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Synthesis of New Cyclopentadienyl–Iron and –Ruthenium Benzenethiolate, Thiol, and Thioether Complexes[†]

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Reactions between CpRu(L)(L′)Cl and (n-Bu)$_3$SnSPh were used to prepare ten compounds: CpRu(CO)$_2$SPh, CpRu(CO)(PPh$_3$)SPh, CpRu(PPh$_3$)(P(OMe)$_3$)SR (R = Ph, tol), and CpRu(L)(L′)SPh (L = L′ = PPh$_2$OMe, PPh(OMe)$_2$, P(OMe)$_3$, P(O-i-Pr)$_3$, PMe$_3$; (L)(L′) = dppe). Alkylation at the thiolate ligand using methyl iodide yielded the thioether complexes (salts) [CpRu(L)$_2$(PhSMe)]X (L = PPh$_2$OMe, X = PF$_6$; L = PPh(OMe)$_2$ or P(OMe)$_3$, X = I). Oxidation of CpRu(CO)$_2$SPh by NOPF$_6$ gave [(CpRu(CO)$_2$)$_2$(μ-PhSSPh)](PF$_6$)$_2$, while AgPF$_6$ oxidation of CpRu(L)$_2$SPh yielded the 17-electron species [CpRu(L)$_2$SPh]PF$_6$ (L = PMe$_3$, P(OMe)$_3$; L$_2$ = dppe). The reaction of CpRu(P(OMe)$_3$)$_2$Cl, PhSH, and AgPF$_6$ gave [CpRu(P(OMe)$_3$)$_2$(PhSH)]PF$_6$; this air-sensitive species was deprotonated by lithium diisopropylamide to form CpRu(P(OMe)$_3$)$_2$SPh. An iron complex, [CpFe(P(OMe)$_3$)$_2$(PhSH)]PF$_6$, was prepared in a similar manner and shown to air-oxidize to [CpFe(P(OMe)$_3$)$_2$SPh]PF$_6$.

Introduction

Organometallic complexes with thiolate (SR$^-$) ligands have been known for over 60 years.[1] Thiolates have been found to be versatile ligands, coordinating to one, two, or three metals; when coordinated to two or more metals, they are an important structural component in metal cluster species. Coordinated to a single metal, thiolate groups are known to undergo chemistry at the sulfur center, including protonation–deprotonation and oxidation–reduction, a complement to traditional chemistry for these complexes centered on the metal.

Research carried out in our group involving cyclopentadienyl–iron thiolate complexes has illustrated this chemical behavior at thiolate ligands. Protonation at sulfur[2] and oxidation at this center with dimerization via sulfur–sulfur bond formation[3,4] in iron carbonyl complexes are noted, as is alkylation of the thiolate ligand.[5] In related complexes with phosphine ligands, oxidation at the metal center has been found to occur; this is a consequence of increased electron richness of the complexes resulting from the greater donor ability of the phosphines relative to carbonyls.[3,6,7]

In this study, we have directed attention to mononuclear cyclopentadienyl–ruthenium thiolate complexes. Only limited consideration of such species preceded this study. The synthesis of the compounds CpRu(CO)$_2$SR (R = Me, Bz, Ph) was described by Killops and Knox.[8] More recently, the chemistry of CpRu(PPh$_3$)$_2$SH has been reported by Amarasekera et al.[9] and syntheses of CpRu(PPh$_3$)(L)SR (R = n-Pr, i-Pr, tol; L = PPh$_3$, CO) were reported by Shaver et al.[10] The opportunity to extend work in this area was presented by the availability of a number of CpRu(L)(L′)Cl (L, L′ = phosphines, phosphites, CO) compounds[11,12] and a route for their conversion to CpRu(L)(L′)SR complexes using organotin thiolate reagents.[13] We have followed this lead to prepare 10 ruthenium thiolate complexes described in this paper. We further report the protonation, alkylation, and oxidation chemistry of these species. In addition, new chemistry of a related iron complex is briefly mentioned.

Experimental Section

The following materials were prepared according to the procedures given in the literature: CpRu(L)$_2$Cl (L = PPh$_3$,[11] P(O-i-Pr)$_3$,[12] PMe$_3$,[12] CO,[14] PPh$_2$OMe,[12] PPh(OMe)$_2$,[12] P(OMe)$_3$;[12] L$_2$ = dppe[12]), CpRu(CO)(PPh$_3$)Cl;[16] CpRu(PPh$_3$)(P(OMe)$_3$)Cl,[15] CpFe(P(OMe)$_3$)$_2$I,[17] (n-Bu)$_3$SnSPh.[13] A sample of (n-Bu)$_3$SnStol was prepared by an analogous procedure. Other starting materials were commercial samples. Solvents were dried prior to use. All reactions were performed under dry N$_2$. Glassware was oven-dried prior to use.

Infrared spectra were recorded on a Beckman IR 4230 spectrometer. All ^{1}H NMR spectra were measured on an IBM-WP-200 spectrometer. Melting points were measured with a Thomas-Hoover Unimelt apparatus and are not corrected.

Whenever possible, the new complexes were characterized by an accurate parent peak mass measurement. Mass spectra were recorded on a Kratos MS-80 mass spectrometer with a heated solids inlet port and electron impact (ei) ionization. In these instances, particular care was taken to verify purities of samples using ^{1}H NMR spectroscopy, with these data also serving as further confirmation of the molecular stoichiometry. When it was not possible to use this characterization, elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

New Cyclopentadienyl–Ruthenium Thiolate Complexes. CpRu(CO)$_2$SPh. This known complex[8] was previously prepared by a different route. A solution of CpRu(CO)$_2$Cl (0.50 g, 1.9 mmol) and (n-Bu)$_3$SnSPh (0.78 mL, 2.3 mmol) in 25 mL of methanol was heated at reflux for 3 h. After the solution was cooled, the solvent was removed on a rotary evaporator and chromatography (alumina/hexane) of the resulting red oil gave a single fraction that was collected. The solid obtained on evaporation of the solvent was purified by crystallization from hexane at −78 °C. The product was isolated as yellow plates, 0.24 g (38%), mp 87–90 °C. MS: m/e = 331.9438; calcd for C$_{13}$H$_{10}$O$_2$RuS m/e = 331.9436. IR (CDCl$_3$): ν(CO) 2040, 1988 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.37 (s, 5 H, Cp), 6.9–7.5 (m, 5 H, Ph).

CpRu(CO)(PPh$_3$)SPh. A solution of CpRu(CO)(PPh$_3$)Cl (0.244 g, 0.432 mmol) and (n-Bu)$_3$SnSPh (0.2 mL, 0.6 mmol) in 20 mL of methanol was heated at reflux for 3 h. After the solution was cooled, the solvent was removed on a rotary evaporator. Chromatography (alumina/20% acetone/CH$_2$Cl$_2$) of the resulting red oil initially gave a colorless fraction containing (n-Bu)$_3$SnCl and unreacted (n-Bu)$_3$SnSPh. The first red band that eluted from the column was evaporated to dryness, and the solid obtained was purified by crystallization from

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[†] Standard abbreviations: Me = methyl, Ph = phenyl, Cp = η^5-cyclopentadienyl, n-Bu = n-butyl, tol = p-tolyl; dppe = 1,2-bis(diphenylphosphino)ethane.

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CH_2Cl_2/hexane. The product, CpRu(CO)(PPh_3)SPh, was isolated as orange crystals, 0.035 g (12%), mp 193–194 °C. MS: *m/e* = 566.0054; calcd for $C_{30}H_{25}OPRuS$ *m/e* = 566.0395. IR (CH_2Cl_2): ν(CO) 1947s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.92 (s, 5 H, Cp), 6.85 (d, *J* = 8.7 Hz, 1 H, SPh), 7.00 (t, *J* = 8.7 Hz, 2 H, SPh), 7.41 (m, 17 H, PPh_3 and SPh).

A second band was eluted from the column with acetone and was evaporated to dryness. Purification of the residue by crystallization from CH_2Cl_2/hexane gave 0.124 g (51% recovery) of pale orange powder. This was identified as CpRu(CO)(PPh_3)Cl by comparison of its ^1H NMR and infrared spectra with those of the starting compound.

CpRu(CO)(PPh_3)SPh was also prepared by heating at reflux a solution of CpRu(CO)(PPh_3)Cl (0.099 g, 0.18 mmol) and NaSPh (0.029 g, 0.22 mmol) in 10 mL of methanol for 20 h. The reaction mixture was worked up in a similar manner. The products were identified by IR and ^1H NMR spectroscopy as CpRu(CO)(PPh_3)SPh (0.072 g, 63%) and CpRu(CO)(PPh_3)Cl (0.008 g, 8%).

CpRu(dppe)SPh. A solution of CpRu(dppe)Cl (2.25 g, 3.8 mmol) and (n-Bu)$_3$SnSPh (1.5 mL, 4.5 mmol) in 50 mL of methanol was heated at reflux for 1.5 h. Upon cooling, the product precipitated from solution and was collected by filtration. After being washed with two 10 mL portions of hexane, the product, an orange powder, was dried to give 1.91 g (76%), mp 188–189 °C. MS: *m/e* = 674.0895; calcd for $C_{37}H_{34}P_2RuS$ *m/e* = 674.0886. ^1H NMR ($CDCl_3$): δ 2.22 (m, 2 H) and 2.84 (m, 2 H) CH_2CH_2, 4.70 (s, 5 H, Cp), 6.4–7.7 (m, 25 H, Ph).

CpRu(PPh_3)(P(OMe)$_3$)SPh. A solution of CpRu(PPh_3)(P(OMe)$_3$)Cl (0.192 g, 0.327 mmol) and (n-Bu)$_3$SnSPh (0.15 mL, 0.42 mmol) in 15 mL of methanol was heated at reflux for 4 h. After the solution was cooled, the solvent was removed on a rotary evaporator. Chromatography (alumina/acetone) of the residue first gave a colorless fraction containing (n-Bu)$_3$SnCl and (n-Bu)$_3$SnSPh. A single orange band was collected from the column, and the fraction was evaporated to dryness. Purification of the residue by crystallization from CH_2Cl_2/hexane at −25 °C gave 0.134 g (62%) of orange crystals, mp 161–163 °C. Anal. Calcd for $C_{32}H_{34}O_3P_2RuS$: C, 58.09; H, 5.18. Found: C, 57.39; H, 5.34. ^1H NMR ($CDCl_3$): δ 3.34 (d, J_{PH} = 10 Hz, 9 H, P(OMe)$_3$), 4.59 (s, 5 H, Cp), 6.77 (t, *J* = 6 Hz, 1 H, SPh), 6.90 (t, *J* = 5 Hz, 2 H, SPh), 7.31 (m, 9 H, PPh_3), 7.49 (m, 8 H, PPh_3 and SPh).

The following compounds were prepared by an analogous procedure.

CpRu(PPh_3)(P(OMe)$_3$)Stol: yellow powder, 49%, mp 125 °C. MS: *m/e* = 662.0799 ($M^+ - CH_2$), 661.0749 ($M^+ - CH_3$); calcd for $C_{33}H_{36}O_3P_2RuS$ *m/e* = 676.08972. ^1H NMR ($CDCl_3$): δ 2.17 (s, 3 H, tolyl methyl), 3.35 (d, J_{PH} = 10 Hz, 9 H, P(OMe)$_3$), 4.54 (s, 5 H, Cp), 6.68 (d, *J* = 6 Hz, 2 H, Stol), 7.30 (m, 11 H, PPh_3 and Stol), 7.44 (m, 6 H, PPh_3).

CpRu(PPh_2OMe)$_2$SPh: orange powder, 73%, mp 91–92 °C. MS: *m/e* = 708.0954; calcd for $C_{37}H_{36}O_2P_2RuS$ *m/e* = 708.0948. ^1H NMR ($CDCl_3$): δ 3.08 (br s, 6 H, POMe), 4.34 (s, 5 H, Cp), 7.25 (m, 17 H), 7.42 (m, 4 H), 7.52 (m, 4 H, PPh and SPh).

CpRu(PPh(OMe)$_2$)$_2$SPh: yellow crystals, 66%, mp 119–120 °C. MS: *m/e* = 616.0534; calcd for $C_{27}H_{32}O_4P_2RuS$ *m/e* = 616.0526. ^1H NMR ($CDCl_3$): δ 3.45 (m, 12 H, POMe), 4.54 (s, 5 H, Cp), 6.7–7.7 (m, 15 H, Ph).

CpRu(P(OMe)$_3$)$_2$SPh: yellow crystals, 52%, mp 59–61 °C. MS: *m/e* = 524.0120; calcd for $C_{17}H_{28}O_6P_2RuS$ *m/e* = 524.0112. ^1H NMR ($CDCl_3$): δ 3.58 (d, J_{PH} = 3 Hz, 9 H, POMe), 3.62 (d, J_{PH} = 3 Hz, 9 H, POMe), 4.89 (s, 5 H, Cp), 6.9–7.6 (m, 5 H, Ph).

An alternative route to this compound was also found. A solution of CpRu(P(OMe)$_3$)$_2$Cl (0.50 g, 1.1 mmol), PhSH (0.13 mL, 1.3 mmol), and NaOEt (0.08 g, 1.2 mmol) in 200 mL of ethanol was heated at reflux for 12 h. A similar workup resulted in 0.12 g (21%) of CpRu(P(OMe)$_3$)$_2$SPh, identified by mp and ^1H NMR spectroscopy.

CpRu(P(O-*i*-Pr)$_3$)$_2$SPh: yellow plates, 65%, mp 109–111 °C. MS: *m/e* = 692.1998; calcd for $C_{29}H_{52}O_6P_2RuS$ *m/e* = 692.1984. ^1H NMR ($CDCl_3$): δ 1.23 (t, *J* = 7 Hz, 12 H, CH(CH_3)$_2$), 4.78 (s, 5 H, Cp), 4.81 (m, 2 H, CH(CH_3)$_2$), 6.8–7.7 (m, 5 H, Ph).

CpRu(PMe_3)$_2$SPh: 70%, mp 96–98 °C. MS: *m/e* = 428.0425; calcd for *m/e* $C_{17}H_{28}P_2RuS$ = 428.0418. ^1H NMR ($CDCl_3$): δ 1.41 (d, J_{PH} = 4 Hz, 9 H, PMe), 1.43 (d, J_{PH} = 4 Hz, 9 H, PMe), 4.61 (s, 5 H, Cp), 6.6–7.5 (m, 5 H, Ph).

NMR Study of the Reaction of CpRu(P(OMe)$_3$)$_2$Cl and (n-Bu)$_3$SnSPh. An NMR tube was charged with CpRu(P(OMe)$_3$)$_2$Cl and 1.9 equiv of (n-Bu)$_3$SnSPh and evacuated. Methanol-d_4 was distilled into the tube. The tube was sealed under vacuum and placed in a 68 °C oil bath. The tube was removed to record ^1H NMR spectra at t = 0, 30, 90, 190, 290, 700, and 1050 min. Two new cyclopentadienyl proton peaks grew in at δ 5.08 and 4.92 as the concentration of the starting material (δ 4.85) decreased. The ratio of the peaks at δ 4.85, 4.92, and 5.08 was 10:15:1 after 1050 min. Confirmation that the peak at δ 4.92 was due to CpRu(P(OMe)$_3$)$_2$SPh was obtained by comparison with the spectrum of a known sample. The peak at δ 5.08 is probably due to the likely intermediate [CpRu(P(OMe)$_3$)$_2$((n-Bu)$_3$SnSPh)]Cl.

New Cyclopentadienyl–Ruthenium Thioether Complexes. [CpRu(PPh_2OMe)$_2$(MeSPh)]PF_6. A solution of CpRu(PPh_2OMe)$_2$Cl (0.294 g, 0.465 mmol) and (n-Bu)$_3$SnSPh (0.20 mL, 0.56 mmol) in 20 mL of methanol was heated at reflux for 19 h. After the solution was cooled, the solvent was removed on a rotary evaporator. Chromatography (alumina/acetone) of the residue initially gave a clear fraction containing (n-Bu)$_3$SnCl and unreacted (n-Bu)$_3$SnSPh. A single red band containing CpRu(PPh_2OMe)$_2$SPh was collected from the column. The solution changed color from reddish orange to pale orange upon treatment with MeI (0.15 mL, 2.4 mmol). After addition of NH_4PF_6 (0.2 g, 1 mmol), the solution was stirred for 10 min and then evaporated to dryness. The residue was extracted with CH_2Cl_2, and the extracts were concentrated to an oil. Crystallization of the oil from ethyl acetate gave yellow powder, 0.243 g (60%), mp 141 °C dec. Anal. Calcd for $C_{38}H_{39}F_6O_2P_3RuS$: C, 52.64; H, 4.53. Found: C, 52.24; H, 4.70. ^1H NMR ($CDCl_3$): δ 2.56 (s, 3 H, SMe), 3.15 (t, J_{PH} = 5.9 Hz, 6 H, POMe), 4.57 (s, 5 H, Cp), 6.97 (m, 4 H), 7.10 (m, 4 H), 7.38 (m, 15 H), 7.45 (m, 2 H).

[CpRu(PPh(OMe)$_2$)$_2$(MeSPh)]I. A solution of CpRu(PPh(OMe)$_2$)$_2$SPh (0.120 g, 0.195 mmol) and MeI (0.1 mL, 2 mmol) in 20 mL of CH_2Cl_2 was stirred briefly. The solution was concentrated to a volume of 5 mL, treated with 15 mL of Et_2O, and cooled at −25 °C. Filtration of the resulting precipitate gave 0.141 g (96%) of yellow-green crystals, mp 125–127 °C. Anal. Calcd for $C_{28}H_{35}IO_4P_2RuS$: C, 44.39; H, 4.66. Found: C, 44.64; H, 4.76. ^1H NMR ($CDCl_3$): δ 2.50 (s, 3 H, SMe), 4.41 (t, J_{PH} = 6 Hz, 6 H, POMe), 4.52 (t, J_{PH} = 6 Hz, 6 H, POMe), 4.87 (s, 5 H, Cp), 7.28 (m, 4 H), 7.40 (m, 9 H), 7.60 (m, 2 H).

[CpRu(P(OMe)$_3$)$_2$(MeSPh)]I. A solution of CpRu(P(OMe)$_3$)$_2$Cl (0.227 g, 0.506 mmol) and (n-Bu)$_3$SnSPh (0.2 mL, 2 mmol) in 20 mL of methanol was heated at reflux for 14.5 h. After the solution was cooled, the solvent was removed in vacuo and the residue was dissolved in a minimum amount of acetone. Chromatography (alumina/10% acetone/hexane) of the residue initially gave a colorless fraction containing (n-Bu)$_3$SnCl and unreacted (n-Bu)$_3$SnSPh. A single orange band, containing CpRu(P(OMe)$_3$)$_2$SPh, eluted from the column text. The orange fraction was concentrated to an oil, and the oil was dissolved in 20 mL of CH_2Cl_2. The color of the orange solution changed to greenish yellow after treatment with MeI (0.07 mL, 1 mmol). The solution was stirred for several minutes and then concentrated to an oil. The oil was crystallized from CH_2Cl_2/Et_2O at −25 °C to give 0.177 g (52%) of yellow crystals, mp 98 °C. Anal. Calcd for $C_{18}H_{31}IO_6P_2RuS$: C, 32.51; H, 4.70. Found: C, 32.17; H, 4.72. ^1H NMR ($CDCl_3$): δ 2.81 (s, 3 H, SMe), 3.61 (t, J_{PH} = 5.6 Hz, 18 H, P(OMe)$_3$), 4.98 (s, 5 H, Cp), 7.38 (m, 3 H, SPh), 7.54 (m, 2 H, SPh).

Oxidation of Cyclopentadienyl–Ruthenium Thiolate Complexes. [(CpRu(CO)$_2$)$_2$$\mu$-PhSSPh](PF$_6$)$_2$. A solution of CpRu(CO)$_2$SPh (0.3 g, 0.9 mmol) and $NOPF_6$ (0.15 g, 0.86 mmol) in 20 mL of CH_2Cl_2 was stirred for 45 min with gas being evolved, and a precipitate formed during this time. This solid was collected and then recrystallized from CH_3CN/Et_2O to give 0.21 g (49%) of yellow powder, mp 145–147 °C. Anal. Calcd for $C_{26}H_{20}F_{12}O_4P_2Ru_2S_2$: C, 32.77; H, 2.10; S, 6.72. Found: C, 32.89; H, 2.37; S, 6.86. IR (KBr): ν(CO) 2062, 2028 cm^{-1}. ^1H NMR (CD_3CN): δ 5.34 (s, 5 H, Cp), 7.7–7.95 (m, 5 H, Ph).

[CpRu(dppe)SPh]PF_6. A solution of CpRu(dppe)SPh (0.3 g, 0.45 mmol) and $AgPF_6$ (0.11 g, 0.45 mmol) in 25 mL of acetone was stirred at ambient temperature for 15 min. The resulting blue solution was filtered and evaporated to an oil. Crystallization of the residue from CH_2Cl_2/Et_2O yielded 0.31 g (85%) of blue powder, mp 100 °C dec. Anal. Calcd for $C_{37}H_{34}F_6P_3RuS$: C, 54.28; H, 4.16; P, 11.37. Found: C, 54.06; H, 4.33; P, 11.59.

A similar procedure was used to prepare the following complexes.

[CpRu(PMe_3)$_2$SPh]PF_6: blue crystals, 73%, mp 87–90 °C. Anal. Calcd for $C_{17}H_{28}F_6P_3RuS$: C, 35.66, H, 4.90; P, 16.26. Found: C, 35.58; H, 4.96; P, 16.45.

[CpRu(P(OMe)$_3$)$_2$SPh]PF_6: green solid, 41%, mp 119–122 °C. Anal. Calcd for $C_{17}H_{28}F_6O_6P_3RuS$: C, 30.54; H, 4.19; P, 13.92. Found: C, 30.32; H, 4.11; P, 13.71.

New Cyclopentadienyl–Iron and –Ruthenium Thiol Complexes. [CpFe(P(OMe)$_3$)$_2$(PhSH)]PF_6 and [CpFe(P(OMe)$_3$)$_2$SPh]PF_6. A solution of CpFe(P(OMe)$_3$)$_2$Cl (0.097 g, 0.38 mmol) and $AgPF_6$ (0.188 g, 0.379 mmol) in 15 mL of methanol was stirred for 2 h at ambient temperature. A precipitate formed, and the solution was filtered into a flask containing PhSH (0.1 mL, 1 mmol). A small amount of black precipitate formed in the flask, and the solution was carefully filtered. The filtrate was concentrated to an oily residue; crystallization of the residue from Et_2O yielded 0.081 g (34%) of [CpFe(P(OMe)$_3$)$_2$(PhSH)]PF_6, an air-sensitive brown solid, mp 122–124 °C. Anal. Calcd for $C_{17}H_{29}F_6FeO_6P_3S$: C, 32.71; H, 4.68. Found: C, 32.07; H, 4.27. ^1H NMR ($CDCl_3$): δ 3.74 (t, J_{PH} = 5 Hz, 18 H, P(OMe)$_3$), 4.45 (s, 5 H, Cp), 7.35 (m, 3 H, SPh), 7.46 (m, 2, H, SPh).

When the filtrate from the above reaction was exposed to air, the color of the solution quickly changed from yellow-brown to dark purple. The purple solution was slowly evaporated to an oil. Purification of this material by crystallization from CH_2Cl_2/Et_2O yielded 0.029 g (4%) of $[CpFe(P(OMe)_3)_2SPh]PF_6$ as black needles, mp 146 °C. Anal. Calcd for $C_{17}H_{28}F_6FeO_6P_3S$: C, 32.76; H, 4.53. Found: C, 32.56; H, 4.84.

$[CpRu(P(OMe)_3)_2(PhSH)]PF_6$. A solution of $CpRu(P(OMe)_3)_2Cl$ (0.262 g, 0.584 mmol) and NH_4PF_6 (0.198 g, 1.22 mmol) in 20 mL of methanol was treated with PhSH (0.2 mL, 2 mmol). The solution was heated at reflux for 14 h. After the solution was cooled, the solvent was removed in vacuo and the residue was extracted with 20 mL of CH_2Cl_2. The solution was concentrated and the resulting oil crystallized from Et_2O to give air-sensitive yellow crystals, 0.296 g (76%), mp 110–112 °C. Anal. Calcd for $C_{17}H_{29}F_6O_6P_3RuS$: C, 30.50; H, 4.37. Found: C, 31.18; H, 4.66. IR (KBr): $\nu(PF_6)$ 845s cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.62 (t, $J_{PH} = 6$ Hz, 18 H, $P(OMe)_3$), 4.92 (s, 5, H, Cp), 7.42 (m, 5 H, SPh).

Reaction of $[CpRu(P(OMe)_3)_2(PhSH)]PF_6$ and Base, Monitored by NMR Spectroscopy. $[CpRu(P(OMe)_3)_2(PhSH)]PF_6$ + Lithium Diisopropylamide (LDA). An NMR tube was charged with 0.021 g (0.032 mmol) of $[CpRu(P(OMe)_3)_2(HSPh)]PF_6$ and an excess of LDA. After evacuation, chloroform-d_1 was distilled into the tube. The tube was frozen and sealed under vacuum and then warmed to room temperature. An ^1H NMR spectrum was identical with that of $CpRu(P(OMe)_3)_2SPh$. ^1H NMR ($CDCl_3$): δ 3.63 (t, $J_{PH} = 6$ Hz, 18 H, $P(OMe)_3$), 4.93 (s, 5 H, Cp), 7.35 (m, 3 H, SPh), 7.50 (m, 2, H, SPh).

Discussion

Ten thiolate complexes, CpRu(L)(L′)SR (L, L′ = phosphine, phosphite, CO; R = Ph, tol) were prepared from the reaction of $(n\text{-}Bu)_3SnSR$ and CpRu(L)(L′)Cl in methanol (eq 1). Typically,

$$CpRu(L)(L')Cl + (n\text{-}Bu)_3SnSR \rightarrow CpRu(L)(L')SR + (n\text{-}Bu)_3SnCl \quad (1)$$

$$R = Ph{:}\ L = L' = CO,\ PPh_2OMe,\ PPh(OMe)_2,\ P(OMe)_3,\ P(O\text{-}i\text{-}Pr)_3,\ PMe_3;\ (L)(L') = dppe;\ L = CO,\ L' = PPh_3$$

$$R = Ph,\ tol{:}\ L = P(OMe)_3;\ L' = PPh_3$$

solutions of these reactants were heated at reflux for several hours. After cooling, chromatography (alumina/acetone) separated $(n\text{-}Bu)_3SnCl$ and unreacted $(n\text{-}Bu)_3SnSPh$ from $CpRu(L)_2SPh$. The isolated complexes are air-stable orange solids. Generally, yields of the pure isolated materials were good (38–76% in this work), with apparent losses coming in purification steps. All of the compounds listed are new except for $CpRu(CO)_2SPh$.[8] Alternative syntheses for $CpRu(CO)(PPh_3)SPh$ and $CpRu(P(OMe)_3)_2SPh$ were provided; the former used NaSPh, while in the latter, PhSH and NaOEt were used to generate $[SPh]^-$ as a source of the thiolate group.

It had previously been suggested that reactions of the tin thiolate reagent occur in a two-step process.[18] Initially, displacement of chloride ion is assumed, giving a thioether complex (coordination via sulfur), $[CpRu(L)(L')((n\text{-}Bu)_3SnSR)]Cl$; this step is then followed by displacement of the tri-n-butyltin group from sulfur by Cl^-. To test for the possibility of an intermediate species, we monitored the reaction of $CpRu(P(OMe)_3)_2Cl$ and $(n\text{-}Bu)_3SnSPh$ in methanol-d_4 by ^1H NMR spectroscopy. Depletion in the quantity of starting complex, as measured by the cyclopentadienyl proton resonance intensity (δ 4.85), was accompanied by the formation of two species. One was the product, $CpRu(P(OMe)_3)_2SPh$, with a cyclopentadienyl proton resonance at $\delta = 4.92$. The cyclopentadienyl proton resonance of the second species was at lower field, $\delta = 5.08$. The chemical shift of this resonance is typical of a cationic complex. Attempts to isolate this species failed.

Oxidation of $CpRu(L)_2SPh$ by $AgPF_6$ readily forms stable blue 17-electron complexes. The complexes $[CpRu(dppe)SPh]PF_6$, $[CpRu(PMe_3)_2SPh]PF_6$, and $[CpRu(P(OMe)_3)_2SPh]PF_6$ are assumed to exist as monomers and, being paramagnetic, were identified only by chemical analysis. Similar oxidations of analogous iron compounds have been reported previously.[3,4,6,7] Oxidation of $CpRu(CO)_2SPh$ by $NOPF_6$ produced a yellow, diamagnetic complex, $[(CpRu(CO)_2)_2(\mu\text{-}PhSSPh)](PF_6)_2$. A similar iron compound, $[(CpFe(CO)_2)_2(\mu\text{-}PhSSPh)](PF_6)_2$, formed by the same reaction has been reported.[3,4] Note also that the oxidation of $CpRu(PPh_3)_2SH$ is reported to yield $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ via the proposed intermediate $[CpRu(PPh_3)_2]_2(\mu\text{-}HSSH)^{2+}$.[9] The better donor phosphine ligands help to stabilize the Ru(III) center; hence the complexes $[CpRu(L)_2SPh]PF_6$ (L_2 – dppe; L = PMe_3, $P(OMe)_3$) were isolated as monomeric radical species. In the case of $[(CpRu(CO)_2)_2(\mu\text{-}PhSSPh)](PF_6)_2$ oxidation occurs at the sulfur center and the resultant radical dimerizes to achieve the 18-electron (Ru(II)–Ru(II)) configuration.

A very rapid reaction of $CpRuL_2SPh$ (L = PPh_2OMe, $PPh(OMe)_2$, $P(OMe)_3$) with MeI was indicated by a color change from orange to yellow (eq 2). The products, thioether complexes,

$$CpRu(L)_2SPh + MeI \rightarrow [CpRu(L)_2(PhSMe)]I \quad (2)$$

$$L = PPh_2OMe,\ PPh(OMe)_2,\ P(OMe)_3$$

can be isolated as yellow to greenish yellow powders as iodide or PF_6^- salts. The $CpRuL_2SR$ complexes thus have similar chemistry to their iron analogues. King and Bisnette[19] found that $CpFe(CO)_2SMe$ reacted with MeI to form $[CpFe(CO)_2(Me_2S)]I$, and our group had reported reactions between CpFe(CO)LSPh (L = PMe_3, PPh_2Me, PPh_3, PPh_2OMe, $PPh(OMe)_2$, $P(OPh)_3$, $P(OMe)_3$) and EtBr.[5] The complex $CpRu(PPh_3)_2SH$ was similarly alkylated by $MeOSO_2CF_3$ to form $[CpRu(PPh_3)_2(MeSH)]OSO_2CF_3$.[9]

The ruthenium thiol complex $[CpRu(P(OMe)_3)_2(PhSH)]PF_6$ was prepared in 76% yield by heating a methanol solution of $CpRu(P(OMe)_3)_2Cl$, PhSH, and NH_4PF_6 at reflux for 14 h, and isolated as air-sensitive, pale yellow crystals (eq 3). It is known

$$CpRu(P(OMe)_3)_2Cl + PhSH + NH_4PF_6 \rightarrow [CpRu(P(OMe)_3)_2(PhSH)]PF_6 + NH_4Cl \quad (3)$$

that $CpRuL_2Cl$ complexes (L = phosphine) readily undergo solvolysis reactions with displacement of the chloride ion by MeOH, CH_3CN, or DMSO.[20-23] The replacement of chloride ion by HSPh is a logical extension of that work. The simplicity of this method provides significant advantages for the preparation of ruthenium thiol complexes. Isolated examples of metal thiol complexes are rare,[24] although the syntheses of $[CpRu(PPh_3)_2(RSH)]^+$ (R = Me, n-Pr) have been reported.[9] The electron richness of the $[CpRu(PPh_3)_2]^+$ moiety is believed to play a significant role in the stability of these complexes.

The iron thiol complex $[CpFe(P(OMe)_3)_2(HSPh)]PF_6$ was prepared by first abstracting the iodide ion from $CpFe(P(OMe)_3)_2I$ with $AgPF_6$ and treating the filtered solution with HSPh. This complex was isolated as an air-sensitive brown solid. A solution of $[CpFe(P(OMe)_3)_2(PhSH)]PF_6$ is oxidized by air to yield a black paramagnetic solid, $[CpFe(P(OMe)_3)_2SPh]PF_6$.

One property of the thiol complexes that we were interested in was their acidity. The complex $[CpFe(CO)_2(HSPh)]BF_4$ has been shown to be a strong acid.[25] Similarly, $[CpMo(CO)_3(HStol)]BF_4$, $[\eta^5\text{-}C_9H_7W(CO)_3(HStol)]BF_4$, $[\eta^5\text{-}C_9H_7W(CO)_3(HStol)]AsF_6$, and $[CpW(CO)_2(P(OPh)_3)(HStol)]BF_4$ are also strong acids.[26] The complexes prepared in this work are much more basic than their carbonyl analogues, presumably because of the electron richness of the metal center. It was possible to deprotonate $[CpRu(P(OMe)_3)_2(HSPh)]PF_6$ with LDA in chloroform-d_1. According to an ^1H NMR spectrum of the reaction, $CpRu(P(OMe)_3)_2SPh$ is formed immediately upon mixing these reagents.

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