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Preliminary communication

INTRODUCTION OF THE PENTAKIS(METHOXYCARBONYL)-CYCLOPENTADIENYL LIGAND IN STANNOCENE CHEMISTRY

FRANZ X. KOHL, EWALD SCHLÜTER and PETER JUTZI*
Fakultät für Chemie der Universität Bielefeld, Universitätsstrasse, D-4800 Bielefeld 1 (F.R.G.)

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Summary

Decamethylstannocene reacts with pentakis(methoxycarbonyl)cyclopentadiene with elimination of pentamethylcyclopentadiene, yielding pentakis(methoxycarbonyl)pentamethylstannocene and decakis(methoxycarbonyl)stannocene.

As we reported, the reaction of decamethylstannocene, $(C_5Me_5)_2Sn$, with acids HX leads to pentamethylcyclopentadiene and compounds of the composition C_5Me_5SnX [1,2,3], and depending on the nucleophilicity of X^- whether the products are ionic ($C_5Me_5Sn^+\ X^-$) or covalent ($C_5Me_5Sn—X$) [3].

Because of its acidic character, pentakis(methoxycarbonyl)cyclopentadiene [4] reacts with decamethylstannocene (I) as expected, to replace a permethylated Cp ligand by a methoxycarbonyl-substituted Cp derivative. The reaction of I with equimolar amounts of the acidic compound in benzene yields pentakis(methoxycarbonyl)pentamethylstannocene (II) as a pale yellow precipitate, which after recrystallisation from CH_2Cl_2 gives colourless rhombic crystals.

$$\begin{array}{ccc} (C_5Me_5)_2Sn & \xrightarrow[-HC_5Me_5]{+\ HC_5(COOMe)_5} & C_5Me_5SnC_5(COOMe)_5 \\ \text{(I)} & & \text{(II)} \end{array}$$

$$\begin{array}{ccc} (C_5Me_5)_2Sn & \xrightarrow[-2HC_5Me_5]{+2\ HC_5(COOMe)_5} & [C_5(COOMe)_5]_2Sn \\ \text{(I)} & & \text{(III)} \end{array}$$

With two equivalents of pentakis(methoxycarbonyl)cyclopentadiene in CH_2Cl_2 as solvent there is also a very slow replacement of the second permethylated Cp ligand. Within a few days, decakis(methoxycarbonyl)stannocene (III)

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crystallizes in solvent-containing, colourless cubes from a solution of decamethylstannocene (I) and the acidic compound. The solvent-free product is obtained in colourless needles by recrystallization from acetonitrile. The identities of this compound and of the mixed metallocene II are confirmed by analytical and spectroscopic data [5].

Studies of the bonding in the stannocenes II and III are not complete. The mass spectra of the mixed metallocene II [5] exhibit covalent interactions between tin and the methoxycarbonyl-substituted Cp system in the gas phase: The M^+ species and also a $C_5(COOMe)_5Sn^+$ fragment appear, although very weak in comparison to the $C_5Me_5Sn^+$ cation. Nevertheless, the insolubility of II in benzene and toluene as well as cryoscopic molecular weight determinations in nitrobenzene [5] indicate ionic character, and the poor nucleophilic activity of the $C_5(COOMe)_5^-$ anion [4] would be consistent with dissociation into $C_5Me_5Sn^+$ $C_5(COOMe)_5^-$.

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References and Notes

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5 II: Analysis: Found: C, 48.25; H, 4.83; mol. weight (cryoscopical, 5.8×10^{-3} M solution in nitrobenzene): 367. $C_{25}H_{30}O_{10}Sn$ calcd.: C, 49.29; H, 4.96%; formula weight: 609.2. ^{1}H NMR (CH_2Cl_2, ext.-TMS): 2.05 ppm (s; 15H; C_5Me_5), 3.74 ppm (s; 15H; $C_5(COOMe)_5$). Mass spectrum (200°C) m/e (I_r of the organometallic fragments): 610 (1; M^+), 475 (6; $C_5(COOMe)_5Sn^+$), 255 (100; $C_5Me_5Sn^+$). III: Analysis: Found: C, 43.22; H, 3.46. $C_{30}H_{30}O_{20}Sn$ calcd.: C, 43.45; H, 3.65%. ^{1}H NMR (CD_3CN, ext.-TMS): 3.75 ppm (s).