

PI-SIGMA REARRANGEMENTS OF PI-CYCLOPENTADIENYL

GROUP: REACTION OF TITANOCENE DICHLORIDE

WITH DIMETHYLSULFOXIDE¹

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The reaction between titanocene dichloride and dimethylsulfoxide at 70°C under argon resulted in the π - σ rearrangement of both cyclopentadienyl groups.

A number of sigma (σ) - pi (π) rearrangements of organotransition metals have been reported,² but, only a few involving cyclopentadienyl groups have been observed. No non-fluxional π - σ rearrangements of cyclopentadienyl groups have been reported.³

We wish to report the first evidence for the π - σ rearrangement of π -cyclopentadienyl groups bonded to titanium, which occurs during the reaction of titanocene dichloride (π -Cp₂TiCl₂) with dimethylsulfoxide (DMSO).

A saturated solution of π -Cp₂TiCl₂ in DMSO⁴ was heated at 70°C in an HA100 nmr probe. The sharp singlet at τ 3.3 slowly decreased in size as a new signal centered at τ 3.45 appeared. After 6 hours, the signal due to the π -Cp protons had completely disappeared from the reaction mixture. Closer analysis of the signal at τ 3.45 revealed this to be the AA'BB' portion of an AA'BB'X pattern. Cooling the reaction mixture to room temperature did not regenerate the starting compound. Further evidence for the π - σ rearrangement of the cyclopentadienyl groups was obtained by isolation of a maleic anhydride adduct⁵ of cyclopentadiene from addition of maleic anhydride to the reaction mixture.

Addition of benzene to the reaction mixture resulted in the precipitation of white crystals, **I**, which were highly hygroscopic and decomposed at 120°C. No solvent was found for **I**. The i.r. and elemental analysis suggested that compound **I** did not contain any cyclopentadienyl group and was a DMSO complex of titanium, TiCl(DMSO)₄.⁶

Addition of diethyl ether to a DMSO solution containing the sigma bonded species resulted in a pale violet precipitate. The precipitate was further purified by reprecipitation with

diethyl ether from DMSO solution. The pale violet amorphorous powder became brown upon drying under vacuum, dec. 315°C. Anal. Calculated for $C_{10}H_{10}TiCl_2 \cdot 4DMSO$: C, 38.50; H, 6.06; S, 22.82; Ti, 8.56; Cl, 12.66 Found⁷: C, 37.05; H, 6.34; S, 25.73; Ti, 8.58; Cl, 12.52; i.r. (cm^{-1}) (KBr): 3400(s,br), 2994(s), 1613(m), 1420(vs), 1046-990(vs), 949(s,br) and 775(s,br). The nmr spectrum (DMSO) of the compound exhibited signals at: τ 3.05(1H,t), 3.50(2H,d), and 7.0(18-24H,s,coord.DMSO). Although probable structures for this compound can be proposed, the final structure elucidation must await X-ray diffraction analysis upon successful crystallization of the compound.

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References

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4. DMSO was dried over Linde 4Å molecular sieves and purified by repeated vacuum distillation.
5. M. J. Bennett, Jr., F. A. Cotton, A. Davidson, J. W. Fuller, S. J. Lippard and S. M. Morehouse, J. Amer. Chem. Soc., **88**, 4371(1966).
6. The m.p. of the adduct was 199-201°C. The parent peak in the mass spectrum was at m/e 164.
7. The repeated analysis was not consistent. $C_{10}H_{10}TiCl_2 \cdot 4DMSO$ was the best formulation for the results of the elemental analysis.

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