

A Stable Methylzirconium Compound

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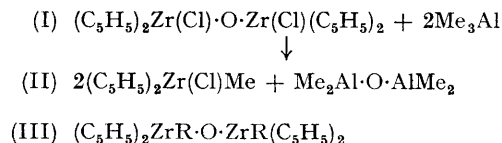
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WE report the preparation of the first stable alkylzirconium compound, namely chlorobis(cyclopentadienyl)(methyl)zirconium (II) by the route shown in equation (1). A mixture of dichloro- μ -oxotetra(cyclopentadienyl)dizirconium (I)^{1,2} and trimethylaluminium (2 mols.) in benzene was heated at 65–70° for 3.5 hr. After evaporation of benzene, the residue was dissolved in tetrahydrofuran; subsequent treatment with light petroleum gave a solid whose proton magnetic resonance (p.m.r.) spectrum showed no significant aluminium–methyl resonance. Crystallization from benzene–petroleum afforded the methylzirconium compound (53%), decomp. 191–193°. Elemental analyses, molecular-weight determination and spectroscopic measurements were consistent with structure (II).

The p.m.r. spectrum (in benzene, with tetramethylsilane as internal reference) shows two sharp peaks at δ 0.42 (presumed to be due to ZrCH_3)³ and 5.78 p.p.m. (π - C_5H_5), of which the intensities

are in the ratio 3:10. Structure (III; $\text{R} = \text{Me}$) is excluded by the infrared spectrum, which lacks the intense absorption at 750–775 cm^{-1} associated with the Zr-O-Zr system.^{1,2,4}

The methylzirconium compound (II) is rapidly hydrolysed by water to give methane in quantitative yield, together with the oxide (I).



While this work was in progress Brainina, Dvoryantseva, and Freidlina⁴ announced the preparation of two arylzirconium compounds (III; $\text{R} = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$), by the reaction of aryl-lithium reagents with either (I) or dichlorobis(cyclopentadienyl)zirconium.

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¹ E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, 1964, **154**, 1113.

² A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailes, *Austral. J. Chem.*, 1965, **18**, 173.

³ T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104; similar data are reported for methyl derivatives of other transition metals.

⁴ E. M. Brainina, G. G. Dvoryantseva, and R. Kh. Freidlina, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 1375