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Synthesis, Reactivity, and Characterization of Ruthenocenes Bearing Pentazincated Cyclopentadienyl Ligands

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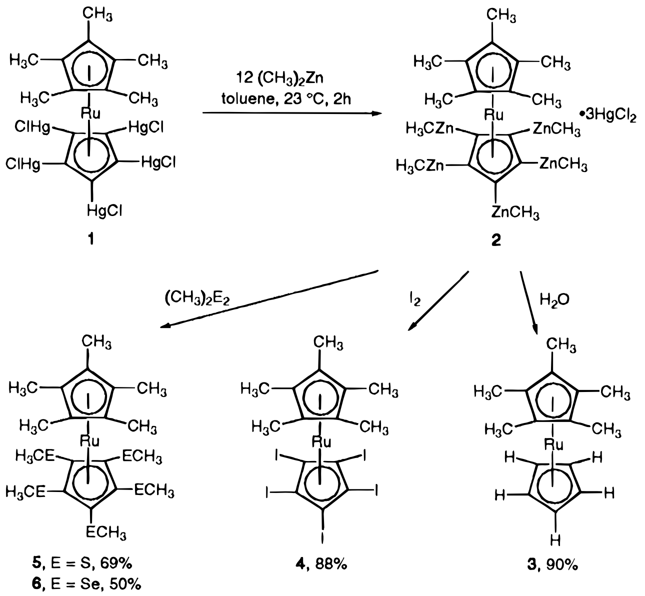
Summary: Treatment of pentakis(chloromercurio)pentamethylruthenocene or decakis(chloromercurio)ruthenocene with dimethylzinc affords ruthenocenes containing pentazincated cyclopentadienyl ligands. The reactivity of the perzincated ruthenocenes is presented, along with insight into the structures of these species.

Aromatic compounds in which all of the hydrogens on the aromatic ring have been replaced by metal substituents represent an extremely rare class of molecules.[1−5] Recently, we reported the preparation and characterization of perlithiated ruthenocenes[2] and permagnesiated ruthenocenes.[3] However, treatment of the perlithiated and permagnesiated ruthenocenes with most electrophiles afforded hydrogen-substituted ruthenocene derivatives by abstraction of hydrogen from the solvent.[4] Accordingly, we sought to examine the preparation of other permetalated ruthenocenes that might exhibit more useful reactivity. Organozinc compounds are well-known to be less reactive than analogous organolithium or organomagnesium compounds,[6] and zinc-substituted ruthenocenes might be less prone to abstract hydrogen atoms from solvents. Herein, we report the synthesis and reactivity of two ruthenocene derivatives bearing pentazincated cyclopentadienyl ligands and offer insight into the solid state and solution structures of these species. To the best of our knowledge, these are the first perzincated aromatic compounds. Furthermore, the perzincated ruthenocenes react with several moderate electrophiles to afford persubstituted derivatives and, thus, represent a promising new class of synthetic intermediates.

Scheme 1. Preparation and Reactions of 2



Treatment of pentakis(chloromercurio)pentamethylruthenocene[3] (**1**) with dimethylzinc (ca. 12 equiv) in toluene at 23 °C for 2 h led to the formation of a yellow-orange suspension containing a perzincated pentamethylruthenocene (**2**, Scheme 1).[7] Hydrolysis of **2** with water afforded pentamethylruthenocene[8a] (**3**, 90%), while D_2O quench gave pentamethylruthenocene (95%) with 86% deuterium incorporation. By contrast, **1** did not react with water under similar conditions. These results unambiguously confirm the complete replacement of the carbon−mercury bonds of **1** with carbon−zinc bonds. Treatment of **2** with iodine afforded pentaiodopentamethylruthenocene[8b] (**4**, 88%). To gain further insight, **2** was treated with methyl disulfide in toluene at 111 °C for 6 days to afford pentakis(methylthio)pentamethylruthenocene (**5**, 69%). Analogous treatment with methyl diselenide gave pentakis(methylseleno)pentamethylruthenocene (**6**, 50%).[7] Exposure of **1** to similar reaction conditions with methyl disulfide or methyl diselenide gave only decomposition. As a comparison, refluxing of the pentamagnesiated pentamethylruthenocene[3] in neat methyl disulfide afforded (methylthio)pentamethylruthenocene (65%) and bis(methylthio)pentamethylruthenocene (16%).[7] Treat-

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(1) For leading references, see: Winter, C. H.; Seneviratne, K. N.; Bretschneider-Hurley, A. *Comm. Inorg. Chem.* **1996**, *19*, 1.

(2) Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1994**, *116*, 6468.

(3) Seneviratne, K. N.; Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 5506.

(4) Bretschneider-Hurley, A.; Winter, C. H. Manuscript in preparation.

(5) See also: Morton, M. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 7005.

(6) For a recent overview of organozinc chemistry, see: Erdik, E. *Organozinc Reagents in Organic Synthesis*; CRC Press: Boca Raton, FL, 1996.

(7) Complete preparative procedures and spectral and analytical data for the new compounds are presented in the Supporting Information. Preparation of **5**: A 100-mL Schlenk flask was charged with **1** (0.500 g, 0.339 mmol) and toluene (50 mL). A 2.0 M solution of dimethylzinc in toluene (2.03 mL, 4.06 mmol) was added to the resulting suspension. The mixture was stirred for 2 h at room temperature. Then methyl disulfide (1.00 mL, 11.1 mmol) was added, and the mixture was refluxed for 6 days. After addition of water to quench any remaining dimethylzinc, the volatile components were removed under reduced pressure. The crude product was extracted with dichloromethane (50 mL). The resultant extract was filtered through a medium-porosity glass frit. The dichloromethane eluent was applied to a 2.5 cm × 15 cm column of silica gel. Elution with toluene, followed by removal of solvent under reduced pressure, afforded **5** as a light yellow solid (0.125 g, 69%): dec point (sealed tube) 170 °C; ^1H NMR ($CDCl_3$, δ) 1.72 (s, $C_5(C\boldsymbol{H}_3)_5$), 2.39 (s, $C_5(SC\boldsymbol{H}_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 92.38 (s, $\mathbf{C}_5(SCH_3)_5$), 89.47 (s, $\boldsymbol{C}_5(CH_3)_5$), 20.69 (s, $C_5(S\boldsymbol{C}H_3)_5$), 10.08 (s, $C_5(\mathbf{C}H_3)_5$); MS (20 eV) *m/e* 532 (M^+, 100%), 517 ($M^+ - CH_3$, 97%). Anal. Calcd for $C_{20}H_{30}RuS_5$: C, 45.17; H, 5.69. Found: C, 44.59; H, 5.66.

(8) (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.

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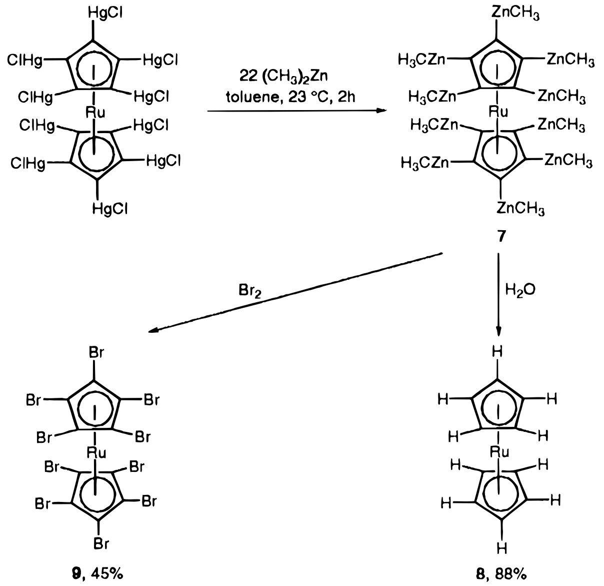
Scheme 2. Preparation and Reactions of 7



ment of pentalithiopentamethylruthenocene with methyldisulfide in tetrahydrofuran gave only pentamethylruthenocene.[4]

When **2** was initially prepared in THF, it precipitated as a yellow powder.[9] After filtration and drying, however, the yellow powder was sufficiently soluble in THF-d_8 to allow analysis by NMR spectroscopy. In the ^{1}H NMR spectrum at −90 °C, the $C_5(CH_3)_5$ methyl groups showed at least five broad resonances between δ 1.92 and 2.13 while a broad singlet for the methyl groups attached to zinc was observed at δ 0.13.[10a] The integration between the two types of methyl groups was 1:1. Carbon, hydrogen, chlorine, and mercury microanalyses were conducted on isolated **2**.[10b] The results were consistent with a formulation of $(C_5(ZnCH_3)_5)(C_5(CH_3)_5Ru)\cdot 3HgCl_2$, where there are three mercury(II) units per metallocene. This formula gives an 82% isolated yield for **2**. A ruthenocene of the formula $Cp_2Ru\cdot 3HgCl_2$ has been structurally characterized[11] and consists of a polymeric array held together by mercury−ruthenium and mercury−chlorine interactions.

The facile formation of a pentazincated pentamethylruthenocene suggested that a decazincated ruthenocene should be obtained in a similar manner. Accordingly, treatment of decakis(chloromercurio)ruthenocene[3] with dimethylzinc (ca. 22 equiv) in toluene at 23 °C gave a bright yellow suspension of a decazincated ruthenocene (**7**, Scheme 2).[7,12] Hydrolysis with water afforded ruthenocene (**8**, 94%), while the reaction with D_2O gave ruthenocene (95%) with 88% deuterium in the cyclopentadienyl ligands.[12] Addition of bromine gave decabromoruthenocene (**9**, 45%).[8b] While **7** is depicted as decakis(methylzinco)ruthenocene for simplicity, its structure is probably more complicated by analogy with **2**. Unfortunately, **7** was insoluble in toluene or tetrahydrofuran and could not be studied by NMR spectroscopy.

In conclusion, pentazincated pentamethylruthenocene and decazincated ruthenocene have been made by treatment of the permercurated analogs with dimethylzinc. Hydrolysis studies are uniquely consistent with complete replacement of the mercury atoms, since ruthenocenyl mercurials do not react with water under similar conditions. Importantly, treatment of the pentazincated pentamethylruthenocene with methyl disulfide and methyl diselenide afforded exclusively persubstituted products, whereas the pentalithiated and pentamagnesiated analogs gave products resulting from extensive hydrogen abstraction from the solvent. These experiments suggest that perzincated metallocenes should be more useful synthetically than perlithiated or permagnesiated analogs. This is a significant point, since organomagnesium and organolithium reagents are used much more frequently in synthesis than are organozinc reagents. Initial NMR studies show that isolated **2** is not a single pure compound in solution, while microanalysis results demonstrate that it has a composition with three mercuric ions per ruthenium atom. A possible structure for **2** is one where the chlorines and methyl groups are statistically scrambled over the zinc and mercury sites. Further studies are in progress to probe the structure and reactivity of perzincated metallocenes as well as related perzincated aromatic compounds.

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Supporting Information Available: Text giving synthetic procedures, spectroscopic data, and analytical data for the new compounds amd ^{1}H NMR spectra of **2** (8 pages). Ordering information is given on any current masthead page.

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(9) Generation of **2** in toluene-d_8, tetrahydrofuran-d_8, and methylsulfoxide-d_6 led to precipitation, which precluded spectroscopy of the material prepared in situ.

(10) (a) The ^{1}H NMR spectrum at 23 °C showed broad resonances for the $C_5(CH_3)_5$ group between δ 2.00−2.30 and, similarly, broad resonances for the methyls attached to zinc between δ 0.15−0.60. The low solubility of **2** precluded measurement of the ^{13}C NMR spectrum. (b) Anal. Calcd for $C_{20}H_{30}Cl_6Hg_3RuZn_5$: C, 16.22; H, 2.28; Cl, 9.37; Hg, 39.20. Found: C, 15.88; H, 2.00; Cl, 14.06; Hg, 39.78.

(11) Gusev, A. I.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1971**, 12, 1121. See also: Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1972**, *11*, 2912.

(12) Preparation and hydrolysis of **7**: A 100-mL Schlenk flask was charged with decakis(chloromercurio)ruthenocene (0.650 g, 0.252 mmol) and toluene (50 mL). A 2.0 M solution of dimethylzinc in toluene (2.77 mL, 5.54 mmol) was added to the resulting suspension. The mixture was stirred for 2 h at room temperature. Then water (0.30 mL, 17 mmol) was added, and the mixture was stirred for an additional 0.5 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane (50 mL). The dichloromethane extract was applied to a 4-cm pad of silica gel on a coarse glass frit. Elution with dichloromethane (50 mL), followed by removal of the solvent under reduced pressure, afforded a solid that contained mercury impurities. The solid was dissolved in hexane (50 mL), and the resultant solution was applied to a 2.5 cm × 15 cm column of silica gel. Elution with hexane (100 mL), followed by removal of the solvent under reduced pressure, afforded ruthenocene (0.0547 g, 94%): ^{1}H NMR ($CDCl_3$, δ) 4.56 (s, $C_5\boldsymbol{H}_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 70.02 (s, $\boldsymbol{C}_5H_5$).