(method b).

5. Synthesis of (η^5-$C_5H_4CO_2^-$)Fe^+(η^6-C_6Me_6) (7). **6d** (472 mg, 1 mmol) was dissolved in 50 mL of ethanol, and 40 mg of NaOH (1 mmol) was added. A large excess of acetone was then added to the solution. the zwitterion precipitates at −20 °C, the $NaPF_6$ salt being still soluble. Pure **7** (200 mg, 53%) was obtained as a yellow powder. The absence of $NaPF_6$ in these samples was checked by infrared spectroscopy (no PF band at ν_{PF} = 855 cm^{-1}). However, the zwitterion is obtained as a trihydrate. ^1H NMR (CD_3CN, δ, Me_4Si): 4.66 (t, 2 H, C_5H_4), 4.39 (t, 2 H, C_5H_4), 2.39 (s, 18 H, $C_6(CH_3)_6$), 2.32 (s, H_2O). ^{13}C NMR (D_2O, δ, DSS): 173.1 (CO_2), 101.3 ($C_6(CH_3)_6$), 88.7 (substituted CpC), 82.2 (Cp); 80.2 (Cp), 18.4 ($C_6(CH_3)_6$). Infrared (Nujol, cm^{-1}): 1650 (s, ν_{CO}), 3400 (s, ν_{OH}). Mössbauer parameters (293 K): QS = 1.86 mm s^{-1}; IS = 0.54 mm s^{-1}. Anal. Calcd for $C_{18}H_{22}O_2Fe{\cdot}3H_2O$: C, 56.85; H, 7.42; Fe, 14.68. Found: C, 56.64; H, 7.28; Fe, 15.00.

6. Synthesis of (η^5-$C_5H_4CO_2^-$)Fe^I(η^6-C_6Me_6) (9) from 7. (a) Characterization by EPR Spectroscopy. **7** (10 mg, 0.031 mmol) were mixed with 10 mg of $LiAlH_4$ (0.27 mmol). The well-ground mixture was introduced into an EPR tube. The latter was purged with argon and then cooled to −50 °C; 2 mL of degassed THF, previously cooled to −50 °C, was added. EPR spectrum at 133 K: g_x = 1.9990; g_y = 2.0647; g_z = 1.8969.

(b) Synthesis and Characterization of 9. In a Schlenk tube, 652 mg of **7** (2 mmol), 23 g of 1% Na/Hg (10 mmol), and 100 mL of degassed THF were introduced. After 2 h of reduction at 20 °C, the purple suspension was isolated by transfer into another Schlenk tube. The purple precipitate was filtered and rinsed with 10 mL of THF. **9** was slightly THF soluble; 412 mg (60%) of powder was obtained. **9** was extremely air-sensitive in solution and in the solid state: upon contact with air, it was instantaneously transformed to **7**. Infrared (Nujol, cm^{-1}): 1625 (s, ν_{CO}). Mössbauer parameters (77 K): QS = 1.54 mm s^{-1}; IS = 0.83 mm s^{-1}. Anal. Calcd for $C_{18}H_{22}O_2FeNa$: C, 61.91; H, 6.35. Found: C, 61.75; H, 6.39.

7. Reduction of [(η^5-$C_5H_4CO_2H$)Fe(η^6-C_6Me_6)]$^+PF_6^-$ (6). (a) Characterization of (η^5-$C_5H_4CO_2H$)Fe^I(η^6-C_6Me_6) (8). Cation **6** (10 mg, 0.021 mmol) and 10 mg of $LiAlH_4$ (0.27 mmol) were mixed and introduced into an EPR tube; the latter was purged with argon and cooled to −50 °C. Degassed THF (2 mL) was introduced at −50 °C. In 1 min, the solution turned green-blue; the tube was then cooled to 77 K. EPR (135 K): g_x = 2.0024; g_y = 2.0659; g_z = 1.9296 (these values are characteristic of Fe^I sandwichs).

(b) Characterization of (η^5-$C_5H_4CO_2^-$)Fe^+(η^6-C_6Me_6) (7). In a Schlenk tube, 170 mg of **6** (0.36 mmol), 4.1 g of 1% Na/Hg (1.8 mmol of Na) and 10 mL of degassed THF were introduced under argon at 20 °C. The solution immediately became blue, indicating the formation of the neutral Fe^I compound **8**. After 15 min of reduction at 20 °C, the blue color of the solution disappeared; 100 mL of pentane was added to impede further reduction. After filtration, 150 mg of a yellow powder was recovered. The infrared spectrum showed a strong band at 1650 cm^{-1} (ν_{CO}), characteristic of the zwitterionic compound **7**. The absence of ν_{CO} at 1730 cm^{-1} and of ν_{OH} at 3400 cm^{-1} indicated that **6** has been fully reduced. A strong PF band at 855 cm^{-1} indicated the presence of $NaPF_6$. The latter was removed by recrystallization from acetone, and **7** was identified by comparison with an authentic sample.

(c) Synthesis and Characterization of (η^5-$C_5H_4CO_2^-$)Fe^I(η^6-C_6Me_6) (9). In a Schlenk tube, 472 mg of **6** (1 mmol), 11.5 g of 1% Na/Hg (5 mmol of Na), and 100 mL of degassed THF were introduced under argon at 20 °C. The solution immediately became blue, and this color disappeared after 15 min; then the suspension progressively turned purple. After 2 h of reduction at 20 °C, the purple suspension was transferred to another Schlenk tube to remove the amalgam and then filtered. A purple powder (250 mg) was obtained, which still contained $NaPF_6$. Washing several times with THF did not remove all the $NaPF_6$. On the other hand, the extremely air-sensitive compound **9** was not stable in acetone or in acetonitrile. It has been characterized by Mössbauer spectroscopy (see above) and by an EPR spectrum at 3.5 K of a solid-state sample (*g* = 1.9725; for a solution spectrum, see above).

Acknowledgment. We are grateful to Professor F. Varret and Dr. J.-P. Mariot (University of le Mans) for recording Mössbauer spectra and for their stimulating interest, F. Le Floc'h (Brest) for his kind EPR assistance, and Dr. S. Sinbandhit (Centre de Mesures Physiques, Rennes) for diligent help in recording NMR spectra. The "Pontifica Universidad Catolica de Chile" and the "Ministère des Affaires Etrangères" have provided funding facilities for the sabatical leave of E.R.E. D.A. also wishes to thank UNESCO for funding (PNUD program) and the Chilian University for kind hospitality. A DGRST grant to V.G. is acknowledged.

Reaction of Decamethylstannocene with Lithium Alkyls

Peter Jutzi* and Bernd Hielscher

Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld, FRG

Received April 30, 1986

The attack of alkyllithiums on (η^5-Me_5C_5)$_2$Sn (**1**) resulted in an overall nucleophilic substitution at the tin atom with pentamethylcyclopentadienide as the leaving group. Thus, the reaction of **1** with $(Me_3Si)_2CHLi$ yielded Me_5C_5Li and $(Me_3Si)_2CH)_2Sn$ (**2**). Treatment of **1** with MeLi produced Me_5C_5Li and apparently a mixture of oligomeric stannylenes $[Me_2Sn]_n$; the initial formation of a short-lived [bis(pentamethylcyclopentadienyl)alkyltin]lithium species (η^1-Me_5C_5)$_2$Sn(Me)Li (**3**) was demonstrated by trapping experiments with methyl iodide and methyl-d_3 iodide, which yielded (η^1-Me_5C_5)$_2Sn(CH_3)_2$ (**4**) and (η^1-Me_5C_5)$_2Sn(CH_3)(CD_3)$ (**5**), respectively. The intermediate **3** is postulated also during reduction of (η^1-Me_5C_5)$_2$Sn(Me)Cl (**6**) with $Li_2C_8H_8$.

Introduction

The use of the cyclopentadienyl ligand in tin(II) chemistry led to the first synthesis of a monomeric diorganotin(II) species, dicyclopentadienyltin,[1] the parent compound of what has become a long series.[2] Since the compound is a π-complex with tin as central atom, it was named stannocene in analogy to the well-known iron compound. Investigation of its reactions with electrophiles

---

[1] (a) Fischer, E. O.; Grubert, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1956**, *11B*, 423. (b) Dave, L. D.; Evans, D. F.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3684.

[2] (a) Jutzi, P.; Hielscher, B. *J. Organomet. Chem.* **1985**, *291*, C25 and references therein. (b) Kohl, F. X.; Schlüter, E.; Jutzi, P.; Krüger, C.; Wolmershäuser, G.; Hofmann, P.; Stauffert, P. *Chem. Ber.* **1984**, *117*, 1178 and references therein.

0276-7333/86/2305-2511$01.50/0

revealed that an attack at the cyclopentadienyl system is followed by loss of a ligand, yielding ionic or covalent tin(II) species of composition CpSnX,[3] while reactions at the tin center gave rise to tin(IV) compounds.[4] Just as in the case of an electrophilic attack, stannocene and its derivatives might provide sites for nucleophilic attack, not only at the periphery of the molecule but also at the metal center. While it is well established that the protons of the cyclopentadienyl ring can be metalated readily,[5] an interaction between nucleophiles and the central tin atom has not yet been clearly demonstrated. To avoid competition with the cyclopentadienyl protons, permethylated stannocene[6] is a more appropriate substrate for the study of nucleophilic substitution at the central tin atom. We have examined reactions of decamethylstannocene with alkyllithiums and report experimental evidence for the formation of a [bis(η^1-pentamethylcyclopentadienyl)alkyltin]lithium intermediate.

Results and Discussion

Treatment of decamethylstannocene (1) with lithium alkyls resulted in immediate precipitation of lithium pentamethylcyclopentadienide. The corresponding formation of a substituted diorganotin compound was first proved in the reaction of 1 with 2 equiv of [bis(trimethylsilyl)methyl]lithium (eq 1). A pentane-soluble compound was isolated and identified as bis[bis(trimethylsilyl)methyl]tin(II) (2), a substance already reported by Lappert and co-workers.[7] Probably because of redistribution reactions of organotin(II) compounds,[3b] treatment of 1 with an equimolar amount of this alkyllithium reagent also yielded 2, while part of the starting material remained unchanged (eq 2). Compound 2 was crystallized from the extract, and NMR, spectra of the noncrystallizing orange-red oil showed it to consist mainly of decamethylstannocene (1). Reactions of 1 with such alkyllithiums as methyllithium, *n*-butyllithium, or *tert*-butyllithium in a 1:1 ratio always yielded red-orange suspensions. Generally, after evaporation of the solvents, the residue was digested with pentane and filtered, leaving insoluble lithium pentamethylcyclopentadienide, which then was treated with trimethyltin chloride to yield (η^1-pentamethylcyclopentadienyl)trimethyltin[8] or treated with methanol to give pentamethylcyclopentadiene, both identified spectroscopically. Unreacted decamethylstannocene (1) was crystallized from the pentane extracts. According to eq 1 the conversion of 1 was completed with 2 equiv of the alkyllithium reagent. The corresponding diorganotin compounds, known to form complex mixtures of $[\text{R}_2\text{Sn}]_n$,[9] were detected spectroscopically for R = Me.

$$\underset{\mathbf{1}}{(\eta^5\text{-Me}_5\text{C}_5)_2\text{Sn}} + 2\text{RLi} \rightarrow 2\text{Me}_5\text{C}_5\text{Li} + \underset{\mathbf{2}}{\text{R}_2\text{Sn}} \qquad (1)$$

$$\underset{\mathbf{1}}{(\eta^5\text{-Me}_5\text{C}_5)_2\text{Sn}} + \text{RLi} \rightarrow \text{Me}_5\text{C}_5\text{Li} + {}^1/_2\underset{\mathbf{1}}{(\eta^5\text{-Me}_5\text{C}_5)_2\text{Sn}} + {}^1/_2\underset{\mathbf{2}}{\text{R}_2\text{Sn}} \qquad (2)$$

$$\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$$

For the course of the reactions given in eq 1 and 2, various mechanisms are possible. Besides a simple substitution following an $\text{S}_\text{N}2$-type mechanism, the formation of a cyclopentadienyl-containing (triorganotin)lithium intermediate might also be postulated. In general, triorganotin–alkali-metal species with various alkyl or aryl ligands, e.g., (triphenyltin)lithium, are known to be in equilibrium with the corresponding diorganotin and organolithium compounds.[10] NMR spectra of a mixture of stannocene and lithium cyclopentadienide suggested an exchange of cyclopentadienyl groups in solution,[11] but this does not appear to be a conclusive argument for the formation of a [tris-η^1-cyclopentadienyl)tin]lithium intermediate. For the case in point, the precipitation of the insoluble $\text{Me}_5\text{C}_5\text{Li}$ would influence such an equilibrium and result in the formation of R_2Sn compounds.

As (triorganotin)lithium compounds are known to react with alkyl halides to form organotin(IV) species, we intended to trap an intermediate by addition of methyl iodide to the reaction mixture from 1 and the alkyllithium reagent. But no such reaction was detected, and the compounds isolated were $\text{Me}_5\text{C}_5\text{Li}$ and the remaining 1. Hence, any (triorganotin)lithium intermediate might be only a short-lived species that would have to be trapped in situ.

Upon treatment of decamethylstannocene (1) with methyllithium in the presence of methyl iodide, no precipitation of lithium pentamethylcyclopentadienide was observed. From the pentane extract of the evaporated reaction mixture a pale yellow compound was crystallized, bis(η^1-pentamethylcyclopentadienyl)dimethyltin (4). Replacing the trapping agent by methyl-d_3 iodide yielded the mixed methyl-d_3 methyl compound 5 exclusively (eq 3).

$$\underset{\mathbf{1}}{(\eta^5\text{-Me}_5\text{C}_5)_2\text{Sn}} + \text{MeLi} \xrightarrow[-\text{LiI}]{\text{RI}} (\eta^1\text{-Me}_5\text{C}_5)_2\text{Sn(Me)R} \qquad (3)$$

$$\mathbf{4}\text{: R = Me} \qquad \mathbf{5}\text{: R = Me-}d_3$$

The origin of 4 and 5 from an oxidative addition reaction of the alkyl halide followed by methylation of the resulting organotin(IV) iodide can be ruled out since methyl iodide and 1 do not react markedly—in contrast to the unsubstituted stannocene.[12] Thus, we conclude the initial step to be the attack of the alkyllithium agent, i.e., mechanism involving a [bis(η^1-pentamethylcyclopentadienyl)methyltin]lithium intermediate.

Surprisingly, the reaction of 1 with *n*-butyllithium instead of methyllithium in the presence of an excess of methyl iodide also yielded the dimethyl derivative 4 (eq 4). Compound 4 was formed at various temperatures and

$$\underset{\mathbf{1}}{(\eta^5\text{-Me}_5\text{C}_5)_2\text{Sn}} + n\text{-BuLi} \xrightarrow[-n\text{-BuI}/-\text{LiI}]{\text{MeI(excess)}} \underset{\mathbf{4}}{(\eta^1\text{-Me}_5\text{C}_5)_2\text{SnMe}_2} \qquad (4)$$

ratios of methyl iodide; a maximum yield was reached at

---

[3] (a) Bos, K. D.; Bulten, E. J.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1975**, *99*, 71. (b) Kohl, F. X.; Jutzi, P. *Chem. Ber.* **1981**, *144*, 488. (c) Dory, T. S.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *J. Organomet. Chem.* **1985**, *281*, C1.

[4] (a) Bos, K. D.; Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1974**, *67*, C13. (b) Schröer, U.; Albert, H. J.; Neumann, W. P. *J. Organomet. Chem.* **1975**, *102*, 291. (c) Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141.

[5] (a) Bulten, E. J.; Budding, A. H. *J. Organomet. Chem.* **1978**, *157*, C3. (b) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239. (c) Cowley, A. H.; Jutzi, P.; Kohl, F. X.; Lasch, J. G.; Norman, N. C.; Schlüter, E. *Angew. Chem.* **1984**, *96*, 603.

[6] Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757.

[7] Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

[8] Davison, A.; Rakita, P. E. *Inorg. Chem.* **1970**, *9*, 289.

[9] Neumann, W. P. *The Organic Chemistry of Tin*; Wiley-Interscience: New York, 1970.

[10] (a) Flitcroft, N.; Kaesz, H. D. *J. Am. Chem. Soc.* **1963**, *85*, 1377. (b) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 181; **1963**, *28*, 237. (c) Tamborski, C.; Ford, F. E.; Lehn, W. L.; Soloski, E. J. *Org. Chem.* **1962**, *27*, 619. (d) Aylett, B. J. *Organometallic Compounds*; Chapman and Hall: London, 1979; Vol. I, Part 2, p 264.

[11] Bos, K. D.; Bulten, E. J.; Meinema, H. A.; Noltes, J. G. *J. Organomet. Chem.* **1979**, *168*, 159.

[12] Schröer, U.; Albert, H. J. *J. Organomet. Chem.* **1973**, *60*, C6.

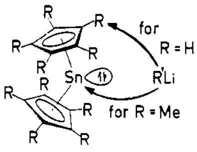


Figure 1. Sites for a nucleophilic attack at stannocene.

−60 °C by using a 50% excess of methyl iodide (3 equiv relative to n-BuLi), while lower amounts of the alkyl halide and higher temperatures favored the formation of Me_5C_5Li with incomplete conversion of 1 just as in eq 2. However, no bis(η^1-pentamethylcyclopentadienyl)-n-butylmethyltin was observed. The formation of the dimethyl derivative 4 apparently arose from an initial metal–halogen exchange between n-butyllithium and the trapping agent.

Because (triorganotin)lithium species can be formed by reaction of a triorganotin halide and lithium metal,[4] the reduction of bis(η^1-pentamethylcyclopentadienyl)organotin halide ought to yield the same intermediate and undergo identical reactions. To study this, we prepared bis(η^1-pentamethylcyclopentadienyl)methyltin chloride (**6**) from methyltin trichloride and lithium pentamethylcyclopentadienide (eq 5). Compound **6** was then reduced with dilithium cyclooctatetraenide (eq 6). After insoluble lithium pentamethylcyclopentadienide was separated, decamethylstannocene (**1**) was isolated from the soluble material; the corresponding, also soluble tin(II) species was detected spectroscopically.

$$MeSnCl_3 \xrightarrow[-2LiCl]{2Me_5C_5Li} \underset{\mathbf{6}}{(\eta^1\text{-}Me_5C_5)_2Sn(Me)Cl} \tag{5}$$

$$\underset{\mathbf{6}}{(\eta^1\text{-}Me_5C_5)_2Sn(Me)Cl} \xrightarrow[-LiCl \atop -C_8H_8]{Li_2C_8H_8} Me_5C_5Li + {}^1/_2\underset{\mathbf{1}}{(\eta^5\text{-}Me_5C_5)_2Sn} + {}^1/_2n[Me_2Sn]_n \tag{6}$$

Since, the reduction of bis(η^1-pentamethylcyclopentadienyl)methyltin chloride (**6**) with dilithium cyclooctatetraenide yielded the same mixture of Me_5C_5Li, **1**, and $[Me_2Sn]_n$ as the conversion of **1** with equimolar amounts of methyllithium, it was concluded that these products had the same origin: an intermediate [bis(η^1-pentamethylcyclopentadienyl)methyltin]lithium (**3**). Unfortunately, trapping experiments failed, probably because of fast side reactions between methyl iodide and the reducing agent.

Conclusion

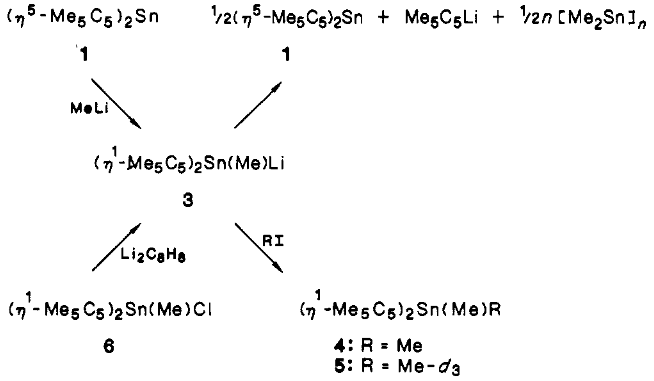
For the nucleophilic alkyllithiums the stannocene molecule provides two sites of attack: the protons of the cyclopentadienyl ligands and the central tin atom (see Figure 1). While unsubstituted stannocene undergoes metalation of cyclopentadienyl protons,[3] the permethylated stannocene **1** is attacked only at the central tin atom. The reaction products strongly suggest the formation of a bis(η^1-pentamethylcyclopentadienyl)-substituted (triorganotin)lithium intermediate (see Scheme I). In the presence of methyl iodide, the intermediate is trapped, yielding tin(IV) compounds; otherwise loss of lithium cyclopentadienide takes place to give substituted diorganotin species.

Experimental Section

All reactions were performed in an atmosphere of dried, oxygen-free argon using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified.

Melting points were determined with a Büchi 510 capillary melting point apparatus. ^{1}H NMR spectra were recorded on Varian EM 360 L (60-MHz) and Bruker AM 300 (300-MHz) spectrometers; ^{13}C NMR spectra (75-MHz, ^{1}H-decoupled) and ^{119}Sn NMR spectra (112-MHz, ^{1}H-decoupled) were also recorded on the Bruker AM 300 spectrometer. Mass spectra were obtained from a Varian 311 A spectrometer (70 eV, 300-μA emission); only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen) or the analytical laboratory of the Universität Bielefeld.

Scheme I



Bis[bis(trimethylsilyl)methyl]tin(II) (2) from 1.[6] During 20 min, a 0.60 M solution of [bis(trimethylsilyl)methyl]lithium[7] in diethyl ether (25.0 mL, 15.0 mmol) was added to a solution of decamethylstannocene[6] (1) (2.92 g, 7.50 mmol) in diethyl ether (100 mL) at 0 °C. The dark red suspension was allowed to warm to room temperature and stirred for 1 h. After evaporation of the solvent in vacuo, the residue was extracted with pentane (100 mL). Concentrating the solution and cooling to −20 °C yielded 2.13 g (65%) of brick-chrome crystals: mp 136–138 °C; ^{1}H NMR (C_6D_6) δ 1.74 (s, 1 H, $(Me_3Si)_2CH$), 0.23 (s, 18 H, $(Me_3Si)_2CH$); $^{13}C\{^1H\}$NMR (C_6D_6) δ 48.0 ($(Me_3Si)_2CH$), 4.1 ($(Me_3Si)_2CH$). Anal. Calcd for $C_{14}H_{38}Si_4Sn$ (437.49): C, 38.43; H, 8.75. Found: C, 38.36; H, 8.62.

Bis(η^1-pentamethylcyclopentadienyl)dimethyltin (4). A solution of decamethylstannocene (1) (2.28 g, 5.86 mmol) and methyl iodide (1.00 mL, 16.1 mmol) in tetrahydrofuran (40 mL) was cooled to −80 °C and treated with a 0.93 M solution of methyllithium in ether (6.27 mL, 5.86 mmol). The bright yellow solution turned to a pale yellow suspension, which cleared up again upon warming slowly. The solvents were removed in vacuo, and the residue was extracted with petroleum ether (30 mL). Within 72 h at 5 °C, a colorless oil separated which was removed and decanted; concentrating the solution and cooling to −20 °C yielded 1.88 g (77%) of colorless scales: mp 78 °C; ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 30 H, $^3J_{^{117,119}Sn-H} = 20.7$ Hz, Me_5C_5), −0.14 (s, 6 H, Me_2Sn, $^2J_{^{119}Sn-H} = 44.9$ Hz, $^2J_{^{117}Sn-H} = 43.0$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 120.2 (Me_5C_5), 12.1 (Me_5C_5), −8.2 (Me_2Sn); $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ 29; MS, m/e (relative intensity) 420 ($M^{\bullet+}$, 1.7), 285 ($Me_5C_5SnMe_2^+$, 100), 255 ($Me_5C_5Sn^+$, 71.9), 135 ($Me_5C_5^+$, 99.0). Anal. Calcd for $C_{22}H_{36}Sn$ (419.22): C, 63.03; H, 8.66. Found: C, 63.17; H, 8.65.

Compound 4 from 1 and n-BuLi in the Presence of Methyl Iodide. A solution of decamethylstannocene (1) (3.24 g, 8.32 mmol) and methyl iodide (1.55 mL, 25.0 mmol) in tetrahydrofuran (50 mL) was cooled to −60 °C and treated with a 1.58 M solution of n-butyllithium in hexane (5.27 mL, 8.33 mmol). After the suspension was allowed to warm slowly, the solvent was evaporated in vacuo. The residue was digested with pentane (60 mL), and the mixture was stored at 5 °C for 72 h before the insoluble material was filtered. Concentration the solution and cooling to −20 °C yielded 2.40 g (69%) of 4: mp 78 °C; ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 30 H, Me_5C_5, $^3J_{^{119}Sn-H} = 21.0$ Hz; $^3J_{^{117}Sn-H} = 20.3$ Hz), −0.14 (s, 6 H, Me_2Sn, $^2J_{^{119}Sn-H} = 45.0$ Hz, $^2J_{^{117}Sn-H} = 43.0$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 120.2 (Me_5C_5), 12.1 (Me_5C_5), −8.3 (Me_2Sn); $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ 30.

Bis(η^1-pentamethylcyclopentadienyl)methyl(trideuteriomethyl)tin (5). A solution of decamethylstannocene (3.01 g, 7.73 mmol) and methyl-d_3 iodide (2.00 g, 13.8 mmol) in tetrahydrofuran (150 mL) cooled to −60 °C was treated with a 1.62 M solution of methyllithium in diethyl ether (4.78 mL, 7.74

mmol). The mixture was allowed to warm slowly and stirred for 15 h at room temperature. The solvents were removed in vacuo, and the residue was extracted with pentane (50 mL). Concentrating the solution and cooling to −20 °C yielded 1.62 g (50%) of pale yellow crystals: mp 77 °C; ^{1}H NMR (CDCl$_3$) δ 1.73 (s, 30 H, Me_5C_5, $^3J_{^{117,119}Sn-H}$ = 20.4 Hz), −0.02 (s, 3 H, Me_2Sn, $^2J_{^{119}Sn-H}$ = 44.6 Hz, $^2J_{^{117}Sn-H}$ = 42.8 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 120.4 (Me_5C_5), 12.0 (Me_5C_5), −8.4 (Me_2Sn); ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ 31; MS, *m/e* (relative intensity) 423 ($M^{\bullet+}$, 1.1), 288 ($Me_5C_5SnMe(Me\text{-}d_3)^+$, 80.7), 255 ($Me_5C_5Sn^+$, 68.8), 135 ($Me_5C_5^+$, 100). Anal. Calcd for $C_{22}H_{33}D_3Sn$ (422.24): C, 62.58; H (D), 9.31. Found: C, 62.61; H, 9.45.

Bis(η^1-pentamethylcyclopentadienyl)methyltin Chloride (6). Methyltin trichloride (27.9 g, 116 mmol) was added during 30 min to an ice-cooled suspension of lithium pentamethylcyclopentadienide, prepared from a solution of 31.6 g (232 mmol) of pentamethylcyclopentadiene in tetrahydrofuran (about 700 mL) and a 1.55 M solution of *n*-butyllithium in hexane (155 mL, 232 mmol). The clear yellow solution was stirred for 20 h. Removal of the solvents in vacuo and extraction of the residue with 250 mL of petroleum ether were followed by concentrating and cooling the solution to −30 °C to yield 22.3 g (44%) of yellow crystals: mp 82–90 °C; ^{1}H NMR (CDCl$_3$) δ 1.76 (s, 30 H, Me_5C_5, $^3J_{^{117,119}Sn-H}$ = 28.5), −0.04 (s, 3 H, MeSn, $^2J_{^{117,119}Sn-H}$ = 44.0 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 122.0 (Me_5C_5), 11.9 (Me_5C_5), −5.9 (MeSn); ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ 43; MS, *m/e* (relative intensity) 440 ($M^{\bullet+}$, 1.8), 305 ($Me_5C_5Sn(Me)Cl^+$, 9.5), 255 ($Me_5C_5Sn^+$, 4.4), 135 ($Me_5C_5^+$, 100). Anal. Calcd for $C_{21}H_{33}SnCl$ (439.64): C, 57.37; H, 7.56. Found: C, 57.65; H, 7.60.

Reduction of 6 with Dilithium Cyclooctatetraenide. A solution of **6** (5.36 g, 12.3 mmol) in tetrahydrofuran (20 mL) was treated at −50 °C with the reagent, prepared from lithium dispersion (170 mg, 24.5 mmol) and cyclooctatetraene (1.39 mL, 12.3 mmol) in tetrahydrofuran (25 mL). The green-brown mixture was allowed to warm slowly, and stirring was continued for 6 days. After removal of the solvent in vacuo, the residue was extracted with 50 mL of petroleum ether. Concentrating the solution and cooling to −20 °C yielded a crude product. Recrystallization from pentane (cooling to −80 °C required) gave 529 mg (22%) of decamethylstannocene; ^{1}H NMR (CDCl$_3$) δ 2.10 (s, $^3J_{^{117,119}Sn-H}$ = 3.6 Hz); ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ −2141. Anal. Calcd for $C_{20}H_{30}Sn$ (389.15): C, 61.72; H, 7.77. Found: C, 61.50; H, 7.82.

Acknowledgment. We express our thanks to F. X. Kohl for valuable discussions during preparation of the manuscript.

Registry No. 1, 68757-81-3; 2, 41823-72-7; 4, 104834-02-8; 5, 104807-97-8; 6, 104807-98-9; [bis(trimethylsilyl)methyl]lithium, 41823-71-6; methyllithium, 917-54-4; *n*-butyllithium, 109-72-8; lithium pentamethylcyclopentadienide, 51905-34-1; dilithium cyclooctatetraenide, 37609-69-1; methyltin trichloride, 993-16-8.

Chemistry of Oxophilic Transition Metals. 2.[†,‡] Novel Derivatives of "Titanocene" and "Zirconocene"

Tomas Cuenca, Wolfgang A. Herrmann,* and Terence V. Ashworth

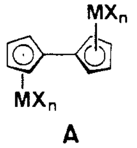
Anorganisch-chemisches Institut der Technischen Universität München, D-8046 Garching, Germany

Received April 23, 1986

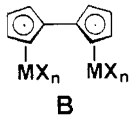
Reduction of dichlorobis(η^5-cyclopentadienyl)titanium(IV) (**3**) with 1.5 equiv of sodium amalgam (Na/Hg) gives the dinuclear η^5:η^5-fulvalene complex **4** of composition $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ and the "titanocene" **5** in 40% yield each; both compounds represent Ti(III) species. The chloro-bridged complex **4** undergoes quick oxidation upon exposure to air, thus yielding the Ti(IV) derivative $[(\eta^5\text{-}C_5H_5)TiCl]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}O)$ (**6**). Reduction of **4** with lithium triethylhydridoboranate cleanly gives "titanocene" **5**, with the latter compound representing a good starting material for the synthesis of the sulfido-bridged fulvalene complex $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}S)]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (**7**). Compound **7** in turn undergoes a sulfur/oxygen exchange reaction when treated with molecular oxygen; in this case, the oxo-/sulfido-bridged derivative $[(\eta^5\text{-}C_5H_5)Ti]_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$ (**8**) is formed.

Introduction

The chemistry of organometallic compounds containing fulvalene ligands has seen a considerable development in the past few years. This particular ligand allows the design of dinuclear complexes in which the metals can be in trans or cis position to each other as shown in A and B, respectively. Such compounds have been proposed as models in organic synthesis, and they may be attractive as sources of active centers in various catalytic processes.



A



B

Three general synthetic procedures have been devised to prepare fulvalene complexes of transition metals: (i) coupling of cyclopentadienyl ligands,[1] (ii) reactions with the fulvalene dianion,[2] and (iii) reaction of dihydrofulvalene with metal carbonyls.[3] ^{1}H NMR spectroscopy provides a convenient tool of characterizing fulvalene compounds: the presence of a plane of symmetry through the C1–C1' bond in the fulvalene ligand gives rise to an A_2B_2 spin system (sometimes AA'BB') which is observed as two triplets or pseudotriplets. When this plane of symmetry is absent, four multiplets of an ABCD spin system are rather observed.

Fulvalene complexes of the group IV (4[9]) transition metals have been confined, until recently, to compounds

---

[†] This paper is dedicated to Professor R. Usøn on the occasion of his 60th birthday.

[‡] For part 1 of this series, see ref 5.

(1) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676 and references cited therein.

(2) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788. Smart, J. C.; Curtis, C. J. *J. Amer. Chem. Soc.* **1977**, *99*, 3518. McKinney, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 603. Köhler, F. H.; Doll, K. H.; Prössdorf, W.; Müller, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 151. Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1973**, *49*, C43. Le Vanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009.

(3) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

0276-7333/86/2305-2514$01.50/0