Facile and Reversible Homolysis of Iron–Germanium, –Tin, and –Lead Bonds by Lewis Bases

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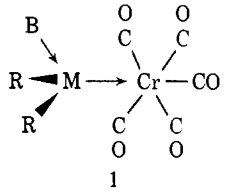
Abstract: Molecules of the general formula $[R_2MFe(CO)_4]_2$, M = Ge, Sn, or Pb, readily and reversibly undergo homolytic cleavage by relatively weak Lewis bases to produce tetracarbonyliron complexes of the general formula base$\cdot R_2M \rightarrow Fe(CO)_4$. The relative cleavage propensity for metals is Ge > Sn $\geq$ Pb and for bases is pyridine > acetone > tetrahydrofuran > diethyl ether. It is seen that diaryl- and dialkylgermylenes, -stannylenes, and -plumbylenes, when coordinated to a transition metal, can still function as strong Lewis acids.

Divalent group IV molecules are of considerable interest to chemists, and as a parallel to the rapidly expanding coordination chemistry of divalent carbon,[1] we began to explore the possibility of synthesizing analogous complexes of silylenes, germylenes, stannylenes, and plumbylenes.[2] The ultimate goal of such studies is to better understand the nature of highly reactive, divalent group IV radicals[2,3] *via* their coordination compounds.[4]

We recently reported[5] on dialkylgermanium and tin pentacarbonylchromium systems, which form complexes which we formulated as **1**. This proposal has



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M = Ge, Sn; B = Lewis base

now been verified by X-ray diffraction.[6] These complexes possess a number of properties differing sharply from the more classical Ge(IV) and Sn(IV) transition metal compounds[7] and from potentially homologous carbene complexes.[1] One of the most apparent of these properties is the requirement[5,8] of a molecule of base, B, for stabilization of the "germylene" and "stannylene" complexes. Evidence that such a ligation pattern may have considerable generality is provided by the following systematic generation of analogous germanium, tin, and lead tetracarbonyliron complexes *via* a novel homolysis reaction of metal–metal bonds, which readily (and reversibly) cleaves molecules of the general formula $[R_2MFe(CO)_4]_2$, M = Ge, Sn, or Pb, yielding molecules of the general formula $B\cdot R_2MFe(CO)_4$.

Experimental Section

The synthesis and handling of all organometallics were carried out under an atmosphere of prepurified nitrogen. All common solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Pyridine was stored over Davison 4 Å molecular sieves and then under nitrogen and was refluxed and distilled from barium oxide.

Synthesis. $[R_2MFe(CO)_4]_2$ molecules, M = Ge, Sn, or Pb, could all be synthesized by the reaction of $Na_2Fe(CO)_4$[9] with the corresponding R_2MCl_2 compound in THF (tetrahydrofuran). Work-up consisted of evaporation of the solvent and extraction with hexane (R = alkyl) or toluene (R = aryl). The filtered extract for R = alkyl was reduced in volume until crystallization commenced and then slowly cooled to $-78°$ to obtain the crystalline product. Hexane or pentane was employed for succeeding recrystallizations. In the case of R = aryl, the toluene solution was reduced in volume, hexane was added until cloudiness, and the mixture crystallized by slowly cooling to $-78°$. Subsequent recrystallization of aryl compounds was performed in toluene–hexane or CH_2Cl_2–hexane mixtures. The known $[R_2MFe(CO)_4]_2$ compounds (where R = CH_3, M = Ge;[10] R = CH_3, M = Sn;[11] R = C_4H_9, M = Pb;[12] R = C_6H_5, M = Ge;[13] R = C_6H_5, M = Sn;[14] and R = C_6H_5, M = Pb[15]) were identified by melting point, infrared spectrum, or by elemental analysis, if insufficient data were available in the literature reference.

The following preparation of a new compound illustrates the details of the $Na_2Fe(CO)_4$ + R_2SnCl_2 reaction procedure.

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(1) (a) E. O. Fischer, *Pure Appl. Chem.*, 30, 353 (1972); (b) O. S. Mills, *ibid.*, 20, 127 (1969); (c) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972); (d) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972).

(2) We follow the nomenclature adopted for divalent silicon: W. H. Atwell and R. D. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(3) (a) P. L. Timms, *Prep. Inorg. React.*, **4**, 59 (1968); (b) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *Fortsch. Chem. Forsch.*, **26**, 1 (1972); (c) J. D. Donaldson, *Progr. Inorg. Chem.*, **8**, 287 (1967); (d) W. P. Neumann, "The Organic Chemistry of Tin," Wiley, New York, N. Y., 1970, Chapter 14; (e) W. P. Neumann, *Angew. Chem., Int. Ed. Engl.*, **2**, 165 (1963); (f) W. P. Neumann and K. Kühlein, *Justus Liebigs Ann. Chem.*, **683**, 1 (1965), and references therein; (g) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(4) G. Schmid and H. J. Balk, *Chem. Ber.*, **103**, 2240 (1970). A dichlorosilylene complex.

(5) (a) T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 7090 (1971); (b) T. J. Marks, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR-23; (c) T. J. Marks, *Proc. Int. Conf. Coord. Chem.*, **14**, 4 (1972).

(6) F. A. Cotton, private communication. We are grateful to Professor Cotton for agreeing to undertake the study of the complex in which R = *tert*-butyl and B = pyridine.

(7) (a) E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev., Sect. A*, 227 (1970); (b) J. F. Young, *Advan. Inorg. Chem. Radiochem.*, **11**, 92 (1968); (c) F. G. A. Stone in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968, p 283 .

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(10) O. Kahn and M. Bigorgne, *C. R. Acad. Sci., Ser. C*, **262**, 906 (1966).

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(12) F. Hein, H. Pobloth, and E. Heuser, *Z. Anorg. Allg. Chem.*, **254**, 138 (1947).

(13) E. H. Brooks and W. A. G. Graham, Proceedings, 4th International Conference Organometallic Chemistry, Paper A2, Bristol, July 1969.

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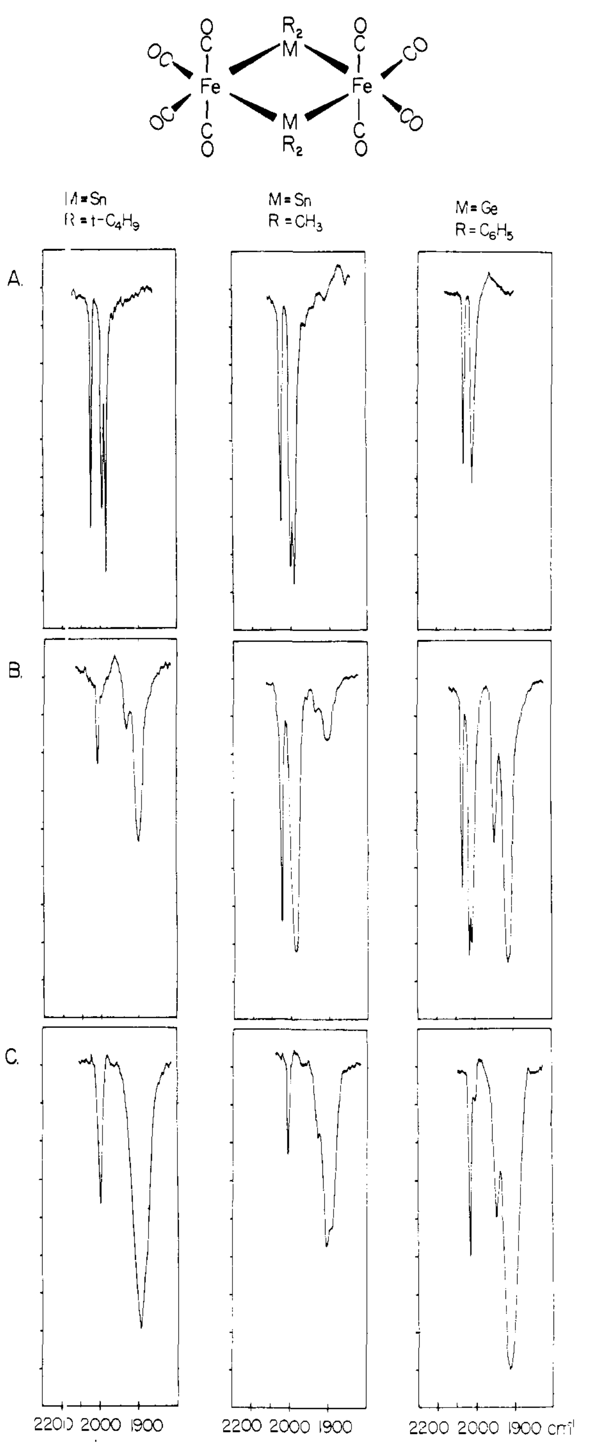

Figure 1. Infrared spectra in the C–O stretching region as a function of solvent: A, hydrocarbon (cyclohexane or benzene); B, tetrahydrofuran; C, pyridine.

Di-μ-dimethylstannylene-bis(tetracarbonyliron). To 2.0 g (9.1 mmol) of $Na_2Fe(CO)_4$ suspended in 60 ml of THF at −60°, was added 2.5 g (8.0 mmol) of $(t\text{-}C_4H_9)_2SnCl_2$,[16] and the mixture, with stirring, was allowed to warm to room temperature over a period of 5 hr. After an additional 2 hr of stirring, the solvent was removed from the red-orange mixture *in vacuo*. The oily orange residue was next extracted with 50 ml of warm hexane, the extract suction filtered through diatomaceous earth under nitrogen, and the residue washed with (3 × 10 ml portions) hexane. The combined filtrate was evaporated to *ca.* 50 ml (yellow solid began to precipitate) and was then cooled to −78° over a period of 10 hr. Next, the supernatant was removed from the solid product *via* syringe and the product washed with 10 ml of precooled (−78°) hexane. After the material was dried under high vacuum, the hexane recrystallization procedure was repeated to yield 1.6 g (50%) of golden yellow platelets (the melting point showed slow decomposition beginning at 170°).

Anal. Calcd for $C_{24}H_{36}Fe_2Sn_2O_8$: C, 35.95; H, 4.54. Found: C, 36.24; H, 4.60.

(Pyridine-dimethylgermylene)tetracarbonyliron. To 200 mg (0.37 mmol) of $[(CH_3)_2GeFe(CO)_4]_2$ was added 5 ml of pyridine, and the resulting solution was suction filtered under nitrogen. The orange filtrate was then slowly evaporated (5 hr) under a stream of nitrogen to yield a thick, dark red oil. Scratching induced crystallization, and the dark orange product was then washed with 5 ml of hexane and blown dry under a nitrogen stream, to yield 240 mg (92%) of dark orange crystals; infrared spectrum (Nujol mull): ν_{CO} (cm^{-1}) at 2010 m, 1920 sh, 1990 vs.

Anal. Calcd for $C_{11}H_{11}NFeGeO_4$: C, 37.78; H, 3.18; N, 4.01. Found: C, 37.14; H, 3.15; N, 3.95.

(Pyridine-di-*tert*-butylstannylene)tetracarbonyliron. The above procedure was followed with 200 mg (0.25 mmol) of $[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2$ to yield 210 mg (88%) of orange-brown microcrystalline material.

Anal. Calcd for $C_{17}H_{23}NSnFeO_4$: C, 42.54; H, 4.84; N, 2.92; Fe, 11.64. Found: C, 40.62; H, 4.74; N, 2.61; Fe, 11.30.[17]

Infrared spectrum (Nujol mull): ν_{CO} (cm^{-1}) at 2010 m, 1930 m, sh, 1885 vs.

Attempted Synthesis of (Pyridine-dimethylstannylene)tetracarbonyliron. The above procedure was employed with 200 mg (0.32 mmol) of $[(CH_3)_2SnFe(CO)_4]_2$. When the resulting red oil crystallized and was washed with hexane, the crystalline product was considerably lighter in color than in the above two cases. An infrared spectrum (Nujol mull) was identical with that of the starting material, *i.e.*, ν_{CO} (cm^{-1}) 2045 m and 1975 vs.

Di-μ-dimethylstannylene-bis[(tributylphosphine)tricarbonyliron]. This is a modified version of the procedure used for $[(C_4H_9)_2SnFe(CO)_3P(C_2H_5)_3]_2$.[18] To 2.0 g (3.16 mmol) of $[(CH_3)_2SnFe(CO)_4]_2$ in 50 ml of dry benzene was added 3.0 ml (*ca.* 16 mmol) of tributylphosphine. The mixture was stirred under reflux until infrared spectra indicated that the starting material had been consumed (48 hr). Next, the benzene solution was evaporated to about 10 ml under a stream of nitrogen. This solution was applied to a column of Merck acid-washed alumina prepared in hexane. Elution with hexane produced a single yellow band which was collected under nitrogen. Evaporation of the eluate under vacuum resulted in an oily yellow solid consisting of the desired product and what was assumed to be $[(C_4H_9)_3P]_2Fe(CO)_3$ (ν_{CO} = 1876 cm^{-1}). Repeated recrystallization from hexane at −78° yielded $[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$ as a pale yellow, crystalline solid, 250 mg (8%) (mp, slow decomposition beginning at 120°).

Anal. Calcd for $C_{34}H_{66}Sn_2Fe_2P_2O_6$: C, 41.58; H, 6.79. Found: C, 41.39; H, 6.88.

Instrumental Measurements. Cryoscopic molecular weight measurements were performed on an apparatus[19] constructed by Professor D. F. Shriver of this Department. Osmometric determinations were performed under argon on a Mecrolab osmometer equipped with an inert atmosphere inlet accessory. Conductivity measurements were made with an Industrial Instruments Model RC 16B1 conductivity bridge (at 1000 Hz) and a Yellow Springs Instruments YSI3400 conductivity cell. The cell was part of a vacuum-tight Schlenk apparatus which allowed measurements to be performed under nitrogen. We thank Professor F. Basolo for the use of this appartus.

Nmr studies were performed on a Varian T-60 (60 MHz) or a Bruker HFX-90 (90 MHz) instrument. Samples were prepared under nitrogen using dry, degassed solvents.

Routine infrared spectra were recorded on a Beckman IR-5 spectrophotometer and were calibrated with polystyrene film. Analytical work was performed on a Beckman IR-9 instrument which had been previously calibrated. Sample solutions were protected from the air at all times, and spectra were run in the evacuable so-

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(16) C. K. Chu and J. D. Murray, *J. Chem. Soc. A*, 360 (1971).

(17) Carbon analyses were consistently low and varied widely for the same sample from laboratory to laboratory. The result given here is that of Miss H. Beck, Northwestern University Analytical Services Laboratory.

(18) M. Bigorgne and O. Kahn, *J. Organometal. Chem.*, 10, 137 (1967).

(19) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 159.

Table I. Solution Infrared Data[a] for $[R_2MFe(CO)_4]_2$ Molecules

R_2M	Hydrocarbon	Tetrahydrofuran[b]	Pyridine[b]
$(t\text{-}C_4H_9)_2Sn$	2045 s, 1994 s, 1984 vs	2018 ms, 1940 m, 1900 vs	2005 s, 1896 vs
$(CH_3)_2Sn$	2050 s, 2000 s, 1990 vs	*c*, 1936 w, 1906 m	2010 s, 1928 m, sh, 1903 vs, 1895 sh
$(C_6H_5)_2Sn$	2060 s, 2008 vs	2028 m, 1945 w, 1915 s	2021 s, 1934 sh, 1907 vs
$(CH_3)_2Ge$	2061 s, 2007 vs	*c*, 1939 s, 1908 vs	2021 s, 2040 m, sh, 1908 vs
$(C_6H_5)_2Ge$	2065 s, 2018 vs	2029 s, 1948 m, 1914 vs	2030 s, 1947 m, 1912 vs
$(n\text{-}C_4H_9)_2Pb$	2038 s, 1990 s, 1980 vs	*c*, 1945 vw, 1914 w	2012 m, 1908 s
$(C_6H_5)_2Pb$	2049, 2020 w, sh, 2000 vs	2029 m, 1951 m, 1925 s, 1900 sh	2025 s, 1945 m, sh, 1909 vs
$[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$	2000 w, 1975 s, 1938 vs	No monomer observed	1839 s[d]

[a] In cm^{-1}; m = medium, s = strong, w = weak, sh = shoulder. [b] Only the bands for the cleavage product are given. [c] Overlap with dimer band prevented observation. [d] All molecules were *ca.* 100% dissociated in pyridine except this one (*ca.* 40% dissociated).

Table II. Conductivity and Solution Molecular Weight Data for $[R_2MFe(CO)_4]_2$ Molecules

R_2M	Molecular weight[a]	Solvent	Ref	Molar conductivity,[b] $ohm^{-1}\ cm^2\ mol^{-1}$
$(t\text{-}C_4H_9)_2Sn$	880 (804)	Benzene	*c*	0.37
	389	Pyridine	*c*	
$(CH_3)_2Ge$	579 (541)	Benzene	*c*	0.19
	254	Pyridine	*c*	
$(CH_3)_2Sn$				0.070
$(n\text{-}C_4H_9)_2Pb$	950 (979)	Benzene	12	0.12
$(C_6H_5)_2Ge$				0.065
$(C_6H_5)_2Pb$	"Dimeric" (1059)	Benzene	15b	
$[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$	1026 (982)	Benzene	*c*	

[a] Quantity in parentheses is the calculated value for the dimer. [b] For 0.005 *M* (in dimer) pyridine solutions. [c] This work. Benzene solutions were studied by osmometry or cryoscopy and pyridine solutions by cryoscopy.

dium chloride cells previously described[20] or in demountable, balanced, nitrogen-flushed IRtran-2 cells. Several of the phenyl compounds were found to slowly react with sodium chloride. Nujol mulls were prepared under a blanket of nitrogen. In all cases several scans were made of each spectrum to monitor any decomposition which might be growing in, or, in the case of quantitative equilibrium studies, to ensure that the system had attained equilibrium. These quantitative studies were performed on THF solutions. It was assumed that the extinction coefficient determined for a solution of $(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot THF$ of known concentration (the corresponding dimer dissociates completely in THF) was the same for all cleavage complexes. The extinction coefficient for *undissociated* dimers in THF was obtained from data on solutions of $[(C_4H_9)_2PbFe(CO)_4]_2$ at known concentrations—this molecule dissociates to a small extent.

Results

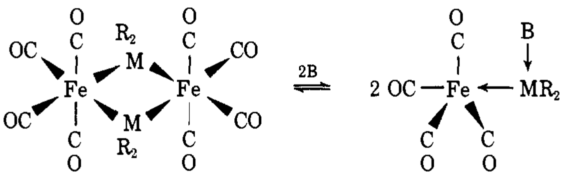
Though a variety of chemical transformations have been employed to obtain $[R_2MFe(CO)_4]_2$ molecules,[10–15] few appear to be either general or convenient. For this study, these molecules were synthesized *via* the reaction

$$Na_2Fe(CO)_4 + R_2MCl_2 \longrightarrow [R_2MFe(CO)_4]_2$$

which, when the tetracarbonylferrate dianion is employed as a pure, white powder,[9a] proceeds cleanly and in high yield.

The structure of these dimers has been well established in the solid state[21] and is schematized at the top of Figure 1. Likewise, vibrational studies[10,14b,18] (also see Table I) and colligative properties (Table II) indicate that the integrity of this structure persists in noncoordinating solvents. All of these molecules possess considerable (for metal carbonyl compounds) thermal and chemical stability. Thus, it was with some enthusiasm that we noted the changes which took place in the infrared spectra on going from noncoordinating to coordinating solvents, as illustrated in Figure 1.

We interpret these changes as manifestations of the equilibrium 1, which requires what is formally an unprecedented type of homolytic cleavage reaction for metal–metal bonds. The cleavage products, **3**, are completely analogous to the pentacarbonylchromium "germylene" and "stannylene" complexes.[5] We offer the following proof for such a deduction. First, the infrared spectra (Figure 1, Table I) of the cleavage products, **3**, in the structurally diagnostic C–O stretching region are in excellent accord with approximately C_{3v} (trigonal bipyramidal) $LFe(CO)_4$ molecules.[22] Indeed, the band patterns are quite similar, though lower in frequency, to known tetracarbonyliron carbene complexes.[23] The spectra are also strikingly similar to the



(1)

2 **3**

2a, M = Ge; R = CH_3
b, M = Ge; R = C_6H_5
c, M = Sn; R = CH_3
d, M = Sn; R = $t\text{-}C_4H_9$
2e, M = Sn; R = C_6H_5
f, M = Pb; R = $n\text{-}C_4H_9$
g, M = Pb; R = C_6H_5

B = THF, pyridine, acetone, acetonitrile, diethyl ether, dimethylformamide

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(20) T. J. Marks, *J. Chem. Educ.*, **48**, 167 (1971).

(21) (a) C. J. Gilmore and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1387 (1972); (b) J. C. Zimmer and M. Huber, *C. R. Acad. Sci., Ser. C*, 267, 1685 (1968); (c) C. J. Fritchie, R. M. Sweet, and R. Schunn, *Inorg. Chem.*, **6**, 749 (1967).

(22) (a) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960); (b) L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969); (c) G. Bor, *Inorg. Chim. Acta*, **1**, 81 (1967); (d) A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.*, **3**, 341 (1965).

(23) (a) K. Öfele and C. G. Kreiter, *Chem. Ber.*, **105**, 529 (1972); (b) E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Müller, and E. Winkler, *ibid.*, **105**, 162 (1972). (c) In the chromium system,[5] observed frequencies were also somewhat lower than in the corresponding

Table III. Pmr Data for $[R_2MFe(CO)_4]_2$ Molecules

R_2M	Solvent	Chemical shifts[a]	$J_{^{117,119}Sn-CH_3}$[b]
$(t\text{-}C_4H_9)_2Sn$	Benzene	8.35	79.1
	Pyridine	8.95	67.2
$(CH_3)_2Sn$	Benzene	8.95	43.0
	Pyridine	9.0	41.2
$(CH_3)_2Ge$	Benzene	8.70	
	Pyridine	8.90	
$(n\text{-}C_4H_9)_2Pb$[c]	Benzene	6.80 (2 H) "triplet," 7.90 (2 H) multiplet 8.40 (2 H) multiplet; 8.93 (3 H) "triplet"	
$[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$	Benzene	8.40 (*ca.* 18 H) multiplet 8.95 (*ca.* 15 H) multiplet	

[a] In τ, estimated error ±0.025 ppm. [b] In Hz, estimated error ±0.4 Hz. Measured from the center of the satellite. [c] No ^{207}Pb satellites were observed.

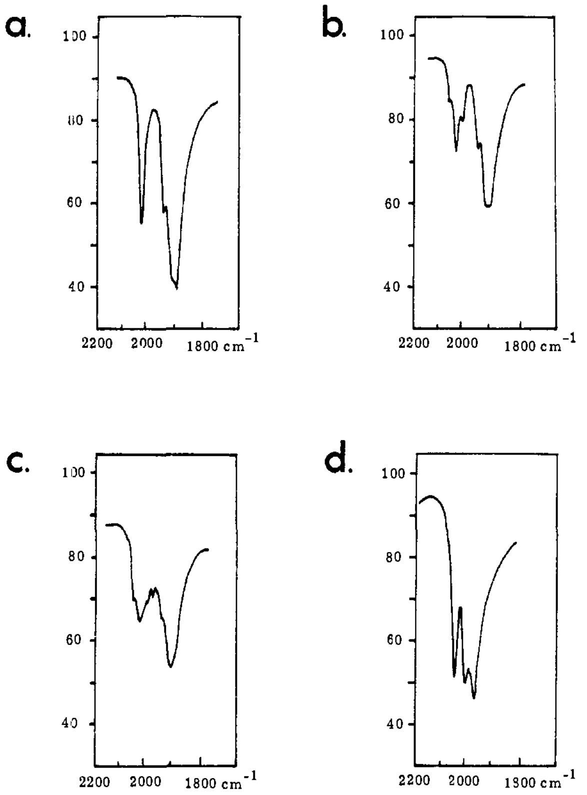

Figure 2. Nujol mull infrared spectra illustrating the solid-state transformation of $(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot$pyridine to $[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2$ at 80° (10^{-3} mm): a, start; b, after 4 hr; c, after 10 hr; d, after 30 hr, identical with $[(t\text{-}C_4H_9)_2SnFe(CO)_4]_2$.

closely related anionic compounds $(C_6H_5)_3SiFe(CO)_4^-$ [24] and $(C_6H_5)_3SnFe(CO)_4^-$.[25] When the molecule $[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$ is cleaved in pyridine, the product exhibits a single strong C–O stretch in the infrared spectrum at 1839 cm^{-1}, indicative of the near D_{3h} symmetry expected for a *trans*-LL'Fe(CO)$_3$ complex.[22] Further proof of equilibrium 1 is provided by colligative data (Table II) which indicate essentially complete dissociation of the dimers in pyridine. That equilibrium 1 does not involve solvent-induced ***heterolytic*** cleavage reactions, which have been previously observed[26] for some group IV metal–transition metal compounds, is demonstrated by the low electrical conductivities[26b] observed for our systems in pyridine (Table II).[27–29] Proton nmr data (Table III) featuring a decrease in the magnitude of $J_{^{117,119}Sn-CH_3}$ in coordinating solvents suggest a somewhat lower valence state for tin[30] in the cleavage product; similar observations were made in the pentacarbonylchromium system.[5] Also several of the adducts, **3**, could be isolated (*vide infra*) and their stoichiometry was precisely that suggested by equilibrium 1. The ^{119}Sn Mössbauer parameters for the tin containing adducts are similar to those of the pentacarbonylchromium dialkyltin complexes.[5] The unusually large quadrupole splitting is again evident.[31,32] The above facts provide strong support for the chemical/structural model represented by equilibrium 1.

It is next appropriate to discuss kinetic and thermodynamic aspects of reaction 1. In all cases, save that of $[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$, equilibrium 1 was attained in the time required to prepare solutions, fill cells, and record spectra (*ca.* 5 min). For the tributylphosphine substituted molecule, about 15 min was required for equilibration in pyridine. It was possible in several cases to isolate the adducts, **3**. For B = THF, evaporation of the solvent *in vacuo* regenerated the corresponding dimers; however, for stronger bases such as pyridine, the adducts of **2a** and **2d** could be isolated. These gave up pyridine in the solid state under more vigorous conditions to again regenerate the dimers; an example is presented in Figure 2. Proton nmr spectra of either of the adducts in benzene-d_6 with added dimer revealed discrete methyl resonances for **2** and **3**. This indicated that equilibrium 1 is slow on the nmr timescale at room temperature and experimentally accessible concentrations (*ca.* 0.01 *M*). However, when excess pyridine is incrementally added to benzene-d_6 solutions of the adducts, broadened, averaged pyridine resonances are observed which grad-

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carbene complexes. (d) The lowest frequencies yet reported for an analogous carbene complex (2043 m, 1962 m, 1927 s cm^{-1}) are for (1,3-dimethylimidazolinylidene)tetracarbonyliron.[23a]

(24) Th. Kruck, E. Job, and U. Klose, *Angew. Chem., Int. Ed. Engl.*, 7, 374 (1968); ν_{CO} (THF) at 2007, 1906, and 1880 cm^{-1}.

(25) Th. Kruck and B. Herber, *ibid.*, **8**, 679 (1969); ν_{CO} (Nujol mull) at 2001, 1923, 1897, and 1877 cm^{-1}.

(26) (a) A. Davison and J. E. Ellis, *J. Organometal. Chem.*, **36**, 113 (1972); (b) J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4562 (1969).

(27) For typical strong electrolyte data in pyridine, see D. S. Burgess and C. A. Kraus, *ibid.*, 70, 706 (1948), and references therein.

(28) Conductivities are slightly higher in dimethylformamide. Presumably the high dielectric constant facilitates heterolysis.[26b]

(29) The curved Λ *vs.* $\sqrt{C}$ plot for 2d in pyridine is characteristic of a weak electrolyte: W. G. Castellan, "Physical Chemistry," Addison-Wesley, Reading, Mass., 1964, Chapter 27.

(30) (a) N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, **85**, 1377 (1963); (b) D. E. Fenton and J. J. Zuckerman, *ibid.*, **90**, 6226 (1968).

(31) (a) B. Y. K. Ho, T. J. Marks, and J. J. Zuckerman, to be submitted for publication. (b) $(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot$pyridine: IS = 2.01; QS = 3.44 mm/sec; $(t\text{-}C_4H_9)_2SnFe(CO)_4\cdot$pyridine: IS = 1.82, QS = 3.06 mm/sec. Isomer shifts are relative to $BaSnO_3$. We thank Professor Zuckerman for these measurements.

(32) (a) J. J. Zuckerman, *Advan. Organometal. Chem.*, **9**, 22 (1970); (b) R. V. Parish, *Progr. Inorg. Chem.*, **15**, 101 (1972).

ually shift toward the positions for free pyridine. Thus, the base molecules are substitutionally quite labile, as found in the chromium system.[5]

The relative abilities of various bases to cleave the dimers, **2**, and the position of equilibrium 1 with base held constant, were also examined. Because it was not possible to calculate infrared extinction coefficients in a number of solvents, owing to the fact that these calculations (see Experimental Section) require that one dimer in the series **2a**–**2g** be completely and one negligibly dissociated, only a qualitative statement can be made concerning relative tendencies to cleave (that is, the position of equilibrium 1), *viz.*, pyridine > acetone > THF > diethyl ether. This ordering parallels the affinity of $(CH_3)_3SnCl$ for the same bases.[33] It was also possible to obtain quantitative data on the relative dissociation of **2a**–**2g** in a single solvent, THF. The results (Table IV) reveal two obvious trends. First, the propensity for cleavage decreases on descending group IV, *i.e.*, Ge > Sn ≥ Pb. This observation could reflect differences in electronegativity, hence acidity, as well as differences in the strengths of the heteronuclear metal–metal bonds. However, most qualitative observations[7] suggest that lead–transition metal bonds are weaker than those involving germanium or tin. Secondly, there is apparently a significant steric effect, the bulky *tert*-butyl group favoring dissociation. Structural data[21] also indicate that steric repulsion could, in some cases, be considerable. The promotion of cleavage by phenyl relative to methyl may reflect both steric and electronic effects. That tributylphosphine substitution for carbon monoxide markedly decreases the dissociation of **2b** is probably due to the increased electron density on iron, which lessens the acidity of the tin.

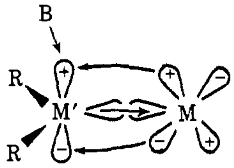
Table IV. Dissociation of $[R_2MFe(CO)_4]_2$ Molecules in Tetrahydrofuran

R_2M	10^2K_{dissoc}[a]	% dissociation[b]
$(t\text{-}C_4H_9)_2Sn$		100.0
$(C_6H_5)_2Ge$	1.58	46.1
$(CH_3)_2Ge$	0.765	35.2
$(C_6H_5)_2Sn$	0.586	31.6
$(C_6H_5)_2Pb$	0.577	31.3
$(CH_3)_2Sn$	0.599	11.5
$(n\text{-}C_4H_9)_2Pb$	0.0174	6.4
$[(CH_3)_2SnFe(CO)_3P(C_4H_9)_3]_2$		<2.0

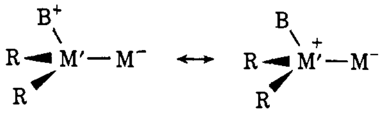
[a] Defined as K_{dissoc} = [monomer]^2/[dimer]. [b] Calculated for a 0.01 *M* solution.

Discussion

This work demonstrates that certain metal–metal bonded systems can be readily cleaved by relatively weak Lewis bases to yield base-coordinated germylene, stannylene, and plumbylene complexes. Besides representing what may be part of an extensive new class of homolysis reactions for metal–metal bonds, this reaction pattern further substantiates the growing evidence[5,8,34] that coordinated divalent group IV metal and metalloid species can behave simultaneously as strong, coordinatively unsaturated Lewis acids and strong Lewis bases. There are also indications that carbene complexes can exhibit similar behavior.[35] Whether complexes of this type are best regarded and named as derived from coordination compounds of divalent group IV radicals, A, in which π back-bonding from the transition metal is insufficient alone to quench the acidity of the empty p orbital, or whether an ylide structure, B, involving a clearly tetravalent group IV species is a more accurate representation, still presents a problem.[36] In any case, it is evident that the molecule of base is a necessary and integral part of these dialkyl and diaryl "germylene," "stannylene," and "plumbylene" complexes. Whether this conclusion can be generalized to include reaction intermediates or systems with strong π-donating rather than alkyl and aryl residues is under investigation.



A



B

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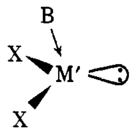
(33) T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3921, 5730 (1966).

(34) (a) T. J. Marks and A. M. Seyam, *J. Organometal. Chem.*, **31**, C62 (1971); (b) M. D. Curtis and R. C. Job, *J. Amer. Chem. Soc.*, **94**, 2153 (1972); (c) G. Schmid and R. Boese, *Chem. Ber.*, **105**, 3306 (1972).

(35) (a) C. G. Kreiter, Summer Inorganic Chemistry Symposium, Buffalo, N. Y., June 1972; (b) F. R. Kreissl, C. G. Kreiter, and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 643 (1972); (c) J. Keeton, R. Mason, and D. R. Russell, *J. Organometal. Chem.*, **33**, 259 (1971); these "ylide" compounds prepared from a platinum–cyclopropyl molecule can also be envisioned as pyridine coordinated ethylidene complexes.

(36) (a) Formulation A is also formally derived from a structural moiety that is ubiquitous in divalent tin chemistry[2]



See also, R. E. Rundle and D. H. Olson, *Inorg. Chem.*, **3**, 596 (1964). (b) A referee has pointed out that acceptance of representation B classifies the observed homolytic cleavage as a special case of known[26] heterolytic cleavage reactions. (c) ^{119}Sn Mössbauer and ESCA data suggest that the actual oxidation state of the group IV atom in these complexes is closer to four than to two,[31] but that the electronic structure does differ appreciably from most group IV metal–transition metal compounds.