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# Chemistry of Cyclopentadienyl–Ruthenium and –Osmium Complexes. 3. New High-Yield Syntheses of Ruthenocenes and Osmocenes. The Crystal and Molecular Structures of Decamethylruthenocene $[Ru(\eta^5\text{-}C_5Me_5)_2]$ and Decamethylosmocene $[Os(\eta^5\text{-}C_5Me_5)_2]$

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The reaction of $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ ($C_8H_{12}$ = cycloocta-1,5-diene) with cyclopentadienylthallium in dimethoxyethane gives $[Ru(\eta^5\text{-}C_5H_5)_2]$ (**1**) in 78% yield. A generalized route from $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ and $[Sn\text{-}n\text{-}Bu_3(C_5R_5)]$ (R = H, Me) in ethanol at 80 °C gives **1** and $[Ru(\eta^5\text{-}C_5Me_5)_2]$ (**2**) (yields 75% and 70%, respectively). Correspondingly $[\{Os(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ reacts with $[Sn\text{-}n\text{-}Bu_3(C_5H_5)]$ in methanol at 65 °C to afford $[Os(\eta^5\text{-}C_5H_5)_2]$ (**3**) in 72% yield. Decamethylosmocene, $[Os(\eta^5\text{-}C_5Me_5)_2]$ (**4**), is obtained in 82% yield by the direct reaction between pentamethylcyclopentadiene and $Na_2[OsCl_6]$ in ethanol. Mixed-ligand ruthenocenes, $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ (**5**) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ (**6**), are obtained by the treatment of the labile ruthenium(II)–cyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ with the appropriate cyclopentadienyl anions ($C_5H_4Me^-$, $C_5Me_5^-$) in tetrahydrofuran at 25 °C. The reactions of $[M(\eta^5\text{-}C_5Me_5)_2]$ (M = Ru, Os) with halogens $X_2$ (X = Br, I) give the ruthenium(IV) and osmium(IV) cations $[M(\eta^5\text{-}C_5Me_5)_2X]Y$ (M = Ru, X, Y = Br, **7**; M = Ru, X = I, Y = $I_3$, **8**; M = Os, X, Y = Br, **9**; M = Os, X = I, Y = $I_3$, **10**). Strong acids reversibly protonate the electron-rich centers in **2** and **4** giving the cationic hydride complexes $[M(\eta^5\text{-}C_5Me_5)_2H]^+$. The complexes **1**–**10** have been characterized by elemental analysis and by spectroscopic (IR and $^1H$ and $^{13}C$ NMR) techniques. The crystal and molecular structures of **2** and **4** have been determined by single-crystal X-ray diffraction. Crystals of these sandwich complexes are isostructural, space group $P2_1/m$. Abnormally high thermal parameters indicate the presence of disorder across the mirror plane. Although the position of the molecules across the crystallographic mirror plane implies a $D_{5h}$ (eclipsed) molecular geometry in both cases, this may only reflect the average structure. The average metal–carbon distances are 2.17 (1) and 2.18 (1) Å for Ru–C and Os–C, respectively; $d$(C–C) = 1.43 (1) Å and $d$(C–C(Me)) = 1.52 (1) Å. In both structures there is a slight bending of the methyl groups (approximately 0.07 Å) away from the mean plane through the cyclopentadienyl ring.

## Introduction

Although the chemistry of ferrocene has developed rapidly since its discovery in 1951 that of ruthenocene has received relatively little attention[1,2] and the chemistry of osmocene remains virtually unexplored.[2,3] This may largely be attributed to the lack of convenient synthetic routes which produce these complexes both in high yields and in substantial amounts.[1-3]

Only low yields of ruthenocene are obtainable from $Ru(acac)_3$ and $(C_5H_5)MgBr$[4] and from the ligand exchange route via ferrocene and anhydrous $RuCl_3$.[5] Although useful yields of ruthenocene are obtained from the reaction of cyclopentadienylsodium with ruthenium trichloride–ruthenium metal mixtures ("partially chlorinated ruthenium")[6] or $[RuCl_2(\text{dimethyl sulfoxide})_4]$,[7] the most convenient route reported to date remains the direct reaction between ruthenium trichloride and cyclopentadiene in ethanol solution.[8] A significant variation on this route relies on zinc as a mild reducing system,[9] a procedure that has recently been employed in order to improve the scale on which this synthesis can be performed.[10] Ruthenium trichloride also forms the most convenient starting point for the only two reported syntheses of decamethylruthenocene; the one involves the direct reaction between the ruthenium salt and pentamethylcyclopentadiene in ethanol or methanol,[11] while the second, based on the original Vitulli synthesis of ruthenocene, relies upon the use of zinc as a reductant.[12] From both these procedures the yields are poor (10–18%). Since the first reported synthesis of osmocene in 1959 by Fischer and Grubert,[13]

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there has been little reported interest in the chemistry of osmocene.[3] Consequently the only reliable synthesis remains the original procedure, the reaction of $OsCl_4$ with excess $NaC_5H_5$, a procedure which affords only 23% of the metallocene.

On the basis of the above discussion, it is thus apparent that to date, there are few reliable, and no general, high-yield syntheses of the metallocenes of ruthenium and osmium. Herein we report on the first generalized synthesis of ruthenocenes and mixed-ligand ruthenocenes and the first high-yield syntheses of osmocene and decamethylosmocene. These procedures make available, for the first time, large amounts of decamethylruthenocene, osmocene, and decamethylosmocene, and of mixed-ligand ruthenocenes, for studies of their physical and chemical properties. A preliminary account of some of this work has already been published.[14]

## Experimental Section

All the reactions were routinely performed by using standard Schlenk techniques under an inert atmosphere of nitrogen or argon and by using dry and deoxygenated solvents. Cyclopentadienyl thallium was purchased from Strem Chemicals and was purified by sublimation immediately prior to use. Pentamethylcyclopentadiene (Fluka A.G., Switzerland, or Strem Chemicals Inc.) was used as purchased. $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$,[15] $[\{Os(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$,[16] and $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$[17] ($C_8H_{12}$ = cycloocta-1,5-diene) were all prepared by the literature methods. The reagents $K[C_5H_4Me]$,[18] $K[C_5Me_5]$,[18] $[Sn\text{-}n\text{-}Bu_3(C_5H_5)]$,[21] and $[Sn\text{-}n\text{-}Bu_3(C_5Me_5)]$[21] were prepared by modification of published procedures. $^1H$ NMR spectra were recorded at 500.13 MHz and $^{13}C$ NMR spectra at 125.72 MHz, in both cases using a Bruker WM 500 instrument and a probe temperature of 303 K. Microanalyses were performed by the microanalytical section of the Analytical Division of the NCRL.

**Preparation of $[Ru(\eta^5\text{-}C_5H_5)_2]$ (1).** (a) $[Sn\text{-}n\text{-}Bu_3(C_5H_5)]$ (32.0 g, 90 mmol) was added to a suspension of $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ (8.4 g, 30 mmol) in ethanol (150 mL) under an inert atmosphere and the resulting mixture heated under reflux for 48 h during which time the brown ruthenium polymer reacted into solution. The hot reaction solution was filtered in air and then cooled to room temperature. The pale yellow solid which crystallized on cooling was collected by filtration and thoroughly washed with cold ethanol (2 × 20 mL) followed by diethyl ether (2 × 20 mL). Analytically pure $[Ru(\eta^5\text{-}C_5H_5)_2]$ was obtained by recrystallization of the crude product from either hot acetone or hot ethanol: yield 5.2 g (22.5 mmol, 75%); $^1H$ NMR ($CDCl_3$) $\delta$ 4.55 (s, $C_5H_5$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 70.1 (s, $C_5H_5$). Anal. calcd for $C_{10}H_{10}Ru$: C, 51.93; H, 4.36. Found: C, 51.89; H, 4.35.

(b) A suspension of $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ (1.4 g, 5.0 mmol) and cyclopentadienylthallium (2.7 g, 10.0 mmol) in dimethoxyethane was refluxed under an inert atmosphere for 1 h. The hot reaction mixture was filtered in air, and the solvent was then removed under vacuum. The resulting solid residue was extracted with diethyl ether (4 × 20 mL). Evaporation of the solvent from these extracts yielded the crude product; yield 0.9 g (3.9 mmol, 78%). Analytically pure 1 was obtained by recrystallization as in (a) above.

**Preparation of $[Ru(\eta^5\text{-}C_5Me_5)_2]$ (2).** A mixture of $[\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ (5.6 g, 20.0 mmol) and $[Sn\text{-}n\text{-}Bu_3(C_5Me_5)]$ (23.2 g, 44.0 mmol) in ethanol (150 mL) was heated under reflux for 1.5 h during which time the suspension of the brown ruthenium polymer reacted into solution. The solution was filtered hot and then cooled to 0 °C. The resultant white crystalline precipitate was collected by filtration and washed with cold ethanol (15 mL) and diethyl ether (2 × 10 mL). Analytically pure $[Ru(\eta^5\text{-}C_5Me_5)_2]$ was readily obtained by recrystallization of the crude product from hot ethanol: yield 5.2 g (14.0 mmol, 70%); $^1H$ NMR ($CDCl_3$) $\delta$ 1.63 (s, $C_5Me_5$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 82.9 (s, $C_5Me_5$), 10.0 (s, $C_5Me_5$). Anal. Calcd for $C_{20}H_{30}Ru$: C, 64.55; H, 8.14. Found: C, 64.78; H, 8.36.

**Preparation of $[Os(\eta^5\text{-}C_5H_5)_2]$ (3).** $[Sn\text{-}n\text{-}Bu_3(C_5H_5)]$ (14.5 g, 43.0 mmol) was added to a stirred suspension of $[\{Os(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ (2.6 g, 7.0 mmol) in methanol (70 mL) and heated under reflux for 15 h. The reaction solution was filtered hot and then cooled to −10 °C. The white crystalline solid which forms is separated by filtration and washed with cold methanol (5 mL). Analytically pure $[Os(\eta^5\text{-}C_5H_5)_2]$ was obtained by recrystallization from hot methanol: yield 1.60 g (5.0 mmol, 72%). $^1H$ NMR ($CDCl_3$) $\delta$ 4.70 (s, $C_5H_5$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 63.6 (s, $C_5H_5$). Anal. Calcd for $C_{10}H_{10}Os$: C, 37.49; H, 3.15. Found: C, 37.71; H, 2.96.

**Preparation of $[Os(\eta^5\text{-}C_5Me_5)_2]$ (4).** Pentamethylcyclopentadiene (0.54 g, 4.0 mmol) was added to $Na_2[OsCl_6]$ (0.90 g, 2.0 mmol) in ethanol (50 mL) and the resultant mixture heated at reflux for 2 h. The solution was filtered hot and then cooled to −10 °C. The crop of colorless needle-like crystals was collected by filtration and washed with cold methanol (5 mL). Analytically pure $[Os(\eta^5\text{-}C_5Me_5)_2]$ was obtained by recrystallization of the crude product from methanol–diethyl ether mixtures: yield 0.76 g (1.6 mmol, 82%); $^1H$ NMR ($CDCl_3$) $\delta$ 1.70 (s, $C_5Me_5$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 77.8 (s, $C_5Me_5$), 10.3 (s, $C_5Me_5$). Anal. Calcd for $C_{20}H_{30}Os$: C, 52.14; H, 6.56. Found: C, 52.49; H, 6.75.

**Preparation of $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ (5).** A solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (0.31 g, 1.0 mmol) and freshly prepared $K[C_5H_4Me]$ (1.2 mmol) in air- and peroxide-free tetrahydrofuran (30 mL) was stirred at 25 °C for 1 h. The reaction solvent was removed under reduced pressure and the solid residue extracted with diethyl ether (2 × 50 mL). Cooling of the ether solution gave a pale yellow crystalline solid. Analytically pure $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ was obtained by recrystallization from hot methanol: yield 0.13 g (0.53 mmol, 53%). $^1H$ NMR ($CDCl_3$) $\delta$ 4.51 (m, 2 H, $C_5H_4Me$), 4.45 (s, 5 H, $C_5H_5$), 4.36 (m, 2 H, $C_5H_4Me$), 1.92 (s, 3 H, $C_5H_5Me$). Anal. Calcd for $C_{11}H_{12}Ru$: C, 53.86; H, 4.93. Found: C, 53.62; H, 4.85.

**Preparation of $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ (6).** In a procedure similar to that outlined for 5 above (except that 1.0 mmol of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ was treated with 1.2 mmol of $K[C_5Me_5]$), $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ was obtained as a white crystalline solid: yield 0.25 g (0.68 mmol, 68%); $^1H$ NMR ($CDCl_3$) $\delta$ 4.13 (s, 5 H, $C_5H_5$), 2.77 (s, 15 H, $C_5Me_5$). Anal. Calcd for $C_{15}H_{20}Ru$: C, 59.78; H, 6.69. Found: C, 59.99; H, 6.88.

**Preparation of $[Ru(\eta^5\text{-}C_5Me_5)_2Br]Br$ (7).** A solution of 2 (0.37 g, 1.0 mmol) in chloroform (50 mL) was treated with $Br_2$ (0.16 g, 1.0 mmol; solution in 50 mL of $CHCl_3$, dropwise addition at room temperature). On completion of the bromine addition, the reaction mixture was stirred at room temperature for a further 2 h. The solvent was removed under reduced pressure, giving a green crystalline solid. Recrystallization from methanol–diethyl ether gave analytically pure $[Ru(\eta^5\text{-}C_5Me_5)_2Br]Br$: yield 0.32 g (0.60 mmol, 60%); $^1H$ NMR ($CDCl_3$) $\delta$ 1.95 (s, $C_5Me_5$). Anal. Calcd for $C_{20}H_{30}Br_2Ru$: C, 45.21; H, 5.69; Br, 30.08. Found: C, 44.91; H, 5.45; Br, 29.68.

**Preparation of $[Ru(\eta^5\text{-}C_5Me_5)_2I]I_3$ (8).** A solution of 2 (0.56 g, 1.5 mmol) in $CCl_4$ (20 mL) at 25 °C was treated over a period of 5 min with iodine (0.76 g, 3.0 mmol; solution in 60 mL of $CCl_4$). The reaction mixture was stirred for a further 30 min at 25 °C. The yellow precipitate which formed in the reaction was filtered and washed with $CCl_4$ (10 mL). Recrystallization from dichloromethane–diethyl ether gave pure $[Ru(\eta^5\text{-}C_5Me_5)_2I]I_3$: yield 1.22 g (1.38 mmol, 92%); $^1H$ NMR ($CD_2Cl_2$) $\delta$ 2.06 (s, $C_5Me_5$). Anal. Calcd for $C_{20}H_{30}I_4Ru$: C, 27.32; H, 3.44; I. 57.74. Found: C, 27.39; H, 3.40; I, 58.40.

**Preparation of $[Os(\eta^5\text{-}C_5Me_5)_2Br]Br$ (9).** A procedure similar to that outlined for 7 above (except using 1.01 g (2.2 mmol) of

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**Table I. Crystal Data and Details of the Crystallographic Analyses**

| | [Ru($\eta^5$-$C_5Me_5$)$_2$] | [Os($\eta^5$-$C_5Me_5$)$_2$] |
|---|---|---|
| $M_r$ | 371.5 | 460.6 |
| space group | $P2_1/m$ | $P2_1/m$ |
| $a$, Å | 7.718 (1) | 7.741 (1) |
| $b$, Å | 14.646 (2) | 14.621 (3) |
| $c$, Å | 8.617 (1) | 8.617 (2) |
| $\beta$, deg | 106.50 (1) | 106.50 (1) |
| $U$, Å$^3$ | 933.96 | 935.10 |
| $Z$ | 2 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.321 | 1.636 |
| $\lambda$(Mo K$\alpha$), Å | 0.71069 | 0.71069 |
| $\mu$, cm$^{-1}$ | 7.41 | 65.31 |
| $F(000)$ | 388 | 452 |
| scan mode | $\omega-2\theta$ | $\omega-\theta$ |
| scan speed variable | 5.49°/min (max) | 5.50°/min (max) |
| scattering range | $3° \leq \theta \leq 30°$ | $3 \leq \theta \leq 30°$ |
| measd intensities | 3000 | 2986 |
| intensities with $F_0 \geq 4\sigma(F_0)$ | 2113 | 2316 |
| cryst dimens, mm | 0.54 × 0.50 × 0.37 | 0.40 × 0.36 × 0.38 |
| weighting scheme | $1/\sigma^2(F_o)$ | $1/\sigma^2(F_o)$ |
| $R$ | 0.0366 | 0.0348 |
| $R_w$ | 0.0365 | 0.0331 |
| $(\Delta/\sigma)_{max}$ | 0.001 | 0.001 |
| $\Delta\rho_{max}$, e Å$^{-3}$ | 0.43 | 1.84 |

**4** and 0.40 g (2.5 mmol) of $Br_2$) gave pure [Os($\eta^5$-$C_5Me_5$)$_2$Br]Br: yield 0.85 g (1.37 mmol, 63%); $^1$H NMR ($CDCl_3$) $\delta$ 2.06 (s, $C_5Me_5$). Anal. Calcd for $C_{20}H_{30}Br_2Os$: C, 38.72; H, 4.87; Br, 25.76. Found: C, 38.19; H, 4.80; Br, 26.57.

**Preparation of [Os($\eta^5$-$C_5Me_5$)$_2$I]$I_3$ (10).** A solution of iodine (1.3 g, 5.0 mmol) in $CCl_4$ (100 mL) was added over 5 min to a solution of **4** (1.01 g, 2.2 mmol) in $CH_2Cl_2$ (20 mL). The reaction mixture was stirred at room temperature for a further 1 h, and then the solvent was removed under vacuum. The solid residue was redissolved in $CH_2Cl_2$ (100 mL), and excess iodine was removed by washing the solution with aqueous potassium iodide solutions (5 portions, 2 g of KI in 20 mL of water each). The $CH_2Cl_2$ solution was dried over anhydrous sodium sulfate and filtered. Methanol (30 mL) was added to the filtrate and the dichloromethane boiled off. Cooling of the methanol solution to room temperature yielded a crop of brown crystals. Analytically pure [Os($\eta^5$-$C_5Me_5$)$_2$I]$I_3$ was obtained by recrystallization of the crude product from hot toluene: yield 1.8 g (1.9 mmol, 85%); $^1$H NMR ($CDCl_3$) $\delta$ 2.12 (s, $C_5Me_5$). Anal. Calcd for $C_{20}H_{30}I_4Os$; C, 24.81; H, 3.12; I, 52.42. Found: C, 24.91; H, 3.11; I, 53.42.

**Collection of Diffraction Data for [Ru($\eta^5$-$C_5Me_5$)$_2$] (2) and [Os($\eta^5$-$C_5Me_5$)$_2$] (4).** Crystals of both **2** and **4** were grown by slow evaporation from diethyl ether solutions over a period of 3–4 weeks. Examination of the crystals under a stereomicroscope in polarized light showed extinction of the polarized beam propagated along two of the morphological axes of the crystal, but not the third. This unique direction was later found to correspond with the crystallographic *a* axis. Preliminary oscillation and Weissenberg photographs established that the crystals were single, monoclinic, and conforming to space group $P2_1$ or $P2_1/m$. Suitable single crystals were mounted on an Enraf-Nonius CAD-4 diffractometer for data collection. The [Os($\eta^5$-$C_5Me_5$)$_2$] crystal was ground to a sphere (radius 0.19 mm). Data were corrected for background, Lorentz, and polarization factors as well as the absorption, on the basis of azimuthal scans of nine reflections.[23]

**Structure Solution and Refinement.** The structures were solved by conventional heavy-atom techniques using the program SHELX.[24] Crystal data and details of the crystallographic analyses are given in Table I. Refinement was done by using SHELX 76[24] on the CDC-750 of the Centre for Computing Services, CSIR. Since the ruthenium and four carbons appeared on the crystallographic mirror plane at ($x$, $^1/_4$, $z$), 12 independent carbons had to be placed. These showed up in the first difference Fourier. Refinement of the trial structure using isotropic temperature factors yielded a slightly distorted structure at $R = 0.08$. In addition, strong satellite peaks were observed on each side of all carbon atoms. This became more apparent when the $C_5Me_5$ groups were fixed as rigid bodies across the mirror plane, with idealized geometry [$d$(C–C) = 1.422 Å; $d$(C–C(Me)) = 1.501 Å; C–C–C(Me) = 120°] and a common isotropic temperature factor ($R = 0.09$). These features revealed disorder in the structure, like the static rotational disorder across the mirror plane in the structure of anthracene-tetracyanobenzene.[25] However, attempts to refine a disorder model using the methods developed before[25] or refinement in the alternate space group $P2_1$ did not lead to a significantly better fit. This could reflect limitations on the rigid-body thermal constraints, which could allow extra degrees of freedom, such as variation in C–C bond length and out-of-plane bending of the methyl groups. It was therefore decided to describe the average structure by allowing all atoms to refine with anisotropic temperature factors, despite their unusually large magnitudes for carbon atoms in the mirror plane. Final fractional atomic coordinates and anisotropic temperature parameters for [Ru($\eta^5$-$C_5Me_5$)$_2$] and [Os($\eta^5$-$C_5Me_5$)$_2$] are listed in Tables II and III. Hydrogen atoms were not placed.

## Results and Discussion

**Synthesis of Metallocenes.** Since the discovery of ruthenocene by Wilkinson[4] in 1952, a diverse range of synthetic procedures have been devised to complement the original (low-yield) synthesis from Ru(acac)$_3$ and ($C_5H_5$)MgBr.[1,2] In principle, ruthenocene should be obtainable (like ferrocene) from a wide range of ruthenium salts and compounds, and to a certain extent this is the case. However, the difference lies in that whereas ferrocene is nearly always obtained in high yields, ruthenocene is usually obtained either in poor yield or, if the yields are good, in small batch processes which apparently can only be scaled up with a not inconsiderable attendant loss of ruthenium.

The most convenient route to ruthenocene reported to date remains the direct reaction between commercially available ruthenium trichloride and cyclopentadiene in ethanol solution,[8] optionally using zinc as a mild reducing agent.[9,10] Seemingly simple "$RuCl_3 \cdot xH_2O$", however, has several disadvantages as a synthetic precursor, including variable composition and oxidation state and the need for a reducing step (mediated, for example, by excess $C_5H_6$ or by zinc dust), all of which combine to produce the variable (low) yields and scale-up problems associated with the direct route to ruthenocene.

As part of our attempt to develop the chemistry of cyclopentadienyl–ruthenium and –osmium complexes along lines more general than that presently possible using the limited number of synthetic precursors currently available,[1,2] we sought high-yield, large-scale, but at the same time, reproducible syntheses of ruthenium and osmium metallocenes. We considered that ruthenium trichloride, being the most readily available of the commercial ruthenium salts, should form the basis of the route, but by its high-yield conversion to a suitable ruthenium(II) precursor to ruthenocene, it would be possible to eliminate the problems associated with the use of ruthenium trichloride itself. The polymeric ruthenium(II) complex [{Ru($\eta^4$-$C_8H_{12}$)$Cl_2$}$_x$],[15] obtainable in quantitative yield from almost any grade of commercial ruthenium trichloride and excess cycloocta-1,5-diene in ethanol solution, fulfilled these requirements.

Thus, treatment of [{Ru($\eta^4$-$C_8H_{12}$)$Cl_2$}$_x$] with cyclopentadienylthallium in dimethoxyethane or with [Sn-*n*-

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**Table II**

a. Fractional Coordinates (×10$^4$; ×10$^5$ for Ru) and Equivalent Isotropic Temperature Factors (Å$^2$; ×10$^3$; ×10$^4$ for Ru) for [Ru($C_5Me_5$)$_2$]

| | $x/a$ | $y/b$ | $z/c$ | $U$(eq) | | $x/a$ | $y/b$ | $z/c$ | $U$(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Ru | 7976 (6) | 25000 | 29191 (6) | 378 (3) | C(11) | 3361 (8) | 3588 (4) | 6112 (7) | 70 (3) |
| C(1) | 3260 (6) | 2983 (3) | 4666 (6) | 44 (2) | C(21) | 3307 (9) | 4277 (4) | 2590 (9) | 78 (4) |
| C(2) | 3216 (6) | 3283 (4) | 3079 (6) | 50 (3) | C(31) | 3298 (13) | 2500 | 369 (11) | 86 (7) |
| C(3) | 3225 (9) | 2500 | 2102 (9) | 51 (4) | C(41) | −1710 (8) | 3588 (4) | 4886 (8) | 71 (4) |
| C(4) | −1616 (6) | 2991 (3) | 3473 (3) | 48 (2) | C(51) | −1752 (10) | 4273 (5) | 1341 (11) | 91 (5) |
| C(5) | −1638 (6) | 3283 (4) | 1900 (7) | 57 (3) | C(61) | −1766 (14) | 2500 | −852 (11) | 103 (7) |
| C(6) | −1629 (10) | 2500 | 940 (9) | 60 (5) | | | | | |

b. Anisotropic Temperature Factors (Å$^2$; ×10$^3$; ×10$^4$ for Ru) for [Ru($C_5Me_5$)$_2$]

| | $U$(11) | $U$(22) | $U$(33) | $U$(23) | $U$(13) | $U$(12) |
|---|---|---|---|---|---|---|
| Ru | 376 (3) | 422 (4) | 380 (3) | 0 | 121 (2) | 0 |
| C(1) | 43 (2) | 40 (2) | 53 (3) | −4 (2) | 8 (2) | −6 (2) |
| C(2) | 40 (2) | 59 (3) | 68 (3) | 19 (3) | 13 (2) | −8 (2) |
| C(3) | 34 (3) | 111 (7) | 48 (4) | 0 | 21 (3) | 0 |
| C(4) | 40 (2) | 55 (3) | 62 (3) | 4 (2) | 20 (2) | 9 (2) |
| C(5) | 43 (3) | 85 (4) | 69 (4) | 29 (3) | 18 (3) | 18 (3) |
| C(6) | 37 (4) | 164 (10) | 38 (4) | 0 | 9 (3) | 0 |
| C(11) | 85 (4) | 69 (4) | 71 (4) | −28 (3) | 9 (3) | 1 (3) |
| C(21) | 91 (4) | 73 (4) | 127 (6) | 48 (4) | 27 (4) | −21 (3) |
| C(31) | 76 (6) | 211 (13) | 55 (5) | 0 | 34 (5) | 0 |
| C(41) | 84 (4) | 74 (4) | 97 (4) | −22 (4) | 48 (4) | 11 (3) |
| C(51) | 97 (5) | 120 (6) | 164 (7) | 95 (6) | 60 (5) | 52 (4) |
| C(61) | 81 (6) | 275 (17) | 50 (6) | 0 | 12 (5) | 0 |

**Table III**

a. Fractional Coordinates (×10$^4$; ×10$^5$ for Os) and Equivalent Isotropic Temperature Factors (Å$^2$; X10$^3$; ×10$^4$ for Os) for [Os($C_5Me_5$)$_2$]

| | $x/a$ | $y/b$ | $z/c$ | $U$(eq) | | $x/a$ | $y/b$ | $z/c$ | $U$(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Os | 8008 (4) | 25000 | 29331 (4) | 374 (2) | C(11) | 3387 (11) | 3579 (6) | 6101 (10) | 68 (5) |
| C(1) | 3253 (7) | 2984 (4) | 4670 (7) | 43 (3) | C(21) | 3358 (15) | 4256 (6) | 2567 (14) | 82 (7) |
| C(2) | 3248 (8) | 3277 (5) | 3103 (8) | 53 (3) | C(31) | 3326 (17) | 2500 | 424 (15) | 82 (9) |
| C(3) | 3196 (12) | 2500 | 2102 (11) | 56 (5) | C(41) | −1693 (11) | 3567 (6) | 4886 (11) | 74 (5) |
| C(4) | −1620 (7) | 2979 (4) | 3485 (7) | 50 (3) | C(51) | −1761 (16) | 4256 (8) | 1342 (13) | 93 (9) |
| C(5) | −1643 (8) | 3289 (5) | 1924 (8) | 60 (4) | C(61) | −1773 (19) | 2500 | −798 (16) | 97 (10) |
| C(6) | −1631 (13) | 2500 | 967 (12) | 63 (6) | | | | | |

b. Anisotropic Temperature Factors (Å$^2$; ×10$^3$; ×10$^4$ for Os) for [Os($C_5Me_5$)$_2$]

| | $U$(11) | $U$(22) | $U$(33) | $U$(23) | $U$(13) | $U$(12) |
|---|---|---|---|---|---|---|
| Os | 393 (2) | 408 (2) | 353 (2) | 0 | 101 (1) | 0 |
| C(1) | 47 (3) | 39 (3) | 46 (3) | −2 (3) | 11 (3) | 0 (2) |
| C(2) | 42 (3) | 60 (4) | 67 (4) | 14 (3) | 10 (3) | −2 (3) |
| C(3) | 57 (6) | 83 (7) | 40 (5) | 0 | 13 (4) | 0 |
| C(4) | 45 (3) | 59 (4) | 54 (3) | 3 (3) | 18 (3) | −1 (3) |
| C(5) | 50 (4) | 85 (5) | 59 (4) | 23 (4) | 8 (3) | 7 (4) |
| C(6) | 42 (5) | 147 (12) | 46 (6) | 0 | 15 (5) | 0 |
| C(11) | 73 (5) | 67 (5) | 70 (5) | −19 (4) | 2 (4) | 7 (4) |
| C(21) | 85 (7) | 70 (7) | 148 (11) | 52 (7) | 31 (7) | −8 (6) |
| C(31) | 52 (7) | 165 (16) | 72 (8) | 0 | 21 (6) | 0 |
| C(41) | 77 (6) | 71 (6) | 94 (6) | −7 (5) | 37 (5) | 7 (4) |
| C(51) | 92 (7) | 107 (10) | 149 (12) | 73 (8) | 37 (9) | 40 (8) |
| C(61) | 56 (8) | 235 (22) | 69 (9) | 0 | 2 (7) | 0 |

$Bu_3(C_5H_5)$] in boiling ethanol gives, after product workup, high yields of ruthenocene [Ru($\eta^5$-$C_5H_5$)$_2$] (**1**). In a similar manner decamethylruthenocene [Ru($\eta^5$-$C_5Me_5$)$_2$] (**2**) has been prepared in 70% yield by the action of [Sn-*n*-$Bu_3$($C_5Me_5$)] on [{Ru($\eta^4$-$C_8H_{12}$)$Cl_2$}$_x$]. The most notable features of these reactions are the reproducibly high yields of metallocene product and the fact that the preparations can be carried out successfuly on both small and large scales. It is also to be noted that unreacted tin reagent (together with the byproduct of the synthesis [Sn-*n*-$Bu_3Cl$]) may be recovered from the mother liquors of the reactions by distillation techniques and regenerated by using standard procedures.[22] Both **1** and **2** have been characterized on the basis of elemental analysis and spectroscopic properties.

The first reported synthesis of osmocene by Fischer and Grubert[13] in 1959, the extended reflux of $OsCl_4$ with $NaC_5H_5$ in tetrahydrofuran or dimethoxyethane, remains, despite the disappointingly low yields of metallocene, the only reliable synthesis of this compound. We were thus encouraged by the results obtained for ruthenocene to explore a similar route to osmocene. Indeed, the polymer [{Os($\eta^4$-$C_8H_{12}$)$Cl_2$}$_x$][16] reacts with [Sn-*n*-$Bu_3$($C_5H_5$)] in refluxing methanol to give [Os($\eta^5$-$C_5H_5$)$_2$] (**3**) (yield 70%). In common with the ruthenium reactions, this provides a simple reproducible route to the metallocene, successful even on a scale of several grams.

In contrast, attempts to synthesize the new metallocene, decamethylosmocene, by the corresponding reaction of [Sn-*n*-$Bu_3$($C_5Me_5$)] with [{Os($\eta^4$-$C_8H_{12}$)$Cl_2$}$_x$] led only to the osmium–hydride complex [($\eta^5$-$C_5Me_5$)Os($\eta^4$-$C_8H_{12}$)H][14,26] (yield 80%). Although this compound can be converted quantitatively to the corresponding chloride [($\eta^5$-$C_5Me_5$)-

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[26] Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B., unpublished results.

**Table IV. Bond Lengths (Å) and Angles (deg)**

a. $[Ru(C_5Me_5)_2]$

Bond Lengths

| | | | |
|---|---|---|---|
| Ru-C(1) | 2.180 (4) | Ru-C(2) | 2.161 (4) |
| Ru-C(3) | 2.181 (6) | Ru-C(4) | 2.173 (4) |
| Ru-C(5) | 2.164 (5) | Ru-C(6) | 2.145 (7) |
| C(1)-C(1′) | 1.415 (9) | C(1)-C(2) | 1.427 (7) |
| C(1)-C(11) | 1.512 (7) | C(2)-C(3) | 1.424 (6) |
| C(2)-C(21) | 1.522 (7) | C(3)-C(31) | 1.510 (11) |
| C(4)-C(4′) | 1.438 (9) | C(4)-C(5) | 1.417 (7) |
| C(4)-C(41) | 1.518 (7) | C(5)-C(6) | 1.415 (7) |
| C(5)-C(51) | 1.523 (9) | C(6)-C(61) | 1.518 (12) |

Bond Angles

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(11) | 126.2 (5) | C(1)-C(2)-C(3) | 108.4 (5) |
| C(1)-C(2)-C(21) | 124.4 (5) | C(3)-C(2)-C(21) | 126.7 (6) |
| C(2)-C(3)-C(31) | 126.3 (4) | C(5)-C(4)-C(41) | 127.1 (5) |
| C(4)-C(5)-C(6) | 108.3 (6) | C(4)-C(5)-C(51) | 125.0 (7) |
| C(6)-C(5)-C(51) | 126.6 (6) | C(5)-C(6)-C(61) | 125.8 (4) |

b. $[Os(C_5Me_5)_2]$

Bond Lengths

| | | | |
|---|---|---|---|
| Os-C(1) | 2.175 (5) | Os-C(2) | 2.178 (6) |
| Os-C(3) | 2.169 (9) | Os-C(4) | 2.176 (5) |
| Os-C(5) | 2.175 (6) | Os-C(6) | 2.145 (10) |
| C(1)-C(1′) | 1.414 (10) | C(1)-C(2) | 1.416 (7) |
| C(1)-C(11) | 1.488 (9) | C(2)-C(3) | 1.419 (8) |
| C(2)-C(21) | 1.514 (10) | C(3)-C(31) | 1.478 (14) |
| C(4)-C(4′) | 1.402 (12) | C(4)-C(5) | 1.414 (8) |
| C(4)-C(41) | 1.497 (9) | C(5)-C(6) | 1.419 (8) |
| C(5)-C(51) | 1.495 (12) | C(6)-C(61) | 1.49 (2) |

Bond Angles

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(11) | 126.4 (6) | C(1)-C(2)-C(3) | 109.2 (6) |
| C(1)-C(2)-C(21) | 126.3 (7) | C(3)-C(2)-C(21) | 124.4 (7) |
| C(2)-C(3)-C(31) | 126.6 (4) | C(5)-C(4)-C(41) | 126.2 (6) |
| C(4)-C(5)-C(6) | 107.0 (7) | C(4)-C(5)-C(51) | 127.2 (8) |
| C(6)-C(5)-C(51) | 125.8 (7) | C(5)-C(6)-C(61) | 125.5 (4) |

$Os(\eta^4\text{-}C_8H_{12})Cl]$,[14,26] further reaction of either of these with $[Sn\text{-}n\text{-}Bu_3(C_5Me_5)]$ or other cyclopentadienylating agents (e.g., $LiC_5Me_5$) to give decamethylosmocene could not be achieved. (The eventual product of the reaction of $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ with $[Sn\text{-}n\text{-}Bu_3(C_5Me_5)]$ was $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})H]$. It is possible that this reaction occurs via the intermediacy of $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})(\eta^1\text{-}C_5Me_5)]$.) These results lead us to propose that the reactions between the polymers $[\{M(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ (M = Ru, Os) and the $[Sn\text{-}n\text{-}Bu_3(C_5R_5)]$ (R = H, Me) reagents to give the metallocenes **1**–**3** probably proceeds via intermediates similar to $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})X]$ above. No direct evidence for the intermediacy of such species in these reactions has, however, been found, even with equimolar additions of $[Sn\text{-}n\text{-}Bu_3(C_5R_5)]$ reagent to the polymers (which give only correspondingly lower yields of the metallocenes). As indirect evidence though, the cyclooctadiene ligands in the complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (R = H,[17,27] Me) have been found to be highly labile in acetone or ethanol solution, reacting rapidly with $[Sn\text{-}n\text{-}Bu_3(C_5R_5)]$ to give **1** and **2** in high yield. We thus suggest that the introduction of the first cyclopentadienyl moiety into $[\{M(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ (M = Ru, Os) is the rate-determining step and that the high lability of the cyclooctadiene ligand in the intermediate half-sandwich complex $[(\eta^5\text{-}C_5R_5)M(\eta^4\text{-}C_8H_{12})Cl]$ results in rapid further reaction with the tin reagent to give the metallocene product. The failure to synthesize decamethylosmocene from $[\{Os(\eta^4\text{-}C_8H_{12})Cl_2\}_x]$ is thus attributable to the unusual stability of both $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})H]$ and $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ to cyclooctadiene displacement.

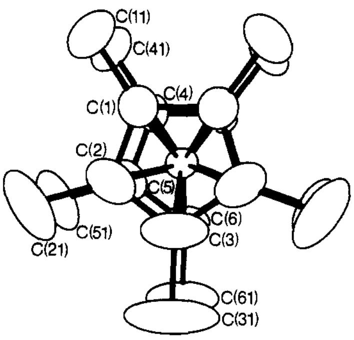

**Figure 1.** The structure of $[Ru(\eta^5\text{-}C_5Me_5)_2]$ projected on to the cyclopentadienyl planes, showing thermal ellipsoids drawn at the 50% level.

With use of the reactive half-sandwich complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ as an intermediate, a series of mixed-ligand metallocenes have been synthesized. Thus, reaction with the cyclopentadienylating reagents $K[C_5H_4Me]$ and $K[C_5Me_5]$ in tetrahydrofuran gives $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ (**5**) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ (**6**) in moderate to good yield. This procedure represents, to date, the most general approach to the synthesis of mixed-ligand ruthenocenes and should be widely applicable.

The stability of the complexes $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})X]$ suggested that an alternative synthetic route to decamethylosmocene which avoided intermediates of this type could be more successful. Thus, the reaction of $Na_2[OsCl_6]$ directly with pentamethylcyclopentadiene in refluxing ethanol gives decamethylosmocene $[Os(\eta^5\text{-}C_5Me_5)_2]$ (**4**) in 80% yield. Reaction of $H_2[OsCl_6]$ with pentamethylcyclopentadiene under similar experimental conditions also gives **4** although in this case the yield is only ca. 25% and the osmium(IV) species $[Os(\eta^5\text{-}C_5Me_5)_2Cl]Cl$ is a significant contaminant.

**Structures of Decamethylruthenocene and Decamethylosmocene.** Because of the continuing interest in the structural chemistry of metallocenes and their derivatives,[1-3,28] the X-ray crystal structures of **2** and **4** have been determined.

In symmetrical metallocenes $[M(\eta^5\text{-}C_5R_5)_2]$ (M = Fe, Ru, Os; R = H, Me) the polarization of the metal ion in the field of the two five-membered rings would be expected to favor an eclipsed ($D_{5h}$) arrangement of the rings.[29] The polarizability of the metal ions in these complexes increases as $P(Fe) < P(Ru) < P(Os)$, and thus the eclipsed form of the complexes is expected to be stabilized in the order $[Fe(\eta^5\text{-}C_5R_5)_2] < [Ru(\eta^5\text{-}C_5R_5)_2] < [Os(\eta^5\text{-}C_5R_5)_2]$ (R = H, Me). A stable orthorhombic form of ferrocene containing only eclipsed ($D_{5h}$) molecules has been reported,[30] and for ruthenocene[31] and osmocene[32] only the eclipsed forms have been observed in the solid state. Calculations of the induction energy arising from the polarization of the metal ions show that the eclipsed forms of ferrocene and ruthenocene are stabilized by 4.5 and 4.7 kJ $mol^{-1}$ respectively, relative to the staggered forms.[29] Thus, in the absence of significant intramolecular steric interactions eclipsed ($D_{5h}$) configurations would be expected for the $[M(\eta^5\text{-}C_5Me_5)_2]$ (M = Fe, Ru, Os) complexes. However, for decamethylferrocene, a staggered conformation of the

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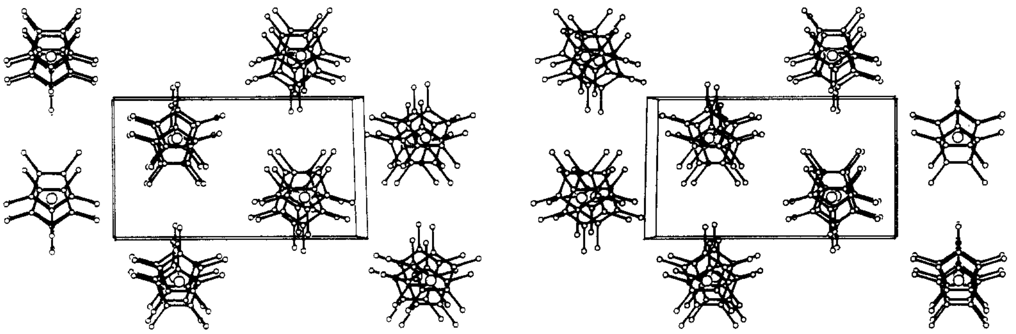

**Figure 2.** Stereoscopic drawing to show the $[Ru(\eta^5\text{-}C_5Me_5)_2]$ unit cell in (100) projection. The *c* axis is across and *b* up the page.

$C_5Me_5$ moieties has been reported[33,34] and calculated to be 4.2 kJ mol$^{-1}$ more stable than the eclipsed form. In this complex unfavorable intramolecular methyl–methyl interactions are presumably responsible for the adoption of the staggered conformation. For decamethylruthenocene (**2**) and decamethylosmocene (**4**) the greater separation of the cyclopentadienyl rings (interplanar distances of 3.60 (1) and 3.61 (1) Å, respectively, relative to 3.31 Å in decamethylferrocene) accommodate the eclipsed conformation with no more significant steric interactions than in the staggered iron analogue. Thus the closest approach of two methyl centres in either of the two eclipsed structures is ca. 3.78 (1) Å compared with interligand methyl–methyl contacts of 3.79 (1)–3.85 (1) Å[33,34] in the staggered iron analogue.

Therefore, whereas in the iron analogue the steric strain introduced by methyl–methyl contacts in an eclipsed conformation outweights the polarization stabilization and results in the adoption of a staggered conformation, in the ruthenium and osmium analogues the greater polarization stabilization and reduced steric strain compared to the iron analogue combine to favor the eclipsed conformation.

The metal atom and carbon atom C(3), C(31), C(6), and C(61) (Figure 1) lie on the crystallographic mirror plane in $P2_1/m$, and the molecule has $D_{5h}$ symmetry. Anisotropic thermal parameters of the carbon atoms, however, are as high as 0.275 and 0.375 Å$^2$ for the methyl carbon atoms of **2** and **4**, respectively. This implied disorder could arise from a random distribution of $D_{5h}$ molecules rotationally slightly displaced from the mirror plane, but indistinguishable from a random distribution of $D_{5d}$ molecules. Calculation of the lattice energy as a function of concerted molecular fragment rotation using methods developed previously[35] are consistent with the expected disorder. Another physical manifestation of the rotational disorder is the absence of extinction in polarized light along the crystallographic *a* axis. The $C_5Me_5$ moieties lie parallel to the *c* axis with an angle of 16° between the plane normal and the *z* axis (Figure 2). Viewed along [100] the crystal therefore *appears* to be isotropic. The crystals are predicted to undergo a phase transition on cooling, probably by a mechanism similar to that proposed, and observed for ferrocene.[35]

Despite accurate reflection data, possible disorder precludes a detailed comparison of molecular geometry of the compounds. However, the bond lengths and angles are compatible with previously reported structures. For example, *d*(Ru–C) = 2.17 (1) Å compared with 2.186 (3) Å in ruthenocene[31] and *d*(Os–C) = 2.18 (1) Å compared with 2.19 (1) Å in osmocene.[32]

**Oxidations.** Ferrocene readily undergoes oxidation reactions,[36] and it is thus surprising, considering that the higher oxidation states in the 4d and 5d metals are favored compared to the 3d metals, that relatively little work has been reported on the oxidation of ruthenocene and osmocene derivatives.[1-3]

In a similar manner to ruthenocene,[1,2] halogens cleanly oxidize **2** and **4** to the corresponding ruthenium(IV) and osmium(IV) cations $[Ru(\eta^5\text{-}C_5Me_5)_2X]Y$ (X, Y = Br, **9**; X = I, Y = $I_3$, **10**) and $[Os(\eta^5\text{-}C_5Me_5)_2X]Y$ (X, Y = Br, **11**; X = I, Y = $I_3$, **12**). Complexes **9–12** have been characterized by elemental analysis and by $^1$H NMR spectroscopy. The X-ray crystal structure of $[Ru(\eta^5\text{-}C_5H_5)_2I]I_3$ has been reported by Gray et al.,[36] and presumably **9–12** have similar bent sandwich structures. (One interesting difference though would relate to possible greater interligand steric repulsion due to the cyclopentadienyl methyl groups in **9–12**.)

Further, in accordance with the known reactivity patterns of ruthenocene and osmocene,[1-3] the electron-rich metal centers in **2** and **4** are reversibly protonated by strong acids. With $CF_3COOH$ in $CDCl_3$, the hydride cations $[M(\eta^5\text{-}C_5Me_5)_2H]^+$ are inferred from the high-field $^1$H NMR resonances at $\delta$ −8.30 (M = Ru) and −15.67 (M = Os) (M = Ru, $C_5\mathit{Me}_5$, $\delta$ 1.84; M = Os, $C_5\mathit{Me}_5$, $\delta$ 2.10). Similar results have been obtained with $HPF_6$ in $CDCl_3$. No attempt has been made to isolate these compounds.

## Conclusion

The procedures described here represent the first generalized syntheses of ruthenocenes and mixed-ligand ruthenocenes and the first high-yield syntheses of osmocene and decamethylosmocene. Thus, for the first time, large amounts of decamethylruthenocene, osmocene, and decamethylosmocene and also of mixed-ligand ruthenocenes are now available for studies of their physical, chemical, and technological properties.

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**Registry No.** **1**, 1287-13-4; **2**, 84821-53-4; **3**, 1273-81-0; **4**, 100603-32-5; **5**, 33270-46-1; **6**, 100462-22-4; **7**, 100462-14-4; **8**, 104293-23-4; **9**, 100462-15-5; **10**, 104293-25-6; Sn-*n*-$Bu_3(C_5H_5)$, 3912-86-5; $\{Ru(\eta^4\text{-}C_8H_{12})Cl_2\}_x$, 50982-13-3; $TlC_5H_5$, 34822-90-7;

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**Supplementary Material Available: Available**: Listings of observed and calculated structure factors for decamethylruthenocene and decamethylosmocene (19 pages). Ordering information is given on any current masthead page.

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# Dynamics of Internal Motion in Nonacarbonyl($\eta^6$-mesitylene)tetracobalt and Nonacarbonyl($\eta^6$-triptycene)tetracobalt. Carbonyl Scrambling and Rotation about the Triptycene–Cobalt Axis

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Variable-temperature $^{13}C$ NMR studies of noncarbonyl($\eta^6$-triptycene)tetracobalt (1) and nonacarbonyl($\eta^6$-mesitylene)tetracobalt (2) are reported. The rate constants of carbonyl group exchange between bridging, equatorial, and axial sites have been determined from a line-shape analysis of the spectra, and it is found that the relative rates of the bridging–equatorial, bridging–axial, and axial–equatorial transposition processes in both compounds are markedly temperature-dependent. The plots of ln $k$ vs. $1/T$ of both compounds show crossover regions in which the $\Delta G^{\ddagger}$ values of the three processes are almost the same: 10.8 kcal mol$^{-1}$ at 225 K for 1 and 13.3 kcal mol$^{-1}$ at 285 K for 2. Rotation about the triptycene–cobalt axis in 1 is faster than carbonyl scrambling over the temperature range examined, 178–308 K. The activation energy for rotation is $E_a$ = 8.2 kcal mol$^{-1}$.

The molecular structure of nonacarbonyl($\eta^6$-triptycene)tetracobalt (1) shows clear evidence of strong repulsive interactions between the $Co_4(CO)_9$ fragment and the proximal ring of the triptycene moiety.[2] The same interactions are expected to manifest themselves in a substantial barrier to rotation about the arene–metal axis: although such barriers are generally quite low,[3] bulky substituents have the effect of increasing the activation energy.[4,5] In the case of 1, this internal motion is accompanied by the scrambling of terminal and bridging carbonyl groups on the three basal cobalt atoms. In this paper we report the results of a variable-temperature NMR study whose aim was to obtain a quantitative measure of the energy barriers for all of these processes.

## Results and Discussion

As a first step, we investigated the kinetics of carbonyl scrambling in nonacarbonyl($\eta^6$-mesitylene)tetracobalt (2),[6] a $\pi$ complex related to 1 in which rotation about the arene–cobalt axis is NMR-invisible because of molecular $C_3$ or $C_{3v}$ symmetry (Figure 1).[7] The 62.83-MHz $^{13}C$ NMR

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