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Photochemical Properties of the Cyclopentadienyl(η^6-benzene)ruthenium(II) Cation. The Synthesis and Reactions of a Synthetically Useful Intermediate: the Cyclopentadienyltris(acetonitrile)ruthenium(II) Cation

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Photolysis of $RuCp(benzene)^+$ in CH_3CN at 313 nm gives a quantitative yield of $[RuCp(CH_3CN)_3]^+$ which is isolated as the PF_6^- salt. The quantum yield for this reaction is 0.4 ± 0.04. The thermal substitution chemistry of this complex is remarkably rich. When the reaction conditions are varied (temperature and solvent), one, two, or three of the CH_3CN molecules can be selectively replaced. For example, with $P(OCH_3)_3$ as the incoming ligand, reaction of $[RuCp(CH_3CN)_3]PF_6$ with an excess of $P(OCH_3)_3$ in acetonitrile at room temperature gives a quantitative yield of $[RuCp(CH_3CN)_2(P(OCH_3)_3)]PF_6$. Further treatment of this monophosphite complex with an excess of $P(OCH_3)_3$ for several days at room temperature yields quantitatively $[RuCp(CH_3CN)(P(OCH_3)_3)_2]PF_6$. Finally, refluxing this bisphosphite complex with an excess of $P(OCH_3)_3$ for several hours in dichloroethane yields $[RuCp(P(OCH_3)_3)_3]PF_6$. $[CpRu(CH_3CN)_3]^+$ also reacts with a variety of unsaturated hydrocarbons to yield compounds in which all three acetonitrile molecules have been replaced. Compounds synthesized by this method include: $[CpRu(\eta^6\text{-hexamethylbenzene})]PF_6$, $[CpRu(\eta^6\text{-[2.2]-}p\text{-cyclophane})]PF_6$, $[CpRu(\eta^6\text{-}p\text{-dichlorobenzene})]PF_6$, and $[CpRu(\eta^6\text{-cyclooctatetraene})]PF_6$. Finally, photolysis of $RuCp(benzene)^+$ in degassed CH_2Cl_2 in the absence of potential ligands leads to no net photoreaction. However, the addition of $P(OCH_3)_3$ or $P(OEt)_3$ to a CH_2Cl_2 solution of $RuCp(benzene)^+$ yields on photolysis $RuCp(P(OR)_3)_3^+$. Photolysis of $RuCp(benzene)^+$ in CH_2Cl_2 in the presence of $P(OPh)_3$ yields no observable products. This contrasts the behavior found for the photolysis of $FeCp(p\text{-xylene})^+$ which, under identical conditions, leads to the efficient formation of $FeCp(P(OPh)_3)_3^+$. These results are interpreted in terms of differences in the degree of unsaturation in the reactive intermediates in the Fe and Ru systems.

Introduction

We have recently begun an investigation of the photochemical properties of transition metal arene complexes. In recent publications,[1,2] we have reported our studies on the cyclopentadienyl(arene)iron(II) cations. Visible light photolysis of these ions in a variety of solvents leads to efficient reactions in which the arene ring is replaced by three monodentate ligands or one tridentate ligand. In the absence of a suitable ligand, photolysis leads to the formation of ferrocene and Fe(II).[3]

We now wish to report the extension of these studies to the Ru(II) analogue, cyclopentadienyl(benzene)ruthenium(II) hexafluorophosphate, $[CpRu(\eta^6\text{-benzene})]PF_6$. These studies have led us to the photochemical synthesis of $CpRu(CH_3CN)_3PF_6$, which due to the lability of the coordinated acetonitrile molecules, is a useful starting material for the synthesis of compounds containing the $CpRu^{II}$ group. Previous synthetic methods which have been extensively exploited in $CpFe^{II}$ chemistry[4] have not generally been useful in the development of the analogous chemistry of the $CpRu^{II}$ moiety although M. I. Bruce and co-workers have recently made several interesting observations.[5] We feel that the synthetic methods illustrated here for several new compounds containing the $CpRu^{II}$ group may be extended to the preparation of a large variety of other $CpRu^{II}$ compounds that are otherwise unavailable.

Experimental Section

General Data. All small scale synthetic photolyses were performed at 20 ± 2 °C in a quartz test tube equipped with a magnetic stir bar and serum stopper. The unfiltered output of a 175-W medium-pressure mercury lamp was used as a light source. Before photolysis, the solutions were degassed by bubbling them with nitrogen for approximately 15 min. For bulk photolyses and the quantum yield determination, different optical arrangements were used (vide infra).

Cyclooctatetraene was prepurified by passage through a short alumina column. All other reagents were purchased and used without additional purification. Solvents used were of spectroscopic quality. Proton NMR spectra were recorded on a Varian Associates CFT-20 spectrometer equipped with a 79.5-MHz proton accessory. All NMR spectra were recorded in acetone-d_6 and are referenced to Me_4Si (internal standard). UV–visible spectra were recorded on a Cary 17D spectrophotometer. IR spectra were recorded on a Perkin-Elmer 297. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

Preparation of Complexes. $[CpRu(\eta^6\text{-benzene})]PF_6$. The compound [CpRu(bz)]Cl was prepared from $RuCl_3{\cdot}1\text{–}3H_2O$ via the procedure of Zelonka and Baird.[6] This compound was dissolved in water and filtered. The filtrate was treated with an aqueous solution of NH_4PF_6, precipitating $[CpRu(bz)]PF_6$ as a tan colored solid. The tan solid was then dissolved in acetone and eluted through a short alumina column. The brown impurity remained at the top of the column. Sometimes the product had a very faint yellow coloration. This color could be removed by dissolving the compound in a 50/50 mixture of dichloromethane/acetone and eluting through a second column of alumina. The product in both cases is obtained by evaporating the solvent on a rotary evaporator. In a typical preparation, 3.4 g of $RuCl_3{\cdot}3H_2O$ yielded 3.2 g of white crystalline $[CpRu(bz)]PF_6$ (61% yield): mp 288–290 °C with decomposition; ^1H NMR τ 4.46 (s, Cp, 5 H), τ 3.65 (s, bz, 6 H). Anal. Calcd for $C_{11}H_{11}RuPF_6$: C,

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33.94; H, 2.85. Found: C, 34.07; H, 2.96.

[CpRu(P(OCH$_3$)$_3$)$_3$]PF$_6$. [CpRu(P(OCH$_3$)$_3$)$_3$]PF$_6$ was prepared by irradiating a solution containing 54.2 mg of [CpRu(bz)]PF$_6$ and 966 mg of P(OCH$_3$)$_3$ in 10 mL of dichloromethane for 4.5 h. Initially, all of the CpRu(bz)PF$_6$ was not dissolved; however, as the reaction proceeded, dissolution was complete. Upon completion of the photolysis, the solvent was evaporated and the product was crystallized from CH$_2$Cl$_2$/hexane. A 81.1-mg sample of [CpRu(P(OCH$_3$)$_3$)$_3$]PF$_6$ (85% yield) was recovered as a white powder: mp 242–244 °C with decomposition; NMR τ 4.61 (q, Cp, 5 H, $J = 1$ Hz), τ 6.27 (complex pattern, CH$_3$, 27 H, $J_{\mathrm{POCH}} = 11.5$ Hz).[7] Anal. Calcd for C$_{14}$H$_{32}$O$_9$P$_4$F$_6$Ru: C, 24.61; H, 4.72. Found: C, 24.42; H, 4.71.

[CpRu(P(OCH$_2$CH$_3$)$_3$)$_3$]PF$_6$. [CpRu(P(OCH$_2$CH$_3$)$_3$)$_3$]PF$_6$ was prepared by irradiating a solution containing 55.5 mg of [CpRu(bz)]PF$_6$ and 1.64 g of P(OCH$_2$CH$_3$)$_3$ in 10 mL of dichloromethane. After 5.5 h of photolysis, the solvent was evaporated and the residue was crystallized from CH$_2$Cl$_2$/hexane. A 79.8-mg sample of [CpRu(P(OCH$_2$CH$_3$)$_3$)$_3$]PF$_6$ was collected as a white powder (69% yield): mp 212–214 °C with decomposition; ^{1}H NMR τ 4.73 (q, Cp, 5 H, $J = 0.9$ Hz), τ 5.89 (m, CH$_2$, 18 H), τ 8.70 (t, CH$_3$, 27 H, $J = 7$ Hz). Anal. Calcd for C$_{23}$H$_{50}$O$_9$P$_4$F$_6$Ru: C, 34.12; H, 6.22. Found: C, 34.08; H, 6.24.

[CpRu(CH$_3$CN)$_3$]PF$_6$. [CpRu(CH$_3$CN)$_3$]PF$_6$ was prepared by irradiating a solution (514.2 mg of [CpRu(bz)]PF$_6$, 120 mL of CH$_3$CN) in the quartz water jacket of an immersion lamp. The jacket was stoppered and the solution degassed by bubbling with N$_2$ for several minutes. The stirred solution was irradiated with the output of a 400-W Ace-Hanovia medium-pressure Hg lamp for 22 h. After irradiation, the solvent was evaporated, yielding 569.4 mg of product (100% yield): mp 117–118 °C with decomposition; ^{1}H NMR τ 5.69 (s, Cp, 5 H), τ 7.48 (s, CH$_3$, 9 H). Anal. Calcd for C$_{11}$H$_{14}$N$_3$RuPF$_6$: C, 30.42; H, 3.25. Found: C, 29.75; H, 3.12.

[CpRu(CH$_3$CN)$_2$CO]PF$_6$. [CpRu(CH$_3$CN)$_3$]PF$_6$ (105.1 mg) was dissolved in 10 mL of CH$_3$CN. This solution was bubbled with CO for about 20 min at room temperature. Upon evaporation of the solvent, 97.4 mg of [CpRu(CH$_3$CN)$_2$(CO)]PF$_6$ (96% yield) was recovered as yellow crystals: mp 159–161 °C with decomposition; NMR τ 4.65 (s, Cp, 5 H), τ 7.40 (s, CH$_3$, 6 H); IR $\bar{\nu}$(CO) 2004 cm^{-1} (CH$_3$CN solution). Anal. Calcd for C$_{10}$H$_{11}$N$_2$ORuPF$_6$: C, 28.51; H, 2.63. Found: C, 29.36; H, 2.73.

[CpRu(CH$_3$CN)$_2$P(OCH$_3$)$_3$]PF$_6$. A solution of 53.1 mg of [CpRu(bz)]PF$_6$ in 10 mL of CH$_3$CN was irradiated for 3.5 h, at which time the formation of CpRu(CH$_3$CN)$_3$$^+$ was judged to be complete. To this solution was added 1 mL of trimethyl phosphite, and the mixture was stirred for 5 min. The solvent was evaporated, and ether was added to the remaining oil. After a few minutes crystals of [CpRu(CH$_3$CN)$_2$P(OCH$_3$)$_3$]PF$_6$ formed: 62.1 mg (88% yield); mp 107–108 °C with decomposition; ^{1}H NMR τ 5.17 (d, Cp, 5 H, $J = 0.9$ Hz), τ 6.34 (d, POCH$_3$, $J = 11.9$ Hz), τ 7.46 (d, NCCH$_3$, 6 H, $J = 1.4$ Hz). Anal. Calcd for C$_{12}$H$_{20}$RuP$_2$O$_3$F$_6$N$_2$: C, 27.96; H, 3.90. Found: C, 27.65; H, 4.01.

[CpRu(CH$_3$CN)(P(OCH$_3$)$_3$)$_2$]PF$_6$. A solution of [CpRu(CH$_3$CN)$_2$P(OCH$_3$)$_3$]PF$_6$ (29.3 mg) and 0.5 mL of trimethyl phosphite in 15 mL of dichloromethane was stirred for 22 h. Evaporation of the solvent yielded a yellow oil, which on addition of diethyl ether yielded [CpRu(CH$_3$CN)(P(OCH$_3$)$_3$)$_2$]PF$_6$ (34.1 mg) as yellow crystals in 100% yield: mp 144–146 °C; ^{1}H NMR τ 4.84 (t, Cp, 5 H, $J = 1$ Hz), τ 6.30 (apparent t, POCH$_3$, 18 H, $J_{\mathrm{POCH}} = 11.7$ Hz), τ 7.49 (t, NCCH$_3$, 3 H, $J = 1.3$ Hz). Anal. Calcd for C$_{19}$H$_{38}$RuP$_3$O$_6$F$_6$N: C, 26.01; H, 4.37. Found: C, 25.82; H, 4.14.

[CpRu(η^6-hexamethylbenzene)]PF$_6$. A 53.5-mg sample of [CpRu(CH$_3$CN)$_3$]PF$_6$ and 91.6 mg of hexamethylbenzene were dissolved in 15 mL of dichloroethane and refluxed under N$_2$ for 21 h. Evaporation of the solvent yielded a residue which was washed several times with hexane to remove unreacted hexamethylbenzene. Elution of the residue with acetone on a short alumina column yielded on evaporation 35 mg (60% yield) of white crystalline [CpRu(η^6-hexamethylbenzene)]PF$_6$. Further elution of the column with CH$_3$OH afforded an additional amount of product of lower purity. 1st fraction: mp 302–305 °C with decomposition; ^{1}H NMR τ 4.83 (s, Cp, 5 H), τ 7.52 (s, CH$_3$, 18 H). Compares favorably to literature values.[8]

[CpRu(η^6-PCP)]PF$_6$. [CpRu(CH$_3$CN)$_3$]PF$_6$ (49.5 mg) and [2.2]-*p*-cyclophane (84.2 mg) were dissolved in 15 mL of dichloroethane. This solution was refluxed under N$_2$ for 17.5 h, and the solvent was evaporated. The residue was crystallized from dichloromethane/hexane affording 50 mg (85% yield) of tan microcrystalline product: mp 266–267 °C with decomposition; ^{1}H NMR τ 3.09 (s, arene protons on complexed ring, 4 H), τ 4.38 (s, arene protons on uncomplexed ring Ru, 4 H), τ 4.82 (s, Cp, 5 H), τ 6.86 (m, CH$_2$ protons, 8 H). Anal. Calcd for C$_{21}$H$_{21}$RuPF$_6$: C, 48.56; H, 4.07. Found: C, 48.41; H, 4.09.

[CpRu(η^6-*p*-dichlorobenzene)]PF$_6$. A solution of [CpRu(CH$_3$CN)$_3$]PF$_6$ (51.6 mg) and *p*-dichlorobenzene (176.2 mg) in 15 mL of dichloroethane was refluxed under N$_2$ for 15 h. The solution turned brown, and some insoluble brown material was observed. The solvent was evaporated, and the residue was washed with hexane several times. The product was dissolved in acetone and eluted down a short alumina column. Evaporation of the solvent yielded 35.9 mg (66% yield) of white CpRu(η^6-*p*-dichlorobenzene)PF$_6$: mp 248–250 °C with decomposition; ^{1}H NMR τ 3.04 (s, aromatic protons, 4 H), τ 4.22 (s, Cp, 5 H). Anal. Calcd for C$_{11}$H$_9$Cl$_2$RuPF$_6$: C, 28.84; H, 1.98. Found: C, 29.02; H, 2.01.

[CpRu(η^6-C$_8$H$_8$)]PF$_6$. [CpRu(η^6-C$_8$H$_8$)]PF$_6$ was prepared in two steps. A solution of 50.6 mg of [CpRu(bz)]PF$_6$ in 10 mL of CH$_3$CN was irradiated for 4 h and 20 min, at which time the formation of CpRu(CH$_3$CN)$_3$$^+$ was judged to be complete. Then 0.5 mL of cyclooctatetraene was added to this solution, and the mixture was stirred for 10 min. The solvent was evaporated, yielding 49.8 mg of yellow crystalline [CpRu(η^6-C$_8$H$_8$)]PF$_6$ (92% yield): mp 228–230 °C with decomposition; ^{1}H NMR τ 4.25 (s, Cp, 5 H), cyclooctatetraene protons τ 3.05 (m, H^{3,4}, 2 H), τ 3.96 (overlapping multiplets, H^{1,2,5,6} 4 H), τ 4.89 (m, H^{7,8}, 2 H). Anal. Calcd for C$_{13}$H$_{13}$RuPF$_6$: C, 37.60; H, 3.16. Found: C, 38.03; H, 3.36.

[CpRu(CO)(η^4-C$_8$H$_8$)]PF$_6$. [CpRu(CH$_3$CN)$_2$CO]PF$_6$ (32.6 mg) and 0.6 mL of cyclooctatetraene were dissolved in 15 mL of dichloroethane. After reflux under N$_2$ for 19 h, the solvent was evaporated. Crystallization of the product from dichloromethane/hexane yielded 23.2 mg of [CpRu(η^4-C$_8$H$_8$)CO]PF$_6$ (68% yield) as yellow crystals: mp 175–177 °C with decomposition; ^{1}H NMR τ 4.12 (s, Cp, 5 H), cyclooctatetraene protons τ 3.62 (m, H^{1,4}, 2 H), τ 3.94 (m, H^{2,3}, 2 H), τ 4.24 (m, H^{5,8}, 2 H), τ 4.85 (doublet of multiplets, H^{6,7}, 2 H); IR $\bar{\nu}$(CO) 2053 cm^{-1} (KBr pellet). The coordination mode of the cyclooctatetraene ligand (i.e., 1–4-η^4 or 1,2:5,6-η^4) is not certain, although chemical shift arguments favor the η^{1-4} coordination mode, which we adopt here in our assignment. Anal. Calcd for C$_{14}$H$_{13}$RuOPF$_6$: C, 37.93; H, 2.96. Found: C, 38.02; H, 2.97.

Reactions. Attempted Thermal Reaction of [CpRu(bz)]PF$_6$ with CH$_3$CN. A solution of 28 mg of [CpRu(bz)]PF$_6$ in 15 mL of CH$_3$CN was refluxed under N$_2$ in the dark for 52 h. The solvent was then removed, yielding 25.2 mg of a white solid. A proton NMR spectrum of the recovered solid showed it to be pure [CpRu(bz)]PF$_6$.

Attempted Thermal Reaction of [CpRu(bz)]PF$_6$ with Trimethyl Phosphite. A solution of [CpRu(bz)]PF$_6$ (35.1 mg) and 1 mL of P(OCH$_3$)$_3$ in 15 mL of dichloromethane was refluxed under N$_2$ for 42 h in the dark. The solvent was evaporated, and the product was washed with diethyl ether to remove excess P(OCH$_3$)$_3$. The 30.4 mg of white, crystalline solid was verified to be CpRu(bz)]PF$_6$ by recording its proton NMR spectrum.

Photochemical Reaction of [CpRu(bz)]PF$_6$ with P(OPh)$_3$. A solution of 51.8 mg of [CpRu(bz)]PF$_6$ and 845 mg of P(OPh)$_3$ in 15 mL of dichloromethane was placed in a quartz test tube, degassed by bubbling with N$_2$, and irradiated for 5 h. The solvent was removed, and the residue was redissolved in dichloromethane and precipitated upon addition of hexane. A proton NMR of the product showed it to be pure [CpRu(bz)]PF$_6$.

Photochemical Reaction of [CpRu(bz)]PF$_6$ with P(OCH(CH$_3$)$_2$)$_3$. A solution of 966 mg of triisopropyl phosphite and 54.2 mg of [CpRu(bz)]PF$_6$ in 15 mL of dichloromethane was degassed by N$_2$ bubbling and irradiated for 5 h. The solvent was removed and the product washed with hexane. The proton NMR spectrum recorded of the solid product indicated it to be a 1:1 mixture of [CpRu(P(OCH(CH$_3$)$_2$)$_3$)$_3$]PF$_6$ and CpRu(bz)PF$_6$.

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Thermal Reaction of [CpRu(CH_3CN)$_3$]PF_6 with P(OPh)$_3$. A solution containing 55 mg of [CpRu(CH_3CN)$_3$]PF_6 and 0.5 mL of P(OPh)$_3$ in 15 mL of dichloroethane was refluxed under nitrogen for 22 h. Evaporation of the solvent yielded a yellow brown oil which was repeatedly washed with diethyl ether and hexane to remove the excess P(OPh)$_3$. The proton NMR spectrum of the oil revealed three major signals in the region where cyclopentadienyl protons generally occur. A singlet was observed at τ 4.42 which we assign to the cyclopentadienyl proton resonance of the [CpRu(η^6-P(OPh)$_3$]$^+$ cation in which the triphenyl phosphite ligand is bound in an η^6 fashion through a phenyl ring. Both the chemical shift and the lack of ^{31}P spin–spin splitting are consistent with this assignment. A triplet τ 5.43 (J = 1.1 Hz) and a quartet τ 5.04 (J = 1.0 Hz) were also observed. These resonances are assigned as the cyclopentadienyl proton signals from CpRu(P(OPh)$_3$)$_2$(CH_3CN)$^+$ and CpRu(P(OPh)$_3$)$_3$$^+$, respectively. Consistent with this assignment, a triplet resonance at τ 7.57 (J = 1.2 Hz) is assigned to the acetonitrile methyl group in CpRu(P(OPh)$_3$)$_2$$CH_3CN$)$^+$. These three compounds appear to be produced in approximately equal amounts.

Attempted Thermal Reaction of [CpRu(η^6-cyclooctatetraene)]PF_6 with CO. A solution of [CpRu(η^6-cyclooctatetraene)]PF_6 in acetone-d^6 in an NMR tube was bubbled with carbon monoxide for 10 min. Proton NMR analysis of the reaction mixture revealed signals due to only the starting material, [CpRu(η^6-cyclooctatetraene)]PF_6.

Reaction of [CpRu(CH_3CN)$_2$P(OCH_3)$_3$]PF_6 with Toluene. A 1.0-mL sample of toluene and 28 mg of [CpRu(CH_3CN)$_2$P(OCH_3)]PF_6 were dissolved in 15 mL of dichloroethane. This solution was refluxed under N_2 for 19 h. The solvent and excess toluene were removed by rotary evaporation. Proton NMR analysis of the yellow solid revealed that [CpRu(η^6-toluene)]PF_6 and [CpRu(P(OCH_3)$_3$)$_2$$CH_3CN$]$PF_6$ were present in approximately a 1:1 ratio. The presence of these compounds was confirmed by comparison with proton NMR spectra of authentic samples.

Quantum Yield Measurement for the Conversion of CpRu(benzene)$^+$ to CpRu(CH_3CN)$_3$$^+$. The 313-nm radiation was isolated from the output of a 100-W medium-pressure mercury lamp using an Oriel interference filter. Reineckate actinometry[9] was performed before and after photolysis of the ruthenium solutions, giving an average light intensity of 6.27 × 10^{-7} einsteins/min. The quantum yield for the photochemical reaction

$$[\mathrm{CpRu(bz)}]\mathrm{PF_6} \xrightarrow[\mathrm{CH_3CN}]{h\nu} [\mathrm{CpRu(CH_3CN)_3}]\mathrm{PF_6} + \mathrm{bz} \quad (1)$$

was determined by irradiating solutions containing 7 mg of [CpRu(bz)]PF_6 in 3 mL of CH_3CN in a quartz cell. The cell was equipped with a magnetic stir bar and stoppered. The solution was degassed by bubbling with nitrogen saturated with acetonitrile for about 10 min. The amount of product formed was determined by measuring the absorption spectrum of the reaction mixture at 5- or 10-min intervals. During each photolysis period, the percent conversion to product was less than 5%. When the quantum yield was calculated, corrections were applied for incomplete absorption of light by the solution and the absorption of light by the product, [CpRu(CH_3CN)$_3$]PF_6.[10] The quantum yield for this reaction is 0.40 ± 0.04.

Electronic Spectra. The electronic spectra of [CpRu(bz)]PF_6 and [CpRu(CH_3CN)$_3$]PF_6 were recorded in acetonitrile: [CpRu(bz)]PF_6 λ 320 nm (ϵ = 136 M^{-1} cm^{-1}); [CpRu(CH_3CN)$_3$]PF_6, λ 309 nm (ϵ = 860 M^{-1} cm^{-1}), λ 365 nm (ϵ = 1071 M^{-1} cm^{-1}).

Results and Discussion

The behavior of [CpRu(bz)]PF_6 somewhat parallels that of the iron system previously studied.[1,2] In both the iron and ruthenium systems, attempted reactions with trialkyl phosphites in refluxing dichloroethane led only to recovery of starting material. Replacement of the arene ring by three trialkyl phosphite (alkyl = methyl, ethyl) ligands could be affected in both systems by photolysis of CpM(arene)$^+$ in CH_2Cl_2 containing trialkyl phosphite. However, [CpRu(bz)]PF_6 exhibited a ligand selectivity in the photochemical reaction that was not observed in the iron system. For example, photolysis of [CpRu(bz)]PF_6 in the presence of P(OPh)$_3$ yielded no [CpRu(P(OPh)$_3$)$_3$]PF_6. By contrast, the facile photochemical replacement of *p*-xylene from [CpFe(η^6-*p*-xylene)]PF_6 was observed when CH_2Cl_2 solutions containing the iron complex and P(OPh)$_3$ were irradiated, yielding [CpFe(P(OPh)$_3$)$_3$]PF_6 in excellent chemical yield.

Although the observed differences in photochemical reactivity between the iron the ruthenium complexes were not anticipated, the results suggest that the intermediates produced upon photolysis may differ in their degree of association of the arene ring with the metal center. Since the Ru–P bonds would be expected to be of similar strength for trimethyl phosphite or triphenyl phosphite, and the cone angle of triphenyl phosphite is much greater than that of either trimethyl phosphite or triethyl phosphite,[11] we prefer to ascribe these observed reactivity differences to kinetic effects rather than thermodynamic effects.[12] To probe these kinetic effects, [CpFe(*p*-xylene)]PF_6 and [CpRu(bz)]PF_6 were irradiated under analogous conditions in the presence of triisopropyl phosphite, a ligand which is slightly more basic than trimethyl phosphite, but with approximately the same cone angle as triphenyl phosphite.[11] Photolysis of [CpFe(*p*-xylene)]PF_6 in the presence of triisopropyl phosphite gave [CpFe(P(OCH(CH_3)$_2$)$_3$)$_3$]PF_6 in good yield.[13] However, replacement of benzene in [CpRu(bz)]PF_6 by triisopropyl phosphite proceeded in about 50% conversion to [CpRu(P(OCH(CH_3)$_2$)$_3$)$_3$]PF_6. These conditions would have affected total replacement of benzene in the ruthenium complex by trimethyl phosphite. Thus, it appears that both the steric and electronic properties influencing the nucleophilicity of the incoming ligand may be important in determining the efficiency of the ring replacement reactions in the ruthenium system.

Other differences have been observed in the photochemical reactivity of the iron and ruthenium systems. When [CpFe(bz)]PF_6 is irradiated in acetonitrile, the iron-containing products are Fe(II) and ferrocene.[3] Our previous results, which illustrate that the replacement of the *p*-xylene ligand with three monodentate ligands readily occurs, suggest that CpFe(CH_3CN)$_3$$^+$ may be formed as an intermediate in this reaction with subsequent decomposition to Fe(II) and ferrocene. However, when [CpRu(bz)]PF_6 is irradiated in CH_3CN, a stable compound, [CpRu(CH_3CN)$_3$]PF_6, is formed with a quantum yield of 0.4 ± 0.04. (The spectral changes observed on photolysis are illustrated in Figure 1.) [CpRu(CH_3CN)$_3$]PF_6 is air stable in the solid state and in acetonitrile solution, although it decomposes slowly in other solvents such as acetone or methylene chloride.

Since acetonitrile ligands in many metal complexes are readily replaced,[14] we suspected that the facile thermal displacement of one or more acetonitrile ligands from the complex [CpRu(CH_3CN)$_3$]PF_6 could be accomplished and lead to reactions of synthetic utility. This was borne out by experiment. Further, control of the degree of substitution was attained by controlling the reaction conditions.

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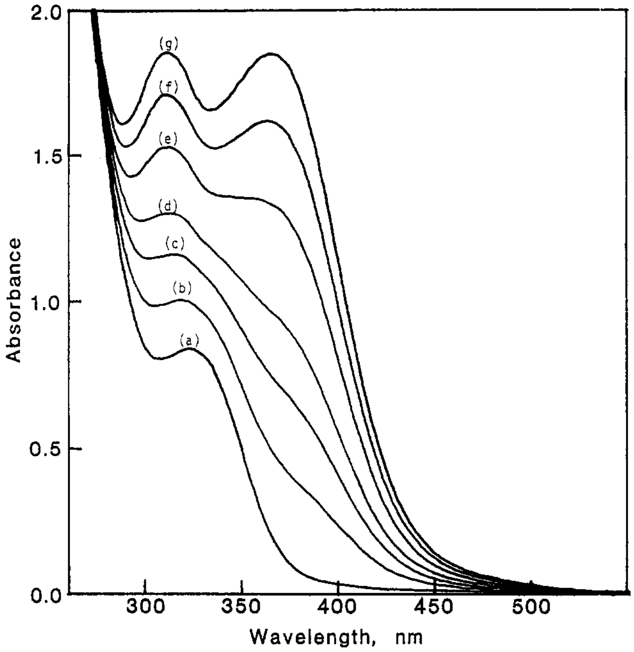

Figure 1. The photolysis of $[CpRu(bz)]PF_6$ in acetonitrile (see text for experimental details): curve a, 0 min; curve b, 5 min; curve c, 10 min; curve d, 15 min; curve e, 25 min; curve f, 35 min; curve g, 45 min.

For example, in acetonitrile solution at room temperature, one acetonitrile molecule in the complex is rapidly replaced upon addition of excess $P(OCH_3)_3$ or CO, to produce $[CpRu(CH_3CN)_2L]PF_6$. Isolation of both $[CpRu(CH_3CN)_2CO]PF_6$ and $[CpRu(CH_3CN)_2P(OCH_3)_3]PF_6$ was accomplished in high yield with no indication of the formation of $[CpRu(CH_3CN)L_2]^+$ or $[CpRuL_3]^+$. Controlled substitution of a second acetonitrile molecule was affected by treatment of $[CpRu(CH_3CN)_2P(OCH_3)_3]PF_6$ with excess $P(OCH_3)_3$ again at room temperature but in CH_2Cl_2 solution. The trisubstituted complex $[CpRu(P(OCH_3)_3)_3]^+$ can then be obtained from $[CpRu(P(OCH_3)_3)_2(CH_3CN)]^+$, by reaction with an excess of $P(OCH_3)_3$ in refluxing dichloroethane.

Formally trisubstituted products are also isolated in the reaction of $[CpRu(CH_3CN)_3]PF_6$ with arenes (*p*-dichlorobenzene, hexamethylbenzene, and [2.2]-*p*-cyclophane). Although it appears that the reaction sequence (reactions 2 and 3) is inefficient, the other syntheses of $[CpRu(arene)]^+$ cations lack generality.

$$[CpRu(bz)]PF_6 \xrightarrow[CH_3CN]{h\nu} [CpRu(CH_3CN)_3]PF_6 + bz \tag{2}$$

$$[CpRu(CH_3CN)_3]PF_6 + arene \xrightarrow[dichloroethane]{\Delta} [CpRu(arene)]PF_6 + 3CH_3CN \tag{3}$$

One method of synthesis begins with ruthenocene using $Al/AlCl_3/H_2O$ to promote the replacement of one cyclopentadienyl ligand with an arene.[8] This method often gives rearrangement of the arene, and the yields are generally low. Another synthetic route to $CpRu(arene)^+$ complexes involves the reaction of cyclohexadienes with $RuCl_3$ to form $[(arene)RuCl_2]_2$ compounds.[15] Treatment of these chloride-bridged dimers with TlCp produces $[CpRu(arene)]Cl$.[6] The major drawback to this method is the unavailability of appropriately substituted cyclohexadienes. Our method of preparing $[CpRu(arene)]PF_6$ compounds involves the reaction of $[CpRu(CH_3CN)_3]PF_6$ with the appropriate arene in refluxing dichloroethane. The yields of these preparative reactions are high (between 60% and 85%), and the complications observed in the previously discussed reactions do not occur.

Nonaromatic unsaturated hydrocarbons are also able to displace all three acetonitrile ligands from $[CpRu(CH_3CN)_3]^+$. The η^6-cyclooctatetraene complex, $[CpRu(\eta^6\text{-}COT)]PF_6$, was isolated in 92% yield from the reaction of $[CpRu(CH_3CN)_3]PF_6$ with cyclooctatetraene, the reaction in this case being complete in 10 min at room temperature.

The order of reagent addition to $[CpRu(CH_3CN)_3]PF_6$ in some cases was found to allow control of the nature of the final product. Although carbon monoxide failed to react with $[CpRu(\eta^6\text{-}COT)]PF_6$ at room temperature, the reaction of $[CpRu(CH_3CN)_2CO]PF_6$ with cyclooctatetraene in refluxing acetonitrile gave a 68% yield of $[CpRu(\eta^4\text{-}C_8H_8)CO]PF_6$ after recrystallization.

Isolation of the $[CpRu(\eta^4\text{-}C_8H_8)CO]PF_6$ complex suggested that stable η^4-arene complexes might be available via the reaction of $[CpRu(CH_3CN)_2P(OCH_3)_3]PF_6$ with toluene in refluxing dichloroethane. However, the products observed in this reaction were $[CpRu(toluene)]PF_6$ and $[CpRu(P(OCH_3)_3)_2CH_3CN]PF_6$. The desired complex, $[CpRu(\eta^4\text{-}toluene)P(OCH_3)_3]PF_6$, may have been formed as an intermediate during the course of the reaction, subsequently releasing $P(OCH_3)_3$ to form $[CpRu(toluene)]PF_6$. This would also account for the formation of $[CpRu(P(OCH_3)_3)_2CH_3CN]PF_6$ by reaction of the released $P(OCH_3)_3$ with $CpRuP(OCH_3)_3(CH_3CN)_2^+$.

Conclusions

The chemistry of $CpRu^{II}$ compounds has not been extensively explored in contrast to $CpFe^{II}$ chemistry which has been the subject of hundreds of papers.[4] This is in part due to the lack of a convenient, general method for the introduction of the $CpRu^{II}$ unit into a molecule. Currently, most $CpRu^{II}$ complexes are prepared from $CpRu(P(Ph)_3)_2Cl$.[5] This reagent is prepared in two steps from $RuCl_3{\cdot}3H_2O$ with an overall yield of only 26%.[16,17] Fortunately, the efficient displacement of chloride or one triphenylphosphine from $CpRu(P(Ph)_3)_2Cl$ can be accomplished by varying the reaction conditions.[5] However, displacement of both triphenylphosphines from the complex has been observed in very few cases. The direct photolysis of $[CpRu(bz)]PF_6$ in CH_2Cl_2 or the thermal replacement of acetonitrile from the complex $[CpRu(CH_3CN)_3]PF_6$ should provide the convenient synthetic methodology needed to prepared a large variety of $CpRu^{II}$ complexes.

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Registry No. $[CpRu(\eta^6\text{-}benzene)]PF_6$, 72812-91-0; $[CpRu(P(OCH_3)_3)_3]PF_6$, 71397-30-3; $[CpRu(P(OCH_2CH_3)_3)_3]PF_6$, 80049-59-8; $[CpRu(CH_3CN)_3]PF_6$, 80049-61-2; $[CpRu(CH_3CN)_2(CO)]PF_6$, 80049-63-4; $[CpRu(CH_3CN)_2P(OCH_3)_3]PF_6$, 80049-65-6; $[CpRu(CH_3CN)(P(OCH_3)_3)_2]PF_6$, 80049-67-8; $[CpRu(\eta^6\text{-}hexamethylbenzene)]PF_6$, 72804-78-5; $[CpRu(\eta^6\text{-}PCP)]PF_6$, 80049-69-0; $[CpRu(\eta^6\text{-}p\text{-}dichlorobenzene)]PF_6$, 80049-71-4; $[CpRu(\eta^6\text{-}C_8H_8)]PF_6$, 80049-73-6; $[CpRu(CO)(\eta^4\text{-}C_8H_8)]PF_6$, 80049-75-8.

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