

Preparation of Biscyclopentadienylmagnesium by Means of a Titanium Complex Catalyst

By TARO SAITO

(Department of Chemistry, The University of Tokyo, Hongo, Tokyo, Japan)

Summary Biscyclopentadienylmagnesium was prepared under mild conditions using cyclopentadienyltitanium trichloride as a catalyst

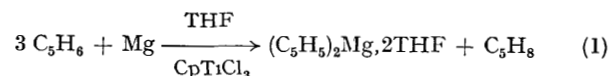
The usual method of the preparation of biscyclopentadienylmagnesium (Cp_2Mg) from magnesium metal and cyclopentadiene in an inert atmosphere requires temperatures of 500–600°. Treatment of magnesium metal, unlike calcium,² with cyclopentadiene in tetrahydrofuran (THF) does not produce Cp_2Mg . A titanium–magnesium complex $\text{TiNMg}_2\text{Cl}_2$, THF was reported to catalyze the formation of MgH_2 from Mg and H_2 under mild conditions.³

We found that the presence of a catalytic amount of cyclopentadienyltitanium trichloride (CpTiCl_3) in the reaction mixture of cyclopentadiene and magnesium in THF facilitates the formation of $\text{Cp}_2\text{Mg} \cdot 2\text{THF}$ even at 0°. Cp_2Mg is easily obtained by heating the tetrahydrofuran adduct to remove THF followed by sublimation.

Thus, cyclopentadiene (13.2 g, 2×10^{-1} mol) was treated with magnesium turnings (4.9 g, 2×10^{-1} mol) in THF (100 ml) in the presence of CpTiCl_3 (0.88 g, 4×10^{-3} mol) at room temperature under argon or nitrogen for 48 h. Unchanged magnesium metal was filtered off and volatile constituents in the filtrate were evaporated off leaving a viscous residue. The black residue (I) was extracted with diethyl ether and on cooling the solution a crystalline precipitate was formed which was recrystallized from diethyl ether to form colourless needles. These were very air-sensitive and decomposed at 84–95° *in vacuo*. Magnesium analysis and IR and ^1H NMR spectra indicated that the crystals were $\text{Cp}_2\text{Mg} \cdot 2\text{THF}$. The ^1H NMR spectrum of $\text{Cp}_2\text{Mg} \cdot 2\text{THF}$ in C_6D_6 shows signals due to the C_5H_5 protons at τ 3.80 and THF protons at τ 6.8 and 8.8 (multiplet) (ratio of areas C_4H_8 : $\text{C}_3\text{H}_5\text{O}$ 5 : 8). THF was removed by heating at 120° and vacuum sublimation of the residue gave a crystalline compound, identified as Cp_2Mg by mp (175°), magnesium analysis, and IR, mass, and ^1H NMR spectra.

It is possible to obtain Cp_2Mg directly from the black residue (I) by heating and extracting with n-hexane (ca 60% yield based on magnesium).

Cyclopentene was quantitatively formed during the reaction and no hydrogen gas evolved. These facts accord with equation (1).



Other titanium complexes such as Cp_2TiCl_2 and $(\text{THF})_2\text{TiCl}_4$ were much less satisfactory as catalysts. The presence of an equimolar amount of iodine or dibromoethane instead of CpTiCl_3 did not catalyze the reaction. The reaction of CpTiCl_3 with excess of magnesium in THF gave a black solution and unchanged active magnesium. Magnesium was separated from the solution and fresh THF and cyclopentadiene were added. Although the magnesium was so active as to react violently with methanol at room temperature, no reaction of cyclopentadiene with the magnesium occurred at room temperature. On the other hand, the titanium complex solution catalysed the reaction of cyclopentadiene and ordinary magnesium turnings. These reactions may be interpreted in terms of catalysis by a titanium complex, *i.e.* the reaction of cyclopentadiene with magnesium is not fully explained by the exposure of the reactive magnesium surface alone but more likely by catalysis by a titanium–magnesium complex. The composition of the titanium complex formed by the reaction of CpTiCl_3 and Mg in THF under argon was found to be $\text{Cp}_2\text{Ti}_2\text{Mg}_2\text{Cl}_3 \cdot 2\text{THF}$.⁴

The present reaction is considered to be a special case of 'diene–magnesium compounds' which were reported recently.⁵

(Received, September 23rd, 1971 Com 1670)

¹ W. A. Barber, *Inorg Synth*, 1960, 6, 11

² E. O. Fischer and G. Stölzle, *Chem Ber*, 1961, 94, 2187

³ A. Yamamoto, M. Ookawa, and S. Ikeda, *Chem Comm*, 1969, 841

⁴ M. Shimo, T. Saito, and Y. Sasaki, unpublished work

⁵ M. Yang, K. Yamamoto, N. Otake, M. Ando, and K. Takase, *Tetrahedron Letters*, 1970, 44, 3843