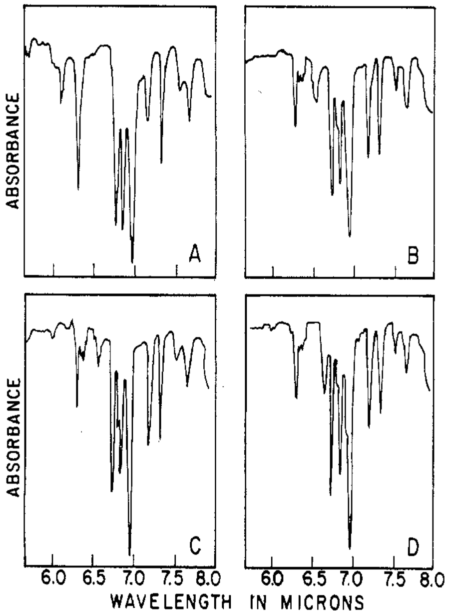

Figure 2.—Infrared spectra of 2-*cis*-propenylphenyldiphenylphosphine (*cis*-PP) and its group VI metal complexes in deuteriochloroform solution: A, *cis*-PP; B, (*cis*-PP)Mo(CO)$_4$; C, (*cis*-PP)Cr(CO)$_4$; D, (*cis*-PP)W(CO)$_4$.

metal–olefin bond strength.[14] Frequency lowerings as high as 187 cm^{-1} have been reported for Pt(II) complexes;[26] however, $\Delta\nu_{C=C}$ usually lies below 150 cm^{-1} and depends upon the nature of the olefin as well as the metal.[14,27]

In the case of the group VI metal complexes of *cis*-PP, determination of $\Delta\nu_{C=C}$ is simplified by the absence of bands in the region between 1480 and 1580 cm^{-1} in the infrared spectrum of the uncoordinated ligand (Figure 2). The new band that appears in this region in the spectra of the group VI metal complexes has been assigned to the coordinated C=C stretching vibration (Table II) giving a $\Delta\nu_{C=C}$ of 140, 122, and 118 cm^{-1} for W(0), Cr(0), and Mo(0), respectively. Therefore, metal–olefin bond strength appears to vary with the metal in this homologous series in the order W > Cr > Mo. This observation is in agreement with the order of M–C force constants determined for the group VI metal hexacarbonyls[28] and also fits in with the somewhat greater stability observed for the tungsten complexes of the simple monoolefins as compared with those of the other group VI metals.[29]

Acknowledgment.—This work was supported in part by the National Science Foundation in the form of a postdoctoral fellowship awarded to L. V. I. The authors also wish to thank Drs. C. Heathcock, M. Jorgenson, and H. Rapoport for the use of their equipment and for helpful discussions.

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[26] R. E. Yingst and B. E. Douglas, *Inorg. Chem.*, **3**, 1177 (1964).

[27] E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961).

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Organometallic Compounds with Metal–Metal Bonds. IV. Pentacarbonylmanganese and Pentacarbonylrhenium Derivatives of Silicon, Germanium, Tin, and Lead. Preparation and Infrared and Nuclear Magnetic Resonance Studies[1]

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Received June 18, 1966

Carbonyl stretching frequencies and force constants calculated by the Cotton–Kraihanzel method are reported for the compounds $(C_6H_5)_3M$–$M'(CO)_5$ (M = Si, Ge, Sn, Pb; M' = Mn, Re) and for trimethyltin, trichlorotin, and tribromotin derivatives of manganese and rhenium. From a comparison of the force constants with those of related compounds, it is concluded that the trihalogenotin group is a strong π-acceptor ligand. The nmr spectra of the trimethyltin compounds and of $(CH_3)_2Sn[M'(CO)_5]_2$ are reported and the trend in proton–tin coupling constants is discussed in terms of enhanced s character in the tin–transition metal bond.

Introduction

Many compounds are now known in which the congeners of carbon in main group IV are covalently bonded to transition metals.[2] In descending this group, one passes from the extensively studied organometallic compounds to the newer field of metal–metal bonding. It appeared that the study of trends in this series would be of value.

The compounds R_3M–$M'(CO)_5$ (R = CH_3, C_6H_5, or halogen; M = Si, Ge, Sn, or Pb; M' = Mn or Re) form a particularly suitable series for such an investigation. The nature of the M–M' interaction can be

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[1] Presented in part at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965. Part III of this series: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

[2] For leading references, *cf.* H. R. H. Patil and W. A. G. Graham, *ibid.*, **5**, 1401 (1966).

inferred, at least semiquantitatively, from carbonyl stretching force constants; these are in turn obtained by application of the Cotton–Kraihanzel approximate force constant method.[3] Fortunately, this method has been applied to a number of halogeno,[4] alkyl, and fluoroalkyl[5] derivatives of $Mn(CO)_5$ and $Re(CO)_5$, as well as to $HMn(CO)_5$.[6] Force constant values for compounds with these more conventional ligands are thus available and provide essential reference points against which values for $R_3M–M'(CO)_5$ can be compared.

Several of the compounds investigated spectroscopically in this work have been reported previously, and details of their preparation, which is for the most part straightforward, are not repeated here.

Experimental Section

Infrared spectra were determined using a Perkin-Elmer 337 (grating) spectrometer. The carbonyl region (2200–1700 cm^{-1}) was recorded in expanded form on a Texas Instruments Servo-Riter recorder so that 100 cm^{-1} occupied about 13 cm of chart paper. The spectra thus obtained were of excellent quality, and the Model 337 instrument offers the advantage of an uninterrupted scan from 4000 to 1200 cm^{-1}, without the usual change of grating or order at the critical 2000-cm^{-1} point. Each expanded spectrum was calibrated above and below the region of interest by introducing gas cells containing carbon monoxide or deuterium bromide into the sample beam at the appropriate times during a continuous run. Sample bands were then measured by interpolation using CO band no. 31 and DBr band no. 13 as reference points.[7] The linearity of the wavenumber scale in this interval was established using gaseous deuterium chloride. The deviation between duplicate spectra did not exceed 1 cm^{-1}, and the accuracy of the figures quoted (relative to the calibration gases) is well within the limits ± 1 cm^{-1}. The solvent in all cases was cyclohexane.

The nmr measurements were made on Varian A-60 or HA-100 (field-frequency lock) instruments, the latter being used for coupling constant measurements. The nmr data are given in Table I.

TABLE I

NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS[a]

Compound	τ[b]	Coupling constants, cps: $J(^{117}Sn–CH_3)$	$J(^{119}Sn–CH_3)$	$J(^{207}Pb–CH_3)$
$(CH_3)_3SnMn(CO)_5$[c]	9.54	46.2	48.3	. . .
$(CH_3)_2ClSnMn(CO)_5$	9.06	43.9	45.8	. . .
$(CH_3)_3PbMn(CO)_5$	8.99	. . .	. . .	43.5
$(CH_3)_3SnRe(CO)_5$	9.58	44.7	46.7	. . .
$(CH_3)_2Sn[Mn(CO)_5]_2$	9.17	34.9	36.7	. . .
$(CH_3)_2Sn[Re(CO)_5]_2$	9.14	34.9	36.7	. . .
$(CH_3)_2Pb[Mn(CO)_5]_2$[d]	8.28	. . .	. . .	16.2

[a] In $CHCl_3$ or $CDCl_3$. [b] Chemical shift in ppm relative to tetramethylsilane. [c] $J(^{13}CH_3) = 129.2$ cps. [d] In toluene.

Starting materials were either commercially available or prepared by standard methods. Reactions were carried out in a nitrogen atmosphere in general accordance with Gorsich's procedures[8] where $NaMn(CO)_5$ and $NaRe(CO)_5$ were involved.

$(C_6H_5)_3Si–Mn(CO)_5$. Method A.—Triphenylsilane (2.61 g, 10 mmoles) and manganese carbonyl (1.96 g, 5 mmoles) were refluxed in methylcyclohexane for 140 hr. The progress of the reaction was followed by infrared spectroscopy, which gave evidence of a new band near 2100 cm^{-1} after about 24 hr. To a 35-ml aliquot of the methylcyclohexane solution was added 10–15 g of Florisil (100–200 mesh) and the solvent was removed at reduced pressure on a rotary evaporator. The adsorbed sample was then placed on a 2.2 × 17 cm Florisil column made up with hexane. Elution with hexane yielded first a yellow band ($Mn_2(CO)_{10}$ by infrared), followed slowly by a colorless oil ($(C_6H_5)_3SiH$). Continued elution with hexane–benzene (1:1) yielded $C_6H_5Si–Mn(CO)_5$, which was recrystallized from hexane. The over-all yield was about 8%.

Method B.—Triphenylsilane (1.50 g, 5.8 mmoles) and manganese carbonyl (1.0 g, 2.6 mmoles) were heated in a sealed, evacuated tube at 160–165°, during which two liquid layers were present and gas evolution was noted at the interface. After 35 hr the tube was cooled and opened, and unreacted $Mn_2(CO)_{10}$ was sublimed off under high vacuum. The residue was recrystallized from hexane affording $(C_6H_5)_3Si–Mn(CO)_5$ (0.41 g, 35%).

$(C_6H_5)_3Si–Re(CO)_5$.—This compound was prepared by the sealed-tube reaction of $(C_6H_5)_3SiH$ and $Re_2(CO)_{10}$ under the conditions described above. The product was isolated by chromatography on Florisil; hexane eluted $Re_2(CO)_{10}$, then slowly $(C_6H_5)_3SiH$, and finally $(C_6H_5)_3Si–Re(CO)_5$ was eluted with hexane–benzene (1:1). Two recrystallizations from hexane afforded the pure product.

$(CH_3)_3Sn–Mn(CO)_5$.—Trimethyltin chloride (12.0 g, 60 mmoles) in 50 ml of anhydrous tetrahydrofuran (THF) was added to a stirred solution of $NaMn(CO)_5$ prepared in 200 ml of THF from 11.7 g of $Mn_2(CO)_{10}$ (30 mmoles) by stirring over an excess of 1% sodium amalgam. The mixture was stirred for 3 hr at room temperature. Removal of THF at reduced pressure left a pale green residue which was extracted with a THF–water mixture. The extract was saturated with NaCl and the layers were separated. The water layer was extracted with $CHCl_3$ and the combined organic layers were evaporated at reduced pressure. This residue was recrystallized from pentane at −78° with filtration of the crystals (mp 26–27°) in a cold room. Sublimation at 0° under high vacuum onto a −78° probe yielded the pure compound (yield *ca.* 80%).

$(CH_3)_2ClSn–Mn(CO)_5$.—This compound was prepared in 50–60% yield by the slow addition of $(CH_3)_2SnCl_2$ to an equimolar amount of $NaMn(CO)_5$, the THF solution being allowed to stand overnight in a refrigerator before workup. On one occasion when the addition was rapid and the overnight delay was omitted, the product was $(CH_3)_2Sn[Mn(CO)_5]_2$.

Discussion

Most of the compounds reported here for the first time require little comment; they have the expected stability and are prepared in the usual way[8] by displacement reactions such as

$$(CH_3)_3SnCl + Na^+Mn(CO)_5^- \longrightarrow (CH_3)_3Sn–Mn(CO)_5 + NaCl$$

The reaction of triphenylchlorosilane in this way yields a red, air-sensitive product which was assumed[8] to be $(C_6H_5)_3Si–Mn(CO)_5$. We confirm that a red, air-sensitive substance is formed in this reaction; it is not the anticipated product, however, and the course of the reaction remains obscure.

Authentic $(C_6H_5)_3Si–Mn(CO)_5$ and its rhenium analog are colorless, air-stable compounds, prepared for the first time in this work by the reaction of triphenylsilane with manganese or rhenium carbonyl at an elevated temperature. The presumed reactions are

$$(C_6H_5)_3SiH + (OC)_5Mn–Mn(CO)_5 \longrightarrow (C_6H_5)_3Si–Mn(CO)_5 + HMn(CO)_5$$

$$(C_6H_5)_3SiH + HMn(CO)_5 \longrightarrow H_2 + (C_6H_5)_3Si–Mn(CO)_5$$

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[3] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[4] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[5] J. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 389 (1965).

[6] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2736 (1964).

[7] International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth and Co. Ltd., London, 1961.

[8] R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

TABLE II

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Mp, °C		Color	Analyses, %			
				Carbon		Hydrogen	
	Obsd[a]	Lit.		Calcd	Found	Calcd	Found
$(C_6H_5)_3SiMn(CO)_5$[b]	160–163	New compd	White	60.79	60.99	3.33	3.46
$(C_6H_5)_3GeMn(CO)_5$	161–164	162–164[c]	White	55.37	55.44	3.03	3.18
$(C_6H_5)_3SnMn(CO)_5$	150–152	148–150[d]	White				
$(CH_3)_3SnMn(CO)_5$	26–27	New compd	White	26.78	27.37	2.53	2.88
$(CH_3)_2ClSnMn(CO)_5$	94.5–96.5	New compd	White	22.17	22.32	1.59	1.56
$Cl_3SnMn(CO)_5$	173–174	168 dec[d]	White				
$Br_3SnMn(CO)_5$	146–148	145–147[d]	Pale yellow	10.85	11.14	0.00	0.00
$(C_6H_5)_3PbMn(CO)_5$	142–144	146–148[d]	Pale yellow				
$(C_6H_5)_3SiRe(CO)_5$	156.5–158.5	New compd	White	47.17	47.70	2.58	2.60
$(C_6H_5)_3GeRe(CO)_5$	157.5–158.5	New compd	White	43.8	44.0	2.4	2.4
$(C_6H_5)_3SnRe(CO)_5$[e]	144.5–146	142–143[f]	White	40.8	41.8	2.2	2.8
$(CH_3)_3SnRe(CO)_5$	51–58	New compd	White	19.6	19.8	1.9	2.0
$Cl_3SnRe(CO)_5$[g]	>250 dec	220 dec[f]	White	10.9	11.4	0.0	0.0
$Br_3SnRe(CO)_5$[h]	265 dec	New compd	White	8.8	9.4	0.0	0.1
$(C_6H_5)_3PbRe(CO)_5$	133–135	New compd	Pale yellow	36.1	36.8	2.0	2.1

[a] Kofler hot stage. [b] Exact mass for $^{12}C_{23}{}^{1}H_{15}{}^{16}O_5{}^{28}Si^{55}Mn$: calcd, 454.0069; found (MS-9), 454.0066. [c] D. Seyferth, H. P. Hofmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1,** 227 (1962). [d] R. D. Gorsich *J. Am. Chem. Soc.*, **84,** 2486 (1962). [e] Mol wt calcd, 676; found (Mechrolab osmometer, CH_2Br_2), 666. [f] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Proc. Acad. Sci. USSR, Chem. Sect.*, **156,** 502 (1964). [g] Cl calcd, 19.2; found, 20.8. [h] Br calcd, 35.1; found, 36.1.

TABLE III

CARBONYL STRETCHING FREQUENCIES, ASSIGNMENTS, AND APPROXIMATE FORCE CONSTANTS

Compound	Frequencies, cm^{-1}			Force constants,[a] mdynes/A			Cm^{-1}	
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i	B_1 (calcd)	B_1 (found)
$(C_6H_5)_3SiMn(CO)_5$	2098	2003[b]	2003[b]	16.36	16.67	0.236	2032	2030
$(C_6H_5)_3GeMn(CO)_5$	2097	2006	2002[c]	16.33	16.70	0.227	2034	2032
$(C_6H_5)_3SnMn(CO)_5$	2093	2002	2002	16.34	16.64	0.226	2030	2027
$(CH_3)_3SnMn(CO)_5$	2089	1991	1998	16.29	16.49	0.240	2021	. . .[d]
$(CH_3)_2ClSnMn(CO)_5$	2101	2006	2015	16.57	16.72	0.234	2035	2039
$Cl_3SnMn(CO)_5$	2126	2046	2039	16.91	17.31	0.204	2070	. . .[d]
$Br_3SnMn(CO)_5$	2122	2043	2037	16.88	17.26	0.201	2067	2060[d]
$(C_6H_5)_3PbMn(CO)_5$	2091	2003[e]	2003[e]	16.35	16.64	0.218	2030	2029
$(C_6H_5)_3SiRe(CO)_5$	2118	2012	2003	16.36	16.88	0.267	2045	2044
$(C_6H_5)_3GeRe(CO)_5$	2118	2014	2000	16.31	16.91	0.264	2046	2047
$(C_6H_5)_3SnRe(CO)_5$	2114	2012	2003	16.36	16.86	0.257	2043	2042
$(CH_3)_3SnRe(CO)_5$	2108	2003	2003	16.38	16.72	0.261	2035	2014
$Cl_3SnRe(CO)_5$	2141	2044	2030	16.78	17.37	0.249	2074	2077[d]
$Br_3SnRe(CO)_5$	2143	2046	2030	16.78	17.40	0.250	2076	2070[d]
$(C_6H_5)_3PbRe(CO)_5$	2114	2015	2001	16.31	16.90	0.251	2046	2044

[a] Force constants k_1, k_2, and k_i are as defined by F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84,** 4432 (1962). All frequencies measured in cyclohexane. [b] Asymmetric due to very weak shoulder on high-frequency side. [c] Medium shoulder. [d] Indistinct; position uncertain. [e] Asymmetric due to very weak shoulder on low-frequency side.

or

$$2HMn(CO)_5 \longrightarrow H_2 + (OC)_5Mn\text{–}Mn(CO)_5$$

This preparative method was suggested by the facile reaction of the Si–H bond with dicobalt octacarbonyl.[9] The latter reaction proceeds at room temperature, and it is not surprising that the generally more stable manganese and rhenium carbonyls require higher temperatures. Thus, the silicon–manganese bond, now that it has been prepared, is found to have a stability fully equal to that of its germanium and tin analogs. It is of interest that the reaction of SiH_4 with $HMn(CO)_5$ afforded very air-sensitive colored solids, from which it was evidently not possible to isolate a silicon–manganese compound.[10]

Physical properties and analytical data of the compounds are reported in Table II.

In discussing the infrared spectra of $R_3M\text{–}Mn(CO)_5$ and $R_3M\text{–}Re(CO)_5$, the symmetry is taken as C_{4v}; this is a convenient and generally adopted[3,5,11] idealization. For C_{4v} symmetry, three infrared-active carbonyl stretching modes are expected ($2\,A_1 + E$) as well as one Raman-active mode (B_1). Many of the compounds of Table III show three main infrared stretching modes. There is little question[3,11] that the medium-intensity band at highest frequency is an A_1 mode, designated $A_1^{(2)}$ in Cotton's notation.[4,12] The strongest absorption is expected to be the E mode, and the lower frequency A_1 mode ($A_1^{(1)}$) may lie at higher or lower frequency than E, or be accidentally degenerate with E.[3,11] The three possibilities are shown in Figures 1–3. To our knowledge, these are the first examples to be re-

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(9) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87,** 1133 (1965).

(10) A. G. Massey, A. J. Park, and F. G. A. Stone, *ibid.*, **85,** 2021 (1963).

(11) L. E. Orgel, *Inorg. Chem.*, **1,** 25 (1962).

(12) In Orgel's notation,[11] the high-frequency and low-frequency A_1 bands are designated A_1^{1b} and A_1^{1a}, respectively.

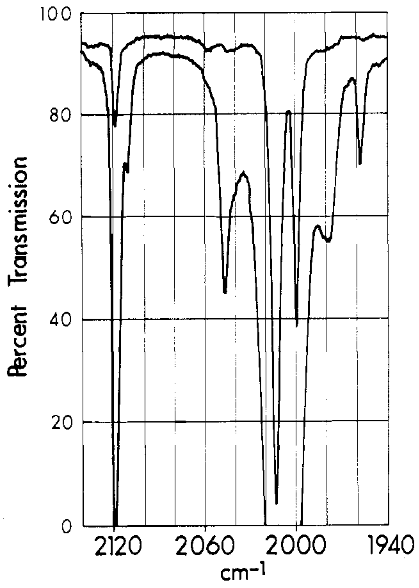

Figure 1.—Carbonyl stretching region of the infrared spectrum of $(C_6H_5)_3Ge-Re(CO)_5$ in cyclohexane: upper curve, 1 mg/ml; lower curve, 9 mg/ml; 0.5-mm cells.

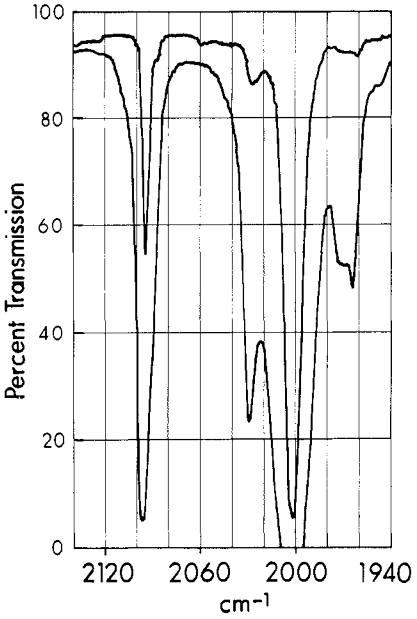

Figure 2.—Carbonyl stretching region of the infrared spectrum of $(C_6H_5)_3Sn-Mn(CO)_5$ in cyclohexane: upper curve, 0.8 mg/ml; lower curve 14 mg/ml; 0.5-mm cells.

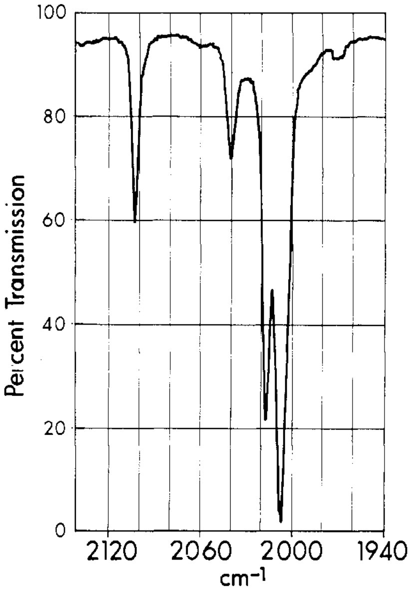

Figure 3.—Carbonyl stretching region of the infrared spectrum of $(CH_3)_2ClSn-Mn(CO)_5$ in cyclohexane: 0.7 mg/ml; 0.5-mm cells.

ported of an $LM(CO)_5$ compound in which $A_1^{(1)}$ actually does occur at higher frequency than E.

The fact that the true symmetry of the molecule is lower than C_{4v} can result in the appearance of the B_1 mode in the infrared and the splitting of the doubly degenerate E mode. A band assignable as B_1 appears in many of the spectra of Table III; using the values of the three stronger bands, the Cotton–Kraihanzel equations enable the position of the B_1 absorption to be calculated. Agreement between the calculated and observed positions of this band is satisfactory, thus confirming the assignments of Table III. In the trihalogeno and trimethyl derivatives, which perhaps approach cylindrical symmetry most closely, the B_1 mode is almost imperceptible; it is readily apparent in the triphenyl derivatives and strongest in $(CH_3)_2ClSn-Mn(CO)_5$, the least symmetrical compound studied. In no case, however, was the asymmetry sufficient to produce any observable splitting of the E band, as has been observed recently in a number of fluorocarbon derivatives of manganese and rhenium pentacarbonyls.[5]

We next consider the implications of the approximate force constant values for the metal–metal bonding in these molecules. Of fundamental importance is the fact that in molecules $LMn(CO)_5$, the ligand L and the CO *trans* to it can both undergo π bonding with the same two transition metal d orbitals (d_{xz} and d_{yz} if we take the z axis along the fourfold axis). This π interaction will involve back donation of manganese d_{xz} and d_{yz} electrons to the vacant antibonding CO orbitals; the concomitant reduction in the CO bond order will be reflected in a smaller stretching force constant for the *trans* CO (k_1 in Cotton's notation[3]). If the ligand L can also accept metal d_π electrons into suitable π-type orbitals, it will in effect compete with the *trans* CO for d electrons of the transition metal. The π-acceptor capability of L, then, will also influence k_1; the greater the π bonding to L, the less electron density enters the antibonding orbitals of the *trans* CO and the greater the CO stretching force constant.

For guidance in interpreting the force constants of the $R_3M-M'(CO)_5$ compounds, data for a number of reference compounds are collected in Table IV. The most striking feature is the high k_1 values for the Cl_3Sn and Br_3Sn ligands. The values of 16.9 and 16.8 mdynes/A for the manganese and rhenium compounds, respectively, are the highest yet recorded for a carbonyl derivative of these metals. Of all the compounds to which this treatment has been applied, a higher k_1 has been found only for *cis*-$(F_3P)_3Mo(CO)_3$, in which the value 16.98 mdynes/A is reported.[4] We believe that the high k_1 values associated with Cl_3Sn and Br_3Sn ligands provide strong evidence in support of the idea that these groups behave as π acceptors. A similar conclusion has been reached by Parshall[13] from quite different evidence; using ^{19}F nmr studies, he characterized the Cl_3Sn^- ligand as a weak σ-donor and a strong π-acceptor ligand in platinum(II) complexes. The vacant 5d orbitals of tin were considered to overlap filled platinum 5d orbitals in the π-acceptor component of the tin–platinum bond.

TABLE IV

COMPARISON OF APPROXIMATE FORCE CONSTANTS FOR SELECTED COMPOUNDS[a]

Compound	Force constants, mdynes/A		
	k_1	k_2	k_i
$(C_6H_5)_3P:Au-Mn(CO)_5$[b]	15.69	16.02	0.246
$CH_3Mn(CO)_5$[c]	16.11	16.82	0.252
$ClMn(CO)_5$[d]	16.22	17.48	0.222
$(C_6H_5)_3Sn-Mn(CO)_5$	**16.34**	**16.64**	**0.226**
$HMn(CO)_5$[e]	16.42	16.93	0.258
$HCF_2CF_2Mn(CO)_5$[c]	16.51	17.33	0.236
$Cl_3Sn-Mn(CO)_5$	**16.91**	**17.31**	**0.204**
$CH_3Re(CO)_5$[c]	16.00	16.91	0.292
$ClRe(CO)_5$[d]	15.99	17.47	0.293
$(C_6H_5)_3Sn-Re(CO)_5$	**16.36**	**16.86**	**0.257**
$HCF_2CF_2-Re(CO)_5$[c]	16.50	17.35	0.282
$Cl_3Sn-Re(CO)_5$	**16.78**	**17.37**	**0.249**

[a] Recalculated using frequencies and assignments given in reference cited; values differ slightly in some cases from those calculated in reference. Cyclohexane solution except as noted. Compounds under discussion in boldface. [b] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964). Measured in CCl_4. We find the same frequencies in cyclohexane. [c] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965). [d] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *ibid.*, **1**, 933 (1962); in CCl_4. [e] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

Among the triphenyl derivatives of Table II, one observes remarkably little variation in the force constant values, and only two representative triphenyl compounds are shown in Table IV. The variety of the interaction possible in stable metal–metal bonds can be gauged from the rather low k_1 value observed in the gold–manganese compound (k_1 = 15.69 mdynes/A).[14] Parshall has suggested that halide ligands have a net π-donor effect in platinum(II) complexes,[13] and on the basis of force constant data, it is tempting to suggest that the $(C_6H_5)_3P:Au$ ligand may serve as a π *donor* in its manganese derivative.[15] The possibility that a ligand might function as a π donor has also been considered by Lewis, who suggested, however, that it was most likely to occur with metals in higher oxidation states.[16]

Some significance can also be attached to the k_2 and k_i values of Table IV. The value of k_2 (the stretching force constant of the four CO groups *cis* to L in $LM(CO)_5$) might be expected to depend largely on the inductive effect of the ligand; unlike *trans* CO, the *cis* CO groups have no direct π interconnection with the ligand *via* a common set of d orbitals of the central metal atom. With this assumption, one can arrange the ligands in a reasonable series of increasing inductive withdrawal ability: $(C_6H_5)_3P:Au < (C_6H_5)_3Sn < CH_3 < H < Cl_3Sn < HCF_2CF_2 < Cl$. Finally, as anticipated,[4] k_i (the stretching interaction force constant) decreases as the π population of the central metal is drawn off by the ligand (increasing k_1).

The classical evidence for multiple-bond character has been bond shortening relative to the sum of "single-bond radii." The latter quantity is very much in doubt for transition metals in low oxidation states, but some interesting conclusions can be drawn from the limited structural data available. For the appropriate manganese radius, we take half the Mn–Mn distance in $Mn_2(CO)_{10}$,[17] 1.46 A. For tin, an appropriate covalent radius is half the Sn–Sn distance in the cyclic hexamer of diphenyltin,[18] or 1.39 A. The expected tin–manganese bond length would be 2.85 A. In the compound $(C_6H_5)_2Sn[Mn(CO)_5]_2$, the Sn–Mn distance has been found[19] to be 2.70 ± 0.01 A, an appreciable shortening. An even more pronounced shortening is observed[20] in *trans*-$(C_6H_5)_3Sn-Mn(CO)_4P(C_6H_5)_3$, where the Sn–Mn distance is 2.55 ± 0.02 A; it may be that the weak π-acceptor capability of triphenylphosphine enhances π bonding between tin and manganese, resulting in a shorter bond.

We next draw attention to the nmr results of Table I. The trends in chemical shifts and coupling constants are similar to those previously pointed out.[21] Successive replacement of methyl groups in tetramethyltin decreases the proton–tin coupling constants [$J(^{117}Sn-CH_3)$ and $J(^{119}Sn-CH_3)$]; a similar trend is observed in the methyllead derivatives. This has been interpreted to mean that the bonding orbital of tin or lead to a transition metal is richer in s character than the 25% implied in a strict sp^3 hybridization. Although the entire picture is oversimplified, one could use the assumptions put forward by Kaesz[22] to estimate that the tin orbital bonding to manganese would have about 33% s character. It is of interest that for $(CH_3)_3SnMn(CO)_5$, the symmetric and asymmetric tin–carbon

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(13) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964); **88**, 704 (1966).

(14) A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 3407 (1965).

(15) A referee has pointed out that the maximum difference in k_1 values among the compounds of Table IV is about 6% and that limitations of the force field employed could easily lead to errors in force constants greater than this. It may be that the value of the technique results from a cancellation of errors in closely related series of compounds. Since the gold–manganese compound is substantially different from the other compounds of Table IV, the comparison is less likely to be meaningful, and the referee tends to distrust the explanation we tentatively advance here. We hope that studies now in progress using ^{19}F nmr of pentafluorophenyl derivatives (M. G. Hogben, R. S. Gay, and W. A. G. Graham, *J. Am. Chem. Soc.*, **88**, 3457 (1966)) will aid in clarifying the π bonding in compounds of this type.

(16) J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965).

(17) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963); see also the discussion by R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965), footnote 21.

(18) D. H. Olson and R. E. Rundle, *Inorg. Chem.*, **2**, 1310 (1963).

(19) B. T. Kilbourne and H. M. Powell, *Chem. Ind.* (London), 1578 (1964).

(20) R. F. Bryan, *Proc. Chem. Soc.*, 232 (1964).

(21) H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965); *Inorg. Chem.*, **5**, 1401 (1966).

(22) H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961). $J(^{119}Sn-CH_3)$ = 48.3 cps observed for $(CH_3)_3SnMn(CO)_5$ implies 22.5% s character in each $Sn-CH_3$ orbital based on Kaesz's linear relation. Thus the residual s character for the Sn–Mn orbital is 100 − (3 × 22.5) = 32.5%.

stretching frequencies lie at 503 and 520 cm^{-1}, respectively. These values fall near the straight lines drawn by Brown and Morgan[23] relating Sn–C stretching frequencies to $J(^{119}Sn-CH_3)$. Indeed, there is a striking similarity of the coupling constants and Sn–C stretching frequencies for $(CH_3)_3Sn-Sn(CH_3)_3$ and $(CH_3)_3Sn-Mn(CO)_5$.[24]

Acknowledgment.—We are indebted to Professor F. W. Birss and to Mrs. Kathleen Simpson, who prepared computer programs for the force constant calculations. We thank Mr. R. S. Gay and Mrs. H. R. H. Patil for assistance. This work was supported in part by the National Research Council of Canada.

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(23) T. L. Brown and G. L. Morgan, *Inorg. Chem.*, **2**, 736 (1963).

(24) NOTE ADDED IN PROOF.—Since the submission of this paper, the compound $(CH_3)_3Sn-Mn(CO)_5$ has been reported by H. C. Clark and J. H. Tsai, *ibid.*, **5**, 1407 (1966). In a private communication, Professor Clark has agreed that the 1960-cm^{-1} band observed in the spectrum of his compound is a ^{13}C satellite of the E mode; under improved resolution, he observes at 1996 cm^{-1} the band which we have assigned as $A_1^{(1)}$.

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Organometallic Compounds with Metal–Metal Bonds. V. An Investigation of Tris(tetracarbonylcobalt)tin(IV) Derivatives[1]

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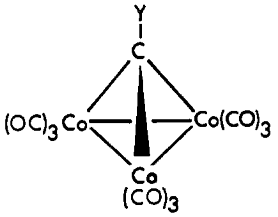
Received July 11, 1966

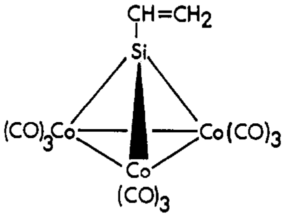
The preparation and infrared spectra of $RSn[Co(CO)_4]_3$ (R = C_6H_5, CH_3, $CH_2{=}CH$, n-C_4H_9) and $XSn[Co(CO)_4]_3$ (X = Cl, Br, I) are described. Their mass spectra are reported, and from this evidence their formulation as *tetra*carbonylcobalt derivatives (III) is conclusively established. Their structures thus differ from the carbon and silicon compounds (I and II) which possess a pyramidal CCo_3 or $SiCo_3$ skeleton with cobalt–cobalt bonds.

Introduction

The reaction of dicobalt octacarbonyl with various trihalogenomethyl compounds X_3CY (Y = CH_3, Cl, F, C_6H_5, COOH, etc.) is reported[2] to give rise to tris(tricarbonylcobalt) derivatives to which the structure I was assigned, largely on the basis of infrared studies.[3]



I



II

The compounds I are intensely purple in color and of high stability. A rational mechanism for their formation, as King[4] has pointed out, would involve successive displacements of the three halogens by tetracarbonylcobalt anion, followed by loss of carbon monoxide by the unstable tris(tetracarbonylcobalt) intermediate; concomitant formation of cobalt–cobalt bonds (two per cobalt atom) would preserve the inert gas configuration for the metal atoms. It is of interest that the CCo_3 nucleus characteristic of I arises also when binuclear acetylene complexes $Co_2(CO)_6(RC{\equiv}CH)$ are treated with acid.[5]

The thermal stability and chemical inertness of these CCo_3 clusters are surprising, since very low stability is a characteristic of the isolated cobalt–carbon σ bond.[6] On the other hand, a much greater stability is exhibited by compounds in which cobalt is covalently bonded to such main group metals as gallium,[7] indium,[7] silicon,[8] germanium,[9] tin,[9] and lead.[10] Thus it appeared that an examination of compounds containing the MCo_3 unit, in which M is a fourth-group element heavier than carbon, would be of interest.

Reaction of tetravinylsilane with dicobalt octacarbonyl has been reported[11] to produce the silicon analog, II, so formulated on the basis of analysis and infrared spectrum. It would be reasonable to expect that the heavier congeners of carbon and silicon would follow a similar pattern in forming $RM[Co(CO)_3]_3$ derivatives having cobalt–cobalt bonds.[12] We find, however, that tin gives rise to a different structural type, $RSn[Co(CO)_4]_3$, which does not possess cobalt–cobalt

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(1) Presented in part at the 49th Canadian Chemical Conference, Saskatoon, Saskatchewan, Canada, June 5–9, 1966. For Part IV, see W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(2) W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 169 (1961); G. Bor, L. Marko, and B. Marko, *Chem. Ber.*, **95**, 333 (1962).

(3) This structure has now been confirmed by X-ray methods: P. W. Sutton and L. F. Dahl, private communication, May 1966.

(4) R. B. King, *Advan. Organometal. Chem.*, **2**, 244 (1964).

(5) U. Krüerke and W. Hübel, *Chem. Ind.* (London), 1264 (1960).

(6) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **13b**, 122 (1958); the much more stable σ-bonded fluorocarbon derivatives are an exception: P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

(7) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

(8) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(9) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

(10) F. Hein and W. Jehn, *Ann.*, **684**, 4 (1965).

(11) S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, 82 (1962).

(12) Although the compound n-$C_4H_9Sn[Co(CO)_3]_3$ has been claimed (S. D. Ibekwe and M. J. Newlands, *Chem. Commun.*, 114 (1965)), we have not been able to substantiate this finding.