ondary carbon.[8] The stability of **1** and **3** may, of course, be partly due to their inability to disproportionate to olefin and alkane. Our results demonstrate in a direct fashion that alkyl shifts in carbon radicals are slow (or they are disfavored at equilibrium), and our decay rates in those cases where they are first order may be interpreted as minimum values for this rearrangement. Chemical evidence had previously supported this contention.[9,10]

The mechanism of decay of these radicals is not yet known. The obvious possibilities are inter- or intramolecular hydrogen abstraction or methyl elimination. In a preliminary attempt to study the products from **1** we treated *t*-Bu_2CHCl with sodium. The reaction was slow and it required 90 min of refluxing in octane to produce a change in the vpc trace. After this time only a small portion of the chloride had reacted. A number of products had formed, some with short and some with long retention times. One product had the retention time of 2,2,4-trimethyl-3-pentene. One of three peaks with a long retention time had a mass spectral pattern consistent with the formation of a dimer of **1** or *t*-$Bu_2CH_2C(Me_2)\dot{C}H_2$, though no parent ion was formed so the molecular weight could not be determined. However, this product, along with some other products of similar volatility, was also formed when *t*-Bu_2CH_2 was allowed to react with *tert*-butoxy (from di-*tert*-butyl hyponitrite) at ambient temperatures and when chlorinated *t*-Bu_2CH_2 (primary:secondary, 6:1) was allowed to react with sodium.

The rapid, bimolecular, decay of **2** appears anomalous. Perhaps the methyl groups in **2** are better able to avoid each other when **2** dimerizes than when **1** attempts to do so, because of the larger size of the silicon atoms. We are actively studying these and other similar aliphatic radicals.

Acknowledgment. We are extremely grateful to Professor Martin Stiles for providing the sample of tri-*tert*-butylmethane for these experiments.

---

[8] However, the $Me_3C\dot{C}H_2$ radical and other primary alkyl radicals as well as $Me_3C\dot{C}Me_2$ decay by rapid bimolecular processes.[7]

[9] J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959), and references cited.

[10] J. J. Gajewski and L. T. Burka, *J. Amer. Chem. Soc.*, **94**, 8865 (1972), and references cited.

[11] N.R.C.C. Postdoctoral Fellow 1971–1972.

G. D. Mendenhall,[11] K. U. Ingold*
Division of Chemistry, National Research Council of Canada
Ottawa, Ontario, Canada
Received December 6, 1972

Preparation of Di-π-cyclooctatetraene Complexes of Uranium, Thorium, and Plutonium by Direct Reaction of the Metals with Cyclooctatetraene[1]

Sir:

We report the practical preparation of the di-π-cyclooctatetraene complexes of uranium, thorium, and plutonium by direct reaction of the finely divided metals with cyclooctatetraene. These organometallic sandwich compounds have been prepared previously by reaction of cyclooctatetraene dianion with UCl_4,[2] $ThCl_4$,[3] and $[(C_2H_5)_4N]_2PuCl_6$,[4] respectively, in accord with the common preparation of metallocene compounds by reaction of a ligand anion with a metal salt.

Previous preparations of metallocenes from the free metal include the treatment of magnesium[5] or iron[6] with cyclopentadiene at 300–600° to produce $Mg(C_5H_5)_2$ and $Fe(C_5H_5)_2$, respectively, in reactions that may require the prior formation of cyclopentadienyl salts with liberation of hydrogen. A more direct transition metal analogy to our synthesis is the preparation of dibenzenechromium, $Cr(C_6H_6)_2$, in centigram amounts by the co-condensation of vapors of chromium and benzene onto a cold surface.[7]

The present experiments made use of pyrophoric uranium prepared from uranium hydride as described by Seaborg and Katz.[8] Several cycles of formation and decomposition of the hydride gave a finely divided reactive metal.

Reactions were generally run in sealed Pyrex tubes with care taken to exclude air and water. Uranium hydride was formed and decomposed on a vacuum line, and dried and degassed cyclooctatetraene was condensed into an intermediate volumetrically calibrated tube and then onto the uranium. The Pyrex tube containing the uranium–cyclooctatetraene mixture was sealed off and heated in a tube furnance. Yields of $U(C_8H_8)_2$ were determined by triturating the sample with tetrahydrofuran under an inert atmosphere and measuring the absorbance of the 615-nm peak. The presence of uranocene was established unambiguously by the characteristic cascade of bands in the 600–700-nm region.[2] The reaction could be run with either uranium or cyclooctatetraene as the limiting reagent. The highest yield observed, 57%, was obtained in an experiment with excess uranium at 150° for 2.5 hr. The product was also isolated by sublimation from the crude reaction mixture.

An interesting and significant feature of this preparation is the apparent catalytic effect of traces of mercury. Yields were low in the complete absence of mercury; the presence of a mercury manometer on the vacuum line is sufficient to provide the catalytic effect. One especially noteworthy feature of this effect is that previous studies of the mercury–uranium system[9] indicate that their mutual solubility is very small.

The analogous thorium compound, di-π-cyclooctatetraenethorium(IV) or thorocene[3] was formed in the same fashion *via* heating finely divided thorium metal, prepared from thorium hydride, with cyclooctatetraene at 150°. Due to its relative insolubility the thorocene formed was characterized by placing the reaction product inside a quartz cuvette and subliming a thin film of thorocene on the walls of the cuvette. The thorocene isolated in this manner showed a uv spectrum identical

---

[1] Supported in part by National Science Foundation Grant No. GP-31803.

[2] A. Streitwieser, Jr., and U. Muller-Westerhoff, *J. Amer. Chem. Soc.*, **90**, 7364 (1968); A. Streitwieser, Jr., U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *J. Amer. Chem. Soc.*, submitted for publication.

[3] A. Streitwieser, Jr., and N. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7528 (1969).

[4] D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *J. Amer. Chem. Soc.*, **92**, 4841 (1970).

[5] W. A. Barber, *J. Inorg. Nucl. Chem.*, **4**, 373 (1957).

[6] S. A. Miller, J. A. Tebboth, and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

[7] P. L. Timms, *Chem. Commun.*, 1033 (1969); *J. Chem. Educ.*, **49**, 782 (1972).

[8] G. T. Seaborg and J. J. Katz, "The Actinide Elements," McGraw-Hill, New York, N. Y., 1954, p 138 ff.

[9] A. F. Messing and O. C. Dean, ORNL-2871, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1969; Y. Kobayashi and T. Ishimori, *J. Inorg. Nucl. Chem.*, **31**, 981 (1969).

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.

Acknowledgment. We thank Dr. N. Edelstein and Dr. T. Parsons for the use of thorium and plutonium metals.

(10) B. Kanellakopulos, E. O. Fischer, E. Dornberger, and F. Baumgartner, *J. Organometal. Chem.*, **24**, 507 (1970).

(11) E. O. Fischer and Y. Hristidu, *Z. Naturforsch. B*, **17**, 275 (1962).

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

Received January 22, 1973

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

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

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**, $(OC)_5$-

---

(1) C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulku, *J. Amer. Chem. Soc.*, **88**, 4286 (1966).

(2) E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev., Sect. A*, 227 (1970); M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968); 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, Cambridge, England, 1968; N. S. Vyazankin, G. A. Razuvaev, and O. A. Kruglaya, *Organometal. Chem. Rev., Sect. A*, 323 (1968).

(3) *Cf.* H. M. J. C. Creemers and J. G. Noltes, *Recl. Trav. Chim. Pays-Bas*, **84**, 1589 (1965); H. M. J. C. Creemers, F. Verbeck, and J. G. Noltes, *J. Organometal. Chem.*, **8**, 469 (1967); W. P. Neumann and B. Schneider, *Angew. Chem.*, **76**, 891 (1964); H. M. J. C. Creemers and J. G. Noltes, *Recl. Trav. Chim. Pays-Bas*, **84**, 590 (1965); W. P. Neumann, B. Schneider, and R. Sommer, *Justus Liebigs Ann. Chem.*, **692**, 1 (1966); *ibid.*, **692**, 12 (1966); H. M. J. C. Creemers, Ph.D. Thesis, University of Utrecht, 1967, and references cited therein.

(4) (a) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 1133 (1965); A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1640 (1967); W. Jetz and W. A. G. Graham, *ibid.*, **89**, 2773 (1967); W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966); W. Jetz and W. A. G. Graham, *ibid.*, **10**, 1159 (1971); A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 3469 (1971), and references cited therein. (b) E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Amer. Chem. Soc.*, **90**, 3587 (1968); R. Ball, M. J. Bennett, E. H. Brooks, W. A. G. Graham, J. Hoyano, and S. M. Illingworth, *Chem. Commun.*, 592 (1970); S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *ibid.*, 1297 (1969); S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 3469 (1971), and references cited therein, (c) J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *Chem. Commun.*, 965 (1967); J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 264 (1967); S. A. R. Knox and F. G. A. Stone, *ibid.*, 3147 (1970), and references cited therein.

(5) S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 2442 (1972); A. G. Massey, A. J. Park, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **85**, 2021 (1963); N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc. A*, 1130 (1966); R. D. George, K. M. Mackay, and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1505 (1972); R. D. George, K. M. Mackay, and S. R. Stobart, *ibid.*, 974 (1972), and references cited therein.

(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]

(7) R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2486 (1962); J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1365 (1967).

(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.