

Synthesis, Spectroscopic Characterization, and Reactivity of Ruthenocenes Bearing Pentamagnesiated Cyclopentadienyl Ligands

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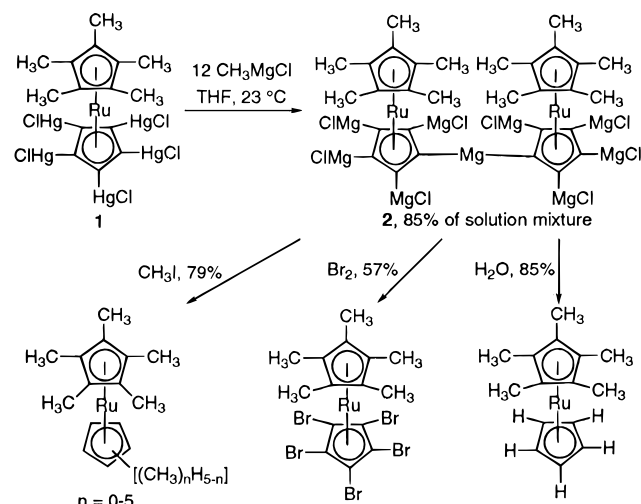
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Grignard reagents rank among the most widely used and studied class of organometallic compounds.¹ Although numerous aliphatic and aromatic Grignard reagents have been prepared, there are very few examples of aromatic compounds bearing two or more magnesium groups directly bonded to aromatic carbons.² In the case of polymagnesiated compounds made from hexahalobenzenes, the thermal stability of higher magnesiated species is limited by the facile elimination of magnesium halide to afford benzyne. Polymagnesiated metallocenes are restricted to dimagnesiated ferrocenes.³ Recently, we reported the synthesis of pentamethylpentalithioruthenocene and decalithioruthenocene.⁴ However, subsequent work in our laboratory has revealed that complexes containing pentalithiated cyclopentadienyl ligands are too reactive and thermally unstable to allow extensive use in synthesis.⁵ We reasoned that replacement of lithium by main group metals with less reactive carbon–metal bonds might lead to species with higher thermal stability and more tractable reactivity patterns. Herein we report the synthesis, characterization, and reactivity of permagnesiated ruthenocenes based upon the ruthenocene and pentamethylruthenocene skeletons. To the best of our knowledge, these are the first examples of permagnesiated aromatic compounds. The new ruthenocenes are remarkably stable, yet readily react to form new substituted derivatives. NMR studies indicate that the permagnesiated ruthenocenes exist as dimers and higher oligomers and that conversion from lower to higher oligomers is facile.

Treatment of pentakis(chloromercurio)(pentamethyl)ruthenocene⁶ (**1**) with methylmagnesium chloride (12 equiv) in tetrahydrofuran at 23 °C for 1 h led to its dissolution, giving a clear yellow–orange solution containing a pentamagnesiated pentamethylruthenocene (Scheme 1). Hydrolysis of this solution with H₂O afforded pentamethylruthenocene^{7a} (85%), while D₂O quench gave pentamethylruthenocene (97%) with 87% deute-

Scheme 1



rium content in the cyclopentadienyl ligand. Carbon–mercury bonds in ruthenocenes are stable to water under the reaction conditions, which supports a pentamagnesiated formulation and rules out structures containing carbon–mercury bonds. Addition of bromine gave pentabromopentamethylruthenocene^{7b} (57%). Additional evidence for a magnesiated species was obtained from reaction with methyl iodide, which gave a mixture of methylated ruthenocenes between pentamethylruthenocene and decamethylruthenocene (79% total yield).⁶ Grignard reagents are well known to react with alkyl iodides by electron transfer pathways.⁸

Given the likelihood that a pentamagnesiated ruthenocene was being formed, we sought to characterize this species by spectroscopic methods. Treatment of **1** with methylmagnesium chloride (12 equiv) in tetrahydrofuran-*d*₈ at ambient temperature, followed by ¹H and ¹³C{¹H} NMR analysis, revealed 85% of a major product **2** with a ¹H NMR resonance for the Cp* ligand at δ 2.06 and 15% of at least five minor products with Cp* resonances at δ 2.13, 2.12, 2.11, 2.10, and 2.08.⁹ No cyclopentadienyl C–H bonds were observed in the ¹H NMR spectrum, indicating that the magnesiated ruthenocenes contained ≤2% of hydrogen on the cyclopentadienyl ligands. The ¹³C{¹H} NMR spectrum of **2** showed resonances due to the Cp* ligand at 84.40 (C–CH₃), and 16.32 (C–CH₃) ppm. Resonances from the magnesiated cyclopentadienyl ligand were observed at 123.35, 121.78, and 118.67 ppm, with intensities of approximately 2:1:2. A reasonable structure for **2** that is consistent with all of the data is a dimer with eight terminal chloromagnesium groups and one diruthenocenyilmagnesium unit.¹⁰ The ipso-carbons in phenyl magnesium halides^{11a} and

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(6) Experimental procedures for the synthesis of new compounds are given in the supporting information. Small amounts of iodinated methyl ruthenocenes (3–11% total yields) were observed in the methylation product mixtures. For data, see supporting information.

(7) (a) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, 3, 274. (b) Winter, C. H.; Han, Y.-H.; Heeg, M. J. *Organometallics* **1994**, 13, 3009.

(8) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice Hall: New York, 1954; pp 1032–1046.

(9) Also observed were dimethylmercury (¹H NMR δ 0.11 (J_{H–Hg} = 52.0 Hz); ¹³C{¹H} NMR 20.14 (J_{C–Hg} = 345 Hz) ppm), excess methylmagnesium chloride (¹H NMR δ –1.82; ¹³C{¹H} NMR –16.80 ppm), and methyl chloride (¹H NMR δ 3.10; ¹³C{¹H} NMR 48.93 ppm; contaminant in methylmagnesium chloride). Several small peaks around the Cp* methyl and ring carbon regions could not be assigned in the ¹³C{¹H} NMR and are probably associated with the five minor products.

(10) (a) For a discussion of the Schlenk equilibria, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; pp 159–161. (b) Cyclic oligomers with 1,2,4- or 1,2,3-MgCl groups would also give 2:1:2 intensity peaks for the magnesiated carbons and must be considered as possible structures for **2**. However, the proposed dimer is a simpler and, we feel, more likely structure.

(11) (a) Screttas, C. G.; Micha-Screttas, M. J. *Organomet. Chem.* **1985**, 290, 1. Allen, P. E. M.; Fisher, M. C. *Eur. Polym. J.* **1985**, 21, 201. (b) Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. J. *Phys. Chem.* **1969**, 73, 1624. (c) For ¹³C NMR shifts (109.1–112.1 ppm for C–Ti) of metallocenes bearing Ti(NEt₂)₃ substituents, see: Bürger, H.; Kluss, C. J. *Organomet. Chem.* **1973**, 56, 269. *Z. Anorg. Chem. Allg. Chem.* **1976**, 423, 112.

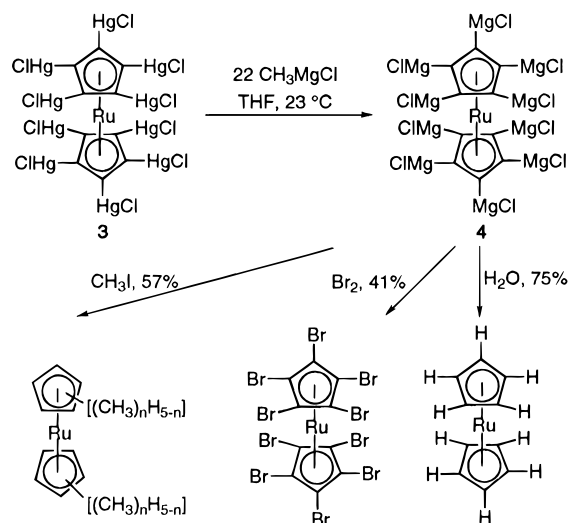
diphenylmagnesium^{11b} are found to resonate about 30–35 ppm downfield from benzene. The positions of the magnesiated carbon resonances (34.27–38.95 ppm downfield from C–CH₃) are thus appropriate for an aromatic magnesium compound.^{11c} The minor compounds could not be identified due to their low concentrations but are probably higher oligomers.

The isolation of **2** was attempted. A tetrahydrofuran solution prepared as above was treated with a large excess of hexane, resulting in the precipitation of a yellow–ochre powder. Analysis of the powder by ¹H NMR spectroscopy in tetrahydrofuran-*d*₈ revealed at least 12 broad Cp* methyl resonances between δ 2.13–1.81, of which **2** (δ 2.06) was a minor component.¹² It was not possible to obtain a ¹³C{¹H} NMR spectrum with sufficient signal to noise to allow structural assignments, due to the low concentration of each of the components. However, we propose that the isolated material corresponds to a mixture of oligomers^{10a} that results from elimination of magnesium chloride from **2**. This mixture is further evidence of the tendency of pentamagnesiated ruthenocenes to form oligomers. Infrared spectroscopy suggested that tetrahydrofuran was associated with the isolated powder, but the exact amount could not be assigned by the ¹H NMR spectrum because of residual hydrogen content in the tetrahydrofuran-*d*₈. The reactivity of the isolated powder was similar to that of the compound generated in solution. Hydrolysis afforded pentamethylruthenocene (65%), while bromination with bromine gave pentabromopentamethylruthenocene (54%) and tetrabromopentamethylruthenocene⁴ (13%).

The simple synthesis of **2** and its higher oligomers suggested that a decamagnesiated ruthenocene should be accessible. Accordingly, treatment of decakis(chloromercurio)ruthenocene (**3**)⁶ with methylmagnesium chloride (ca. 22 equiv) in tetrahydrofuran at 23 °C gave a turbid light brown solution containing a decamagnesiated ruthenocene **4** (Scheme 2). Attempts to record NMR spectra of **4** in tetrahydrofuran-*d*₈ failed due to its low solubility. Although **4** is denoted as a monomer herein for simplicity, its low solubility and analogy with **2** suggest a dimeric or higher oligomeric structure. Hydrolysis of **4** afforded ruthenocene (75%), while treatment of **4** with bromine (ca. 20 equiv) gave decabromoruthenocene¹³ (41%). Methylation of **4** by refluxing in neat methyl iodide gave about 15 methylated ruthenocenes (57% total yield), as determined by GLC and GLC/MS.⁶

Several significant inferences can be made from the above results. First, and perhaps most surprising, is that ruthenocenes bearing pentamagnesiated cyclopentadienyl ligands are stable and can be easily isolated and manipulated at ambient temperature. The complexes described herein are substantially more robust than the perliithiated analogs we described earlier,⁴ implying that permagnesiated aromatic compounds and permetalated aromatic compounds containing other main group metals will exhibit similar or possibly higher thermal stability. Such stability contradicts conventional wisdom,^{14,15} which would predict that placement of adjacent electropositive metals on

Scheme 2



aromatic molecules should be extremely unfavorable due to repulsion between the carbanionic sites. Second, NMR spectroscopy suggests that the permagnesiated ruthenocenes exist preferentially as dimers or higher oligomers. The facile formation of oligomers is in contrast to traditional Grignard reagents, which favor monomeric formulations in ether solvents.^{16,17} Finally, despite the unusual placement of five or ten contiguous magnesium substituents about a metallocene skeleton, initial studies suggest that the permagnesiated ruthenocenes react like typical organomagnesium reagents. Thus, the complete range of reactivity associated with Grignard reagents and diorganomagnesium compounds may be expected for permagnesiated cyclopentadienyl complexes and aromatic compounds.¹ The above predictions are being investigated in our laboratory.¹⁸

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for the new compounds (16 pages). Ordering information is given on any current masthead page.

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(17) For a structural discussion of di-Grignard compounds, see: Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 990.

(18) For an initial disclosure of a hexamagnesiated benzene, see: Winter, C. H.; Kur, S. A. *Abstracts of Papers*, 210th National Meeting of the American Chemical Society, Chicago, IL, August 20–24, 1994; INOR 475.

(12) Data for isolated solid: IR (Nujol, cm⁻¹): 1337 (m), 1308 (w), 1249 (m), 1257 (s), 1240 (m), 1172 (s), 1029 (vs, THF C–O), 949 (m), 915 (s), 881 (vs), 722 (s), 687 (s), 670 (s). Anal. Found: C, 24.68; H, 4.07; Cl, 30.06. For comparison, calcd for (C₅(MgCl)₅)(C₅(CH₃)₅)Ru: C, 30.27; H, 2.54; Cl, 29.79.

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