
$(CH_3)_3SnC_6H_5$[a]	2.75[i] (m), 2.6–3.0[j,a]	50.5	52.9
	9.72[i] (s), 9.75[j,a]	52.3[d]	54.6[d]
$(CH_3)_3SnC_6H_5Cr(CO)_3$[b]	4.72[i] (m), 4.8–5.0[j,a]	53.0	55.4
	9.60[i] (s), 9.68[j,a]		
$(CH_3)_3SnC_6H_5Mo(CO)_3$[b]	4.54,[i] 4.43[k] (m)	53.1	55.7
	9.67,[i] 9.62[k] (s)		
$(CH_3)_3CC_6H_5$[a,e]	2.80[i] (m)		
	8.68[i] (s)		
$(CH_3)_3CC_6H_5Cr(CO)_3$[a,e]	4.73[i] (m)		
	8.68[i] (s)		
$(CH_3)_3CC_6H_5Mo(CO)_3$[a]	4.42[k] (m)		
	8.72[k] (s)		
$(CH_3)_3SiC_6H_5$[a,e]	2.72[i] (m), 2.5–2.9[j,a]		
	9.78[i] (s), 9.74[j,a]		
$(CH_3)_3SiC_6H_5Cr(CO)_3$[a,e]	4.77[i] (m), 4.5–5.0[j,a]		
	9.70[i] (s), 9.69[j,a]		
p-$[(CH_3)_3Sn]_2C_6H_4$[c]	2.58[i] (m)	51.6	53.8
	9.64[i] (s)		
p-$[(CH_3)_3Sn]_2C_6H_4Cr(CO)_3$[c]	4.86[i] (m)	52.9	55.3
	9.60[i] (s)		
$(CH_3)_2Sn(C_6H_5)_2$[c]	2.49[i] (m)	52.2	54.4
	9.45[i] (s)	53.0[d]	55.4[d]
$(CH_3)_2(C_6H_5)SnC_6H_5Cr(CO)_3$[c]	2.61[i] (m)	53.8	56.1
	4.76[i] (m)		
	9.35[i] (s)		
$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$[b]	4.67[k] (m)	55.5	58.1
	9.55[k] (s)		
$(CH_3)_3SnCH_2C_6H_5$[c]	2.92,[k] 2.94[i] (m)	49.9	52.3
	7.60,[k] 7.65[i] (s)	59.4[f]	62.3[f]
	9.84,[k] 9.89[i] (s)		
$(CH_3)_3SnCH_2C_6H_5Cr(CO)_3$[c]	4.87[k] (m, br)	51.6	53.6
	7.97[k] (s)	54.5[f]	56.8[f]
	9.87[k] (s)		
$CH_3CH_2C_6H_5$[c]	2.76[i] (m), 2.77[g]		
	7.30[i] (q), 7.32[g]		
	8.68[i] (t), 8.75[g]		
$CH_3CH_2C_6H_5Cr(CO)_3$[c]	4.83[i] (m)		
	7.58[i] (q)		
	8.78[i] (t)		
p-$CH_3CH_2C_6H_4NO_2$[h]	1.97 (d)		
	2.70 (d)		
	7.26 (q)		
	8.73 (t)		

[a] TMS internal standard. [b] $CHCl_3$ internal standard. [c] *p*-Dioxane internal standard. [d] Reference 14. [e] G. A. Moser, M.S. Thesis, Bucknell University, 1968. [f] Methylene protons. [g] "High-Resolution NMR Spectra Catalogue," Vol. 2, Varian Associates, Palo Alto, Calif., spectrum No. 505; solvent, $CDCl_3$, reference, TMS. [h] "Nuclear Magnetic Resonance Spectra," Sadtler Research Laboratories, Inc., Philadelphia, Pa., spectrum no. 5040; solvent, CCl_4, reference, TMS. [i] CCl_4 solvent. [j] T. F. Jula and D. Seyferth, *Inorg. Chem.*, **7**, 1245 (1968). [k] $CDCl_3$ solvent.

The $J(^{117,119}Sn-C-^1H_2)$ values for benzyltrimethyltin decrease by 4.9 and 5.5 Hz, respectively, on complex formation. Although this is a larger change than for the other ligands in absolute magnitude, it is difficult to attribute this to direct interaction between the two metal atoms since the change is in the opposite

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(20) M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nucl. Chem.*, **29**, 1177 (1967); R. V. Parish and R. H. Platt, *Chem. Commun.*, 1118 (1968); *J. Chem. Soc. A*, 2145 (1969); T. Chivers and J. R. Sams, *Chem. Commun.*, 249 (1969).

(21) D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **90**, 6226 (1968).

(22) R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965).

(23) J. J. Zuckerman, "Mössbauer Effect Methodology," Vol. 3, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, p 15; *Advan. Organometal. Chem.*, **9**, 21 (1971).

(24) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964).

TABLE

MASS SPECTRA: FRAGMENT ASSIGNMENTS[a] AND

m/e	p-$[(CH_3)_3Sn]_2C_6H_4$	p-$[(CH_3)_3Sn]_2C_6H_4Cr(CO)_3$ (II)	*m/e*	$(CH_3)_3SnCH_2C_6H_5$	$(CH_3)_3SnCH_2C_6H_5Cr(CO)_3$ (IV)
540		$[(CH_3)_3Sn]_2C_6H_4(CO)_3^+$ (24.0)			
525		$(CH_3)_2SnC_6H_4Sn(CH_3)_3Cr(CO)_3^+$ (5.3)			
484		$(CH_3)_3SnC_6H_4Sn(CH_3)_3Cr(CO)^+$ (44.0)			
456		$(CH_3)_3SnC_6H_4Sn(CH_3)_3Cr^+$ (100)			
441		$(CH_3)_2SnC_6H_4Sn(CH_3)_3Cr^+$ (2.0)			
426		$(CH_3)_2SnC_6H_4Sn(CH_3)_2Cr^+$ (5.3)			
410		$(CH_3)SnC_6H_4Sn(CH_2)(CH_3)Cr^+$ (3.3)			
404	$(CH_3)_3SnC_6H_4Sn(CH_3)_3^+$ (8.1)				
389	$(CH_3)_3SnC_6H_4Sn(CH_3)_2^+$ (100)	$(CH_3)_3SnC_6H_4Sn(CH_3)_2^+$ (26.0)	391		$(CH_3)_3SnCH_2C_6H_5Cr(CO)_3^+$ (27.2)
379		$SnC_6H_4SnCHCr^+$ (10.7)	376		$(CH_3)_2SnCH_2C_6H_5Cr(CO)_3^+$ (2.7)
365		$SnC_6H_3SnCr^+$ (12.0)			
359	$(CH_3)_2SnC_6H_4SnCH_3^+$ (13.3)	$(CH_3)_2SnC_6H_4SnCH_3^+$ (10.0)			
344	$CH_3SnC_6H_4SnCH_3^+$ (14.7)	$CH_3SnC_6H_4SnCH_3^+$ and $(Sn_2C_4H_6)Cr^+$ (3.3)			
329	$CH_3SnC_6H_4Sn^+$ (10.5)	$CH_3SnC_6H_4Sn^+$ (8.0)	335		$(CH_3)_3SnCH_2C_6H_5Cr(CO)^+$ (17.7)
314	$SnC_6H_4Sn^+$ (6.0)	$SnC_6H_4Sn^+$ (6.0)	320		$(CH_3)_2SnCH_2C_6H_5Cr(CO)^+$ (4.5)
			307		$(CH_3)_3SnCH_2C_6H_5Cr^+$ (100)
303		$SnCHSnCr^+$ (3.3)			
290		Sn_2Cr^+ (4.0)			
			292		$(CH_3)_2SnCH_2C_6H_5Cr^+$ (4.1)
276		$(CH_3)(CH_2)SnC_6H_4Cr^+$ (7.4)	276		$(CH_2)SnCH_2C_6H_5Cr^+$ (21.4)
			263		$HSnCH_2C_6H_5Cr^+$ (9.1)
261		$CH_2SnC_6H_4Cr^+$ (7.4)	255	$(CH_3)_3SnCH_2C_6H_5^+$ (12.5)	
247		$SnC_6H_4Cr^+$ (14.0)			
225	$(CH_3)_2SnC_6H_4^+$ (4.9)		240	$(CH_3)_2SnCH_2C_6H_5^+$ (14.2)	$(CH_3)_2SnCH_2C_6H_5^+$ (2.7)
224		$CH_2SnC_3H_3Cr^+$ (12.0)	224	$CH_3SnCH_2C_6H_4^+$ (8.3)	
			215		$[(CH_3)_2SnCH_2]Cr^+$ (2.7)
210		$SnC_3H_3Cr^+$ (13.3)	210	$SnCH_2C_6H_5^+$ (7.5)	$SnCH_2C_6H_5^+$ (5.9)
			201		$(CH_3)_2SnCr^+$ (10.9)
196		$SnC_6H_5^+$ (7.4)	196	$SnC_6H_5^+$ (8.3)	
195	$SnC_6H_4^+$ (5.5)				
187	$(CH_3)_2SnC_6H_4Sn(CH_3)_2^{2+}$ (9.8)				
			185		CH_2SnCr^+ (5.9)
172	$CH_3SnC_6H_4SnCH_3^{2+}$ (4.9)				
171		$SnCr^+$ (4.7)	171		$SnCr^+$ (3.6)
164	$(CH_3)_3Sn^+$ (8.8)	$(CH_3)_3Sn^+$ (6.6)	164	$(CH_3)_3Sn^+$ (100)	$(CH_3)_3Sn^+$ (6.4)
149	$(CH_3)_2Sn^+$ (5.5)				
134	CH_3Sn^+ (18.2)	CH_3Sn^+ (10.0)	134	CH_3Sn^+ (20.8)	CH_3Sn^+ (5.0)
119	Sn^+ (11.5)	Sn^+ (6.6)	119	Sn^+ (10.0)	Sn^+ (2.7)

[a] Relative to ^{119}Sn, ^{52}Cr, and ^{96}Mo. [b] Because of the complexity and wide mass-distribution of the polyisotopic Sn–Mo-bearing

direction to that observed in the methyltin protons on complex formation by the other ligands. Also, the QS in the Mössbauer spectrum is the smallest of all complexes studied. Dreiding models show that by rotation about the carbon–phenyl bond, the tin atom can be directed either toward or away from the side of the phenyl ring which holds the tricarbonylchromium group. If the solid-state situation is such that the tin and the tricarbonylchromium group are on the same side of the phenyl ring, and if this situation arises because of metal–metal interactions, then the QS should be enhanced. Free rotation in solution may account for the observed changes in the coupling constants of the methylene protons.

Ultraviolet Spectra.—The absorption spectra of the complexes were measured in the 220–800-nm region (see data in Experimental Section). All show bands at 317–323 and 258–270 nm in addition to an exceptionally strong charge-transfer band just below 220 nm. The two bands at ~320 and ~265 nm show no characteristic differences in either position or intensity from those observed for tricarbonylchromium complex of other ligands.[25]

Mass Spectra.—The prominent peaks observed in the mass spectra of these complexes are given in Table III. Tin-bearing fragment ions are easily identified because of the distinctive polyisotopic distribution for that element. No peaks of *m/e* greater than the molecular weight are observed; this is consistent with the monomeric nature of the molecules in solution. In all the chromium complexes save one (complex VI), the most abundant peak was the one corresponding to loss of three CO groups; for VI the most abundant peak corresponds to the loss of three CO groups and a $Cr(CO)_3$ moiety. For III, the most abundant fragment has lost $Mo(CO)_3$ plus one methyl group from tin. In all the chromium complexes save one (complex V) a relatively strong (4–10%) peak at *m/e* 171 can be assigned to $SnCr^+$. Even-electron ions such as $(CH_3)_3Sn^+$ and CH_3Sn^+ tend to be abundant, and loss of C_6H_6 is seen in complexes V and VI [$(C_6H_5)_2SnCr^+ \rightarrow SnC_6H_4Cr^+$] as has been observed before in studies of organotin compounds in the mass spectrometer.[26] Complex II fragments to give both $SnCrSn^+$ and $SnCr^+$ ions in 4 and 4.7% relative abundance. This fragmentation of the organic part of the molecules to leave the $SnCr^+$ and $SnCrSn^+$ fragments may be interpreted to support the idea that under the dilute, gas-phase, ionic conditions which prevail in the mass

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(25) (a) R. Ecoli and A. Mangini, *Ric. Sci.*, **28**, 2135 (1958); *Chem. Abstr.*, **53**, 10947*g* (1959); (b) F. Calderazzo, R. Ecoli, and A. Mangini, *ibid.*, **29**, 2615 (1959); *Chem. Abstr.*, **54**, 14929*e* (1960); (c) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962); (d) G. A. Moser, M.S. Thesis, Bucknell University, 1968.

(26) D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. A*, 1759 (1967).

III

RELATIVE ABUNDANCES (MOST INTENSE PEAK = 100)

m/e	$(CH_3)_3SnC_6H_5Cr(CO)_3$ (I)	$(CH_3)_3SnC_6H_5Mo(CO)_3$ (III)[b]	*m/e*	$(CH_3)_2C_6H_5SnC_6H_5Cr(CO)_3$ (V)	$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$ (VI)
			575		$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2^+$ (16.1)
			489		$(OC)CrC_6H_5SnC_6H_5Cr(CO)_3^+$ (21.5)
			461		$(OC)CrC_6H_5SnC_6H_5Cr(CO)_2^+$ (21.5)
			439	$(CH_3)_2C_6H_5SnC_6H_5Cr(CO)_3^+$ (15.2)	
421		$(CH_3)_3SnC_6H_5Mo(CO)_3^+$ (33)	424	$(CH_3)C_6H_5SnC_6H_5Cr(CO)_3^+$ (1.0)	
406		$(CH_3)_2SnC_6H_5Mo(CO)_3^+$ (<5)	407		$(CH_3)_2Sn[C_6H_5Cr]_2^+$ (31.2)
393		$(CH_3)_3SnC_6H_5Mo(CO)_2^+$ (13)			
378		$(CH_3)_2SnC_6H_5Mo(CO)_2^+$ (35)			
377	$(CH_3)_3SnC_6H_5Cr(CO)_3^+$ (30.0)[c]				
365		$(CH_3)_3SnC_6H_5MoCO^+$ (12)			
362	$(CH_3)_2SnC_6H_5Cr(CO)_3^+$ (3.0)[c]		355	$(CH_3)_2C_6H_5SnC_6H_5Cr^+$ (100)	$(CH_3)_2C_6H_5SnC_6H_5Cr^+$ (100)
337		$(CH_3)_3SnC_6H_5Mo^+$ (50)	340	$CH_3C_6H_5SnC_6H_5Cr^+$ (1.0)	
334	$(CH_3)_2SnC_6H_5Cr(CO)_2^+$ (1.0)[c]				
322		$(CH_3)_2SnC_6H_5Mo^+$ (40)	325	$C_6H_5SnC_6H_5Cr^+$ (13.5)	$C_6H_5SnC_6H_5Cr^+$ (25.9)
321	$(CH_3)_3SnC_6H_5Cr(CO)^+$ (36.6)[c]				
307		$CH_3SnC_6H_5Mo^+$ (5)			
306	$(CH_3)_2SnC_6H_5Cr(CO)^+$ (4.7)				
293	$(CH_3)_3SnC_6H_5Cr^+$ (100)[c]		288	$(CH_3)Sn(C_6H_5)_2^+$ (58.0)	$(CH_3)Sn(C_6H_5)_2^+$ (8.6)
292		$SnC_6H_5Mo^+$ (12)			
278	$(CH_3)_2SnC_6H_5Cr^+$ (2.3)[c]				
263	$CH_3SnC_6H_5Cr^+$ (13.3)[c]				
248	$SnC_6H_5Cr^+$ (11.3)[c]				
			247	$SnC_6H_4Cr^+$ (9.4)	$SnC_6H_4Cr^+$ (22.6)
229		$C_6H_5Mo(CO)_2^+$ (17)			
226	$(CH_3)_2SnC_6H_5^+$ (33.3)	$(CH_3)_2SnC_6H_5^+$ (100)	226	$(CH_3)_2SnC_6H_5^+$ (6.8)	
210	$CH_2SnC_6H_5^+$ (12.3)	$CH_2SnC_6H_5^+$ (25)	210	$CH_2SnC_6H_5^+$ (11.0)	$CH_2SnC_6H_5^+$ (10.5)
196	$SnC_6H_5^+$ (33.3)	$SnC_6H_5^+$ (40)	196	$SnC_6H_5^+$ (31.3)	$SnC_6H_5^+$ (52.8)
185	CH_2SnCr^+ (7.3)				
171	$SnCr^+$ (6.0)		171		$SnCr^+$ (10.0)
164		$(CH_3)_3Sn^+$ (11)			
149		$(CH_3)_2Sn^+$ (11)	149	$(CH_3)_2Sn^+$ (5.7)	
134		CH_3Sn^+ (17)	134	CH_3Sn^+ (5.7)	CH_3Sn^+ (5.6)
119	Sn^+ (4.7)	Sn^+ (24)	119	Sn^+ (18.7)	Sn^+ (13.3)

fragments, intensity comparisons are less precise in this case. [c] Analogous fragment of III 44 mass units greater.

TABLE IV

VIBRATIONAL SPECTRA IN THE 500–550-CM^{-1} REGION[a]

Compd	Type of spectrum	ν_{asym}(Sn–CH$_3$)	ν_{sym}(Sn–CH$_3$)	δ(M–CO)
$(CH_3)_2Sn(C_6H_5)_2$[b]	Ir	530 s	517 m	
	Raman	534 w, sh, dp	521 vs, p	
$(CH_3)_2C_6H_5SnC_6H_5Cr(CO)_3$	Ir	534 s,[c,f] 536[d,f]	522 m[c,d]	
	Raman[e]	536 m[f]	522 vs	
$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$	Ir	530 s,[c,g] 534 [d]	. . .	544 w, sh[c]
	Raman[e]	. . .	530 s, 531 p[d]	545 w, sh
$(CH_3)_3SnC_6H_5$[b]	Ir	526 s	508 m	
$(CH_3)_3SnC_6H_5Cr(CO)_3$	Ir	532 s,[c] 536[d]	512 m,[c] 514[d]	539 s[c]
$(CH_3)_3SnC_6H_5Mo(CO)_3$	Ir	535 s,[c] 536[d]	519 m,[c] 508[d]	542 s[c]
p-$[(CH_3)_3Sn]C_6H_4$	Ir	526 s,[c] 530[d]	510 m,[c] 514[d]	
p-$[(CH_3)_3Sn]C_6H_4Cr(CO)_3$	Ir	532 s,[c] 536[d]	514 m[c,d]	537 w, sh[c]
$(CH_3)_3SnCH_2C_6H_5$[b]	Ir	525 s	507 m	
$(CH_3)_3SnCH_2C_6H_5Cr(CO)_3$	Ir	527 s,[c] 532[d]	510 m[c,d]	535 s[c]

[a] All frequencies in cm^{-1}. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; p, polarized; dp, depolarized. [b] Neat liquid. [c] Nujol mull. [d] CHCl$_3$ solution. [e] Polycrystalline solid. [f] Also δ(Cr–CO). [g] Possibly also δ(Cr–CO).

spectrometer, some sort of interaction between the two metals is present.

Infrared and Laser-Raman Spectra.—The infrared and Raman spectra of complexes V and VI above 550 cm^{-1} are in excellent agreement with the recently published spectra of π-$C_6H_6Cr(CO)_3$,[27] except for the appearance of additional bands that are assignable as CH$_3$ internal modes, and these spectra are not tabulated here.[28] The carbonyl stretching regions of the solid-state spectra evidence factor group effects, which have been previously noted for similar compounds,[27,29] but all absorptions occur in the frequency range expected for arenemetal carbonyls. No bands occur in the bridging carbonyl region. This is also true for the other complexes studied.

The laser-Raman and infrared spectra in the range 500-550 cm^{-1} of the complexes studied are presented in Table IV; the infrared spectra of V, VI, and the cor-

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[27] D. M. Adams and A. Squire, *J. Chem. Soc. A*, 814 (1970).

[28] The complete spectra (4000–200 cm^{-1}) are available on request from T. V. L., II.

[29] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc. A*, 2077, 2224 (1969).

responding ligand are shown in Figure 2. Assignments in this spectral range are complicated because modes that are approximately describable as Cr–CO bends and as Sn–CH_3 stretches both occur. However, in the spectra of dimethyldiphenyltin(IV), only tin–methyl stretches will appear, and a strong, polarized Raman shift is measured at 521 cm^{-1} with a weak depolarized shoulder at 534 cm^{-1}. These fundamentals also are measured in the infrared, with an inversion in intensity, and they are assigned as the symmetric and asymmetric Sn–CH_3 stretches, respectively. A similar modal pattern is found for $(CH_3)_2C_6H_5SnC_6H_5Cr(CO)_3$, but the intense Cr–CO bending fundamental that occurs at 533 cm^{-1} in the infrared spectrum of π-$C_6H_6Cr(CO)_3$[27] may also contribute to the absorption at that frequency. Weak Raman lines attributable to Cr–CO bends occur at 543 and 537 cm^{-1} in the spectrum of π-$C_6H_6Cr(CO)_3$;[27] these appear only weakly in the spectra reported here and are depolarized. The infrared spectra of other methyl-containing complexes exhibit a strong asymmetric tin–methyl stretch at *ca.* 530 cm^{-1} and a weaker symmetric stretch 16–20 cm^{-1} lower in frequency, with the exception of $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$, for which a discrete symmetric stretching mode cannot be distinguished in absorption (Figure 2). A strong, polarized Raman mode is measured at 530 cm^{-1} for the latter compound, which indicates that the asymmetric and symmetric Sn–CH_3 stretching fundamentals have apparently become degenerate. Such a change is anomalous in view of the invariant pattern in this spectral region for all the other closely related molecules studied. Although the behavior could be attributed to purely electronic effects without structural modification, a more plausible explanation would invoke a distortion of the Sn–C_4 tetrahedron. Complex VI exhibits an identical spectrum in solution, indicating that structural changes, if such occur, are of intramolecular origin. A reasonable possibility is a steric flattening of the tetrahedron to approach a trans-planar structure. The observed degeneracy of course precludes determination of whether the fundamentals can be described by centrosymmetric selection rules.

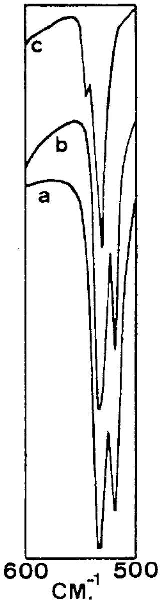

Figure 2.—Infrared absorption spectra in the tin–methyl stretching region for $(CH_3)_2Sn(C_6H_5)_2$ (curve a), $(CH_3)_2C_6H_5SnC_6H_5Cr(CO)_3$ (V, curve b), and $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$ (VI, curve c).

Summary

The evidence obtained from ir, nmr, and Mössbauer spectroscopies indicates that any direct interaction between the tin atom and the transition metal in the complexes studied must be weak.[30] The mass spectra may indicate some Sn–Cr interactions in the fragment ions under the dilute, gas-phase conditions found in the mass spectrometer. The infrared and laser-Raman spectra indicate that, for complex VI, distortion from a tetrahedral arrangement of the four groups about the tin must be considered, possibly a sterically induced flattening. Such an arrangement could lead to efficient packing of the molecules in the crystal lattice. However, to ascribe any structural modification to crystalline forces seems unjustified in view of the apparent persistence of the structure in solution. Intramolecular "end bridging" for a carbonyl group to place the tin atom in a *trans*-$Sn(CH_3)_2(C_6H_5)_2O_2$ octahedral environment seems to be ruled out by the Mössbauer data which indicate four-coordination, the unshifted ν(CO) frequencies and the nmr J(Sn–C–H_3) values consistent with four-coordination, while intermolecular bridging is inconsistent with the monomeric nature of the molecules in solution and in the gas phase. Extensive π-electron delocalization may be possible in this arrangement, but the ultraviolet spectrum of VI shows λ_{max} values unshifted from those of the other complexes studied, though ϵ is somewhat larger. A single-crystal X-ray study of VI is now underway; it is hoped that this will provide a definite answer to these unresolved questions.

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(30) NOTE ADDED IN PROOF.—We have recently measured the tin-119 nmr chemical shifts of the complexes reported here by ^1H–^{119}Sn double-resonance techniques. Complexation in I–III and V–VI decreases the tin shift by *ca.* 30 ppm per $Cr(CO)_3$ group, while in IV, where tin is insulated by a methylene group, the effect of complexation is only −4 ppm. Population of the tin 5d orbitals would be expected to raise, not lower, the shift: P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, submitted for publication.