Permercuration of Ferrocenes and Ruthenocenes. New Approaches to Complexes Bearing Perhalogenated Cyclopentadienyl Ligands

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Treatment of ferrocene with mercuric trifluoroacetate (10 equiv) and mercuric oxide (5 equiv) in 1:1 diethyl ether/ethanol afforded decakis[(trifluoroacetoxy)mercurio]ferrocene (60%) as a yellow-orange powder. Reaction with cupric chloride dihydrate in acetone yielded mixtures of partially chlorinated ferrocenes, of which decachloroferrocene was a minor component. Treatment of ferrocene with mercuric acetate (10 equiv) in refluxing dichloroethane for 18 h afforded decakis(acetoxymercurio)ferrocene (95%). Halogenation of decakis(acetoxymercurio)ferrocene with cupric chloride dihydrate in acetone, potassium tribromide in water, or potassium triiodide in water afforded decachloroferrocene (27%), decabromoferrocene (60%), and decaiodoferrocene (67%), respectively. Examination of the ^{1}H NMR spectra of crude decachloroferrocene and decabromoferrocene revealed small amounts ($\leq$5%) of partially halogenated ferrocenes, which suggested that decakis(acetoxymercurio)ferrocene was not completely decamercurated. Treatment of ruthenocene with mercuric acetate (10 equiv) in refluxing dichloroethane afforded decakis(acetoxymercurio)ruthenocene (88%). Reaction of decakis(acetoxymercurio)ruthenocene with cupric chloride dihydrate in acetone, potassium tribromide in water, or potassium triiodide in water afforded decachlororuthenocene (73%), decabromoruthenocene (47%), and decaiodoruthenocene (39%), respectively. Inspection of the ^{1}H NMR spectra of crude decachlororuthenocene and decabromoruthenocene showed no resonances that could be attributed to partially halogenated ruthenocenes, which indicates that decakis(acetoxymercurio)ruthenocene was $\geq$98% decamercurated. Treatment of pentamethylruthenocene with mercuric acetate in 1:1 diethyl ether/ethanol afforded pentakis(acetoxymercurio)pentamethylruthenocene (88%). Pentakis(acetoxymercurio)pentamethylruthenocene showed hindered rotation of the mercury–acetate groups in the ^{1}H NMR spectra. Halogenation afforded pentachloropentamethylruthenocene (67%), pentabromopentamethylruthenocene (35%), and pentaiodopentamethylruthenocene (60%). Treatment of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) with mercuric acetate ($\geq$3 equiv) in 1:1 diethyl ether–ethanol afforded (η^5-1,2,3-tris(acetoxymercurio)indenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (99%), which could be brominated and iodinated to afford (η^5-1,2,3-tribromoindenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (29%) and (η^5-1,2,3-triiodoindenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (66%). The structure of (η^5-1,2,3-triiodoindenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) was determined, showing that it crystallized in the monoclinic space group $P2_1/c$, with cell dimensions a = 15.934(3) Å, b = 10.308(4) Å, c = 12.530(5) Å, β = 93.53(2)°, V = 2054(1) Å^3, and Z = 4.

Introduction

The mercuration of aromatic compounds, in which a carbon–hydrogen bond is replaced by a carbon–mercury bond, is one of the fundamental processes that these compounds undergo.[1] The carbon–mercury bond can be cleaved by a wide variety of electrophiles to afford functionalized products that would be difficult to prepare by other methodologies.[1,2] While the monomercuration of benzenoid compounds is the most prevalent reaction mode, polymercuration and even complete replacement of the aromatic hydrogens has been observed in electron rich systems. For example, benzene, anisole, furan, thiophene, and other aromatics can be permercurated upon treatment with mercuric salts at elevated temperatures.[3] These permercurated compounds can be efficiently transformed to the corresponding persubstituted species upon treatment with electrophiles.

Correspondingly less is known about the mercuration of organometallic compounds bearing aromatic ligands.[4,5] Most of the mercuration studies have centered on ferrocene,[4] which undergoes mono- and dimercuration upon treatment with mercuric acetate. Several other brief reports have appeared describing the mono- and dimercuration of ruthenocene,[5a] the mono- and dimercuration of cyclopentadienylmanganese tricarbonyl,[5b]

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(1) For leading references, see: Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer-Verlag: Berlin, 1985.

(2) For leading references, see: Jensen, F. R.; Rickborn, B. *Electrophilic Substitution of Organomercurials*; McGraw-Hill: New York, 1968. Larock, R. C. *Tetrahedron* **1982**, 3289.

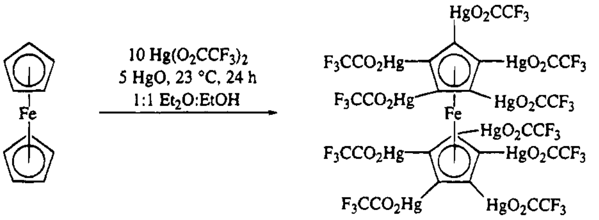
(3) For leading references see: Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1976**, *29*, 627. *J. Organomet. Chem.* **1974**, *67*, C1. O'Connor, G. N.; Crawford, J. V.; Wang, C.-H. *J. Org. Chem.* **1965**, *30*, 4090. Ciusa, R.; Grilla, G. *Gazz. Chim. Ital.* **1927**, *57*, 323. Paolini, O.; Silbermann, B. *Ibid.* **1915**, *45*, 385.

and the tetramercuration of (butadiene)iron tricarbonyl.[5c] 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.[6a] Additionally, 1,1′-dimethylferrocene was octamercurated under similar conditions.[6b] Cyclopentadienylmanganese tricarbonyl is pentamercurated upon treatment with mercuric trifluoroacetate.[6c]

We have recently disclosed that ruthenocene[7a] and pentamethylruthenocene[7b] undergo permercuration of the unsubstituted cyclopentadienyl ligands with mercuric acetate to afford metallocenes bearing pentakis(acetoxymercurio)cyclopentadienyl ligands. Herein we report a detailed study of the decamercuration of ferrocene and ruthenocene, the pentamercuration of pentamethylruthenocene, and the selective trimercuration of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II). Additionally, the use of these species in the preparation of perchloro-, perbromo-, and periodocyclopentadienyl complexes is described. The combined results demonstrate a general strategy for the permercuration of iron and ruthenium metallocenes and further show that many of these permercurated complexes can serve as useful precursors to persubstituted metallocenes.

Results

Mercuration and Halogenation of Ferrocene. Careful reproduction of the reported procedure for the decamercuration of ferrocene (10 equiv of $Hg(O_2CCF_3)_2$, diethyl ether/ethanol, 25 °C)[6a] afforded a gray-green solid, which, unlike the reported material (purported to be soluble in DMF, alcohols), was completely insoluble in all solvents that were examined. The reaction solution became deep green, which suggested that ferrocene had been oxidized to a ferrocenium ion under the reaction conditions. To circumvent such problems, the mercuration was carried out in the presence of 5 equiv of mercuric oxide, whose anticipated role was to keep the reaction medium neutral by reacting with the trifluoroacetic acid. Indeed, the mixture remained yellow-orange throughout the reaction under these conditions. The desired decakis[(trifluoroacetoxy)mercurio]ferrocene (**1**, 60%) was isolated as a yellow-orange powder after filtration of the reaction mixture and precipitation with water (eq 1). Upon isolation, **1** exhibited an extremely low solubility in common solvents. Complex **1** was characterized by infrared and ^{19}F NMR spectroscopy and C, H, and Hg microanalysis. The infrared spectrum showed absorptions characteristic of the HgO_2CCF_3 group at 1668 (ν_{CO}, vs), 1429 (ν_{CO}, m), 1379 (m), 1203 (s), 1126 (s), 830 (m), 802 (m), and 717 (m) cm^{-1}. For comparison, mercuric trifluoroacetate showed absorptions at 1675 (ν_{CO}, vs), 1429 (ν_{CO}, m), 1379 (m), 1203 (s), 1126 (s), 830 (m), 795 (m), and 717 (m) cm^{-1}. The ^{19}F NMR spectrum of **1** in acetone showed a single peak at −74.62 ppm. By comparison, mercuric trifluoroacetate showed a singlet at −73.16 ppm. The extremely low molar solubility of **1** precluded solution analysis by ^{13}C and ^{199}Hg NMR spectroscopy.



(1)

1, 60%

Attempted chlorination of **1** with cuprous chloride in acetone afforded ca. 25% yield of a yellow powder. ^{1}H NMR showed resonances at δ 4.59, 4.48, and 4.36, in a 12:34:54 ratio, suggesting a mixture of partially chlorinated ferrocenes. The mass spectrum of the yellow powder showed a very weak intensity mass envelope (ca. 1–2%, relative to the base peak at 492) for decachloroferrocene (*m/e* 526), and strong mass envelopes for nonachloroferrocene (*m/e* 492) and octachloroferrocene (*m/e* 458). The weak mass envelope at *m/e* 526 implied that decachloroferrocene was only a minor product at best (decachloroferrocene showed a strong M$^+$ at *m/e* 526 (25% versus *m/e* 492 base peak)). Halogenation of **1** using potassium tribromide in water also afforded a small amount of yellow powder that was a mixture of at least four partially brominated ferrocenes. Hence, **1** is not a useful precursor to perhalogenated ferrocenes. The above analyses suggest that **1** is either a mixture of partially mercurated ferrocenes or undergoes significant protiodemercuration during the halogenation processes.

Since perhalogenated ferrocenes could not be prepared from **1**, other permercurated ferrocenes were sought. In particular, ferrocene undergoes mono- and dimercuration upon treatment with mercuric acetate in polar organic solvents.[8] The mercuration process stops at the dimercurated stage, apparently due to the insolubility of 1,1′-bis(acetoxymercurio)ferrocene. We envisioned that ferrocene might undergo decamercuration with mercuric acetate provided that the low solubility of 1,1′-bis(acetoxymercurio)ferrocene could be overcome. Accordingly, ferrocene was treated with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane for 18 h, during which time a yellow precipitate formed. Filtration afforded decakis(acetoxymercurio)ferrocene (**2**, 95%) as an insoluble powder (eq 2).

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(4) For leading references, see: Fung, C. W.; Roberts, R. M. G. *Tetrahedron* **1980**, 3289. Floris, B.; Illuminati, G. *Coord. Chem. Rev.* **1975**, *16*, 107. Kitching, W. *Organomet. Chem. Rev.* **1968**, *3*, 35. Makarova, L. G. In *Organometallic Reactions*; Becker, E. I., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1970; Vol. 1, p 119. Popov, V I.; Lieb, M.; Haas, A. *Ukr. Khim. Zh.* **1990**, *56*, 1115. See also: Nesmeyanov, A. N.; Anisimov, K. N.; Valuava, Z. P. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1962**, 1683. Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

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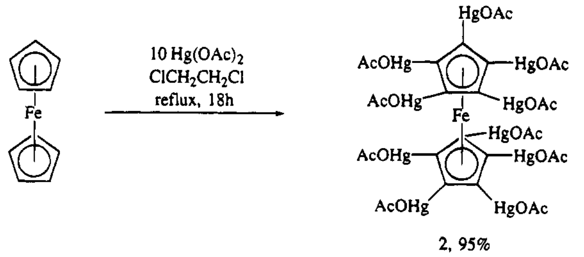
(8) For leading references, see: Rausch, M. D.; Klemann, L. P.; Siegel, A.; Kovar, R. F.; Gund, T. H. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 193.



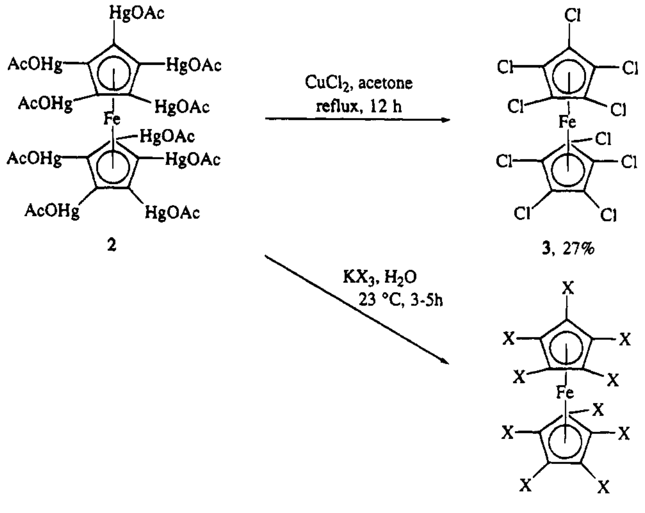
(2)

2, 95%

Complex **2** was characterized by infrared spectroscopy and C and H microanalysis. The infrared spectrum showed absorptions characteristic of the HgO_2CCH_3 group at 1570, 1393, 1358, 1310, and 682 cm^{-1}. For comparison, mercuric acetate showed strong absorptions at 1555, 1400, 1330, and 653 cm^{-1}. The carbon and hydrogen microanalysis results hovered around the calculated values, but could not be obtained within ±0.4%. Unfortunately, the complete insolubility of **2** precluded any further purification. The above data for **2** did not conclusively establish its decamercurated nature, since only absorptions arising from the HgO_2CCH_3 functionality were observed in the infrared spectrum. Additionally, the calculated C and H microanalysis values were not strongly dependent upon the degree of mercuration (e.g., Anal. Calcd for **2**: C, 13.00; H, 1.09. Anal. Calcd for octamercurated ferrocene ($C_{26}H_{26}FeHg_8O_{16}$): C, 13.85; H, 1.16).

In order to probe the degree of mercuration of **2**, the reaction with halogenating agents was examined (Scheme 1). Treatment of **2** with cupric chloride dihydrate (ca. 50 equiv) in refluxing acetone for 12 h afforded decachloroferrocene (**3**, 27%) as a yellow powder upon workup. It was identified by mass spectrometry and by comparison of its melting point with the reported value.[9] Complex **3** was soluble in hexane and dichloromethane and could be easily extracted from the reaction residue. Careful examination of crude **3** showed minor ^1H NMR resonances at δ 4.59 and 4.48, which probably correspond to partially chlorinated ferrocenes, in analogy with the product mixture obtained upon chlorination of **1**. However, these resonances disappeared upon column chromatography, followed by crystallization from hexane. Complex **3** was thus obtained as a pure material. We estimate that the amount of partially chlorinated ferrocenes was ≤5%, since they were easily separted from **3** and could not be isolated in enough quantity for characterization. Treatment of **2** with potassium tribromide (prepared from potassium bromide and bromine) in water afforded decabromoferrocene (**4**, 60%) as a yellow powder after workup. Its structure was evident from the spectroscopic, analytical, and mass spectrometric data. Again, careful examination of the ^1H NMR spectrum of crude **4** showed resonances at δ 4.64 and 4.44, which might correspond to partially brominated ferrocenes. Iodination of **2** with potassium triiodide (prepared from potassium iodide and iodine) in water afforded decaiodoferrocene (**5**, 67%) as a yellow powder. Unlike **3** and **4**, which were quite soluble in dichloromethane, chloroform, and hexane, **5** exhibited a very low solubility in dichloromethane. Additionally, the solubility characteristics of **5** were very similar to those of mercuric iodide, which was produced in the formation of **5**. As a result, it was not possible to obtain **5** that was totally free of mercuric iodide, despite varied attempts. However, the infrared spectrum, mass spectrum, and microanalysis are consistent with the decaiodoferrocene formulation.

Scheme 1. Halogenation of 2



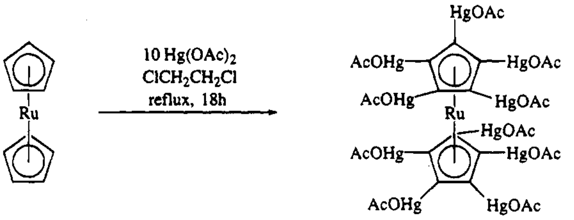
2

3, 27%

X = Br 4, 60%
X = I 5, 67%

Mercuration and Halogenation of Ruthenocene. Given the simple decamercuration of ferrocene it was tempting to examine the analogous decamercuration of ruthenocene. However, ruthenocene ($E° = 1.03$ V[10]) has a substantially more positive oxidation potential than ferrocene ($E° = 0.47$ V[10]), which indicates that ruthenocene is less electron rich than ferrocene. As a result, the mercuration of ruthenocene might not proceed with the same facility as observed with ferrocene.

Treatment of ruthenocene with mercuric acetate (10 equiv) in refluxing dichloroethane for 18 h afforded decakis(acetoxymercurio)ruthenocene (**6**) in 88% yield as an off-white solid which precipitated from the reaction medium (eq 3). Complex **6** was insoluble in all common solvents, which prevented its analysis by NMR methods. The complex was characterized by microanalysis and infrared spectroscopy. In particular, the infrared spectrum revealed strong absorptions characteristic of the HgO_2CCH_3 functionality at 1570, 1403, 1382, 1337, and 643 cm^{-1}. By comparison, mercuric acetate showed strong absorptions at 1555, 1400, 1330, and 653 cm^{-1} in the infrared spectrum. In analogy with **2**, the C and H microanalysis results for **6** hovered near those expected for a decamercurated structure, but were not within the ±0.4% limit. Again, the calculated values were not strongly dependent upon the degree of mercuration (e.g., Anal. Calcd for **6**: C, 12.79; H, 1.07. Anal.



(3)

6, 88%

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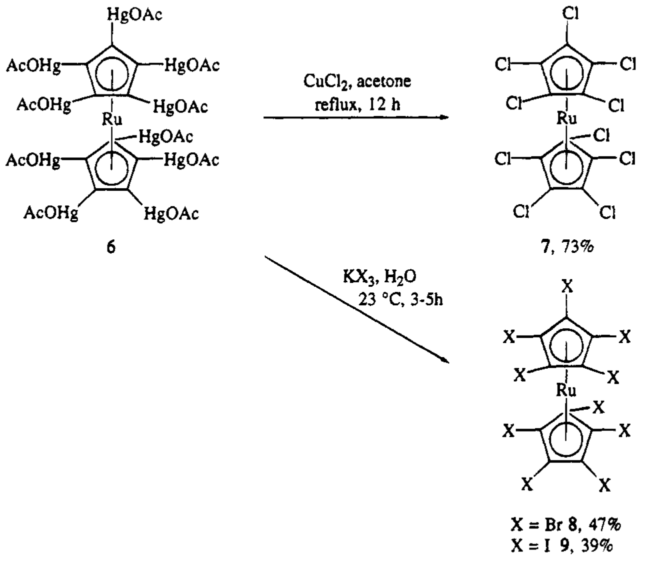
(9) Hedberg, F. L.; Rosenberg, H. *J. Am. Chem. Soc.* **1973**, *95*, 870.

(10) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4690.

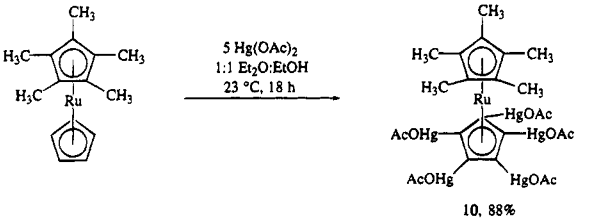
Scheme 2. Halogenation of 6



Calcd for octamercurated ruthenocene ($C_{26}H_{26}Hg_8$-$O_{16}Ru$): C, 13.58; H, 1.14).

The fully mercurated nature of **6** was confirmed by its reaction with halogenating agents (Scheme 2). Treatment of **6** with cupric chloride dihydrate (50 equiv) in refluxing acetone for 12 h afforded decachlororuthenocene (**7**)[9] in 73% yield as a white crystalline solid, after workup. ^{1}H NMR analysis of crude **7** showed no signals that could be attributed to partially chlorinated ruthenocenes. This indicates that **6** is $\geq$98% decamercurated. Reaction of **6** with potassium tribromide and potassium triiodide (prepared from KX and X_2 in water) afforded decabromoruthenocene (**8**, 47%) and decaiodoruthenocene (**9**, 39%) as white and yellow-ochre solids, respectively. The structures of **7**–**9** were evident from their spectral and analytical data.

Mercuration and Halogenation of Pentamethylruthenocene. Treatment of pentamethylruthenocene with mercuric acetate (5 equiv) in 1:1 ethanol/diethyl ether as ambient temperature for 18 h afforded a white precipitate of pentakis(acetoxymercurio)pentamethylruthenocene (**10**, 88%), which was obtained as an analytically pure powder after filtration and vacuum drying (eq 4). The structure of **10** was established by ^{1}H NMR, infrared spectroscopy, and microanalysis and from reactivity studies (vide infra). Unlike **1**, **2**, and **6**, **10** was soluble in chloroform and could be subjected to NMR analysis. The ^{1}H NMR spectrum showed no cyclopentadienyl C—H resonances between δ 4 and 5, which indicated that **10** was $\geq$98% pentamercurated. An experiment was performed in which pentamethylruthenocene was reacted with 1 equiv of mercuric acetate in 1:1 ethanol/diethyl ether for 18 h. Workup afforded **10** (18%) and recovered pentamethylruthenocene (78%). This experiment indicates that the rates of mercuration for the intermediate mercurated species are all faster than the initial mercuration of pentamethylruthenocene.



(4)

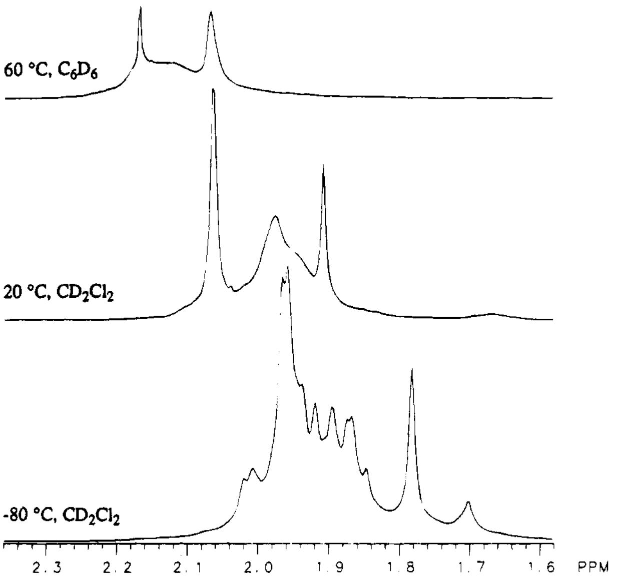


Figure 1. Variable temperature ^{1}H NMR spectra for **10**.

The ^{1}H NMR spectrum of **10** was complicated (Figure 1). At ambient temperature in dichloromethane-d_2, four signals were observed. Upon cooling to −80 °C, at least 12 resonances were obtained. The 60 °C spectrum in benzene-d_6 showed two singlets at δ 2.22 and 2.12. We propose that this behavior arises from acetate isomerism that occurs when the oxygen or methyl is either pointed up toward the Cp* ring or away from it. At low temperatures, this would result in a statistical mixture of eight possible isomers and would account for the complicated nature of the observed spectrum. At 60 °C carbonyl rotation is fast on the NMR time scale. This proposed model is based upon the crystal structure of phenylmercuric acetate,[11] which shows a nearly linear C—Hg—O bond (170°) with the plane of the acetate group approximately perpendicular to the plane of the aromatic ring. The observed hindered rotation indicates that substantial steric interactions are present in the permercurated cyclopentadienyl ligand. Interconversion of the isomers probably occurs by an "interlocking" mechanism, similar to that proposed for hexaisopropylbenzene[12a] and pentaisopropylcobaltocenium hexafluorophosphate.[12b]

Treatment of **10** with cupric chloride dihydrate (ca. 25 equiv) in refluxing acetone afforded pentachloropentamethylruthenocene (**11**, 67%) as a white crystalline powder (Scheme 3). Analogous halogenation of **10** with either potassium tribromide or potassium triiodide (prepared from X_2 and KX at 25 °C) in water afforded off-white pentabromopentamethylruthenocene (**12**, 35%), and bright yellow pentaiodopentamethylruthenocene (**13**, 60%), respectively, upon workup. The structures of **11**–**13** were evident from their spectral and analytical data. We have previously reported the crystal structure of $\mathbf{13}\cdot0.25CCl_4$.[7b] Complex **11** has been prepared in 75%

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(11) Kamenar, B.; Penavic, M. *Inorg. Chim. Acta* **1972**, *6*, 191.

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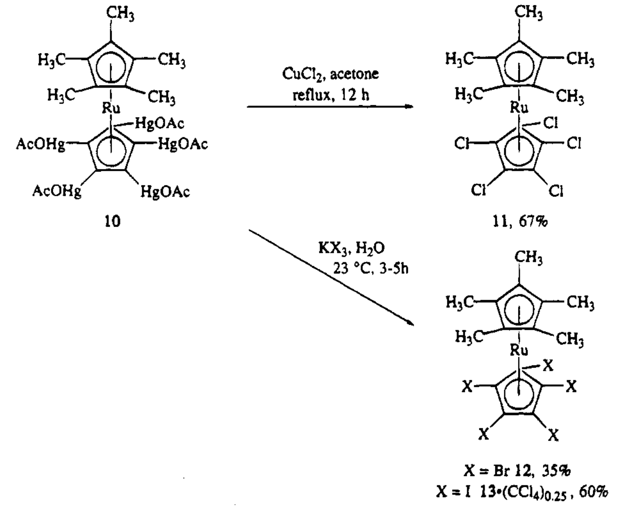
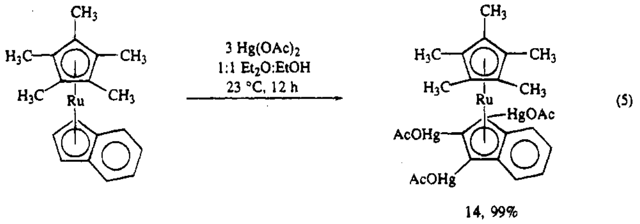
Scheme 3. Halogenation of 10



yield from the dichloro(pentamethylcyclopentadienyl)-ruthenium(III) oligomer and tetrachlorodiazocyclopentadiene.[13]

Mercuration and Halogenation of (η^5-Pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II). The facile permercuration of ferrocene, ruthenocene, and pentamethylruthenocene suggested that it should be possible to mercurate cyclopentadienyl ligands containing functional substituents. In particular, ligands with delocalized π-systems, such as indenyl, might undergo complete mercuration of the ligands or might only be mercurated at the C—H bonds directly attached to the metal. In order to probe these possibilities, the mercuration of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) was investigated.

Treatment of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II)[13] with mercuric acetate (3 equiv) in ethanol/diethyl ether at ambient temperature for 12 h afforded (η^5-1,2,3-tris(acetoxymercurio)indenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (**14**, 99%) as a yellow microcrystalline solid (eq 5). The selective



1,2,3-trimercuration in **14** was evident from the ^{1}H NMR spectrum, which showed the 1,2,3-protons to be absent. The six-membered ring hydrogens were observed as doublets at δ 6.96 and 6.77, while the acetate methyls appeared as a broad singlet at δ 2.13 and the Cp* methyls appeared as a sharp singlet at δ 1.57. Attempts to heptamercurate (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) with mercuric acetate (7 equiv) in ethanol/diethyl ether at ambient temperature gave only **14**. Hence, only the hydrogen-bearing carbons directly attached to the metal are activated toward mercuration.

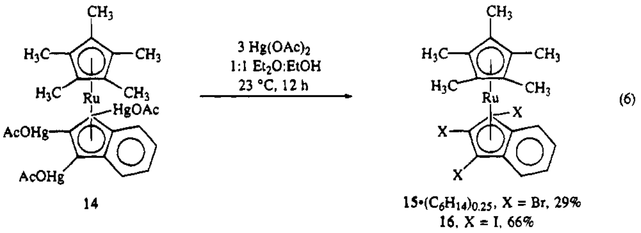
An experiment was performed in which (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) was treated with 1 equiv of mercuric acetate under conditions otherwise identical to the preparation of **14**. Removal of the solvent, followed by analysis of the residue by ^{1}H NMR, indicated a 24:11:21:36 ratio of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II), (η^5-pentamethylcyclopentadienyl)(η^5-1-(acetoxymercurio)indenyl(ruthenium(II), (η^5-pentamethylcyclopentadienyl)(η^5-bis(acetoxymercurio)indenyl)ruthenium(II), and **14**. The monomercurated adduct was selectively mercurated in the 1-position of the indenyl ligand, as determined by the two doublets observed in the ^{1}H NMR spectrum for the 2,3-indenyl hydrogens (δ 4.95 (J = 2.4 Hz), 4.36 (J = 2.4 Hz)). Mercuration in the 2-position of the indenyl ligand would give rise to a singlet for the 1,3-hydrogens. The dimercurated product showed a singlet of δ 4.23 for the indenyl proton. It was not possible to distinguish between the 1,2- and 1,3-dimercurated indenyl products, since both would show a singlet for the indenyl hydrogen on the five-membered ring. The mercury—acetate methyls were observed as an unresolved singlet at δ 2.13 for all three mercurated compounds.

Table 1. Crystallographic Data for 16

formula	$C_{19}H_{19}I_3Ru$	fw	729.14
a, Å	15.934(3)	space group	$P2_1/c$
b, Å	10.308(4)	T, °C	22
c, Å	12.530(5)	λ, Å	0.71073 Å
β, deg	93.53(2)	ϱ(calc), g·cm^{-3}	2.358
V, Å^3	2054(1)	μ, cm^{-1}	52.11
Z	4	transm coeff	0.329−0.217
R^a	0.044	$R_w{}^a$	0.050

[a] $R = (\sum|\Delta F|)/\sum|F_o|$; $R_w = [(\sum w|\Delta F|^2)/\sum wF_o{}^2]^{1/2}$.

Treatment of **14** with KX_3 (from KX and X_2, X = Br, I) in water/methanol (3:1) for 0.5 h afforded (1,2,3-tribromoindenyl)(pentamethylcyclopentadienyl)ruthenium(II)•0.25(C_6H_{14}) (**15**•0.25C_6H_{14}, 29%) and (1,2,3-triiodoindenyl)(pentamethylcyclopentadienyl)ruthenium(II) (**16**, 66%) as yellow powders (eq 6). The structures of **15**•0.25C_6H_{14} and **16** were assigned on the basis of their spectral and analytical data. Additionally, the crystal structure of **16** was determined (vide infra). Complex **15**•0.25C_6H_{14} was isolated as a stable hexane solvate. The amount of solvate was estimated by C and H microanalysis and by integration of the ^{1}H NMR hexane resonances against the Cp* methyl resonance. The hexane solvate did not change after vacuum drying at 60 °C (0.01 mmHg) for 24 h.



Structure of (1,2,3-Triiodoindenyl)(pentamethylcyclopentadienyl)ruthenium(II). The crystal structure of **16** was determined in order to characterize its molecular geometry. X-ray data were collected under the conditions summarized in Table 1. Bond lengths, bond angles, and positional parameters are summarized in Tables 2 and 3. A perspective view is shown in Figure 2. Further structural data are contained in the supplementary material.

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[13] Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130.

Table 2. Bond Lengths (Å) and Bond Angles (deg) for 16

I(1)–C(1)	2.077(8)	I(2)–C(2)	2.056(8)
I(3)–C(3)	2.079(9)	Ru–C(1)	2.158(8)
Ru–C(2)	2.166(8)	Ru–C(3)	2.147(8)
Ru–C(4)	2.226(8)	Ru–C(5)	2.230(8)
Ru–C(10)	2.172(9)	Ru–C(11)	2.15(1)
Ru–C(12)	2.162(9)	Ru–C(13)	2.14(1)
Ru–C(14)	2.16(1)	Ru–Cp(1)	1.815(8)
Ru–Cp(2)	1.800(8)	C(1)–C(2)	1.43(1)
C(10)–C(11)	1.36(1)	C(1)–C(5)	1.43(1)
C(10)–C(14)	1.40(2)	C(2)–C(3)	1.42(1)
C(10)–C(15)	1.51(2)	C(3)–C(4)	1.44(1)
C(11)–C(12)	1.39(1)	C(4)–C(5)	1.44(1)
C(11)–C(16)	1.51(2)	C(4)–C(9)	1.43(1)
C(12)–C(13)	1.42(2)	C(5)–C(6)	1.43(1)
C(12)–C(17)	1.50(2)	C(6)–C(7)	1.35(1)
C(13)–C(14)	1.42(2)	C(7)–C(8)	1.34(1)
C(13)–C(18)	1.51(2)	C(8)–C(9)	1.35(2)
C(14)–C(19)	1.47(2)		
I(1)–C(1)–C(2)	126.3(6)	I(1)–C(1)–C(5)	124.1(6)
I(2)–C(2)–C(1)	126.4(6)	I(2)–C(2)–C(3)	126.5(6)
I(3)–C(3)–C(2)	127.2(6)	I(3)–C(3)–C(4)	122.8(6)
Cp(1)–Ru–Cp(2)	179.1(4)	C(1)–C(2)–C(3)	107.0(7)
C(10)–C(11)–C(16)	126(1)	C(1)–C(5)–C(4)	107.7(7)
C(10)–C(14)–C(13)	106(1)	C(1)–C(5)–C(6)	132.8(8)
C(10)–C(14)–C(19)	129(1)	C(2)–C(1)–C(5)	109.2(7)
C(11)–C(10)–C(14)	108.8(9)	C(2)–C(3)–C(4)	109.2(7)
C(11)–C(10)–C(15)	126(1)	C(3)–C(4)–C(5)	106.9(7)
C(11)–C(12)–C(13)	105.1(9)	C(3)–C(4)–C(9)	134.5(8)
C(11)–C(12)–C(17)	128(1)	C(4)–C(5)–C(6)	119.5(7)
C(12)–C(11)–C(16)	123(1)	C(4)–C(9)–C(8)	117.8(9)
C(12)–C(13)–C(14)	109(1)	C(5)–C(4)–C(9)	118.5(8)
C(12)–C(13)–C(18)	123(1)	C(5)–C(6)–C(7)	117.2(9)
C(13)–C(12)–C(17)	127(1)	C(6)–C(7)–C(8)	124(1)
C(13)–C(14)–C(19)	125(1)	C(7)–C(8)–C(9)	123(1)
C(14)–C(10)–C(15)	125(1)	C(10)–C(11)–C(12)	111(1)
C(14)–C(13)–C(18)	128(1)		

Table 3. Atomic Positional Parameters for 16

atom	*x*	*y*	*z*
I(1)	0.18352(5)	0.16258(6)	0.08679(6)
I(2)	0.41338(4)	0.23981(8)	0.18622(7)
I(3)	0.40485(5)	0.51693(8)	0.39719(6)
Ru	0.24915(4)	0.50732(6)	0.15364(5)
C(1)	0.2229(5)	0.3081(8)	0.1930(7)
C(2)	0.3078(5)	0.3376(8)	0.2279(7)
C(3)	0.3048(5)	0.4394(9)	0.3038(7)
C(4)	0.2181(5)	0.4685(8)	0.3214(6)
C(5)	0.1674(5)	0.3856(8)	0.2515(6)
C(6)	0.0779(6)	0.3923(9)	0.2520(8)
C(7)	0.0453(6)	0.482(1)	0.3161(8)
C(8)	0.0921(7)	0.562(1)	0.3798(8)
C(9)	0.1767(7)	0.5612(9)	0.3855(7)
C(10)	0.2800(8)	0.7057(9)	0.1127(8)
C(11)	0.3268(6)	0.623(1)	0.0560(9)
C(12)	0.2759(8)	0.5447(9)	−0.0106(8)
C(13)	0.1924(7)	0.583(1)	0.0077(9)
C(14)	0.1950(7)	0.683(1)	0.086(1)
C(15)	0.313(1)	0.809(1)	0.190(1)
C(16)	0.4215(8)	0.618(1)	0.058(1)
C(17)	0.302(1)	0.445(1)	−0.089(1)
C(18)	0.116(1)	0.526(2)	−0.052(2)
C(19)	0.121(1)	0.746(2)	0.128(1)

The complex consists of staggered η^5-pentamethylcyclopentadienyl and essentially η^5-1,2,3-triiodoindenyl ligands. It is unusual for the cyclopentadienyl ligands in a ruthenocene to be staggered;[14] such a configuration in **16** is undoubtedly due to interannular interactions between the sterically demanding iodo substituents and the methyl groups. There was a slight slippage of the 1,2,3-triiodoindenyl ligand toward η^3-bonding. The iodinated ruthenium–carbon bonds (Ru–C(1) 2.158(8) Å, Ru–C(2) 2.166(8) Å, Ru–C(3) 2.147(8) Å) were shorter than the benzenoid ruthenium–carbon bonds (Ru–C(4) 2.226(8) Å, Ru–C(5) 2.230(8) Å), although the differences are at the edge of experimental uncertainty. The carbon–iodine bond lengths averaged 2.070 Å. The carbon–carbon bond lengths in the five-membered ring averaged 1.42 Å, while the average length in the six-membered ring was 1.39 Å. The ruthenium–carbon distances in the pentamethylcyclopentadienyl ligand averaged 1.40 Å, while the average carbon(ring)–carbon(methyl) bond length was 1.50 Å. The ruthenium–cyclopentadienyl centroid distances were 1.815(8) Å (1,2,3-triiodoindenyl ligand) and 1.800 Å (pentamethylcyclopentadienyl ligand).

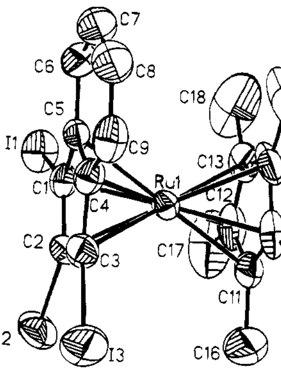

Figure 2. Perspective view of **16**.

Discussion

Treatment of ferrocene with mercuric trifluoroacetate (10 equiv) in diethyl ether/ethanol according to the method of Boev and Dombrovskii[6a] did not afford the decamercurated complex **1**, but rather gave a totally insoluble gray-green powder. We found that complex **1** could be synthesized in 60% yield by adding 5 equiv of mercuric oxide (to keep the reaction medium at or near neutral pH) and by dropwise addition of ferrocene to the mercuric acetate suspension over 4 h. Despite a successful synthesis of **1**, chlorination and bromination yielded mixtures of partially halogenated ferrocenes. In the chlorination of **1**, the mass spectrum indicated that decachloroferrocene was only a minor product and that nonachloroferrocene and octachloroferrocene were the major products. The observation of partially halogenated ferrocenes suggests that **1** is either partially mercurated or that substantial protiodemercuration occurs upon halogenation. The analytical data for **1** are consistent with a decamercurated formulation, since **1** gave a single resonance in the ^{19}F NMR and a reasonable mercury analysis was obtained. It is possible that some of the mercury groups are hydrolyzed by HX present in the halogenation reaction mixtures.

Treatment of ferrocene with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane afforded the decamercurated ferrocene **2** in 95% yield. Complex **2** is insoluble in all common solvents and could not be characterized by NMR methods. The available characterization methods (IR, mp, C and H microanalysis) could not conclusively establish the degree of mercuration in **2**. As a result, halogenation reactions were used

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[14] For selected structure determinations of ruthenocenes, see: Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1980**, *B36*, 2946. Liles, D. C.; Shaver, A.; Singleton, E.; Wiege, M. B. *J. Organomet. Chem.* **1985**, *288*, C33. Trotter, J. *Acta Crystallogr.* **1963**, *16*, 571. Small, G.; Trotter, J. *Can. J. Chem.* **1964**, *42*, 1746. Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 125. Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261.

to probe the extent of substitution. Chlorination of **2** with cupric chloride dihydrate in refluxing acetone afforded decachloroferrocene **3** in 27% yield after column chromatography and crystallization from hexane. Inspection of the ^1H NMR of crude **2** revealed two resonances that could be attributed to partially chlorinated ferrocenes. Similar partially brominated ferrocenes were observed in crude **4**. Although we were unable to quantify the amount of these partially substituted species, we estimate that they constitute $\leq 5\%$ of the crude products. This suggests that **2** is 90–95% decamercurated, with the remainder of the material being nonamercurated and octamercurated ferrocenes. Alternatively, the halogenation conditions lead to a small amount of protiodemercuration, which gives the partially halogenated ferrocenes. We favor the former possibility for several reasons. The decamercurated ruthenocene **6**, unlike **2**, gives decahaloruthenocenes containing $\leq 2\%$ of partially substituted ruthenocenes. Protiodemercuration, if an operating reaction path, should occur in **2** and **6** to roughly similar extents. The lack of partially halogenated ruthenocenes from **6** argues against protiodemercuration. In addition, the microanalyses for **2** could not be obtained within the ±0.4% limit, despite a number of attempts, indicating a formulation other than the idealized decamercurated structure. We propose that the extremely insoluble nature of heavily mercurated ferrocenes leads to the premature precipitation of complexes that still contain cyclopentadienyl C–H bonds. Such insolubility could afford a small amount of octamercurated and nonamercurated impurities in **2**.

Ruthenocene reacts with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane to afford the decamercurated ruthenocene **6**. Like **2**, this compound was completely insoluble in common solvents and was characterized by infrared spectroscopy, melting point, and C and H microanalysis. Treatment of **6** with halogenating agents afforded the decahaloruthenocenes **7**–**9** in 39–73% yields. The ^1H NMR spectra of crude **7** and **8** did not show any resonances between δ 4 and 5, indicating that **6** is $\geq 98\%$ decamercurated. The complete mercuration of **6** is in contrast to the partial mercuration that appears to be present in **2**. We suggest that **6** is more soluble than **2** and that partially mercurated ruthenocenes are able to remain in solution long enough to get completely mercurated. While we have no solubility data for mercurated ferrocenes and ruthenocenes, the iodide complexes **5** and **9** provide a useful comparison. Decaiodoferrocene **5** is completely insoluble in all organic solvents and could not be purified further, while decaiodoruthenocene **9** exhibited low, but real, solubility in dichloromethane and other organic solvents. It appears that decasubstituted metallocenes with large element substituents (e.g., I, HgX) have low solubilities in organic solvents but that the greater interannular distance in ruthenocenes allows for more efficient solvation.

Mercuration of pentamethylruthenocene with mercuric acetate (5 equiv) affords the pentamercurated complex **10** in 88% yield. Unlike the decamercurated metallocenes, **10** exhibits moderate solubility in dichloromethane and other organic solvents and could be analyzed by NMR methods. In particular, the mercury–acetate groups were found to exhibit hindered rotation on the NMR time scale (Figure 1). At −80 °C in dichloromethane-d_2, a large number of acetate and Cp* methyl resonances were observed. At room temperature in dichloromethane-d_2, there were fewer resonances, while at 60 °C in benzene-d_6 two relatively sharp resonances were found. We propose that this behavior can be explained by a slowly interconverting mixture of eight possible isomers that occur due to acetate isomerism. That is, the plane of the acetate groups will be approximately perpendicular to the cyclopentadienyl plane, which places the acetate methyl group either up toward the Cp* ligand or away from it. Since a methyl group and a carbonyl oxygen are roughly isosteric, a statistical distribution of the isomers can be expected. It was not possible to resolve all 16 resonances at the low temperature limit, because the methyl chemical shift region was narrow (ca. δ 1.7–2.1). However, at 60 °C, the spectrum shows a relatively sharp singlet for the acetate methyls and another singlet for the Cp* methyls, which is consistent with rapid interconversion of the isomers on the NMR time scale. It should be noted that a very broad resonance was present in the 60 °C ^1H NMR spectrum centered at δ 2.12, in addition to the singlets observed at δ 2.16 and 2.06. This resonance disappeared upon heating the sample to 100 °C in toluene-d_8, but decomposition of **10** became evident upon reaching this temperature.

Treatment of pentamethylruthenocene with 1 equiv of mercuric acetate afforded **10** (18%) and recovered pentamethylruthenocene (78%). This experiment indicates that the first mercuration is the slowest step and that each subsequent mercuration is faster than the first. This is a dramatic indication of the reactivity of metallocenes toward permercuration. Seemingly conflicting reports have suggested that the HgOAc group is a strong electron-withdrawing substituent on an arene ring ($\sigma_p = 0.40$)[15] and also that the HgX group possesses a negligible electronic effect as an aromatic substituent.[16] If the HgOAc group is electron withdrawing, then a possible rationale for the observed permercuration could be the strong σ,π-hyperconjugation associated with a carbon–mercury bond,[17] which would stabilize the adjacent positive charge involved in each mercuration step. We have recently reported that pentakis(acetoxymercurio)cyclopentadienylmanganese tricarbonyl shows slightly lower infrared carbonyl stretches than cyclopentadienylmanganese tricarbonyl, which establishes that mercury is electron donating relative to hydrogen.[18] Thus, the increasing rate of mercuration with increasing mercury substitution is probably an electronic effect that reflects the more electron rich character of the intermediate mercurated species.

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[15] Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; pp 439–540. See also: Yagupolskii, L. M.; Popov, V. I.; Kondratenko, N. V.; Konovalov, E. V. *Russ. J. Org. Chem.* **1974**, *10*, 278. Kravtsov, D. N.; Kvasov, B. A.; Golovchenko, L. S.; Fedin, E. I. *J. Organomet. Chem.* **1972**, *36*, 227.

[16] For leading references, see: Adcock, W.; Hegarty, B. F.; Kitching, W.; Smith, A. J. *J. Organomet. Chem.* **1968**, *12*, P21. Kitching, W.; Adcock, W.; Hegarty, B. F. *Aust. J. Chem.* **1968**, *21*, 2411. See also: Perrin, C.; Westheimer, F. H. *J. Am. Chem. Soc.* **1963**, *85*, 2773. Gowenlock, B. G.; Trotman, J. *J. Chem. Soc.* **1955**, 1454.

[17] For a theoretical description of this effect, see: Scherr, P. A.; Glick, M. D.; Siefert, J. H.; Bach, R. D. *J. Am. Chem. Soc.* **1975**, *97*, 1782. Bach, R. D.; Scherr, P. A. *Tetrahedron Lett.* **1973**, 1099.

[18] Kur, S. A.; Heeg, M. J.; Winter, C. H. *Organometallics* **1994**, *13*, 1865.

The reaction of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) with excess mercuric acetate (7 equiv) was investigated to determine if the indenyl ligand could be heptamercurated. It was found that the indenyl ligand was selectively trimercurated in the 1,2,3-positions to afford complex **14**. Hence, only cyclopentadienyl C—H bonds directly attached to a metal are activated toward mercuration. Like **10**, **14** was soluble in dichloromethane and other organic media. Unlike **10**, however, the −80 °C ^{1}H NMR spectrum in dichloromethane-d_2 was nearly identical to the spectrum at 20 °C. The lack of temperature dependence in the spectra implies a much lower degree of steric congestion in **14** than is present in **10**. Treatment of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) with 1 equiv of mercuric acetate afforded a mixture of the mono-, di-, and trimercurated indenyl complexes, in addition to some unreacted starting indenyl complex. The observation of partially mercurated complexes in the reaction of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) with 1 equiv of mercuric acetate is in contrast to the analogous mercuration of pentamethylruthenocene. Pentamethylruthenocene reacted with 1 equiv of mercuric acetate to give **10** (18%) and recovered pentamethylruthenocene (78%). We suggest that the reduced reactivity of the indenyl complex toward mercuration can be attributed to the lower aromaticity of indenyl versus cyclopentadienyl ligands. The aromatic six-membered ring in the indenyl ligand competes with the five-membered ring for electron density in order to achieve fully aromatic character and thus reduces the aromaticity of the five-membered ring.

Treatment of **14** with brominating and iodinating agents afforded the 1,2,3-trihaloindenyl complexes **15**$\cdot 0.25C_6H_{14}$ and **16**. To the best of our knowledge, these constitute the first examples of complexes bearing 1,2,3-trihaloindenyl ligands. It is not easy to envision alternate syntheses of **15**$\cdot 0.25C_6H_{14}$ and **16**, which illustrates the power of polymercuration strategies in organometallic synthesis. The structure of **16** was determined and is the first structurally characterized complex bearing a 1,2,3-triiodoindenyl ligand. The structural parameters were largely normal, except for the slight slippage of the 1,2,3-triiodoindenyl toward η^3-bonding to ruthenium.

A significant achievement in this work has been the development of simple synthetic routes to perhalometallocenes. In general, pentahalocyclopentadienyl ligands have been notoriously difficult to synthesize and have remained rare.[9,19] A useful comparison can be made regarding the preparation of decachloroferrocene **3** and decachlororuthenocene **7**. Hedberg and Rosenberg first prepared **3** and **7** by repetitive lithiation/chlorination of ferrocene and ruthenocene to provide these decahalometallocenes in 7% and 14% yields, respectively.[9] By contrast, our methodology affords **3** and **7** in 26% and 64% overall yields, for a two-step sequence from ferrocene and ruthenocene. In addition, the mercurated complexes are easily transformed to perbromocyclopentadienyl and periodocyclopentadienyl complexes upon treatment with cupric bromide dihydrate, potassium tribromide, or potassium triiodide.

In summary, iron and ruthenium metallocenes are easily permercurated by treatment with mercuric acetate in refluxing 1,2-dichloroethane or diethyl ether/ethanol. In the case of ferrocene, the decamercurated product that is obtained contains 5−10% of partially mercurated materials, which lead to partially substituted ferrocenes upon halogenation. By contrast, ruthenocene, pentamethylruthenocene, and (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) are completely permercurated upon treatment with the appropriate number of equivalents of mercuric acetate in either refluxing 1,2-dichloroethane or ethanol/diethyl ether. The permercurated ruthenocenes can be halogenated with cupric chloride dihydrate or cupric bromide dihydrate in acetone, potassium tribromide in water, or potassium triiodide in water to afford moderate to good yields of the perhalometallocenes. The combined results demonstrate that permercurated metallocenes are easy to prepare and serve as useful precursors to species that would be difficult to prepare by existing methods. Hence, permercurated cyclopentadienyl complexes should not be viewed as exotic species, but rather as accessible and potentially useful synthetic tools.

Experimental Section

General Considerations. The mercuration reactions were performed under an atmosphere of nitrogen using Schlenk techniques. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Diethyl ether was distilled from a purple solution of sodium benzophenone ketyl. Reagent grade 1,2-dichloroethane, acetone, ethanol, and water were used as received. Chloroform-d, dichloromethane-d_2, benzene-d_6, and toluene-d_8 were purified by vacuum transfer from 4-Å molecular sieves. Ferrocene, pentamethylcyclopentadiene, indene, mercuric acetate, mercuric trifluoroacetate, cupric chloride dihydrate, cupric bromide dihydrate, sodium thiosulfate, potassium iodide, and iodine were used as received from Aldrich Chemical Co. Ruthenocene[20] and (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II)[13] were prepared by literature methods.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained at 500, 300, 126, and 75 MHz in chloroform-d, unless otherwise noted. ^{19}F NMR spectra were obtained at 282 MHz in the indicated solvents. ^{199}Hg NMR spectra were obtained at 53.7 MHz in chloroform using previously reported parameters.[21] Infrared spectra were obtained using potassium bromide as the medium. Mass spectra were obtained in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Decakis[(trifluoroacetoxy)mercurio]ferrocene (1). A 100-mL Schlenk flask was charged with mercuric trifluoroacetate (1.2 g, 2.8 mmol), mercuric oxide (0.30 g, 1.4 mmol), ethanol (7.5 mL), diethyl ether (7.5 mL),

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[19] For examples of synthetic routes, see: Reimer, K. J.; Shaver, A. *Inorg. Chem.* **1975**, *14*, 2707. Hermann, W. A.; Huber, M. *J. Organomet. Chem.* **1977**, *140*, 55. Day, V. W.; Reimer, K. J.; Shaver, A. *J. Chem. Soc., Chem. Commun.* **1975**, 403. Brown, G. M.; Hedberg, F. L.; Rosenberg, H. *Ibid.* **1972**, 5. Priebsch, W.; Hoch, M.; Rehder, D. *Chem. Ber.* **1988**, *121*, 1971. Hughes, R. P.; Curnow, O. J. *J. Am. Chem. Soc.* **1992**, *114*, 5895.

[20] Winter, C. H.; Pirzad, S.; Graf, D. D.; Cao, D. H.; Heeg, M. J. *Inorg. Chem.* **1993**, *32*, 3654.

[21] Bach, R. D.; Vardhan, H. B.; Rahman, A. F. M. M.; Oliver, J. P. *Organometallics* **1985**, *4*, 846.

and a stir bar and was fitted with a rubber septum. A solution of ferrocene (0.052 g, 0.28 mmol) in 1:1 ethanol/diethyl ether (15 mL) was loaded into a syringe equipped with a 12-in. needle. The ferrocene was added by syringe pump to the mercuric trifluoroacetate/mercuric oxide mixture at ambient temperature over 4 h. The solution was stirred for an additional 20 h. The reaction mixture was filtered through a 1-cm pad of Celite on a coarse glass frit to afford a clear yellow-orange solution. This solution was poured into water (100 mL) to afford a yellow-orange precipitate. The solid was collected by filtration onto a medium-porosity glass frit. Vacuum drying afforded **1** as a yellow-orange powder (0.56 g, 60%): dec range, with evolution of elemental mercury, 200–210 °C; IR (KBr, cm^{-1}) 1668 (ν_{CO}, vs), 1429 (ν_{CO}, m), 1379 (m), 1203 (s), 1126 (s), 830 (m), 802 (m), 717 (m); ^{19}F NMR (acetone-d_6, δ) −74.62 (s, CF$_3$). Anal. Calcd for $C_{20}F_{30}FeHg_{10}O_{20}$: C, 10.88; H, 0.00; Hg, 60.56. Found: C, 9.51; H, 0.00; Hg, 60.43.

Decakis(acetoxymercurio)ferrocene (2). A 250-mL round-bottomed flask, equipped with condenser, stir bar, and rubber septum, was charged with ferrocene (0.186 g, 1.00 mmol), mercuric acetate (3.187 g, 10.0 mmol), and 1,2-dichloroethane (100 mL). The mixture was refluxed for 18 h, during which time a yellow precipitate formed. The precipitate was collected on a medium-porosity glass frit and was washed with hexane (40 mL). Vacuum drying afforded **2** as a yellow powder (2.630 g, 95%): dec range, with evolution of elemental mercury, 260–270 °C; IR (KBr, cm^{-1}) 1570 (ν_{CO}, vs), 1393 (ν_{CO}, s), 1358 (m), 1310 (m), 1006 (w), 682 (m). Anal. Calcd for $C_{30}H_{30}Hg_{10}O_{20}Fe$: C, 13.00; H, 1.09. Found: C, 14.31; H, 1.40.

Decachloroferrocene (3). A 250-mL round-bottomed flask was charged with **2** (2.00 g, 0.721 mmol), cupric chloride dihydrate (6.15 g, 36.07 mmol), and acetone (120 mL). The resultant mixture was refluxed for 12 h. The volatiles were removed under reduced pressure to give a dark oily solid. The solid was extracted with hexane (100 mL). The hexane extract was applied to a 30-cm column of silica gel on a coarse glass frit, and the column was eluted with hexane (100 mL) to afford a lemon yellow solution. Removal of the volatile components under reduced pressure, followed by vacuum drying and crystallization from hexane at −20 °C, afforded **3** as a yellow powder (0.104 g, 27%): mp (sealed tube) 245–246 °C dec (lit.[9] mp 245–246 °C dec); IR (KBr) 1392 (m), 1383 (m), 1353 (s), 1315 (w), 1096 (w), 934 (w), 818 (w), 700 (s), 679 (w), 573 (w), 505 (w), 417 (m); $^{13}C\{^1H\}$ NMR (CDCl$_3$, ppm) 84.50 (s, $\boldsymbol{C}_5Cl_5$); MS (20 eV) *m/e* 526 (M$^+$, 25%), 495 (M$^+$ − Cl, 100%), 460 (M$^+$ − 2Cl, 26%). The isotope distribution pattern of the parent mass envelope was identical with the calculated pattern.

Decabromoferrocene (4). A 100-mL round-bottomed flask was charged with **2** (1.39 g, 0.50 mmol) and potassium tribromide (prepared from potassium bromide (0.595 g, 5.00 mmol) and bromine (0.256 mL, 5.00 mmol) in water (50 mL)). The resultant mixture was stirred at ambient temperature for 3 h, during which time a yellow solid formed. The crude product was collected on a medium-porosity glass frit and was washed with methanol (20 mL). The solid was then extracted with dichloromethane to afford a yellow solution. This solution was applied to a 30-cm column of silica gel on a coarse glass frit. Elution with dichloromethane (50 mL) afforded a clear yellow solution. Removal of the volatile components, followed by vacuum drying and crystallization from hexane at −20 °C, afforded **4** as a yellow powder (0.294 g, 60%): mp (sealed tube) 150 °C; IR (KBr, cm^{-1}) 1379 (s), 1302 (s), 1274 (w), 580 (s); MS (20 eV) *m/e* 975 (M$^+$, 19%), 895 (M$^+$ − Br, 100%), 816 (M$^+$ − 2Br, 12%). The isotope distribution pattern of the parent mass envelope was identical with the calculated pattern. Anal. Calcd for $C_{10}Br_{10}Fe$: C, 12.32; H, 0.00. Found: C, 12.12; H, 0.00.

Decaiodoferrocene (5). A 100-mL round-bottomed flask was charged with potassium iodide (0.830 g, 5.00 mmol), iodine (0.635 g, 5.00 mmol), and water (50 mL). The resultant mixture was stirred at ambient temperature and then **2** (1.386 g, 0.50 mmol) was added. The mixture was stirred at ambient temperature for 5 h, during which time a yellow powder formed. The crude product was collected on a medium-porosity glass frit and was washed with aqueous potassium iodide (0.1 M, 100 mL), water (20 mL), and methanol (100 mL) to remove mercury impurities. The residue was placed in a paper thimble and was extracted with acetone for 24 h to remove any additional mercury impurities. Vacuum drying of the resultant solid afforded **5** as a yellow powder (0.485 g, 67%): IR (KBr, cm^{-1}) 1238 (m), 513 (m); MS (20 eV) *m/e* 1192 (M$^+$ − 2I, 2%). Anal. Calcd for $C_{10}I_{10}Fe$: C, 8.31; H, 0.00. Found: C, 7.50; H, 0.26.

Decakis(acetoxymercurio)ruthenocene (6). In analogy with the preparation of **2**, ruthenocene (0.231 g, 1.00 mmol) was reacted with mercuric acetate (3.187 g, 10.0 mmol) in 1,2-dichloroethane (100 mL) to afford **6** as an off-white powder (2.492 g, 88%): dec range, with evolution of elemental mercury, 200–220 °C; IR (KBr) 1570 (ν_{CO}, vs), 1403 (ν_{CO}, vs), 1337 (w), 1014 (w), 917 (w), 643 (s). Anal. Calcd for $C_{30}H_{30}Hg_{10}O_{20}Ru$: C, 12.79; H, 1.07. Found: C, 13.50; H, 1.29.

Decachlororuthenocene (7). In analogy with the preparation of **3**, **6** (1.00 g, 0.355 mmol) was reacted with cupric chloride dihydrate (3.03 g, 17.8 mmol) in acetone (80 mL) to afford **7** as a white powder (0.149 g, 73%): mp >300 °C (sublimes; lit. mp[9] >300 °C, sublimes): $^{13}C\{^1H\}$ NMR (CDCl$_3$, ppm) 91.46 (s, $\boldsymbol{C}_5Cl_5$); IR (KBr, cm^{-1}) 1386 (m), 1351 (s), 1310 (m), 1095 (w), 928 (w), 811 (w), 703 (s), 564 (w), 409 (s); MS (20 eV) *m/e* 576 (M$^+$, 100%), 541 (M$^+$ − Cl, 24%). The isotope distribution pattern of the parent mass envelope was identical with the calculated pattern.

Decabromoruthenocene (8). In analogy with the preparation of **4**, **6** (1.146 g, 0.407 mmol) was reacted with potassium bromide (0.484 g, 4.07 mmol) and bromine (0.208 mL, 4.07 mmol) in water (50 mL) to afford **8** as an analytically pure white powder (0.194 g, 47%): mp (sealed tube) >300 °C; $^{13}C\{^1H\}$ NMR (CDCl$_3$, ppm) 84.51 (s, $\boldsymbol{C}_5Br_5$); IR (KBr, cm^{-1}) 1379 (m), 1302 (s), 1274 (w), 589 (s); MS (20 eV) *m/e* 1020 (M$^+$, 100%), 941 (M$^+$ − Br, 3%), 862 (M$^+$ − 2Br, 15%). The isotope distribution pattern of the parent mass envelope was identical with the calculated pattern. Anal. Calcd for $C_{10}Br_{10}Ru$: C, 11.77; H, 0.00. Found: C, 11.90; H, 0.00.

Decaiodoruthenocene (9). In analogy with the preparation of **5**, **6** (1.409 g, 0.50 mmol) was reacted with potassium iodide (0.830 g, 5.00 mmol) and iodine (1.269 g, 5.00 mmol) in water (50 mL) to afford **9** as an yellow-ochre powder (0.292 g, 39%): dec range (sealed tube)

240–260 °C; $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm) 69.94 (s, $\boldsymbol{C}_5I_5$); IR (KBr, cm^{-1}) 1246 (m), 506 (m); MS (20 eV) *m/e* 1110 ($M^+ - 3I$, 3%), 983 ($M^+ - 4I$, 12%). The isotope distribution pattern of the $M^+ - 3I$ mass envelope was identical with the calculated pattern. Anal. Calcd for $C_{10}I_{10}Ru$: C, 8.06; H, 0.00. Found: C, 7.92; H, 0.20.

Pentakis(acetoxymercurio)pentamethylruthenocene (10). A 250-mL round-bottomed flask was charged with pentamethylruthenocene (0.904 g, 3.00 mmol), mercuric acetate (4.78 g, 15.0 mmol), ethanol (100 mL), diethyl ether (50 mL), and a stir bar and was fitted with a rubber septum. The solution was stirred at ambient temperature for 18 h, during which time an off-white solid precipitated. The precipitate was collected on a medium glass frit and was washed successively with ethanol (20 mL), ether (20 mL), and hexane (20 mL). Vacuum drying afforded **10** as an analytically pure off-white powder (4.19 g, 88%): dec range, with evolution of elemental mercury, 230–250 °C; IR (KBr, cm^{-1}) 2957 (w), 2894 (w), 1570 (ν_{CO}, vs), 1400 (ν_{CO}, s), 1372 (s), 1323 (m), 1013 (m), 914 (w), 682 (m), 640 (m); ^1H NMR (CD_2Cl_2, 23 °C, δ) 2.07 (s), 1.98 (s, broad), 1.95 (s, broad), 1.92 (s). Anal. Calcd for $C_{25}H_{30}Hg_5O_{10}Ru$: C, 18.83; H, 1.90. Found: C, 18.84; H, 1.93.

Pentachloropentamethylruthenocene (11). A 250-mL round-bottomed flask, equipped with condenser, stir bar, and rubber septum, was charged with **10** (1.07 g, 0.671 mmol), cupric chloride dihydrate (2.06 g, 16.8 mmol), and acetone (100 mL). The resultant mixture was refluxed for 15 h. The volatile components were removed under reduced pressure to give an oily black solid. The residue was extracted with hexane (100 mL). The hexane extract was applied to a 3-cm column of silica gel on a coarse glass frit and the column was eluted with hexane to afford a colorless solution. Removal of the hexane under reduced pressure, followed by vacuum drying, afforded **11** as a white powder (0.214 g, 67%): mp (sealed tube) >300 °C; lit. mp[13] >300 °C); ^1H NMR ($CDCl_3$, δ) 1.69 (s, $C_5(C\boldsymbol{H}_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 91.06 (s, $\boldsymbol{C}_5Cl_5$), 87.14 (s, $\boldsymbol{C}_5(CH_3)_5$), 8.86 (s, $C_5(\boldsymbol{C}H_3)_5$); MS (20 eV) *m/e* 472 (M^+, 5%), 437 ($M^+ -$ Cl, 100%). The isotope distribution pattern of the parent mass envelope was identical with the calculated pattern.

Pentabromopentamethylruthenocene (12). A 100-mL round-bottomed flask was charged with potassium bromide (0.192 g, 1.61 mmol), bromine (0.082 mL, 1.59 mmol), water (25 mL), methanol (25 mL), and a stir bar. The resultant mixture was stirred at ambient temperature for 0.5 h and then **10** (0.427 g, 0.268 mmol) was added. The mixture was stirred at ambient temperature for 3 h, during which time a white precipitate formed. The crude product was collected on a medium-porosity glass frit and was successively washed with saturated aqueous sodium thiosulfate (250 mL) and saturated aqueous potassium iodide (250 mL) to remove mercury impurities. The precipitate was then extracted with dichloromethane (50 mL) to afford a colorless solution. This solution was applied to a 2-cm pad of silica gel on a coarse glass frit and elution with dichloromethane (50 mL) afforded a colorless solution. Removal of the volatiles under reduced pressure afforded **12** as an analytically pure off-white powder (0.065 g, 35%): dec point (sealed tube) 270 °C; IR (KBr) 2963 (w), 2951 (w), 2909 (m), 2853 (w), 1468 (m), 1444 (m), 1379 (s), 1298 (s), 1269 (m), 1125 (w), 1065 (w), 1026 (s), 940 (w), 785 (w), 758 (w), 570 (vs), 452 (m); ^1H NMR ($CDCl_3$, δ) 1.65 (s, $C_5(C\boldsymbol{H}_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 91.21 (s, $\boldsymbol{C}$—CH_3), 80.09 (s, $\boldsymbol{C}$—Br), 8.25 (s, $\boldsymbol{C}H_3$); HRMS calcd for $C_{15}H_{15}Br_5Ru$, 691.6130; found, 691.6139. Anal. Calcd for $C_{15}H_{15}Br_5Ru$: C, 25.89; H, 2.17. Found: C, 25.70; 2.05.

Pentaiodopentamethylruthenocene ($13\cdot 0.25CCl_4$). A 100-mL round-bottomed flask was charged with potassium iodide (0.311 g, 1.87 mmol), iodine (0.237 g, 1.87 mmol), water (25 mL), methanol (25 mL), and a stir bar. The resultant mixture was stirred at ambient temperature for 0.5 h, and then **10** (0.427 g, 0.268 mmol) was added. A bright yellow precipitate formed immediately. The crude product was collected on a medium-porosity glass frit and was successively washed with saturated aqueous sodium thiosulfate (250 mL) and saturated aqueous potassium iodide (250 mL) to remove mercury impurities. The precipitate was then extracted with dichloromethane (50 mL) to afford a bright yellow solution. This solution was applied to a 2-cm pad of silica gel on a coarse glass frit, and elution with dichloromethane (50 mL) afforded a bright yellow solution. Removal of the volatiles under reduced pressure afforded a yellow powder (0.117 g, 60%). An analytical sample was crystallized from hexane/carbon tetrachloride to provide bright yellow needles of **$3\cdot 0.25CCl_4$**: dec point (sealed tube) 190 °C; IR (KBr) 2962 (w), 2944 (w), 2898 (m), 2848 (w), 1467 (m), 1443 (m), 1377 (s), 1253 (s), 1114 (w), 1066 (w), 1023 (s), 902 (m), 785 (w), 763 (w), 733 (m), 579 (w), 510 (vs), 446 (m); ^1H NMR ($CDCl_3$, δ) 1.58 (s, $C_5(C\boldsymbol{H}_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 90.71 (s, $\boldsymbol{C}$—CH_3), 62.45 (S, $\boldsymbol{C}$—I), 7.06 (s, $\boldsymbol{C}H_3$). Anal. Calcd for $C_{15}H_{15}I_5Ru\cdot(CCl_4)_{0.25}$: C, 18.90; H, 1.56. Found: C, 18.92; 1.52.

(η^5-1,2,3-Tris(acetoxymercurio)indenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (14). A 100-mL round-bottomed flask, equipped with stir bar and rubber septum, was charged with (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) (0.300 g, 0.852 mmol), mercuric acetate (0.815 g, 2.56 mmol), ethanol (25 mL), and diethyl ether (25 mL). The mixture was stirred at ambient temperature for 12 h. Removal of the solvent under reduced pressure afforded a yellow powder. The solid was washed with hexane (100 mL) and was then dissolved in dichloromethane (100 mL). The dichloromethane solution was filtered through a 1-cm pad of Celite on a coarse glass frit to give a clear light yellow solution. Removal of the solvent under reduced pressure afforded **14** as a light yellow microcrystalline powder (0.953 g, 99%): dec point (sealed tube) 170 °C; IR (KBr, cm^{-1}) 2957 (w), 2894 (w), 1562 (ν_{CO}, vs), 1400 (ν_{CO}, vs), 1372 (m), 1020 (w), 731 (w), 682 (w), 640 (w); ^1H NMR ($CDCl_3$, δ, 22 °C) 6.96 (broad s, Ind $C_6\boldsymbol{H}_2H_2'$), 6.77 (broad s, Ind $C_6H_2\boldsymbol{H}_2'$), 2.13 (s, 3 $Hg(O_2CC\boldsymbol{H}_3)$), 1.57 (s, $C_5(C\boldsymbol{H}_3)_5$); ^{199}Hg NMR ($CDCl_3$, ppm, 23 °C, neat $HgMe_2$ = 0 ppm) −574 (s, 2 ***Hg***OAc), −619 (s, ***Hg***OAc). Anal. Calcd for $C_{25}H_{28}O_6Hg_3Ru$: C, 26.64; H, 2.50. Found: C, 26.70; H, 2.64.

(η^5-1,2,3-Tribromoindenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II)·0.25(C_6H_{14}) ($15\cdot 0.25C_6H_{14}$). In a manner similar to the preparation of **14**, potassium bromide (0.158 g, 1.33 mmol), bromine (68.5 μL, 1.33 mmol), and (η^5-1,2,3-tris(acetoxymercurio)indenyl(η^5-pentamethylcyclopentadienyl)ruthenium(II) (0.500 g, 0.443 mmol) were reacted to afford **16**·0.25C_6H_{14} as an analytically pure yellow powder (0.077 g, 29%): dec temperature 220 °C; IR (KBr, cm^{-1}) 2963 (w), 2949 (w), 2901 (s), 2852 (w), 1464 (m), 1446 (m), 1377 (s), 1351 (m), 1278 (m), 1190 (m), 1024 (s), 916 (s), 785 (m), 733 (s), 655 (m), 603 (s); ^1H NMR ($CDCl_3$, δ, 22 °C) 7.09 (m, Ind $C_6\boldsymbol{H}_2H_2'$), 7.05 (m, Ind $C_6H_2\boldsymbol{H}_2'$), 1.45 (s, $C_5(C\boldsymbol{H}_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm, 22 °C) 123.73 (s, Ind $\boldsymbol{C}$—H), 122.77 (s, Ind $\boldsymbol{C}$—H), 90.73 (Ind quat $\boldsymbol{C}$), 86.43 (s, $\boldsymbol{C}_5(CH_3)_5$), 85.74 (s, $\boldsymbol{C}$—Br), 73.88 (s, 2 $\boldsymbol{C}$—Br), 8.39 (s, $C_5(\boldsymbol{C}H_3)_5$). Anal. Calcd for $C_{19}H_{19}Br_3Ru$·0.25C_6H_{14}: C, 40.38; H, 3.72. Found: C, 40.58; H, 3.42. The amount of hexane solvate was verified by integration of the hexane ^1H NMR resonances against the pentamethylcyclopentadienyl resonance. The amount of hexane solvate did not change after vacuum drying of the solid at 60 °C (0.01 mmHg) in a drying pistol for 24 h.

(η^5-1,2,3-Triiodoindenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (16). A 250-mL round-bottomed flask, equipped with stir bar and rubber septum, was charged with potassium iodide (0.368 g, 2.22 mmol), iodine (0.563 g, 2.22 mmol), water (30 mL), and methanol (10 mL). The resultant mixture was stirred at ambient temperature for 0.5 h. (η^5-1,2,3-Tris(acetoxymercurio)indenyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (0.500 g, 0.443 mmol) dissolved in acetone (20 mL) was slowly added to the potassium triiodide solution. A yellow precipitate formed during the addition. The solution was stirred for 5 min after the addition was complete. The yellow precipitate was collected on a medium-porosity glass frit and was air dried. The precipitate was dissolved in hexane (100 mL), and the resultant yellow solution was dried over anhydrous magnesium sulfate. The solution was filtered through a 3-cm pad of silica gel on a coarse glass frit, and the pad was eluted with additional hexane (100 mL). Removal of the hexane under reduced pressure afforded **17** as an analytically pure yellow powder (0.213 g, 66%): dec point (sealed tube) 250 °C; IR (KBr, cm^{-1}) 2961 (w), 2944 (w), 2900 (s), 2850 (w), 1460 (m), 1441 (m), 1377 (s), 1346 (m), 1292 (m), 1261 (m), 1238 (w), 1188 (m), 1067 (w), 1025 (m), 989 (w), 906 (s), 767 (w), 734 (vs), 632 (m), 592 (m); ^1H NMR ($CDCl_3$, δ, 22 °C) 6.99 (s, Ind $C_6\boldsymbol{H}_2\boldsymbol{H}_2'$), 1.37 (s, $C_5(C\boldsymbol{H}_3)_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm, 22 °C) 124.88 (s, Ind $\boldsymbol{C}$—H), 124.23 (s, Ind $\boldsymbol{C}$—H), 95.45 (Ind quat $\boldsymbol{C}$), 86.01 (s, $\boldsymbol{C}_5(CH_3)_5$), 67.68 (s, $\boldsymbol{C}$—I), 49.29 (s, 2 $\boldsymbol{C}$—I), 7.62 (s, $C_5(\boldsymbol{C}H_3)_5$). Anal. Calcd for $C_{19}H_{19}I_3Ru$: C, 31.30; H, 2.63. Found: C, 31.36; H, 2.56.

Crystal Structure Determination of 16. Crystallographic data were collected on a Nicolet P2$_1$ diffractometer at room temperature. Out of 4285 total reflections, 2834 were observed and used for refinement. The structure was refined in a full matrix with all non-hydrogen atoms described anisotropically. Cell constants were derived from 24 high angle reflections. Absorption corrections were applied by employing empirical methods. Hydrogen atom positions were calculated or observed and held fixed. Neutral atom scattering factors were taken from ref 22a. Local modifications of Sheldrick's computer programs were used in the solution and refinement (SHELX-76, SHELXTL).[22b,c] Additional crystallographic parameters are given in the supplementary material. No correction for secondary extinction was deemed necessary.

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Supplementary Material Available: Tables S1–S3, listing full experimental details for data collection and refinement, thermal parameters, and hydrogen positional parameters for **16** (3 pages). Ordering information is given on any current masthead page.

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