CONCLUSIONS

1. The methods of PMR spectroscopy have been used to study the reactions of dipropylmercury, di-n-butylmercury, tetraethyltin, tetrapropyltin, and diisobutylgermanium with triarylmethane salts.

2. Hydride displacement from the metalorganic compound to the triarylmethyl cation proceeds in phase with the breaking of the carbon-metal and β-carbon-hydrogen bonds.

LITERATURE CITED


CATALYSTS FOR HOMOGENEOUS OLEFIN HYDROGENATION BASED ON
MACROMOLECULAR COMPLEXES OF TRANSITION-METAL IONS WITH
COPOLYMERS OF STYRENE AND AMINO-ACID MALEIMIDES

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Macromolecular metal-complex catalysts (MMC) have become objects of interest in the discussion of various problems of both theoretical and practical significance [1-3]. Olefin hydrogenation processes can be actively catalyzed by MMC's prepared through the interaction of PdCl₂ with copolymers of styrene and the maleimides of certain amines and amino acids [4]. Readily available chiral copolymers serve as the basis for asymmetric olefin hydrogenation catalysts such as those used for the preparation of chiral amino acids [5, 6].

The present work was a study of the nature and properties of MMC's formed through the interaction of Pd(II) and Rh(III) chloride complexes with copolymers of styrene and the maleimide of S-phenylalanine (SMPh), and the activity of the forms resulting from MMC treatment with H₂ and NaBH₄. The MMC's involved in this work had the following compositions: [PdCl₂·NaCl,L₄,0](Pd(II)--SMPh), [RhCl₃(H₂O),₅,L₁,₇](Rh(III)--SMPh), and [Am₂PdCl₂,L₄,₅](Am₂PdCl₂--SMPh), Am being d-α-methylbenzylamine and L the monomer unit of S- or RS-SMPh.

EXPERIMENTAL

The copolymers of styrene with the amino-acid maleimides were synthesized by the methods of [5]. S-SMPh: yield 83%, $[\eta] 0.74$ (dioxane, 25°C); $[\alpha]_D 63.1^\circ$ (dimethoxyethane, 85.5°C) (dimethylformamide)). Found: N 3.91; COOH 12.63%. $C_{21}H_{16}O_4N$. Calculated: N 4.01; COOH 12.88%. RS-SMPh: yield 86%; $[\eta] 0.98$ (dioxane, 25°C). Found: N 3.97; COOH 12.71%. $C_{21}$ $H_{16}O_4N$. Calculated: N 4.01; COOH 12.88%.

In preparing the Pd(II)–SMPh, 2 mmoles each of S-SMPh, PdCl$_2$, and NaCl were dissolved in 40 ml of ethanol and the resulting solution allowed to stand overnight at ~20°C. At this end of this time, the solution was evaporated to dryness, the residue taken up in 20 ml of anhydrous acetone, the mixture filtered, and the complex brought down with 200 ml ether. The precipitated complex was washed with ether, again precipitated from acetone solution with ether, and finally vacuum dried over KOH at ~20°C. The yield of complex was 76.1%, $[\alpha]_D 150.2^\circ$ (dimethoxyethane). Found: N 3.11; Cl 6.20; Pd 6.00%. $[PdCl_2 \cdot NaCl, L_{10.4}]_n$, where L is the S-SMPh monomer unit. $C_{21}H_{16}O_4N$. Calculated: N 3.43; Cl 6.52; Pd 6.51%.

Rh(III)–SMPh was prepared by dissolving 2 mmole S-SMPh and 2 mmole RhCl$_3$ · 3H$_2$O in 30 ml acetone and allowing the resulting mixture to stand overnight at ~20°C. The complex was twice brought down with ether from acetone solution and finally vacuum dried over KOH at ~20°C; yield 75%, $[\alpha]_D 25.0^\circ$ (DMFA). Found: C 48.75; H 4.80; Cl 12.75; Rh 11.50%. $[RhCl_3(H_2O)_3, N_{1.7}]_n$, L being the S-SMPh monomer unit. $C_{21}H_{16}O_4N$. Calculated: C 49.50; H 4.44; Cl 12.30; Rh 11.88%.

Dichlorobis(d-α-methylbenzylamino)palladium(II) was prepared by the procedure given in [7]. Found: N 6.16; Pd 24.9%. $C_{14}H_{22}N_2Cl_2Pd$. Calculated: N 6.52; Pd 25.1%.

Am$_2$PdCl$_2$–SMPh was prepared by mixing solutions containing 1 eq of Am$_2$PdCl$_2$ and 4.5 eq of RS-SMPh, calculated on a per SMPh monomer unit.