ther, since our methods do not distinguish between H(Tc,Mn)(CO)$_5$ and ·(Tc,Mn)(CO)$_5$.

Summary

It has been shown that the ·Tc(CO)$_5$ radical is formed by the β decay of Mo(CO)$_6$ and that this radical displays several of the properties which would be expected of it. Its stability in the solid Mo(CO)$_6$ matrix is greater than that of the analogous ·Mn(CO)$_5$ in Mn$_2$(CO)$_{10}$. It seems to be rapidly destroyed by NO gas present during the early stages of the chemical workup and to be somewhat sensitive to atmospheric oxygen. The ·Tc(CO)$_5$ radical reacts slowly with ·Mn(CO)$_5$ to produce a species which is likely TcMn(CO)$_{10}$ and reacts rapidly with IMn(CO)$_5$ to produce ITc(CO)$_5$. The results suggest that some species such as HTc(CO)$_5$ may also be involved.

Acknowledgments. The impetus for parts of this work arose from a discussion with Professor A. Wojcicki, during which he very kindly gave us experimental information on his recently discovered photochemical preparation of ·Mn(CO)$_5$. The financial support of the National Research Council of Canada is gratefully acknowledged.

Registry No. ·Tc(CO)$_5$, 41375-71-7; Mo(CO)$_6$, 14040-11-0; ·Mn(CO)$_5$, 15651-51-1; TcMn(CO)$_{10}$, 41375-72-8; IMn(CO)$_5$, 14879-42-6; ITc(CO)$_5$, 41375-73-9; Mn$_2$(CO)$_{10}$, 10170-69-1.

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, and State University of New York at Albany, Albany, New York 12222

Tin-119m Mossbauer and X-Ray Photoelectron (ESCA) Studies of Tin Oxidation State and Bonding in Base-Dialkyltin Pentacarbonylchromium and Tetracarbonyliron Complexes

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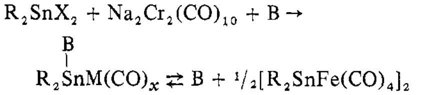
^{119m}Sn Mossbauer, ^{119}Sn–^{1}H three-bond nmr coupling constants, and Sn 3d$_{5/2}$ ESCA electron binding energy data for the compounds $(t\text{-}C_4H_9)_2SnM(CO)_x\cdot B$, where for M = Fe, $x = 4$ and B = DMSO and pyridine and for M = Cr, $x = 5$ and B = THF, DMSO, and pyridine, favor a tin(IV) formulation. The Mossbauer QS values for M = Cr compounds (3.4–4.1 mm/sec) are the largest thus far recorded for four-coordinated organotin compounds. Explanations based upon ylide structures are proposed.

Introduction

Recent attempts at synthesizing the analogs of metal carbonyl "carbene" complexes[2] from dialkyltin dihalides and $Na_2Cr_2(CO)_{10}$[3] have resulted in products shown to have structure I, which are also obtained from homolytic cleavage of the tin-iron bonds in the cyclic $[R_2SnFe(CO)_4]_2$ dimer by base[4,5] (eq 1). X-Ray crystal structure determination of

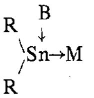


$$R_2SnX_2 + Na_2Cr_2(CO)_{10} + B \rightarrow \overset{\overset{B}{|}}{R_2SnM(CO)_x} \rightleftarrows B + {}^1/_2[R_2SnFe(CO)_4]_2 \qquad (1)$$

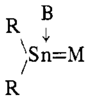
I

M = Cr, $x = 5$
M = Fe, $x = 4$
B = THF, DMSO, py

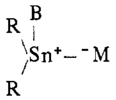
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot C_5H_5N$ shows the base molecule bonded to the tin atom in good accord with this formulation.[6] Compounds I bear an obvious conceptual relationship to the desired, three-coordinated "stannylene" complexes by simple removal of the neutral base molecule, but experimentally such a process in the iron case results in reconversion to the dimer,[5] and in the chromium case the syntheses of I do not proceed in noncoordinating solvents, nor has it been possible to remove the base from any of the known examples without decomposition.[3,4,6a] A number of electronic configurations can be drawn to represent the bonding of I, *i.e.*



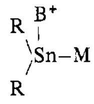
Ia



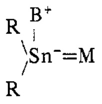
Ib



Ic



Id



Ie

where M is a transition metal carbonyl. Structure Ia represents both base and "stannylene" molecules acting as Lewis bases (σ donors); structure Ib includes back-donation from the filled d orbitals of the transition metal. In Ia and Ib the tin atom is in a subvalent, tin(II) oxidation state. Structure Ic represents tin as making four formal covalent bonds in an ylide form; in structure Id the positive charge is delocalized onto the base molecule, and in structure Ie back-donation from the filled d orbitals of the transition metal is shown. In structures Ic–Ie the tin atom is viewed as in a formal oxidation state of 4. The relatively small magnitudes of $J(^{117,119}Sn\text{-}C\text{-}^1H)$ for compounds I where R = CH$_3$ [for M = Cr and

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(1) (a) Northwestern University. (b) State University of New York at Albany.

(2) (a) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 16, 487 (1972); (b) E. O. Fischer, *Pure Appl. Chem.*, 30, 353 (1972); (c) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972).

(3) T. J. Marks, *J. Amer. Chem. Soc.*, 93, 7090 (1971).

(4) T. J. Marks, *Proc. Int. Conf. Coord. Chem.*, 14, 4 (1972).

(5) T. J. Marks and A. R. Newman, *J. Amer. Chem. Soc.*, 95, 769 (1973).

(6) M. D. Brice and F. A. Cotton, *J. Amer. Chem. Soc.*, 95, 4529 (1973).

(6a) Note Added in Proof. By the use of bulky R groups and a different synthetic route, it recently has been reported possible to prepare $R_2SnCr(CO)_5$ compounds: P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 317 (1973).

$x = 5$, $J = 23.0$ Hz for B = THF;[3] for M = Fe and $x = 4$, $J = 41.2$ Hz for B = py[5]], the fact that the tin moiety can be replaced by triphenylphosphine,[3] and the air sensitivity of the compounds[3,5] suggest that the tin atom might be in a subvalent state. Lowered values of ν(C-O) in the infrared spectra[3-5] indicate that the $B \cdot R_2Sn$ ligand unit is a strong electron donor. The need for more definitive studies to understand the electronic structures of these unusual compounds was recognized. ^{119m}Sn Mossbauer spectroscopy[7] and X-ray photoelectron spectroscopy (ESCA)[8] have proved useful in probing the electronic situation at the tin atom in tin-transition metal compounds.[9-11] We present here the results of studies of a series of $(t\text{-}C_4H_9)_2SnM(CO)_x \cdot B$ compounds, where B = base and M = Fe ($x = 4$) and Cr ($x = 5$), employing these spectroscopic techniques.

Results and Discussion

Table I presents ^{119m}Sn Mossbauer data for a number of compounds of formula I, along with other related tin compounds in which the tin atom is accepted to be tin(IV). Bis(cyclopentadienyl)tin(II), $(h^5\text{-}C_5H_5)_2Sn$,[12a] and its BF_3 adduct[12b] serve as unambiguous examples of a tin(II) derivative and its Lewis acid complex.

It can be generalized that tin(II) compounds exhibit isomer shift (IS) values greater than that of β-tin metal (IS = 2.56 mm/sec), while those of tin(IV) compounds fall below.[7a] Conventional tin-transition metal compounds of the formula $R_nSn[M(CO)_x]_{4-n}$, where R is an organic group, have IS values in the range 1.35-2.00 mm/sec with respect to $BaSnO_3$ for $n = 1\text{-}3$,[7a] but shifts to higher velocity are generally observed as n decreases,[9] and the highest IS values are found for the $n = 0$ compounds; for example, in $Sn[h^5\text{-}C_5H_5Fe(CO)_2]_4$, IS = 2.14 mm/sec, and in the central tin atom of $(CH_3)_2SnFe_2(CO)_8\mathit{Sn}Fe_2(CO)_8Sn(CH_3)_2$, IS = 2.20 mm/sec.[7a,13]

Quadrupole splitting (QS), which is a measure of the deviation of the electronic environment at the tin atom from cubic symmetry, varies considerably in tin-transition metal compounds, where many examples in which the tin atom is substituted by organic groups alone fail to exhibit any resolvable splitting at all. QS values are never above 1.4 mm/sec, even in the case of perfluorophenyl substitution in $R_nSn[M(CO)_x]_{4-n}$ systems, but QS values are large as 2.60 and 2.84 mm/sec have been found for derivatives with one or two halogen atoms at tin, respectively.[14]

Reference to Table I reveals two important features of the ^{119m}Sn Mossbauer data. First, the observed IS values for the $(t\text{-}C_4H_9)_2SnM(CO)_x \cdot B$ compounds fall on the same side of the IS for tin metal as does that of $(t\text{-}C_4H_9)_2SnCl_2$ and clearly into the region normally associated with the organic derivatives of tin(IV), including the conventional organotin-transition metal complexes, although to the high end of the $R_nSn[M(CO)_x]_{4-n}$ range.[14a] Second, the QS values are clearly larger than any thus far observed for four-coordinated tin structures,[7] and their magnitudes increase in the order pyridine < DMSO < THF. The Mossbauer spectrum of $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot THF$ is shown in Figure 1.

Table II presents ESCA binding energy data for the tin $3d_{5/2}$ electrons in the $(t\text{-}C_4H_9)_2SnM(CO)_x \cdot B$ compounds along with some model compounds. These data should, in nonionic lattices, reflect the total charge on the tin atom.[8,11,15] The most noteworthy feature of these data is that, within experimental error, the $(t\text{-}C_4H_9)_2SnM(CO)_x \cdot B$ compounds have the same binding energies as conventional tin-transition metal compounds.[11] The tin $3d_{5/2}$ electron binding energy of only one tin(II) compound, $[(C_2H_5)_4N] \cdot SnCl_3$, has been published thus far,[11] and it is not known at this time whether the ESCA experiment can distinguish between tin oxidation states.[15a] The scale of the data of our compounds (486.7-487.1 ± 0.2 eV) lies within the range of data for known tin(IV) compounds (486.3-488.3 eV)[11,15] but outside the value for the $SnCl_3^-$ salt (485.7 ± 0.1 eV).[11,15-17]

The Mossbauer and ESCA results can now be compared with other spectroscopic data for compounds I. $J(^{117,119}Sn\text{-}C\text{-}^1H)$ values are generally accepted as a measure of s-electron character in the orbitals directed by the tin atom toward carbon in a closely related series of four-coordinated organotin compounds,[18] and the concept has been tested recently by measurement of $J(^{117,119}Sn\text{-}^{13}C)$ values in variously substituted aryltrimethyltin compounds.[19] Examination of available data suggests that this same criterion may be applied to protons on β-methyl groups, although the two coupling constants are of opposite sign.[20] $^3J(^{119}Sn\text{-}C\text{-}C\text{-}^1H)$ for $(t\text{-}C_4H_9)_2SnCl_2$ is 114 Hz and for the tin-transition metal compounds is in the order $[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2 >$ I(M = Fe) > I(M = Cr) (see Table I). There is some indication that the Mossbauer IS values follow a trend opposite to this, but the differences are near the limit of experimental confidence.[21]

We begin our interpretation by returning to structures Ia-

(7) (a) J. J. Zuckerman, *Advan. Organometal. Chem.*, 9, 21 (1970); (b) P. J. Smith, *Organometal. Chem. Rev., Sect. A*, 5, 373 (1970); (c) R. V. Parish, *Progr. Inorg. Chem.*, 15, 101 (1972).

(8) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlson, I. Lindgren, and B. Lindberg, "ESCA; Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967.

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

(10) D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 8, 1771 (1969).

(11) G. W. Parshall, *Inorg. Chem.*, 11, 433 (1972).

(12) (a) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 91, 6885 (1969); (b) *ibid.*, 92, 2577 (1970).

(13) IS values for certain neutral Rh-Sn systems are claimed to be even higher, falling in the range 2.1-2.4 mm/sec [R. V. Parish and P. J. Rowbotham, unpublished results, quoted in ref 7c, p 189], but all are below the β-tin value, and the compounds can be regarded as containing tin making four covalent bonds.

(14) G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, *J. Chem. Soc., Dalton Trans.*, 2025 (1972).

(14a) Note Added in Proof. The recently prepared $(C_5H_5)_2Sn(py)Fe(CO)_4$ has been shown by nmr to contain monohapto-bound cyclopentadienyl groups, characteristic of Sn(IV) and corroborating the assignment of the tin atoms reported here: P. G. Harrison and J. A. Richards, private communication.

(15) W. E. Swartz, P. H. Watts, Jr., E. R. Lippencott, J. C. Watts, and J. E. Huheey, *Inorg. Chem.*, 11, 2632 (1972).

(15a) Note Added in Proof. However, this frequency probably cannot be related to oxidation state in a straightforward manner: P. A. Grutsch, M. V. Zeller, and T. P. Frehlner, *Inorg. Chem.*, 12, 1431 (1973).

(16) The actual extent of agreement cannot be judged accurately without Madelung corrections[17] for the ionic compounds in ref 11 and 15.

(17) (a) Reference 8, Chapter V; (b) C. S. Fradley, S. B. M. Hagstrom, M. E. Klein, and D. A. Shirley, *J. Chem. Phys.*, 48, 3779 (1968); (c) J. J. Jack and D. M. Hercules, *Anal. Chem.*, 43, 729 (1971).

(18) R. C. Poller, "The Chemistry of Organotin Compounds," Academic Press, New York, N. Y., 1970, p 233.

(19) (a) C. D. Schaeffer, Jr., and J. J. Zuckerman, *J. Organometal. Chem.*, 47, C1 (1973); (b) *ibid.*, in press.

(20) (a) Reference 18, p 241; (b) L. Verdonck and G. P. Van der Kelen, *Bull. Soc. Chim. Belg.*, 76, 258 (1967); (c) G. Barbieri and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1327 (1972); (d) S. E. Ulrich and J. J. Zuckerman, unpublished results.

(21) The J values in the Fermi contact mechanism measure the distribution of s-electron density along bonding axes, *i.e.*, in an anisotropic way, while the Mossbauer IS values reflect the total isotropic $|\psi_{ns}(0)|^2$ at the tin nucleus.

Table I. ^{119m}Sn Mossbauer and ^{1}H Nmr Coupling Constant Data

Compd[a]	mm/sec				$^3J(^{119}$Sn-C-C-^{1}H) ± 0.3, Hz
	IS ± 0.06[b]	QS ± 0.12	Γ_1	Γ_2	
$(h^5\text{-}C_5H_5)_2Sn$[c]	3.74[c]	0.86[c]			
$(h^5\text{-}C_5H_5)_2Sn\cdot BF_3$[d]	3.79[d]	0.90[d]			
$t\text{-}C_4H_9Sn(CH_3)_3$	1.41	0.00	1.11		65.7[e]
$(t\text{-}C_4H_9)_2SnCl_2$	1.79	3.07	1.16	1.23	114
$[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2$	1.83	1.16	0.85	1.36	79.1
$(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot$DMSO	1.87	3.45	1.14	1.09	70.0
$(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot$py	1.82	3.06	1.34	1.12	67.2
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$THF	2.11	4.14	1.32	1.14	56.0
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$DMSO	1.98	3.60	1.31	1.62	58.0
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$py	2.01	3.44	1.31	1.17	59.5

[a] THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, and py = pyridine. [b] Measured at 77°K relative to Ba^{119}SnO$_3$. None of the compounds listed here shows a spectrum at ambient temperature. [c] Reference 12a. [d] Reference 12b. [e] M. Gielen, M. de Clercq, and B. de Poorter, *J. Organometal. Chem.*, 34, 305 (1972).

Table II. ESCA Data[a]

Compd	Sn 3d$_{5/2}$ binding energy ± 0.2, eV[b]
$[(CH_3)_2SnFe(CO)_4]_2$	486.9
$[(C_6H_5)_2SnFe(CO)_4]_2$	486.8
$[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2$	487.1
$(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot$DMSO	487.0
$(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot$py	487.1
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$THF	486.7
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$DMSO	487.0
$(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$py	486.7

[a] Recorded at −100 ± 5°. [b] C 1s binding energy taken to be 285.0 eV.

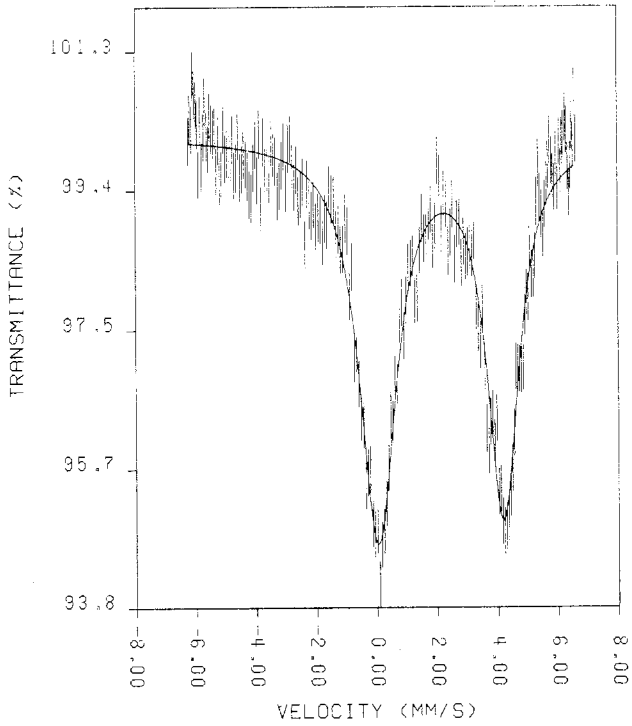

Figure 1. ^{119}Sn Mossbauer spectrum of $(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$THF at 77°K *vs.* Ba^{119}SnO$_3$.

Ie, where Ia and Ib portray the use of the lone pair available in the common three-coordinated tin(II) structure[22] in a σ-donor interaction with M. Three-coordination, provided by a molecule of base or by catenation in the solid state is the dominant feature of tin(II) structural chemistry,[22,23] and the Lewis base activity of the lone pair has been demonstrated in the BF$_3$ adduct of $(h^5\text{-}C_5H_5)_2Sn$.[12b] However, our Mossbauer IS, ESCA, and nmr coupling constant data rule out any description of compounds I requiring tin as tin(II). The only truly tin(II) transition metal complex thus far known, chlorobis[bis(1,2-diphenylphosphino)ethane]cobalt(II) trichlorostannate (IS = 3.10 ± 0.06 mm/sec), adopts an ionic form in the crystal with a remote SnCl$_3^-$ group.[24]

Structures Ic–Ie portray an ylide in which the tin atom contributes one electron to each of four two-electron σ bonds, one to an anionic transition metal fragment, and one to a cationic base molecule, to produce a situation similar to that found in the conventional four-coordinated tin–transition metal compounds. The formal oxidation state of the tin in these structures is tin(IV), with the principal difference between systems I and the more conventional derivatives being that the "base" is usually a halide or an organic anion. The anionic compounds $[Cl_3SnCr(CO)_5]^-$ [25] and $[(C_6H_5)_3SnFe(CO)_4]^-$ [26] can be viewed as precursors to systems I by replacement of Cl$^-$ or R$^-$ with a neutral base molecule such as THF, DMSO, or pyridine. The unprecedented large QS values we observe for compounds I apparently arise from the charge separation in the resulting ylide. According to this approach, changing from the neutral bases through Cl$^-$ to R$^-$ should decrease the QS as the base becomes more comparable to the transition metal moiety. The lack of resolvable QS in many $R_nSn[M(CO)_x]_{4-n}$ compounds presumably reflects the equivalence of R and M(CO)$_x$ in donor or base strength.

We likewise interpret the differences in the data for the three base molecules of our series—THF, DMSO, and pyridine—as a measure of the base strength of these moieties toward the remainder of the molecules or of their ability to delocalize the positive charge in structures Ic–Ie. The same order, py > DMSO > THF, is expected for both qualities. Localizing the charge onto the tin atom in going from pyridine to THF has the effect of increasing the IS slightly, but the effect on the QS is very pronounced. Delocalization from THF back to pyridine reduces the electric field gradient at the tin nucleus and lowers the QS. Thus structure Ic would make a larger contribution in the THF derivative, as would structures Id and Ie for the pyridine analog for each metal.

Differences between the iron and chromium systems are also of interest. Compounds I for M = Fe show smaller IS

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(22) J. D. Donaldson, *Progr. Inorg. Chem.*, 8, 287 (1966).

(23) B. Y. K. Ho and J. J. Zuckerman, *J. Organometal. Chem.*, 49, 1 (1973).

(24) J. K. Stalick, D. W. Meek, B. Y. K. Ho and J. J. Zuckerman, *J. Chem. Soc., Chem. Commun.*, 630 (1972).

(25) J. K. Ruff, *Inorg. Chem.*, 6, 1502 (1967).

(26) T. Kruck and B. Herber, *Angew. Chem., Int. Ed. Engl.*, 7, 374 (1968).

and QS and larger $^3J(^{119}Sn\text{-}C\text{-}C\text{-}^1H)$ for a given base. In our view this reflects the greater ability of the $Fe(CO)_4$ group to accomodate negative charge or to act as a σ acceptor. This would lead to a reduced QS through the more effective delocalization of imbalanced charge from tin, a reduced IS through a reduction in charge density at the tin nucleus, and an increased $^3J(Sn\text{-}H)$ through an isovalent rehybridization at the tin atom which would direct a hybrid orbital with more p character toward the iron atom, leaving a greater amount of s character directed along the bonding axes to carbon.

Structure Ie may be more important for chromium than for iron, since earlier transition metals are expected to be better able to engage in π back-bonding. Reference can be made to the lower $\nu(C{=}N)$ frequencies (by 40–70 cm^{-1}) for pentacarbonylchromium isocyanide complexes, suggesting increased flow of electron density into the $-N{=}C$ π^* orbitals as compared with tetracarbonyliron complexes.[27] The contribution of structure Ie would be expected to increase the QS because of the more acute concentration of charge imbalance in the tin-base molecule portion of the compound.

Thus the bonding in compounds I can be described by major contributions from structures Ic–Ie. Admixture of analogous electronic structures successfully rationalizes bonding trends in the carbene complexes.[2a] The principal difference between the carbon systems and those of its lower cogeners in the fourth group then lies in the means of stabilization preferred. All isolable carbene complexes necessarily contain atoms with lone-pair electrons adjacent to the carbene carbon (internal stabilization[2a]), but reports in the literature suggest that a second series of complexes in which carbon makes four bonds instead of three is becoming known.[28] These ylide complexes of the transition metals are the direct analogs of our compounds I where stabilization is provided by a bonded molecule of base and are probably best described as containing tetravalent carbon. This suggests that the true, three-coordinated stannylene complexes are likely to be found to be those in which an atom with lone-pair electrons is adjacent to tin to provide internal stabilization.[29]

Experimental Section

Compounds I were synthesized as described previously[3-5] and were handled with rigorous exclusion of air.

Mossbauer Studies. Data were collected using our cam-drive, constant-acceleration spectrometer at 77°K *vs.* $Ba^{119m}SnO_3$ (New England Nuclear Corp.). Our curve-fitting procedure has been previously described.[30]

ESCA Studies. Spectra were recorded on an AEI-ES100B spectrometer. All air-sensitive samples were prepared, mounted, and introduced into the instrument using a nitrogen-filled glove bag attached to the entry port. Spectra were recorded at $-100 \pm 5°$ to prevent sublimation or loss of base. Several scans were made of each sample to ensure reproducibility and to check for possible X-ray damage, and all data reported represent average values derived from a minimum of three determinations. A PDP-8S computer, interfaced with the spectrometer, was employed for time averaging when necessary. Samples were deliberately exposed to air after recording spectra and rerun to determine the effect of oxidation. Relative binding energies were calculated using the C 1s line (taken to be at 285.0 eV) as the standard. It was assumed in these calculations that Madelung corrections would not significantly affect the relative binding energies in a closely related series of compounds.

Acknowledgment. We thank the National Science Foundation under Grants GP-16,544 (B. Y. K. H., D. L. T., and J. J. Z.) and GP-30,623X (G. W. G. and T. J. M.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this research.

Registry No. $t\text{-}C_4H_9Sn(CH_3)_3$, 3531-47-3; $(t\text{-}C_4H_9)_2SnCl_2$, 19429-30-2; $[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2$, 40827-47-2; $(t\text{-}C_4H_9)_2SnFe(CO)_4 \cdot DMSO$, 40925-20-0; $(t\text{-}C_4H_9)_2SnFe(CO)_4 \cdot py$, 40832-35-7; $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot THF$, 40904-68-5; $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot DMSO$, 40904-69-6; $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot py$, 40904-70-9; $[(CH_3)_2SnFe(CO)_4]_2$, 15615-58-4; $[(C_6H_5)_2SnFe(CO)_4]_2$, 29889-95-0.

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(27) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley–Interscience, New York, N. Y., 1969, p 25.

(28) (a) P. A. Arnup and M. C. Baird, *Inorg. Nucl. Chem. Lett.*, 5, 65 (1969); (b) C. Kruger, B. L. Barnett, and Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 10, 841 (1971); (c) F. R. Kreissl, C. G. Kreiter, and E. O. Fisher, *ibid.*, 11, 643 (1972); (d) J. Keeton, R. Mason, and D. R. Russell, *J. Organometal. Chem.*, 33, 259 (1971); (e) F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fisher, *Chem. Ber.*, 106, 1262 (1973).

(29) (a) Recent chemical[29b] and spectroscopic [29c] results lead to an interpretation of the three-coordinated carbon–transition metal compounds as onium complexes; (b) A. Davison and D. L. Reger, *J. Amer. Chem. Soc.*, 94, 9237 (1972); (c) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972).

(30) N. W. G. Debye, D. E. Fenton, S. E. Ulrich, and J. J. Zuckerman, *J. Organometal. Chem.*, 28, 339 (1971).