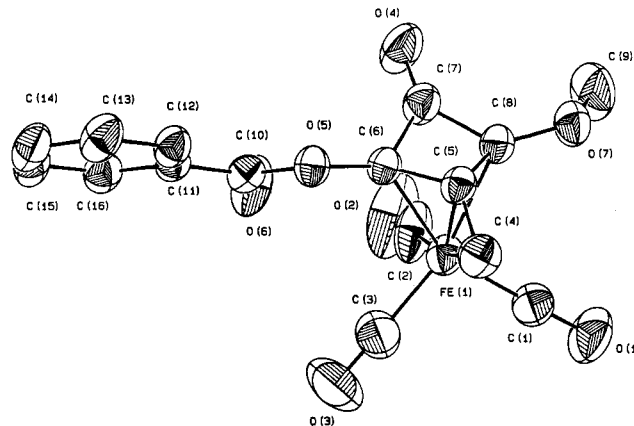platinum compounds. These results are consistent with the proposal that α-silyl elimination and the formation of silyl(silylene) complexes occur early in the catalytic redistribution of hydridodisilanes by platinum complexes.[2b-c,17] Further experiments along these lines are in progress.

Supplementary Material Available: Spectroscopic characterizations of new compounds and complete tables of positional parameters, bond lengths and angles, and least-squares planes for **1b** (21 pages); a listing of structure factors for **1b** (40 pages). Ordering information is given on any current masthead page.

(17) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263–9264. (b) Ojima, I.; Inaba, S. I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7–C8.

A Novel Synthesis of Functional, Cyclic (Trimethylenemethane)tricarbonyliron Complexes by the Reactions of α-Substituted Allenyllithium Reagents with Pentacarbonyliron

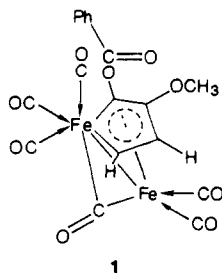**Dietmar Seyferth,* Lea L. Anderson, and William M. Davis**

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Summary: The reaction of (α-methoxyallenyl)lithium with pentacarbonyliron at −78 °C, followed by addition of an acid chloride, gives organoiron products in which the organic ligand is composed of a four-membered ring, three carbon atoms of which plus an exo ═CH₂ group make up a trimethylenemethane unit which is bonded to an Fe(CO)₃ moiety, [η⁴-RC(O)OCC(═CH₂)C(OMe)C═O]Fe-(CO)₃. The allenyllithium reagents CH₂═C═C(SMe)Li and CH₂═C═C(NMe₂)Li form similar products in their reactions with Fe(CO)₅.

In earlier work, we found the reaction of (α-methoxyallenyl)lithium with Fe₃(CO)₁₂, followed by addition of benzoyl chloride, to give as an unexpected product, the ferrole **1**, whose structure was established by X-ray crys-


1

tallography.[1] In a continuation of this study, we have

Figure caption

Figure 1. ORTEP representation of compound **2a** (40.0% probability ellipsoids). Hydrogen atoms are omitted for clarity. Important bond distances (Å): Fe–C(3), 1.785 (6); Fe–C(1), 1.785 (5); Fe–C(2), 1.792 (6); Fe–C(5), 1.944 (4); Fe–C(6), 2.068 (4); Fe–C(8), 2.128 (4); Fe–C(4), 2.208 (4); O(5)–C(6), 1.382 (5); O-(4)–C(7), 1.202 (5); O(7)–C(9), 1.416 (6); C(4)–C(5), 1.388 (6); O(1)–C(1), 1.146 (5); O(2)–C(2), 1.134 (6); O(3)–C(3), 1.137 (6); C(6)–C(7), 1.493 (6); C(7)–C(8), 1.497 (6); O(7)–C(8), 1.337 (5). Important bond angles (deg): C(6)–C(7)–C(8), 85.1 (4); C(5)–C-(8)–C(7), 90.4 (4); C(8)–C(5)–C(6), 89.8 (4); C(5)–C(6)–C(7), 90.5 (4); C(4)–C(5)–C(6), 127.0 (4); C(4)–C(5)–C(8), 128.7 (4).

investigated the reaction of (α-methoxyallenyl)lithium with Fe(CO)₅.

The CH₂═C═C(OMe)Li reagent was prepared[2] by the reaction of methoxyallene[3] with an equimolar quantity of n-butyllithium in THF at −78 °C (all operations under nitrogen). In a typical experiment, a 100-mL flask with a side arm, equipped with a stir bar and a rubber septum, was charged with 15 mL of dry THF and 5.00 mmol of Fe(CO)₅. The solution was cooled to −78 °C, and then 5.40 mmol of (α-methoxyallenyl)lithium in 5 mL of THF, also at −78 °C, was cannulated into the Fe(CO)₅ solution. The resulting mixture was stirred for 1 h at −78 °C, during which time a color change from light orange to orange-red was noted. After the mixture had been allowed to warm to room temperature (giving a dark red solution), it was stirred for 1 h more and then 5.40 mmol of benzoyl chloride was added. The reaction mixture was stirred at room temperature for some hours, and then the solvent was removed at reduced pressure. The residual red oil was passed through a thin pad of silicic acid (elution with 8:1 dichloromethane/pentane). The product was isolated from the eluate by preparative TLC (silica gel, 1:1 v/v dichloromethane/pentane) as air-stable, yellow crystals, mp 93–94 °C (0.74 g, 43% yield). A similar reaction, carried out with a slow stream of carbon monoxide bubbling through the reaction mixture until such time as the benzoyl chloride was added, gave this product in 68% yield. On the basis of its analysis, EI mass spectrum, and ¹H and ¹³C NMR spectra[4] the product was identified as **2a**, a (tri-

(1) Seyferth, D.; Archer, C. M.; Dewan, J. C. *J. Organomet. Chem.* **1986**, *308*, C5.

(2) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*, 1st ed.; Elsevier: Amsterdam, 1981, p 92.
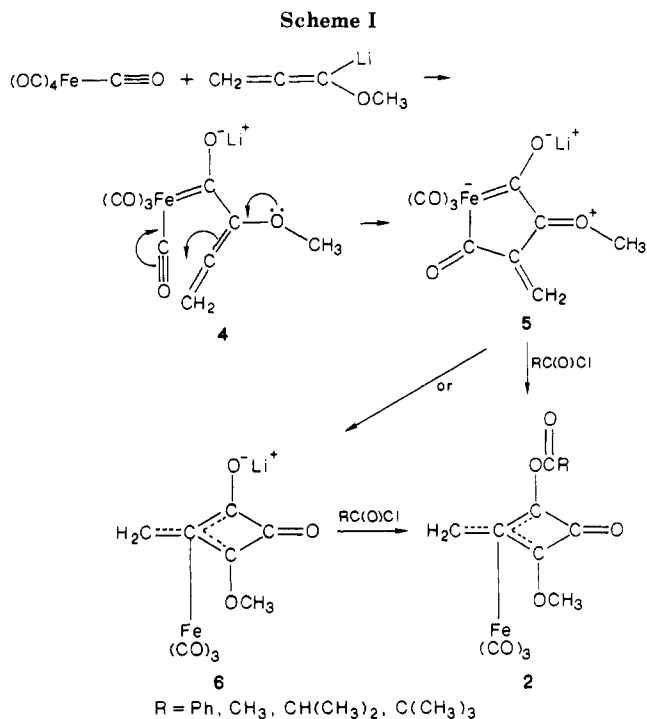
(3) Reference 2, p 23.

(4) Anal. Calcd for C₁₆H₁₀O₇Fe: C, 51.92; H, 2.73. Found: C, 51.85; H, 2.77. EI mass spectrum: inter alia, M⁺ and M⁺ − nCO (n = 1–4) fragment ions. IR (CCl₄, cm⁻¹): ν(C═O), 1780, 1755, 1745; terminal C═O, 2085 (vs), 2005 (vs), 2000 (vs). ¹H NMR (CDCl₃, 300 MHz): δ 3.81 (s, 3 H, OCH₃), 4.22 (d, ²J_gem = 2.39 Hz, 1 H, ═CH₂), 4.43 (d, ²J_gem = 1.52 Hz, 1 H, ═CH₂), 7.43 (t, J = 7.82 Hz, 2 H, Ph), 7.59 (t, J = 7.43 Hz, 1 H, Ph), 7.99 (d, J = 8.28 Hz, 2 H, Ph). ¹³C NMR (CDCl₃, 75.4 MHz): δ_C 60.40 (q, J = 146.3 Hz, OCH₃), 69.48 (t, J = 166.5 Hz, ═CH₂), 94.09 (s, COC(O)Ph), 108.77 (s, C═CH₂), 123.90 (s, COCH₃), 127.50 (s, ipso Ph), 128.54 (d, J = 153.1 Hz, Ph), 130.03 (d, J = 166.5 Hz, Ph), 133.98 (d, J = 157.1 Hz, Ph), 163.12 (s, COC(O)Ph), 170.15 (s, CH₃OCC═O), 205.43, 206.25, 208.90 (all s, Fe─CO).

2a, R = Ph
b, R = CH₃
c, R = CH(CH₃)₂
d, R = C(CH₃)₃
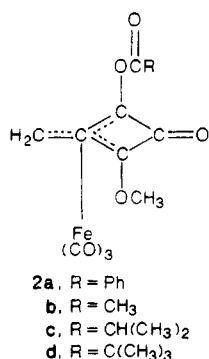
methylenemethane)tricarbonyliron derivative. An X-ray structure determination provided confirmation.[5] The structure of **2a** is shown in the ORTEP plot in Figure 1 which gives important bond distances and angles. The four-membered ring incorporating C(5), C(6), C(7), and C(8) is π-bonded to the iron atom by three of its carbon atoms, C(6), C(5), and C(8), as well as through the methylene carbon atom C(4). This unit can be regarded as a tri-methylenemethane moiety. With regard to the indicated ligand binding to iron, the model that gave the best statistical analysis was the one in which the exocyclic =CH₂ unit, rather than the =O, was bound to the iron atom. The relevant C–C distances, C(5) to C(4), C(8), and C(6), are 1.388 (6), 1.432 (6), and 1.434 (5) Å, respectively. These may be compared with the C–C distances from the central carbon atom in (phenyltrimethylenemethane)tri-carbonyliron (**3**), 1.405 (13), 1.406 (13), and 1.436 (12) Å.[6] The bond angles of the trimethylenemethane units in **2a** and **3** cannot be compared because the presence of the four-membered ring in **2a** results in contraction of the angle C(6)–C(5)–C(8) to 89.8 (4)° and expansion of angles C(4)–C(5)–C(8) and C(4)–C(5)–C(6) to 128.7 (4)° and 127.0 (4)°, respectively. The ring itself is slightly puckered with a torsion angle of 15.0 (3)°.

The mechanism of formation of **2** is of interest but at present is not well understood and requires more study. It will be noted that only two of the carbon atoms of the four-membered ring in **2**, C(5) and C(8), are derived from the (α-methoxyallenyl)lithium reagent. The other two must have as their origin CO ligands of the Fe(CO)₅. The most reasonable first step of the process by which **2** is formed is the addition of the organolithium reagent to a CO ligand of the Fe(CO)₅ (Scheme I), a reaction which has precedent through the work of E. O. Fischer and his co-workers.[7,8] It is clear that the reaction does not stop there. In view of our lack of experimental evidence concerning further details of the reaction course, the most economical sequence is given in Scheme I. The ring closure of intermediate **4** will be facilitated by the electron-donating substituent in the α-position. The cyclic species **5** may be a stable intermediate, and addition of the electrophile then

(5) Crystal data for compound **2a**: orthorhombic, a = 13.113 (3) Å, b = 28.681 (5) Å, c = 8.589 (1) Å, V = 3230 (1) Å³, Z = 8, space group Pbca (No. 61), μ = 9.63 cm⁻¹. Data in the range 3.00° < 2θ < 50.00° were collected at 23 °C by using Mo Kα radiation on a Rigaku AFC6R diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included in the structure factor calculations in idealized positions (d_{C-H} = 0.95 Å). All other atoms were refined anisotropically. An absorption correction was not necessary. Final R = 0.040 and R_w = 0.040 for 1684 observed reflections [$4F_o^2/\sigma^2(F_o^2)$] and 217 variables. The largest peak in the final difference Fourier map was 0.33 e/Å³.

(6) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1969**, *8*, 401.

(7) Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

(8) For a recent example involving the addition of Me₃CC(O)Li to Fe(CO)₅ see: Dötz, K.-H.; Wenicker, U.; Müller, G.; Alt, H. G.; Seyferth, D. *Organometallics* **1986**, *5*, 2570.

Scheme I

R = Ph, CH₃, CH(CH₃)₂, C(CH₃)₃

may induce reductive elimination to form **2**. Alternatively, **5** may not be stable and may be converted to anion **6** by reductive elimination. In that case, **2** will be formed by reaction of the electrophile with **6**.

As noted in Scheme I, other acid chlorides have been used to convert the anionic intermediate, whatever it may be, to a neutral product.[9] Furthermore, this chemistry is applicable to other α-substituted allenyllithium reagents. For instance, a similar reaction of (α-thiomethoxy-allenyl)lithium, CH₂=C=C(SMe)Li, with Fe(CO)₅ at –78 °C, followed by reaction with isobutyryl chloride, gave **7** in 42% yield when the reaction was carried out in a stream of carbon monoxide. As in the case of **2**, compound **7** was
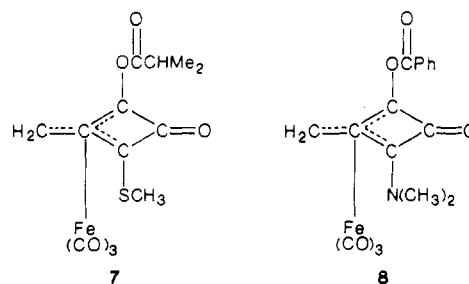
identified on the basis of its analysis, EI mass spectrum, and ¹H and ¹³C NMR spectra.[9] Also, the reaction of CH₂=C=C(NMe₂)Li with Fe(CO)₅ at –78 °C in a stream of CO, followed by addition of benzoyl chloride, gave **8** in 11% yield.[9,10] We have not been able to obtain a similar product from such reactions using allenyllithium itself. It would seem that the electron-donating OMe, SMe, and NMe₂ substituents are required for the subsequent steps in the process outlined in Scheme I.

Supplementary Material Available: A table of characterizing data for new compounds and an X-ray structure report for

(9) Characterization data (analysis, IR, ¹H and ¹³C NMR, and EI mass spectra) are given for all new compounds in the supplementary material.

(10) The low yield of **8** most likely is due to reaction of the tertiary amine function with benzoyl chloride to give a benzoylammonium salt.

compound 2a, including experimental details and crystal data and tables of positional and thermal parameters, general temperature factor expressions, bond distances and angles, torsion angles, intermolecular contacts up to 3.60 Å, and intensity data (27 pages); a listing of observed and calculated structure factors (20 pages) ordering information is given on any current masthead page.

Synthesis and Characterization of {2,6-Bis[(dimethylamino)methyl]phenyl}tin(II) Chloride and {2,6-Bis[(dimethylamino)methyl]phenyl}4-tolyltin(II), the First Example of a Mixed Diaryltin(II) Compound

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Summary: The bis ortho-chelated aryltin(II) chloride Sn^{II}Cl[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6] (1) has been synthesized which has both in the solid state (X-ray) and in solution (^{1}H, ^{13}C, and ^{119}Sn NMR) a Ψ-trigonal-bipyramidal structure. Reaction of 1 with 4-tolyllithium gives the first example of a mixed diaryltin(II) compound, Sn^{II}[C$_6$H$_3$-(CH$_2$NMe$_2$)$_2$-2,6](C$_6$H$_4$Me-4) (2), which readily undergoes oxidative addition reactions with electrophiles MeI and I$_2$.

Previously we have shown that the, potentially tridentate, monoanionic 2,6-bis[(dimethylamino)methyl]phenyl group, i.e. [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6], may be used to prepare organotransition-metal compounds in which the metal has an unusual oxidation state for an organometallic compound, e.g. Fe(III)[1], Ni(III),[2] and Co(II).[3] Moreover, this aryl ligand allows the isolation of reactive intermediates; for example, {2,6-bis[(dimethylamino)methyl]phenyl}-platinum iodide reacts with I$_2$ to give a complex in which I$_2$ is end-on coordinated to the platinum atom.[4]

We have extended our work with [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6] to the preparation of divalent organotin compounds. Although a Mössbauer spectroscopic study of SnCl-[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6] and some related species that were assumed to be diaryltin(II) compounds has been published, this paper contains no further structural information.[5] This is unfortunate since {2,6-bis[(dimethylamino)-methyl]phenyl}tin(II) compounds are of potential interest
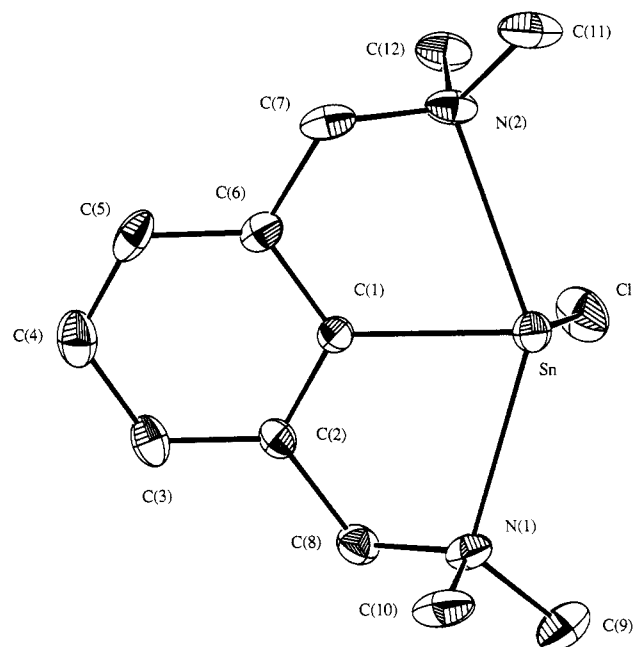
Figure 1. ORTEP drawing of 1. Bond distances (Å): Sn–C(1), 2.158 (8); Sn–Cl, 2.488 (3); Sn–N(1), 2.525 (8); Sn–N(2), 2.602 (8). Bond angles (deg): C(1)–Sn–Cl, 95.0 (3); C(1)–Sn–N(1), 71.9 (3); C(1)–Sn–N(2), 71.5 (3); Cl–Sn–N(1), 86.3 (2); Cl–Sn–N(2), 92.2 (3).

for two reasons. In the first place, intramolecular Sn–N coordination should stabilize the tin(II) state and this is likely to have interesting stereochemical consequences, and secondly, the synthesis of unknown mixed RR′Sn species might be accessible via RSnCl. We here report our first results in this area.

The reaction of Li[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6] with SnCl$_2$, in a 1:1 molar ratio, in Et$_2$O/THF (eq 1), affords {2,6-bis-[(dimethylamino)methyl]phenyl}tin chloride (1) which is obtained, after workup, as a white solid[6] in quantitative yield.
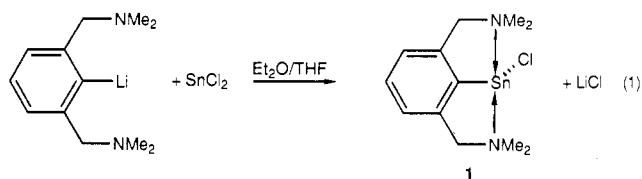
We have now fully characterized this interesting aryl-tin(II) chloride. Compound 1 is readily soluble in hydrocarbon and ether solvents, and molecular weight determinations[6] (cryoscopy in benzene) indicate that it is a monomer in solution. Single crystals of 1, suitable for an X-ray structure determination, were grown from a diethyl ether solution at –25 °C. Crystals of 1 are monoclinic with space group $P2_1/n$ with four molecules in a unit cell of dimensions a = 9.7649 (4) Å, b = 9.3651 (5) Å, c = 16.0712 (6) Å, and β = 97.303 (5)°. The structure determination and refinement[7a] reveal a monomeric structure in the solid

*To whom correspondence should be addressed.

(1) de Koster, A.; Kanters, J. A.; Spek, A. L.; van der Zeijden, A. A. H.; van Koten, G.; Vrieze, K. *Acta Crystallogr., Sect. C* **1985**, *C41*, 893.

(2) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379.

(3) van der Zeijden, A. A. H.; van Koten, G. *Inorg. Chem.* **1986**, *25*, 4723.

(4) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010.

(5) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.

(6) Anal. Calcd for C$_{12}$H$_{19}$ClN$_2$Sn (1): C, 41.72; H, 5.54; N, 8.11; Cl, 10.26; mol wt, 345.4. Found: C, 41.88; H, 5.52; N, 7.99; Cl, 10.11; mol wt, (cryoscopic in benzene), 350. Anal. Calcd for C$_{19}$H$_{26}$N$_2$Sn (2): C, 56.89; H, 6.53; N, 6.98; mol wt, 401.1. Found: C, 56.96; H, 6.48; N, 6.81; mol wt (cryoscopic in benzene), 391. Anal. Calcd for C$_{20}$H$_{29}$IN$_2$Sn (3): C, 44.23; H, 5.38; N, 5.16. Found: C, 44.58; H, 5.21; N, 5.03. Anal. Calcd for C$_{13}$H$_{22}$I$_2$N$_2$Sn (4): C, 26.98; H, 3.83; N, 4.84. Found: C, 26.71; H, 3.74; N, 4.81.