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ansa-METALLOCENE DERIVATIVES

V *. SYNTHESIS OF TETRAMETHYLETHYLENE-BRIDGED TITANOCENE AND ZIRCONOCENE DERIVATIVES VIA REDUCTIVE FULVENE COUPLING

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Summary

Titanocene and zirconocene derivatives with an interannular tetramethylethylene bridge can be made by reductive coupling of 6,6-dimethylfulvene with sodium amalgam, sodium anthracenide, or magnesium metal/CCl_4 as reducing agents and subsequent reaction of the anionic tetramethyldicyclopentadienylethane product with $TiCl_3$ or $ZrCl_4$ in THF.

Introduction

Convenient synthetic routes to *ansa*-metallocene derivatives, in which the ligand framework is stabilized by the presence of an interannular chelate ring, continue to be of interest. Previously we have shown that the 1,2-dicyclopentadienylethane ligand can be obtained in reasonable yields if the otherwise predominant formation of spiro-heptadiene products [2] is avoided by treating the ethylenediamine-activated cyclopentadienylmagnesium reagents with 1,2-dibromoethane [3]. Here we report a preparation of tetramethylethylene-bridged titanocene and zirconocene derivatives via reductive coupling of 6,6-dimethylfulvene.

Reductive coupling of dimethylfulvene with metallic sodium has been utilized by Rinehart et al. [4] to prepare tetramethylethylene-bridged ferrocene; the preparation was not described in detail, however, and yields were reported as low (cf. [5]). Later, Sullivan and Little [6] described an attempt to prepare tetramethylethylene-bridged titanocene dichloride by an analogous reaction, which, however, gave bis(isopropylcyclopentadienyl)titanium dichloride as the major product, from which the de-

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* For Part IV see ref. 1.

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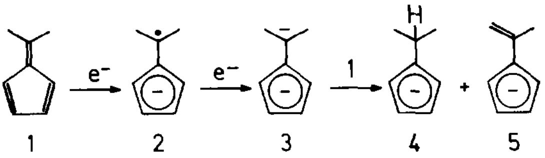
sired *ansa*-titanocene derivative, probably formed in minor amounts, could not be separated. Similar results have been obtained in our laboratory. The formation of isopropylcyclopentadienyl anion (4), which hinders these reduction reactions, is most likely due to over-reduction of the fulvene to a dianionic species (3), which is then protonated, e.g. by H^+-abstraction from dimethylfulvene *.



From electrochemical data available on these and related reduction processes [8], it appeared that formation of such a dianion, which occurs at potentials only slightly more negative than that of the monoanion, might be avoided by use of milder reducing agents with reduction potentials of less than ca. -2 volts.

Results

In accord with the reasoning above, we find that reduction of fulvene with the rather strongly reducing sodium naphthalene anion (E° -2.50 V [11]) in tetrahydrofuran (THF) still yields, after subsequent reaction with $TiCl_3 \cdot THF$ and appropriate work-up, a mixture of diisopropyl- and tetramethylethylene-titanocene dichloride (^1H NMR signals at 1.23 ppm (d, 12H, 7 Hz), 3.23 ppm (m, 2H), 6.36 ppm (m, 8H); and at 1.45 ppm (s, 12H), 6.21 ppm (t, 4H, 2.55 Hz), 6.87 ppm (t, 4H, 2.55 Hz), respectively), whereas use of the less strongly reducing sodium anthracenide (E° $-$ 1.96 V [11]) in an analogous reaction yields the tetramethylethylene-bridged titanocene dichloride without detectable amounts of the diisopropyl side-product. However, the regenerated anthracene is difficult to separate from the product.

Similarly, sodium amalgam, which is less reducing than sodium metal by almost one volt, reduces dimethylfulvene in THF during about one week to an anionic product, from which, after reaction with $TiCl_3 \cdot 3THF$ and oxidative work-up with HCl, the desired tetramethylethylene-bridged titanocene dichloride can be obtained in 33% yield free from any unbridged isopropyl derivative.

This reaction can also be conducted in a one-pot fashion by stirring a THF solution containing dimethylfulvene and $TiCl_3 \cdot 3THF$ over a sodium amalgam mirror. In this case, the reduction is complete after 16 h, and yields, after appropriate work-up, 35% of NMR-spectrally and analytically pure tetramethylethylene-bridged titanocene dichloride.

Finally, we have observed that treatment of dimethylfulvene with Mg metal and CCl_4 yields a white precipitate, which, in the light of its elemental composition and its quantitative hydrolysis to pure 2,3-dimethyl-2,3-dicyclopentadienebutane, is probably a bifunctional Grignard reagent of composition $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$. This material is obtained in 25% yield (based on dimethylfulvene). Its

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* For discussions on intermediates and reaction mechanisms involved in reductions of fulvene to various types of products, see refs. 7–10.

reaction with $TiCl_3 \cdot 3THF$ in THF affords analytically pure $(CH_3)_4C_2(C_5H_4)_2TiCl_2$ in 63% yield after work-up. Similarly, $(CH_3)_4C_2(C_5H_4)_2ZrCl_2$ is obtained in 33% yield, by treatment of the Grignard reduction product with $ZrCl_4$ in THF.

Bridged metallocene derivatives with central transition metals from other groups are also accessible via reaction of the Grignard intermediate $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$ with various transition metal halide compounds [12].

Experimental

The following synthetic operations, except for the final purification steps of titanium(IV) and zirconium(IV) products were conducted with exclusion of air by Schlenk techniques on a vacuum manifold. Solvents were thoroughly dried, freed from dissolved O_2, and stored under Ar.

1. $(CH_3)_4C_2(C_5H_4)_2TiCl_2$ *via reduction of 6,6-dimethylfulvene with sodium amalgam*

Sodium amalgam is freshly prepared by adding 0.6 g (25 mmol) Na metal to 47.2 g Hg metal in a 250 ml side-arm flask. While still warm, the amalgam is spread over the interior of the reaction flask and allowed to solidify to an amalgam mirror. To this is slowly added a solution of 1.1 g (10 mmol) 6,6-dimethylfulvene [13] in 70 ml THF containing 1.85 g (5 mmol) $TiCl_3 \cdot 3THF$ [14]. After stirring overnight at room temperature, the solution is decanted from the liquefied mercury and cooled to −40°C; 2 ml of 6 *M* HCl (ca. 12 mmol) is added and the mixture allowed to warm to room temperature. After 4–5 hours, the resulting red solution is evaporated to dryness. The residue is taken up in CH_2Cl_2 *, freed from brownish impurities by addition of pentane and concentrated to a small volume. From this saturated CH_2Cl_2 solution, the *ansa*-titanocene dichloride is obtained, as a microcrystalline, red powder by addition of methylcyclohexane. Yield: 585 mg (35.3%, based on dimethylfulvene).

The product is characterized by ^1H NMR signals (in $CDCl_3$) at 1.45 ppm (s, 12H); 6.21 ppm (t, 4H, 2.55 Hz) and 6.87 ppm (t, 4H, 2.55 Hz), by a mass spectrum with parent ion at m/e 328–334 and appropriate isotope distribution for $C_{16}H_{20}TiCl_2$, and by its elemental analysis: Found: C, 57.91; H, 6.24; Cl, 21.21. $C_{16}H_{20}TiCl_2$ calcd.: C, 58.03; H, 6.09; Cl, 21.41%.

2. $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$

To 7.2 g (0.3 mol) of magnesium turnings, a solution of 31.8 g (0.3 mol) 6,6-dimethylfulvene in 80 ml THF, containing 7.0 g (45.5 mmol) CCl_4 is added (during 15–20 min) at such a rate that vigorous reaction is maintained. Upon cooling to room temperature a yellowish/cream-colored suspension is obtained. After stirring overnight, the suspension is decanted from remaining Mg metal, filtered off, washed with diethyl ether (ca. 80 ml; until most of the color has been removed) and then pentane, and dried in vacuo. The product which corresponds in its composition to $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4.2THF$ is obtained as a colorless, somewhat air-sensitive powder. Yield: 24.1 g (38 mmol; 25%, based on dimethyl-

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* Occasionally these solutions turned green. In this case the solution was treated with HCl gas, freed from any precipitates, and further purified as described above.

fulvene). Elemental analysis: Found: C, 59.58; H, 7.92; Mg, 7.71; Cl, 10.79. $C_{32}H_{52}O_4Mg_2Cl_2$ calcd.: C, 61.96; H, 8.45; Mg, 7.84; Cl, 11.43%.

In analogous experiments with higher or lower ratios of CCl_4/Mg, with different addition rates or reaction temperatures and with different organic halide compounds as Mg metal activators, yields were generally lower than for the procedure described above.

This Grignard compound can be hydrolyzed in ethereal suspension with 0.1 *M* HCl. Quantitative back-titration indicates that 2 mmol of HCl are consumed by 630 mg of the Grignard compound. This formula weight is in accord with the presence of 4.2 mmol of THF per mmol of bifunctional Grignard compound. From the diethyl ether phase, 2,3-dimethyl-2,3-dicyclopentadienebutane can be obtained by evaporation and recrystallisation of the residue from pentane solution. This compound gives rise to a parent ion with $m/e = 214$, corresponding to the composition $C_{16}H_{22}$. Its ^{1}H NMR spectrum (in CCl_4) is complicated by the presence of several tautomers: 1.12 ppm (d, 12H, 1.8 Hz); 2.65 and 2.80 ppm (m, ca. 4H), 5.90, 6.17 and 6.33 ppm (m, ca. 6H).

3. $(CH_3)_4C_2(C_5H_4)_2TiCl_2$ *via* $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$

A mixture of 4.1 g; (6.5 mmol) of the Grignard product, 2.4 g (6.5 mmol) of $TiCl_3 \cdot 3THF$, and 100 ml of THF is refluxed for 3–4 h, cooled to −40°C, and worked up, after addition of 4 ml of 6 *M* HCl, as described above, to give 1.4 g (4.2 mmol) of $(CH_3)_4C_2(C_5H_4)_2TiCl_2$ (63% yield, based on $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$).

4. $(CH_3)_4C_2(C_5H_4)_2ZrCl_2$ *via* $(CH_3)_2C_2(C_5H_4MgCl)_2 \cdot 4THF$

THF (ca. 80 ml) is condensed, at −80°C onto 6.3 g (10 mmol) of $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$ and 2.3 g (10 mmol) of $ZrCl_4$, and the mixture is warmed to room temperature and refluxed for ca. 4 h.

The resulting yellow solution is cooled to room temperature and evaporated to dryness. The residue is taken up in 150 ml $CHCl_3$ and 5 ml concentrated HCl, whereupon the $CHCl_3$ solution turns blue-green. The $CHCl_3$ phase is separated, the aqueous phase washed twice with ca. 50 ml $CHCl_3$ saturated with concentrated HCl *. The combined $CHCl_3$ phases are dried with Na_2SO_4, evaporated to dryness, taken up in 100 ml diethyl ether, acidified with HCl gas, freed from insoluble, dark impurities, concentrated to ca. 50 ml and cooled to −80°C. A dark precipitate, which appears after ca. 16 h is collected, washed with 5 ml pentane and dried. Further recrystallisation from HCl-containing ether/pentane mixtures (1/1) yields 0.94 g (25%) of a grayish, crystalline product. When pentane and the pentane washings are added to the ethereal mother liquor to a total volume of ca. 100 ml, cooling to −80°C yields a second crop of 0.31 g (8%) of $(CH_3)_4C_2(C_5H_4)_2ZrCl_2$.

$(CH_3)_4C_2(C_5H_4)_2ZrCl_2$ is characterized by ^{1}H NMR signals (in $CDCl_3$) at 1.45

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* If these $CHCl_3$ solutions are washed with H_2O and worked up without addition of HCl, the color changes to light-brown and a light-brown material is obtained which (in $CDCl_3$) shows four quartets (instead of two triplets) cyclopentadienyl ^{1}H NMR signals at 5.89, 6.10, 6.27 and 6.50 ppm and two (instead of one) H_3C-singlets at 1.38 and 1.47 ppm, with a proton ratio of 2/2/2/2/6/6. This and a parent ion at *m/e* 692/694 indicate that this material is $[(CH_3)_4C_2(C_5H_4)_2ZrCl]_2O$. Upon addition of HCl gas to its $CHCl_3$ solutions, it is quantitatively reconverted to $(CH_3)_4C_2(C_5H_4)_2ZrCl_2$, in accord with earlier observations on $[(C_5H_5)_2ZrCl]_2O$ [15,16].

ppm (s, 12 H), 6.14 ppm (t, 4H, 2.65 Hz) and 6.66 ppm (t, 4H, 2.65 Hz), by a mass spectrum with parent ion at m/e 372–278 with appropriate isotope distribution for $C_{16}H_{20}ZrCl_2$. Elemental analysis: Found: C, 51.27; H, 5.43; Cl, 18.98. $C_{16}H_{20}ZrCl_2$ calcd.: C, 51.32; H, 5.38; Cl, 18.94%.

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