$(CO)_8L_2$.[2,4] The only comparable values of k_1' for different substituents show that $P(OPh)_3 > PBu_3$ for stage II of reaction with Br_2 and $PPh_3 \gtrsim PBu_3$ for stage II of reaction with I_2. This suggests that the substituent effect may be fully manifested in the rapid preequilibrium formation of the adducts complex·X_2 rather than in the slow stage of the reactions. In all reactions for which comparison is possible the rate constants for reaction with Br_2 are greater than for reaction with I_2 or ICl. Finally, the values of β_1' are generally much greater than those observed for reactions of $Mn_2(CO)_8L_2$.[2,4]

While the trends shown in some of these reactions are not as clear-cut or pronounced as those shown by the reactions of $Mn_2(CO)_8L_2$,[2,4] the general form of the kinetic behavior leads us to propose that the same mechanism is operating, namely, that there is a rapid preassembly of one or more halogen molecules around the surface of the complex and that these weaken the metal–metal bonds by attracting electron density from the metal–metal-bonding orbitals (which are the HOMO).[8] This attraction is probably transmitted through the CO ligands.[2,4] When the metal–metal bonds have been sufficiently weakened (by either the number or strength of the interactions with the halogen molecules), they undergo spontaneous fission (homolytic or heterolytic),[2] and halogen molecules are present to react very rapidly with the fragments formed. There is no evidence (for or against) as to whether the attraction of electrons from the HOMOs is quantized, i.e., whether a single electron is transferred to form $(\text{complex}^{+}\cdot)(X_2^{-}\cdot)(X_2)_{n-1}$, and this remains a distinct possibility.[18]

The ease with which some of these metal–metal-bonded carbonyls can attract several halogen molecules shows that they can act as quite strong polydentate Lewis bases[2,17] toward halogens. In the Ru_3 complexes, as with the Mn_2 complexes, it is those that are substituted with $P(OPh)_3$ that show the formation of adducts with the highest number of halogen molecules.[2,4] The reason for this is not clear.

The activation parameters (Table II) for bimolecular attack of I_2 on $Ru_3(CO)_9(PPh_3)_3 \cdot I_2$ are quite compatible with the mechanism being proposed, but little can be said until further values are available.

The kinetics of stages II and III of reaction of ICl with $Ru_3(CO)_9(PPh_3)_3$ have not been discussed in detail because it is not clear exactly what the reactant complexes are. It is interesting, however, that stage II involves a path that is clearly *second* order in [complex]. Similar behavior is shown at high values of c_0 in the first stage of reaction of Br_2 with this complex and in the reaction[19] of I_2 with $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$. It therefore seems that in some cases activation of the metal–metal bonds can be accomplished by bringing two molecules of complex together, though a halogen molecule, sandwiched between them, may be a requirement for this.

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Registry No. $Ru_3(CO)_9(PPh_3)_3$, 15663-31-7; $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$, 12258-07-0; $Ru_3(CO)_9[P(OPh)_3]_3$, 50661-53-5; I_2, 7553-56-2; Br_2, 7726-95-6; ICl, 7790-99-0; $Ru(CO)_3(PPh_3)I_2$, 76648-27-6; $Ru(CO)_3(PPh_3)Br_2$, 76648-28-7; $Ru(CO)_3(P\text{-}n\text{-}Bu_3)I_2$, 76613-62-2; $Ru(CO)_3(P\text{-}n\text{-}Bu_3)Br_2$, 76613-63-3; $Ru(CO)_3[P(OPh)_3]I_2$, 76613-64-4; $Ru(CO)_3[P(OPh)_3]Br_2$, 76613-65-5.

Supplementary Material Available: A table of kinetic data (6 pages). Ordering information is given on any current masthead page.

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Low Oxidation State, σ-Bonded Organometallic Derivatives of Indium(I)

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The organoindium compounds $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$, whose formulas indicate indium in the +1 oxidation state, have been prepared and characterized by elemental analyses, cryoscopic molecular weight measurements in benzene solution, and infrared and ^1H NMR spectral data. The novel indium(I) compounds were prepared from $In(CH_2SiMe_3)_3$ and NaH in the appropriate solvent by an apparent reductive elimination reaction. The nature of the specific indium(I) product was dependent on the reaction solvent. When either aromatic or hydrocarbon solvents were used, a hexameric species, $[NaIn(CH_2SiMe_3)_2]_6$, was formed. The product from dimethoxyethane, $[NaIn(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe]_x$, exhibited an association which was concentration dependent. Structures which involve indium–indium bonds are proposed to account for the observed molecular association as well as the chemical and spectral properties.

Introduction

The organometallic derivatives of the main-group metals in low oxidation states provide unique synthetic challenges and opportunities. Cyclopentadienylindium(I), $In(C_5H_5)$,[1,2] represents the only previously known organometallic, low oxidation state compound of indium. The preparative reaction invovles the reagents $InCl_3$ and NaC_5H_5 in ether solution. The indium(I) product was believed to be formed by the reduction of $In(C_5H_5)_3$ by the cyclopentadienyl anion.[2] Unfortunately, little more is known about the nature of the apparent reduction reaction. An X-ray structural study[3] of $In(C_5H_5)$ has shown the compound to exist as a linear polymer with the cyclopentadienyl ring exhibiting η^5 coordination, rather than as a simple σ-bonded organometallic species.

The initial goal of our synthetic studies in indium chemistry was the preparation of a kinetically stable, σ-bonded, low

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oxidation state compound by a well-defined reduction process. The reductive elimination reaction is used in transition-metal chemistry to prepare compounds which have been reduced by units of two,[4] the common oxidation state difference observed in main-group element chemistry. Thus, our challenge was to define a set of ligands, reagents, and reaction conditions which would lead to a reduction reaction and produce a kinetically stable indium(I) compound. The chemistry of the hydride derivatives of the heavier main-group metals suggest the occurrence of facile reduction reactions at a metallic center.[5-7] Thus, a controlled reduction reaction of hydride derivative was considered a possible route to a low oxidation state compound provided the organic ligands on the metal could minimize the availability of associative and dissociative low-energy decomposition pathways for the product. The organic ligands CH_2SiMe_3 and $CH(SiMe_3)_2$ are known to satisfy these requirements.[8] Thus, the reactions of $In(CH_2SiMe_3)_{3-x}Cl_x$ (x = 0–2) with alkali metal hydrides were investigated as possible routes to σ-bonded, organometallic, low oxidation state indium compounds.

In this paper we report the synthesis and characterization of the indium(I) compounds with the simplest formulas, $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$. The nature of the synthetic reaction path, the unusual properties of these novel compounds, and their possible structures based on available data are discussed. Historically, it is important to note that these indium(I) compounds were prepared and characterized prior to the previously reported analogous gallium(I) derivatives.[9] The indium compounds were studied before the gallium compounds because the low oxidation state is observed to be more readily prepared and more stable for the heavier members of a periodic group of main-group elements.

Experimental Section

Materials. All compounds described in this investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or a purified nitrogen or argon atmosphere. The solvents were purified by refluxing with an appropriate drying agent and vacuum distilled just prior to use. The drying agent for the solvents dimethoxyethane and tetrahydrofuran was sodium–benzophenone ketyl and for benzene and hexane was sodium ribbon. The hexane was certified to be free of alkenes. The alkali-metal hydrides were purchased from Alfa Inorganics as oil dispersions. The oil was removed by repeated extractions with dry pentane. Tris((trimethylsilyl)methyl)indium(III), $In(CH_2SiMe_3)_3$, was prepared from $InCl_3$ or InI_3 by a standard Grignard reaction in diethyl ether.[10]

Analyses. The new ((trimethylsilyl)methyl)indium(I) compounds were analyzed for indium by EDTA titration.[11] The percentages of sodium were determined by standard atomic absorption procedures using a Perkin-Elmer Model 503 spectrometer. The moles of CH_2SiMe_3 groups per mole of indium was determined by quantitatively converting the ligand into $Si(CH_3)_4$ by reaction of the organoindium(I) compound with anhydrous HCl in 95% ethanol. $Si(CH_3)_4$ was separated from all other volatile components in the reaction mixture by passage through a −78 °C trap and into a −196 °C trap on the vacuum line and weighed. The purity of $Si(CH_3)_4$ was confirmed by vapor pressure measurements and ^1H NMR and infrared spectroscopy. All analytical data are given in appropriate sections.

Molecular Weight Studies. Molecular weight measurements were obtained cryoscopically in benzene by using an instrument similar to that described by Shriver.[12] The molecular weight data are given in appropriate sections.

Infrared and ^1H NMR Spectra. The infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer. The spectra were recorded as Nujol mulls using CsI plates. The absorption intensities were measured by using the method of Durkin, Glore, and DeHayes.[13]

The ^1H NMR spectra were recorded at 100 MHz and ambient temperature by using a Jeolco Model MH-100 spectrometer. All chemical shifts (τ) are given in ppm and are referenced to tetramethylsilane as 10.00 ppm.

All spectroscopic data are given in appropriate sections.

Syntheses of $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$. The low oxidation state compounds $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ were prepared from $In(CH_2SiMe_3)_3$ and NaH in hexane (or benzene) or dimethoxyethane, respectively. In a typical synthetic reaction, an argon-purged flask charged with 1.81 g (4.83 mmol) of $In(CH_2SiMe_3)_3$ dissolved in 5.0 mL of hexane was equipped with a water-cooled condenser and magnetic stir bar. NaH (0.486 g, 20.2 mmol) was added by means of a side-arm dumper, and the resultant mixture was refluxed for 16 h. Then, the reaction mixture was filtered and extracted twice with the reaction solvent to remove the indium(I) product from the excess NaH. Vacuum distillation of the reaction solvent at 25 °C left a colorless solid, $NaIn(CH_2SiMe_3)_2$ (1.398 g, 4.48 mmol, 93.0% yield on the basis of $In(CH_2SiMe_3)_3$). The tetramethylsilane produced in the preparative reaction was identified by infrared and NMR data. For quantitative measurement of the $Si(CH_3)_4$ produced, a preparative reaction was run in a sealed tube equipped with a break-seal side arm with toluene as solvent. The yield of $Si(CH_3)_4$ was 0.956 mol/mol of $In(CH_2SiMe_3)_3$ consumed. The product, $NaIn(CH_2SiMe_3)_2$, was completely characterized as described in a following section.

When dimethoxyethane was used as a reaction solvent, $In(CH_2SiMe_3)_3$ and NaH were observed to react completely in 16 h at room temperature. The indium(I) product was isolated by filtration from excess NaH, followed by removal of solvent as previously described. The yield of product was consistently greater than 90% for every reaction. The properties of $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ as described in the following section were unique in comparison to those of $NaIn(CH_2SiMe_3)_2$. Successful syntheses of the two indium(I) products were always obtained in greater than 90% yields. Quantities of $In(CH_2SiMe_3)_3$ varied from 0.2 to 3.0 g and mole ratios of $NaH/In(CH_2SiMe_3)_3$ varied from 3.0 to 12.0. The use of diethyl ether at reflux as reaction conditions lead to incomplete reaction. It was not possible to quantitatively separate the indium(I) product from unreacted $In(CH_2SiMe_3)_3$.

Characterization and Properties of $NaIn(CH_2SiMe_3)_2$. The product $NaIn(CH_2SiMe_3)_2$ was completely characterized by available methods. The compound does not melt upon heating but undergoes a series of irreversible color transitions which are indicative of decomposition: 130 ± 5 °C, yellow; 165 ± 5 °C, orange; 195 ± 5 °C, red; 240 ± 5 °C, black. Anal. Calcd for $NaIn(CH_2SiMe_3)_2$: In, 36.9; Na, 7.37; mol of CH_2SiMe_3/mol of In, 2.00. Found: In, 36.4; Na, 7.71; mol of CH_2SiMe_3/mol of In, 1.95. Typical solvents for $NaIn(CH_2SiMe_3)_2$ include hexane, benzene, methylene chloride, diethyl ether, and tetrahydrofuran. The compound is insoluble in cold acetonitrile.

The following cryoscopic molecular weight data were observed for benzene solutions. $NaIn(CH_2SiMe_3)_2$ (formula wt 312) [calculated molality monomer, (observed molecular weight), extent of association]: 0.205, (2028), 6.5; 0.171, (2048), 6.6; 0.102, (1767), 5.7. The solubility of $NaIn(CH_2SiMe_3)_2$ precluded molecular weight measurements at higher concentrations. The limitations of the instrument prevented measurements at lower concentrations.

The infrared spectral data (frequency, cm^{-1}) are as follows (bands due to the mulling agents have been omitted) (intensity: s, strong; m, medium; w, weak; sh, shoulder): 1265 (s), 1254 (vs), 965 (s), 865 (vs), 839 (vs), 762 (s), 735 (s), 695 (m), 565 (m), 480 (m), 400 (m).

The ^1H NMR data (τ, ppm (identity)) in benzene solution are 9.55 (Me₃–Si), 9.83 (CH_2–Si), and 11.23 (CH_2–Si). These lines are slightly broader than those observed for other ((trimethylsilyl)methyl)indium(I) and -indium(III)[10] compounds.

Characterization and Properties of $NaIn(CH_2SiMe_3)_2{\cdot}$

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$MeOC_2H_4OMe$. The compound $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ had very different properties in comparison with $NaIn(CH_2SiMe_3)_2$. The colorless compound had a melting point of 103–105 °C. Anal. Calcd for $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$: In, 28.6; Na, 5.72; mol of CH_2SiMe_3/mol of In, 2.00. Found: In, 28.5; Na, 5.72; mol of CH_2SiMe_3/mol of In, 2.04. Typical solvents of the compound include benzene, methylene chloride, diethyl ether, and tetrahydrofuran. The compound is insoluble in hexane.

The following cryoscopic molecular weight data were observed for benzene solutions. $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ (formula weight 402) [calculated molality monomer, (observed molecular weight), apparent extent of association]: 0.114, (1220), 3.03; 0.0688, (773), 1.92; 0.0578, (488), 1.21; 0.0480, (412), 1.02; 0.0441, (385), 0.958; 0.0270, (425), 1.06.

The infrared spectral data (cm^{-1}) are (bands due to mulling agents have been omitted) 1245 (vs), 1201 (w), 1133 (m), 1090 (s), 1038 (w), 1026 (w, sh), 932 (s), 859 (vs), 828 (vs), 757 (s), 730 (m), 682 (m), 561 (w), 477 (m), and 435 (w, sh).

The ^1H NMR chemical shift data in benzene solution are [τ, ppm (identity)] 9.55 (Me_3–Si) and 10.22 (CH_2–Si). All lines were sharp.

Attempted Reactions of Indium Compounds with Various Alkali-Metal Hydrides. The following reactions were attempted, but in all cases the reagents were recovered unchanged and no products were detected. The reagents $In(CH_2SiMe_3)_3$ and LiH were combined in refluxing hexane (16 h) and dimethoxyethane (72 h). Similarly, the indium(I) product $NaIn(CH_2SiMe_3)_2$ did not react with NaH in refluxing hexane or dimethoxyethane.

The reactions of KH with $In(CH_2SiMe_3)_3$ in benzene at 50 °C or dimethoxyethane at room temperature were also investigated. In both cases, $Si(CH_3)_4$ was formed, but no product indicative of $KIn(CH_2SiMe_3)_2$ could be isolated. The indium appeared to have been converted into an insoluble black solid, possibly finely divided indium metal. It is noteworthy that KH was also observed to react with $NaIn(CH_2SiMe_3)_2$ in hexane for 16 h at 60 °C to form a similar insoluble black solid. Unreacted $NaIn(CH_2SiMe_3)_2$ could not be isolated from the reaction mixture.

The reagents $[In(CH_2SiMe_3)_2Cl]_2$ and NaH reacted at room temperature to give a noncondensable gas, probably hydrogen, and a similar insoluble black solid in either diethyl ether or dimethoxyethane. If hexane was used as the reaction medium, no reaction was observed. The $[In(CH_2SiMe_3)_2Cl]_2$ was recovered unchanged. Identifiable indium containing products could not be obtained from the reaction of $In(CH_2SiMe_3)Cl_2$ with NaH in dimethoxyethane.

Results and Discussion

A novel class of organometallic indium(I) compounds as exemplified by $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ have been prepared by an apparent reductive elimination reaction and fully characterized. Kinetically stable indium(I) compounds could only be prepared from $In(CH_2SiMe_3)_3$ and NaH in a hydrocarbon solvent (hexane or benzene) or dimethoxyethane by a stoichiometric reaction as summarized by the idealized equation (1). The preparative reaction is experimentally attractive. The indium(I) product is soluble in the reaction solvent and easily separated from the excess insoluble metal hydride and volatile $Si(CH_3)_4$. Essentially quantitative yields of both products were obtained in all reactions.

$$In(CH_2SiMe_3)_3 + NaH \xrightarrow{\text{solvent}} NaIn(CH_2SiMe_3)_2 + Si(CH_3)_4 \tag{1}$$

The preparative reaction involves an oxidation–reduction process. Indium(III) is reduced to indium(I). Tetramethylsilane must be the product of the oxidation process. Available data are consistent with the hypothesis that the redox process occurs as a facile nonradical reductive elimination reaction of an indium(III) hydride intermediate (see eq 2 and 3). A similar reaction scheme supported by analogous data was proposed for the formation of gallium(I) compounds.[9] When NaD was used as a reagent, the deuterium was quantitatively incorporated into tetramethylsilane as Me_3SiCH_2D as shown by mass spectral data. There are many experimental observations which suggest that a major factor controlling reactivity in the ((trimethylsilyl)methyl)indium system is the ease of formation of the indium(III) hydride intermediate. The reductive elimination reaction is probably very facile because no indium hydride intermediates were ever detected as reaction products. Thus, the relative magnitude of the lattice energy of the metal hydride and the Lewis acidity of the indium(III) reactant must be important. The general order of reactivity of the metal hydrides follows lattice energy: LiH < NaH < KH. Lithium hydride does not react with $In(CH_2SiMe_3)_3$, presumably because the high lattice energy precludes reaction. The dimer[10] $[In(CH_2SiMe_3)_2Cl]_2$ does not react with NaH in hexane because the indium compound is not a sufficiently strong Lewis acid to form the hydride intermediate. The dimer is coordinatively saturated with chlorine bridges and sufficiently stable that $N(CH_3)_3$ does not even form a stable adduct.[10] The metal hydride, KH, with the lowest lattice energy gave surprising results. The potassium derivative $KIn(CH_2SiMe_3)_2$ could not be prepared. Instead, a black solid, indicative of finely divided indium metal, and $Si(CH_3)_4$ were the final products. These results suggest that $KIn(CH_2SiMe_3)_2$ might be formed but reacts further with excess KH. This hypothesis is supported by the observation that KH also reacts with $NaIn(CH_2SiMe_3)_2$ to form a similar black solid and a noncondensable gas, probably hydrogen. Another possible conclusion is that $In(CH_2SiMe_3)$ might be a kinetically unstable species.

$$In(CH_2SiMe_3)_3 + NaH \rightarrow NaIn(CH_2SiMe_3)_3H \tag{2}$$

$$NaIn(CH_2SiMe_3)_3H \xrightarrow[\text{elimination}]{\text{reductive}} NaIn(CH_2SiMe_3)_2 + Si(CH_3)_4 \tag{3}$$

The new indium(I) compounds have properties of typical covalent substances and are soluble in hydrocarbon and aromatic solvents. The compound $NaIn(CH_2SiMe_3)_2$ is a colorless solid at room temperature but upon heating to about 130 °C, it starts to undergo a sequence of nonreversible color changes indicative of decomposition. The cryoscopic molecular weight data for $NaIn(CH_2SiMe_3)_2$ in benzene solution indicate that the compound exists as a hexameric species. Molecular association of the monomeric units can occur by metal–metal bonds using the available electron pair and vacant orbital on each indium(I) atom. An alternative association scheme would require alkyl bridge bonding, which seems less likely. There are no examples of indium compounds which are associated in solution by alkyl bridge bonding,[14] and we have no supportng data for this type of bonding. Thus, metal–metal bonding can be proposed. Similar metal–metal bonding schemes have been suggested for the dimeric and trimeric gallium(I)[9] and related dimeric tin(II)[15] compounds. The two possible arrangements for six $NaIn(CH_2SiMe_3)_2$ formula units are an octahedral cluster with $In(CH_2SiMe_3)_2$ units at each corner or a 12-membered ring. The bulky (trimethylsilyl)methyl groups would provide a hydrocarbon sheath to minimize intermolecular interactions and enhance the solubility of the compound in hydrocarbon and aromatic solvents. A crystallographic study will be required to define the structure.

The ^1H NMR spectrum of $[NaIn(CH_2SiMe_3)_2]_6$ in benzene or hexane solution has three lines, one large line and two smaller lines of equal intensity. The most intense line is assigned to the methyl–silicon protons. The two smaller lines at higher field are related to the protons of the methylene groups bound to indium. The integrated intensity ratio of the larger line to the two smaller ones is 9:2 as required by the CH_2SiMe_3 ligand. The two magnetically distinct lines for the

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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 $NaIn(CH_iSiMe_3)_2{\cdot}MeOC_2H_4OMe$ 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.

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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]

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

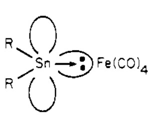
$$n = 1 \text{ or } 2$$

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

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).

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

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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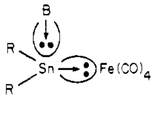

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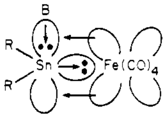

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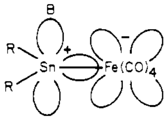

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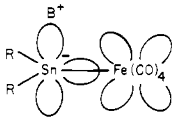

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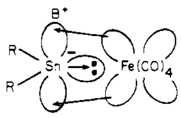

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