

Highly Fluxional Arene Cyclooctatetraene Complexes of Zerovalent Iron, Ruthenium, and Osmium. Single-Crystal X-ray Study of (Cyclooctatetraene)(hexamethylbenzene)ruthenium(0), $\text{Ru}(\eta^6\text{-HMB})(1\text{-}4\text{-}\eta\text{-COT})^1$

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Complexes of general formula $\text{M}(\text{arene})(\text{COT})$ ($\text{M} = \text{Fe, Ru, Os}$; arene = C_6H_6 , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, HMB) have been prepared by reaction of COT^{2-} with bis(η^6 -arene)iron(II) salts $[\text{Fe}(\text{arene})_2](\text{PF}_6)_2$ or with (η^6 -arene)ruthenium(II) or -osmium(II) halide derivatives such as $[\text{RuCl}_2(\text{arene})_2]$, $\text{OsCl}_2(\text{C}_6\text{H}_6)(\text{CH}_3\text{CN})$, and $\text{Os}_4\text{Cl}_9(1,3,5\text{-C}_6\text{H}_3\text{Me}_3)_3$. Yields range from 15 to 50%, decreasing in the orders $\text{Fe} > \text{Ru} > \text{Os}$ and $\text{HMB} > \text{C}_6\text{H}_3\text{Me}_3 > \text{C}_6\text{H}_6$. The complex $\text{Ru}(\text{HMB})(\text{COT})$ crystallizes in space group $P2_1/n$ with $a = 8.8460$ (6) Å, $b = 18.0622$ (10) Å, $c = 10.8181$ (4) Å, $\beta = 91.49$ (2)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least-squares methods to $R = 0.047$ for 1746 reflections. The complex contains a slightly nonplanar η^6 -HMB ring and a hinged 1-4- η -COT ring, the dihedral angle between the coordinated and uncoordinated diene sections of the latter being 45.4°. The mean distances from ruthenium to the arene carbon atoms and to the inner and terminal carbon atoms of the bound diene unit are 2.203, 2.120, and 2.233 Å, respectively. The Ru-C(diene) distances are significantly shorter than those reported for $\text{Ru}(\text{CO})_3(\text{COT})$, implying that COT is more firmly bound in the arene complexes than in the tricarbonyl. Variable-temperature ^1H and ^{13}C NMR measurements show that the COT ring is more fluxional in the arene complexes than in the corresponding tricarbonyls, the estimated difference in activation energy for rearrangement for the ruthenium complexes being about 2 kcal/mol. This may be a consequence of increased back-bonding to the COT ring in the arene complexes, leading to a transition state for rearrangement close to COT^{2-} .

Introduction

In its mononuclear complexes with d^8 transition elements, cyclooctatetraene commonly behaves either as a chelating 1,5-diene (1,2,5,6- η bonding) or as a conjugated 1,3-diene (1-4- η bonding).² The first alternative is favored for d^8 metals in +1 or +2 oxidation states, e.g., $\text{PtR}_2(\text{COT})$ ^{3,4} ($\text{R} = \text{halide}$ or alkyl), $[\text{RhCl}(\text{COT})]_2$,⁵ and $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{COT})$ ($\text{M} = \text{Co, Rh, Ir}$),⁶ while the second alternative is adopted in complexes of zerovalent iron and ruthenium, e.g., $\text{M}(\text{CO})_3(\text{COT})$ ($\text{M} = \text{Fe, Ru}$),^{7,8} $\text{Fe}(\eta^6\text{-COT})(\eta^4\text{-COT})$,⁹ and $\text{Fe}(\text{CO})(\eta^4\text{-COT})(\eta^4\text{-C}_4\text{H}_6)$.¹⁰ In the case of $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-COT})$ ($\text{M} = \text{Rh, Ir}$), both 1-4- η and 1,2,5,6- η isomers can be detected, the latter being thermodynamically the more stable.¹¹ Without exception, the 1-4- η - C_8H_8 complexes show only one proton or ^{13}C resonance in their NMR spectra at room temperature, but only in the case of $\text{M}(\text{CO})_3(\text{COT})$ ($\text{M} = \text{Fe, Ru, Os}$) have low-temperature limiting spectra been obtained.¹²⁻¹⁴ The fluxional behavior inferred from line-shape analysis of the iron and ruthenium complexes is a sequence of 1,2 shifts of the metal with its associated ligands relative to the ring. It has also been claimed¹⁵ that $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(1,2,5,6\text{-}\eta\text{-COT})$ is

fluxional at elevated temperature as a result of interchange of coordinated and uncoordinated double bonds. In this paper¹⁶ we report the preparation, structural characterization, and fluxional behavior of the complexes $\text{M}(\eta^6\text{-arene})(\eta^4\text{-COT})$ ($\text{M} = \text{Fe, Ru, Os}$) which can be compared directly with the isoelectronic series $\text{M}(\text{CO})_3(\text{COT})$ ($\text{M} = \text{Fe, Ru, Os}$) and $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{COT})$ ($\text{M} = \text{Co, Rh, Ir}$).

Experimental Section

All reactions were carried out in a nitrogen atmosphere by using standard techniques for handling air-sensitive materials, and solvents were dried and deoxygenated before use. IR spectra were measured as Nujol mulls on cesium iodide plates on a PE 457 spectrophotometer. Proton NMR spectra were recorded at 34 °C on either a Varian HA-100 or Jeolco MH-100 instrument using $(\text{CH}_3)_4\text{Si}$ as internal reference. Variable-temperature ^{13}C and ^1H spectra were obtained on either a Jeolco FX-60 (15.04 MHz for ^{13}C) or Bruker HX-270 (67.89 MHz for ^{13}C) instrument. Mass spectra were measured on an MS-902 instrument operating at 70 eV. Microanalyses were carried out in the microanalytical laboratories of this school, of the John Curtin School of Medical Research, and of CSIRO (Parkville, Victoria). Analyses and spectroscopic data (mass, IR and ^1H NMR) are in Table I; ^{13}C NMR data are in Table II.

Literature procedures were followed to prepare 1-*tert*-butyl-1,4-cyclohexadiene,¹⁷ 1,3,5-trimethyl-1,4-cyclohexadiene,^{18,19} $[\text{Fe}(\text{arene})_2](\text{PF}_6)_2$ (arene = benzene, mesitylene, or HMB),^{20,21} $[\text{RuCl}_2(\text{arene})_2]$, and $\text{RuCl}_2(\text{arene})\text{py}$ (arene = benzene, *p*-cymene, or mesitylene).^{19,22}

Preparations. Bis(hexamethylbenzene)dichloro- μ -chloro-diruthenium(II), $[\text{RuCl}_2(\text{HMB})]_2$. (a) $[\text{RuCl}_2(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)]_2$ (1.0 g, 1.63 mmol) was stirred with molten HMB (ca. 10 g) for 2 h. The mixture was allowed to cool to room temperature, and the excess of

- (1) Abbreviations: Me, methyl; *t*-Bu, *tert*-butyl; HMB, hexamethylbenzene; COT, cyclooctatetraene; COD, 1,5-cyclooctadiene; NBD, norbornadiene; py, pyridine; acac, 2,4-pentanedionato.
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Table I. Analyses and Selected Spectroscopic Data (Mass, IR, and ^1H NMR) for Complexes $\text{M}(\text{arene})(\text{COT})^a$

M	arene	% calcd		% found		M^+ mass	$\nu(\text{C}=\text{C})$, cm^{-1}	arene resonances, ppm	C_8H_8 resonances, ppm
		C	H	C	H				
Fe	C_6H_6^b	70.6	5.9	70.9	5.9	238	1520	4.81 (s, 6, C_6H_6)	5.21 (s)
Fe	$\text{C}_6\text{H}_3\text{Me}_3$	72.9	7.1	72.6	7.0	280	1515	1.92 (s, 9, Me), 4.54 (m, 3, C_6H_3)	4.92 (s)
Fe	C_6Me_6	74.5	8.1	75.0	8.4	322	1515	1.83 (s, 18, Me)	4.90 (s)
Ru	C_6H_6	59.4	5.0	59.8	5.5	283	1530	4.71 (s, 6, C_6H_6)	5.33 (s)
Ru	$\text{C}_6\text{H}_5-t\text{-Bu}$	63.7	6.5	63.7	6.6	340	1530	0.92 (s, 9, $t\text{-Bu}$), 4.81 (m, 5, C_6H_5)	5.27 (s)
Ru	$\text{C}_6\text{H}_3\text{Me}_3$	62.8	6.2	62.7	6.3	325	1530	1.81 (s, 9, Me), 4.52 (s, 3, C_6H_3) ^c	5.20 (s)
Ru	C_6Me_6	65.4	7.1	65.6	7.0	367	1530	2.12 (s, 18, Me) ^{c,d}	4.91 (s) ^{c,d}
Os	C_6H_6	^e	^e	^e	^e	374	^e	4.78 (s, 6, C_6H_6)	5.43 (s)
Os	$\text{C}_6\text{H}_3\text{Me}_3$	49.5	5.0	49.3	4.8	416	1561	1.93 (s, 9, Me), 4.64 (s, 3, C_6H_3)	5.32 (s)

^a Parent-ion masses refer to the peak containing the most abundant metal isotope (^{56}Fe , ^{102}Ru , ^{192}Os) and agree with the calculated values in all cases. IR data refer to Nujol mulls, the $\nu(\text{C}=\text{C})$ band due to the free double bonds of coordinated COT being of medium intensity. Chemical shifts (δ) are measured at 100 MHz at 34 °C in C_6D_6 except where stated otherwise. ^b % Fe: calcd, 23.5; found, 22.7. ^c Spectrum unchanged at -145 °C in $\text{CHF}_2\text{Cl}/\text{CF}_2\text{Cl}_2$. ^d Measured in CDCl_3 at 34 °C. ^e Quantity of sample insufficient for elemental analysis or measurement of IR spectrum.

Table II. $^{13}\text{C}\{^1\text{H}\}$ NMR Data for $\text{M}(\text{arene})(\text{COT})^a$

complex	arene resonances	C_8H_8 resonances ^b
$\text{Fe}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$	81.3 (C_6H_3), 20.4 (CH_3) ^c	91.5
$\text{Fe}(\text{C}_6\text{Me}_6)(\text{COT})$	16.2 (CH_3) ^c	90.4
$\text{Ru}(\text{C}_6\text{H}_5-t\text{-Bu})(\text{COT})$	109.3, 79.9, 79.3, 78.2 (C_6H_5), 34.2 (CMe_3), 30.9 (CMe_3)	91.9
$\text{Ru}(\text{C}_6\text{Me}_6)(\text{COT})$	17.3 (CH_3) ^c	91.6 ^d
$\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$	87.5 (C_6Me_3), 71.8 (C_6H_3), 20.8 (CH_3)	90.6 ^e

^a ^{13}C chemical shifts (δ) measured at 15.04 MHz in CD_2Cl_2 at -90 °C except where stated otherwise. ^b Sharp singlets except where stated otherwise. ^c Quaternary aromatic carbon resonances not observed, probably because they are beneath the C_8H_8 resonance. ^d Remains a sharp singlet at -100 °C (67.89 MHz). ^e Sharp singlet at -70 °C; signal broadened on cooling and disappeared into base line at -100 °C, at both 15.04 and 67.89 MHz.

HMB was removed by washing with *n*-hexane. The remaining red-brown microcrystalline solid was dried in vacuo to give $[\text{RuCl}_2(\text{HMB})_2]$, mp 270 °C (0.87 g, 80%). If necessary, the product could be further purified by crystallization from a chloroform solution which had been chromatographed on silica gel.

(b) $[\text{RuCl}_2(1,5\text{-COD})_n]$ (0.5 g) was stirred with HMB (10 g) at 170 °C for 3 h. The mixture was allowed to cool to room temperature and was extracted with chloroform (25 mL). After removal of much unreacted $[\text{RuCl}_2(\text{COD})]_n$ by filtration, the solution was set aside for 3 days. The red crystals were filtered off, washed with benzene, and dried in vacuo to give $[\text{RuCl}_2(\text{HMB})_2]$ (50 mg, 9%). ^1H NMR (CDCl_3): δ 7.97 (s, Me). IR (cm^{-1} , Nujol): 299 s, 258 br ($\nu(\text{Ru}-\text{Cl})$). Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{Cl}_4\text{Ru}_2$: C, 43.1; H, 5.4; Cl, 21.2; mol wt 669. Found: C, 42.2; H, 5.3; Cl, 21.9; mol wt (osmometry, CHCl_3 , 34 °C) 690.

Bis(*tert*-butylbenzene)dichlorodi- μ -chloro-diruthenium(II), $[\text{RuCl}_2(\text{C}_6\text{H}_5-t\text{-Bu})_2]$. A solution of hydrated ruthenium chloride (1.5 g) in ethanol (50 mL) was heated under reflux with 1-*tert*-butyl-1,4-cyclohexadiene (3 mL) for 4 h to give dark brown crystals and an orange solution. After filtration, the solution deposited orange crystals. The dark brown solid was extracted with ethanol in a Soxhlet apparatus. The orange crystals which separated from the ethanol on cooling were combined with the first crop to give 0.5 g of $[\text{RuCl}_2(\text{C}_6\text{H}_5-t\text{-Bu})_2]$. ^1H NMR (CD_2Cl_2): δ 1.26 (s, 9, $t\text{-Bu}$), 5.53 (t), 5.71 (unsym d) (spacing 6 Hz, 5, C_6H_5). Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{Cl}_4\text{Ru}_2$: C, 39.3; H, 4.6; Cl, 23.2. Found: C, 39.25; H, 4.8; Cl, 23.3.

(Arene)Osmium Chloride Complexes.^{23,24} Osmium tetroxide (1 g) was heated under reflux with concentrated HCl (25 mL) for 48 h. On evaporation in vacuo, a mixture of orange crystals and orange-yellow oil was obtained, which was used without further puri-

fication or identification in the following preparations.

(i) The residue was dissolved in ethanol (50 mL), 1,3-cyclohexadiene (6 mL) was added, and the solution was heated under reflux overnight. Solvents were removed in vacuo, and the brown residue was extracted with acetonitrile (20 mL). Addition of ether gave yellow crystals of (acetonitrile)(benzene)dichloroosmium(II), $\text{OsCl}_2(\text{C}_6\text{H}_6)(\text{CH}_3\text{CN})$, in ca. 40% yield. Rubezhov et al.²⁴ report the formation of the solvent-free dimer, $[\text{OsCl}_2(\text{C}_6\text{H}_6)]_2$, under the same conditions. ^1H NMR (CD_3CN): δ 5.95 (s, C_6H_6). Anal. Calcd for $\text{C}_7\text{H}_9\text{Cl}_2\text{Os}$: C, 22.5; H, 2.5; Cl, 22.2. Found: C, 22.0, 22.3, 22.2, 22.5; H, 2.7, 2.6, 2.5, 3.0; Cl, 22.7.

(ii) Reaction as above using 1,3,5-trimethyl-1,4-cyclohexadiene (4 mL) in place of 1,3-cyclohexadiene gave, after heating under reflux overnight, yellow microcrystals of empirical formula Os_4Cl_9 (mesitylene)₃, which were insoluble in all organic solvents except Me_2SO . ^1H NMR ($\text{Me}_2\text{SO}-d_6$): δ 2.23 (s, 9, CH_3), 5.77 (s, 3, C_6H_3). Anal. Calcd for $\text{C}_7\text{H}_9\text{Cl}_2\text{Os}_4$: C, 22.5; H, 2.5; Cl, 22.2. Found: C, 22.0, 22.3, 22.2, 22.5; H, 2.7, 2.6, 2.5, 3.0; Cl, 22.7.

COT Complexes. (η^4 -Cyclooctatetraene)(η^6 -mesitylene)iron(0), $\text{Fe}(1,3,5\text{-C}_6\text{H}_3\text{Me}_3)(\text{COT})$. COT (0.16 g, 1.5 mmol) was added to small pieces of freshly cut lithium metal (0.021 g, 3 mg-atoms) in ether (10 mL), and the mixture was stirred at room temperature until all the metal had dissolved. The stirred yellow-brown solution of Li_2COT was cooled to -78 °C and treated with $[\text{Fe}(\text{C}_6\text{H}_3\text{Me}_3)_2](\text{PF}_6)_2$ (0.586 g, 1 mmol). Stirring was continued for 0.5 h at -78 °C, and then solvent was removed in vacuo, the temperature not being allowed to exceed 0 °C. The solid residue was extracted with *n*-hexane to give a red-brown solution which, after filtration, concentration, and cooling to -78 °C, gave black crystals of $\text{Fe}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ in yields of 20–35%.

The analogous benzene complex $\text{Fe}(\text{C}_6\text{H}_6)(\text{COT})$, was prepared similarly from $[\text{Fe}(\text{C}_6\text{H}_6)_2](\text{PF}_6)_2$ as black crystals in yields of 15–30%.

(η^4 -Cyclooctatetraene)(η^6 -hexamethylbenzene)iron(0), $\text{Fe}(\text{HMB})(\text{COT})$. Cyclooctatetraene (0.23 g, 2.2 mmol) was added to small pieces of lithium metal (0.028 g, 4 mg-atoms) in freshly distilled THF (15 mL), and the mixture was stirred at room temperature to give a green solution of Li_2COT . On addition of $[\text{Fe}(\text{HMB})_2](\text{PF}_6)_2$ (0.400 g, 0.8 mmol) black crystals of bis(hexamethylbenzene)iron(0), $\text{Fe}(\text{HMB})_2$, were deposited. An excess of COT (0.25 mL) was added, and the mixture was stirred at 40 °C for 20 h. Solvent was removed in vacuo, and the residue was treated as described above to give black, crystalline $\text{Fe}(\text{HMB})(\text{COT})$ (0.09 g, 47%).

(η^4 -Cyclooctatetraene)(η^6 -mesitylene)ruthenium(0), $\text{Ru}(1,3,5\text{-C}_6\text{H}_3\text{Me}_3)(\text{COT})$. (i) COT (0.23 g, 2.2 mmol) was added to small pieces of potassium metal (0.17 g, 4.4 mg-atoms) in freshly distilled THF (15 mL) at -30 °C. The solution was stirred for 2 h, treated with $[\text{RuCl}_2(\text{C}_6\text{H}_3\text{Me}_3)_2]$ (0.5 g, 0.94 mmol), and stirred at -30 °C for a further 4 h. Solvent was removed in vacuo, and the residue was extracted with *n*-hexane to give an orange solution. Concentration under reduced pressure and cooling to -78 °C gave orange crystals of $\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ (0.21 g, 25%).

Use of the pyridine complex $\text{RuCl}_2(\text{C}_6\text{H}_3\text{Me}_3)\text{py}$ in place of $[\text{RuCl}_2(\text{C}_6\text{H}_3\text{Me}_3)_2]$ gave the same product in 28% yield.

(ii) To a solution of Li_2COT in THF was added the yellow acetylacetonate complex $\text{RuCl}(\text{acac})(\text{C}_6\text{H}_3\text{Me}_3)$ (0.100 g, 0.28 mmol), which had been prepared by treatment of $[\text{RuCl}_2(\text{C}_6\text{H}_3\text{Me}_3)_2]$ with thallium(I) acetylacetonate in dichloromethane.²⁵ After the solution

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was stirred at room temperature for 0.5 h, solvent was removed in vacuo and the residue was extracted with *n*-hexane. Concentration and cooling of the yellow solution gave orange-yellow crystals of $\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ (0.051 g, 56%).

Similarly prepared in 55% yield from $[\text{RuCl}_2(\text{HMB})]_2$ and K_2COT was the orange-red, crystalline HMB complex $\text{Ru}(\text{HMB})(\text{COT})$.

(η^6 -Benzene)(η^4 -cyclooctatetraene)ruthenium(0), $\text{Ru}(\text{C}_6\text{H}_6)(\text{COT})$. Treatment of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$ or its pyridine adduct with K_2COT or Li_2COT in THF gave $\text{Ru}(\text{C}_6\text{H}_6)(\text{COT})$ in low yield, contaminated with oily impurities. A more successful procedure was as follows.

A suspension of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$ (0.200 g, 0.4 mmol) in dichloromethane (15 mL) was treated with thallium(I) acetylacetonate (ca. 0.5 g, excess), and the mixture was stirred at room temperature for 2 h. After filtration to remove precipitated TiCl_4 , the solution was evaporated to dryness in vacuo to give a reddish yellow solid.²⁵ This was dissolved in freshly distilled THF (5 mL), and the solution was added to a solution of Li_2COT in THF. Workup as described above gave red crystals of $\text{Ru}(\text{C}_6\text{H}_6)(\text{COT})$ (0.078 g, 35%).

(Arene)(cyclooctatetraene)osmium(0) Complexes. The reaction of $\text{Os}_4\text{Cl}_9(\text{C}_6\text{H}_3\text{Me}_3)_3$ (0.150 g, 0.1 mmol) with Li_2COT in THF was worked up as usual to give orange-yellow crystals of $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ (0.022 g, 17%).

A similar reaction between $\text{OsCl}_2(\text{C}_6\text{H}_6)(\text{CH}_3\text{CN})$ and Li_2COT gave a few milligrams of orange-yellow $\text{Os}(\text{C}_6\text{H}_6)(\text{COT})$, which was characterized spectroscopically.

Collection of X-ray Intensity Data and Solution and Refinement of the Structure of $\text{Ru}(\text{HMB})(\text{COT})$. Crystals of suitable quality were obtained from *n*-hexane. Absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) from preliminary Weissenberg and precession photographs established the space group as $P2_1/n$. The cell dimensions were determined by a least-squares fit to the four angles optimized on a Picker FACS-1 four-circle diffractometer, for each of 12 reflections with $2\theta > 70^\circ$ (λ (Cu $K\alpha_1$) = 1.5405 Å). The estimated standard deviations of the cell dimensions are derived from the least-squares procedure.

Crystal data for $\text{C}_{20}\text{H}_{26}\text{Ru}$: $M_r = 367.5$, monoclinic, space group $P2_1/n$ (nonstandard setting of $P2_1/c$ (C_{2h}^5 , No. 14)) with $a = 8.8460$ (6) Å, $b = 18.0622$ (10) Å, $c = 10.8181$ (4) Å, $\beta = 91.49$ (2)°, $V_c = 1727.9$ Å³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 8.8$ cm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 760$, $t = 23 \pm 1$ °C, approximate crystal dimensions $0.015 \times 0.015 \times 0.025$ cm.

The preliminary results of this structure determination, reported earlier,¹⁶ were based on intensities measured with Cu $K\alpha$ radiation. Because highly irregular crystal shape precluded the application of an absorption correction ($\mu(\text{Cu } K\alpha) = 75.2$ cm⁻¹), we report here the refinement based on intensities measured with Mo $K\alpha$ radiation ($\mu = 8.8$ cm⁻¹). Intensities for reflections with $3^\circ < 2\theta < 60^\circ$ were recorded with monochromated (graphite, $2\theta_m = 12.16^\circ$) Mo $K\alpha$ radiation, by using a $\theta/2\theta$ scan (2°/min) from 0.85° below the α_1 maximum to 0.85° above the α_2 maximum, with stationary-background measurements (10 s) on each side of the scan. The 1746 unique reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption.

Scattering factors for the atoms and the anomalous dispersion correction for Ru were taken from ref 26. The coordinates of the nonhydrogen atoms were determined by conventional "heavy-atom" methods and refined initially by a block-diagonal least-squares procedure with unit observational weights. Methyl hydrogen atoms were located from a difference Fourier synthesis but were fixed in positions computed from the optimized²⁷ molecular geometry. The positional parameters of the cyclooctatetraene hydrogen atoms were located initially from the difference map and were refined subsequently. All hydrogen atoms were included in the structure factor calculations with an isotropic temperature factor equal to that of the atom to which they were bound. Anisotropic temperature factors were refined for nonhydrogen atoms. Full-matrix least-squares refinement with ob-

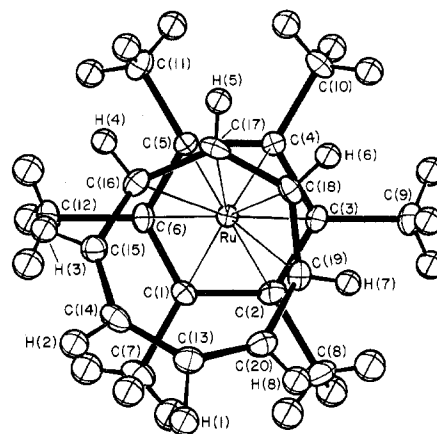


Figure 1. Molecular geometry and atom numbering in $\text{Ru}(\text{HMB})(\text{COT})$. Methyl hydrogen atoms are unlabeled for clarity. Thermal ellipsoids are scaled to include 10% probability.

servational weights w , where $w^{-1/2} = [\sigma^2(I)/(Lp)^2 + 0.002|F_o|^4]^{1/2}/2|F_o|$,²⁸ converged with R of 0.047 for the 1746 reflections ($R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2} = 0.050$). The function minimized was $\sum w(|F_o| - |F_c|)^2$ throughout. There was no serious dependence of $w(|F_o| - |F_c|)^2$ on either $|F_o|$ or $(\sin \theta)/\lambda$. The maximum shift in the final cycle was 0.1 σ , and the standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$,²⁸ was 1.30. An inspection of $|F_o|$ and $|F_c|$ showed no evidence of extinction.

A difference map computed at the end of the refinement showed a peak of $0.8 \text{ e}/\text{\AA}^{-3}$ in the region of the Ru atom, but there were no other features with an absolute value greater than $0.4 \text{ e}/\text{\AA}^{-3}$. Final atomic coordinates are listed in Table III, and the atom numbering is shown in Figure 1. The molecular packing is illustrated in Figure 2. A listing of observed and calculated structure factor amplitudes [$\times 10$ (electrons)] is available (see paragraph at end of paper regarding supplementary material).

Computer Programs. Those programs used were part of the ANUCRYS package collected, modified, or written by Dr. D. Taylor and Dr. P. O. Whimp. The programs were SETUP3 (data reduction incorporating correction for crystal "decay"), SORTER (sorting and averaging program), ANUFOR (Fourier program from a modification of the University of Canterbury Fourier Program²⁹), TOMPAB (analytical³⁰ absorption correction program written by Dr. J. D. Bell), BLKLSQ and FULNNN (block-diagonal and full-matrix least-squares program based on Prewitt's SFLS-5³¹ as modified by Dr. B. M. Foxman), HYDGEN (program for calculating hydrogen atom positions modified from a program by H. Hope and U. C. Davis), ORTEP₂,³² ORFFE3,³³ MEANPL (mean-plane program³⁴ from a program by M. F. Pippy), PUBTAB (source of the structure factor listing), and LISTER (source of coordinate and thermal parameter listings). All calculations were performed on the UNIVAC 1108 of The Australian National University Computer Services Centre.

Results

Reaction of cyclooctatetraene dianion, COT^{2-} , with bis-(arene)iron(II) salts, $[\text{Fe}(\text{arene})_2](\text{PF}_6)_2$, or with appropriate (arene)ruthenium(II) or -osmium(II) halide complexes such

(25) The structure of (arene)ruthenium acetylacetonates will be discussed elsewhere: Bennett, M. A.; Matheson, T. W.; Stevens, M. R., unpublished work.

(26) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99, 149.

(27) The optimized positions of the three hydrogen atoms were determined in terms of the C-C(methyl)-H torsion angles, α , $\alpha + 120^\circ$, $\alpha + 240^\circ$, a C-H bond length of 0.95 Å, and a C-C-H angle of 109° . The torsion angles were found to alternate such that $\alpha = 90^\circ$ ($\pm 5^\circ$) for C(7), -90° for C(8), and so on through to -90° for C(12).

(28) Lp is the Lorentz-polarization correction, m is the number of observations (1746), and n is the number of parameters (214). The net intensity $I = P - (B_1 + B_2)t_p/t_b$ and $\sigma(I) = P + (B_1 + B_2)t_p^2/t_b^2$, where P is the peak count, B_1 and B_2 are the background counts, t_p is the peak scan time, and t_b is the total background counting time.

(29) Based on modification of FORDAP (A. Zalkin, University of California) by R. Dellaca.

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(34) Using the method described by: Blow, D. M. *Acta Crystallogr.* **1960**, *13*, 168.

Table III. Final Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations (in Parentheses) for Ru(HMB)(COT)

ATOM	X/A	Y/B	Z/C	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
RU	0.2374(11)	0.1351(11)	0.2455(11)	0.0121(11)	0.0027(11)	0.0081(11)	-0.0001(11)	0.0005(11)	-0.0005(11)
C(1)	0.2289(13)	0.0130(4)	0.2540(10)	0.0216(21)	0.0029(3)	0.0111(10)	-0.0003(7)	0.0021(13)	-0.0002(6)
C(2)	0.3715(12)	0.0341(5)	0.2037(9)	0.0183(17)	0.0034(3)	0.0131(12)	0.0028(6)	0.0008(12)	-0.0008(5)
C(3)	0.3770(10)	0.0822(5)	0.1019(8)	0.0138(14)	0.0038(3)	0.0117(10)	0.0001(6)	0.0030(10)	-0.0023(5)
C(4)	0.2405(10)	0.1120(4)	0.0485(7)	0.0169(14)	0.0031(3)	0.0086(8)	-0.0003(5)	0.0008(9)	-0.0015(4)
C(5)	0.0987(10)	0.0876(5)	0.0939(8)	0.0151(14)	0.0037(3)	0.0097(9)	0.0002(6)	-0.0012(9)	-0.0010(4)
C(6)	0.0967(11)	0.0393(5)	0.1955(9)	0.0162(16)	0.0034(3)	0.0125(11)	-0.0019(6)	0.0028(11)	-0.0016(5)
C(7)	0.2278(16)	-0.0390(6)	0.3648(11)	0.0388(29)	0.0040(4)	0.0188(15)	0.0008(9)	0.0025(18)	0.0023(6)
C(8)	0.5194(13)	0.0064(7)	0.2634(12)	0.0225(22)	0.0076(7)	0.0213(18)	0.0049(10)	-0.0027(16)	0.0013(8)
C(9)	0.5287(12)	0.1064(6)	0.0506(11)	0.0176(17)	0.0050(4)	0.0202(18)	0.0009(7)	0.0059(13)	-0.0017(6)
C(10)	0.2445(13)	0.1655(6)	-0.0590(8)	0.0292(22)	0.0049(4)	0.0099(10)	-0.0017(8)	0.0019(13)	0.0007(5)
C(11)	-0.0460(12)	0.1136(6)	0.0337(10)	0.0173(17)	0.0063(5)	0.0155(13)	-0.0012(7)	-0.0030(12)	-0.0021(6)
C(12)	-0.0566(13)	0.0154(6)	0.2480(12)	0.0231(21)	0.0052(5)	0.0236(19)	-0.0042(8)	0.0064(16)	-0.0003(7)
C(13)	0.3200(17)	0.1770(7)	0.5816(12)	0.0276(27)	0.0059(5)	0.0128(14)	0.0000(9)	-0.0019(16)	-0.0001(7)
C(14)	0.1651(18)	0.1789(6)	0.5762(10)	0.0342(30)	0.0042(4)	0.0099(12)	0.0025(9)	0.0064(16)	0.0005(5)
C(15)	0.0653(14)	0.1832(6)	0.4828(11)	0.0221(20)	0.0054(5)	0.0117(12)	0.0013(8)	0.0026(14)	0.0001(6)
C(16)	0.0713(12)	0.1996(6)	0.3530(11)	0.0166(17)	0.0046(4)	0.0145(14)	0.0012(7)	0.0001(13)	-0.0021(6)
C(17)	0.1682(16)	0.2442(6)	0.2839(10)	0.0315(28)	0.0034(4)	0.0077(10)	0.0028(9)	0.0010(14)	0.0003(5)
C(18)	0.3265(15)	0.2424(6)	0.2858(11)	0.0235(22)	0.0038(4)	0.0117(13)	-0.0035(8)	0.0024(15)	-0.0003(6)
C(19)	0.4152(12)	0.1933(6)	0.3607(10)	0.0167(17)	0.0047(4)	0.0112(12)	-0.0019(7)	0.0013(11)	-0.0022(5)
C(20)	0.4199(14)	0.1768(6)	0.4891(12)	0.0209(21)	0.0051(5)	0.0150(15)	0.0003(8)	-0.0026(15)	0.0001(6)
ATOM	X/A	Y/B	Z/C	B(A ²)	ATOM	X/A	Y/B	Z/C	B(A ²)
H(1)	0.369(10)	0.166(5)	0.675(8)	7.4	H(23)	0.566	-0.002	0.349	9.0
H(2)	0.123(11)	0.171(5)	0.646(8)	6.8	H(31)	0.600	0.068	0.060	7.2
H(3)	-0.033(10)	0.168(5)	0.472(9)	6.5	H(32)	0.516	0.118	-0.035	7.2
H(4)	-0.019(10)	0.196(4)	0.305(8)	6.0	H(33)	0.565	0.149	0.095	7.2
H(5)	0.133(10)	0.276(5)	0.240(8)	5.8	H(41)	0.246	0.138	-0.133	6.6
H(6)	0.357(10)	0.272(5)	0.234(8)	6.0	H(42)	0.158	0.196	-0.057	6.6
H(7)	0.500(9)	0.186(4)	0.321(8)	5.5	H(43)	0.333	0.195	-0.051	6.6
H(8)	0.568(10)	0.164(6)	0.505(9)	6.7	H(51)	-0.030	0.123	-0.052	7.0
H(11)	0.138	-0.068	0.362	8.7	H(52)	-0.121	0.076	0.042	7.0
H(12)	0.313	-0.071	0.363	8.7	H(53)	-0.078	0.158	0.072	7.0
H(13)	0.232	-0.011	0.439	8.7	H(61)	-0.088	-0.029	0.208	8.3
H(21)	0.549	-0.038	0.224	9.0	H(62)	-0.044	0.007	0.334	8.3
H(22)	0.596	0.043	0.254	9.0	H(63)	-0.129	0.053	0.233	8.3

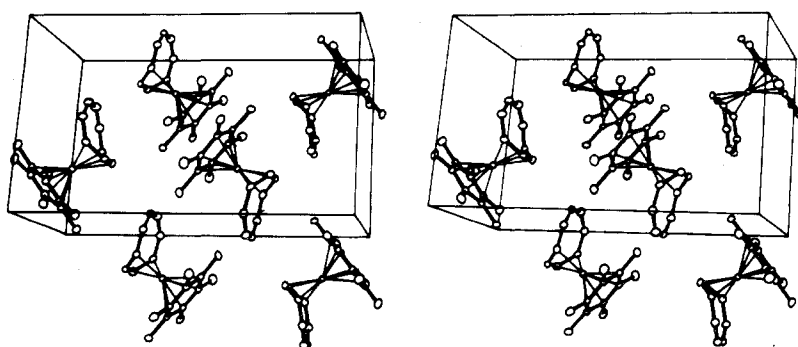


Figure 2. Unit cell packing for Ru(HMB)(COT) viewed approximately along *a*.

as $[\text{MCl}_2(\text{arene})]_2$ ($\text{M} = \text{Ru}$, arene = C_6H_6 , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, HMB; $\text{M} = \text{Os}$, arene = C_6H_6) or $\text{Os}_4\text{Cl}_9(\text{C}_6\text{H}_3\text{Me}_3)_3$ gives crystalline complexes $\text{M}(\text{arene})(\text{COT})$, which can be purified by low-temperature recrystallization from hexane or isopentane or, more wastefully, by high-vacuum sublimation. A similar procedure has been used previously to prepare η^6 -COT complexes of ruthenium(0) and osmium(0) of the type $\text{M}(\text{diene})(\eta^6\text{-COT})$ ($\text{M} = \text{Ru}$, Os ; diene = 1,5-COD, NBD) from $[\text{MCl}_2(\text{diene})]_n$.³⁵ In our system, yields are generally in the range 15–50%, decreasing in the orders $\text{Fe} > \text{Ru} > \text{Os}$ and $\text{HMB} > 1,3,5\text{-C}_6\text{H}_3\text{Me}_3 > \text{C}_6\text{H}_6$. The modest yields in the case of Ru and Os may be due in part to the poor solubility of the arene metal halide precursors (arene = C_6H_6 , $\text{C}_6\text{H}_3\text{Me}_3$) in solvents such as ether or THF. Reaction of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$ with COT^{2-} gave only a small yield of $\text{Ru}(\text{C}_6\text{H}_6)(\text{COT})$ contaminated with inseparable oily impurities, but conversion of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$ into a more soluble acetylacetonato derivative and subsequent reaction with COT^{2-} gave ca. 35% of the pure product.

The initial product precipitated from reaction of $[\text{Fe}(\text{HMB})_2]^{2+}$ with COT^{2-} is the known³⁶ zerovalent iron complex $\text{Fe}(\text{HMB})_2$, which subsequently reacts with COT to give $\text{Fe}(\text{HMB})(\text{COT})$. It seems likely that all the reactions in the iron series involve highly reactive species $\text{Fe}(\text{arene})_2$ ³⁷ formed by two one-electron reductions with COT^{2-} .

The iron complexes $\text{M}(\text{arene})(\text{COT})$ are almost black in the solid state and give deep red-brown solutions; the ruthenium and osmium complexes are orange in solution and in the solid state. As usual, air sensitivity decreases markedly on descending the triad, and the arene COT complexes of iron and ruthenium are considerably more air sensitive than the corresponding tricarbonyls.

The proton and ¹³C resonances of coordinated COT in all the complexes are singlets at room temperature, and the IR spectra show a weak to medium intensity $\nu(\text{C}=\text{C})$ absorption at ca. 1530–1560 cm^{-1} , assignable to the free double bonds of a fluxional 1-4- η -COT ring; cf. $\text{Fe}(\text{CO})_3(1\text{-}4\text{-}\eta\text{-COT})$ (1562 cm^{-1}),³⁸ $\text{Fe}(1\text{-}4\text{-}\eta\text{-COT})(1\text{-}6\text{-}\eta\text{-COT})$ (1527 cm^{-1}),³⁹ $\text{Fe}(1\text{-}4\text{-}\eta\text{-COT})(\text{C}_4\text{H}_6)(\text{CO})$ (1571 cm^{-1}),⁴⁰ and $\text{Ru}(\text{CO})_3(1\text{-}4\text{-}\eta\text{-COT})$ (1561 cm^{-1}).⁴¹ In contrast, $\nu(\text{C}=\text{C})$ for the uncomplexed double bonds in 1,2,5,6- η -COT is about 1640 cm^{-1} .²⁻⁵ The presence of a 1-4- η -COT ring in $\text{Ru}(\text{C}_6\text{Me}_6)(\text{COT})$ has been confirmed by a single-crystal X-ray study (see below). Attempts to slow down the fluxional process re-

sponsible for averaging the COT ¹H and ¹³C environments have been only partially successful. The COT proton singlets of $\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ and $\text{Ru}(\text{HMB})(\text{COT})$ remain sharp even at -145°C (100 MHz), whereas $\text{Ru}(\text{CO})_3(\text{COT})$ has reached its limiting spectrum under the same conditions.¹³ Similarly, the COT ¹³C singlets of $\text{Ru}(\text{C}_6\text{H}_5\text{-}t\text{-Bu})(\text{COT})$ and $\text{Ru}(\text{C}_6\text{Me}_6)(\text{COT})$, measured at 15.04 and 67.89 MHz, respectively, remain sharp at -100 to -110°C , whereas $\text{Ru}(\text{C}_6\text{O})_3(\text{COT})$ attains a limiting ¹³C NMR spectrum at -120°C (25.035 MHz).¹² However, in both 15.04- and 67.89-MHz ¹³C NMR spectra of $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$, the COT singlet broadens at about -90°C and collapses into the base line from -100 to -120°C . Clearly, studies at temperatures lower than those available to us at present are required to obtain limiting spectra for $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$. The higher barrier to fluxional behavior in the osmium compound relative to its iron and ruthenium analogues is also observed in the $\text{M}(\text{CO})_3(\text{COT})$ series, since $\text{Os}(\text{CO})_3(\text{COT})$ attains its limiting 100-MHz ¹H NMR spectrum at -100°C .¹⁴ Taking the coalescence temperature for $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ as -100°C and assuming that the average chemical shift difference ($\Delta\nu$) between the coordinated and uncoordinated carbon atoms in the limiting spectrum is the same as that in $\text{Ru}(\text{CO})_3(\text{COT})$ at -126°C , viz., 50.9 Hz, we can use the relationship $k = \pi(\Delta\nu)/2^{1/2}$ to calculate the rate of rearrangement of $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ at -100°C as 113 s^{-1} . Assuming further that the frequency factor in the Arrhenius equation $k = A \exp(-E/RT)$ is equal to that for $\text{Ru}(\text{CO})_3(\text{COT})$, viz., $10^{13.3 \pm 0.1}$,¹³ we estimate the activation energy for the assumed 1,2-rearrangement process in $\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$ to be about 9 kcal/mol. A similar calculation for $\text{Ru}(\text{HMB})(\text{COT})$, assuming -145°C to be the coalescence temperature, gives an upper limit for the Arrhenius activation energy of 6.6 kcal/mol, which can be compared with the value of 8.6 ± 0.1 kcal/mol for $\text{Ru}(\text{CO})_3(\text{COT})$.¹³

Structure of Ru(HMB)(COT). The molecule has only approximate *m* symmetry (Figure 1) and contains the metal atom bound to an approximately planar η^6 -HMB ligand and to a 1-4- η -COT ring in the now-familiar tub conformation (defined by planes *b*, *c*, and *d* in Table V) which is almost hinge shaped. Bond length and angle data are in Table IV, and the results of some mean-plane calculations are in Table V. The dihedral angle between the coordinated and uncoordinated diene sections is 45.4° (cf.: $\text{Fe}(\text{CO})_3(\text{COT})$, 42.5° ;⁷ $\text{Ru}(\text{CO})_3(\text{COT})$, 43.7° ;⁸ $\text{Fe}(\eta^6\text{-COT})(\eta^4\text{-COT})$, 33° ;⁹ $\text{Fe}(\text{CO})(\eta^4\text{-COT})(\eta^4\text{-C}_4\text{H}_6)$, 43° ¹⁰). The plane of the coordinated diene fragment of $\text{Ru}(\text{HMB})(\text{COT})$ makes an angle of 8.8° with the HMB mean plane; cf. 5.2° for the η^4 -HMB ring in $\text{Ru}(\eta^6\text{-HMB})(\eta^4\text{-HMB})$.⁴² The mean metal-carbon bond lengths to the inner and outer carbon atoms of the bonded diene fragment are 2.120 (10) (Ru-C(17), Ru-C(18)) and 2.233 (10) Å (Ru-C(16), Ru-C(19), respectively (Table IV). These

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Table IV. Bond Lengths (Å) and Angles (Deg) with Estimated Standard Deviations (in Parentheses)

Ru-C(1)	2.210 (8)	C(1)-C(7)	1.523 (14)
Ru-C(2)	2.219 (8)	C(2)-C(8)	1.528 (13)
Ru-C(3)	2.214 (8)	C(3)-C(9)	1.530 (13)
Ru-C(4)	2.172 (8)	C(4)-C(10)	1.504 (12)
Ru-C(5)	2.205 (8)	C(5)-C(11)	1.497 (13)
Ru-C(6)	2.200 (8)	C(6)-C(12)	1.540 (13)
Ru-C(16)	2.234 (10)	mean ^a	1.520 (16)
Ru-C(17)	2.115 (10)	C(1)-C(2)-C(3)	120.6 (9)
Ru-C(18)	2.126 (10)	C(2)-C(3)-C(4)	120.3 (8)
Ru-C(19)	2.232 (9)	C(3)-C(4)-C(5)	118.9 (7)
C(13)-C(14)	1.371 (16)	C(4)-C(5)-C(6)	119.4 (8)
C(14)-C(15)	1.327 (16)	C(5)-C(6)-C(1)	122.6 (9)
C(15)-C(16)	1.435 (15)	C(6)-C(1)-C(2)	118.0 (9)
C(16)-C(17)	1.413 (16)	mean ^a	120.0 (15)
C(17)-C(18)	1.400 (16)	C(7)-C(1)-C(2)	119.0 (10)
C(18)-C(19)	1.423 (15)	C(7)-C(1)-C(6)	122.9 (11)
C(19)-C(20)	1.420 (16)	C(8)-C(2)-C(1)	120.2 (9)
C(20)-C(13)	1.352 (16)	C(8)-C(2)-C(3)	119.1 (10)
C(13)-H(1)	1.11 (8)	C(9)-C(3)-C(2)	120.7 (9)
C(14)-H(2)	0.86 (9)	C(9)-C(3)-C(4)	119.0 (9)
C(15)-H(3)	0.92 (8)	C(10)-C(4)-C(3)	121.0 (8)
C(16)-H(4)	0.95 (8)	C(10)-C(4)-C(5)	120.0 (8)
C(17)-H(5)	0.80 (8)	C(11)-C(5)-C(4)	120.1 (8)
C(18)-H(6)	0.83 (8)	C(11)-C(5)-C(6)	120.5 (9)
C(19)-H(7)	0.88 (8)	C(12)-C(6)-C(5)	119.5 (9)
C(20)-H(8)	0.83 (8)	C(12)-C(6)-C(1)	117.9 (9)
mean ^a	0.90 (10)	mean ^a	120.0 (12)
C(1)-C(2)	1.438 (13)	C(20)-C(13)-C(14)	129.8 (12)
C(2)-C(3)	1.405 (13)	C(13)-C(14)-C(15)	132.7 (12)
C(3)-C(4)	1.430 (12)	C(14)-C(15)-C(16)	135.7 (12)
C(4)-C(5)	1.429 (12)	C(15)-C(16)-C(17)	132.1 (10)
C(5)-C(6)	1.403 (12)	C(16)-C(17)-C(18)	126.8 (10)
C(6)-C(1)	1.399 (13)	C(17)-C(18)-C(19)	124.0 (10)
mean ^a	1.417 (16)	C(18)-C(19)-C(20)	133.6 (10)
		C(19)-C(20)-C(13)	136.1 (11)

^a Here and in the text this refers to the straight (unweighted) mean; the value in parentheses is the standard deviation of the sample distribution if the sample size is greater than three but is the individual esd otherwise.

are significantly shorter than the corresponding distances in Ru(CO)₃(COT) (2.182 (6), 2.265 (6) Å) but are closer to the metal-η⁴-arene distances in Ru(η⁶-HMB)(η⁴-HMB) (2.117 (7), 2.179 (7) Å).⁴² The C-C bond lengths in the bound diene fragment of Ru(HMB)(COT) (1.400 (16) (central), 1.423 (15), 1.413 (16) Å (outer)) do not differ significantly from each other, in contrast to the case for Ru(CO)₃(COT) (1.394 (12) (central), 1.443 (8) Å (outer)).⁸ However, it is not possible to draw any conclusion from this because the larger standard deviations in Ru(HMB)(COT) mean there are no significant differences between equivalent bond lengths (central or outer) for the two complexes. The C-C distances in the uncoordinated diene fragment are surprisingly close to equality (1.371 (16) (central), 1.327 (16), 1.352 (16) Å (outer)), the central bond being significantly shorter than that expected for the usual central C-C distance of a *cis*-1,3-butadiene group (1.46-1.47 Å).⁴³ A similar though less marked trend is evident in the corresponding distances in Ru(CO)₃(COT) (1.419 (8) (central), 1.332 (8) Å (outer)).^{8,44} The conclusion implied by these observations, that some electron delocalization occurs over the entire COT ring, is supported by a comparison of the C-C bond lengths which connect the two diene fragments (mean values 1.428 (15) Å in Ru(HMB)(COT) and 1.445 (9) Å in Ru(CO)₃(COT)) with the equivalent lengths (mean 1.496

Table V

Mean Planes and Distances (Å) of Atoms from the Planes		
plane	atoms defining plane	distances (in square brackets)
a	C(1), C(2), C(3), C(5), C(6)	C(1) [-0.01], C(2) [0.01], C(3) [0.00], C(4) [-0.06], C(5) [0.00], C(6) [0.01], C(7) [-0.01], C(8) [0.00], C(9) [-0.02], C(10) [-0.12], C(11) [0.03], C(12) [0.02]
b	C(16), C(17), C(18), C(19)	C(15) [-0.84], C(16) [0.00], C(17) [0.00], C(18) [0.00], C(19) [0.00], C(20) [-0.82], H(4) [0.43], H(5) [-0.04], H(6) [0.05], H(7) [0.40], Ru [1.634]
c	C(13), C(14), C(15), C(20)	C(13) [-0.01], C(14) [0.01], C(15) [0.00], C(20) [0.00], H(1) [0.15], H(2) [0.14], H(3) [0.31], H(8) [0.20]
d	C(16), C(19), C(20), C(15)	C(16) [0.00], C(19) [0.00], C(20) [0.00], C(15) [0.00], H(4) [0.19], H(7) [0.19], H(8) [0.16], H(3) [0.32]
Dihedral Angles between Planes (Deg)		
	Ru(COT)(HMB)	Ru(CO) ₃ (COT)
a,b	9.7	
b,d	35.7	40.8
b,c	45.4	48.7
c,d	9.7	7.9

Torsion Angles (Deg) of the C-C(COT) Bonds in Ru(COT)(HMB)
 C(14)-C(15) 11.9 C(15)-C(16) 30.7 C(16)-C(17) 52.8
 C(17)-C(18) 0.5 C(18)-C(19) 52.7 C(19)-C(20) 29.2
 C(20)-C(13) 16.1 C(13)-C(14) 2.2

Å) in [1,4-bis(*o*-diphenylphosphino)phenyl]-1,3-butadiene]-carbonylruthenium(0), Ru(CO){*o*-Ph₂PC₆H₄-*c*-CH=CH-*t*-CH=CHC₆H₄PPh₂-*o*}⁴⁵ where conjugation beyond the diene segment is sterically disfavored. Bond angles in the COT ring of Ru(HMB)(COT) do not differ significantly from those in Ru(CO)₃(COT).

The positions of the COT hydrogen atoms in Ru(HMB)(COT), although refined, are poorly determined. It is clear, however, that H(4) and H(7) do not lie in the plane defined by the bound diene carbon atoms C(16), C(17), C(18), and C(19) but are displaced toward the ruthenium atom, whereas the central carbon atoms C(17) and C(18) exhibit approximate trigonal planar coordination. Similar distortions have been reported for the coordinated diene moieties in Fe(CO)(η⁴-COT)(η⁴-C₄H₆),¹⁰ Mn(CO)(η⁴-C₄H₆)₂,⁴⁶ and the Fe(CO)₃ complex of sorbic acid.⁴⁷

The absence of a hexad axis through the metal atom implies that the HMB ligand need not possess exact *D*_{6h} symmetry, and deviations from this symmetry are evident. The Ru-C(4) distance (2.172 (8) Å) is significantly shorter than the mean (2.210 (7) Å) of the other five Ru-C(HMB) distances. The latter five carbon atoms lie in a plane (Table V), whereas C(4) and C(10) are displaced respectively 0.06 and 0.12 Å away from the plane toward the ruthenium atom. The C(4)-C(10) vector makes an angle of 87.9° with the plane normal. On the basis of the esd for a single measurement there are no significant differences between the C-C(arene) bond lengths. There is no evidence of a twofold distortion as reported for the ring in Cr(CO)₃(η⁶-HMB),⁴⁸ or of alternately long and

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(44) The anomalously long central bond distance of 1.536 Å for the uncoordinated diene fragment of Ru(CO)₃(COT) reported in ref 8 is believed to be in error. The value given here has been computed from the coordinates and cell constants reported in ref 8. Other bond lengths in ref 8 appear to be correct.

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short bonds around the ring as in $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)$.⁴⁹ In the present case, π -electron localization could arise only from the slight departure from *m* symmetry of the entire molecule, not from the nonplanarity of the HMB ring (which would retain a mirror plane). The angles in the HMB ligand are unexceptional and show no significant trends associated with the nonplanarity of the ring.

Departures from planarity of η^6 -arenes in their ruthenium complexes have been reported for $\text{Ru}^{\text{II}}\text{Cl}_2(\text{arene})(\text{PMePh}_2)$ (arene = C_6H_6 or *p*- $\text{MeC}_6\text{H}_4\text{CHMe}_2$)⁵⁰ and for $\text{Ru}^0(\text{C}_6\text{H}_6)(\text{COD})$.⁵¹ In the first case, the bonds from the metal to the two adjacent ring carbon atoms which are trans to the tertiary phosphine are longer than those to the other four; this was attributed⁵⁰ to the larger trans influence of PMePh_2 relative to Cl^- . In the second case, the bonds from ruthenium to the 1,4-carbon atoms which are trans to the coordinated double bonds are shorter than those to the other four; no explanation for this effect has been offered. In the present instance, carbon atom C(4) is staggered with respect to the central C–C bond of the coordinated diene fragment and is not trans to any of the carbon atoms in this unit, so that C(4) may be able to compete more effectively than the other arene carbon atoms for π -electron density on ruthenium.

The relative orientations of the methyl groups in the HMB ligand, which, although not refined, are accurate to within $\pm 5^\circ$, minimize nonbonded interactions between hydrogen atoms of adjacent groups. There are no exceptionally short intramolecular nonbonded contacts. The intermolecular packing (Figure 2) seems to exert little influence on the molecular geometry. The most significant nonbonded contacts have been deposited, but none are exceptionally short.

Discussion

The COT ring in the $\text{M}(\text{arene})(\text{COT})$ complexes of the iron triad adopts the 1–4- η -bonding mode, and there is no evidence for alternatives such as those found in $\text{Os}(\text{CO})_3(1,2,3,6-\eta\text{-COT})$ ⁵² or $\text{M}(\text{C}_5\text{Me}_5)(1,2,5,6-\eta\text{-COT})$ ($\text{M} = \text{Rh}, \text{Ir}$).¹¹ The absence of 1,2,5,6- η bonding is surprising in view of the thermal stability of complexes such as $\text{Ru}(\text{arene})(1,5\text{-COD})$ (arene = C_6H_6 , HMB)^{53,54} and $\text{Ru}(\text{HMB})(\text{C}_2\text{H}_4)_2$.⁵⁴ It is not clear why the isoelectronic M–arene (iron triad) and M– C_5Me_5 (cobalt triad) fragments should differ in this way, because their σ/π -bonding abilities are generally assumed to be similar.

Extended Hückel calculations have suggested⁵⁵ that the σ -bonding abilities of the $\text{M}(\text{CO})_3$ and M–arene moieties to a main-group probe are about equal. In contrast, the M–arene moiety π -overlaps more effectively than does $\text{M}(\text{CO})_3$, because in the latter the key d_{xz} and d_{xy} orbitals are delocalized into vacant π^* orbitals on CO. This assertion is supported by the significant shortening of the Ru–C(COT) bond lengths in $\text{Ru}(\text{HMB})(\text{COT})$ relative to those in $\text{Ru}(\text{CO})_3(\text{COT})$ and also by the similar trend in Cr–C(arene) distances in $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ (2.14 Å)⁵⁶ and $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)$ (2.23 Å).⁴⁹ However, in the “sandwich” complexes, the possibility of some contribution to the metal–ring bonding from direct overlap of the ligand π orbitals cannot be excluded. Thus, the perpendicular distance from the center of the C(17)–C(18) bond of Ru-

(HMB)(COT) to the arene plane is 3.50 Å, which approaches the interplanar separations of ca. 3.40 Å observed in organic molecular donor–acceptor complexes.

The tighter binding of the diene moiety in $\text{Ru}(\text{HMB})(\text{COT})$ than in $\text{Ru}(\text{CO})_3(\text{COT})$ implied by the Ru–diene distances is not reflected in the C–C distances of the diene, equivalent distances being equal within experimental error. It has been suggested^{57,58} that increasing the back-bonding to a 1,3-diene should cause a change from approximate equality to a long–short–long pattern of the C–C bond lengths, similar to that of the first excited configuration of free butadiene. Whereas C–C distances in $\text{Fe}(\text{CO})_3(1,3\text{-diene})$ complexes are usually equal within experimental error, those in similar $\text{M}(\text{C}_5\text{H}_5)\text{-}(1,3\text{-diene})$ complexes appear to display the expected long–short–long pattern, presumably owing to the weaker π -acceptor ability of C_5H_5 relative to CO. Clearly, accurate structural studies of complexes containing $\text{M}(\text{CO})_3$, $\text{M}(\text{arene})$, and $\text{M}(\text{C}_5\text{H}_5)$, respectively, bound to the same 1,3-diene are required to further test the validity of this hypothesis.

At first sight it is surprising that the stronger bonding of COT in the arene complexes relative to the tricarbonyl complexes should result in a lowering of the barrier to 1,2 rearrangement. The coalescence temperatures for the ring protons in the isoelectronic complexes $\text{Mn}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)$ and $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)]^+$ are about 20 and -50°C , respectively, indicating a difference in activation energies of 3–8 kcal/mol.⁵⁹ In this case, the complex with the stronger back-bonding has the higher activation energy to its fluxional behavior. The apparent contradiction can be reconciled by assuming that the important factor is the aromaticity of the transition state for bond shifting. In the C_7H_7 complexes, the ring in the cationic iron system looks more like a tropylium ion than that in the neutral manganese complex, which may be closer to the antiaromatic C_7H_7^- .⁵⁹ In contrast, the increased back-bonding to the COT ring in $\text{M}(\text{arene})(\text{COT})$ relative to $\text{M}(\text{CO})_3(\text{COT})$ may cause the eight-membered ring to approach more closely the aromatic system COT^{2-} , either in the ground state or in the transition state for rearrangement. As noted above, there is some evidence from the C–C bond lengths in the uncoordinated diene moiety that delocalization over the whole COT ring is more extensive in $\text{Ru}(\text{HMB})(\text{COT})$ than in $\text{Ru}(\text{C}(\text{O})_3)(\text{COT})$. The fact that the ^{13}C NMR COT resonances of the $\text{M}(\text{arene})(\text{COT})$ complexes are about 10 ppm to higher field than those of the corresponding tricarbonyls is also consistent with this assertion. On the basis of the aromaticity hypothesis, we predict that the rate of rearrangement of $[\text{M}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)]^+$ should be greater than that of $[\text{M}(\text{arene})(\eta^5\text{-C}_7\text{H}_7)]^+$ ($\text{M} = \text{Fe}, \text{Ru}$). Unfortunately, we have so far been unable to prepare the latter species.

Finally, we note that our rough estimate of about 6–7 kcal/mol for the Arrhenius activation energy of the presumed 1,2 shift in $\text{Ru}(\text{arene})(\text{COT})$ complexes may be of the same order as the barrier to internal rotation about the metal–arene ring axis; cf. values of ca. 5 kcal/mol for reorientation of five-membered rings in substituted ferrocenes.^{60,61} Thus, if there is any significant direct overlap of arene and COT π orbitals, the two processes could be to some extent interdependent.

Registry No. $\text{Fe}(\text{C}_6\text{H}_6)(\text{COT})$, 72765-35-6; $\text{Fe}(\text{C}_6\text{H}_3\text{Me}_3)(\text{COT})$, 72765-34-5; $\text{Fe}(\text{C}_6\text{Me}_6)(\text{COT})$, 72765-33-4; $\text{Ru}(\text{C}_6\text{H}_6)(\text{COT})$, 62422-34-8; $\text{Ru}(\text{C}_6\text{H}_5\text{-}i\text{-Bu})(\text{COT})$, 72765-32-3; $\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)$ -

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RuCl₂(C₆H₃Me₃)py, 52490-90-1; RuCl(acac)(C₆H₃Me₃), 72778-73-5; [RuCl₂(HMB)]₂, 67421-02-7; [RuCl₂(C₆H₆)₂], 37366-09-9; RuCl₂(C₆H₆)py, 68012-51-1.

Supplementary Material Available: Listings of structure factor amplitudes and nonbonded contacts (7 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of ((Trimethylsilyl)methyl)gallium(III) Compounds

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A series of neutral organogallium(III) compounds which incorporate the (trimethylsilyl)methyl ligand, Ga(CH₂SiMe₃)_nX_{3-n} (n = 3, 2, 1; X = Cl, Br), have been prepared and fully characterized by elemental analyses, ¹H NMR and infrared spectroscopy, molecular weight data, solubility properties, and Lewis acid-base chemistry. The parent compound Ga(CH₂SiMe₃)₃ was prepared from GaCl₃ by a standard Grignard reaction in diethyl ether. The halogen derivatives were prepared from Ga(CH₂SiMe₃)₃ by elimination reactions with HCl or HBr and exchange reactions with GaCl₃ or GaBr₃. The following molecular formulas are supported by all available data: Ga(CH₂SiMe₃)₃, [Ga(CH₂SiMe₃)₂Cl]_x, [Ga(CH₂SiMe₃)₂Br]₂, [Ga(CH₂SiMe₃)Cl]₂, and [Ga(CH₂SiMe₃)Br]₂. It is noteworthy that the (trimethylsilyl)methyl ligand significantly influences the chemistry of only Ga(CH₂SiMe₃)₃ and [Ga(CH₂SiMe₃)₂Cl]_x. The Lewis acidity of Ga(CH₂SiMe₃)₃ has been greatly diminished as diethyl ether can be readily removed by simple vacuum distillation. The chemical and physical properties of Ga(CH₂SiMe₃)₂Cl, which could only be prepared in low yield by the elimination reaction, suggest that the compound might have an unusual structure. A "ladder" polymer or a linear polymer with one bridging chlorine atom per gallium atom is proposed. All other ((trimethylsilyl)methyl)gallium-halogen compounds have properties analogous to those of other known organogallium-halogen compounds.

Introduction

The enhanced thermal stability of the ((trimethylsilyl)methyl)metal compounds and their potential for unusual chemistry as imposed by the steric restraints of the organometallic ligand provide the impetus for synthesizing new compounds.^{1,2} The (trimethylsilyl)methyl derivatives of the group 3 elements, boron,³ aluminum,⁴ and indium,¹ have been prepared and fully characterized. The boron derivative,³ B(CH₂SiMe₃)₃, is readily made from BF₃·O(C₂H₅)₂ by a standard Grignard reaction in refluxing diethyl ether solution. Available data suggest that B(CH₂SiMe₃)₃ has a trigonal-planar structure. The aluminum compound,⁴ Al(CH₂SiMe₃)₃, prepared from Hg(CH₂SiMe₃)₂⁵ and aluminum foil, exists as a mixture of monomeric and dimeric species in benzene solution. Only in the case of indium¹ has a series of (trimethylsilyl)methyl derivatives In(CH₂SiMe₃)_xCl_{3-x} (x = 1, 2, 3) been studied. The parent compound, In(CH₂SiMe₃)₃, prepared by the Grignard reaction, exists as a monomeric three-coordinate species. The chloroindium derivatives¹ were prepared from In(CH₂SiMe₃)₃ by means of exchange reactions with InCl₃ or elimination reactions with HCl. Available data suggest that both the mono- and dichloroindium derivatives exist as chlorine-bridged dimers, but [In(CH₂SiMe₃)Cl]₂ probably has more extensive association in the solid state.¹ It is noteworthy that neither chloroindium compound formed a

stable adduct with any base examined in a Lewis acid-base study. The bases included N(CH₃)₃, CH₃CN, O(C₂H₅)₂, tetrahydrofuran, and dimethoxyethane.

An attempt to prepare Ga(CH₂SiMe₃)₃ from gallium metal and Hg(CH₂SiMe₃)₂ was surprisingly unsuccessful.⁴ Considering the success of the Grignard reaction for the preparation of the boron³ and indium¹ derivatives and the subsequent ease of removing diethyl ether from In(CH₂SiMe₃)₃, the Grignard reaction of GaCl₃ was investigated. In this paper we report the high yield synthesis of Ga(CH₂SiMe₃)₃. The diethyl ether was very readily removed. Additional experiments lead to the syntheses of a series of neutral organogallium(III) compounds which incorporate the (trimethylsilyl)methyl ligand, Ga(CH₂SiMe₃)_nX_{3-n} (X = Cl, Br; n = 1, 2, 3). All compounds have been fully characterized by elemental analyses, infrared spectra, molecular weight data, solubility properties, ¹H NMR data, and Lewis acid-base studies. Our results suggest that the (trimethylsilyl)methyl ligand introduces new chemical properties, reactivities, and structures in some of these organogallium(III) compounds.

Experimental Section

All compounds described in this investigation were extremely oxygen and moisture sensitive and were manipulated in a vacuum line or a purified nitrogen or argon atmosphere. The solvents and reagents were purified by conventional means. New compounds were analyzed for gallium by EDTA titration.⁶ Chlorine and bromine were determined by standard gravimetric procedures.

Synthesis of Ga(CH₂SiMe₃)₃. The compound Ga(CH₂SiMe₃)₃ was prepared from GaCl₃ and the Grignard reagent⁷ Me₃SiCH₂MgCl in diethyl ether solution. An argon-purged flask, containing 10.000 g (56.796 mmol) of GaCl₃ and 200 mL of ether, was equipped with

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