methylene protons could probably arise from the positioning of the sodium ions about six of the 12 edges of an octahedral cluster. However, the lack of any unusual infrared lines would rule out Na–HC interactions.

The indium(I) compound with a bound dimethoxyethane molecule, $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$, has a distinct and unique set of properties when compared with $[NaIn(CH_2SiMe_3)_2]_6$. The compound can be prepared from $In(CH_2SiMe_3)_3$ and NaH in dimethoxyethane or by adding dimethoxyethane to $[NaIn(CH_2SiMe_3)_2]_6$. However, dimethoxyethane cannot be removed quantitatively from $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ to reform the hexameric species. The colorless dimethoxyethane adduct has a sharp melting point to a colorless liquid at 103–105 °C. The cryoscopic molecular weight study indicates that the molecular species which exist in solution are concentration dependent. An apparent monomeric species was present in dilute solution. At the highest concentrations studied, a trimeric species was indicated. These data suggest that either an equilibrium between monomer, dimer, and trimer exists in solution, or alternatively, the $[NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_3$ trimer remains in tact but with various numbers of bound dimethoxyethane molecules. It is of interest to note that neither tetrahydrofuran, diethyl ether, or trimethylamine react with $[NaIn(CH_2SiMe_3)_2]_6$ to form stable adducts analagous to $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$. The hexamer can be recovered unchanged after the base is removed. These observations might suggest that the sodium ion is the reactive site for dimethoxyethane. Similar conclusions were reached in the study of $NaGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$.[9] We might also conclude from our observations of the $[NaIn(CH_2SiMe_3)_2]_6$–$[NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]$ systems that the hexamer has a measure of kinetic lability for formation of less associated species.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Registry No. $[NaIn(CH_2SiMe_3)_2]_6$, 76566-83-1; $[NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_3$, 76529-83-4; $[NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_2$, 76529-85-6; $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$, 76529-87-8; $In(CH_2SiMe_3)_3$, 69833-15-4; NaH, 7646-69-7; KH, 7693-26-7.

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Reduction of a Mixed-Metal Bimetallic, $[Fe(CO)_4(SnR_2)]_2$, in Lewis Bases

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The complex $[Fe(CO)_4(SnR_2)]_2$ in strong Lewis bases (B) establishes an equilibrium with an unbridged monomer adduct $[Fe(CO)_4(SnR_2\{B\})]$. For B = THF, C_5H_4N, and $4\text{-}MeC_5H_4NO$, the monomer adduct undergoes two-electron reduction in the presence of strong hydridic reagents such as sodium hydride or by treatment with sodium amalgam. The complexes produced are formulated as $[Fe(CO)_4(SnR_2)]^{2-}$ where the reduction process may be viewed as populating a nonbonding sp^3 lone-pair orbital on tin with possible π back-bonding. The iron-57 Mössbauer spectrum exhibits a doublet ($\delta = 0.061$ mm/s, $\Delta = 1.498$ mm/s) in the region of iron(–II) when the complex is isolated from THF, and a doublet ($\delta = 0.169$ mm/s, $\Delta = 1.502$ mm/s) in the region of iron(–I) when the complex is isolated with $4\text{-}MeC_5H_4NO$, while the tin-119 Mössbauer spectrum exhibits a doublet ($\delta = 1.54$ mm/s, $\Delta = 1.19$ mm/s) in the region normally associated with tin(IV). Iron and tin each appear spectroscopically to undergo formal one-electron reduction. The complexes $[Fe(CO)_4(SnR_2)]^{2-}$ have been isolated as sodium salts that show tight ion pairing in CH_3CN. In solution base appears to be cation associated, and crystalline complexes contain base.

Introduction

Heavy-metal analogues of transition-metal carbenes $[Fe(CO)_4(SnR_2)]_2$ exist, if R is sufficiently nonbulky, in equilibrium in the presence of Lewis bases with a monomer adduct presumably via an η^1-stannylene, as shown in (1) and (2).[1,2]

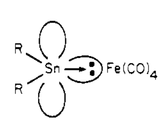
$$\underset{\text{dimer}}{[Fe(CO)_4(\eta^2\text{-}SnR_2)]_2} \rightleftarrows (2/n)[Fe(CO)_4(\eta^1\text{-}SnR_2)]_n \qquad n = 1 \text{ or } 2 \tag{1}$$

$$\underset{\text{monomer}}{[Fe(CO)_4(\eta^1\text{-}SnR_2)]} + \text{Lewis base (B)} \rightleftarrows [Fe(CO)_4(SnR_2\{B\})] \tag{2}$$

Marks and co-workers further established[1,2] that the lability of the associated base is rapid on the ^1H NMR time scale and that the equilibrium position is mainly controlled by the base strength. This process can be thought of formally as base exchange represented by (3).

$$[Fe(CO)_4(SnR_2\{B\})] + B' \rightleftarrows [Fe(CO)_4(SnR_2\{B'\})] + B \qquad \text{equilibrium position and rate(fast)} \propto B \tag{3}$$

This bimetallic system contains two Mössbauer-active nuclei, and so effective spectroscopic evidence can be presented that allows estimation of the charge on both metals and the asymmetry about each metal. Tin exhibits an isomer shift in $[Fe(CO)_4(SnR_2\{B\})]$ consistent with Sn(IV), with large but widely varying degrees of quadrupole splitting depending on the base.[3] Of the bonding modes **4**–**9** considered, structure **7** which involves charge separation such that the iron atom can better approach d^{10}-electron configuration best represents



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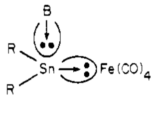

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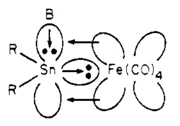

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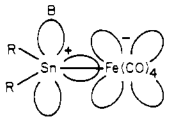

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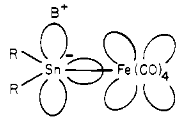

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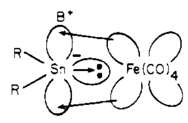

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the monomer adduct when B = THF.

Completely different chemistry is observed when the group 4 metal is surrounded by bulky substituents.[4-7] In this case these complexes are not base associated and exhibit reactivity similar to dialkyl carbenes; that is, they displace coordinated carbon monoxide and triorganophosphines and insert into metal–alkyl, metal–hydride, and metal–halide bonds.[5] Lappert and co-workers have therefore established that in complexes such as $[Fe(CO)_4(SnR_2)]$ ($R = CH(SiMe_3)_2$) the vacant tin p_π orbital may be rendered inaccessible by steric crowding.

We wish to present evidence that $[Fe(CO)_4(SnR_2)]_2$ (R = nonbulky alkyl) in the presence of strong Lewis bases undergoes a base exchange reaction with hydride ion to yield hydrogen gas, producing the complex $Na_2[Fe(CO)_4(SnR_2)]$ (B = tetrahydrofuran and 4-picoline *N*-oxide have been isolated).

Experimental Section

All complexes were handled under rigorous air-free conditions with use of standard techniques.[8] Solvents were dried and deoxygenated thoroughly prior to use. Infrared spectra were recorded on a Beckman IR 4230 spectrophotometer in the form indicated with use of polystyrene as reference. The ^1H NMR spectra were measured on a Varian EM-390. Tin-119 Mössbauer spectra was carried out as described elsewhere[9] with the use of a $BaSnO_3$ source. Iron-57 Mössbauer spectra were performed on an apparatus described previously[10] with a sodium nitroprusside dihydrate standard. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Inc., NY. Solution conductivities were obtained in acetonitrile on a Yellow Springs Institute Model 31 conductivity bridge.

The compounds $[Fe(CO)_4(SnR_2)]_2$[2] and $Na_2[Fe(CO)_4]\cdot 1.5(\text{dioxane})$[11] were synthesized by literature methods. The compounds R_2SnCl_2, 4-picoline *N*-oxide, NaH, solvents, and $LiEt_3BH$ were obtained from commercial sources. Tetrahydrofuran and pyridine were dried in the usual manner[8] and then distilled from NaH.

Synthesis of $Na_2[Fe(CO)_4(SnMe_2)]$ (B = 4-MeC_5H_4NO). A round-bottom flask is charged with $[Fe(CO)_4(SnMe_2)]_2$ (4.0 g, 6.31 mmol), 4-picoline *N*-oxide (1.38 g, 12.62 mmol), and sodium hydride (1.15 g, 50 mmol). Then THF was added at room temperature, and the solution was stirred. Rapid H_2 gas (2 mol equiv) evolution occurred even at temperatures as low as −20 °C. The hydrogen gas was collected on a Toeppler pump and identified by chemical ionization mass spectrometry, and no infrared absorptions could be found. The reaction was complete within 5 min, and the resulting golden yellow solution was then filtered. Yellow crystalline $Na_2[Fe(CO)_4(SnMe_2)]\cdot 4\text{-}MeC_5H_4NO$ (2.40 g) was isolated from a THF/diethyl ether solution at −78 °C and collected and dried. The crystals melted at ca. 80 °C and darkened, and gas was evolved at 105 °C under an N_2 atmosphere. The complex was washed with 50 mL of diethyl ether, but the color of the complex remained unchanged. IR (KBr): 3370 (s, br), 1970 (s), 1870 (vs, br), 1605 (w, br), 1470 (m, w sh), 1370 (w), 1210 (s), 1168 (w), 1090 (w), 1030 (w), 815 (s), 747 (s), and 600 (s) cm^{-1}. NMR (CD_3CN): δ 7.9 (2, br d), 8.07 (2, br s), 2.36 (3, s), 0.93 (1.30, $Sn\{^3J_{SnCH} = 24\ Hz\}$) and 0.28 (2.12, $Sn\{^3J_{SnCH} = 24\ Hz\}$) ($\delta$ relative to Me_4Si). Mössbauer (^{57}Fe): $\delta = 0.169$ mm/s, $\Delta = 1.502$ mm/s. Anal. Calcd for $Na_2[Fe(CO)_4(SnMe_2)]\cdot 1.75CH_3C_5H_4NO$: C, 35.75; H, 3.30; N, 4.42. Found: C, 36.13; H, 2.82; N, 4.72.

Synthesis of $Na_2[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]\cdot 4\text{-}CH_3C_5H_4NO$. From a reaction containing $[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]_2$ (4.0 g, 5.81 mmol), NaH (1.15 g, 50 mmol), and 4-picoline *N*-oxide (12.67 g, 11.62 mmol) in THF (20 mL) was isolated pale tan crystalline $Na_2[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2\{4\text{-picoline } N\text{-oxide}\})]$ (0.47 g). The complex was obtained by an identical procedure to $Na_2[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]\cdot 4\text{-}CH_3C_5H_4NO$. IR (KBr): ν_{CO} 1995 (m) and 1900 (s, br) cm^{-1}.

Synthesis of $Na_2[Fe(CO)_4(SnMe_2)]\cdot THF$. A flask is charged with solid $[Fe(CO)_4(SnMe_2)]_2$ and excess NaH to which liquid base THF at room temperature was added. Rapid H_2 evolution (2 mol equiv) occurred and the solution changed from yellow to dark golden yellow/orange. Filtration and evaporation under vacuum yielded a red oil which became a red crystalline material with pumping over the period of 1–2 days (10^{-5} torr). The infrared spectrum of the solid is identical with its solution spectrum. Redissolving the crystals in solvent yields identical infrared and ^1H NMR spectra. Further drying over 1 week at 10^{-5} torr yields a pale yellow crystalline solid that dissolves completely in THF to give identical spectra. The conditions were as follows: $[Fe(CO)_4(SnMe_2)]_2$, 1.0 g, 1.58 mmol; NaH, 120 mg; THF, 5 mL; yield $Na_2[Fe(CO)_4(SnMe_2)]\cdot THF$, 0.9 g, 66%. IR (THF): ν_{CO} 1982 (m), 1887 (sh), 1868 (s) and 1829 (w) cm^{-1}; (KBr) 2976 (2), 2883 (w), 2031 (w), 1983 (s, br), 1853 (vs, br), 1608 (w), 1440 (w), 1380 (s), 1253 (w), 1168 (w), 1106 (w), 1043 (w), 868 (w), 753 (w), 614 (s) cm^{-1}. NMR (THF): δ 0.10 ($Sn\{^3J_{SnCH} = 21\ Hz\}$) ($\delta$ relative to Me_4Si). Integration of THF gives 0.30 equiv/mol. Mössbauer: Sn(119) $\delta = 1.54$ mm/s, $\Delta = 1.19$ mm/s; Fe(57) $\delta = 0.061$ mm/s, $\Delta = 1.498$ mm/s. Anal. Calcd for $Na_2[Fe(CO)_4(SnMe_2)]\cdot 0.30OC_4H_8$: C, 22.46; H, 2.18. Found: C, 22.05; H, 2.53.

For *B = pyridine* the compound was not isolated out of solution and was synthesized as above. The H_2 gas was measured to be 2.0 mol equiv H_2/dimer. NMR (C_5H_5N): 0.80 ($S\{J = 20\ Hz\}$) (δ relative to Me_4Si).

Reaction of $[Fe(CO)_4(SnMe_2)]_2$ with Sodium Amalgam. A 1.25% (by weight) amalgam of 1.5 g Na in 120 g Hg was prepared, and a THF (30 mL) solution of $[Fe(CO)_4(SnMe_2)]_2$ (750 mg, 1.18 mmol) was added. After 5 h the solution was filtered through celite and the solution infrared and ^1H NMR spectra obtained were identical with those obtained by reaction of $[Fe(CO)_4(SnMe_2)]_2$ with NaH in THF. The compound was isolated as above, yielding $Na_2[Fe(CO)_4(SnMe_2)]\cdot THF$ (720 mg, 64%).

Conductivity Measurements. For the conductivity of $Na_2[Fe(CO)_4(SnMe_2)]\cdot 1.75(4\text{-}CH_3C_5H_4NO)$, a 10^{-3} M acetonitrile solution (45 mg in 100 mL) gave an equivalent conductance of 71 $\Omega^{-1}\ M^{-1}\ cm^{-1}$. For $Na_2[Fe(CO)_4(SnMe_2)]\cdot 0.30THF$ a 1.59×10^{-3} M acetonitrile solution (60.5 mg in 100 mL) gave an equivalent conductance of 109 $\Omega^{-1}\ M^{-1}\ cm^{-1}$. When the conductivity of $Na_2[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]\cdot 4\text{-}CH_3C_5H_4NO$ was measured a 2×10^{-3} M acetonitrile solution (54 mg in 50 mL) gave an equivalent conductance of 81 $\Omega^{-1}\ M^{-1}\ cm^{-1}$.

Low-Temperature Reaction of $LiEt_3BH$ and $[Fe(CO)_4(SnMe_2)]_2$. The reaction was run in an NMR tube (5-mm diameter). A 10^{-2} M solution of $[Fe(CO)_4(SnMe_2)]_2$ (0.634 g in 10 mL of THF) was added (1 mL) to the tube in a glovebox, and the tube was fitted with a septum cap. Under a nitrogen atmosphere maintained via a syringe needle N_2 inlet, a solution of 1 M $LiEt_3BH$ in THF (0.02 mL) was added to the NMR tube kept at −78 °C. The NMR spectra were then run with the septum removed to allow H_2 evolution in a probe that is constantly purged with pure N_2 gas. Reference spectra of 1 M $LiEt_3BH$ and 10^{-2} M $[Fe(CO)_4(SnMe_2)]_2$ were obtained in THF.

Results and Discussion

We have observed the rapid room-temperature reaction of sodium hydride with $[Fe(CO)_4(SnR_2)]_2$ with the evolution of 2 mol equiv of hydrogen gas. This reaction proceeds only in the presence of a Lewis base such as THF, pyridine, or 4-picoline *N*-oxide. A stoichiometric amount of base in a weakly coordinating solvent such as methylene chloride or diethyl ether is sufficient to see rapid reaction as evidenced by gas evolution. In the absence of Lewis bases in either methylene chloride or hexane or the weak base diethyl ether, the hydride reduction reaction does not proceed. Lewis bases cleave the dimer to a monomer adduct,[1,2] which must be necessary before reaction with hydride commences. Since it has been established[1,2] by dynamic ^1H NMR that the base in $[Fe(CO)_4(SnR_2\{B\})]$ is labile, it seems reasonable that the initial stage of reaction involves base loss from the monomer adduct and subsequent reaction with an iron η^1-stannylene ligand either by electron transfer or via the intermediacy of a metal hydride that we could not find evidence for spectroscopically.

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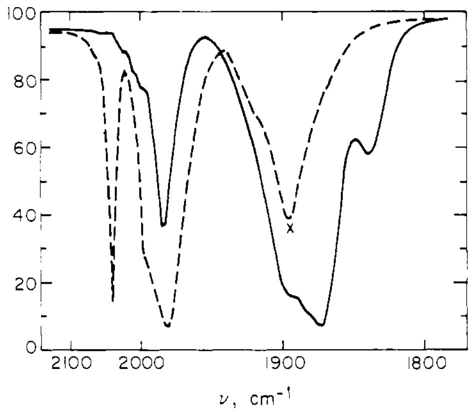
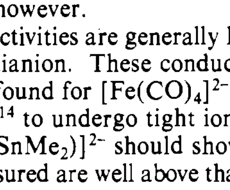


Figure 1. Changes in IR (ν_{CO}) upon reduction (spectra recorded in THF): ---, $[Fe(CO)_4(SnMe_2)]_2$ and $[Fe(CO)_4(SnMe_2\{THF\})]$ (denoted by ×); —, $[Fe(CO)_4(SnMe_2)]^{2-}$.

The infrared spectra in the carbonyl region of the reduced complexes are remarkably similar in appearance to the starting iron dimer with about a 100-cm^{-1} shift toward lower wave numbers, indicative of only a one electron increase at iron.[12] It is less than the decrease that might have been anticipated for formation of a dianion from a neutral complex. These differences are normally[12] in the range of 200 cm^{-1} as exemplified by the two-electron reduction of $[Fe(CO)_5]$ to $[Fe(CO)_4]^{2-}$. The spectra of the carbonyl stretching region for $[Fe(CO)_4(SnMe_2)]\cdot THF$ and the complex produced upon hydride reduction, $[Fe(CO)_4(SnMe_2)]^{2-}$, are shown in Figure 1. Although golden yellow in solution, upon concentration the complex becomes progressively red and crystalline. After being dried extensively at 25 °C (10^{-6} torr), the complex turns pale yellow. Its solid-state (KBr) spectrum shows identical ν_{CO} stretching absorptions, and the complex as either its red or pale yellow form redissolves completely in THF to yield identical infrared solution spectra. Both the ^1H and ^{13}C NMR spectra of $[Fe(CO)_4(SnMe_2)]^{2-}$ in THF and pyridine show small but significant changes. For B = THF the ^1H NMR spectrum after reaction with sodium hydride exhibits a new tin methyl singlet at a shift of 0.5–1.0 ppm upfield toward Me_4Si (more shielding) whereas the ^{13}C NMR spectrum shows a 1-ppm shift upfield. Small $^3J_{SnCH}$ values of 20–25 Hz were observed which are a measure[3] of a decrease in C–Sn–C angle in $[Fe(CO)_4(SnR_2\{B\})]$ and suggestive of sp^3 hybridization as in **10** rather than sp^2. The direction of C–Sn–C angle as a function of $^3J_{SnCH}$ does change from compound series to compound series, however.



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Measured conductivities are generally lower than would be anticipated for a dianion. These conductivities are roughly 40% of the values found for $[Fe(CO)_4]^{2-}$ in THF, which has been established[13,14] to undergo tight ion pairing. In acetonitrile, $[Fe(CO)_4(SnMe_2)]^{2-}$ should show tight ion pairing. Conductivities measured are well above that found for covalent molecules, and roughly 2–3 times that found for $[Fe(CO)_4(Sn\text{-}t\text{-}Bu_2\{C_5H_4N\})]$ (37 Ω^{-1} cm^{-1} mol^{-1}) and 10 times greater than $[Fe(CO)_4(SnMe_2\{C_5H_5N\})]$ (7.0 Ω^{-1} cm^{-1} mol^{-1}).[2]

The compound isolated from the sodium hydride or sodium amalgam reduction of 2:1 $4\text{-}MeC_5H_4NO/[Fe(CO)_4(SnMe_2)]_2$ in THF contains $4\text{-}MeC_5H_5NO$ aryl ring resonances that are broadened. Additional base sharpens the aryl ring protons of 4-picoline *N*-oxide with no free ligand methyl peak observed. Cation–base coordination must be occurring. An attempt to isolate crystalline complexes that are totally free of base was unsuccessful. For B = THF, the isolated complex is nearly base free, but for B = $4\text{-}MeC_5H_4NO$ nearly 2 mol of base are incorporated in the crystalline complex. Isolation of B = THF complex by drying the oil for extended periods removes nearly all the THF. We have examined samples containing as low as 0.30 equiv of THF. A ^1H NMR spectrum of this compound in CD_3CN shows this amount of THF by integration and matches the elemental analysis exactly.

A process that interconverts tin alkyl resonances in the NMR involving bridging–terminal $M'R_2$ (M′ = Si–Sn) interchange has been studied[15,16] for the complex $[Fe(CO)_4(M'R_2)]_2$. Stannylene (η^1) intermediates were proposed. Along with processes that involve temperature-dependent base adduct formation and temperature-dependent association reactions, analysis of solution species is somewhat uncertain at best. There is no change at ca. −50 °C in the tin methyl region for solutions of $[Fe(CO)_4(SnMe_2)]^{2-}$. No good methods for accurately estimating the molecular weight of $[Fe(CO)_4(SnR_2)]^{2-}$ in solution exist because of its ionic nature and labile base association, and we are seeking single-crystal structural data to establish the degree of association, if any.

Studies by Ernst, Marks, and Ibers on a related series of complexes formed by base cleavage of the polymeric $[CdFe(CO)_4]_n$ have established adduct formation as a viable route to a variety of different associated species. The polymer $[CdFe(CO)_4]_n$ which could exist as chains or links which can form cycles is found to undergo base homolysis. In weak base (B = acetone) a tetramer $[CdFe(CO)_4]_4\cdot 2B$ was isolated and characterized.[18] A stronger bidentate base (B = bipyridyl) yields[17] the trimer $[(bpy)CdFe(CO)_4]_3$, while in strong bases (B = THF, NH_3, and pyridine) the complexes $[B_nCdFe(CO)_4]$ (n = 2 or 3) are formed. Charge separation $Cd^{\delta+}\text{–}Fe^{\delta+}$ is proposed in analogy with the complexes $[Fe(CO)_4(SnR_2\{B\})]$ as in **7**, discussed below. We are in the process of exploring the reduction of these mixed-metal systems in Lewis bases.

The ^{119m}Sn Mössbauer spectra have been measured for monomer adducts $[M(CO)_n(SnR_2\{B\})]$ and dimers and isomer shifts from 1.82 to 2.11 mm/s are observed. These isomer shifts are consistent[22,23] with poor electron screening found for tin in its IV oxidation state. Large variance in the size of the quadrupole splitting (Δ), which is a measure of the deviation from cubic symmetry, was noted as a function of base. For $[Cr(CO)_4(Sn\text{-}t\text{-}Bu_2\{B\})]$ the Δ increases py < Me_2SO < THF with exceedingly large values for each. For B = THF, $[Fe(CO)_4(SnR_2\{B\})]$ ^{119}Sn Mössbauer quadrupole splittings are among the largest Δ known for tetravalent tin(IV). The large Δ's in these systems were rationalized on the basis of the charge separation $Sn^{\delta+}\text{–}Fe^{\delta-}$ best depicted as resonance structure **7** of the five resonance structures **5**–**9** considered. Other metal fragments and bases around divalent tin may be

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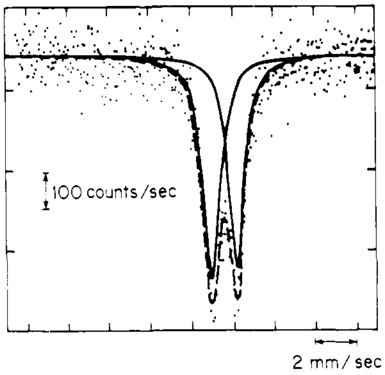

Figure 2. ^{119m}Sn Mössbauer spectrum of $[Fe(CO)_4(SnMe_2)]^{2-}\cdot 0.3THF$ ($\delta = 1.54$ mm/s, $\Delta = 1.19$ mm/s).

better rationalized with other resonance structures of **5–9**. In terms of structure **7**, one may view tin as donating one electron each to four two-electron σ bonds. The small isomer shift of tin systems was attributed[3] to the ability of $Fe(CO)_4$ to act as a good σ acceptor.

The ^{119m}Sn Mössbauer spectrum of $Na_2[Fe(CO)_4(SnMe_2)]$ shown in Figure 2 contains a doublet centered around 1.54 mm/s with a quadrupole splitting of 1.19 mm/s. While the ^{119m}Sn Mössbauer data for $[Fe(CO)_4(SnMe_2\{THF\})]$ is not available, this value is some 0.25–0.3 mm s^{-1} lower than both the dimer $[Fe(CO)_4(Sn\text{-}t\text{-}Bu_2)]$ and the monomer adducts $[Fe(CO)_4(SnMe_2\{B\})]$ and reflects somewhat decreased shielding[20,21] on tin. This isomer shift is still consistent with a value found for tin(IV) but with somewhat reduced shielding at tin as compared to the natural monomer adducts $[Fe(CO)_4(SnR_2\{B\})]$. This resulting dianion has one form of tin environment present which we think argues that in solution it is monomeric. It exhibits considerably less charge separation and deviation from cubic symmetry about the iron–tin bond as exemplified by a reduced quadrupole splitting ($\Delta = 1.19$). The reduced species $[Fe(CO)_4(SnMe_2)]^{2-}$ may, therefore, balance excess charge at iron by enhanced π back-bonding. The observed shielding for the reduced species suggests a low s-electron level at the tin nucleus with the enhanced charge having no effect on screening.

The ^{57}Fe Mössbauer spectrum of $Na_2[Fe(CO)_4(SnR_2)]\cdot xTHF$ shows a doublet with an isomer shift (δ) at +0.061 mm/s from the nitroprusside standard with a quadrupole splitting (Δ) of 1.498 mm/s. When isolated with $4\text{-}MeC_5H_4NO$ as the associated base, the ^{57}Fe Mössbauer spectrum contained a doublet at $\delta = 0.169$ mm/s and $\Delta = 1.502$ mm/s. The isomer shift found in ^{57}Fe Mössbauer spectra is dependent on the oxidation state of iron, but the range for the various oxidation states is smaller than in ^{119}Sn Mössbauer spectra. Representative iron compounds have Mössbauer parameters[22] as follows: $[Fe(\eta^5\text{-}C_5H_5)_2]$, $\delta = 0.79$ mm/s, $\Delta = 2.37$ mm/s; $[Fe(CO)_5]$, $\delta = 0.17$ mm/s, $\Delta = 2.57$ mm/s; $(NEt_4)_2[Fe_2(CO)_8]$, $\delta = 0.16$ mm/s, $\Delta = 2.22$ mm/s; $Na_2[Fe(CO)_4]$, $\delta = 0.09$ mm/s, $\Delta = 0$ mm/s. Our ^{57}Fe Mössbauer value for $[Fe(CO)_4(SnR_2)]^{2-}$ indicated that iron is in a low oxidation state, about as deshielded as Fe(–II) when THF is present in small amounts (0.3 mol equiv) but exactly in the Fe(–I) region when B = $4\text{-}MeC_5H_4NO$ (1.74 mol equiv). The quadrupole splitting is moderate, indicating a reasonable but not large deviation from cubic symmetry at iron.

We favor the representation **10** for the reduced mixed-metal complex $[Fe(CO)_4(SnR_2)]^{2-}$. Spectroscopically our Mössbauer and infrared data suggest formal one-electron reduction at each metal. In **10**, tin(I) has seven electrons and, along with a shared electron from Fe(–I), a filled sp^3 hybrid set. The Fe(–I, d^9) satisfies the EAN rule with the additional electron in the bimetallic bond. The similarity between the light yellow colors of the monomer adducts and the reduced species in solution and as a solid suggests that the electronic structure of iron in $[Fe(CO)_4(SnR_2)]^{2-}$ is very similar to that in $[Fe(CO)_4(SnR_2\{B\})]$.

We sought to establish the intermediacy of a tin hydride or an iron hydride by low-temperature ^1H NMR spectroscopy. We did not consider formyl formation because none has been reported to liberate hydrogen in the presence of hydride; rather, they seem to form various other products.[24,25] Although NaH is inconvenient for this purpose due to its insolubility, this reaction does proceed with other hydride sources. The compound $LiEt_3BH$ (the so-called super hydride) was mixed with $[Fe(CO)_4(SnMe_2)]_2$ in THF at –78 °C and studied at –60, –35, and –10 °C. At –35 °C the monomer adduct is in solution but no new peaks assignable to Sn–H or Fe–H appear. At –10 °C reaction has occurred yielding $[Fe(CO)_4(SnMe_2)]^{2-}$ again with no appearance of metal hydride.

We have studied the reaction visually by slow warm-up of a THF solution of NaH and $[Fe(CO)_4(SnR_2)]_2$ and at low sodium hydride concentration. There is no temperature at which it appears that NaH is consumed without also H_2 gas evolution being observed. Reaction occurs at as low as –20 °C. This does not disprove the existence of an intermediate metal hydride; it only shows that its concentration is not built up and that it was not observed. A bimolecular process involving hydrogen elimination and metal hydrides alone should, we believe, show more temperature dependence.[26-28] Rapid reaction at low temperatures (–20 °C) suggests acid–base behavior or simple electron transfer. At –20 °C the rate of base exchange should be slowed considerably, otherwise reaction should occur at even lower temperatures.

Electron transfer with hydridic reducing agents may involve an unusually labile or protic metal hydride bond. It would not be hard to visualize hydride, a good σ donor but poor π acceptor, being rendered protic attached to a tin atom which has the good σ-acceptor group $Fe(CO)_4$ also attached.

The ligand $SnMe_2H$ is a heavy-metal analogue of carbon containing an α-hydrogen. Studies by Schrock and co-workers have established α-hydride abstraction[26-28] as a principle route to metal alkylidene[29] (carbene) complexes. In addition to α-hydride abstraction, which can be alternatively viewed as deprotonation at carbon, a process termed α-hydrogen is metal abstracted, yielding a metal hydride and a carbene. Green and co-workers have trapped a hydrido carbene complex $[W(\eta^5\text{-}C_5H_5)_2CH_2(H)]^+$ from the alkyl $[W(\eta^5\text{-}C_5H_5)_2CH_3]^+$.[30] Shapley has observed a methyl $\rightleftarrows$ methylene hydride equilibrium in an osmium cluster.[31] The α-elimination process in $Na[Fe(CO)_4(SnMe_2H)]$ would generate a seven-coordinate intermediate which should for a first-row metal be sterically crowded, and we do not favor the intermediacy of an iron hydride. However, without further knowledge of an intermediate of detailed kinetic data, it is impossible to differentiate conclusively between the mechanisms analogous to α-hydride abstraction or elimination or simple electron transfer.

The basicity of an $Fe(CO)_4$ group has been noted before by several authors. Marks and co-workers have discussed[19] charge separation in $[B_nCdFe(CO)_4]_x$ and bond lengthening

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in $[Cr(CO)_5(SnBu_2\{py\})]$ vs. $[Cr(CO)_5(Sn(CH\{SiMe_3\}_2)_2)]$ as a function of hybridization due to adduct formation. Structural distortion from octahedral toward idealized bicapped tetrahedron is attributed to a d^{10}-like configuration at iron. Hoffman, Howell, and Rossi have discussed[32] this distortion for $[Fe(CO)_4X_2]$ (X = halide) where X is strongly σ-electron donating.

Reduction by sodium amalgam of $[Fe(CO)_4(SnMe_2)]_2$ in various bases parallels closely reduction by hydride although the amalgam reduction route appears to be somewhat cleaner.

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Registry No. $Na_2[Fe(CO)_4(SnMe_2)]$, 76705-09-4; $Na_2[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]$, 76705-10-7; $[Fe(CO)_4(SnMe_2)]_2$, 15418-00-5; $[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]_2$, 15613-38-4; $Fe(CO)_4(SnMe_2\{THF\})$, 76705-11-8.

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Preparation and Characterization of $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$: An A-Frame Methylplatinum Complex Cation

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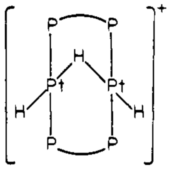
Reaction of $[PtCl_2(dppm)]$, dppm = bis(diphenylphosphino)methane, with methyllithium gives $[PtMe_2(dppm)]$, which, on reaction with HCl, gives $[PtClMe(dppm)]$ and the A-frame complex $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$, both of which have been isolated in pure form. The A-frame complex, previously thought to be a nonionic trimer, was characterized by comparison of its spectral properties (IR and ^1H and ^{31}P NMR) with those of the hexafluorophosphate salt $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ and by conductivity measurements. A third, probably dimeric, form of $[PtClMe(dppm)]$ has been isolated but not structurally characterized.

Introduction

We recently synthesized[2] a series of hydridodiplatinum(II) complex ions, I–III, containing the ligand bis(diphenylphosphino)methane (dppm), and following this we have attempted the synthesis of analogous methyldiplatinum species $[Pt_2Me_nCl_{3-n}(\mu\text{-}dppm)_2]^+$ (n = 1–3). Accounts of the complex $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$, analogous in molecular formula but not in structure with I, have recently been published,[3] and we now report on the complex ion $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$, analogous to II.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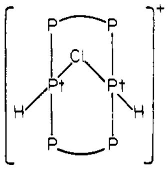
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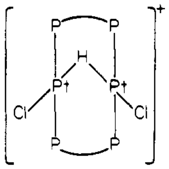
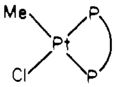
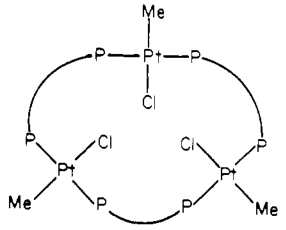

III

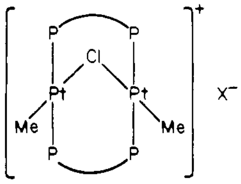
$\widehat{PP} = Ph_2PCH_2PPh_2$

Bennett and coworkers[4] have previously reported methylplatinum derivatives with dppm as ligand. They reported that $[PtClMe(cod)]$ (cod = 1,5-cyclooctadiene) reacted with dppm to give a monomeric form (IV) and an oligomeric form (V) of $[PtClMe(dppm)]$. The oligomeric form was tentatively identified as the trimer V by its molecular weight in chloroform, and this formulation was considered to be consistent with the ^1H and ^{31}P NMR spectra.


IV


V

We have developed routes to pure samples of both the monomeric and previously reported oligomeric forms of $[PtClMe(dppm)]$, and evidence is presented that the oligomeric form is actually an ionic A-frame dimer (VIa).


VIa, $X^- = Cl^-$
b, $X^- = PF_6^-$

Results and Discussion

We find that $[PtMe_2(dppm)]$ is a convenient starting material for the preparation of these chloromethyl complexes and is readily obtained by the action of methyllithium on $[PtCl_2(dppm)]$. It is worth noting that this reaction gives monomeric $[PtMe_2(dppm)]$, identical with the compound

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