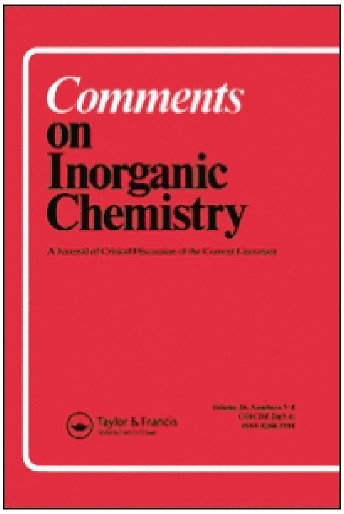

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Permetalated Aromatic Compounds

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Permetalated Aromatic Compounds

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Permetalated aromatic compounds, wherein all aromatic hydrogens in an aromatic molecule are replaced by metal substituents, represent an extremely rare class of molecules. A critical examination of the literature might lead to the conclusion that permetalated aromatic compounds possess limited thermodynamic stability due to strong electrostatic repulsion between adjacent carbanionic sites. However, a recent report detailing the synthesis of hexalithiobenzene, coupled with recent studies on permetalated metallocenes, demonstrate that permetalated aromatic compounds can possess excellent thermodynamic stability. The present state of knowledge concerning the structure and reactivity of hexalithiobenzene, decalithioruthenocene, and decakis(chloromagnesio)ruthenocene is described. The remarkable stability of the existing permetalated compounds implies that many new permetalated systems should be easily synthesized.

Key Words: *organolithium, organomagnesium, mercuration, ruthenocene, ferrocene*

INTRODUCTION

σ-Bonded organometallic compounds rank among the most widely used reactive species in organic synthesis. Of these, organolithium and organomagnesium reagents have achieved a position of special prominence, due to their ease of generation and useful, predictable reactiv-

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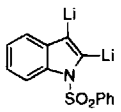
ity.[1] It is almost inconceivable to envision the preparation of a complex organic molecule that does not use an alkyllithium or Grignard reagent at some strategic point in the synthesis. Because of their central importance, considerable effort has been expended toward understanding the structure and reactivity of these reagents.[1]

Conventional wisdom dictates that the introduction of more lithium atoms (or other electropositive metals) onto a monometalated aromatic molecule will be extremely unfavorable due to repulsion between the carbanionic sites. Once generated, such compounds should be exceptionally reactive and difficult to handle. Consistent with this generalization, there are very few known examples of polylithiated aromatic compounds.[2–7] However, we suggest that a critical examination of the literature does not support the traditional picture. For example, the permetalated aromatics **1–5** have been generated from the corresponding perhalogenated precursors and were characterized at varying levels, depending on their stabilities.



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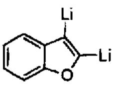

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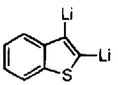

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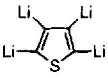

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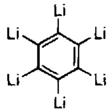


5

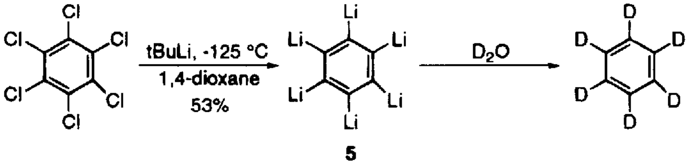
Compounds **1**[2] and **2**[3] undergo ring-opening reactions, even at very low temperatures, and could only be characterized by alkylation of the resultant dianions. The thiophene derivatives **3**[4] and **4**[5] are more resistant to ring opening and can be alkylated to form substituted thiophenes in excellent yields. Hexalithiobenzene **5**[6,7] is reported to be stable to 200°C as a solid. We suggest that there are not necessarily inherent stability problems with permetalated aromatic compounds, but rather, there are few synthetic routes that provide these compounds in pure states.

Recent theoretical studies have identified many new perlithiated carbon compounds that are predicted to be thermodynamically stable. Remarkable examples include CLi_8, CLi_{10}, and CLi_{12}.[8] Tetralithioethylene (C_2Li_4) has been demonstrated to be more acetylene-like than ethylene-like, and has a number of low-energy structures available to it.[9,10] Hexalithiobenzene (**5**) has recently been the subject of several theoretical studies.[11,12] Such studies demonstrate that lithium compounds can exhibit a remarkable range of structures and that these formulations are neither readily predicted nor explained by our present understanding of main group organometallic chemistry. In this area, theory is far ahead of experiment. Most experimental studies reported to date have focused on perlithiated aliphatic carbon species (e.g., CLi_4, C_5Li_4, C_2Li_2, C_4Li_2).[13]

For the purposes of this review, we define a permetalated aromatic compound as an aromatic hydrocarbon derivative in which all of the available carbon–hydrogen bonds on an aromatic ring have been replaced by carbon–metal bonds. Until recently, **1–5** and several permercurated organic species were the only known examples of compounds that fit this definition. Over the last several years, we have been investigating the synthesis and properties of transition metal cyclopentadienyl complexes in which the cyclopentadienyl hydrogens are replaced by main group metals. These permetalated complexes are easily prepared by treatment of a permercurated cyclopentadienyl complex with main group metal alkyls. The permercurated precursors are in turn accessed in nearly quantitative yield by reaction of the parent cyclopentadienyl complex with excess mercury(II) acetate salts. The remarkable stability of the perlithiated and permagnesiated metallocenes is surprising and unexpected. Such stability implies that a large family of permetalated aromatic compounds should be easily synthesized from the corresponding permercurated aromatics. In the following sections we review what is known about permetalated aromatic compounds, describe our recent investigations of perlithiated and permagnesiated ruthenocenes, and offer suggestions about other permetalated aromatic systems that should be readily synthesized.

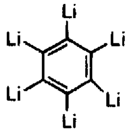
1. HEXALITHIOBENZENE

In 1978, Lagow reported evidence for the preparation of hexalithiobenzene **5** by treatment of hexachlorobenzene with lithium vapor.[6] While the yield was exceedingly low (≤1%), **5** appeared to be stable at ambient temperature. More recently, Lagow has prepared **5** in 53% yield by lithiation of hexachlorobenzene with t-butyllithium [Eq. (1)].[7] It was necessary to run the reaction at low temperature (≤ −105°C) for 24 h in pentane/1,4-dioxane to avoid intermolecular coupling reactions and formation of benzynes by elimination of lithium chloride. The product was initially characterized by deuterolysis to afford hexadeuterobenzene (no yield specified), which was identified by ^{13}C NMR and GLC/MS. Polymeric products from cross-linking and coupling reactions were also observed. The mass spectrum of **5** was measured using both laser desorption ionization/Fourier transform ion cyclotron resonance and traditional electron impact modes. Both techniques gave molecular ions, which is strong evidence for the formation of **5** and for its formulation as a monomeric species in the gas phase. Significantly, a conventional heated inlet was used to introduce **5** into the gas phase in the mass spectrum measured under electron impact conditions, showing that **5** has a high vapor pressure. It was speculated that the high vapor pressure implied a monomeric structure in the solid state.



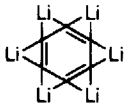
(1)

Xie and Schaefer have reported a theoretical study examining the structure of **5**.[11] The study restricted itself to cyclic and cage topologies and found three structures that were minima. Surprisingly, the structure containing all terminal C–Li bonds (**5**) was found to lie 122 kcal/mol higher in energy than the species where all of the lithiums are bridging. The species with all bridging lithiums (**5a**) was the lowest energy structure that was considered. A more recent theoretical study by Smith did not limit itself to cyclic structures and used a higher level of theory.[12] It was found that a tightly clustered trimer of dilithioacetylene (**5b**) was about 100 kcal/mol lower in energy than the cyclic structure **5a** found by Xie and Schaefer. The energy of **5** was calculated to lie about 157 kcal/mol above structure **5a**. The predicted infrared spectra of **5a** and **5b** are very different. It might be possible to differentiate experimentally between the two structures based upon the infrared spectrum.



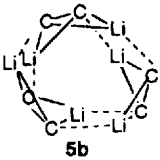
5

+ 157 kcal/mol



5a

0 kcal/mol

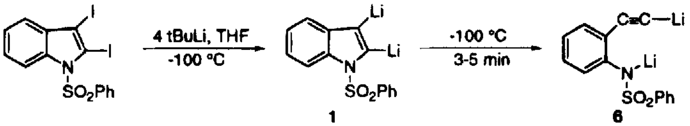


5b

-100 kcal/mol

2. PERLITHIATED 5-MEMBERED HETEROCYCLES

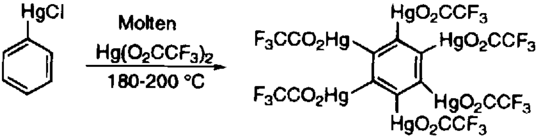
Treatment of 2,3-diiodo-1-(phenylsulfonyl)indole with t-butyllithium at −100°C affords a solution initially containing 2,3-dilithio-1(phenylsulfonyl)indole (**1**).[2] However, **1** rapidly reacts to give the amide acetylide **6**. In fact, treatment of **1** with electrophiles gives high yields of products derived from **6**. Evidence for **1** as a quasi-stable species comes from the protonolysis reaction with ammonium chloride, which gives 1-(phenylsulfonyl)indole in 18% yield. The low thermal stability of **1** is mirrored in the reactions of several other related heterocycles. 2,3-Dilithiobenzofuran **2** was prepared by treatment of 2,3-dibromobenzofuran with n-butyllithium (5 equiv) in diethyl ether.[3] Hydrolysis of **2** at −75°C gave predominantly benzofuran, while at higher temperature (−40°C), hydrolysis afforded substantial amounts of the ring-opening product ortho-ethynyl phenol. 2,3-Dilithiobenzothiophene **3** has been generated from 2,3-dibromobenzothiophene and n-butyllithium and reacts with carbon dioxide to give benzothiophene-2,3-dicarboxylic acid after hydrolysis.[4] No other products were mentioned. Tetralithiothiophene **4** has apparently been generated by treatment of tetrabromothiophene with a large excess of n-butyllithium.[5] The only characterization was its reaction with methyl iodide to yield tetramethylthiophene in 75% yield.



(2)

3. PERMERCURATION OF TRANSITION METAL CYCLOPENTADIENYL COMPLEXES

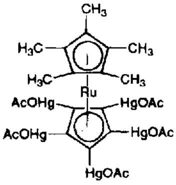
It has been known for many years that many organic aromatic compounds can be permercurated under very mild conditions.[14] These compounds fit our definition for permetalated aromatic compounds. A hexamercurated benzene can be prepared by fusion of phenylmercuric chloride with molten mercuric trifluoroacetate at 180°C [Eq. (3)].[14a] Certain electron-rich substituted benzene derivatives (e.g., anisole, acetanilide) are permercurated upon treatment with either mercuric acetate or mercuric trifluoroacetate in high boiling solvents.[14a] Heterocyclic compounds such as pyrrole,[14b] furan,[14c] and thiophene[14d] can be tetramercurated by reaction with four equivalents of mercuric acetate.



(3)

Correspondingly less is known about the mercuration of organometallic compounds bearing aromatic ligands. Most of the mercuration studies have centered on ferrocene,[15] which undergoes mono- and dimercuration upon treatment with mercuric acetate. Several other brief reports have appeared describing the mono- and dimercuration of ruthenocene,[16a] the mono- and dimercuration of cyclopentadienylmanganese tricarbonyl,[16b] and the tetramercuration of (cyclobutadiene)iron tricarbonyl.[16c] There have been several disclosures regarding the permercuration of cyclopentadienyl ligands bonded to a transition metal. Ferrocene itself has been reported to undergo decamercuration upon treatment with mercuric trifluoroacetate in ethanol/diethyl ether at ambient temperature.[17a] Additionally, 1,1′-dimethylferrocene was octamercurated under similar conditions.[17b] Cyclopentadienylmanganese tricarbonyl is pentamercurated upon treatment with mercuric trifluoroacetate.[17c]

In the past several years, we have reported the synthesis and characterization of permercurated transition metal cyclopentadienyl complexes, including pentakis(acetoxymercurio)pentamethylruthenocene (**7**),[18,20] decakis(acetoxymercurio)ruthenocene (**8**),[19,20] decakis(acetoxymercurio) osmocene (**9**),[21] pentakis(acetoxymercurio)cyclopentadienylmanganese tricarbonyl (**10**),[22] and pentakis(acetoxymercurio)cyclopentadienylrhenium tricarbonyl (**11**).[22] These compounds are easily accessed from the parent hydrogen-substituted complexes by treatment with the appropriate number of equivalents (5 or 10) of mercuric acetate in ethanol/ether (**7**) or refluxing 1,2-dichloroethane (**8–11**). The surprisingly high reactivity of the metallocenes toward permercuration is illustrated by the reaction of pentamethylruthenocene with one equivalent of mercuric acetate, which affords **7** (18%) and recovered pentamethylruthenocene (78%). Thus, the first mercuration is the slowest. Halogenation of **7–10** provides excellent routes to complexes bearing pentachlorocyclopentadienyl, pentabromocyclopentadienyl, and pentaiodocyclopentadienyl ligands. By contrast, **11** decomposes under conditions used to halogenate **7–10**.



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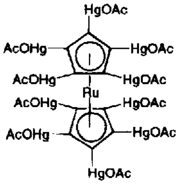

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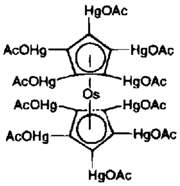

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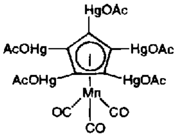

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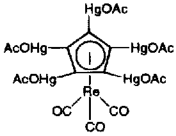
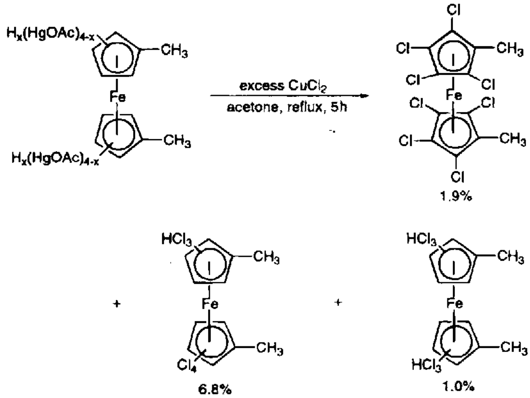


11

Treatment of ferrocene with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane gives a polymercurated ferrocene, which upon chlorination affords a mixture of decachloroferrocene (major component), nonachloroferrocene (minor component), and octachloroferrocene (minor component).[20] By contrast, analogous chlorination of **7–10** yields only compounds containing pentachlorocyclopentadienyl ligands. Thus, ferrocene does not undergo exhaustive mercuration, apparently due to the extreme insolubility of the higher mercurated species. Unfortunately, we were unable to quantify the chlorinated mixture, due to lack of a suitable spectroscopic or analytical assay.

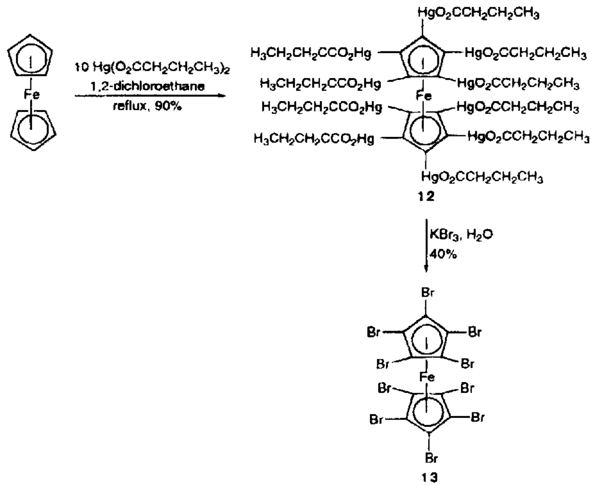
In order to obtain a better estimate of the degree of mercuration, we examined the octamercuration of 1,1-dimethylferrocene with mercuric acetate (8 equiv) in refluxing 1,2-dichloroethane [Eq. (4)].[23]



(4)

Chlorination of the resultant orange solid afforded an inseparable 20:70:10 mixture of 1,1′,2,2′,3,3′,4,4′-octachloro-5,5′-dimethylferrocene (1.9%), 1,1′,2,2′,3,3′,4-heptachloro-5,5′-dimethylferrocene (6.8%), and 1,1′,2,2′,3,3′-hexachloro-5,5′-ferrocene (1.0%). The identity and distribution of the major products were established by a combination of GLC, GLC/MS, and ^{1}H and ^{13}C{^{1}H} NMR analyses. We suggest, based upon the halogenation results, that the mercurated 1,1′-dimethylferrocene is a mixture of about 20% octakis(acetoxymercurio)dimethylferrocene, 70% heptakis(acetoxymercurio)dimethylferrocene, and 10% hexakis(acetoxymercurio)dimethylferrocene.

In the above mercuration attempts with ferrocene, it seemed likely that the failure to undergo complete mercuration was due to the extreme insolubility of the heavily mercurated intermediates. In order to probe this issue, the decamercuration of ferrocene was attempted using mercuric butyrate [Eq. (5)].[24] The idea was that the more lipophilic butyrate groups would keep the intermediate mercurated ferrocenes in solution long enough for decamercuration to occur. Indeed, treatment of ferrocene with mercuric butyrate (12 equiv) in refluxing 1,2-dichloroethane for 18 h afforded an insoluble decamercurated ferrocene **12** as an orange powder. Bromination of the mercurated ferrocene with potassium tribromide gave decabromoferrocene **13**. Analysis of the crude decabromoferrocene showed no resonances that could be attributed to partially brominated ferrocenes, indicating that **12** is ≥ 98% decamercurated.



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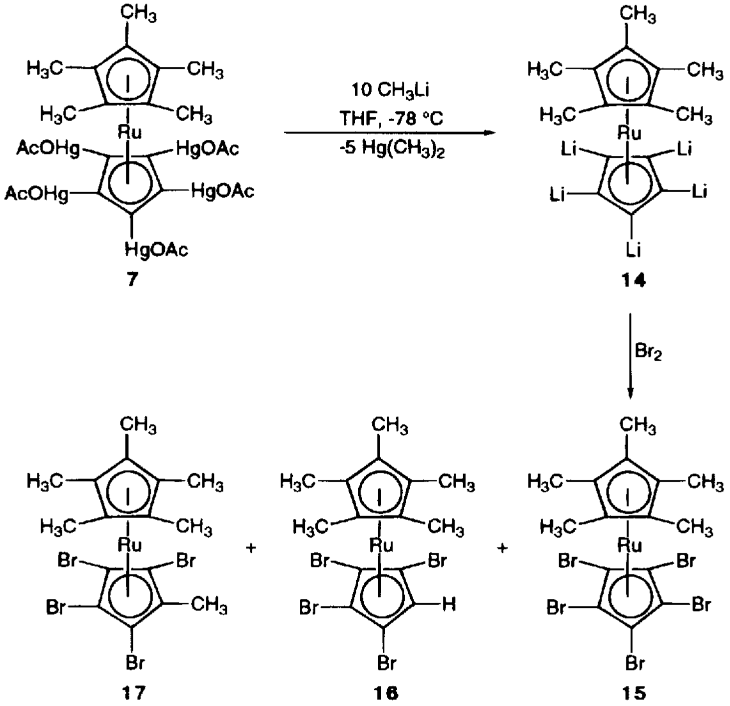
13

(5)

4. PERLITHIATED RUTHENOCENES

Our original goal in the metallocene permercuration project was to develop synthetic routes to decafluoroferrocene and decafluororuthenocene by treatment of the decamercurated metallocenes with electrophilic fluorinating agents. However, extensive fluorination studies revealed that **7** and **8** are destroyed by vigorous fluorinating agents (e.g., F_2, CH_3CO_2F) and are unreactive toward mild electrophilic fluorine sources (e.g., N-fluoropyridinium triflate). We reasoned that introduction of carbon-metal bonds that were more reactive than carbon-mercury bonds might lead to successful reaction with mild fluorinating agents. Lithium was the obvious choice, since lithiocarbons have been extensively used in organic synthesis. However, there was essentially nothing known about perlithiated metallocenes and it was not clear that such compounds would even be stable. Halasa and Tate claimed that mixtures of polylithiated ferrocenes (up to heptalithioferrocene) could be obtained by treatment of ferrocene with n-butyllithium in refluxing hexane.[25] The surprising stability of hexalithiobenzene **5** suggested that a decalithiated metallocene might be robust enough to be synthetically useful. However, the work of Halasa and Tate implied that direct deprotonation of the metallocenes would not be a viable route. It is well known that aromatic mercury compounds react with alkyllithium reagents to afford new aromatic lithium compounds and alkylmercury products.[26] We therefore sought to examine if this reaction could be extended to mercury compounds **7–11** as a method for preparing complexes with pentalithiocyclopentadienyl ligands.

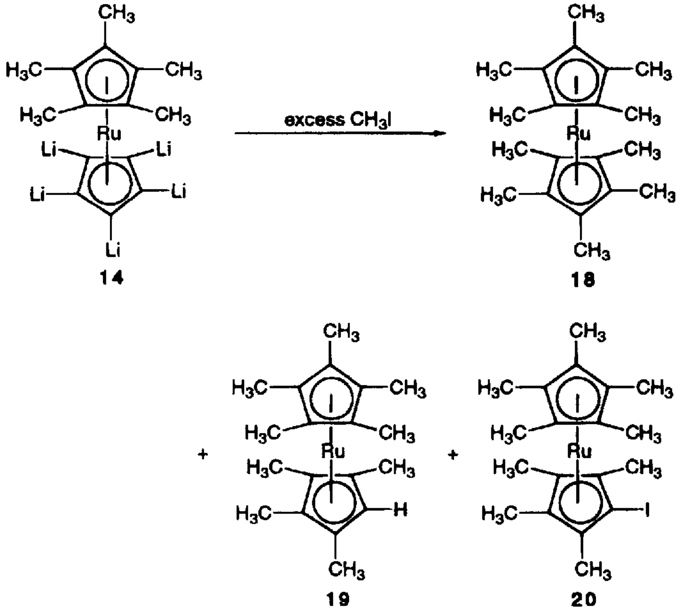
Treatment of **7** with methyllithium (10 equiv) in tetrahydrofuran at –78°C led to an immediate change from a white suspension to a yellow-orange suspension. After stirring for 1 h at –78°C, bromine (13 equiv) was added to the mixture, resulting in bleaching of the yellow-orange color (Scheme 1). Workup as described in the experimental section afforded pentabromopentamethylruthenocene (**15**, 38%), tetrabromopentamethylruthenocene (**16**, 22%), and tetrabromohexamethylruthenocene (**17**, 12%). The mixture of **15–17** was inseparable, despite many attempts, and was characterized by correlation of the ^1H and $^{13}C\{^1H\}$ NMR resonances with those of independently prepared materials. The isolation of the pentasubstituted products **15** and **17** in 50% yield strongly suggested that pentamethylpentalithioruthenocene (**14**) had been produced upon treatment of **7** with methyllithium. We have previously reported that bromination of **7** gives **15** as the exclusive product, so the observation of



SCHEME 1 Preparation and bromination of **14**.

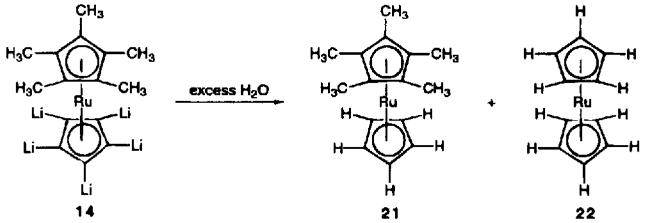
16 and especially **17** upon bromination suggested a different reactive species. In order to probe the thermal stability, **14** was generated as above and was allowed to warm to ambient temperature. After 0.5 h, addition of bromine followed by workup afforded **15** (8%), **16** (3%), and **17** (2%) as the only tractable products. Thus, solutions of **14** in tetrahydrofuran have only limited stability at or near ambient temperature.

In order to probe the nature of **14** further, the reaction with methyl iodide was examined. Generation of **14** as above in tetrahydrofuran, followed by addition of methyl iodide (20 equiv), afforded decamethylruthenocene (**18**, 46%), nonamethylruthenocene (**19**, 14%), and iodononamethylruthenocene (**20**, 21%) as an inseparable mixture after workup [Eq. (6)]. The mixture was characterized by correlation of the ^1H and $^{13}C\{^1H\}$ NMR resonances with those of independently prepared materials.



(6)

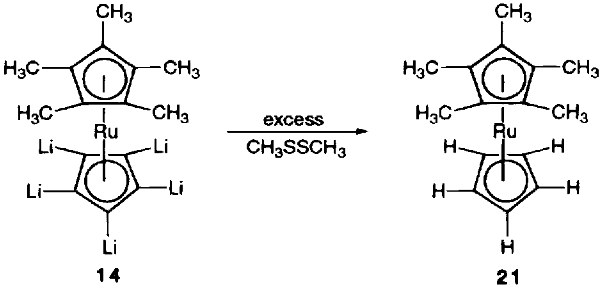
The hydrolysis of **14** was investigated next [Eq. (7)]. Generation of **14** at –78°C as above, followed by addition of H_2O (20 equiv) after 1.0 h, afforded a mixture of pentamethylruthenocene (**21**, 47%) and ruthenocene (**22**, 23%).



(7)

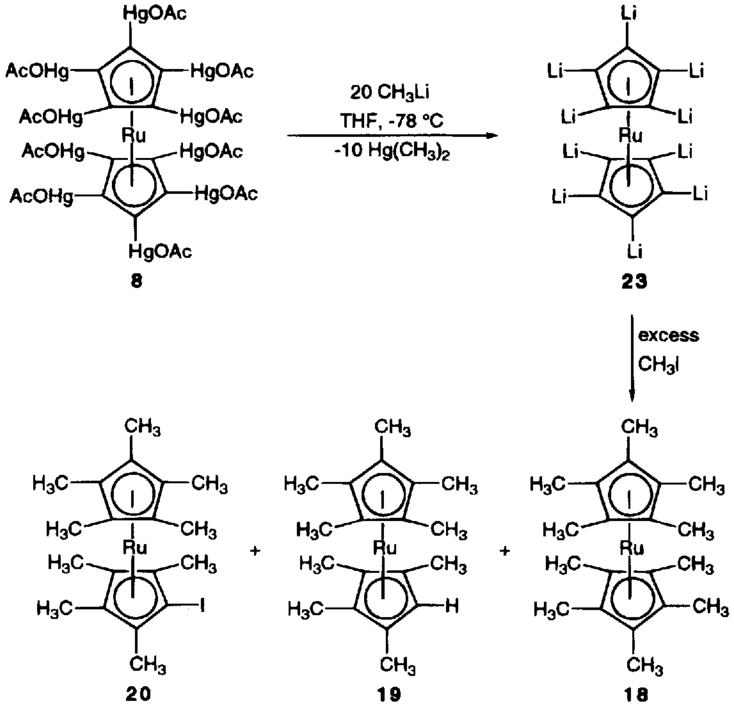
Because **22** was an unexpected product, the reaction mixture was examined in detail. Decamethylruthenocene was not observed within the detection limits of ^1H NMR ($\leq 2\%$), ruling out a ring redistribution reaction. Analysis of the reaction solution by GLC revealed the presence of pentamethylcyclopentadiene, but the yields were only 1–2% versus internal dodecane. An insoluble yellow powder could be isolated from the reaction. Its poor solubility precluded NMR analyses, but mass spectrometry of the powder showed dimethylmercury. The yellow powder is clearly not dimethylmercury (colorless liquid, bp 91–92°C), but dimethylmercury is liberated upon thermolysis. It is possible that the yellow powder contains the remaining pentamethylcyclopentadiene, but we were unable to clarify this issue any further.

Since carbon–lithium bonds are of exceptional utility in synthesis, we sought to explore the reactivity of **14** with other electrophiles. Generation of **14** in tetrahydrofuran at –78°C, followed by addition of dimethyl disulfide and warming to ambient temperature, afforded **21** as the sole tractable product [75%, Eq. (8)]. We have prepared all of the possible thiomethyl-substituted ruthenocenes $(C_5(SCH_3)_nH_{5-n})(C_5(CH_3)_5)Ru$ (n = 1–5) by alternate synthetic routes,[27] and no such resonances were observed in the crude reaction mixture within the detection limits of ^1H NMR. Compound **21** was also the only isolable product obtained upon treatment of **14** with chlorodimethylsilane (43%), trimethyloxonium tetrafluoroborate (10%), triethyloxonium tetrafluoroborate (20%), and xenon difluoride (96%). It is likely that the hydrogen atoms are derived from the solvent; however, all attempts to detect organic products derived from tetrahydrofuran or the electrophiles failed.



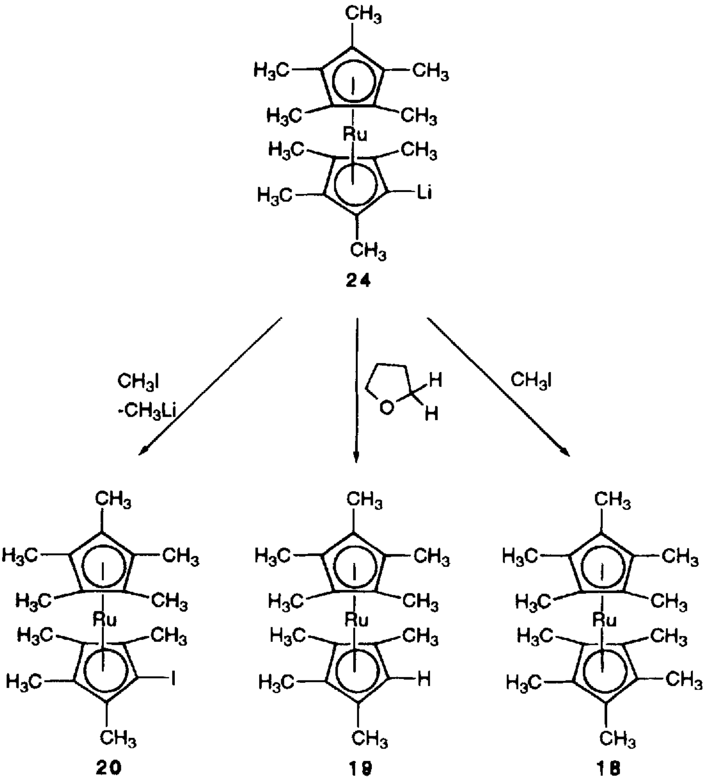
(8)

The facile route to **14** suggests that an analogous strategy should yield a decalithiometallocene. Accordingly, treatment of decakis(acetoxymercurio)ruthenocene **8** with methyllithium (20 equiv) in tetrahydrofuran at –78°C gave an immediate color change from white to red-orange and gave a solution containing decalithioruthenocene (**23**, Scheme 2). After 1 h at –78°C, addition of methyl iodide, followed by warming to ambient temperature and workup, afforded **18** (24%), **19** (24%), and **20** (12%).



SCHEME 2 Preparation and bromination of **23**.

The formation of persubstituted products in moderate to good yields upon treatment of **14** and **23** with simple electrophiles is excellent evidence for the formation of ruthenocenes bearing pentalithiocyclopentadienyl ligands. The similar product mixtures derived from treatment of **14** and **23** with methyl iodide suggest that these reactions proceed through the same intermediate. We propose that the observed product distributions (i.e., **18–20**) can be derived from the penultimate species nonamethyllithioruthenocene (**24**, Scheme 3). Direct methylation of **14** with methyl iodide would give **18**, while proton abstraction from solvent would yield **19**. Complex **19** could also be obtained by proton abstraction from tetrahydrofuran by **14** and **23**, 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 **14** with methyl iodide would afford **20**.[28] The observation



SCHEME 3 Reactions of **24**.

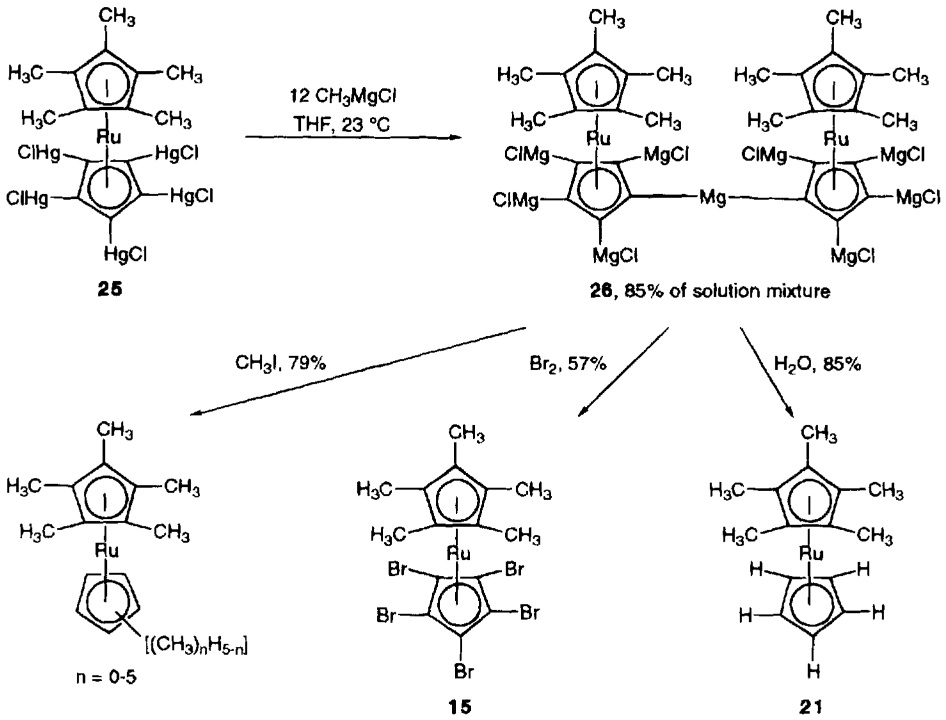
of ruthenocene upon hydrolysis of **14** is puzzling. We propose that **14** may be dimeric or oligomeric in solution via bridging lithium atoms. Such a structure would place two cyclopentadienyl ligands in close proximity to the ruthenium centers and might lead to ligand exchange upon hydrolysis.

5. PERMAGNESIATED RUTHENOCENES

Grignard reagents rank among the most widely used and studied class of organometallic compounds.[29] 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.[30] 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 benzynes. Polymagnesiated metallocenes are restricted to dimagnesiated ferrocenes.[31] The work described above with **14** and **23** has revealed that complexes containing pentalithiated cyclopentadienyl ligands are too reactive and thermally unstable to allow extensive use in synthesis. 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.

Treatment of pentakis(chloromercurio)(pentamethyl)ruthenocene[6] (**25**) 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 4). Hydrolysis of this solution with H_2O afforded **21** (85%), while D_2O quench gave **21** (97%) with 87% deuterium 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 **15** (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). Grignard reagents are well known to react with alkyl iodides by electron transfer pathways.[32]

Given the likelihood that a pentamagnesiated ruthenocene was being formed, we sought to characterize this species by spectroscopic methods. Treatment of **25** with methylmagnesium chloride (12 equiv) in tetrahydrofuran-d_8 at ambient temperature, followed by ^1H and $^{13}C\{^1H\}$ NMR analysis, revealed 85% of a major product **26** 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. 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 $^{13}C\{^1H\}$ NMR spectrum of **26** showed resonances due to the Cp* ligand at 84.40 (*C*–CH$_3$), and 16.32 (C–CH$_3$) 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 **26** that is consistent with all of the data is a dimer with eight

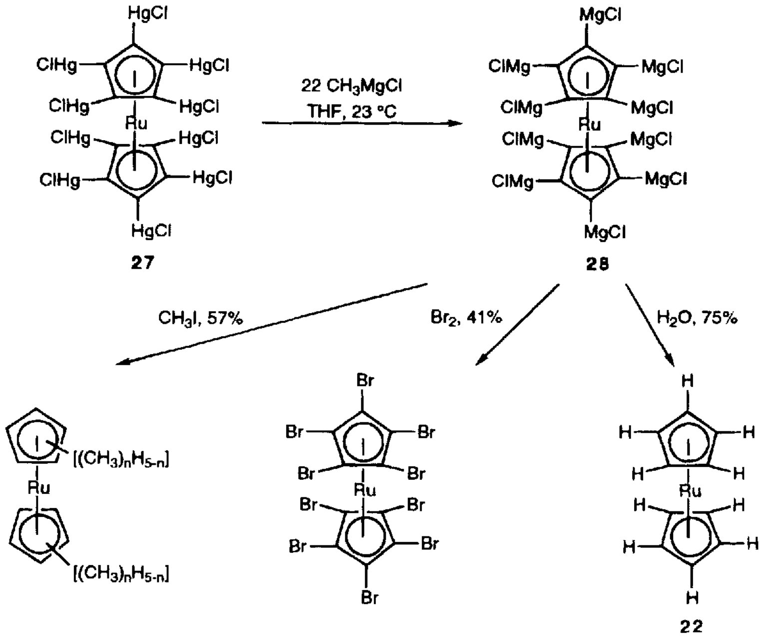


SCHEME 4 Preparation and reactions of **26**.

terminal chloromagnesio groups and one diruthenocenylmagnesium unit (Scheme 4). The ipso-carbons in phenyl magnesium halides[33a] and diphenylmagnesium[33b] 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–CH_3) are thus appropriate for an aromatic magnesium compound. The minor compounds could not be identified due to their low concentrations, but are probably higher oligomers.

The isolation of **26** 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 **26** (δ 2.06) was a minor component. It was not possible to obtain a $^{13}C\{^1H\}$ 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 that results from elimination of magnesium chloride from **26**. 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 tetrabromopentamethylruthenocene (13%).

The simple synthesis of **26** and its higher oligomers suggested that a decamagnesiated ruthenocene should be accessible. Accordingly, treatment of decakis(chloromercurio)ruthenocene (**27**) with methylmagnesium chloride (ca. 22 equiv) in tetrahydrofuran at 23°C gave a turbid light brown solution containing a decamagnesiated ruthenocene **28** (Scheme 5). Attempts to record NMR spectra of **28** in tetrahydrofuran-d_8 failed due to its low solubility. Although **28** is denoted as a monomer herein for simplicity, its low solubility and analogy with **26** suggest a dimeric or higher oligomeric structure. Hydrolysis of **28** afforded ruthenocene (75%), while treatment with bromine (ca. 20 equiv) gave decabromoruthenocene (41%). Methylation of **28** by refluxing in neat methyl iodide gave about 15 methylated ruthenocenes (57% total yield), as determined by GLC and GLC/MS.



SCHEME 5 Preparation and reactions of **28**.

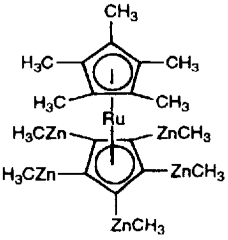
6. DISCUSSION AND CONCLUSIONS

Perhaps the most surprising conclusion that can be drawn from the preceding discussion is that permetalated aromatic compounds can exhibit remarkable thermal stabilities. Prior to Lagow's disclosure of **5**,[6,7] the only permetalated aromatic compounds known were the perlithiated heterocycles **1–4**. These compounds were generated at low temperatures in solution and were not isolated. Furthermore, structures **1–3** undergo a ring-opening reaction upon warming. These observations tend to support the idea that strong electrostatic repulsion between the adjacent carbanionic sites should make perlithiated aromatic compounds thermodynamically unstable. The synthesis of **5** and demonstration of its stability at ambient temperature was the first indication that perlithiated aromatic compounds might have extensive chemistry. While **5** has been the subject of two theoretical studies, there have been no further experimental reports detailing its properties. Thus, the structure and reactivity of **5** and the myriad of related compounds that are easily envisioned remain to be studied.

The compounds **14** and **23** shed some light on how replacement of all aromatic hydrogens by lithiums affects the structure and reactivity of the aromatic skeleton. Both **14** and **23** were insoluble in tetrahydrofuran-d_8, which precluded structural analysis by solution NMR methods. It is likely that the insolubility is a result of oligomerization by bridging carbon–lithium–carbon interactions. Such oligomer formation is common in organolithium compounds and would certainly be reasonable for **14** and **23**. Treatment of **14** and **23** with electrophiles offers the first insight into how perlithiation affects the reactivity of the ruthenocene skeleton. With powerful electrophiles, such as water, bromine, and methyl iodide, persubstitution is the predominant reaction mode. The reaction of **14** and **23** with methyl iodide is particularly illustrative, since the three products obtained (**18**–**20**) illustrate three typical reaction modes available to organolithium compounds [i.e., alkylation (**18**), hydrogen atom abstraction from tetrahydrofuran (**19**), lithium—halogen exchange (**20**)]. With less reactive electrophiles [e.g., $ClSi(CH_3)_2H$, $(CH_3)_3O^+BF_4^-$, XeF_2, $(CH_3)_2S_2$] the exclusive reaction mode observed was hydrogen abstraction from solvent to afford pentamethylruthenocene **21** in yields ranging from 10% to 96%. While hydrogen abstraction from tetrahydrofuran is commonly observed with organolithium reagents, it is surprising that **14** and **23** react in a useful way with only a small range of electrophiles. Further reactivity data are clearly required. It is likely that perlithiated metallocenes [and perhaps other perlithiated aromatic compounds, (**5**?)] will have limited synthetic applications due to hydrogen abstraction from solvents required for their solvation.

The magnesiated ruthenocenes **26** and **28** are easily prepared by treatment of the permercurated ruthenocenes with excess methylmagnesium chloride. Both **26** and **28** are substantially more stable than the lithiated analogs **14** and **23**. For example, a sealed NMR tube containing **26** in tetrahydrofuran-d_8 remained unchanged for 6 months at 23°C. By contrast, **14** decomposes within 0.5 h at 23°C in tetrahydrofuran. The solubility of **26** allowed its solution structure to be probed by NMR methods. Generation of **26** in an NMR tube gave a major species (about 85% of mixture) whose $^{13}C\{^1H\}$ NMR spectrum was consistent with a dimeric structure, as well as **4**–**5** minor species (about 15% total) that are likely higher oligomers. The facile formation of oligomers with **26** is surprising, since traditional Grignard reagents favor monomeric structures in ether solvents.[35] However, Bickelphaupt has noted that di-Grignard compounds with one, two, or three carbons between the two magnesium centers generally exhibit very low solubilities in ether solvents due to shifting of the Schlenk equilibrium toward oligomeric products.[36] Thus, **26** and **28** may bear some structural resemblance to known di-Grignard compounds. Despite the unusual placement of five or ten contiguous magnesium substituents about a metallocene skeleton, initial studies suggest that **26** and **28** react like typical organomagnesium reagents. Thus, the complete range of reactivity associated with Grignard reagents and diorganomagnesium compounds may be expected for permagnesiated aromatic compounds.

The simple formation of **14, 23, 26**, and **28** by treatment of permercurated ruthenocenes with methyllithium or methyl magnesium bromide suggests that similar exchanges of permercurated compounds with other main group metal alkyls should yield new permetalated aromatic compounds. Indeed, treatment of **25** with dimethylzinc, trimethylaluminum, or boron trichloride affords the new persubstituted complexes **29–31**.[37] In addition, the hexametalated benzene derivatives **32** and **33** have been prepared by similar exchanges from hexakis(chloromercurio)benzene.[38] Although **29–33** are denoted as a monomers herein for simplicity, their structures are probably much more complicated and will require considerable experimentation to establish.



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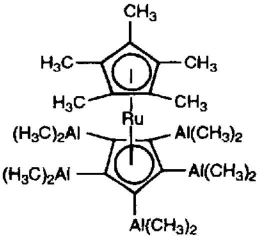

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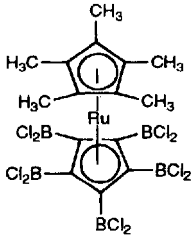

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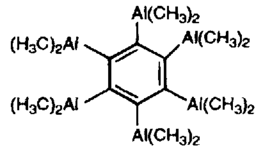

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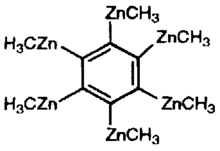

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In the preceding sections, we have described what was known about permetalated aromatic compounds prior to the beginning of our studies and have outlined what we have learned so far about perlithiated and permagnesiated ruthenocenes. Our major contribution to this area has been the discovery that permercurated compounds are easily transformed to other permetalated compounds upon treatment with main group metal alkyls. Such exchanges are rapid, complete, and work for a wide range of metal alkyls. By contrast, permetalated aromatic compounds had previously been limited to lithiated species made by the difficult exchange of an organolithium compound with a perhalogenated aromatic species. While our own studies are just beginning, research in this area should lead to the characterization of molecules that should challenge our current ideas about bonding and structure in main group organometallic molecules. Moreover, development of permetalated aromatic compounds may lead to new reagents for use in synthesis.

Acknowledgments

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