with that of a sublimed film of thorocene prepared from $ThCl_4$ and $K_2C_8H_8$ (λ_{max} at 275 and 333 nm). Yields were not determined in the thorium reaction although they appear to be generally lower than in the uranium reaction.

A similar procedure was used with 1.5 mmol of plutonium, ^{239}Pu. A single small chunk was converted to finely divided metal by several cycles of hydride formation and decomposition and was treated with 0.30 mmol of dried and degassed cyclooctatetraene at 160° for 15 min in the absence of mercury. A red sublimate resulted which had the spectrum reported for $Pu(C_8H_8)_2$.[4]

The present preparations provide a dramatic demonstration of the thermodynamic stability of the actinide cyclooctatetraene complexes. Treatment of pyrophoric uranium with cyclopentadiene under the same conditions used to form uranocene failed to produce any detectable amounts of the known compounds $U(C_5H_5)_3$[10] or $U(C_5H_5)_4$.[11]

Further studies are under way concerning this direct reaction. Experiments are in progress employing other actinide metals and substituted cyclooctatetraenes.

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David F. Starks, Andrew Streitwieser, Jr.*
Department of Chemistry, University of California
Berkeley, California 94720
Lawrence Berkeley Laboratory
Berkeley, California 94720

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Syntheses of Intermetallic Oligomers Employing Transition Metal Substituted Tin and Germanium Hydrides

Sir:

The eventual synthesis of linear polymers having backbones comprised entirely of covalently bonded metal atoms is a long range goal of our laboratory.[1] Our interest in such materials stems from the expectation that a coaxially oriented solid derived from such substances would exhibit anisotropic electron transport properties which would be principally dependent upon the structure of the individual polymer molecules.

Consequently, we are interested in preparing metal–metal bonds by methods which avoid strongly basic conditions that might sever metal chains. Most of the known metal–metal bond forming reactions involve a nucleophilic metal anion reacting with another metal halide.[2] The paucity of alternative methods for preparing metal–metal bonds is not surprising when one considers that the great majority of carbon–carbon bond forming reactions employ p–π orbitals which are energetically disfavored for elements beyond the first short period.

Group IVa (Si, Ge, Sn) hydrides are attractive intermediates for intermetallic syntheses in view of three reactions: (a) the widely reported, base catalyzed, self-coupling of Sn–H groups (eq 1),[3] (b) condensations

$$2R_3SnH \xrightarrow{\text{base}} R_3SnSnR_3 + H_2 \tag{1}$$

between Sn–H and Sn–X groups (eq 2),[3] and (c) the

$$R_3SnH + R_3'SnX \longrightarrow R_3SnSnR_3' + HX \tag{2}$$
$$X = NR_2'',\ NArCHO$$

additions of group IVa hydrides to polynuclear metal carbonyls[4] (*cf.* eq 3). Reaction c is the method of

$$2Ph_2SiH_2 + Co_2(CO)_8 \longrightarrow 2HPh_2SiCo(CO)_4 \tag{3}$$

choice for preparing silicon to transition metal bonds[4a] and a few cases have been reported for simple germanium[4b] and tin hydrides;[4c] however the latter afford low yields and complex mixtures.[4c]

We decided to study transition metal substituted germanium and tin hydrides as models for metal–metal bond forming reactions which might be employed in polymerizations of metallic monomers. At the outset of this work a few examples of transition metal substituted germanium hydrides were known[5] but the tin analogs were not. Reduction of the requisite tin and germanium chlorides[6] with $(i\text{-}Bu)_2AlH$ afforded transition metal substituted tin and germanium hydrides in good to excellent yields (*eg.*, eq 4). Using

$$[(OC)_5Mn]_2SnCl_2 + 2(i\text{-}Bu)_2AlH \xrightarrow{\text{hexane}} H_2Sn[Mn(CO)_5]_2 \tag{4}$$

this method the following hydrides were prepared and characterized:[8] **1**, $(OC)_5MnSnPh_2H$ (oil); **2**, $(OC)_5$-

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(6) Prepared by the metathetical reaction of the appropriate transition metal carbonyl anion with the corresponding tin or germanium chloride. Physical and spectroscopic properties were consistent with the formulations and agreed with those previously reported.[7]

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(8) Characterization of the complexes by elemental analyses, molecular weight measurements, infrared spectra in the ν_{CO} region, and pmr spectra was in agreement with our formulations. For example, the complexes $H_2Sn[Mn(CO)_5]_2$ and $HPh_2GeRe(CO)_5$ show sharp singlets in the pmr spectra for the hydride protons at τ 6.10 and 4.55, respectively.

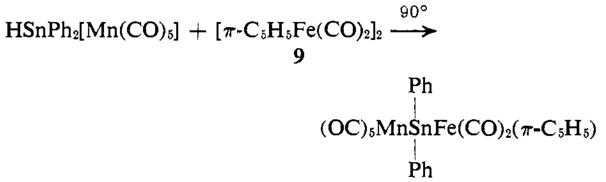
$ReSnPh_2H$ (oil); **3**, $[(OC)_5Mn]_2SnH_2$ (yellow, mp 89–92°); **4**, $[(OC)_5Re]_2SnH_2$ (yellow, mp 94–97°); **5**, $[(OC)_5Mn]_3SnH$ (orange, mp 127–130°); **6**, $(OC)_5MnGePh_2H$ (oil); and **7** $(OC)_5ReGePh_2H$ (white, mp 47–49°). The Ge derivatives **6** and **7** are more stable toward heat and O_2 than the Sn compounds **1–5**. The stability of such tin hydrides appears to be sensitive to the nature of the attached transition metal, and our attempts to prepare tin hydrides containing Co, Mo, W, or Fe substituents were unsuccessful.

Coupling reactions of transition metal substituted silicon, germanium, and tin hydrides have not been previously reported.[9] Having these transition metal–tin hydrides in hand, we first examined tin–tin coupling reactions modeled after those in eq 1 and 2. Both procedures afforded complex, often intractable, mixtures. Careful analysis of these reactions (*cf.* eq 5)

$$(OC)_5MnSnPh_2H + Et_2NSnPh_3 \longrightarrow Et_2NH + Ph_3SnSnPh_3 + Ph_3SnMn(CO)_5 + \text{unidentified products} \quad (5)$$

indicated varying degrees of disproportionation about tin. However, reactions of these tin hydrides with binuclear metal carbonyls were more successful and in some cases selectively afforded metal oligomers. For example the dihydride **3** reacts with $Co_2(CO)_8$ under ambient conditions forming the pentametallic derivative **8** (eq 6). Similarly at 90° the monohydride **1** reacts with the dimeric iron complex **9** to form the trimer **10** (eq 7).

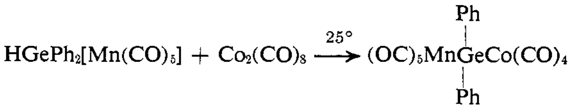
$$\underset{\mathbf{3}}{H_2Sn[Mn(CO)_5]_2} + Co_2(CO)_8 \xrightarrow{25^\circ} \underset{\mathbf{8}}{[(OC)_4Co]_2Sn[Mn(CO)_5]_2} \quad (6)$$



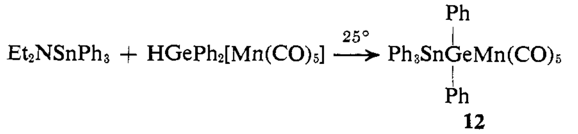
$$HSnPh_2[Mn(CO)_5] + \underset{\mathbf{9}}{[\pi\text{-}C_5H_5Fe(CO)_2]_2} \xrightarrow{90^\circ} (OC)_5Mn\overset{Ph}{\underset{Ph}{Sn}}Fe(CO)_2(\pi\text{-}C_5H_5) \quad (7)$$

10

The moderate thermal instability of these tin hydrides limits the scope of this sort of reaction. For example $Mn_2(CO)_{10}$ fails to react with the dihydride **3** up to 120° at which point **3** undergoes self-coupling forming cyclic oligomers of the type $[Sn[Mn(CO)_5]_2]_n$. Because of this thermal instability we turned our attention to the more robust metal substituted germanium hydrides. $Co_2(CO)_8$ reacts with **6** affording the trimer **11** in high yield (eq 8). These germanium hydrides can also be coupled with tin amido derivatives as illustrated in the formation of **12** (eq 9). When irradiated the manganese substituted germanium hydride **6** undergoes related self-coupling affording the dimer **13**[10] (eq 10)

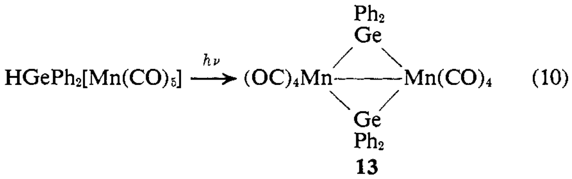


$$\underset{\mathbf{6}}{HGePh_2[Mn(CO)_5]} + Co_2(CO)_8 \xrightarrow{25^\circ} \underset{\mathbf{11}}{(OC)_5Mn\overset{Ph}{\underset{Ph}{Ge}}Co(CO)_4} \quad (8)$$



$$Et_2NSnPh_3 + HGePh_2[Mn(CO)_5] \xrightarrow{25^\circ} Ph_3Sn\overset{Ph}{\underset{Ph}{Ge}}Mn(CO)_5 \quad (9)$$

12

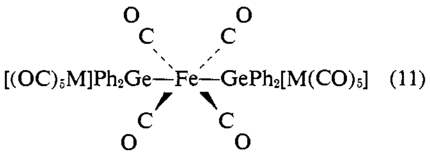


13

which is thought to have the indicated bicyclic structure because of the similarity of its infrared spectrum with that of the structurally characterized silicon analog.[11]

The most interesting reaction is that of $Fe_2(CO)_9$ with **6** and **7** affording the metallic pentamers **14a,b** under mild conditions (eq 11). These new metallic oligomers **8–14** have been characterized by elemental analyses, vibrational spectroscopy, and molecular weight measurements. A trans configuration about iron is most consistent with the ν_{CO} region in the ir spectra of **14a,b**. If this steric assignment (which is currently being examined by X-ray diffraction) is correct, this reaction (eq 11) takes on great importance because difunctional germanium hydrides may react with $Fe_2(CO)_9$ forming linear intermetallic polymers. The apparent transoid nature of the germanium–iron bond forming reaction augers well for directing linear polymerization, avoiding the formation of cycles. We plan to test this hypothesis.

$$2HGePh_2[M(CO)_5] + Fe_2(CO)_9 \longrightarrow$$



14a, M = Mn
b, M = Re

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[9] The following reaction has been observed

$$2HCl_2SiMn(CO)_5 + Mn_2(CO)_{10} \longrightarrow Cl_2Si[Mn(CO)_5]_2$$

J. K. Hoyano and W. A. G. Graham, unpublished results.

[10] Previously prepared by heating Ph_2GeH_2 with $Mn_2(CO)_{10}$ at *ca.* 160°. Note that in reactions of this type transition metal substituted germanium hydrides cannot be isolated (see ref 4b).

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[12] National Research Council of Canada Postdoctoral Fellow.

James P. Collman,* James K. Hoyano,[12] Donald W. Murphy
Department of Chemistry, Stanford University
Stanford, California 94305

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Photochemical Sigmatropic Rearrangement of Boron. Interconversions of Allyl(amino)boranes *via* Occurrence of a 1,3-Aminoboryl Shift

Sir:

One of the more ubiquitous photochemical rearrangement pathways is the 1,3-sigmatropic shift, quantum mechanically and geometrically allowed in the excited state for a suprafacial transfer with configurational retention at the migrating center. Although the actual stereochemistry remains invisible when the migrating group is a π bond and although intimate radical-pair mechanisms rather than concerted reorganizations appear involved in many cases, this formal $[_\pi 2_s + _\sigma 2_s]$