encing chemistry of these complexes seems to be the most informative and internally consistent method of categorizing these and related compounds.

The previous EHMO description of $M(HC\equiv CH)_2(dtc)_2$[1] utilized a M—C(alkyne) distance of 2.03 Å and resulted in a calculated barrier to rotation of 40.3 kcal mol^{-1}. The discrepancy between experimental (ΔG^* of 15.3 kcal mol^{-1}) and calculated energy barriers for $Mo(EtC_2Et)_2(S_2CNMe_2)_2$ was much larger than we had found in $M(CO)(HC\equiv CH)(dtc)_2$ and $M(O)(HC\equiv CH)(dtc)_2$ studies. Although 2.03 Å was the M–C distance reported for $W(CO)(HC\equiv CH)(detc)_2$,[8] structural data for $(\pi\text{-}C_5H_5)Nb(CO)(PhC\equiv CPh)_2$[17] and $(\pi\text{-}C_5H_5)WCl(CF_3C\equiv CCF_3)_2$[19] suggested that a distance of 2.17 Å would be more likely to characterize the bis(alkyne) derivative. The results of such a calculation produced a barrier of 13.2 kcal mol^{-1} for rotation of one

alkyne, much nearer the observed value. The variation in calculated barrier as a function of the M–C distance ($\sim$2.0 kcal mol^{-1}/0.01 Å) is consistent with a strong dependence of the metal–alkyne π-acceptor and π-donor orbital contributions on nuclear separation.

Tricarbonylchromium Complexes of (CH$_3$)$_2$EAr$_2$ Ligands (E = C, Si, Ge, Sn, and Pb; Ar = C$_6$H$_5$, CH$_2$C$_6$H$_5$, and *p*-C$_6$H$_4$CH$_3$)

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Mono- and bis(arene)tricarbonylchromium complexes of (CH$_3$)$_2$E(C$_6$H$_5$)$_2$[Cr(CO)$_3$]$_x$, where E = C, Si, Ge, Sn, and Pb, and (CH$_3$)$_2$Sn(CH$_2$C$_6$H$_5$)$_2$[Cr(CO)$_3$]$_x$ and (CH$_3$)$_2$Sn(C$_6$H$_5$CH$_3$-*p*)$_2$[Cr(CO)$_3$]$_x$, where *x* = 1 (mono) and 2 (bis), are prepared from Cr(CO)$_6$ in diglyme–tetrahydrofuran (THF) solutions or from Cr(CO)$_3$(NH$_3$)$_3$ in refluxing dioxane. Extraction of the mixture of mono and bis complexes with hot hexane or petroleum ether gives the mono complexes, and subsequent recrystallization of the residue from hot benzene gives the bis. Alternatively, the bis complex can be obtained directly from column chromatography on silica gel after sublimation to remove the mono complex. Proton NMR data are recorded for all 15 fourth group homologues, including the tin-119 and lead-207 coupling constants |$^2J(^{119}Sn-C^{-1}H)$| and |$^2J(^{207}Pb-C^{-1}H)$|, respectively, which for the tin derivatives are consistent with monomeric species in solution containing four-coordinated tin atoms. Tin-119m Mössbauer isomer shift (IS) and quadrupole splitting (QS) values also reflect tin(IV) atoms in a four-coordinated environment. Infrared and Raman data are used to assign ν[E(CH$_3$)$_2$] modes in the E = C, Si, Ge, Sn, and Pb ligands and the mono and bis complexes. Intramolecular contact between the oxygen atoms of the tricarbonylchromium moiety and the element-methyl groups is offered as an explanation for the decrease in the intensity of the infrared ν_{sym}(E–CH$_3$) absorption and the increase in the intensity of the corresponding Raman absorption on successive tricarbonylchromium substitution.

A decade ago we synthesized a series of tricarbonylmetal complexes of tin-substituted arene ligands of the general formulas (CH$_3$)$_n$Sn(C$_6$H$_5$)$_{4-n}$[M(CO)$_3$]$_x$, where *n* = 2 or 3 and M = Cr or Mo, [(CH$_3$)$_3$Sn]$_2$C$_6$H$_4$[Cr(CO)$_3$]$_x$, and (CH$_3$)$_3$SnCH$_2$C$_6$H$_5$[Cr(CO)$_3$]$_x$, where *x* = 2 (bis) or 1 (mono), and studied the products by NMR, infrared, laser-Raman, tin-119m Mössbauer, and mass spectroscopies. Mössbauer spectra showed no quadrupole splitting (QS) in any of the free ligands, but small splittings in the complexes which we attributed to enhanced electric field gradients in the tin–phenyl bonds. NMR spectra showed a displacement of chemical shifts of ca. 2 ppm of the aromatic protons in the expected direction on complex formation and only very small differences (1.3–3.7 Hz) in the |$^2J(^{119}Sn-C^{-1}H)$| from the free ligands, consistent with four-coordination at tin in solution where all the complexes are monomeric. Mass spectra indicated that the complexes

are monomeric in the gas phase as well. No drastic frequency shifts occurred in the ν(Sn–C) modes on complex formation.[2]

The spectral properties of the bis(tricarbonylchromium) complex (CH$_3$)$_2$Sn[C$_6$H$_5$Cr(CO)$_3$]$_2$ were remarkable, however. This material exhibited the most intense *m/e* 171 (SnCr$^+$) peak in the mass spectrum, the largest increase in |$^2J(^{119}Sn-C^{-1}H)$| on complexation and the largest value in absolute magnitude as well, and the largest Mössbauer QS value. Most striking, however, were the vibrational spectra in the ν(Sn–C) region. In the infrared spectrum a discrete ν_{sym}(Sn–C) could not be distinguished from the ν_{asym}(Sn–C) band, and in the Raman only a strong, po-

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(2) Poeth, T. P.; Harrison, P. G.; Long, T. V., II; Willeford, B. R.; Zuckerman, J. J. *Inorg. Chem.* **1971**, *10*, 522.

Chart I

Compounds Studied

E = C, Si, Ge, Pb
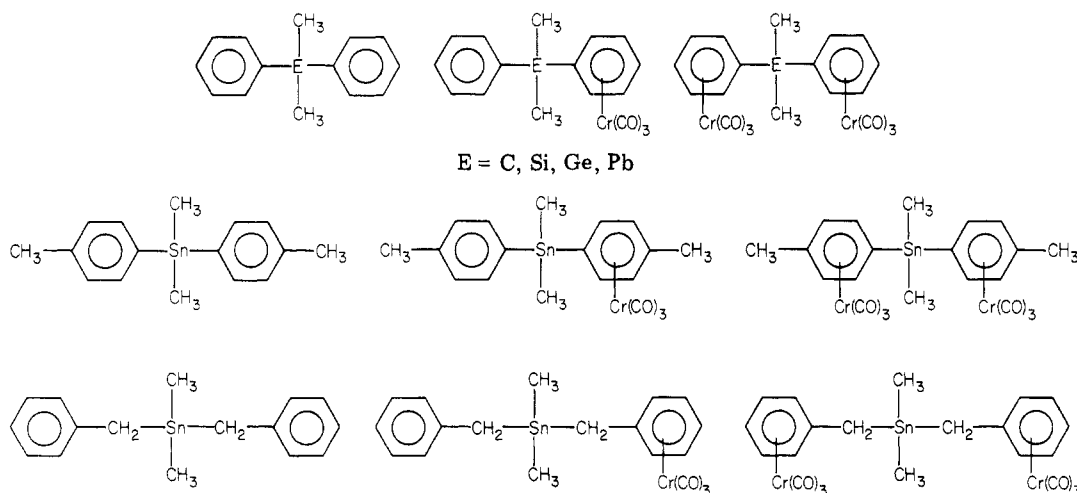
Compounds Previously Reported
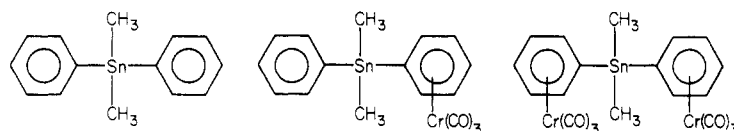

larized mode was recorded at 530 cm^{-1}. The free ligands and other complexes exhibited the expected strong ν_{asym}(Sn–C) absorptions at 536–525 cm^{-1} with a weaker symmetric stretch 16–20 cm^{-1} lower in frequency. In Raman, strong, polarized ν_{sym}(Sn–C) absorptions were recorded at 521–522 cm^{-1} with weak, depolarized shoulders at 536–534 cm^{-1} for the asymmetric stretch. One explanation for the anomalous result for the bis(tricarbonylchromium) complex of dimethyldiphenyltin is a distortion of the SnC$_4$ skeleton arising from the steric requirements of the two bulky transition-metal groups to approach a trans-planar structure at tin which must persist in solution since the vibrational spectra are identical in that phase.[2]

But, as we pointed out at the time, assignments in the 550–500-cm^{-1} range are complicated because Cr–CO bending modes may also occur there, and some combination of the presence of these and purely electronic effects without substantial structural modification may give rise to the patterns observed in the infrared and Raman spectra without recourse to an explanation based upon the operation of centrosymmetric selection rules.[2] Indeed, the tin-119 NMR chemical shift of the bis complex is not different from the others in which the tin resonance shifts downfield by ca. 30 ppm per Cr(CO)$_3$ group complexed to a directly bonded phenyl but only by 4 ppm when the phenyl is insulated from tin by a methylene.[3]

We set out to determine the origin of the curious effect observed in the vibrational spectrum of (CH$_3$)$_2$Sn[(C$_6$H$_5$)Cr(CO)$_3$]$_2$ in two ways. Growing a suitable single crystal proved to be extremely difficult because of twinning, but the structure of this complex has now been solved from a crystal in which there is some disorder. The bond the tin atom makes with its methyl groups is only 6° opened from the tetrahedral, and thus structural distortion cannot lie at the root of the absence of ν_{sym}(Sn–CH$_3$) in the infrared and the degeneracy of the ν_{asym} and ν_{sym}(Sn–CH$_3$) modes in the Raman.[4]

The second approach is through the synthesis of additional examples of the title species; in this paper, we report the synthesis and spectroscopic properties of a homologous series of tricarbonylchromium complexes of arene ligands containing fourth group elements from carbon to lead. These species are depicted below. The interesting electron-impact and chemical ionization properties of this series of compounds have already been reported[5] (Chart I).

Experimental Section

Compounds. The complexes were synthesized from Cr(CO)$_6$[6] in diglyme–tetrahydrofuran (THF) solutions or from Cr(CO)$_3$(NH$_3$)$_3$[7] in refluxing dioxane, using reagent grade materials and with great care to prevent contact with air or moisture. All work with solutions of the complexes was carried out under an atmosphere of prepurified nitrogen. Solvents were saturated with N$_2$. Dioxane was passed through an alumina column, then refluxed over LiAlH$_4$, and distilled under N$_2$. Melting points were measured in sealed evacuated tubes and are uncorrected. All new compounds gave satisfactory elemental analyses as shown in Table I. Microanalytical data were determined by MHW Laboratories, Phoenix, AZ, and at the Microanalytical Laboratory, Department of Chemistry, University of Massachusetts, Amherst, MA.

The general preparation method using Cr(CO)$_3$(NH$_3$)$_3$ (the amount is specified in each case mentioned below) involved refluxing this reagent with the ligand in dioxane (25 mL). The mixture was cooled and filtered and the residue washed with benzene. The solvents were removed under vacuum, leaving a yellow oil which solidified on trituration with hexane or petroleum ether (30–60 °C) and cooling in an ice bath. This crude product, a mixture of mono and bis complexes, was then extracted with

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Table I. Physical Properties and Analytical Data for the Tricarbonylchromium Complexes

compd	mp, °C	formula	anal.							
			calculated				found			
			C	H	Cr	O	C	H	Cr	O
$C_6H_5C(CH_3)_2C_6H_5Cr(CO)_3$	70–72	$C_{18}H_{16}CrO_3$	65.06	4.85	15.65	14.44	65.32	4.76	15.60	14.40
$(CH_3)_2C[C_6H_5Cr(CO)_3]_2$	143–149	$C_{21}H_{16}Cr_2O_6$	53.86	3.44	22.20	20.50	54.50	3.35	22.40	20.45
$C_6H_5Si(CH_3)_2C_6H_5Cr(CO)_3$	63–65	$C_{17}H_{16}CrO_3Si$	58.61	4.63	14.92	13.78	58.57	4.42	14.90	13.75
$(CH_3)_2Si[C_6H_5Cr(CO)_3]_2$	106–108	$C_{20}H_{16}Cr_2O_6Si$	49.58	3.34	21.47		49.54	3.52	21.4	
$C_6H_5Ge(CH_3)_2C_6H_5Cr(CO)_3$	54–56	$C_{17}H_{16}CrGeO_3$	51.96	4.11	13.23		51.70	4.03	12.8	
$(CH_3)_2Ge[C_6H_5Cr(CO)_3]_2$	115–116	$C_{20}H_{16}Cr_2GeO_6$	45.41	3.06	19.66		45.18	3.28	18.7	
$C_6H_5Pb(CH_3)_2C_6H_5Cr(CO)_3$	79–82.5	$C_{17}H_{16}CrO_3Pb$ [a]	38.70	3.06			38.63	3.27		
$(CH_3)_2Pb[C_6H_5Cr(CO)_3]_2$	69–73	$C_{20}H_{16}Cr_2O_6Pb$ [b]	36.20	2.44	15.67		36.02	2.60	15.46	
$C_6H_5CH_2Sn(CH_3)_2CH_2C_6H_5Cr(CO)_3$	84–85	$C_{19}H_{20}CrO_3Sn$	48.85	4.32	11.13		48.63	4.45	11.4	
$(CH_3)_2Sn[CH_2C_6H_5Cr(CO)_3]_2$	189–191	$C_{22}H_{20}Cr_2O_6Sn$	43.81	3.35	17.24		43.61	3.36	17.1	
$p\text{-}CH_3C_6H_4Sn(CH_3)_2C_6H_4CH_3Cr(CO)_3$	81–84	$C_{19}H_{20}CrO_3Sn$	48.85	4.32	11.13		48.63	4.32	11.2	
$(CH_3)_2Sn[C_6H_4CH_3\text{-}p\text{-}Cr(CO)_3]_2$	151–153	$C_{22}H_{20}Cr_2O_6Sn$	43.81	3.35	17.24		43.66	3.21	16.8	

[a] Pb: calcd, 39.28; found, 39.09.   [b] Pb: calcd, 31.22; found, 31.06.

hot hexane or petroleum ether (60–110 °C) and filtered. Cooling the filtrate in an ice bath usually resulted in a precipitate of pure mono complex. The residue from the extraction with hot solvent was dissolved in hot benzene, CHCl₃ or CCl₄, filtered, hexane or petroleum ether (30–60 °C) added to the filtrate, and the filtrate cooled in an ice bath. This usually produced the pure bis complex. Significant variations in this procedure are mentioned explicitly in individual cases.

(2,2-Diphenylpropane)tricarbonylchromium(0). Triamminetricarbonylchromium (2.44 g, 13.1 mmol) and 2,2-diphenylpropane (Aldrich Chemical Co., 1.24 g, 6.31 mmol) were heated under reflux for 7.25 h in a very slow stream of N₂. The residue contained decomposition products and some white crystals (124 mg) which were isolated and identified as $Cr(CO)_6$. The yellow oil formed after removal of solvents was dissolved in THF (ca. 5 mL) and added to a silica gel column (28 × 2 cm) packed in hexane. Elution with hexane followed by benzene produced a single, broad yellow band which was collected, and the solvents were removed under vacuum. Trituration with petroleum ether (bp 30–60 °C) followed by removal of the petroleum ether under vacuum produced 1.46 g of crude product, from which was isolated 0.77 g (37% yield) of the mono complex: mol wt 332 (mass spectrum); mp 70–72 °C; IR (Nujol mull) 1955 (s), 1885 (s), 1855 (s), 1405 (m), 1309 (w), 1248 (w), 1205 (w), 1150 (m), 1081 (w), 1056 (w), 1030 (m), 1014 (w), 811 (m), 791 (w), 761 (s), 720 (w), 700 (s), 659 (s), 629 (s), 614 (m), 562 (w), 540 (m), 529 (s), 478 (m) cm⁻¹; UV maxima (C₆H₁₂) 318 (ε 1.02 × 10⁴), 262 nm (ε 1.02 × 10⁴).

(2,2-Diphenylpropane)bis[tricarbonylchromium(0)]. Treatment as described above yielded 0.27 g (9.0% yield) of pure bis complex: mol wt 468 (mass spectrum); mp 143–149 °C dec; IR (Nujol mull) 1960 (s), 1880 (s), 1855 (s), 1405 (w), 1309 (w), 1234 (w), 1212 (w), 1154 (m), 1078 (w), 1049 (w), 1010 (w), 877 (w), 814 (m), 808 (m), 781 (w), 718 (w), 655 (s), 630 (s), 622 (s), 573 (w), 533 (s), 527 (s), 476 (m) cm⁻¹.

The above two complexes were also prepared in somewhat smaller yields by heating $Cr(CO)_6$ and the ligand in diglyme–THF at 140–150 °C for 10 h, followed by filtration, chromatography on alumina with petroleum ether (30–60 °C), evaporation of the solvent, and trituration of the residue with hexane. The mixture of mono and bis complexes was filtered and dried. Sublimation at 0.05 torr and 105 °C produced pure mono complex (10% yield). The residue was dissolved in benzene and chromatographed on alumina with benzene as the eluent. Evaporation of the solvent under vacuum left pure bis complex (9% yield).

(Dimethyldiphenylsilane)tricarbonylchromium(0). Dimethyldiphenylsaline was prepared in 34% yield by the reaction of phenylmagnesium bromide with phenyldimethylchlorosilane (K and K Laboratories) and in 88% yield by the reaction of methylmagnesium chloride with diphenyldichlorosilane (PCR, Inc.); bp 165–166 °C (18 torr), 84–88 °C (0.25 torr) [lit.[8] bp 177 °C (45 torr), 156–157 °C (15 torr)]. The infrared spectrum was identical to that in the literature.[9]

Dimethyldiphenylsilane (2.15 g, 10.1 mmol) and $Cr(CO)_3(NH_3)_3$ (2.56 g, 13.7 mmol) were refluxed for 6.5 h to give 2.20 g of the crude product or 1.49 g of purified mono complex (42% yield): mol wt 348 (mass spectrum); mp 63–65 °C; IR (Nujol mull) 1950 (s), 1910 (s), 1865 (s), 1425 (w), 1292 (m), 1254 (m), 1167 (w), 1112 (s), 1101 (s), 1018 (w), 998 (w), 990 (m), 914 (w), 839 (s), 817 (s), 780 (s), 733 (s), 707 (m), 694 (m), 653 (s), 645 (w, sh), 632 (s), 617 (s), 534 (s), 469 (s) cm⁻¹.

(Dimethyldiphenylsilane)bis[tricarbonylchromium(0)]. Treatment of the crude product in the usual manner produced 0.23 g of yellow crystals (5.0% yield): mol wt 484 (mass spectrum); mp 106–108 °C; IR (Nujol mull) 1960 (s), 1870 (s), 1290 (m), 1265 (m), 1255 (m), 1163 (w), 1155 (m), 1105 (s), 1017 (m), 990 (m), 973 (w), 942 (w), 883 (w), 841 (s), 814 (s), 783 (s), 720 (w), 705 (w), 658 (s), 623 (s), 615 (s), 532 (s), 472 (s) cm⁻¹.

An alternate procedure yielded the bis complex almost exclusively. Hexacarbonylchromium (9.10 g, 41.4 mmol) and (C-H₃)₂(C₆H₅)₂Si (3.00 g, 14.2 mmol) were heated in diglyme (10 mL) and THF (5 mL) at 150 °C for 61 h. The reaction mixture was cooled and passed through a silica gel column (10 × 2 cm) by using benzene as eluent. Solvents were removed under vacuum to a total volume of 15 mL; addition of hexane (20 mL) caused immediate appearance of crystals. Filtration, washing with hexane, and drying under vacuum gave yellow crystals (4.81 g); vacuum sublimation at 0.01 torr and 90 °C for 96 h removed a very small amount of the mono complex. The residue was chromatographed on a silica gel column with benzene, the eluate concentrated under vacuum, and hexane added. The crystals which separated were filtered, washed with hexane, and dried under vacuum (weight 3.03 g, 44% yield). ¹H NMR and mass spectra revealed the presence of a small amount of an unknown impurity of mol wt 558 characterized by a methyl proton resonance signal at δ 0.44. Solution in hot CHCl₃, filtration, addition of petroleum ether (30–60 °C) to the filtrate, and cooling in an ice bath produced crystals of the pure bis complex which were separated by filtration (65% recovery); the ¹H NMR spectrum of the filtrate showed the absence of the unknown contaminant.

(Dimethyldiphenylgermane)tricarbonylchromium(0). Dimethyldiphenylgermane was prepared in 90% yield by reaction[10] of methylmagnesium chloride with diphenyldichlorogermane (Ventron Corp., Alfa Products): bp 90–100 °C (0.22 torr) [lit.[10,11] bp 145 °C (10 torr), 125–126 °C (3 torr),[12] IR bands (neat liquid) 3060 (s), 3040 (s), 3015 (s), 2985 (s), 2970 (s), 2900 (s), 1950 (m), 1870 (m), 1815 (m), 1575 (m), 1485 (m), 1425 (s), 1325 (m), 1265 (m), 1240 (m), 1092 (s), 1027 (m), 998 (m), 826 (m), 800 (s), 726 (s), 695 (s), 669 (m), 600 (s), 578 (s), 455 (s) cm⁻¹.

Dimethyldiphenylgermane (2.26 g, 8.82 mmol) and $Cr(CO)_3$-$(NH_3)_3$ (3.29 g, 17.6 mmol) were refluxed for 6 h. Workup of the

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(9) "Standard Infrared Spectra"; Sadtler Research Laboratories, Inc.; Philadelphia, PA, 1962; Spectrum No. 1612.

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(12) Kumada, M.; Sakamoto, S.; Ishikawa, M. *J. Organomet. Chem.* **1969**, *17*, 235.

reaction mixture gave 2.76 g of crude product from which 1.18 g of the pure mono complex (34% yield) was isolated: mol wt 394 (mass spectrum based on ^{74}Ge); mp 54–56 °C; IR (Nujol mull) 1980 (s), 1915 (s), 1870 (s), 1296 (w), 1241 (w), 1161 (w), 1095 (m), 1085 (m), 1018 (w), 989 (w), 910 (w), 838 (m), 806 (s), 752 (w), 730 (s), 695 (m), 666 (m), 655 (s), 632 (s), 616 (s), 608 (ms), 585 (m), 535 (s), 477 (m), 438 (m) cm^{-1}.

(Dimethyldiphenylgermane)bis[tricarbonylchromium(0)]. Treatment of the crude product as previously described gave the bis complex (0.87 g, 18% yield): mol wt 530 (mass spectrum based on ^{74}Ge); mp 115–116 °C; IR (Nujol mull) 1970 (s), 1950 (s), 1900 (s), 1875 (s), 1295 (m), 1257 (m), 1247 (m), 1164 (w), 1149 (w), 1079 (m), 1043 (w), 1018 (w), 984 (w), 945 (w), 920 (w), 912 (w), 888 (w), 812 (s), 753 (w), 718 (w), 660 (s), 627 (s), 615 (s), 586 (w), 530 (s), 478 (m) cm^{-1}.

(Dimethyldiphenyllead)tricarbonylchromium(0). Dimethyldiphenyllead was prepared in 73% yield by the reaction of methylmagnesium chloride with diphenyllead dichloride (obtained from Institute for Organic Chemistry TNO, Utrecht, The Netherlands): bp 118–120 °C (0.37 torr) [lit.[13,14] 151–152 °C (2 torr)]; prominent IR bands (neat liquid) 3050 (s), 3005 (s), 2975 (s), 2915 (s), 2290 (m), 1940 (m), 1860 (m), 1805 (m), 1620 (m), 1565 (s), 1470 (s), 1425 (s), 1325 (m), 1300 (m), 1260 (m), 1189 (m), 1162 (m), 1155 (m), 1062 (m), 1018 (m), 997 (m), 753 (m), 720 (s), 695 (s), 490 (m), 479 (m), 470 (s), 435 (s) cm^{-1}.

Dimethyldiphenyllead (3.27 g, 8.38 mmol) and Cr(CO)$_3$(NH$_3$)$_3$ (1.50 g, 8.03 mmol) were heated at reflux for 7 h. The yellow oil obtained after evaporation of solvents did not solidify on trituration with hexane or on chromatographing on silica gel and so was mixed with hexane (20 mL) and saturated with N$_2$, and the solution was allowed to stand in a refrigerator for 10 days. A precipitate formed (0.470 g, 11% yield) which was filtered, washed with hexane, and dried: mol wt 528 (mass spectrum based on ^{208}Pb); mp 79–82.5 °C; IR (Nujol mull) 1970 (s), 1905 (s), 1855 (s), 1291 (w), 1150 (m), 1058 (m), 1042 (w), 1012 (m), 992 (m), 980 (m), 920 (w), 903 (w), 887 (w), 846 (m), 812 (m), 772 (m), 722 (s), 692 (s), 662 (s), 654 (s), 628 (s), 614 (s), 531 (s), 481 (s), 469 (s), 432 (m) cm^{-1}.

This complex was also prepared in 46% yield by a similar process using a larger excess of Cr(CO)$_3$(NH$_3$)$_3$.

(Dimethyldiphenyllead)bis[tricarbonylchromium(0)]. Dimethyldiphenyllead (2.89 g, 7.40 mmol) and Cr(CO)$_3$(NH$_3$)$_3$ (3.22 g, 17.2 mmol) were refluxed for 6.5 h. The usual workup gave 3.10 g of crude product. This was washed with petroleum ether (30–60 °C) (150 mL) and then dissolved in hot CHCl$_3$ (30 mL), and the solution was filtered. Addition of petroleum ether (30–60 °C) and cooling in an ice bath gave 1.47 g of the bis complex (30% yield) which was isolated by filtration, washed, and dried under vacuum: mol wt 664 (mass spectrum based on ^{208}Pb); mp 69–73 °C; IR (Nujol mull) 1965 (s), 1945 (s), 1860 (s), 1299 (m), 1176 (m), 1158 (m), 1040 (w), 1008 (w), 977 (w), 938 (w), 880 (w), 820 (w), 804 (m), 770 (m), 720 (m), 670 (s), 661 (s), 636 (s), 622 (m), 538 (s), 489 (m), 474 (m), 455 (m) cm^{-1}.

(Dibenzyldimethyltin)tricarbonylchromium(0). Dibenzyldimethyltin was prepared by the addition of dimethyltin dichloride (1 mol) in tetrahydrofuran to a solution of benzylmagnesium bromide (3 mol) in ether. The mixture was refluxed for 3 h and then hydrolyzed. The organic layer was separated, the solvent removed in vacuo, and the residue distilled. The fraction boiling at 106 °C (15 torr) solidified on cooling: mp 41–44 °C (lit.[15] mp 26 °C, bp 132–135 °C (1.0 torr); mp 47 °C[16]); IR (Nujol mull) 3060 (m), 3050 (m), 3010 (s), 1595 (s), 1480 (m), 1316 (w), 1248 (w), 1210 (s), 1182 (w), 1157 (w), 1100 (m), 1048 (m), 1030 (m), 999 (w), 897 (m), 797 (m), 752 (s), 697 (s), 616 (m), 562 (w), 528 (m), 511 (m), 441 (m) cm^{-1}.

Dibenzyldimethyltin (1.72 g, 5.21 mmol) and Cr(CO)$_3$(NH$_3$)$_3$ (1.07 g, 5.73 mmol) were refluxed for 7.5 h. The usual workup produced 2.27 g crude product from which was isolated 1.03 g

(42% yield) of the mono complex: mol wt 468 (mass spectrum based on ^{120}Sn); mp 84–85 °C; IR (Nujol mull) 3065 (w), 1965 (s), 1860 (s), 1595 (w), 1520 (w), 1415 (w), 1210 (m), 1192 (w), 1152 (m), 1118 (m), 1038 (w), 1000 (m), 974 (w), 907 (w), 890 (w), 876 (w), 820 (m), 797 (m), 761 (w), 719 (w), 685 (m), 662 (s), 629 (s), 566 (m), 533 (s), 518 (m), 476 (m) cm^{-1}; UV maximum (C$_6$H$_{12}$) 320 nm (ϵ 1.25 × 10^4).

(Dibenzyldimethyltin)bis[tricarbonylchromium(0)] was isolated as described above (0.35 g, 11% yield): mol wt 604 (mass spectrum based on ^{120}Sn); mp 189–191 °C; IR (Nujol mull) 1950 (s), 1880 (s), 1850 (m), 1210 (m), 1192 (w), 1152 (w), 1117 (m), 1037 (m), 1015 (w), 998 (m), 973 (w), 906 (w), 889 (w), 875 (w), 820 (m), 796 (m), 761 (m), 718 (w), 684 (m), 661 (s), 628 (s), 617 (w), 566 (m), 538 (m), 523 (vw), 475 (m) cm^{-1} UV maximum (C$_6$H$_{12}$) 322 nm (ϵ = 6.61 × 10^3).

(Dimethyldi-p-tolyltin)tricarbonylchromium(0). Dimethyldi-p-tolyltin was prepared by a procedure similar to that described above for dibenzyldimethyltin: bp 105–107 °C (0.05 torr) [lit.[17] bp 120–121 °C (0.2 torr), 110–112 °C ($\leq$0.1 torr)[18]]; Prominent IR bands (neat liquid) 3055 (m), 3025 (s), 3005 (s), 2975 (m), 2915 (s), 2860 (m), 1900 (m), 1595 (m), 1495 (m), 1450 (m), 1390 (s), 1320 (m), 1265 (m), 1217 (m), 1191 (s), 1116 (m), 1072 (s), 1020 (m), 791 (s), 748 (s), 617 (m), 576 (s), 530 (s), 516 (s), 477 (s) cm^{-1}.

Dimethyldi-p-tolyltin (1.68 g, 5.09 mmol) and Cr(CO)$_3$(NH$_3$)$_3$ (1.98 g, 10.6 mmol) were refluxed for 11 h. Treatment of the reaction mixture in the manner previously described gave 2.44 g of crude product. The mono complex (1.03 g, 43% yield) was isolated by extraction with hot petroleum ether (30–60 °C). This product still contained a very small amount of the bis complex, so the separation procedure was repeated twice with ca. 75% recovery each time: mol wt 468 (mass spectrum based on ^{120}Sn); mp 81–84 °C; IR (Nujol mull) 1950 (s), 1905 (s), 1860 (s), 1366 (w), 1292 (w), 1213 (w), 1196 (w), 1172 (w), 1071 (m), 1058 (m), 1036 (w), 1018 (w), 989 (w), 960 (w), 886 (w), 846 (m), 790 (s), 752 (m), 664 (s), 634 (s), 628 (s), 578 (m), 532 (vs), 522 (m), 475 (s) cm^{-1}.

(Dimethyldi-p-tolyltin)bis[tricarbonylchromium(0)]. The residue from the petroleum ether extraction above gave 0.77 g (25% yield) of the bis complex: mol wt 604 (mass spectrum based on ^{120}Sn); mp 151–153 °C; IR (Nujol mull) 1960 (s), 1945 (s), 1900 (s), 1850 (s), 1294 (w), 1211 (w), 1205 (w), 1190 (w), 1173 (w), 1098 (w), 1055 (m), 1035 (m), 955 (w), 890 (w), 847 (m), 790 (w), 767 (m), 720 (w), 665 (s), 637 (m), 628 (s), 576 (m), 535 (s), 510 (sh, m), 476 (s) cm^{-1}.

Spectra. Mass spectra were recorded on a Finnegan 3200 quadrupole instrument equipped with a 6110 data system.[5] UV–vis spectra were obtained on cyclohexane solutions using 1-cm cells on a Cary 14 spectrometer. NMR spectra were recorded on Varian A60-A and EM-360 instruments on CDCl$_3$ and CCl$_4$ solutions containing 40–50 mg/mL of sample with tetramethylsilane (Me$_4$Si) or p-dioxane where Me$_4$Si would interfere (222 and 216 Hz at 60 MHz upfield from Me$_4$Si in CDCl$_3$ and CCl$_4$, respectively) as internal standards. Infrared spectra were recorded on a Perkin-Elmer 337 instrument for identification purposes and on Perkin-Elmer 621 and Beckman IR-12 instruments for more precise work. The samples were run as Nujol mulls. Raman spectra were recorded on a Cary 81 instrument using a He–Ne laser, a Cary 83 instrument equipped with an Ar laser, and a Codberg PH-1 instrument equipped with a Spectra Physics Model 165-01 Kr laser in 0.3-mL cuvettes calibrated by an indene spectrum. Tin-119m Mössbauer spectra were measured on camdrive, constant acceleration[22] and Ranger Engineering constant acceleration instruments equipped with an NaI scintillation counter using Ca^{119m}SnO$_3$ (New England Nuclear Corp.) as both source and standard reference material for zero velocity. Velocity calibration was based upon both β-tin and natural iron foils. Data

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Table II. ^{1}H NMR Chemical Shifts of $(CH_3)_2E(C_6H_5)_2$ (where E = C, Si, Ge, and Pb) and Their Complexes[a]

	aromatic		
	uncomplexed	complexed	methyl
$(CH_3)_2C(C_6H_5)_2$[b]	7.07–7.37		1.70[c]
$C_6H_5C(CH_3)_2C_6H_5Cr(CO)_3$[b]	7.13–7.52	4.96–5.62	1.75
$(CH_3)_2C[C_6H_5Cr(CO)_3]_2$[b]		5.02–5.68	1.72
$(CH_3)_2Si(C_6H_5)_2$	7.22–7.73		0.56
$C_6H_5Si(CH_3)_2C_6H_5Cr(CO)_3$	7.24–7.73	4.98–5.70	0.59
$(CH_3)_2Si[C_6H_5Cr(CO)_3]_2$		4.96–5.79	0.61
$(CH_3)_2Ge(C_6H_5)_2$	7.21–7.66[d]		0.64[e]
$C_6H_5Ge(CH_3)_2C_6H_5Cr(CO)_3$	7.17–7.67	5.00–5.61	0.71
$(CH_3)_2Ge[C_6H_5Cr(CO)_3]_2$		5.07–5.62	0.75
$(CH_3)_2Pb(C_6H_5)_2$[f]	7.08–7.74		1.11
$C_6H_5Pb(CH_3)_2C_6H_5Cr(CO)_3$[g]	7.15–7.77	5.03–5.55	1.28
$(CH_3)_2Pb[C_6H_5Cr(CO)_3]_2$[h]		5.03–5.63	1.42

^{a} δ values in CDCl₃ vs. a p-dioxane internal standard unless otherwise specified. Aromatic signals are multiplets and methyl signals sharp singlets. ^{b} Me₄Si internal standard. ^{c} Reported as δ 1.63 in ref 18. ^{d} Reported as δ 7.05–7.6 in ref 12. ^{e} Reported as δ 0.62 in ref 18 and as δ 0.63 in ref 12. ^{f} $|J(^{207}Pb-C-^1H_3)| = 66.5$ Hz. ^{g} $|J(^{207}Pb-C-^1H_3)| = 69.9$ Hz. ^{h} $|J(^{207}Pb-C-^1H_3)| = 74.0$ Hz.

Table III. ^{1}H NMR Chemical Shifts of the Tin Ligands and Complexes[a]

	aromatic			
	uncomplexed[b]	complexed[b]	methyl	methylene
$(CH_3)_2Sn(C_6H_5)_2$[c,d]	7.51[e]		0.55[f]	
$C_6H_5Sn(CH_3)_2C_6H_5Cr(CO)_3$[c,d]	7.39	5.24	0.65	
$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$[d]		5.33	0.45	
$(CH_3)_2Sn(p-CH_3C_6H_4)_2$	7.29[g]		0.47,[h] 2.34[i,j]	
	7.24[c]		0.51,[c] 2.38[c,i]	
$p\text{-}CH_3C_6H_4Sn(CH_3)_2[p\text{-}CH_3C_6H_4Cr(CO)_3]$	7.33	5.20	0.57, 2.35,[i] 2.17[k]	
$(CH_3)_2Sn[p\text{-}CH_3C_6H_4Cr(CO)_3]_2$		5.25	0.64, 2.20	
$(CH_3)_2Sn(CH_2C_6H_5)_2$	7.08, 7.02,[c] 7.08[l]		0.01, 0.01[c]–0.07[l,m]	2.33, 2.32,[c] 2.31[l]
$C_6H_5CH_2Sn(CH_3)_2CH_2C_6H_5Cr(CO)_3$	7.11	5.06	0.07	2.38,[n] 2.01[o]
$(CH_3)_2Sn[CH_2C_6H_5Cr(CO)_3]_2$		5.40,[p] 5.55[l]	0.13,[p] 0.08[l]	2.15[l,p]

^{a} δ values in CDCl₃ vs. p-dioxane (0.05 mL/mL of CDCl₃) as internal standard unless otherwise specified. ^{b} Center of multiplet. ^{c} In CCl₄ solution. ^{d} Reference 2. ^{e} Reported as 444 for the ortho and 435 Hz for the meta protons at 60 MHz vs. Me₄Si in ref 18. ^{f} Reported as 28.2 Hz vs. Me₄Si at 60 MHz in ref 18. ^{g} Reported as 440 for the ortho and 423 for the meta protons at 60 MHz vs. Me₄Si in ref 18. ^{h} Reported as –27.0 Hz vs. Me₄Si at 60 MHz in ref 18. ^{i} Aromatic methyl, uncomplexed. ^{j} Reported as –137.5 Hz vs. Me₄Si at 60 MHz in ref 18. ^{k} Aromatic methyl, complexed. ^{l} In Me₂SO solution. ^{m} Reported as 2.2 Hz vs. Me₄Si at 60 MHz in ref 19. ^{n} Methylene, uncomplexed. ^{o} Methylene, complexed. ^{p} In CDCl₃–Me₂SO solution.

were fitted to Lorentzian curves by standard, nonlinear, least-squares techniques.

Results and Discussion

It is surprisingly rare, even in the intensively worked organometallic chemistry of the elements of the fourth main group, to have a completely homologous set of compounds, carbon to lead, available for study. The present effort includes three such sets, the dimethyldiphenyl-methane, -silane, -germane, -stannane, and -plumbane ligands, $(CH_3)_2E(C_6H_5)_2$, where E = C, Si, Ge, Sn, and Pb, and their mono- and bis(tricarbonylchromium) complexes, $C_6H_5(CH_3)_2EC_6H_5Cr(CO)_3$ and $(CH_3)_2E[C_6H_5Cr(CO)_3]_2$. The five members of each set are expected to be isostructural, with the only changes induced by the larger size of the central atom, E, and its transformation from the archtypical covalent carbon through the metalloidal silicon and germanium to the metallic tin and lead. Properties capable of being measured for all 15 homologues should show a smooth gradation in each series down the fourth periodic group, as well as from the free ligands to the bis complexes.

These expectations are disappointed in both senses by the variation in the parameter most easily measured and most confidently assigned, namely the methyl proton NMR chemical shift. Examination of these values in Table II and for the tin analogues in Table III reveals a scatter in their magnitudes proceeding either from carbon to lead or from ligand to bis complex. The corresponding shifts for the tetramethyl derivatives were used by Allred and

Table IV. Methyltin Coupling Constants of the Ligands and Complexes

	$|^2J(^{119}Sn-C-^1H)|$, Hz
$(CH_3)_2Sn(C_6H_5)_2$[a]	54.4[b,c]
$C_6H_5Sn(CH_3)_2C_6H_5Cr(CO)_3$[a]	56.1[b]
$(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$[a]	58.1[d]
$(CH_3)_2Sn(p\text{-}CH_3C_6H_4)_2$	52.3,[b] 56.1[d]
$p\text{-}CH_3C_6H_4Sn(CH_3)_2\text{-}[p\text{-}CH_3C_6H_4Cr(CO)_3]$	57.5[d]
$(CH_3)_2Sn[p\text{-}CH_3C_6H_4Cr(CO)_3]_2$	58.9[d]
$(CH_3)_2Sn(CH_2C_6H_5)_2$	49.0,[b] 58.4[b] (CH₂) 52.3,[d] 62.4[d] (CH₂) 53.2,[e] 64.9[e] (CH₂)
$C_6H_5CH_2Sn(CH_3)_2CH_2C_6H_5Cr(CO)_3$	53.4[d] 63.5[d,f] (CH₂) 55.7[d,i] (CH₂)
$(CH_3)_2Sn[CH_2C_6H_5Cr(CO)_3]_2$	54.9,[h] 56.4[e] 62.2[e,g] (CH₂)

^{a} Reference 2. ^{b} In CCl₄ solution. ^{c} Reported as 55.4 Hz in ref 18, as 55.8 Hz in ref 19, as 57.3 and 58.5 Hz in ref 20, and as 56 Hz in ref 21. ^{d} In CDCl₃ solution. ^{e} In Me₂SO solution. ^{f} Uncomplexed. ^{g} Complexed. ^{h} In CDCl₃–Me₂SO solution.

Rochow to determine the electronegativities of these elements,[23] but there is no correlation with our shift values.

Tin-119 NMR coupling constants are more straightforward to interpret,[24] and the data in Table IV reveal the

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Table V. Tin-119m Mössbauer Data for the Organotin Ligands and Their Tricarbonylchromium Complexes at 77 K [a]

compd	IS,[b] mm s⁻¹	QS,[c] mm s⁻¹	Γ,[b] mm s⁻¹
(CH₃)₂Sn(C₆H₅)₂	1.27		1.48
C₆H₅(CH₃)₂SnC₆H₅Cr(CO)₃	1.74[d,e]	0.64[d,e]	
(CH₃)₂Sn[C₆H₅Cr(CO)₃]₂	1.75[d,e]	0.89[d,f]	
	1.26[b]	0.93[c]	
(CH₃)₂Sn(p-CH₃C₆H₄)₂	1.29	. . .	0.73
p-CH₃C₆H₄(CH₃)₂Sn(p-CH₃C₆H₄)Cr(CO)₃	1.26	. . .	1.14
(CH₃)₂Sn[(p-CH₃C₆H₄)Cr(CO)₃]₂	1.26	0.74	0.981
(CH₃)₂Sn(CH₂C₆H₅)₂	1.39	. . .	1.23
C₆H₅CH₂(CH₃)₂SnCH₂C₆H₅Cr(CO)₃	1.38	. . .	1.29
(CH₃)₂Sn[CH₂C₆H₅Cr(CO)₃]₂	1.39	0.71	0.85

[a] Vs. Ca ¹¹⁹ᵐSnO₃.   [b] ±0.03 mm s⁻¹.   [c] ±0.06 mm s⁻¹.   [d] Reference 2.   [e] ±0.06 mm s⁻¹.   [f] ±0.12 mm s⁻¹.

Table VI. Infrared and Raman ν(E-CH₃) Assignments for E = Si, Ge, Sn, and Pb

compd	ν_asym(E-CH₃)		ν_sym(E-CH₃)	
	IR[a]	Raman (depol)[b]	IR[a]	Raman (pol)[b]
(CH₃)₂C(C₆H₅)₂	1156 m	1158 w	1028 s	1030 s
C₆H₅(CH₃)₂CC₆H₅Cr(CO)₃	1150 m	c	1080 m	c
(CH₃)₂C[C₆H₅Cr(CO)₃]₂	1154 m	c	. . .	c
(CH₃)₂Si(C₆H₅)₂	774 s	d	640 m	641 w
C₆H₅(CH₃)₂SiC₆H₅Cr(CO)₃	780 s	d	645 w, sh	646 m
(CH₃)₂Si[C₆H₅Cr(CO)₃]₂	783 s	. . .	. . .	649 m
(CH₃)₂Ge(C₆H₅)₂	601 s	605 s	579 s	581 vs[e]
C₆H₅(CH₃)₂GeC₆H₅Cr(CO)₃	608 ms	610 vw	585 m	585 s
(CH₃)₂Ge[C₆H₅Cr(CO)₃]₂	615 s	617 vw	586 w	587 m
(CH₃)₂Sn(C₆H₅)₂[f]	530 s	534 w, sh	517 m	521 vs
C₆H₅(CH₃)₂SnC₆H₅Cr(CO)₃[f]	534 s, 536[g]	536 m	522 vs	522 vs
(CH₃)₂Sn[C₆H₅Cr(CO)₃]₂[f]	530 s, 534[g]	. . .	. . .	530 s, 531[g]
(CH₃)₂Sn(p-CH₃C₆H₄)₂	530 s	534 m	517 s	520 vs
CH₃C₆H₄(CH₃)₂Sn(p-CH₃C₆H₄)Cr(CO)₃	532 vs	537 w	522 m	522 m
(CH₃)₂Sn[(p-CH₃C₆H₄)Cr(CO)₃]₂	535 s	540 w, sh / 545 w, sh[h]	510 sh, m	523 s / 528 m[h]
(CH₃)₂Sn(CH₂C₆H₅)₂	529 ms	528 m	513 m	516 vs
C₆H₅CH₂(CH₃)₂SnCH₂C₆H₅Cr(CO)₃	533 s	533 w	518 m	517 s
(CH₃)₂Sn[CH₂C₆H₅Cr(CO)₃]₂	538 m	536 w / 528 w[h]	523 vw	520 m / 514 m[h]
(CH₃)₂Pb(C₆H₅)₂	480 ms	c	470 ms	c
C₆H₅CH₂(CH₃)₂SnCH₂C₆H₅Cr(CO)₃	490 m	486 vs	479 m	474 s
(CH₃)₂Pb[C₆H₅Cr(CO)₃]₂	489 m	483 m	474 m	471 vs

[a] In Nujol mulls.   [b] In methylene chloride solution.   [c] Not recorded.   [d] Obscured by the strong methylene chloride absorption.   [e] Assigned at 580 cm⁻¹ to ν(Ge-C) in ref 10.   [f] Reference 2.   [g] In chloroform solution.   [h] Microcrystalline solid.

redistribution of s and p orbital character on complexation of the phenyl group. Here there is a smooth progression of increased |²J(¹¹⁹Sn-C-¹H)| values on attaching one and then two chromium tricarbonyl ligands to each of the three tin ligands listed. This reflects a higher s character in the orbital the tin atom directs at the methyl group and hence, given a constant total amount of valence electron s and p character available, more p character in the orbital used to bind the phenyl ring. Thus the tricarbonylchromium moiety in these systems is σ-electron withdrawing. Further experimental confirmation is available in the benzyl derivatives where |²J(¹¹⁹Sn-C-¹H)| for the methylene protons measures the s character in the bond tin directs toward the phenyl and its pendant tricarbonylchromium group. Chromium complexation reduces this value. This fact and the reduced chemical shifts listed in Table III are used to assign the methylene protons attached to the complexed phenyl ring in the mono complex where a direct comparison is available within the same molecule. Of the four tin bonding orbitals, the one with least s character is directed toward the complexed phenyl. The magnitudes of the coupling constants are consistent, at least for these tin derivatives, with four-coordination at the tin atom and hence with monomeric species in solution.[24]

The Mössbauer data in Table V also speak to the situation at the tin atom. The isomer shift (IS) values which are typical for tetraorganotin compounds[25,26] do not change outside of experimental error on mono or bis complexation.[27] None of the free ligands or mono complexes has a clearly resolvable quadrupole splitting (QS) and forcing our fitting program to produce a doublet results, for example, in an improbably small (0.64 mm s⁻¹) value for C₆H₅(CH₃)₂SnC₆H₅Cr(CO)₃. The doublets for the bis complexes, on the other hand, are clearly resolvable, if small. The explanation advanced earlier based upon enhanced electric field gradients along the tin–phenyl σ bonds[2] seems reasonable now and corroborates the NMR coupling constant changes. Recent electrochemical studies show that the two (arene)tricarbonylchromium groups in the bis complex are noninteracting.[28] The QS value of the benzyl derivative is not reduced, even though the tin atom is farther removed from the aryltricarbonylchromium moiety and insulated from its effect by the methylene group.

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It was the anomalous infrared ν(Sn–CH₃) pattern in the tin bis complex, (CH₃)₂Sn[C₆H₅Cr(CO)₃]₂, that caused us to initiate this study in the first place, and we present the corresponding data for the *p*-tolyl- and benzyltin ligands and complexes as well as for the homologous carbon, silicon, germanium, and lead systems in Table VI.

As a rule, as the mass of the metal atom in methyl derivatives of the main group elements increases, the frequency separation of the two expected ν(E–C) modes decreases. For tetramethylsilane, -germane, -stannane, and -plumbane the ν_{asym}, ν_{sym}(E–C), and $\Delta\nu$'s are as follows: 696, 598, 98; 595, 558, 37; 529, 508, 21; 476, 459, 17 cm⁻¹, respectively.[29] Polarization measurements in the Raman guide the assignment of these frequencies, since the totally symmetric (CH₃)₂E ν(E–C) mode is polarized while the asymmetric mode is depolarized.

Assigning the ν(C–CH₃) modes for the –C(CH₃)₂– skeleton has proved notoriously difficult,[30] and no detailed vibrational analysis of the parent ligand 2,2-diphenylpropane is available as a guide. While pairs of bands at 1170 ± 5 and 1170–1140, or at 1210 and 1190, or at 1190 and 1175–1165 cm⁻¹ are said to be characteristic of the –C(CH₃)₂– group, there is disagreement over the origin of these absorptions[30,31] with one source assigning them to ν(C–CH₃).[32] Weak to medium infrared bands are indeed seen at 1188, 1156, 1146, 1109, 1056, and 1028 cm⁻¹ for the free 2,2-diphenylpropane ligand and at 1206, 1157, 1150, 1111, and 1030 cm⁻¹ and at 1214, 1168, 1154, and 1106 cm⁻¹ for the mono and bis complexes, respectively. Five of the six infrared bands of the free ligand are also found in the Raman at 1190 (w) (depol), 1159 (w) (depol), 1148 (vw) (depol), 1114 (w) (pol), and 1030 (s) (pol). Of these only the first two depolarized and last two polarized bands can arise from ν_{asym} and ν_{sym}(C–CH₃), respectively. On the basis of their separation of 128 cm⁻¹ and presence in the ligand and complexes, we assign the Raman 1158- and 1030-cm⁻¹ bands to these modes. The corresponding infrared ν_{sym}(C–CH₃) diminishes in intensity on successive tricarbonylchromium complexation until it disappears in the bis complex.

The anomaly of the stepwise reduction in the intensity of the infrared ν_{sym}(Sn–CH₃) band on mono and bis complexation observed for the dimethyldiphenyltin series is repeated in the closely related *p*-tolyl set where this band is found at 517 (m) and 522 (w) cm⁻¹ in the free ligand and mono complex, respectively. Examination of the bis complex at high resolution reveals only some asymmetry on the ν_{asym}(Sn–CH₃) band at 535 (s) cm⁻¹ which could arise from an overlapped feature 10–15 cm⁻¹ to lower energy. In the Raman spectrum the strong, polarized ν_{sym}(Sn–CH₃) band at 523 cm⁻¹ has a very weak, depolarized shoulder at ca. 540 cm⁻¹, presumably the ν_{asym}(Sn–CH₃) mode. Only a very weak shoulder is seen at ca. 545 cm⁻¹ on the high energy side of the ν_{sym}(Sn–CH₃) band at 528 (m) cm⁻¹ in the Raman spectrum of the bright, chrome-yellow, solid bis complex.

In the isomeric benzyltin derivatives the infrared ν_{sym}(Sn–CH₃) mode at 513 (m) cm⁻¹ in the free ligand again falls in intensity on mono [518 (m) cm⁻¹] and bis [523 (w) cm⁻¹] complexation but is still discernible as a separate

band, even at low resolution. The medium, polarized ν_{sym}(Sn–CH₃) band at 520 cm⁻¹ in the Raman has a weak shoulder at ca. 536 cm⁻¹ of doubtful polarization, presumably the ν_{asym}(Sn–CH₃) mode. These features are seen more clearly in the Raman spectrum of the solid in which they appear at 528 (w) and 514 (m) cm⁻¹. The ν_{asym} and ν_{sym}(Sn–CH₃) modes are assigned at 530 and 515 cm⁻¹, respectively, in ref 15.

This phenomenon is also observed in the germanium series where the ν_{asym} and ν_{sym}(Ge–C) stretching modes have been assigned at 608 (601) and 587 (580) cm⁻¹ in the infrared (Raman), respectively, for dimethyldiphenylgermane.[33] The intensity of the ν_{sym}(Ge–CH₃) mode is diminished relative to the ν_{asym}(Ge–CH₃) absorption stepwise on tricarbonylchromium complexation until in the bis complex the band at 586 cm⁻¹ is very weak. The ν_{asym}(Ge–CH₃) bands in the Raman follow a similar pattern with the depolarized 617-cm⁻¹ band in the bis complex being very weak.

In the lead series a band at ca. 440 cm⁻¹ also appears in the spectra of tetraphenyllead and hexaphenyldilead and hence is not associated with a methyllead mode. Methyllead–carbon stretches are assigned near 476 cm⁻¹,[34] with ν_{asym} and ν_{sym}(Pb–CH₃) at 478 and 459 cm⁻¹, respectively, in tetramethyllead,[35] and at 534 and 523 and 460 and 447 cm⁻¹ in dimethyllead dichloride and dibromide, respectively.[36] However, the chromium–carbon stretching frequency in variously substituted arene chromium tricarbonyl complexes also absorb in this region.[37-41] The assignment in the parent ligand is straightforward, but there is a reversal in expected intensity, the band assigned to ν_{sym}(Pb–CH₃) being more intense than the ν_{asym}. Careful examination of the relevant infrared region at high resolution reveals a third band centered at 485 cm⁻¹, presumably the ν(Cr–CO) mode, which enhances the intensity of the adjacent ν_{sym}(Pb–CH₃) absorption in the infrared, reversing its intensity ratio with the ν_{asym} mode. This third band could not be resolved in the Raman spectra of the mono or the bis complex. In the latter the infrared intensity ratios are most skewed, and so it is likely that the ν(Cr–CO) absorption lies more directly under the ν_{sym}(Pb–CH₃) absorption at 474 cm⁻¹ where it also adds to the intensity of the Raman band at 471 cm⁻¹. Thus because of this complication, it is impossible to test whether the ν_{sym}(Pb–CH₃) mode diminishes in intensity on complexation as do the corresponding modes in the carbon, germanium, and tin series.

The silicon case is still more complex since the ν(Si–CH₃) stretching frequencies are difficult to distinguish from a methyl rocking which absorbs in the same region.[30,32,42] In addition, the spectrum of our parent silicon ligand is particularly rich in bands between 840 and 615 cm⁻¹, the region of interest. In dimethyldichlorosilane the ν_{asym} and

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ν_{sym}(Si–CH$_3$) modes absorb at 805 and 688 cm^{-1}, respectively,[43] and in dimethyldiethynylsilane absorb at 794 (depol) and 701 (pol) cm^{-1}, respectively, in the Raman.[44] In our series we find polarized Raman bands at 641, 646, and 649 cm^{-1} in the free ligand and mono and bis complexes, respectively, which we assign to the ν_{sym}(Si–CH$_3$) mode. These bands increase in intensity on successive complexation. The corresponding band is found at 640 cm^{-1} in the infrared of dimethyldiphenylsilane and as a weaker shoulder at 645 cm^{-1} in its mono complex. The bis complex contains no infrared absorption between 656 and 622 cm^{-1}, and 783-cm^{-1} band which we assign to ν_{asym}(Si–CH$_3$) is likewise absent in the Raman. Thus the intensity anomaly is observed on successive complexation in the silicon series as well.

In conclusion, we see that the diminishing of intensity of the ν_{sym}(E–C) mode in the infrared and increasing in intensity in the Raman on successive mono and bis complexation of the aryl groups by tricarbonylchromium moieties first observed for the series of dimethyldiphenyltin ligand and complexes[2] is general for the carbon, silicon, germanium, and perhaps the lead series, as well as for the closely related pair of isomeric tin ligands, dimethyldibenzyl- and dimethyldi-*p*-tolyltin. These changes are thus observed in four different spectral regions where the frequency differences between the symmetric and asymmetric modes, $\Delta\nu = [\nu_{sym}(E–CH_3) - \nu_{asym}(E–CH_3)]$, decreases from an average of 128 for E = carbon and 134 for silicon to 25 for germanium to 13 for tin to 10 for lead [taking infrared results for the $(CH_3)_2E(C_6H_5)_2$ ligands only].

Close examination of the structural data for the bis complex of dimethyldiphenyltin[4] provides a possible general explanation. While the anomalous spectral properties of this compound cannot be attributed to distortions of the normal geometry at the central tin atom, where the dimethyltin carbon–tin–carbon angle is opened only to 115.5° while the corresponding diphenyltin angle is somewhat closed to 105.7°, the preservation of roughly tetrahedral values at tin gives rise to nonbonded interactions in other parts of this crowded molecule. In particular, the terminal oxygen atoms of one of the carbonylchromium groups is forced into contact with one of the methyltin groups [d(O–H$_3$C) = 3.11 Å vs. sum of the van der Waals radii = 3.40 Å].[45] This represents a maximum distance, since the structure adopted in the solid state has the tricarbonylchromium rotated so that this intramolecular interaction is minimized. In solution, on the other hand, the freer rotation or libration of the tricarbonylchromium group would be expected to bring the carbonyl oxygen atom into yet more severe contact with the tin methyl group.

This contact with and consequent distortion of the symmetry of the methyltin groups with successive tricarbonylchromium substitution affects the frequency and intensity of the methyltin ν_{asym} and ν_{sym}(Sn–C) modes by lowering the basic symmetry (and hence changing the

definitions of these two spectral features) and by changing the relative contributions of the various atomic and molecular motions that produce the observed absorption in the infrared and Raman spectra. The effect is seen as a change in intensity of the infrared ν_{sym}(Sn–C) mode and Raman ν_{asym}(Sn–C) mode which mimics that which would be produced by a flattening of the central atom tetrahedron toward square planarity.

The structures of the five molecules in each of our three series of ligands and mono and bis complexes should be related simply by an expansion of the bond distances to the central atom, E, in the successive E = carbon to lead substitution. In particular, for the intramolecular contact described above, the E-methyl and E-phenyl distances in the system O≡CCrC$_6$H$_5$ECH would be subject to an expansion of E = carbon to lead of ca. 0.8 Å (the difference in the covalent radii of E).[45] The net effect would be to move the carbonyl oxygen atom farther away from the methyl group, and thus the interaction should be least severe for the E = Pb case. However, because of the complex nature of the spectra (see above), it is not certain that the intensity changes are observed in the E = Pb case. For the atoms smaller than tin, the molecules should be more crowded and the interaction more severe. Substitution of a benzyl group should allow additional rotational degrees of freedom for the complexes, but some effect on the intensities of the ν(Sn–C) modes is still seen.

The temperature-dependent solution infrared and Raman spectral studies in the ν(C–H) and ν(Cr–CO) region needed to confirm this suggestion are unfortunately beyond the scope of the present study.

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