Synthesis, Characterization, and Molecular Structure of (η^5-Cyclopentadienyl)(η^4-2,4-cyclopentadien-1-one)ruthenium(II) Complexes

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The complexes $[Ru^{II}Cp(CPD)(CH_3CN)]^+$ (1) and $[Ru^{II}Cp(CPD)]_2^{2+}$ (2) (CPD = 2,4-cyclopentadien-1-one) have been shown to be convenient precursors to derivatives resulting from attack by certain nucleophiles at the rings. With nitriles, pyridine, 4,4′-bipyridine, halides, thiourea, *N*,*N*-dimethylthioformamide, isocyanides, thioethers, and triphenylarsine, substitution at the rings is not observed, but rather conversion to mononuclear products of the type $[Ru^{II}Cp(CPD)(nucleophile)]^{0,+}$. The reactions are remarkably clean, and complexes derived from the alternative mode of attack comprise less than 5% of the product mixture. Details of the preparative procedures, of characterization of the products by NMR and IR spectroscopy, and of the structure determination of the PF_6^- salts of **1** and **2** by X-ray diffraction are reported. **1** crystallizes in the monoclinic space group $P2/_1n$ with a = 11.833(3) Å, b = 11.314(2) Å, c = 12.108(3) Å and β = 118.56(2)°; V = 1435.5(6) Å^3 with ρ_{cal} = 2.00 for Z = 4. Species **1** is monomeric, with each Ru ligated to Cp (η^5 mode), CPD (η^4), and acetonitrile. **2** crystallizes in the monoclinic space group $P2$ with a = 8.569(1) Å, b = 6.667(1) Å, c = 10.561(2) Å, and β = 100.08(2)°; V = 594.0(2) Å^3 *with* ρ_{cal} = 2.19 *for* Z = 2. The structure consists of dimeric species. Each Ru(II) coordination sphere contains an η^5 Cp ring, an η^4 CPD ring, and an oxygen atom from a second CPL ligand. In both structures, the CPD ring is nonplanar.

Introduction

As a free ligand, 2,4-cyclopentadien-1-one (CPD) is stable to dimerization only at low temperatures (4 K, argon matrix),[3,4] but it is known to be quite stable when coordinated to transition metals. Transition metal η^4-complexes of CPD and particularly of its derivatives (CPD*, e.g. tetraalkyl- or tetraaryl-CPD) as coligands have been known for more than 30 years. They are usually made by the reactions of acetylenes with group 8 metal carbonyls and are of the type $[M^0(CPD^*)(CO)_3]$ (M = Fe, Ru)[5-7] and $[M^ICp(CPD^*)]$ (M = Co, Rh).[8,9] Of these, only the complex of iron has been synthesized with the parent CPD ligand.

Recently it was found[10,11] that, in water, the oxidation of Cp in the Ru(IV) complex $[RuCp_2X]^+$ (X = Cl, Br, I) by Ru(IV) itself, or by Ag_2O, provides a new synthetic route to η^4-CPD complexes. Preliminary results on the synthesis of complexes of the types $[Ru^{II}Cp(CPD)(CH_3CN)]^+$ (**1**), $[RuCp(CPD)X]$ (X = Cl, Br, I), and $[Ru^{II}Cp(CPD)]_2^{2+}$ (**2**) were reported.[11] Aside from exhibiting interesting structural features, species of this kind make it possible to investigate reactions of CPD bound η^4 to a metal in a rather high oxidation state. Quite unexpected is the reactivity to certain nucleophiles (e.g. $P(CH_3)_3$, $P(C_6H_5)_3$, SCH_3^-, $SC_6H_5^-$, CN^-) of Cp as a coligand, an effect which we attribute[11] to activation of Cp by the built-in oxidant CPD.

A matter of interest is the differentiation of the two classes of nucleophiles, those which attack at the metal ion and those which attack at the Cp ring. Herein we report on the preparation of complexes formed by substitution at the metal center, some of their properties, and report also the details of the structure determination of the PF_6^- salts of **1** and **2**, the results of which were reported earlier.[11] In what follows the number designations **1** and **2** will also be used for the PF_6^- salts of the respective cations.

Experimental Section

Materials. The syntheses of compounds **1** and **2** are described elsewhere.[10,11] All ligand chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[12] The deuterated solvents were purchased from Aldrich and dried over 4-Å molecular sieves. As a precaution, all experiments were performed under an inert atmosphere in an Ar-filled Vacuum Atmosphere Dri-Lab glovebox. Infrared spectra were obtained on an IBM 98 FTIR instrument with samples prepared as KBr pellets. ^1H NMR spectra were obtained on a Nicolet NT-300WB spectrometer operating at 300 MHz. ^{13}C NMR spectra were recorded on a Varian XL-400 and a Varian Gemimi 200 spectrometer operating at 100.58 and 50.29 MHz, respectively. Microanalyses were done by Galbraith Laboratories, Knoxville, TN, and Desert Analytics, Tucson, AZ.

Syntheses. [RuCp(CPD)(propionitrile)]PF$_6$ (3). This compound was prepared by the procedure described for the acetonitrile complex.[11] Yield: 20%. Anal. Calc for $C_{13}H_{14}NOPF_6Ru$: C, 34.99; H, 3.16; N, 3.14. Found: C, 34.92; H, 3.02; N, 3.17. ^1H NMR (δ, ppm, acetone-d_6, 20 °C): 6.48 (m, 2H), 5.81 (s, 5H), 4.68 (m, 2H), 2.98 (q, 2H), 1.34 (t, 3H). IR (KBr): 2293.8, 2305.4 cm^{-1} (m, ν_{CN}), 1684.4, 1696.0 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(benzonitrile)]PF$_6$ (4) was prepared as above. Yield: 20%. Anal. Calc for $C_{17}H_{14}NOPF_6Ru$: C, 41.31; H, 2.85; N, 2.83; P, 6.26. Found: C, 41.65; H, 2.83; N, 2.94; P, 6.37. ^1H NMR (δ, ppm, acetonitrile-d_3, 20 °C): 7.90–7.60 (m, 5H), 6.27 (m, 2H), 5.65 (s, 5H), 4.69 (m, 2H). IR (KBr): 2276.5 cm^{-1} (m, ν_{CN}), 1693.1 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(pyridine)]PF$_6$ (5). Compound **1**, 100 mg, was dissolved in 5 mL of acetone. A 1-mL portion of pyridine was added, and the solution was stirred at 60 °C for 1 h. Then, diethyl ether was added until a precipitate was formed. The yellow solid was filtered off, washed with diethyl ether, and air-dried. Yield: 75 mg (70%). Anal. Calc for $C_{15}H_{14}NOPF_6Ru$: C, 38.31; H, 3.00; N, 2.98; P, 6.57. Found: C, 38.70; H, 2.99; N, 2.95; P, 6.23. ^1H NMR (δ, ppm, acetone-d_6, 20 °C): 8.96 (m, 2H), 8.09 (m, 2H), 7.57 (m, 2H), 6.48 (m, 2H), 5.77 (s, 5H), 4.67

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(m, 2H). ^{13}C NMR (δ, ppm, acetone-d_6, 20 °C): 181.6 (C=O), 160.8 (py), 140.6 (py), 128.2 (py), 88.1 (CPD), 87.1 (CPD), 76.0 (Cp). IR (KBr): 1682.5 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(pyrazine)]PF$_6$ (6). This compound was prepared as described directly above. Yield: 50%. Anal. Calc for $C_{14}H_{13}N_2OPF_6Ru$: C, 35.68; H, 2.78; N, 5.94. Found: C, 35.80; H, 2.64; N, 5.71. ^{1}H NMR (δ, ppm, acetone-d_6, 20 °C): 9.79 (m, 2H), 9.07 (m, 2H), 6.57 (m, 2H), 5.86 (s, 5H), 4.75 (m, 2H). IR (KBr): 1685.4 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(4,4′-bipyridine)]PF$_6$ (7) was prepared as described directly above. Yield: 75%. Anal. Calc for $C_{20}H_{17}N_2OPF_6Ru$: C, 43.88; H, 3.13; N, 5.12; P, 5.65. Found: C, 43.34; H, 3.12; N, 4.92; P, 5.77. ^{1}H NMR (δ, ppm, acetone-d_6, 20 °C): 9.88 (m, 2H), 9.08 (m, 2H), 7.98 (m, 2H), 7.84 (m, 2H), 6.52 (m, 2H), 5.81 (s, 5H), 4.74 (m, 2H). IR (KBr): 1678.7 cm^{-1} (s, $\nu_{C=O}$).

{[RuCp(CPD)]$_2$(4,4′-bipyridine)}(PF$_6$)$_2$ (8). Compound **1**, 100 mg, and 4,4′-bipyridine, 18 mg, were dissolved in 5 mL of acetone, and the mixture was stirred for 5 h at 60 °C, during which time a greenish precipitate formed. Before filtration, 2 mL of diethyl ether was added to complete the precipitation of **8**, and the solid was washed with diethyl ether and air-dried. Yield: 150 mg (71%). Anal. Calc for $C_{30}H_{26}N_2O_2P_2F_{12}Ru_2$: C, 38.10; H, 3.00; N, 2.98; P, 6.57. Found: C, 38.13; H, 2.87; N, 3.17; P, 6.39. ^{1}H NMR (δ, ppm, acetone-d_6, 20 °C): 9.16 (m, 4H), 8.05 (m, 4H), 6.53 (m, 2H), 5.80 (s, 5H), 4.74 (m, 2H). IR (KBr): 1684 cm^{-1} (s, $\nu_{C=O}$).

RuCp(CPD)I (9). Compound **1**, 50 mg, was dissolved in 2 mL of acetone, and 10-fold molar excess of *n*-tetrabutylammonium iodide was added. The solution was kept at 60 °C for 1 h. Dark-red crystals formed, which were collected on a glass-frit, washed with diethyl ether, and air-dried. Yield: 90%. Anal. Calc for $C_{10}H_9OI$: C, 32.19; H, 2.43. Found: C, 32.32; H, 2.41. ^{1}H NMR (δ, ppm, acetonitrile-d_3, 20 °C): 5.79 (m, 2H), 5.45 (s, 5H), 4.11 (m, 2H). IR (KBr): 1675.8 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(thiourea)]PF$_6$ (10). The reaction mixture consisting of 50 mg of **1** and 30 mg of thiourea dissolved in 5 mL of acetone was stirred at 60 °C for 1 h and then filtered, and diethyl ether was added to the filtrate. A yellow precipitate formed, which was filtered off, washed with diethyl ether, and air dried. Yield: 27 mg (50%). Anal. Calc for $C_{11}H_{13}N_2OSPF_6Ru$: C, 28.27; H, 2.80; N, 5.99; S, 6.86. Found: C, 28.45; H, 2.81; N, 6.17; S, 6.98. ^{1}H NMR (δ, ppm, acetone-d_6, 20 °C): 7.80–7.40 (b, 4H), 6.22 (m, 2H), 5.71 (s, 5H), 4.23 (m, 2H). IR (KBr): 1651.7 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(*N,N*-dimethylthioformamide)]PF$_6$ (11). This compound was prepared in a manner similar to that used for **10**. However, before the resulting solution was treated with diethyl ether, the reaction mixture was chromatographed on an alumina column with acetonitrile as elutant. Yield: 65%. Anal. Calc for $C_{13}H_{16}NOSPF_6Ru$: C, 32.50; H, 3.36; N, 2.91; S, 6.67. Found: C, 31.95; H, 3.33; N, 3.11; S, 6.24. ^{1}H NMR (δ, ppm, acetone-d_6, 20 °C): 9.24 (s, 1H), 6.27 (m, 2H), 5.68 (s, 5H), 4.26 (m, 2H), 3.57 (s, 3H), 3.51 (s, 3H). IR (KBr): 1680.6 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(benzyl isocyanide)]PF$_6$ (12). To a solution of 100 mg of **2** in nitromethane was added 30 μL of benzyl isocyanide, during which the initially dark-red solution turned yellow. On removal of the solvent under vacuum, a brownish oil resulted. Attempts to obtain a solid material failed, and within a day the oil decomposed to some unidentified species. The yield in solution as monitored by ^{1}H NMR in CD_3NO_2, by use of an internal standard, was 100%. ^{1}H NMR (δ, ppm, nitromethane-d_3, 20 °C): 7.55–7 45 (m, 5H), 6.38 (m, 2H), 5.74 (s, 5H), 5.28 (s, 2H), 4.58 (m, 2H).

[RuCp(CPD)(cyclohexyl isocyanide)]PF$_6$ (13). A 10-fold molar excess of cyclohexyl isocyanide was added to a solution of 100 mg of **2** in nitromethane. After the mixture was stirred for 2 h, solids were removed by filtration and diethyl ether was added to the filtrate. Upon overnight standing at -20 °C, a crystalline material was formed. Yield: 50 mg (39%). Anal. Calc for $C_{17}H_{20}NOPF_6Ru$: C, 40.81; H, 4.03; N, 2.80. Found: C, 40.62; H, 4.03; N, 2.98. ^{1}H NMR (δ, ppm, nitromethane-d_3, 20 °C): 6.34 (m, 2H), 5.72 (s, 5H), 4.54 (m, 2H), 2.10–1.40 (m, 11H).

[RuCp(CPD)(1,4-dicyanobenzene)]PF$_6$ (14). A 4-fold molar excess of 1,4-dicyanobenzene was added to a solution of 100 mg of **2** in nitromethane, and the reaction mixture was stirred overnight at 60 °C. The reaction mixture was then filtered, and the filtrate was treated with diethyl ether. A brownish precipitate formed, which was washed with diethyl ether and air-dried. Yield: 80 mg (60%). Anal. Calc for $C_{18}H_{13}N_2OPF_6Ru$: C, 41.63; H, 2.52. Found: C, 40.80; H, 2.72. ^{1}H NMR (δ, ppm, nitromethane-d_3, 20 °C): 8.26–8.24 (m, 2H), 8.17–8.14 (m, 2H), 6.64 (m, 2H), 5.98 (s, 5H), 4.85 (m, 2H).

[RuCp(CPD)(methyl benzyl sulfide)]PF$_6$ (15). A 10-fold molar excess of methyl benzyl sulfide (34.8 μL) was added to a solution of 100 mg of **2** in nitromethane, and the reaction mixture was stirred overnight at 40 °C. The solution was filtered, and the filtrate was treated with diethyl ether. A yellow precipitate formed, which was filtered off, washed with diethyl ether, and air-dried. Yield: 81.2 mg (60%). Anal. Calc for $C_{18}H_{19}OSPF_6Ru$: C, 40.83; H, 3.62; S, 606; P, 5.85. Found: C, 40.64; H, 3.58; S, 5.86; P, 5.75. ^{1}H NMR (δ, ppm, nitromethane-d_3, 20 °C): 7.50–7.40 (m, 5H), 6.69 (m, 2H), 5.79 (s, 5H), 4.50 (b, 2H), 4.15 (b, 2H), 2.47 (s, 3H).

[RuCp(CPD)(diethyl sulfide)]PF$_6$ (16). This compound was prepared in analogy to **15**. Yield: 65%. Anal. Calc for $C_{14}H_{19}OSPF_6Ru$: C, 34.93; H, 3.98; S, 6.66. Found: C, 35.14; H, 4.01; S, 6.55. ^{1}H NMR (δ, ppm, nitromethane-d_3, 20 °C): 6.49 (m, 2H), 5.81 (s, 5H), 4.28 (m, 2H), 2.98 (q, 4H), 1.24 (t, 6H). IR(KBr): 1672 cm^{-1} (s, $\nu_{C=O}$).

[RuCp(CPD)(diphenyl sulfide)]PF$_6$ (17). This compound was prepared in analogy to **15**. Yield: 55%. ^{1}H NMR (δ, ppm, acetone-d_6, 20 °C): 7.67–7.55 (m, 10H), 6.73 (m, 2H), 5.45 (s, 5H), 4.53 (m, 2H).

[RuCp(CPD)(triphenylarsine)]PF$_6$ (18). The reaction mixture, consisting of 200 mg of **2** and 313 mg of triphenylarsine in 5 mL of nitromethane was stirred overnight at 40 °C. Upon addition of diethyl ether, a yellow precipitate appeared, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 172 mg (48%). Anal. Calc for $C_{28}H_{24}OPF_6AsRu$: C, 48.22; H, 3.47; P, 4.44. Found: C, 48.31; H, 3.42; P, 4.32. ^{1}H NMR (δ, ppm, acetone-d_6, 20°C): 7.80–7.50 (m, 15H), 6.56 (m, 2H), 5.60 (s, 5H), 4.18 (m, 2H). ^{13}C NMR (δ, ppm, acetone-d_6, 20 °C): 178.9 (C=O), 86.2 (CPD), 84.0 (CPD), 72.5 (Cp), 134.8 (C_6H_5), 133.6 (C_6H_5), 131.7 (C_6H_5), 129.8 (C_6H_5). IR (KBr): 1688 cm^{-1} (s, $\nu_{C=O}$).

X-ray Crystallography. Crystals of **1** and **2** were grown by vapor diffusion of diethyl ether into a nitromethane solution of the complexes. The crystal data were collected on a Syntex P2$_1$ diffractometer, upgraded to Nicolet R3m specifications,[13] with a graphite monochromator and Mo Kα (λ = 0.710 69 Å) radiation. The orientation matrix and lattice parameters for **1** (**2**) were optimized from a least squares calculation of 25 well-centered high-angle reflections with 24° < 2θ < 34° (30° < 2θ < 33°). Two standard reflections, 200 and 120 (101 and 102), were monitored every 96 reflections and showed no systematic variation. The intensities of 2811 (1972) reflections were measured using a Wycoff scan (0.9° scan range) with scan speeds varying from 6 to 60° (4 to 29.3°) min^{-1} out to 2θ(max) of 45°. The *hkl* ranges were $0 \leq h \leq 12$, $0 \leq k \leq 12$, $-12 \leq l \leq 12$ for **1** and $0 \leq h \leq 11$, $0 \leq k \leq 7$, $-12 \leq l \leq 12$ for **2**. Following the data reduction, 2532 (1866) unique reflections remained, with 2187 (1612) having $|F_o| > 3\sigma(F)$. Empirical absorption corrections for **2** were made with the program XEMP .

In the case of **1**, the positions of the Ru and P atoms were found by direct methods, routine SOLV, with the remaining atoms being found from subsequent electron difference synthesis. The C–H distances were constrained to 0.96 Å, and the thermal parameters fixed at 1.2 times the equivalent isotropic U_{eq} of the corresponding atom. All non-hydrogen atoms were refined anisotropically to final values of $R = 0.0443$ and $R_w = 0.0450$. The refinement included 199 least-squares parameters with a mean value of $\Delta/\sigma = 0.003$ and $g = 0.000\,48$. The goodness of the fit was 1.509 and the final difference map showed a residual of 0.67 e/Å^3 near F(4). No absorption corrections were applied due to the low value of the absorption coefficient (12.46 cm^{-1}).

For **2**, the structural solution was initiated via the location of the Ru atoms from analysis of the Patterson function. Subsequent difference electron density maps led to location of the lighter atoms. The PF_6^-, Cp, and CPD groups were all disordered. The PF_6^- anion disorder involves two orientations related by ca. 45° rotations about the F(1)–P–F(6) axis of the anion with 66(1)% occupation of one orientation (F(3) to F(6)) and 34(1)% occupation of the second orientation (F(3a) to F(6a)). The Cp disorder is also 2-fold, with two orientations (63(2)% for C(1) to C(5) and 37(2)% for C(1a) to C(5a)) related by a rotation of approximately 30° about the normal to the Cp plane. With the similar occupancy factors, it appears the disorders at these sites may be correlated. Finally, the CPD rings exhibit a 2-fold disorder with approximately equal occupancies of each site (46(1)% for C(11) to C(15) and O(1); 54(1)% for C(11a) to C(15a) and O(1a)). Because the CPD rings are in the interior of the Ru dimer, it is not surprising that the site occupancy factors are not the same as those for PF_6^- and Cp species.

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Table I. Crystallographic Data for $[RuCp(CPD)(CH_3CN)]PF_6$ and $[RuCp(CPD)]_2(PF_6)_2$

empirical formula	$C_{12}H_{12}NOPF_6Ru$	$C_{10}H_9OPF_6Ru$
fw	432.3	391.2
space group	$P2_1/n$ (No. 14)	$P2$ (No. 3)
a, Å	11.833(3)	8.569(1)
b, Å	11.314(2)	6.667(1)
c, Å	12.208(3)	10.561(2)
β, deg	118.56(2)	100.08(2)
V, Å^3	1435.5(6)	594.0(2)
Z	4	2
T, °C	22	22
λ, Å	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	2.00	2.19
μ, cm^{-1}	12.40	29.8
transm coeff	a	0.683–0.931
$R(F_o)^b$	0.044	0.065
$R_w(F_o)^c$	0.045	0.089

[a] No absorption correction. [b] $R(F_o) = \sum||F_o| - |F_c||/\sum(F_o)$. [c] $R_w(F_o) = \sum w(|(F_o - |F_c|)^2/\sum w(F_o)^2$.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[RuCp(CPD)(CH_3CN)]PF_6$

atom	x	y	z	U^a
Ru	1308(1)	2116(1)	3345(1)	41(1)
N	528(4)	3785(4)	2906(4)	49(2)
C(1)	81(5)	4698(5)	2727(5)	48(2)
C(2)	−500(6)	5868(5)	2478(6)	59(3)
C(3)	2202(8)	2074(8)	5394(6)	81(4)
C(4)	939(9)	2373(7)	4939(7)	77(4)
C(5)	178(8)	1462(9)	4232(7)	86(4)
C(6)	957(12)	581(7)	4216(7)	93(6)
C(7)	2229(10)	958(9)	4945(7)	96(5)
C(8)	1397(7)	2942(5)	1411(6)	58(3)
C(9)	2588(7)	2649(6)	2534(7)	67(3)
C(10)	2600(8)	1426(7)	2722(7)	76(4)
C(11)	1336(8)	972(5)	1934(6)	64(4)
C(12)	555(7)	1897(6)	1257(6)	61(3)
O	1106(5)	3838(4)	778(4)	79(3)
P	2783(2)	−4005(1)	6090(2)	55(1)
F(1)	4244(4)	−3638(4)	6668(6)	117(3)
F(2)	1314(4)	−4398(4)	5504(4)	88(2)
F(3)	2606(7)	−3247(7)	7024(6)	167(4)
F(4)	2412(6)	−2936(5)	5207(6)	152(4)
F(5)	2897(7)	−4752(6)	5052(7)	167(5)
F(6)	3128(6)	−5155(5)	6906(7)	185(4)

[a] The equivalent isotropic U for Ru, P, and F(1) through F(6) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

In addition, the difference electron maps calculated at this stage showed large residuals in the region between two PF_6^- anions and the C(14) or C(14a) atoms of the CPD rings. The nature of the responsible species is not known. It was modeled as a Ag^+ ion with a site occupancy of 2.7(2)%, and it may correspond to replacement of **2** by $AgRuCp(CPD)^{2+}$.

The final refinement utilized anisotropic thermal parameters only for the Ru, P, and F(1) to F(6) atoms. Hydrogen atoms were not included. Final residuals were $R = 0.056$ and $R_w = 0.089$. The final refinement included 193 least-squares parameters with a mean value of $\Delta/\sigma = 1.45$, and the final difference map showed a residual of 2.0 e/Å^3 near Ru.

All data reduction, including Lorentz and polarization corrections, structure solution and refinement, and graphics were performed using SHELTEX 5.1 software.[14] Crystallographic data may be found in Table I. The final positional parameters for the complexes are given in Tables II and III.

Listings of anisotropic temperature factors and complete bond lengths and angles are available as supplementary material.

Results and Discussion

The ^1H NMR and ^{13}C NMR data are recorded in the Experimental Section, as are some measurements of the carbonyl stretching frequencies. For the nitriles, the $-C{\equiv}N$ stretching frequencies were also determined. In each case, they are shifted to somewhat higher energy than those for the free ligand.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[RuCp(CPD)]_2(PF_6)_2$

atom	x	y	z	U^b
Ru	1756(7)	5000	6903(5)	47(2)
C(1)[a]	386(16)	5450(19)	8480(15)	47(4)
C(2)	1272(17)	3635(23)	8721(15)	45(3)
C(3)	2881(19)	4246(25)	8904(19)	55(5)
C(4)	3063(15)	6321(22)	8745(15)	42(4)
C(5)	1501(17)	7029(25)	8541(19)	56(4)
C(11)	1587(21)	4133(29)	4616(18)	28(4)
C(12)	1875(18)	6283(26)	4983(15)	25(3)
C(13)	3384(23)	6600(34)	5864(21)	42(5)
C(14)	3949(21)	4538(25)	6123(18)	34(4)
C(15)	2811(24)	3040(31)	5500(20)	39(4)
O(1)	708(33)	3713(41)	3774(24)	80(6)
O(1a)	356(12)	6630(17)	3864(10)	34(2)
P	3135(3)	6(7)	2032(2)	57(7)
F(1)	3118(13)	2350(11)	2198(11)	102(4)
F(2)	3138(13)	−2366(10)	1931(10)	90(3)
F(3)	4373(20)	38(14)	3279(14)	205(11)
F(4)	1734(19)	−38(46)	2798(18)	129(8)
F(5)	1853(22)	56(14)	804(14)	134(8)
F(6)	4454(24)	−150(62)	1193(22)	151(11)
F(3a)	4962(12)	76(73)	2003(21)	80(6)
F(4a)	3455(28)	−258(71)	3507(11)	95(9)
F(5a)	1332(13)	236(62)	1930(23)	82(8)
F(6a)	3063(17)	−218(92)	566(13)	112(12)

[a] Only the coordinates of the major components of the structure are listed. [b] The equivalent isotropic U for Ru, P, and F(1) through F(6) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

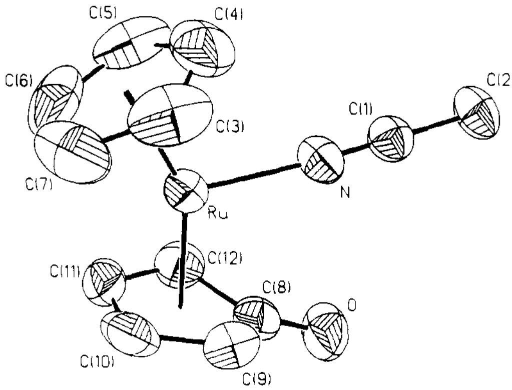

Figure 1. ORTEP drawing of $[RuCp(CpO)(CH_3CN)]^+$ (thermal ellipsoids at 50% probability).

A number of experiments were performed on the reactions of the nucleophiles with **1** in CD_3NO_2 as solvent. The progress of the reaction (at 20 °C) was followed by ^1H NMR measurements, use being made of an internal standard. With equimolar amounts of each reactant, (ca. 1–5 mM) we find quantitative replacement of CH_3CN in each case—and in no case is a product other than that resulting from replacement of CH_3CN observed. The conversion times span a range of a few minutes (halides and isocyanides) to several days for thioethers. The reactivity order we observe is thioethers < pyrazine < pyridine, 4,4′-bipy ≪ thiourea < isocyanides, halides.

Bond distances and selected bond angles for structures of **1** and **2** are given in Tables IV and V.

The average Cp C–C distance in **1** at 1.38 Å is somewhat smaller than those found in RuCp(CPD)Br (1.42 Å),[10] $RuCp_2$ (1.43 Å), and $RuCp_2I^+$ (1.41 Å).[15] The average metal–carbon bond length is 2.20 Å (excluding C(8)) and can be compared to those in $RuCp_2$ (2.21 Å), RuCp(CPD)Br (2.21 Å), and $RuCp_2I^+$ (2.20Å). The CPD skeleton consists essentially of two planes of

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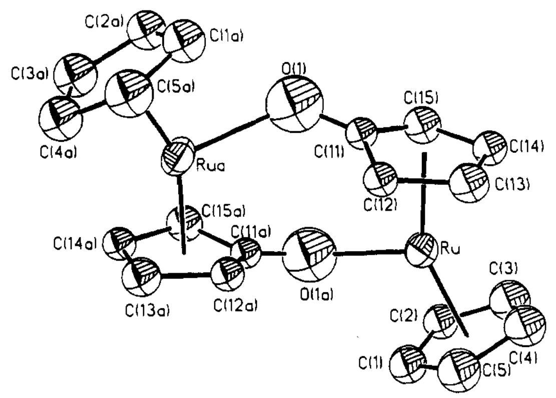

Figure 2. ORTEP drawing of $[\{RuCp(CpO)\}_2]^{2+}$.

Table IV. Bond Lengths (Å) and Bond Angles (deg) for $[RuCp(CPD)(CH_3CN)]PF_6$

Bond Lengths			
Ru-N	2.057(5)	C(3)-C(4)	1.365(13)
Ru-C(3)	2.202(7)	C(3)-C(7)	1.383(14)
Ru-C(4)	2.208(11)	C(4)-C(5)	1.369(12)
Ru-C(5)	2.212(11)	C(5)-C(6)	1.364(15)
Ru-C(6)	2.178(10)	C(6)-C(7)	1.399(15)
Ru-C(7)	2.165(9)	C(8)-C(9)	1.458(8)
Ru-C(9)	2.252(10)	C(8)-C(12)	1.499(10)
Ru-C(10)	2.153(11)	C(9)-C(10)	1.402(10)
Ru-C(11)	2.167(8)	C(10)-C(11)	1.431(10)
Ru-C(12)	2.276(7)	C(11)-C(12)	1.379(9)
N-C(1)	1.133(7)	C(8)-O	1.221(7)
C(1)-C(2)	1.455(8)		
Bond Angles			
N-Ru-C(3)	103.2(3)	C(4)-C(3)-C(7)	107.0(7)
N-Ru-C(4)	81.7(3)	C(3)-C(7)-C(6)	108.0(9)
N-Ru-C(5)	97.7(3)	C(8)-C(9)-C(10)	107.9(5)
N-Ru-C(6)	133.8(4)	C(9)-C(10)-C(11)	108.6(6)
N-Ru-C(7)	139.5(3)	C(10)-C(11)-C(12)	108.4(6)
N-Ru-C(9)	87.2(3)	C(9)-C(8)-C(12)	103.0(5)
N-Ru-C(10)	123.1(3)	C(8)-C(12)-C(11)	107.9(6)
N-Ru-C(11)	121.1(2)	C(9)-C(8)-O	129.5(6)
N-Ru-C(12)	85.5(2)	C(12)-C(8)-O	127.3(6)
C(3)-C(4)-C(5)	109.4(8)	N-C(1)-C(2)	179.2(6)
C(4)-C(5)-C(6)	108.3(8)	Ru-N-C(1)	175.5(6)
C(5)-C(6)-C(7)	107.3(8)		

Table V. Bond Lengths (Å) and Bond Angles (deg) for $[RuCp(CPD)]_2(PF_6)_2$

Bond Lengths			
Rua-O(1)	2.276(27)	C(1)-C(5)	1.416(21)
Ru-O(1a)	2.145(10)	C(2)-C(3)	1.418(22)
Ru-C(1)	2.221(16)	C(3)-C(4)	1.406(22)
Ru-C(2)	2.229(16)	C(4)-C(5)	1.400(19)
Ru-C(3)	2.221(14)	C(11)-C(12)	1.494(26)
Ru-C(4)	2.248(20)	C(12)-C(13)	1.470(26)
Ru-C(5)	2.237(20)	C(11)-C(15)	1.470(24)
Ru-C(12)	2.219(17)	C(13)-C(14)	1.467(28)
Ru-C(13)	2.196(22)	C(14)-C(15)	1.469(26)
Ru-C(14)	2.200(19)	C(11)-O(1)	1.096(30)
Ru-C(15)	2.277(22)	C(11a)-O(1a)	1.351(44)
C(1)-C(2)	1.427(20)		
Bond Angles			
O(1a)-C(1)-Ru	72.7(8)	C(1)-C(2)-C(3)	104.7(13)
O(1a)-C(2)-Ru	79.2(7)	C(2)-C(3)-C(4)	113.1(14)
O(1a)-C(3)-Ru	115.9(8)	C(3)-C(4)-C(5)	103.1(13)
O(1a)-C(4)-Ru	135.5(8)	C(2)-C(1)-C(5)	106.8(12)
O(1a)-C(5)-Ru	105.0(8)	C(1)-C(5)-C(4)	112.1(14)
O(1a)-C(11)-Ru	73.2(8)	C(11)-C(12)-C(13)	112.9(15)
O(1a)-C(12)-Ru	92.7(8)	C(12)-C(13)-C(14)-C(15)	102.0(16)
O(1a)-C(13)-Ru	131.4(8)		
O(1a)-C(14)-Ru	129.5(8)	C(13)-C(14)-C(15)	112.5(15)
O(1a)-C(15)-Ru	91.8(9)	C(11)-C(15)-C(14)	106.9(16)
C(12)-C(11)-O(1)	120.9(21)	C(12)-C(11)-C(15)	104.1(14)
C(15)-C(11)-O(1)	134.5(23)	C(11)-O(1)-Rua	128.8(22)

atoms, one defined by C(9), C(10), C(11), and C(12) (butadiene fragment) and the other defined by C(8), O, C(9), and C(12). The dihedral angle between these two planes is 18.0°. In RuCp(CPD)Br and $Ru(CPD^*)(CO)_3$ (throughout the rest of the paper CPD* = η^4-tetraphenylcyclopentadienone), this angle is 20.6 and 18.0°, respectively.[7,10] This structural form is also encountered in other CPD or substituted CPD complexes.[16,18] The angle between the Cp plane and the butadiene fragment in CPD is 6.0°. The coordinated acetonitrile is practically linear (N-C(1)-C(2) = 179.2°). The C-O distance is 1.221 Å, identical to the distance in RuCp(CPD)Br and very close to that in $Ru(CPD^*)(CO)_3$ (1.224 Å). The Ru-N distance is 2.057 Å. The butadiene fragment of the CPD ring shows the characteristic long-short pattern expected for a ground state butadiene unit, as was found also for the RuCp(CPD)Br complex, which is, however, in contrast to $Fe(CPD)(CO)_3$ or $Ru(CPD^*)(CO)_3$, where all C-C bond distances in CPD or CPD* are equal.[7,16] Disorder problems have led to some difficulties in obtaining precise carbon and oxygen atomic positions in **2**. These problems manifest themselves primarily as an imprecision of the C-C and C-O distances. The average Cp C-C distance of 1.42 Å and the average Ru-C distance of 2.23 Å (excluding C(11)) however are comparable with the data above and are in excellent agreement with corresponding distances in related metallocenes. The angle between the Cp rings is 13.0°. The angle formed between the butadiene fragment and the plane defined by C(12), O, C(11), and C(15) in CPD is 13.7° whereas in the dimer $[Ru(CPD^*)(CO)_2]_2$ this angle is reduced to 6.7°.[19] The average C-O distance is 1.22 Å. Due to the coordination to Ru a somewhat longer distance is expected; e.g., in $[Ru(CPD^*)(CO)_2]_2$ the C-O distance is 1.27 Å. This is in contrast to $[Mo_2(\mu\text{-}C_2Ph_2)(\mu\text{-}CPD^*)(\mu\text{-}C_4Ph_4)(CO)_3]$, a species with a bridging CPD*, where the C-O distance in CPD* is found to be 1.38 Å, suggesting η^5 coordination.[20] We are, however, convinced that the imprecisions in the C=O and Ru—O bond lengths are artifacts arising from the disorder inherent in this crystal. The overall structure is believed to be correct and is in agreement with the spectroscopic and analytical data presented here and in ref 11.

The preparative work shows that both **1** and **2** are convenient precursors to complexes of the type [RuCp(CPD)L] (L = nitriles, isocyanides, thioethers, thiocarbonyls, pyridine, pyrazine, arsines, halides) in either acetone or nitromethane as solvent.

It is noteworthy that the reactions described, involving substitution at the metal, proceed cleanly, without detectable formation (<5%) of products derived from attack at either five-membered ring.[11] Such discrimination, when the complete roster of nucleophiles which have been used is considered, is quite striking.

The ^1H NMR spectra of the RuCp(CPD)$^+$ moiety for all complexes synthesized are very similar and reveal two multiplets in the ranges 6.5–5.8 and 4.8–4.1 ppm, respectively, which can be assigned to the α and β protons of the CPD ring (AA′XX′ system), and a singlet at about 5.8–5.4 ppm, which can be assigned to those of the Cp ring. In contrast, the ^1H NMR spectrum of $Fe(CPD)(CO)_3$ exhibits two apparent triplets at 4.08 and 5.57 ppm, respectively.[16] This can be rationalized by reference to the structural data. The C-C distances of CPD in RuCp(CPD)$^+$ show a characteristic long-short pattern, and thus, since the coupling constant J_{AX} is different from $J_{AX'}$, an AA′XX′ system is encountered. On the other hand, in the complexes of the type $M(CPD^*)(CO)_3$ (M = Fe, Ru), the C-C distances in CPD* are

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approximately equal, and consequently, the coupling constants $J_{AX} \approx J_{AX'}$. A similar triplet pattern is found in the ^1H NMR spectrum of hydroxyruthenocene.[21] The signals of coordinated L are slightly shifted downfield compared to those of free L (e.g., ^1H NMR of coordinated and free CH_3CN in acetone-d_6, respectively: 2.67, 1.97 ppm).

The ^{13}C NMR spectra show a characteristic singlet shifted downfield to about 180 ppm (for L = CH_3CN, pyridine, and triphenylarsine, it is observed at 182.8, 181.6, and 178.9 ppm, respectively) which can be assigned to the ketonic carbon of the CPD ring. In Fe(CPD)$(CO)_3$, the resonances of the CPD carbonyl are found at 173.9 and 174 ppm.[16] The signals of coordinated L are similar to the signals of free L.

In the IR spectrum the carbonyl stretching frequency is found between 1700 and 1650 cm^{-1}. Free 2,4-cyclopentadien-1-one (at 4 K in an argon matrix) shows a strong band at 1709 cm^{-1}.[3] In several complexes of the type M(CPD*)$(CO)_3$ (M = Fe, Ru) the carbonyl band of CPD is also found in the same frequency range.[6,16] In complexes with L = CH_3CN, C_2H_5CN, and C_6H_5CN, the cyanide bands are shifted to somewhat higher energies compared to those of the free molecules. This result suggests that even though in these complexes ruthenium is in the 2+ oxidation state, back-bonding is not a prominent feature of the metal–nitrile interaction in the complexes. This is in large part attributable to the fact that CPD is a coligand, and the indications are that it is strongly electron withdrawing. The net effect is similar to that encountered when the oxidation state of the metal is raised. Thus in $[Os^{IV}Cp_2(CH_3CN)]^{2+}$, the CN stretching frequencies are observed at 2343 and 2361 cm^{-1}.[22]

The ^1H NMR spectrum of **2** in CD_3NO_2, at room temperature, reveals one singlet at 6.09 ppm and two broad lines centered at 6.33 and 5.49 ppm, respectively. At −50 °C the spectrum is resolved into four multiplets and one singlet with a ratio of 1:1:5:1:1 (6.4, 6.20, 6.09, 5.71, 5.27 ppm). The ^{13}C resonance line of the CPD carbonyl is observed at 175.0 ppm. In $[Ru(CPD^*)(CO)_2]_2$ it is found at 170.4 ppm.[19] Fluxional behavior as just described for **2**, however, has not been observed for the dimer $[Ru(CPD^*)(CO)_2]_2$ apparently due to a much higher energy barrier caused by the bulky phenyl substituents. The carbonyl stretching frequency is found at 1568.7 cm^{-1}, ca. 100 cm^{-1} lower than is observed for the mononuclear derivatives. A large decrease is expected on the basis of the structure revealed by the X-ray diffraction studies; binding of the carbonyl oxygen to Ru(II) will favor the accumulation of negative charge on the oxygen, an effect which tends to change the carbonyl to a single bond. A similar effect was observed for $[Fe(CPD)(CO)_2]_2$ and $[Ru(CPD^*)(CO)_2]_2$. The carbonyl stretching frequency for the former compound is observed at 1567 cm^{-1} and for the latter at 1535 cm^{-1}.[5,6,19]

A result of the work on the reactions of nucleophiles with the $Ru^{II}(\eta^5\text{-}Cp)(\eta^4\text{-}CPD)$ entity is the high selectivity shown whether attack is at the metal atom as described in this paper or whether it is at a ring as reported earlier.[11] Perhaps the most striking comparison of this kind is for the reaction of triphenylarsine, in which metal-centered substitution is dominant, and that of triphenylphosphine, in which attack at a ring is favored, where our semiquantitative results suggest a change in relative rates in excess of a factor of 100. Understanding the course of the high selectivity awaits a detailed study of the reaction mechanism, but even in the absence of such a study, a contributing factor suggests itself. It seems likely that in each case the first reaction involves substitution at the metal center, followed in some cases by substitution at a ring. Thus a nucleophile is involved at two stages, and if the effects at each stage reinforce, the effect on the relative rates is magnified. The earlier work[11] in fact shows that the results are sensitive to the nature of the nucleophile which is attached to the metal.

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Supplementary Material Available: Listings of bond angles, anisotropic thermal parameters, and hydrogen atom positions for **1** and complete listings of bond distances and angles as well as coordinates and thermal parameters for all atoms of **2** (11 pages). Ordering information is given on any current masthead page.

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