

Pentamethylpentalithioruthenocene and Decalithioruthenocene

Annette Bretschneider-Hurley and Charles H. Winter*

Department of Chemistry
Wayne State University
Detroit, Michigan 48202

Received March 30, 1994

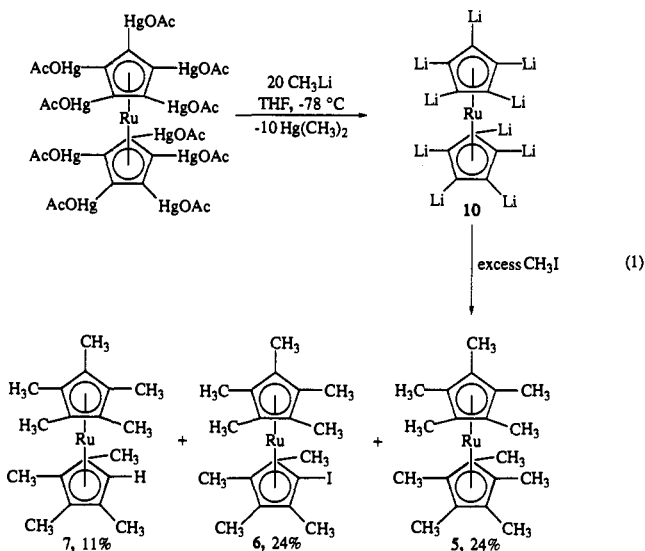
There has been considerable recent synthetic and theoretical interest in perolithiated organic compounds. While numerous polyolithiated aliphatic hydrocarbons have been studied,¹ very little is known about perolithiated aromatic compounds.² Lagow has reported the synthesis of hexalithiobenzene by lithiation of hexachlorobenzene with *tert*-butyllithium and has obtained its mass spectrum.² Monolithiated transition metal cyclopentadienyl complexes are well known and have been widely used as synthetic intermediates in organometallic synthesis.³ However, experimental evidence for complexes containing di-, tri-, or tetralithiated cyclopentadienyl ligands is meager,⁴ and complexes bearing pentalithiocyclopentadienyl ligands remain unknown. Herein we report that treatment of pentakis(acetoxymethyl)pentamethylruthenocene and decakis(acetoxymethyl)decakis(acetoxymethyl)ruthenocene with methyllithium represents a simple route to pentamethylpentalithioruthenocene and decalithioruthenocene. Pentamethylpentalithioruthenocene and decalithioruthenocene constitute the first examples of pentalithiocyclopentadienyl complexes. These species react with simple electrophiles to afford 48–67% yields of persubstituted products. Pentamethylpentalithioruthenocene can be isolated as an orange powder that is stable for short periods at ambient temperature. The results of this study suggest that other pentamethylated cyclopentadienyl complexes should be easily accessible and may constitute a new class of useful reactive species.

Scheme 1 outlines the synthesis and reactions of pentamethylpentalithioruthenocene (**1**). Treatment of pentakis(acetoxymethyl)pentamethylruthenocene⁵ with methyllithium (10 equiv) in tetrahydrofuran at $-78\text{ }^{\circ}\text{C}$ led to the immediate formation of a deep yellow-orange solution containing **1**. After the solution was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$, addition of bromine (ca. 13 equiv) led to rapid (≤ 1 min) bleaching of the orange color. Workup afforded (pentabromo)(pentamethyl)ruthenocene⁵ (**2**, 38%), (pentamethyl)(tetrabromo)ruthenocene⁶ (**3**, 22%), and (methyltetrabromo)(pentamethyl)ruthenocene⁶ (**4**, 12%).⁷ The thermal stability of **1** was investigated by warming a tetrahydrofuran solution to $23\text{ }^{\circ}\text{C}$ prior to bromine addition. Workup afforded

2 (8%), **3** (3%), and **4** (2%). Hence, solutions of **1** have limited stability at $23\text{ }^{\circ}\text{C}$. Treatment of **1** with methyl iodide (ca. 20 equiv) at $-78\text{ }^{\circ}\text{C}$ afforded decamethylruthenocene⁸ (**5**, 46%), (iodotetramethyl)(pentamethyl)ruthenocene⁶ (**6**, 21%), and nonamethylruthenocene⁶ (**7**, 14%). Finally, hydrolysis with water (ca. 20 equiv) gave pentamethylruthenocene (**8**, 46%) and ruthenocene (**9**, 23%).⁹

Complex **1** could be precipitated by addition of hexane at $-78\text{ }^{\circ}\text{C}$ to afford an exceptionally air-sensitive bright orange powder. This material was insoluble in tetrahydrofuran-*d*₈ at $23\text{ }^{\circ}\text{C}$, which precluded NMR analysis.¹⁰ However, treatment of the precipitated powder with bromine in tetrahydrofuran afforded **2** (23%), which indicated that the powder had not decomposed. This experiment also indicates that solid **1** is considerably more stable at $23\text{ }^{\circ}\text{C}$ than is a tetrahydrofuran solution of **1**.

The facile route to **1** suggested that an analogous strategy should afford a decalithiometalloocene. Accordingly, treatment of decakis(acetoxymethyl)decakis(acetoxymethyl)ruthenocene¹¹ with methyllithium (20 equiv) in tetrahydrofuran at $-78\text{ }^{\circ}\text{C}$ gave an immediate color change from white to red-orange and afforded a solution containing decalithioruthenocene (**10**, eq 1). After 1 h at $-78\text{ }^{\circ}\text{C}$, addition of methyl iodide, followed warming to ambient temperature and workup, afforded **5** (24%), **6** (24%), and **7** (12%).



The formation of persubstituted products in 48–67% yields upon treatment of **1** and **10** with simple electrophiles is excellent evidence for the formation of ruthenocenes bearing pentalithiocyclopentadienyl ligands. The similar product mixtures derived from treatment of **1** and **10** with methyl iodide suggest that these reactions proceed through the same intermediate. We propose that the observed product distributions (i.e., **5**, **6**, **7**) can be derived

(7) In order to probe the genesis of the methyl group in **4**, the preparation of **1** was repeated using methyllithium-*d*₃. Analysis by ¹H NMR showed the methyl resonance for the C₅Br₄(CH₃) ligand in **4** to be absent, which suggests that the methyl group originates from methyllithium and not from the Cp* ligand. However, the methyllithium-*d*₃ was available only as the lithium iodide complex, and a new product was observed, in addition to **2–4**. Mass spectral analysis suggests that this product was (iodotetramethyl)(pentamethyl)ruthenocene.

(8) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* 1984, 3, 274. Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Chem. Lett.* 1984, 1161.

(9) Decamethylruthenocene was not observed to the limits of ¹H NMR detection ($\leq 2\%$). GLC analysis of the reaction solution indicated the presence of pentamethylcyclopentadiene in ca. 1–2% yield versus internal dodecane. The remaining pentamethylcyclopentadiene mass balance was possibly present in an insoluble yellow powder that was formed in the reaction. This powder liberated dimethylmercury upon thermolysis, as assayed by mass spectrometry.

(10) Attempts to generate **1** in an NMR tube in tetrahydrofuran-*d*₈ led to precipitation, consistent with its low solubility.

(11) Winter, C. H.; Han, Y.-H.; Ostrander, R. L.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 1161.

(1) For leading references, see: Ivanic, J.; Marsden, C. J. *J. Am. Chem. Soc.* 1993, 115, 7503. Maercker, A. *Angew. Chem., Int. Ed. Engl.* 1992, 31, 584. Dorigo, A.E.; van Eikema Hommes, N. J. R.; Krogh-Jespersen, K.; Schleyer, P.v.R. *Angew. Chem., Int. Ed. Engl.* 1992, 31, 1602. Maercker, A.; Theis, M. *Top. Curr. Chem.* 1987, 138, 1.

(2) (a) Shimp, L. A.; Chung, C.; Lagow, R. J. *Inorg. Chim. Acta* 1978, 29, 77. (b) Baran, J. C., Jr.; Hendrickson, C.; Laude, D. A., Jr.; Lagow, R. J. *J. Org. Chem.* 1992, 57, 3759. (c) Xie, Y.; Schaefer, H. F., III. *Chem. Phys. Lett.* 1991, 179, 563.

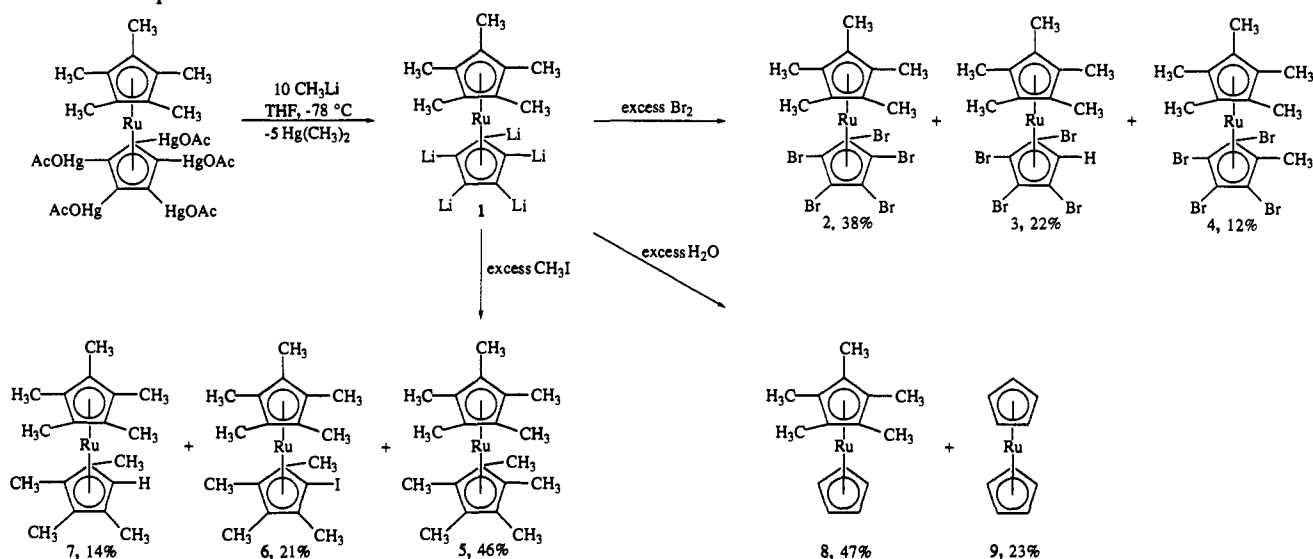
(3) For leading references, see: Rebiere, F.; Samuel, S.; Kagan, H. B. *Tetrahedron Lett.* 1990, 3121. Härter, P.; Boguth, G.; Herdtweck, E.; Riede, J. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1008. Crocco, G. L.; Gladysz, J. A. *Chem. Ber.* 1988, 121, 375. Wright, M. E.; Day, V. W. *J. Organomet. Chem.* 1987, 329, 43. Butler, I. R.; Cullen, W. R.; Rettig, S. *Organometallics* 1986, 5, 1320. Butler, I. R.; Cullen, W. R. *Organometallics* 1986, 5, 2537. Bednarik, L.; Neuse, E. W. *J. Org. Chem.* 1980, 45, 2032. Walczak, M.; Walczak, K.; Mink, R.; Rausch, M. D.; Stucky, G. *J. Am. Chem. Soc.* 1978, 100, 6382. Hedberg, F. L.; Rosenberg, H. *Tetrahedron Lett.* 1969, 4011. Rausch, M. D.; Ciappenelli, D. *J. Organomet. Chem.* 1967, 10, 127.

(4) Halasa, A. F.; Tate, D. P. *J. Organomet. Chem.* 1970, 24, 769. Bednarik, L.; Neuse, E. W. *J. Organomet. Chem.* 1979, 168, C8. See also: Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* 1978, 162, 79. Post, E. W.; Crimmins, T. F. *J. Organomet. Chem.* 1978, 161, C17.

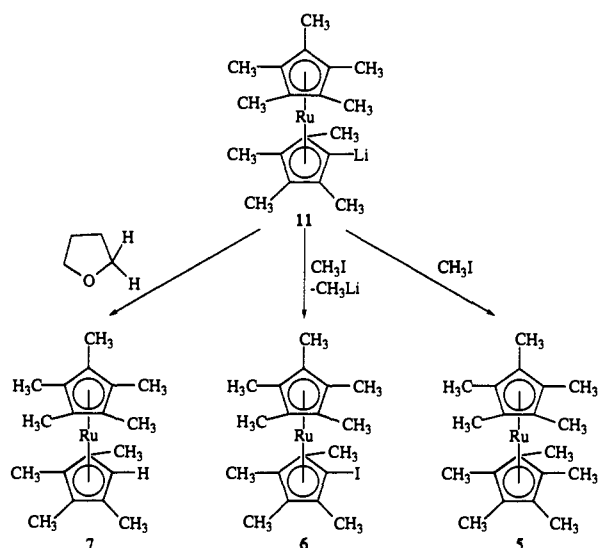
(5) Winter, C. H.; Han, Y.-H.; Heeg, M. J. *Organometallics* 1992, 11, 3169.

(6) Experimental procedures, spectroscopic data, and analytical data for the new complexes are contained in the supplementary material.

Scheme 1. Preparation and Reactions of 1



Scheme 2. Reactions of 11



from the penultimate species nonamethylthioruthenocene (11, Scheme 2). Direct methylation of 11 with methyl iodide would afford 5, while proton abstraction from solvent would afford 7. Complex 7 could also be obtained by proton abstraction from tetrahydrofuran by 1 and 10, although if this pathway were viable, other protonated products (e.g., complexes bearing $C_5X_3H_2$, $C_5X_2H_3$ ligands) should have been isolated. Lithium-halogen exchange of 11 with methyl iodide would afford 6.¹² The observation of ruthenocene upon hydrolysis of 1 is puzzling.⁹ We propose that 1 may be dimeric or oligomeric in solution via bridging lithium atoms. Such a structure would place two cyclopentadienyl

ligands in close proximity to the ruthenium centers and might lead to ligand exchange upon hydrolysis.

In summary, pentamethylpentalithioruthenocene (1) and decalithioruthenocene (10) have been prepared by treatment of the permercurated precursors with methyl lithium in tetrahydrofuran and are surprisingly stable. While the structural parameters of 1 and 10 remain to be determined, treatment with simple electrophiles gives moderate to good yields of persubstituted products. The exchange reaction of permercurated cyclopentadienyl complexes with methyl lithium appears to constitute a general route to perliithiocyclopentadienyl complexes. For example, we have prepared decalithioferrocene, (pentalithiocyclopentadienyl)manganese tricarbonyl, and (pentalithiocyclopentadienyl)rhenium tricarbonyl by lithiation of the permercurated complexes.¹³ We are continuing to study the synthesis, structure, and reactivity of permetalated cyclopentadienyl complexes and will report these results in due course.

Acknowledgment. We thank the Air Force Office of Scientific Research (Contract No. F49620-93-1-0072) for support of this work.

Supplementary Material Available: Synthetic procedures and spectral and analytical data for the new compounds (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(12) For examples of the preparation of organolithiums by exchange of an organoiodide with a different organolithium, see: Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404. Negishi, E.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* **1990**, *55*, 5406. Bailey, W. F.; Patricia, J. *J. Organomet. Chem.* **1988**, *352*, 1.

(13) Bretschneider-Hurley, A.; Winter, C. H., unpublished results, Wayne State University, 1994.