76-4; **2** ((*n* = 2)–S–(*n* = 2)), 87345-77-5; **3** (*n* = 3), 103590-87-0; **3** (*n* = 4), 103590-88-1; **3** (*n* = 5), 103590-89-2; **3** (*n* = 6), 103590-90-5; **3** ((*n* = 2)–O–(*n* = 2)), 103590-91-6; **3** ((*n* = 2)–S–(*n* = 2)), 103590-92-7; **4**, 936-49-2; **5**, 103590-93-8; **6**, 103590-94-9; **7**, 84927-40-2; **9**, 103590-95-0; **10**, 103590-96-1; **11**, 103590-97-2; **12**, 103590-98-3; **13**, 103590-99-4; **14**, 103591-00-0; **15**, 103591-01-1; Ni[**1** (*n* = 3)]$^{2+}$, 103591-02-2; Ni[**1** (*n* = 4)]$^{2+}$, 103591-03-3; Ni[**1** (*n* = 5)]$^{2+}$, 103591-04-4; Ni[**1** (*n* = 6)]$^{2+}$, 103591-05-5; Ni[**1** (*n* = 2)$_2$–O]$^{2+}$, 103591-06-6; 2-chlorotropone, 3839-48-3; 1,2-diaminoethane, 107-15-3; 2-(tosyloxy)tropone, 38768-08-0; 1,3-diaminopropane, 109-76-2; 1,4-diaminobutane, 110-60-1; 1,5-diaminopentane, 462-94-2; 1,6-diaminohexane, 124-09-4; 1,5-diamino-3-oxapentane, 2752-17-2; 1,5-diamino-3-thiapentane, 871-76-1.

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Coordinatively Saturated Cationic Ruthenium(II) Complexes. Preparation, Characterization, and Reaction with Potassium Superoxide

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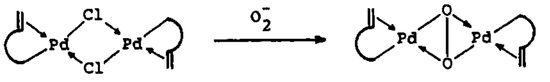
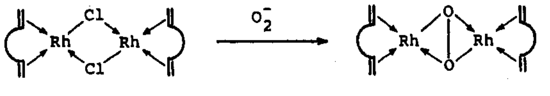
Coordinatively saturated cationic ruthenium(II) complexes, $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Ru^{II}][BF_4]$ (**1**), $[(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)Ru^{II}][BF_4]$ (**2**), $[(1\text{–}5\text{-}\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6H_6)Ru^{II}][BF_4]$ (**3**), $[(1\text{–}5\text{-}\eta^5\text{-}C_7H_9)(\eta^6\text{-}C_6H_6)Ru^{II}][BF_4]$ (**4**), $[(1\text{–}3{:}5,6\text{-}\eta^5\text{-}C_8H_{11})(\eta^6\text{-}C_6H_6)Ru^{II}][BF_4]$ (**5**), and $[(6\text{-EtO–}1\text{–}5\text{-}\eta^5\text{-}C_7H_8)(\eta^6\text{-}C_6H_6)Ru^{II}][BF_4]$ (**7**), are prepared by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with cyclopentadiene, pentamethylcyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, and 1,3,5-cycloheptatriene, respectively, in ethanol in the presence of $AgBF_4$. Superoxide anion attacks at the terminal position of the dienyl moiety of **3–5** to yield ruthenium(0) complexes **8–10**, containing cyclic dienone ligand.

Introduction

Interaction between dioxygen and transition-metal complexes has become an important area of investigation over the last two decades primarily since this may be a key step for catalytic oxygenation reactions.[1] Numbers of peroxo complexes can be obtained by the reaction of molecular oxygen with low-valent transition-metal complexes containing tertiary phosphines or isonitriles as auxiliary ligands. Transfer of coordinated dioxygen to olefins giving epoxides or ketones was examied by interaction of the peroxo complexes with cyanoolefins, and several intermediary peroxometallacyclic adducts were isolated.[2] Not only dioxygen but superoxide (O_2^-) and peroxide (O_2^{2-}), resulting from electron transfer from the metal species to dioxygen, deeply participate in the metal-catalyzed oxidation. In previous papers, we reported that the reaction of coordinatively unsaturated (16 e) palladium(II) and rhodium(I) olefin complexes with superoxide ion (O_2^-) afforded the corresponding μ-peroxo complexes via a nucleophilic attack of superoxide ion on the metal center (eq 1 and 2).[3] Superoxide ion may also attack the metal center of the coordinatively unsaturated (16 e) cationic rhodium(I) complex to yield dimeric peroxo complexes, e.g. $[(1,5\text{-COD})RhO_2]_2$, which liberates cyclooctanone on pyrolysis in benzene solution in the presence of cyclohexene (eq 3).[4] We have also reported the reaction of *tert*-butylperoxide anion (t-BuOO$^-$) with cationic rhodium(I) and palladium(II) complexes.[5] In the reaction with electronically saturated cationic complexes, t-BuOO$^-$ attacks the coordinated olefinic ligand, whereas it attacks the cationic metal center directly in the reaction with the complexes with 16e configurations. Thus, the number of electrons around the metal center, 16 or 18, may determine the reaction site of superoxide ion toward the metal–olefin complex, i.e. at the metal center as opposed to the coordinated olefin. We have expanded our studies to clarify the reaction of superoxide ion with coordinatively saturated metal–olefin complexes. In this paper we describe the preparation and characterization of novel cationic ruthenium complexes of 18-electron configuration and their reactions with superoxide ion.



(1)



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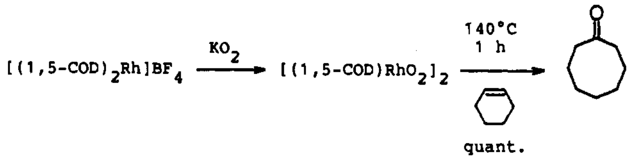

(3)

Experimental Section

All manipulations were carried out under an atmosphere of dry argon, using either standard Schlenk or vacuum techniques. All solvents used were dried by conventional techniques[6] and were distilled under an atmosphere of dry argon prior to use. Unless otherwise noted, all reagents were obtained from commercial suppliers. Potassium superoxide[7] and potassium 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienide[8] were freshly prepared prior to use by the literature procedures. The ruthenium complexes $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$[9] and $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$[10] were prepared

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by the literature procedures. An ultrasonic cleaner, Bransonic 12 (45 kHz/35 W), was used for vigorous agitation of the reaction mixture in the preparation of cationic complexes. A neutral alumina column for chromatography utilized Merck Aluminiumoxid 90 (Art. 1097). Proton and carbon-13 NMR spectra were recorded on either a JEOL FX-100, a JEOL GX-400, or a JEOL GX-500 spectrometer. Correlated 2D NMR spectra were measured on JEOL GX-400 and GX-500 spectrometers. All proton and carbon-13 chemical shifts are reported as δ values relative to internal tetramethylsilane. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet); addition of br indicates a broadened pattern. Infrared spectra were recorded on a Hitachi 260-50 grating spectrophotometer. Melting points were determined on a Büchi melting point determiner 510 in sealed capillaries and are uncorrected. Elemental analyses were performed by the analytical facility in the Research Laboratory of Resources Utilization at Tokyo Institute of Technology and by the Microanalytical Center at Kyoto University.

Preparation of $[(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)Ru][BF_4]$ (1). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.428 g, 0.86 mmol), cyclopentadiene (3 mL, 36.3 mmol), and ethanol (10 mL) were placed in a Schlenk tube filled with dry argon. After addition of a solution of $AgBF_4$ (0.713 g, 3.66 mmol) in 5 mL of ethanol, the reaction mixture was vigorously agitated for 1 h at room temperature by using an ultrasonic cleaner. Filtration of the resulting reaction mixture followed by concentration of the filtrate afforded colorless needles. The product was collected on a fine frit and was successively washed with one 5-mL portion of ethanol and two 5-mL portions of diethyl ether. Drying in vacuo gave 0.203 g (36%) of **1**, mp 246 °C dec. IR (KBr): 3055, 2998, 1439, 1415, 1306, 1053, 1025, 910, 859, 822, 539, 527, 427, 399, 371, 305 cm^{-1}. ^1H NMR ($CDCl_3$–Me_4Si): δ 5.37 (s, 5 H), 6.13 (s, 6 H). ^{13}C NMR ($CDCl_3$–Me_4Si): δ 80.7 (C_5H_5, J_{C-H} = 182.4 Hz), 86.1 (C_6H_6, J_{C-H} = 178.8 Hz).

Preparation of $[(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5Me_5)Ru][BF_4]$ (2). $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ (0.147 g), ethanol (10 mL), and benzene (2 mL) were placed in a Schlenk tube filled with dry argon. A solution of $AgBF_4$ (0.109 g, 0.56 mmol) in 5 mL of ethanol was then added, and the reaction mixture was vigorously agitated for 2 h at room temperature by using an ultrasonic cleaner. Filtration followed by concentration of the filtrate gave a yellow crystalline solid of **2** (0.052 g, 24%), mp 203 °C dec. IR (KBr): 3078, 2984, 2966, 2916, 1479, 1438, 1392, 1285, 1050, 833, 593, 528, 468, 448, 399, 319 cm^{-1}. ^1H NMR (CD_3COCD_3–Me_4Si): δ 2.12 (s, Cp–CH_3, 15 H), 6.08 (s, C_6H_6, 6 H). ^{13}C NMR (CD_3COCD_3–Me_4Si): δ 10.7 (Cp–CH_3), 87.6 (C_5Me_5), 88.3 (C_6H_6).

Preparation of $[(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)Ru][BF_4]$ (3). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.220 g, 0.44 mmol), ethanol (10 mL), and 1,3-cyclohexadiene (1.0 mL, 10.5 mmol) were placed in a Schlenk tube filled with dry argon. $AgBF_4$ (0.363 g, 1.86 mmol) dissolved in 5 mL of ethanol was then added. The mixture was allowed to react for 3 h at ambient temperature by use of an ultrasonic cleaner. The AgCl formed in the reaction was removed by filtration. Pale yellow needles of **3** precipitated from the concentrated filtrate and were collected on a glass frit, washed successively with ethanol and diethyl ether, and dried in vacuo giving 0.111 g (37% yield); mp 201 °C dec. IR (KBr): 3051, 2881, 2824, 1436, 1397, 1301, 1076, 1025, 887, 870, 821, 538, 527, 478, 406, 363 cm^{-1}. ^1H NMR (CD_3OD–Me_4Si): δ 2.34 (m, H_6, 1 H), 2.71 (m, H_6, 1 H), 3.74 (m, H_1 and H_5, 2 H), 5.21 (dd, J = 5.2 and 6.2 Hz, H_2 and H_4, 2 H), 6.32 (s, C_6H_6, 6 H), 6.56 (t, J = 5.2 Hz, H_3, 1 H). ^{13}C NMR ($CDCl_3$–Me_4Si): δ 27.4 (t, J_{C-H} = 133.4 Hz), 38.5 (d, J_{C-H} = 170.0 Hz), 87.6 (d, J_{C-H} = 171.4 Hz), 88.1 (d, J_{C-H} = 171.4 Hz), 90.2 (d, J_{C-H} = 177.3 Hz, C_6H_6). Anal. Calcd for $C_{12}H_{13}BF_4Ru$: C, 41.76; H, 3.79. Found: C, 41.74; H, 3.62.

Preparation of $[(\eta^6\text{-}C_6H_6)(1\text{–}5\text{-}\eta^5\text{-}C_7H_9)Ru][BF_4]$ (4). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.671 g, 1.34 mmol), ethanol (10 mL), and 1,3-cycloheptadiene (1 mL, 9.22 mmol) were placed in a Schlenk tube filled with dry argon. A solution of $AgBF_4$ (1.12 g, 5.73 mmol) in 5 mL of ethanol was then added at once, and the mixture was allowed to react with vigorous agitation for 3 h at room temperature by using an ultrasonic cleaner. Removal of the AgCl formed in the reaction by filtration followed by cooling of the filtrate afforded **4** as yellow plates (0.288 g, 30%), mp 226 °C dec. IR (KBr): 3084, 3012, 2938, 2869, 2837, 1445, 1406, 1359, 1340, 1308, 1286, 1186, 1053, 976, 884, 863, 818, 525, 466, 431, 399, 360, 320 cm^{-1}. ^1H NMR ($CDCl_3$–Me_4Si): δ 1.30 (m, 2 H), 1.95 (m, 2 H), 4.83 (m, 2 H), 5.25 (dd, J = 5.8 and 8.3 Hz, 2 H), 6.15 (s, 6 H), 6.33 (t, J = 5.8, 1 H). ^{13}C NMR (CD_3COCD_3): δ 34.7 (t, J_{C-H} = 129.0 Hz, $C_{6,7}$), 76.0 (d, J_{C-H} = 155.3 Hz, $C_{1,5}$), 89.2 (d, J_{C-H} = 168.5 Hz, $C_{2,4}$), 92.3 (d, J_{C-H} = 178.8 Hz, C_6H_6), 97.6 (d, J_{C-H} = 170.0 Hz, C_3).

Preparation of $[(\eta^6\text{-}C_6H_6)(1\text{–}3\text{:}5,6\text{-}\eta^5\text{-}C_8H_{11})Ru][BF_4]$ (5). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.611 g, 1.22 mmol), 1,5-cyclooctadiene (5 mL, 40.8 mmol), and ethanol (15 mL) were placed in a Schlenk tube filled with dry argon. A solution of $AgBF_4$ (0.983 g, 5.05 mmol) in 5 mL of ethanol was then added, and the reaction mixture was allowed to react with vigorous agitation for 3 h at room temperature by using an ultrasonic cleaner. Filtration of the resultant yellow suspension under an atmosphere of argon and concentration of the filtrate in vacuo followed by cooling of the solution gave complex **5** as yellow plates. The product was successively washed with one 5-mL portion of ethanol and two 5-mL portions of diethyl ether and dried in vacuo. The yield of the crystalline product was 0.479 g (53%); mp 195 °C dec. IR (KBr): 3025, 2940, 2920, 2882, 1438, 1303, 1278, 1080, 1038, 598, 540, 528 cm^{-1}. Anal. Calcd for $C_{14}H_{17}RuBF_4$: C, 45.06; H, 4.59. Found: C, 44.81; H, 4.59.

$[(\eta^6\text{-}C_6H_6)(1\text{–}3\text{:}5,6\text{-}\eta^5\text{-}C_8H_{11})Ru][C_5(CO_2CH_3)_5]$ (6). Complex **5** (0.147 g, 0.39 mmol), $K[C_5(CO_2CH_3)_5]$ (0.163 g, 0.41 mmol), and ethanol (10 mL) were placed in a Schlenk tube. The resulting mixture was allowed to react with stirring for 24 h at room temperature. Filtration and concentration of the filtrate under reduced pressure followed by purification by column chromatography on neutral alumina with acetone gave **6** as a yellow powder (0.088 g, 35%); mp 142 °C. IR (KBr): 3072, 2990, 2946, 2834, 1700, 1450, 1392, 1276, 1178, 1067, 1006, 942, 864, 835, 816, 798, 786, 748, 635, 596, 398, 350 cm^{-1}. ^{13}C NMR ($CDCl_3$–Me_4Si): δ 19.3, 27.9, 28.4, 33.2, 35.9, 51.4, 72.4, 79.5, 84.2, 91.4 (C_6H_6), 117.1, 167.5 (C=O). Anal. Calcd for $C_{29}H_{32}O_{10}Ru$: C, 54.29; H, 5.03. Found: C, 54.16; H, 5.07.

Preparation of $[(\eta^6\text{-}C_6H_6)(C_2H_5O\text{-}\eta^5\text{-}C_7H_8)Ru][BF_4]$ (7). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.356 g, 0.71 mmol), ethanol (10 mL), and cycloheptatriene (3 mL, 29 mmol) were placed in a Schlenk tube charged with dry argon. A solution of $AgBF_4$ (0.560 g, 2.88 mol) in 5 mL of ethanol was then added, and the mixture was stirred for 4 h at room temperature. The AgCl formed in the reaction was removed by filtration. The yellow crystalline solid that precipitated from the concentrated filtrate was collected on a glass frit, washed with ethanol and diethyl ether, and dried in vacuo (0.341 g, 60%); mp 124 °C. IR (KBr): 3059, 2971, 2929, 2865, 1443, 1393, 1357, 1306, 1072, 1031, 861, 819, 542, 527, 400, 357 cm^{-1}. ^1H NMR ($CDCl_3$–Me_4Si): δ 1.22 (t, J = 7.2 Hz, 3 H), 1.40 (m, 1 H), 1.84 (m, 1 H), 3.24–3.68 (m, 3 H), 4.72 (m, 2 H)8 5.27 (dd, J = 6 and 8.4 Hz, 1 H), 5.40 (dd, J = 6 and 7.2 Hz, 1 H), 6.26 (s, 6 H), 6.46 (t, J = 6 Hz, 1 H). ^{13}C NMR ($CDCl_3$–Me_4Si): δ 15.6 (CH_3), 38.1 (CH_2, C_7), 63.9 (OCH_2), 69.7 (OCH_2), 77.9 (CH), 84.6 (CH), 85.9 (CH), 89.0 (CH), 91.6 (C_6H_6), 98.2 (CH, C_3). Anal. Calcd for $C_{15}H_{19}OBF_4Ru$: C, 44.69; H, 4.75. Found: C, 44.77; H, 4.55.

(η-Benzene)(η-cyclohexa-2,4-dien-1-one)ruthenium(0) (8). A Schlenk tube was charged with a magnetic stirrer, 0.134 g (0.39 mmol) of **3**, and 10 mL of dichloromethane. Then 0.183 g (2.58 mmol) of finely powdered KO_2 was added under a positive pressure of dry argon, and the reaction mixture was stirred for 48 h at ambient temperature. Excess KO_2 and KBF_4 formed in the reaction were removed by filtration. Concentration of the filtrate under reduced pressure gave a yellow oil. Purification by column chromatography on neutral alumina with chloroform followed by recrystallization from $CHCl_3/(C_2H_5)_2O$ afforded **8** as yellow prisms (0.030 g, 28%); mp 146 °C dec. IR (KBr): 2990, 2920, 2848, 1620, 1428, 1438, 1280, 1239, 1130, 1108, 1081, 1018, 962, 904, 882, 804, 603, 561, 491 cm^{-1}. ^1H NMR (C_6D_6–Me_4Si): δ 2.56 (m, H_6, 2 H), 2.89 (m, H_5, 1 H), 3.66 (d, $J_{2,3}$ = 5.4 Hz, H_2, 1 H), 4.58 (m, H_4, 1 H), 4.69 (s, C_6H_6, 6 H), 4.96 (ddd, $J_{2,3}$) = 5.4 Hz, $J_{3,4}$ = 3.9 Hz, $J_{3,5}$ = 1.5 Hz, H_3, 1 H). ^{13}C NMR (C_6D_6–Me_4Si): δ 36.2 (t, J_{C-H} = 128.9 Hz), 39.6 (d, J_{C-H} = 156.8 Hz), 60.2 (d, J_{C-H} = 158.3 Hz), 73.8 (d, J_{C-H} = 168.5), 77.1 (d, J_{C-H} = 165.6 Hz), 81.8 (d, J_{C-H} = 174.4 Hz, C_6H_6), 193.4 (s, C=O). Anal. Calcd for $C_{12}H_{12}ORu$: C, 52.74; H, 4.43. Found: C, 52.14; H, 4.40.

(η-Benzene)(η-cyclohepta-2,4-dien-1-one)ruthenium(0) (9). A Schlenk tube was charged with a magnetic stirrer, 0.213 g (0.59 mmol) of **4**, and 10 mL of dichloromethane. To the resulting yellow solution was added finely powdered KO_2 (0.145 g, 2.04 mmol) at room temperature under an atmosphere of dry argon, and the reaction mixture was allowed to react with stirring for 4 h. Excess KO_2 and KBF_4 formed in the reaction were removed by filtration. Concentration of the filtrate under reduced pressure followed by purification of the resultant oily residue by column chromatography on neutral alumina with chloroform afforded **9** (yellow prisms, 0.013 g, 8%) and **11** (yellow needles, 0.048 g, 23%).

9. Mp: 130 °C. IR (KBr): 3072, 3053, 3005, 2964, 2914, 2822, 1613, 1435, 1429, 1381, 1355, 1262, 1216, 1163, 1152, 1131, 1113, 1051, 1042, 1003, 962, 903, 859, 799, 593, 508, 302 cm^{-1}. ^1H NMR ($CDCl_3$–Me_4Si): δ 1.76 (m, $J_{7,7'}$ = 12.3, $J_{7,6}$ = 5.3 Hz, $J_{7,6'}$ = 2.7 Hz, $J_{7,1}$ = 2.0 Hz, H_7, 1 H), 1.83 (ddd, $J_{7',7}$ = 12.3 Hz, $J_{7',6}$ = 12.7 Hz, $J_{7',6'}$ = 5.2 Hz, $H_{7'}$, 1 H), 2.66 (dddd, $J_{6,7}$) = 5.3 Hz, $J_{6,7'}$ = 12.7 Hz, $J_{6,6'}$ = 15.0 Hz, $J_{6,5}$ = 1.0 Hz, H_6, 1 H), 2.95 (dddd, $J_{6',7}$ = 2.7 Hz, $J_{6',7'}$ = 5.2 Hz, $J_{6',6}$ = 15.0 Hz, $J_{6',5}$ = 5.5 Hz, $H_{6'}$, 1 H), 3.28 (ddd, $J_{5,6}$ = 1.0 Hz, $J_{5,6'}$ = 5.5 Hz, $J_{5,4}$ = 7.2 Hz, H_5, 1 H), 3.56 (dd, $J_{2,7}$ = 2.0 Hz, $J_{2,3}$ = 5.6 Hz, H_2, 1 H), 4.69 (dd, $J_{4,5}$ = 7.2 Hz, $J_{4,3}$ = 6.4 Hz, H_4, 1 H), 5.34

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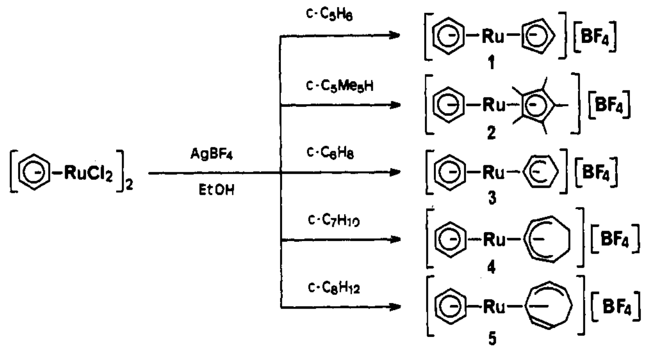
Scheme I



(dd, $J_{3,2}$ = 5.6 Hz, $J_{3,4}$ = 6.4 Hz, H_3, 1 H), 5.39 (s, aromatic, 6 H). ^{13}C NMR ($CDCl_3$–Me_4Si): δ 38.7, 44.3, 51.2, 51.7, 78.2, 81.9, 82.6 (C_6H_6), 210.5 (C=O). Anal. Calcd for $C_{13}H_{14}ORu$: C, 54.34; H, 4.91. Found: C, 54.44; H, 4.90.

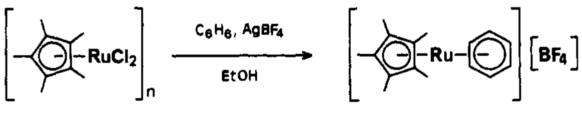
11. ^1H NMR (C_6D_6–Me_4Si): δ 1.55 (m, 2 H), 1.96 (m, 2 H), 3.88 (m, 2 H), 4.33 (dd, *J* = 5.5 and 7.9 Hz, 2 H), 4.90 (t, *J* = 5.5 Hz, 1 H), 2.92 (dt, *J* = 9.6 and 5.5 Hz, 1 H), 3.19 (dd, *J* = 5.5 and 5.4 Hz, 2 H), 4.06 (dd, *J* = 5.4 and 5.0 Hz, 2 H), 4.41 (d, *J* = 9.6 Hz, 1 H), 4.67 (t, *J* = 5.0 Hz, 1 H). Anal. Calcd for $C_{14}H_{16}Cl_2Ru$: C, 47.20; H, 4.53; Cl, 19.90. Found: C, 47.34; H, 4.52; Cl, 19.60.

Reaction of [(η^6-C_6H_6)(1–5-η^5-C_7H_9)Ru][BF_4] with CH_2Cl_2 in the Presence of KOH. Complex **4** (0.065 q, 0.18 mmol), dichloromethane (10 mL), and KOH (0.075 g, 1.34 mmol) were placed in a Schlenk tube filled with dry argon. The mixture was vigorously agitated for 1 day at ambient temperature by using an ultrasonic cleaner. Filtration and concentration of the filtrate under reduced pressure followed by purification by column chromatography on neutral alumina with diethyl ether gave **11** as a yellow powder. Recrystallization from $(C_2H_5)_2O$/*n*-C_5H_{12} (1:1 v/v) afforded yellow needles of **11** (0.072 g, 90%).

(η-Benzene)(η-cycloocta-2,6-dien-1-one)ruthenium(0) (10). A Schlenk tube was charged with a magnetic stirrer, 0.544 g (1.46 mmol) of **5**, and 20 mL of dichloromethane, and the mixture was cooled at −78 °C. After 0.266 g (3.74 mmol) of powdered KO_2 was added, the reaction mixture was gradually warmed to room temperature and allowed to react for 2 h. Excess KO_2 and KBF_4 formed were removed by filtration. Purification using column chromatography on neutral alumina with chloroform, followed by recrystallization from $CHCl_3/(C_2H_5)_2O$ (2:1 v/v), gave **10** as yellow plates (0.205 g, 47%); mp 146 °C dec. IR (KBr): 2995, 2952, 2933, 2861, 2804, 1630, 1443, 1428, 1347, 1262, 1240, 1163, 1130, 962, 880, 861, 780, 553, 520, 383 cm^{-1}. ^1H NMR ($CDCl_3$–Me_4Si): δ 1.52 (ddt, *J* = 14.7, 4.4 and 9.0 Hz, H_4, 1 H), 2.02 (m, H_4, 1 H), 2.21 (m, H_5, 2 H), 2.43 (m, H_8, 2 H), 3.04 (dt, *J* = 8.1 and 6.7 Hz, H_7, 1 H), 3.51 (d, *J* = 8.5 Hz, H_2, 1 H), 3.73 (m, H_6, 1 H), 3.81 (ddd, *J* = 8.5, 9.5, and 4.4 Hz, H_3, 1 H), 5.44 (s, C_6H_6, 6 H). ^{13}C NMR ($CDCl_3$–Me_4Si): δ 29.8 (t, J_{C-H} = 126.0 Hz, C_4), 31.3 (d, J_{C-H} = 163.4 Hz, C_7), 35.7 (t, J_{C-H} = 124.6 Hz, C_8), 36.3 (t, J_{C-H} = 121.6 Hz, C_5), 58.9 (d, J_{C-H} = 159.7 Hz, C_3), 64.1 (d, J_{C-H} = 160.3 Hz, C_6), 64.3 (d, J_{C-H} = 158.3 Hz, C_2), 87.6 (d, J_{C-H} = 171.4 Hz, C_6H_6), 198.3 (s, C_1). Anal. Calcd for $C_{14}H_{16}ORu$: C, 55.80; H, 5.31. Found: C, 54.57; H, 5.29.

Results and Discussion

The reaction of the ruthenium(II) complex [(η^6-C_6H_6)$RuCl_2$]$_2$ with cyclic dienes or triene in the presence of $AgBF_4$ provides a new route to the coordinatively saturated (18 e) cationic complexes containing cyclic dienyl ligands. The cationic ruthenium(II) complexes **1–5** were prepared by the reaction of [(η^6-C_6H_6)$RuCl_2$]$_2$ with cyclopentadiene, pentamethylcyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,5-cyclooctadiene, respectively, in ethanol in the presence of $AgBF_4$ (Scheme I). Complex **7** was formed via a nucleophilic attack of EtO^- at the terminal carbon atom of conjugated triene coordinated by the cationic ruthenium. Complex **2** could alternatively be synthesized by the treatment of [(η^5-C_5Me_5)$RuCl_2$]$_n$[10] with benzene in ethanol in the presence of $AgBF_4$ (eq 4).



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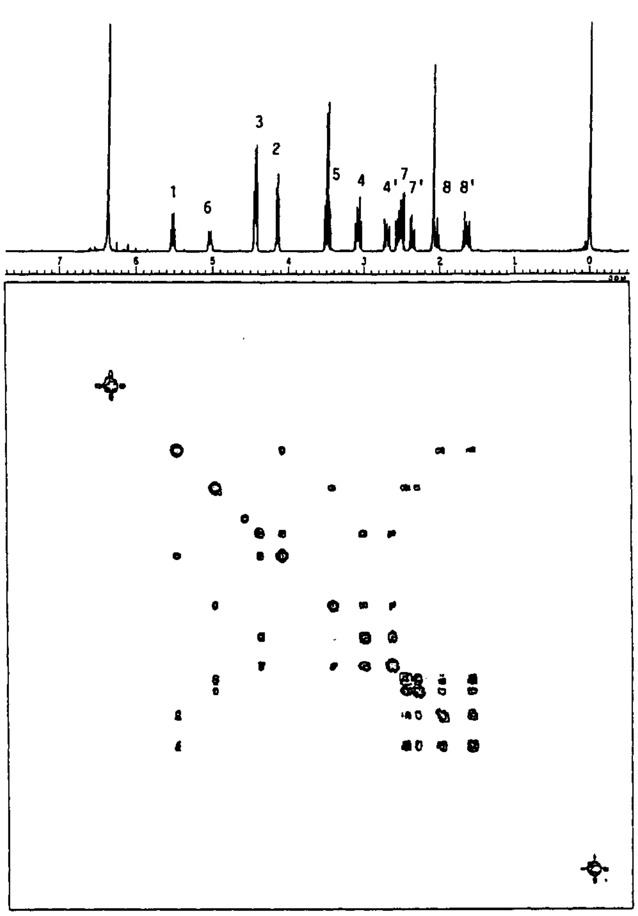

Figure 1. Contour plot of the 400-MHz ^1H COSY spectrum of complex **5**.

These cationic complexes are yellow and sparingly soluble in saturated and aromatic hydrocarbons; therefore, they were recrystallized from acetone or chloroform/diethyl ether. The complexes were characterized by IR and ^1H and ^{13}C NMR spectroscopy as well as by elemental analysis. The ^1H and ^{13}C NMR spectra for the C_8H_{11} ligand of **5** reveal very complicated resonance patterns; 11 multiplets for ^1H and five ^{13}CH and three $^{13}CH_2$ signals are present in the spectra of **5**. The ^1H and ^{13}C NMR spectra resemble those of [(1–3:5,6-η^5-C_8H_{11})Ru^{II}][BPh_4] (**11**),[11] [(1–3:5,6-η^5-C_8H_{11})Ru^{II}][$BPhF_3$] (**12**),[11] [(1–3:5,6-η^5-C_8H_{11})(η^5-C_5Me_5)M^{III}][PF_6] (**13**; M = Rh, Ir),[12] [(1–3:5,6-η^5-C_8H_{11})$(CO)_3M^{II}$][BF_4] (**14**; M = Fe, Ru, Os),[13] and [(1–3:5,6-η^5-C_8H_{11})$_2Ru^{II}$ (**15**).[14] However, the assignment of their resonance peaks partly remains equivocal. Recently, Tkatchenko has reported some analogous cationic cyclooctadienyl complexes [(1–3:5,6-η^5-C_8H_{11})Ru^{II}(L)][Y] (**16**; L = 1,3,5-C_8H_{10}, C_6H_6, 3CO, 3P$(OMe)_3$; Y = PF_6, BF_4).[15] Among them, the NMR parameters of [(1–3:5,6-η^5-C_8H_{11})(η^6-C_6H_6)Ru^{II}][PF_6] resemble those of **5**.

The ^1H and ^{13}C NMR assignments for the 1–3:5,6-η^5-C_8H_{11} ligand were greatly facilitated by the use of 2D homonuclear correlation spectroscopy (COSY) and ^{13}C–^1H chemical shift correlation spectroscopy. The COSY spectrum for [(1–3:5,6-η^5-C_8H_{11})(η^6-C_6H_6)Ru^{II}][BF_4] (**5**) is shown in Figure 1.

A contour plot of the COSY map identifies the spin coupling network of the individual proton signals. The resonance peaks

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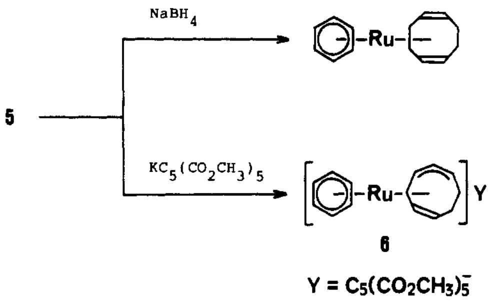
Table I. Proton and Carbon-13 NMR Parameters of **5**[a]

	^{1}H chem shift, ppm	J_{H-H},[b] Hz	^{13}C chem shift, ppm	J_{C-H}, Hz
1	5.50	(1–2) = 7.7, (1–3) = 1.2, (1–8) = 9.3, (1–8′) = 6.6	73.1	144.0
2	4.12	(2–3) = 6.9	80.5	166.0
3	4.41	(3–4) = 9.2, (3–4′) = 5.4	33.9	170.9
4	3.05	(4–4′) = 13.8, (4–5) = 8.9	19.7	135.5
4′	2.67	(4′–5) = 7.2, (4′–6) = 1.0		
5	3.46	(5–6) = 8.7, (5–7′) = 1.4	29.1	170.9
6	5.00	(6–7) = 6.3, (6–7′) = 1.4	85.1	161.0
7	2.50	(7–7′) = 15.3, (7–8) = 9.8, (7–8′) = 13.0	36.5	133.2
7′	2.34	(7′–8) = 1.4, (7′–8′) = 6.6		
8	2.03	(8–8′) = 13.3	28.54	124.5
8′	1.62			

[a] Spectra were measured in acetone-d^6 at 30 °C. [b] Numbers in parentheses represent hydrogens.

Scheme II



at 5.50, 4.12, and 4.41 ppm are assigned to those for η^3-allyl moiety, H_1, H_2, and H_3, respectively. The resonances for olefinic protons, H_5 and H_6, appear at 3.46 and 5.00 ppm.

A contour plot of ^{1}H–^{13}C chemical shift correlation NMR experiment for complex **5** is shown in Figure 2, where cross peaks are observed at positions (ω^H, ω^C) when there is scalar coupling between the proton at ω^H and the ^{13}C nucleus at ω^C.

The ^{13}C resonances at 29.1 and 85.1 ppm show couplings to olefinic protons H_5 at 3.46 ppm and H_6 at 5.00 ppm, respectively. The resonances at 73.1, 80.5, and 33.9 ppm show the cross peaks with protons of η-allyl moiety at 5.50, 4.12, and 4.41 ppm. The magnitude of J_{C-H} for these ^{13}C resonances were well consistent with those for sp^2 carbons. The ^{1}H and ^{13}C chemical shifts and the magnitudes of the J couplings are listed in Table I. It is noteworthy that the resonance peaks for C_3 and C_5 appear in the extraordinary high field, 33.9 and 29.1 ppm, in spite of the sp^2 character of these carbons, whereas those for C_1 and C_6 are observed at 73.1 and 85.0 ppm, respectively.

The structure of complex **5** was also confirmed through the reactions with $NaBH_4$ and $KC_5(CO_2CH_3)_5$ (Scheme II). Complex **5** was converted to well-characterized (η^6-C_6H_6)(1,5-COD)Ru^0 [16] in 80% yield by treatment with $NaBH_4$ in ethanol by way of a nucleophilic addition of H$^-$ at the C_3 position.

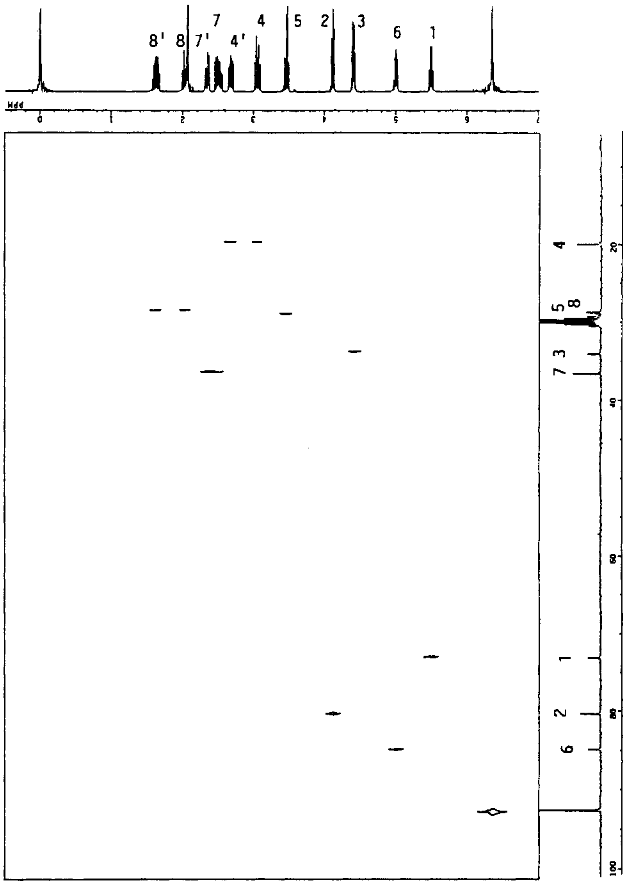
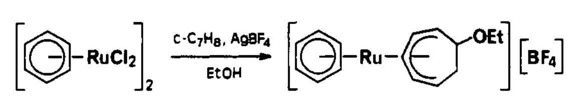


Figure 2. Contour plot of the ^{13}C–^{1}H chemical shift correlation spectrum of complex **5**.

The anion-exchange reaction of **5** with substituted cyclopentadienyl anion gave novel cationic complex **6**. Treatment of **5** with (pentakis(methoxycarbonyl)cyclopentadieneyl)potassium, $[C_5(CO_2CH_3)_5]K$, afforded $[(\eta^6\text{-}C_6H_6)(1\text{-}3{:}5,6\text{-}\eta^5\text{-}C_8H_{11})\text{-}Ru^{II}][C_5(CO_2CH_3)]$ (**6**).

Structures **3** and **4** were also assigned on the basis of ^{1}H and ^{13}C NMR spectra. The ^{1}H and ^{13}C NMR chemical shifts of **3** and **4** are listed in Tables II and III together with those of some analogues.

In the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with cycloheptatriene in the presence of $AgBF_4$ in ethanol, $[(\eta^6\text{-}C_6H_6)(6\text{-}C_2H_5O\text{-}1\text{-}5\text{-}\eta^5\text{-}C_7H_8)Ru^{II}][BF_4]$ (**7**) was formed via a nucleophilic attack of EtO$^-$ on the coordinated cycloheptatriene (eq 5). The key spectral features of **7** that characterize its structure are the ^{1}H and ^{13}C NMR parameters associated with the dienyl ligand. The resonances of the dienyl protons of the 6-C_2H_5O-1–5-η^5-C_7H_8 ligand appeared at δ 4.72 (H_1 and H_5), 5.27 (H_2, or H_4), 5.40 (H_4 or H_2), and 6.46 (H_3). The chemical shifts of these protons are very similar to those of symmetrically coordinated C_7H_9 ligand of **4**. In the ^{13}C NMR of **7**, resonances for five sp^2 carbons attributable to dienyl moiety appear at δ 77.9, 84.6, 85.9, 89.0, and 98.2.



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Many studies on the dioxygen complexes have been reported in the last two decades; however, there are few reported examples of the interaction between coordinated olefin and oxygen. We previously reported the reaction of metal–olefin complexes with negatively charged dioxygen species. Superoxide ion reacted with

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Table II. Proton and Carbon-13 NMR Chemical Shifts of Cyclohexadienyl Ligand

complex	^{1}H NMR, ppm $H_{1,5}$	$H_{2,4}$	H_3	H_6	^{13}C NMR, ppm $C_{1,5}$	$C_{2,4}$	C_3	C_6	ref
$(\eta\text{-}C_6H_7)Ru(\eta\text{-}C_6H_6)^+$	3.74	5.21	6.56	2.34, 2.71	38.5	88.1	87.6	27.4	this work
$(\eta\text{-}C_6H_7)Ru(CO)_3^+$	4.55	6.10	6.90	3.10					17
$(\eta\text{-}C_6H_7)Ru(\eta\text{-}C_5H_5)$	2.55	4.36	5.71	2.55, 2.75					18
$(\eta\text{-}C_6H_7)Ru(CO)_2(EPTB)^+$	4.14	5.55	6.75	3.25					19
$(\eta\text{-}C_6H_7)Ru(PMe_2Ph)(o\text{-phen})^+$					32.7	96.1	95.9	27.5	20
$(\eta\text{-}C_6H_7)Fe(CO)_3^+$	4.27	5.82	7.22	2.57	65.4	103.2	89.9	24.7	21, 22
$(\eta\text{-}C_6H_7)Mn(CO)_3$					50.1	98.0	79.7	24.2	23

Table III. Proton and Carbon-13 NMR Chemical Shifts of Cycloheptadienyl Ligand

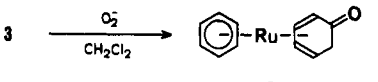
complex	^{1}H NMR, ppm $H_{1,5}$	$H_{2,4}$	H_3	$H_{6,7}$	^{13}C NMR, ppm				ref
$(\eta\text{-}C_7H_9)Ru(\eta\text{-}C_6H_6)^+$	4.83	5.25	6.33	1.30, 1.95	76.0 ($C_{1,5}$)	89.2 ($C_{2,4}$)	97.6 (C_3)	34.7 ($C_{6,7}$)	this work
(2–6-η-bicyclo[5.1.0]octadienyl)-$Ru(PMe_2Ph)_3^+$	3.39 ($H_{2,6}$)	4.62 ($H_{3,5}$)	5.86 (H_4)		80.2 ($C_{2,6}$)	94.7 ($C_{3,5}$)	87.7 (C_4)		24
$(\eta\text{-}C_7H_9)Ru(CO)_3^+$	5.24	6.29	6.90	2.20, 2.62					17
$(\eta\text{-}C_7H_9)Ru(CO)_2(PPh_3)^+$	4.44	5.60	6.85	1.96, 2.45					17
$(\eta\text{-}C_7H_9)Ru(CO)_2(EPTB)^+$	5.88	6.04	6.75	2.00, 2.70					19

Table IV. Proton and Carbon-13 NMR Chemical Shifts of Complexes **8–10**

complex	^{1}H NMR, ppm H_2	H_3	H_4	H_5	H_6	H_7	H_8	C_6H_6	^{13}C NMR, ppm	CO	C_6H_6
8	3.66	4.96	4.58	2.89	2.56			4.69	36.2, 39.6, 60.2, 73.8, 77.1	193.4	81.8
9	3.56	5.34	4.69	3.28	2.66, 2.95	1.76, 1.83		5.39	38.7, 44.3, 51.2, 51.7, 78.2, 81.9	210.5	82.6
10	3.51	3.81	1.52, 2.02	2.21	3.73	3.04	2.43	5.44	29.8, 31.3, 35.7, 36.3, 58.9, 64.1, 64.3	198.3	87.6

coordinatively unsaturated cationic rhodium complex [(1,5-COD)$_2$Rh][BF$_4$] to give a peroxo complex, [(1,5-COD)RhO$_2$]$_2$, via a nucleophilic attack of superoxide on the metal center.[3] Nucleophilic attack of superoxide on the olefinic ligand would therefore be expected in the reaction of superoxide with electronically saturated (18 e) cationic olefin complexes.

Treatment of $[(\eta^5\text{-}C_6H_7)(\eta^6\text{-}C_6H_6)Ru][BF_4]$ (**3**) with KO$_2$ in dichloromethane at room temperature afforded the (cyclohexadienone)ruthenium(0) complex, **8** (eq 6). The IR spectrum of complex **8** exhibits a strong absorption band at 1620 cm^{-1}, ascribed to the stretching vibration of conjugated carbonyl group. The ^{1}H (Table IV) and ^{13}C NMR spectra of **8** show the presence of cyclohexa-2,4-dien-1-one ligand formed as a result of nucleophilic attack of superoxide at the terminal position of cyclohexadienyl ligand.



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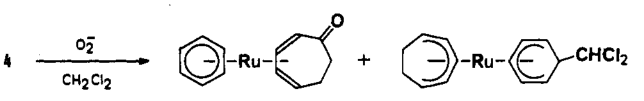
Tautomerization of the coordinated cyclohexa-2,4-dien-1-one to phenol was completely repressed. Cyclohexa-2,4-dien-1-one serving as a 4-electron ligand could form a stable 18-electron complex as a result of the coordination to the $[(\eta^6\text{-}C_6H_6)Ru^0]$ moiety, whereas the η^6-phenol ligand would form a 20-electron complex.

Nucleophilic attack of superoxide on the olefinic ligand was also observed in the reaction of the coordinatively saturated cationic complexes **4** and **5** with KO$_2$. Treatment of **4** with KO$_2$ in dichloromethane gave (benzene)(cycloheptadienone)ruthenium(0) (**9**) together with $(6\text{-}CHCl_2\text{-}1\text{-}5\text{-}\eta^5\text{-}C_6H_6)(1\text{-}5\text{-}\eta^5\text{-}C_7H_9)Ru^{II}$ (**11**) (eq 7).



9 (8%) **11** (23%)

(7)

A strong absorption at 1613 cm^{-1} in the IR spectrum and a resonance signal at 210.5 ppm in the ^{13}C NMR spectrum suggest that complex **9** contains a ketone as ligand. A detailed structural assignment by means of ^{1}H NMR including a decoupling experiment shows that oxygenation occurs at the terminal position of the dienyl moiety in the C$_7$H$_9$ ligand of **4** to yield cyclic dienone. Generality of the reaction mode of superoxide anion toward an electronically saturated cationic complex is demonstrated by the reaction with **5**. Treatment of **5** with KO$_2$ in dichloromethane gave (cyclooctadienone)ruthenium(0) complex **10** in 47% yield (eq 8).

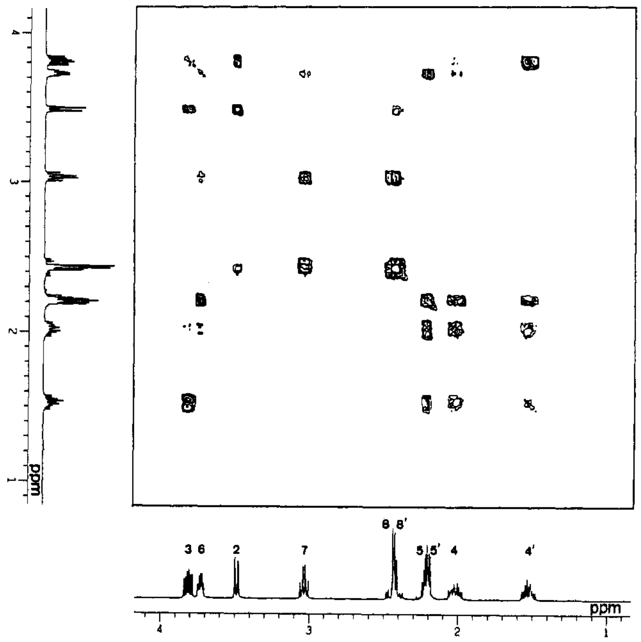
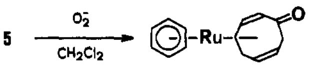


Figure 3. Contour plot of the 500-MHz ^{1}H COSY spectrum of complex **10**.



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10

The structure of the C$_8$H$_{10}$O ligand coordinated in **10** was explicitly assigned as cycloocta-2,6-dien-1-one by means of its COSY spectrum (Figure 3) and ^{13}C–^{1}H chemical shift correlation NMR experiments (Figure 4). The ^{1}H NMR parameters of **10**

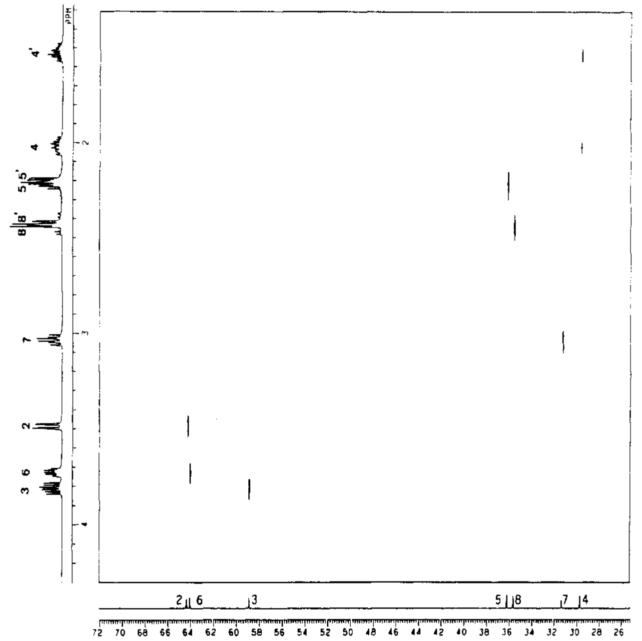
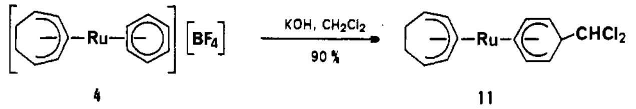


Figure 4. Contour plot of the ^{13}C–^1H chemical shift correlation spectrum of complex **10**.

are listed in Table IV. The formation of (cyclooctadienone)ruthenium(0) complex **10** strongly suggests that the nucleophilic attack of superoxide also occurred at the terminal position, C_3, of the allylic moiety of C_8H_{11} ligand.

The formation of **11** would reasonably be elucidated by the nucleophilic attack of $CHCl_2^-$ on the coordinated benzene. In this reaction, superoxide would act as a base[25] and abstract a proton from dichloromethane to generate $CHCl_2^-$.

Treatment of **4** in dichloromethane in the presence of KOH demonstrates the nucleophilic attack of $CHCl_2^-$ on the coordinated benzene, forming **11** (eq 9).



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Additional investigations of the detailed mechanism of the formation of the cyclic ketone complexes are under way.

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Registry No. **1**, 91753-79-6; **2**, 103438-20-6; **3**, 103438-22-8; **4**, 103438-24-0; **5**, 103438-26-2; **6**, 103438-27-3; **7**, 103438-29-5; **8**, 103438-30-8; **9**, 103438-31-9; **10**, 103438-32-0; **11**, 103438-33-1; $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, 37366-09-9; $[(\eta^5\text{-}C_5Me_5)RuCl_2]$, 92390-47-1; $K[C_5(CO_2CH_3)_5]$, 16691-64-8.

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Protonation of Iron, Ruthenium, and Osmium Hydrides with Fluorocarbon Acids. Stereochemical Rigidity in Seven-Coordinate $[(Ph_3P)_4OsH_3]^+[HC(SO_2CF_3)_2]^-$

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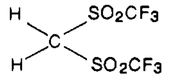
The fluorocarbon acid $H_2C(SO_2CF_3)_2$ has been used to effect protonation of a series of iron, ruthenium, and osmium hydrides. The salts $[(Ph_3P)_3MH(CO)]^+[HC(SO_2CF_3)_2]^-$ (M = Ru, Os) and $[(Ph_3P)_3RuH(CO)]^+[HC(SO_2C_8F_{17})_2]^-$ were prepared from $(Ph_3P)_3MH_2(CO)$ whereas $(Ph_3P)_3Ru(CO)HCl$ yields binuclear $[(Ph_3P)_4Ru_2(CO)_2(\mu\text{-}Cl)_2(\mu\text{-}H)][HC(SO_2CF_3)_2]$. Protonation of $(diphos)_2FeHCl$ and $(diphos)_2FeH_2$ yields $[(diphos)_2FeCl][HC(SO_2CF_3)_2]$ and $[(diphos)_2Fe(\eta^2\text{-}H_2)H][HC(SO_2CF_3)_2]$, respectively. The latter reacts with $(CH_3)_3P$ to form $[(diphos)_2FeHP(CH_3)_3][HC(SO_2CF_3)_2]$. Protonation of the polyhydride $(Ph_3P)_3OsH_4$ in the presence of Ph_3P produces $[(Ph_3P)_4OsH_3][HC(SO_2CF_3)_2]$, whose crystal structure [at −90 °C; $P2_1/n$, a = 14.122 (6) Å, b = 13.636 (1) Å, c = 33.646 (2) Å, β = 90.90 (4)°, Z = 4, R = 0.095] indicates that in it osmium has a distorted, capped octahedral coordination geometry. The cation is stereochemically nonrigid at ≥−80 °C. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the fluxional process, determined by ^{31}P DNMR, are 5.3 ± 0.3 kcal/mol and −16 ± 1 eu.

Introduction

We have previously reported that the fluorocarbon acids **1–3** are useful reagents for the synthesis of novel cationic compounds formed by the protonation of organometallic hydrides and carbonyl hydrides.[1-4] This is because **1–3** are strong, nonoxidizing acids



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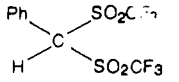

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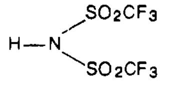

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that, upon proton transfer, form noncoordinating conjugate bases. The bis(trifluoromethylsulfonyl)alkanes **1** and **2** and their higher perfluoroalkyl homologues are nonhygroscopic and may be easily manipulated in air in anhydrous form; **1**, after prolonged exposure to the atmosphere, contains 0.02% water determined by Karl Fischer analysis. Since these fluorocarbon acids are soluble in nondonor solvents such as toluene and dichloromethane, they may be used to study the proton-transfer chemistry of organometallic coordination compounds with minimal or no interference from strong interactions involving electron transfer, adventitious water,

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