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The synthesis of several new cyclopentadienyl-ruthenium t-butyl thiol complexes

Paul M. Treichel *, Richard A. Crane and Kenneth N. Haller
Department of Chemistry, University of Wisconsin - Madison, Madison, WI (U.S.A.)

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Abstract

The air-sensitive complexes $[CpRu(L)(L')(HSBu^t)]PF_6$ ($L = L' = PPh(OMe)_2$, PPh_2OMe, $P(OMe)_3$; $L = PPh_3$, $L' = CO$, $P(OMe)_3$) are prepared by heating methanol solutions of $CpRu(L)(L')Cl$, $HSBu^t$, and NH_4PF_6. The cyclopentadienyl-ruthenium thiol complexes oxidized in air to form paramagnetic complexes, one of which, $[CpRu(PPh_2OMe)_2SBu^t]PF_6$, was isolated and characterized by a single crystal x-ray diffraction study. Crystals are monoclinic with space group $P2_1/c$, $a = 12.8070(25)$, $b = 14.3160(36)$, $c = 20.1768(50)$ Å, $\beta = 97.841(18)°$, and $Z = 4$. Data were refined to $R = 0.0452$ (6248 reflections). The Ru–S(1) bond length was 2.274(1) Å and the Ru–P bond lengths were 2.298(1) and 2.291(1) Å. The synthesis of $CpRu(CO)(PPh_3)SBu^t$ is also reported.

Introduction

Organometallic complexes containing thiols (RSH) as ligands are very rare [1], and the instability of many of these complexes with respect to loss of either H^+ or H_2 has made the study of these compounds difficult [2]. Our interest in thiol complexes began with the preparation of $[CpFe(CO)_2(HSPh)]BF_4$ here in 1981 [3]. The complex, prepared from $CpFe(CO)_2SPh$ and HBF_4, is a strong acid, capable of protonating THF in CH_2Cl_2 solution. Since then, the list of isolated organometallic thiol complexes has been expanded to include $[CpMo(CO)_3(HStol)]BF_4$, $[(\eta^5\text{-}C_9H_7)W(CO)_3(HStol)]BF_4$, $[(\eta^5\text{-}C_9H_7)W(CO)(HStol)]AsF_6$, and $[CpW(CO)_2(P\{OPh\}_3)(HStol)]BF_4$ [4]. These complexes were air-sensitive and were also shown to be strong acids. More recently, the synthesis of $[CpRu(PPh_3)_2(MeSH)]OSO_2CF_3$ and $[CpRu(PPh_3)_2(HSPr^n)]BF_4$ have been reported [5].

Our studies of chloride substitution reactions of $CpRu(L)(L')Cl$ compounds by CH_3CN and DMSO suggested that thiol complexes could be synthesized by a similar procedure, Eq. 1.

$$CpRu(L)(L')Cl + HSR + NH_4PF_6 \rightarrow [CpRu(L)(L')(HSR)]PF_6 + NH_4Cl \qquad (1)$$

(L, L' = phosphine, phosphite, CO; R = alkyl, aryl)

The availability of $CpRu(L)(L')Cl$ with a variety of ligands and the simplicity of the procedure made this method attractive. In this paper, we report the synthesis and study of several new $HSBu^t$ complexes prepared by this route. This work complements our studies of similar ruthenium benzenethiolate and benzenethiol complexes [6]. Solutions of the reported thiol complexes were oxidized by air to form paramagnetic ruthenium(III) complexes. The crystal structure of one of the oxidation products, $[CpRu(PPh_2OMe)_2SBu^t]PF_6$ was determined. We also report the synthesis of a new thiolate complex, $CpRu(CO)(PPh_3)SBu^t$.

Experimental

The following materials were prepared according to the procedures given in the literature: $CpRu(L)(L')Cl$ ($L = PPh_3$, $L' = P(OMe)_3$ [7], $L = CO$, $L' = PPh_3$ [8], $L = L' = PPh_2OMe$, $PPh(OMe)_2$, $P(OMe)_3$ [9]). Other starting materials were commercial samples. Solvents were dried prior to use, all reactions were performed under dry N_2, and all glassware was oven dried.

Infrared spectra were recorded on a Beckman IR 4230 spectrometer. All ^1H NMR spectra were measured on an IBM-WP-200 spectrometer. Melting points were measured with a Thomas–Hoover Unimelt apparatus and were not corrected. Analyses were performed by Galbraith Laboratories, Knoxville, TN.

New cyclopentadienyl-ruthenium thiol complexes

$[CpRu(CO)(PPh_3)(HSBu^t)]PF_6$: A solution of $CpRu(CO)(PPh_3)Cl$ (0.182 g, 0.370 mmol) and NH_4PF_6 (0.092 g, 0.56 mmol) in 20 mL of methanol was treated with $HSBu^t$ (0.1 mL, 0.9 mmol). The solution was heated at reflux for 18 h. After cooling the solution, the solvent was removed in vacuo and the residue was extracted with 20 mL of CH_2Cl_2. The extracts were combined and concentrated to a volume of 3 ml. The product crystallized after the addition of 15 ml of Et_2O to the solution. Filtration of the precipitate gave 0.062 g (24%) of air-sensitive orange-brown crystals, m.p. 204°C. Anal. Found: C, 48.12; H, 4.40. $C_{28}H_{30}F_6OP_2RuS$ calcd.: C, 48.62; H, 4.37%. ^1H NMR ($CDCl_3$): δ 1.27 (s, 9 H, SBu^t), 2.08 (s, 1 H, SH), 5.23 (s, 5 H, Cp), 7.25 (m, 6 H, PPh_3), 7.5 (m, 9 H, PPh_3).

The following complexes were prepared by procedures analogous to the above:

$[CpRu(PPh_3)(P\{OMe\}_3)(HSBu^t)]PF_6$: air-sensitive pale orange needles, 81%, m.p. 198–199°C. Anal. Found: C, 46.26; H, 5.33. $C_{30}H_{39}F_6O_3P_3RuS$ calcd.: C, 45.74; H, 4.99%. ^1H NMR ($CDCl_3$): δ 1.33 (s, 9 H, SBu^t), 3.49 (d, $J(PH) = 11$ Hz, 9 H, $P(OMe)_3$), 4.88 (s, 5 H, Cp), 7.25 (m, 6 H, PPh_3), 7.45 (m, 9 H, PPh_3).

$[CpRu(PPh_2OMe)_2(HSBu^t)]PF_6$: air-sensitive reddish-brown crystals, 64%, m.p. 158–162°C. Anal. Found: C, 50.44; H, 5.02. $C_{35}H_{41}F_6O_2P_3RuS$ calcd.: C, 50.42; H, 4.96%. ^1H NMR ($CDCl_3$): δ 1.32 (s, 9 H, SBu^t), 3.21 (t, $J(PH) = 6$ Hz, 6 H, POMe), 4.64 (s, 5 H, Cp), 7.18 (m, 12 H, PPh_2), 7.45 (m, 8 H, PPh_2).

$[CpRu(PPh\{OMe\}_2)_2(HSBu^t)]PF_6$: air-sensitive pale orange crystals, 56%, m.p. 129–131°C. Anal. Found: C, 38.88; H, 4.97. $C_{25}H_{37}F_6O_4P_3RuS$ calcd.: C, 40.49; H, 5.03%. ^1H NMR ($CDCl_3$): δ 1.35 (s, 9 H, SBu^t), 3.19 (s, 1 H, SH), 3.52 (d, $J(PH) = 11.6$ Hz, 6 H, POMe), 3.55 (d, $J(PH) = 11.7$ Hz, 6 H, POMe), 4.84 (s, 5 H, Cp), 7.40 (m, 10 H, PPh).

$[CpRu(P\{OMe\}_3)_2(HSBu^t)]PF_6$: air-sensitive pale yellow needles, 43%, m.p. 130–135°C dec. Anal. Found: C, 27.77; H, 4.97. $C_{15}H_{33}F_6O_6P_3RuS$ calcd.: C, 27.74; H, 5.12%. IR (KBr): $\nu(SH)$ 2540w, $\nu(PF_6)$ 845s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.36 (s, 9 H, SBu^t), 3.44 (s, 1 H, SH), 3.63 (t, $J(PH) = 5.7$ Hz, 18 H, $P(OMe)_3$), 5.12 (s, 5 H, Cp).

Reaction of [CpRu(P{OMe}$_3$)$_2$(HSBu^t)]PF$_6$ and lithium diisopropylamide (LDA), monitored by ^{1}H NMR

An NMR tube was charged with [CpRu(P{OMe}$_3$)$_2$(HSBu^t)]PF$_6$ (0.023 g, 0.035 mmol) and LDA (0.004 g, 0.04 mmol). After evacuation, chloroform-d_1 was distilled into the tube. The tube was frozen and sealed under vacuum. The ^{1}H NMR spectrum taken immediately upon warming indicated that only CpRu(P{OMe}$_3$)$_2$-SBu^t was produced. ^{1}H NMR (CDCl$_3$): δ 1.24 (s, 9 H, SBu^t), 3.66 (t, J(PH) = 4.7 Hz, 18 H, P(OMe)$_3$), 5.06 (s, 5 H, Cp).

A preparative scale reaction was attempted in order to confirm that the product was CpRu(P{OMe}$_3$)$_2$SBu^t. A solution of [CpRu(P{OMe}$_3$)$_2$(HSBu^t)]PF$_6$ (0.169 g, 0.261 mmol) and LDA (0.031 g, 0.29 mmol) in 15 mL of THF was stirred briefly at ambient temperature. The solvent was removed in vacuo and the resulting orange oil extracted with Et$_2$O. The extracts were combined and slowly evaporated to give 0.027 g of orange crystals. An ^{1}H NMR spectrum indicated the sample was a mixture; the major component, identified by ^{1}H NMR, was CpRu(P{OMe}$_3$)$_2$SBu^t, ^{1}H NMR (CDCl$_3$): δ 1.24 (s, 9 H, SBu^t), 3.66 (t, J(PH) = 5.5 Hz, 18 H, P(OMe)$_3$), 5.08 (s, 5 H, Cp). The sample decomposed upon further attempts to purify it.

Oxidation of [CpRu(PPh$_2$OMe)$_2$(HSBu^t)]PF$_6$ by air

[CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$: A solution of CpRu(PPh$_2$OMe)$_2$Cl (0.293 g, 0.463 mmol) and NH$_4$PF$_6$ (0.107 g, 0.658 mmol) in 20 mL of methanol was treated with HSBu^t (0.3 mL, 2 mmol). The solution was heated at reflux for 0.5 h and then cooled to ambient temperature. The solvent was removed in vacuo and the residue was extracted with several 15 mL portions of CH$_2$Cl$_2$. The extracts were combined and a color change from orange to purple was observed when the solution was exposed to air. The solvent was removed in vacuo and crystallization of the residue from CH$_2$Cl$_2$/Et$_2$O gave 0.195 g (50%) of dark red powder, m.p. 149–157 ° C. Anal. Found: C, 50.30; H, 4.98. $C_{35}H_{40}F_6O_2P_3RuS$ calcd.: C, 50.48; H, 4.84%. IR (KBr): ν(PF$_6$) 845s cm^{-1}.

X-ray diffraction study of [CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$

Deep reddish-purple crystals of [CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$ suitable for X-ray diffraction were grown by vapor diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of [CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$. A crystal measuring 0.1 × 0.1 × 0.2 mm was mounted on a glass fiber with cyanoacrylate glue. Data was collected with a Syntex P3/F diffractometer using graphite-monochromated Mo-K_α radiation, and was corrected for Lorentz and polarization factors. Systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) in the data indicated that the space group was $P2_1/c$. The ruthenium atom was located by the Patterson interpretation section of SHELXTL. The remaining atoms were located by Fourier techniques. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were inserted at calculated positions and the temperature factors were not refined. An empirical absorption correction was applied using XEMP. Final refinement was by least-squares methods (minimizing $\Sigma w(F_o - F_c)^2$) in cascaded large blocks using the appropriate atomic scattering factors [10]. A summary of crystal data and data collection is presented in Table 1. Atom coordinates and equivalent isotropic displacement parameters are contained in Table 2 and selected bond lengths and bond angles are in Table 3. The molecular structure of [CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$ is presented in Fig. 1.

Table 1

Summary of crystal data and data collection for [CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$

λ(Mo-K_α), Å	0.71069
Temperature, K	295
Formula	$C_{35}H_{40}F_6O_2P_3RuS$
Formula weight	832.73
Crystal dimensions, mm	0.1 × 0.1 × 0.2
Space group	$P2_1/c$
a, Å	12.8070(25)
b, Å	14.3160(36)
c, Å	20.1768(50)
α, °	90
β, °	97.841(18)
γ, °	90
d_{calcd}, g/cm^3	1.45
Z	4
Cell volume, Å^3	3664.76
Absorpt. coeff. μ, cm^{-1}	6.62
Scan range, °	4–54.9
Scan type	$\theta-2\theta$
Unique data measured	8409
$F_o > 3\sigma F_o$	6248
Octants	$\pm h, k, l$
No. of parameters in final cycle	448
R	0.0452
R_w	0.0532
Goodness of fit	1.1146

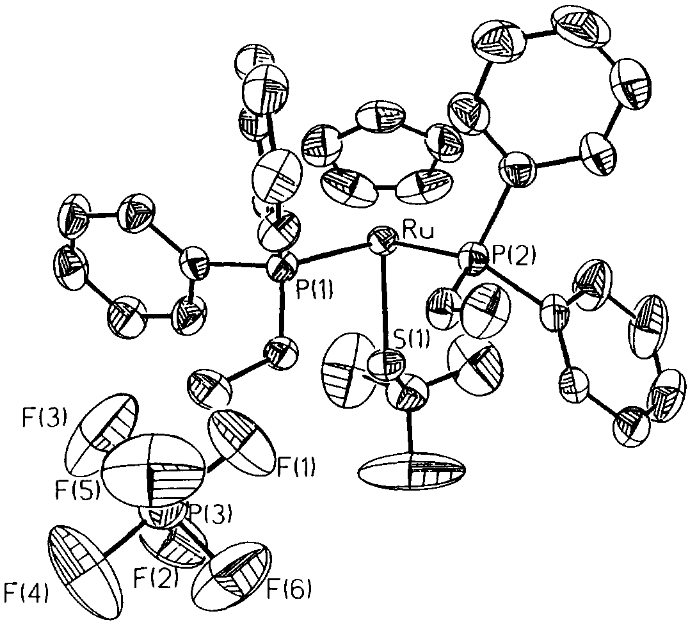

Fig. 1. ORTEP plot of [CpRu(PPh$_2$OMe)$_2$SBu^t]PF$_6$. Thermal ellipsoids of non-hydrogen atoms are plotted at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters for [CpRu(PPh$_2$OMe)$_2$-SBu^t]PF$_6$

	x	y	z	U_{eq}
Ru	2902(1)	3598(1)	1710(1)	310(1)
S(1)	2617(1)	3775(1)	580(1)	403(3)
P(1)	3779(1)	5000(1)	1728(1)	320(3)
P(2)	1307(1)	4304(1)	1753(1)	343(3)
P(3)	3214(1)	9186(1)	730(1)	551(4)
F(1)	2616(3)	8391(3)	1077(2)	1021(16)
F(2)	3446(3)	8424(2)	200(2)	925(15)
F(3)	4251(3)	8873(3)	1177(3)	1474(22)
F(4)	3790(4)	9936(3)	373(3)	1559(26)
F(5)	2969(4)	9923(3)	1256(2)	1411(23)
F(6)	2146(3)	9425(3)	301(2)	1311(20)
O(1)	3398(2)	5673(2)	1108(1)	400(8)
O(2)	1281(2)	5388(2)	1546(1)	425(9)
C(1)	3716(3)	5727(3)	2461(2)	360(11)
C(2)	3156(3)	6569(3)	2391(2)	476(14)
C(3)	2999(4)	7069(3)	2955(3)	603(17)
C(4)	3392(4)	6761(4)	3584(3)	625(18)
C(5)	3950(3)	5934(3)	3660(2)	523(15)
C(6)	4119(3)	5418(3)	3102(2)	434(13)
C(7)	5178(3)	4828(3)	1664(2)	363(12)
C(8)	5987(3)	5074(3)	2157(2)	480(14)
C(9)	7027(3)	4923(3)	2055(3)	583(17)
C(10)	7262(3)	4544(3)	1474(2)	559(16)
C(11)	6459(3)	4306(4)	980(2)	639(18)
C(12)	5423(3)	4432(4)	1078(2)	570(16)
C(13)	4051(4)	6437(3)	935(2)	592(17)
C(14)	820(3)	4297(3)	2560(2)	447(13)
C(15)	−147(4)	3930(4)	2660(3)	724(21)
C(16)	−489(4)	3997(6)	3286(3)	985(29)
C(17)	148(5)	4410(5)	3808(3)	884(26)
C(18)	1112(5)	4763(4)	3724(2)	689(20)
C(19)	1443(4)	4706(3)	3104(2)	535(16)
C(20)	239(3)	3778(3)	1181(2)	401(13)
C(21)	−9(4)	2839(3)	1240(3)	672(19)
C(22)	−782(4)	2431(4)	779(3)	849(25)
C(23)	−1286(4)	2934(4)	267(3)	734(21)
C(24)	−1065(4)	3863(4)	198(2)	642(19)
C(25)	−292(3)	4275(3)	661(2)	478(14)
C(26)	493(4)	6031(3)	1708(3)	625(18)
C(27)	3308(4)	3080(3)	2764(2)	597(17)
C(28)	4191(4)	2987(4)	2455(3)	644(19)
C(29)	3979(5)	2353(4)	1936(3)	761(22)
C(30)	2925(5)	2050(3)	1926(3)	706(21)
C(31)	2525(4)	2507(3)	2441(3)	606(17)
C(32)	2640(4)	2744(3)	26(2)	557(16)
C(33)	1881(7)	2017(5)	178(4)	1157(35)
C(34)	3729(6)	2317(5)	100(5)	1270(39)
C(35)	2339(11)	3116(5)	−645(3)	1902(64)

Table 3

Selected bond lengths (Å) and angles (°) for $[CpRu(PPh_2OMe)_2SBu^t]PF_6$ [a]

Bond lengths (std. dev.)			
Ru-S	2.274(1)	Ru-C(ave)	2.252(5)
Ru-P(1)	2.298(1)	S-C(32)	1.854(5)
Ru-P(2)	2.291(1)		
Bond Angles (std. dev.)			
S-Ru-P(1)	85.9(1)	P(1)-Ru-P(2)	92.9(1)
S-Ru-P(2)	88.1(1)	Ru-S-C(32)	120.1(1)

[a] A complete table of bond lengths and angles is given in the supplementary material.

The cyclopentadienyl-ruthenium thiolate complex, $CpRu(CO)(PPh_3)SBu^t$

A solution of $CpRu(CO)(PPh_3)Cl$ (0.250 g, 0.509 mmol) and $(Bu^n)_3SnSBu^t$ (0.3 mL, 0.8 mmol) in 20 mL of methanol was heated at reflux for 20 h. After cooling the solution, the solvent was removed on a rotary evaporator. Chromatography (alumina/CH_2Cl_2) of the resulting red oil gave a single red band. The solution was evaporated to dryness, and crystallization of the residue from CH_2Cl_2/hexane gave 0.053 g (19%) of $CpRu(CO)(PPh_3)SBu^t$, an orange powder, m.p. 194–195 °C. MS: $m/e = 546.0696$. $C_{28}H_{29}OPRuS$ calcd.: 546.0707. IR (CH_2Cl_2): $\nu(CO)$ 1935 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (s, 9 H, SBu^t), 4.93 (s, 5 H, Cp), 7.37 (m, 9 H, PPh_3), 7.53 (m, 6 H, PPh_3).

Reaction of $CpRu(P\{OMe\}_3)_2Cl$, $(Bu^n)_3SnSBu^t$, *and* NH_4PF_6 *monitored by NMR*

An NMR tube was charged with $CpRu(P\{OMe\}_3)_2Cl$, 0.4 equivalents of $(Bu^n)_3SnSBu^t$, and 1.5 equivalents of NH_4PF_6. Methanol-d_4 was distilled into the tube which was then sealed under vacuum. The tube was placed in a 68 °C oil bath and removed to record spectra at $t = 0$, 3.5, 6.5, 17, 21.5, 28.5, and 41.5 h. A cyclopentadienyl proton peak grew in at δ 5.22 at the concentration of the starting material (δ 4.87) decreased. The ratio of product to starting material was 2 : 10 after heating for 3.5 h. At this point a third cyclopentadienyl proton peak became evident at δ 5.03; this continued to grow for the duration of the experiment with concurrent decreases in the other two peaks. The final product is presumably $[CpRu(P\{OMe\}_3)_2(HSBu^t)]^+$ (δ 5.03), while the intermediate is probably $[CpRu(P\{OMe\}_3)_2\{(Bu^n)_3SnSBu^t\}]^+$ (δ 5.22). Protonation of the thiolate group by NH_4^+ is assumed.

Discussion

Examples of isolated organometallic thiol complexes are rare [1,3–6], and we are pleased to report the synthesis of several new examples. The complexes, $[CpRu(L)(L')(HSBu^t)]PF_6$ (L, L′ = PPh_2OMe, $PPh(OMe)_2$, $P(OMe)_3$; L = PPh_3, L′ = CO, $P(OMe)_3$), were prepared by heating methanol solutions of $CpRu(L)(L')Cl$ in the presence of NH_4PF_6 and an excess of $HSBu^t$, Eq. 2.

$$CpRu(L)(L')Cl + HSBu^t + NH_4PF_6 \rightarrow [CpRu(L)(L')(HSBu^t)]PF_6 + NH_4Cl \quad (2)$$

(L, L′ = PPh_2OMe, $PPh(OMe)_2$, $P(OMe)_3$; L = PPh_3, L′ = CO, $P(OMe)_3$)

The complexes are pale yellow to pale orange air-sensitive crystals, obtained with isolated yields of 24–81%. The apparent air-sensitivity and ease of isolation of the complexes varied with the choice of the phosphine ligand. Among the examples reported here, the complex containing $P(OMe)_3$ was the easiest to handle, while the complex containing PPh_2OMe was the hardest to work with, with respect to oxidative decomposition. Presumably, the reactivity towards oxygen is a function of steric interactions between the ligands on the metal.

The reaction, monitored by NMR, between $CpRu(P\{OMe\}_3)_2Cl$, $(Bu^n)_3SnSBu^t$, and NH_4PF_6 produced two new cyclopentadienyl proton peaks in the ^1H NMR spectrum that were assigned to $[CpRu(P\{OMe\}_3)_2(HSBu^t)]^+$ and $[CpRu(P\{OMe\}_3)_2(\{Bu^n\}_3SnSBu^t)]^+$. A similar reaction, monitored by NMR, between $CpRu(P\{OMe\}_3)_2Cl$ and $(Bu^n)_3SnSPh$ produced new cyclopentadienyl proton peaks that were assigned to $CpRu(P\{OMe\}_3)_2SPh$ and $[CpRu(P\{OMe\}_3)_2(\{Bu^n\}_3SnSPh)]Cl$ [6]. The formation of $[CpRu(P\{OMe\}_3)_2(HSBu^t)]^+$ probably involves protonation of $CpRu(P\{OMe\}_3)_2SBu^t$ by NH_4^+ as it is produced in the reaction mixture. This indicates the relatively high basicity of sulfur in this complex, and as a corollary, the fact that the thiol complex is a weak acid (weaker than NH_4^+). The basicity of the thiolate moiety in these complexes is presumably enhanced by the electron richness of the metal center. A similar argument is used to explain the chemistry of $[CpRu(PPh_3)_2(H_2S)]^+$ and related complexes [5].

The oxidation of organometallic thiol complexes commonly leads to formation of organometallic thiolate complexes. Oxidation of $CpMn(CO)_2(HSBu^t)$ forms $CpMn(CO)_2(SBu^t)$ [11]. Similarly, $[CpRu(PPh_3)_2(H_2S)]OSO_2CF_3$ is oxidized by air to yield $[(CpRu\{PPh_3\}_2)_2(\mu\text{-}S_2)](OSO_2CF_3)_2$ [5]. Solutions of the thiol complex, $[CpRu(PPh_2OMe)_2(HSBu^t)]PF_6$, were oxidized by air to give deep purple solutions of $[CpRu(PPh_2OMe)_2SBu^t]PF_6$, which was isolated as reddish-purple crystals, Eq. 3.

$$\left[CpRu(PPh_2OMe)_2(HSBu^t)\right]PF_6 + \tfrac{1}{2}O_2 \rightarrow \left[CpRu(PPh_2OMe)_2(SBu^t)\right]PF_6 + H_2O \qquad (3)$$

The other thiol complexes prepared in this work were also oxidized by air as was indicated by a color change of the solution from pale orange to blue or green, but the products of these oxidations are intractable oils and were not fully characterized. Previously, the complexes $CpRu(L)_2SPh$ (L_2 = dppe; L = PMe_3, $P(OMe)_3$), had been shown to chemically oxidize to form blue or green complexes $[CpRu(L)_2SPh]^+$ [6].

The structure of $[CpRu(PPh_2OMe)_2SBu^t]PF_6$ was established by a single crystal X-ray diffraction study. The ruthenium atom can be viewed as having a distorted octahedral geometry with the cyclopentadienyl ring occupying three vertices and the remaining three vertices are occupied by the PPh_2OMe and SBu^t moieties. The bond angles are slightly distorted from the idealized 90°. The P(1)–Ru–P(2) angle is 92.9(1)° while the P(1)–Ru–S and P(2)–Ru–S angles are 85.9(1) and 88.1(1)° respectively. These angles are not greatly different from values measured for other related systems [12,13].

The Ru–P(1) and Ru–P(2) bond lengths were 2.298(1) and 2.291(1) Å respectively, shorter than the Ru–P bond length of 2.36 Å found in $[CpRu(PPh_3)_2(SC_2H_4)]OSO_2CF_3$ [12], and also shorter than the Ru–P bond lengths of 2.358 and 2.353 Å found in $[C_5H_4Ru(PPh_3)_2(CH_2SC_4H_3)]BF_4$ [13]. The shorter Ru–P bond length in $[CpRu(PPh_2OMe)_2SBu^t]PF_6$ can be accounted for in part based on the nature of the phosphorus ligand. Metal–phosphorus bond lengths in phosphine substituted compounds are typically 0.06 Å shorter than metal–phosphorus bond lengths in phosphite substituted compounds [14].

The Ru–S bond of 2.274(1) Å in $[CpRu(PPh_2OMe)_2SBu^t]PF_6$ is significantly shorter than the 2.408 Å observed for $C_5H_4Ru(PPh_3)_2(CH_2SC_4H_3)]BF_4$ [13] or the 2.41 Å found in $[CpRu(PPh_3)_2(HSC_3H_7)]BF_4$ [5]. The S–C bond of 1.854(5) Å is significantly longer than the more typical 1.81 Å [15]. The shortening of the Ru–S bond length suggests that there may be significant back bonding interaction between ruthenium and sulfur. The Ru–S bond length is in a range that is reasonable for a bond order of 1.5 [16].

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Supplementary material available. Complete lists of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, hydrogen-atom coordinates (calcd.), observed and calculated structure factors may be obtained from the author upon request.

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