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Direct Synthesis of *ansa*-Metallocenes of Tin and Lead via Metal Vapor Cocondensation

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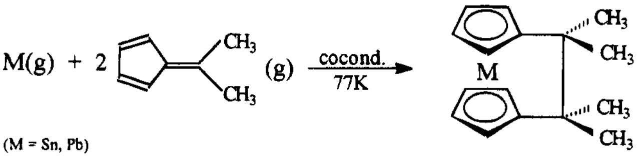
Summary: Tin or lead vapor reacts under cryogenic reaction conditions to give ansa-metallocenes of the respective element via a template synthesis at the metal center. This is one of the very few examples of Pb undergoing a direct synthesis to organometallics.

Introduction

Twenty years ago, *ansa*-ferrocene was prepared by reacting iron atoms with 6,6-dimethylfulvene.[1] This approach was developed further by Edelmann et al., who reacted electropositive metals such as Ca and Sr[2] as well as Sm and Yb[3] as powders with the same fulvene. Meanwhile, *ansa*-zirconocenes became important in homogeneous catalysis for regiospecific polymerization of propylene.[4] The present paper reports the synthesis and characterization of the *ansa*-metallocenes of tin and lead, which are obtained via vapor atom synthesis (MVS).

Results and Discussion

The synthesis of the *ansa*-metallocenes was carried out by cocondensing the gaseous Sn and Pb with an excess of 6,6-dimethylfulvene in a toluene matrix under high vacuum conditions at liquid nitrogen temperature:



For the reaction a stainless steel metal vapor apparatus was used. The MVS machine is distinctly different from standard arrangement.[5] It is equipped with a cooled internal drain in the cocondensation vessel, which allows for the isolation of products under Schlenk-type conditions at low temperature. Details of the construction similar to an earlier report[6] are shown in Figure 1.

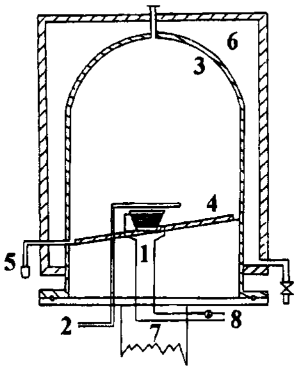


Figure 1. The cocondensation apparatus: (1) crucible; (2) inlet system; (3) cocondensation vessel; (4) internal drain; (5) outlet system; (6) liquid nitrogen; (7) high vacuum pump; (8) power supply.

High-field resonances for the *ansa*-metallocenes in the ^{119}Sn[7] and ^{207}Pb NMR[7] verify that these species are monomeric and low-valent (M^{II}) compounds. ^{1}H and ^{13}C NMR data show that an ethylene bridge connects two Cp rings in one molecule and exclude the $(\eta^5\text{-}C_5H_4CH(CH_3)_2M$ alternative.

The *ansa*-stannocene may be a monomer in the solid state, as is the unsubstituted species,[8] because it is easier to sublime in vacuo and more soluble in benzene compared to the *ansa*-plumbocene, which more likely is polymeric in the solid state.[9]

Experimental Section

All experimental procedures were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques. Solvents were dried by refluxing with the appropriate drying agent and were distilled before use. The metals (Sn and Pb) were purchased from Aldrich Chemical Co. (all minimum 99.5%). 6,6-Dimethylfulvene was prepared according to literature methods.[10]

NMR spectra were recorded at ambient temperatures on JEOL FX 90 (^{1}H) and EX 400 (^{13}C) spectrometers, while ^{119}Sn and ^{207}Pb NMR data were collected on a Bruker ACP 200 instrument. Infrared and Raman spectra were obtained on a Bruker IFS 66V, which is also equipped with an FT Raman part (FRA 106). High-resolution mass spectral analyses were performed on a Finnigan MAT MS 71 operating in the EI mode at 70 eV. The UV/vis spectrum was recorded on a Hitachi 100−60 in a Schlenk-type quartz cell.

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[7] $Cp^*{}_2Sn$ and $Cp^*{}_2Pb$ exhibit resonances at −2129 ppm (^{119}Sn NMR) and −4437 ppm (^{207}Pb NMR). These compounds are monomers in solution as well as in the solid state: Jutzi, P.; Dickbreder, R.; Nöth, H. *Chem. Ber.* **1989**, *122*, 865.

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Preparation of the Compounds. $SnC_{16}H_{20}$ and $PbC_{16}H_{20}$. In a typical experiment, about 75 mmol of the appropriate metal (8.8 g of Sn or 15.4 g of Pb) was vaporized from an alumina crucible at 1300 °C (Sn) or 750 °C (Pb) over 80 min and cocondensed with a mixture of 20 mL of 6,6-dimethylfulvene (0.19 mol) and 60 mL of toluene (0.61 mol) to obtain a low-melting matrix. The pressure, which is measured at the bottom of the cocondensation vessel, was kept below 5×10^{-5} mbar to avoid gas phase reactions of metal atoms and reactants. At the end of the experiment the frozen matrix was warmed to room temperature under an argon atmosphere. The molten reaction mixture flowed through the internal drain into a Schlenk-type tube, which was kept at −80 °C. For a crude isolation, the solvent was evaporated under reduced pressure. Analytically and spectroscopically pure samples were obtained by sublimation of the solid residue at 1×10^{-5} mbar and 130 °C (Sn) or 150 °C (Pb). The resulting white (Sn: 480 mg, 2% yield) or lemon yellow (Pb: 620 mgm, 2% yield) waxlike, air- and moisture-sensitive solids are not suitable for X-ray structure analysis but are fully characterized in solution by spectroscopic methods.

$SnC_{16}H_{20}$: ^1H NMR (C_6D_6; 90 MHz) δ 1.28 (s, 12H, CH_3), 5.75−6.05 (m, 8H, Cp′); ^{13}C NMR (C_6D_6; 400 MHz) δ 28.1 (CH_3), 41.5 (q-C), 106.5, 109.7, 111.7 (Cp′); ^{119}Sn NMR (C_6D_6; 270 MHz) δ −2122 (s); MS (70 eV, EI): *m/z* 332.0569 (obsd) and 332.0587 (calcd) for $^{120}SnC_{16}H_{20}$, 330.0547 (obsd) and 330.0587 (calcd) for $^{118}SnC_{16}H_{20}$, 328.0562 (obsd) and 328.0581 (calcd) for $^{116}SnC_{16}H_{20}$, IR (Nujol and Hostaflon mull) 3074, 2973, 2934, 2866, 1578, 1468, 1378, 1277, 1107, 1057, 986, 744 cm^{-1}; Raman (neat solid) 3100, 2984, 2963, 1455, 1384, 1172, 759, 215, 134 cm^{-1}. Anal. Calcd for $SnC_{16}H_{20}$: Sn, 35.86; C, 58.05; H, 6.09. Found: Sn, 35.91; C, 58.09; H, 6.10.

$PbC_{16}H_{20}$: ^1H NMR (C_6D_6; 90 MHz) δ 1.28 (s, 12H, CH_3), 5.75−6.05 (m, 8H, Cp′); ^{13}C NMR (C_6D_6; 400 MHz) δ 29.1 (CH_3), 41.3 (q-C), 110.8, 110.9 (Cp′) ^{207}Pb NMR (C_6D_6; 270 MHz) δ −4206 (s); UV/vis (in toluene) λ_{max} 365 nm; MS (70 eV, EI) *m/z* 420.1307 (obsd) and 420.1332 (calcd) for $^{208}PbC_{16}H_{20}$, 419.1324 (obsd) and 419.1324 (calcd) for $^{207}PbC_{16}H_{20}$, 418.1356 (obsd) and 418.1310 (calcd) for $^{206}PbC_{16}H_{20}$; IR (Nujol and Hostaflon mull) 3082, 2976, 2931, 2866, 1580, 1466, 1402, 1372, 1107, 1034, 917, 821, 741, 689, 471 cm^{-1}; Raman (neat solid): 3102, 2984, 2962, 2914, 1456, 1373, 1172, 1150, 759, 215, 135 cm^{-1}. Anal. Calcd for $PbC_{16}H_{20}$: Pb, 49.39; C, 45.81; H, 4.80. Found: Pb, 49.49; C, 45.75%; H, 4.76.

An attempt to synthesize *ansa*-germanocene in a similar way produced an insoluble and unsublimable red polymer, which was not examined further.

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