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An unsaturated half-sandwich ruthenium(II) complex containing a dithioimidodiphosphinate ligand

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Abstract

Treatment of $[Cp^*RuCl_2]_x$ ($Cp^* = \eta^5$-C_5Me_5) with $K[N(Ph_2PS)_2]$ afforded $[Cp^*Ru\{N(Ph_2PS)_2\}Cl]$ (**1**). Reduction of **1** with $Li[BEt_3H]$ gave the 16-electron half-sandwich Ru(II) complex $[Cp^*Ru\{N(Ph_2PS)_2\}]$ (**2**). Complexes **1** and **2** have been characterized by X-ray crystallography. The Ru–Cp*(centroid) and average Ru–S distances in **1** are 1.827 and 2.3833(5) Å, respectively. The corresponding bond distances in **2** are 1.739 and 2.379(1) Å. Treatment of **2** with 2-electron ligands L afforded the adducts $[Cp^*Ru\{N(Ph_2PS)_2\}L]$ (L = CO (**3**), 2,6-$Me_2C_6H_4NC$ (**4**), $MeCO_2C{\equiv}CCO_2Me$ (**5**)). Oxidation of **2** with tetramethylthiuram disulfide gave the Ru(IV) complex $[Cp^*Ru\{S_2CNMe_2\}_2][N(Ph_2PS)_2]$ (**6**). The Ru–Cp*(centroid) and average Ru–S distances in **6** are 1.897 and 2.387(1) Å, respectively.

Keywords: Ruthenium; Half-sandwich compound; 16-electron; Sulfur ligand

1. Introduction

Coordinately unsaturated organometallic compounds play important roles as reactive intermediates in homogeneous catalysis. Of interest are 16-electron, half-sandwich Ru(II) complexes that were found to be reactive toward unsaturated organic substrates and small molecules [1]. Coordinately unsaturated Ru(II) cyclopentadienyl (Cp) complexes are usually associated with bulky electron-releasing co-ligands, notably phosphines. 16-electron Ru(II) Cp complexes of the types [CpRu(L)(X)] (L = phosphine, X = mono-anionic ligand) and $[CpRu(L\hat{}L)]^+$ (L = neutral bidentate ligand such as diphosphine and diamine) are well documented. The unsaturation of the CpRu(II) core can also be stabilized by π-donation of colligands [1–3]. Recently, $[Cp^*Ru\{PhC(NBu^t)_2\}]$ ($Cp^* = \eta^5$-C_5Me_5) that shows a nearly planar geometry with the Cp* centroid and the RuN_2 moiety has been isolated [4]. While unsaturated CpRu(II) complexes stabilized by nitrogen [2,4,5] and oxygen [2,6,7] donor ligands are well known, there are few examples of such complexes supported by sulfur ligands.

Dithioimidophosphinates $[N(R_2PS)_2]^-$ (R = alkyl or aryl) (Scheme 1) are versatile ligands that can form stable complexes with a range of transition and main group metal ions [8–12].

Nevertheless, organometallic complexes of Ru containing dithioimidophosphinates have not been well explored [13–18]. Recently, we have demonstrated that the electron-rich $[Ru\{N(R_2PS)_2\}_2]$ core can stabilize a variety of reactive unsaturated species including SO [16], diazene [17], and carbene [18]. As our continuing effort to investigate the catalytic chemistry of electron-rich Ru/S complexes, we set out to prepare unsaturated, half-sandwich Ru dithioimidophosphinate complexes. Although half-sandwich (η^6-arene)Ru(II) [14,15], Cp*Rh(III) [14,15,19], and Cp*Ir(III) [15,19]

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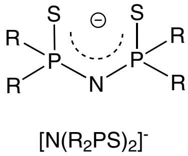


Scheme 1.

complexes with $[N(R_2PS)_2]^-$ have been synthesized, the isoelectronic Cp*Ru(II) analogue is unknown. Herein, we describe the synthesis, crystal structure, and reactivity of the first 16-electron, half-sandwich Ru(II) complex supported by $[N(R_2PS)_2]^-$.

2. Experimental

2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Infrared spectra (KBr) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively, and the scan rate was $100\ mV\ s^{-1}$. Formal potentials were measured in CH_2Cl_2 solutions with 0.1 M $[NBu^n_4][PF_6]$ as supporting electrolyte and reported with reference to the ferrocenium–ferrocene couple ($Cp_2Fe^{+/0}$). Elemental analyses were performed by Medac Ltd., Surrey, UK. The ligand $K[N(Ph_2PS)_2]$ [20] and $[Cp^*RuCl_2]_x$ [21] were prepared according to the literature methods.

2.2. Synthesis of $[Cp^*Ru\{N(Ph_2PS)_2\}Cl]$ (**1**)

A mixture of $[Cp^*RuCl_2]_x$ (60 mg, 0.10 mmol) and $K[N(Ph_2PS)_2]$ (0.20 mmol) in THF (15 ml) was stirred at room temperature for 1 h, during which the brown suspension changed to red solution. The solvent was pumped off, and the residue was washed with Et_2O. Recrystallization from CH_2Cl_2/hexane at room temperature afforded red blocks. Yield: 56 mg, 78%. *Anal.* Calc. for $C_{34}H_{35}ClNP_2RuS_2$: C, 56.7; H, 4.9; N, 2.0. Found: C, 56.3; H, 4.9; N, 1.8%.

2.3. Synthesis of $[Cp^*Ru\{N(Ph_2PS)_2\}]$ (**2**)

To a solution of **1** (72 mg, 0.10 mmol) in THF (20 ml) was added $Li[BEt_3H]$ (0.1 ml, 1 M in THF) at −78 °C. Upon warming room temperature, the color change from red to purple was observed. The purple solution was stirred for 2 h at room temperature. The solvent was pumped off and the oil was extracted with hexane. Concentration and cooling at −10 °C gave purple crystals. Yield: 38 mg, 55%. *Anal.* Calc. for $C_{34}H_{35}NP_2RuS_2 \cdot H_2O$: C, 58.1; H, 5.3; N, 2.0. Found: C, 58.3; H, 5.0; N,2.0%. ^1H NMR (300 MHz, C_6D_6): $\delta = 8.14$ (m, 8H, Ph), 7.08 (m, 12H, Ph), 1.27 (s, 15H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta = 29.33$ (s) ppm.

2.4. Synthesis of $[Cp^*Ru\{N(Ph_2PS)_2\}(CO)]$ (**3**)

CO gas was bubbled slowly through a solution of **2** (70 mg) in hexane (20 ml) for 1 min, during which time the color changed from purple to yellow. A yellow precipitate was formed after the solution was stirred for ca. 1 h. The yellow solid was collected and recrystallized from CH_2Cl_2/hexane to give yellowish orange crystals. Yield: 27 mg, 38%. *Anal.* Calc. for $C_{35}H_{35}NOP_2RuS_2$: C, 59.0; H, 5.0; N, 2.0. Found: C, 58.9; H, 5.0; N, 2.0%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.95$ (m, 8H, Ph), 7.36 (m, 12H, Ph), 1.51 (s, 15H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 37.18$ (s) ppm. IR (KBr, cm^{-1}): 1929 [$\nu(C\equiv O)$].

2.5. Synthesis of $[Cp^*Ru\{N(Ph_2PS)_2\}(L)]$ (L = xylNC) where xyl = 2,6-dimethylphenyl (**4**), $MeO_2CC\equiv CCO_2Me$ (**5**)

To a solution of **2** (70 mg) in hexane (20 ml) was added 1 equivalent of L at 0 °C. The resulting mixture was stirred at room temperature for 15 min, during which time the color changed from purple to yellow. The solution was evaporated to dryness and the residue recrystallized from THF/Et_2O at −10 °C to give orange solids.

4: Yield: 29 mg, 35%. *Anal.* Calc. for $C_{43}H_{46}N_2P_2RuS_2$: C, 63.1; H, 5.7; N, 3.4. Found: C, 63.5; H, 5.7; N, 3.3%. ^1H NMR (300 MHz, C_6D_6): $\delta = 8.25$–8.20 (m, 8H, Ph), 7.05–6.83 (m, 12H, Ph), 6.75–6.74 (m, 3H, xyl), 2.24 (s, 6H, Me), 1.57 (s, 15H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta = 32.03$ (s) ppm. IR (KBr, cm^{-1}): 2045 [$\nu(C\equiv N)$].

5: Yield: 35 mg, 42%. *Anal.* Calc. for $C_{40}H_{41}NO_4P_2RuS_2$: C, 58.0; H, 5.0; N, 1.7. Found: C, 57.2; H, 5.2; N, 1.9%. ^1H NMR (300 MHz, $CDCl_3$): 7.85–7.58 (m, 8H, Ph), 3.69 (s, 6H, Me), 1.35 (s, 15H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 34.67$ (s) ppm. IR (KBr, cm^{-1}): 1887 [$\nu(C\equiv C)$], 1706, 1698, 1688 [$\nu(C=O)$].

2.6. Synthesis of $[Cp^*Ru(S_2CNMe_2)_2][N(Ph_2PS)_2]$ (**6**)

To solution of **2** (68 mg, 0.1 mmol) in THF (10 ml) was added 1 equivalent of tetramethylthiuram disulfide and the mixture was stirred at room temperature overnight. The solvent was pumped off and the oil was washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O afforded reddish brown crystals. Yield: 26%. *Anal.* Calc. for $C_{36}H_{52}N_3P_2RuS_6 \cdot 2H_2O$: C, 50.0; H, 5.3; N, 4.4. Found: C, 49.5; H, 5.2; N, 4.1%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.16–8.09$ (m, 8H, Ph), 7.21–7.16 (m, 12H, Ph), 3.20 (s, 12H, Me), 1.49 (s, 15H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 35.82$ (s) ppm.

2.7. X-ray crystallography

A summary of crystallographic data and experimental details for [Cp*Ru{N($Ph_2PS)_2$}Cl] (**1**), [Cp*Ru{N($Ph_2PS)_2$}] (**2**), and [Cp*Ru($S_2CNMe_2)_2$][N($Ph_2PS)_2$] · 1/2H_2O (**6** · 1/2H_2O) are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 100(2) K. The collected frames were processed with the software SAINT [22]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL [23] software package. Non-hydrogen atoms were refined anisotropically. The Cp* ligand in **6** was found to be disordered, and the carbon atoms C(1)–C(10) are split into two sites of 0.7 and 0.3 occupancies. In addition, one of the phenyl groups in the [N($Ph_2PS)_2]^-$ anion is disordered. The disordered carbon atoms C(83)–C(85) are split into two sites of 0.6 and 0.4 occupancies. Selected bond lengths and angles for complexes **1**, **2** and **6** are listed in Tables 2 and 3.

3. Results and discussion

3.1. Half-sandwich Ru(III) and Ru(II) complexes with $[N(PR_2S)_2]^-$

The synthesis and reactivity of Cp*Ru complexes with [N($Ph_2PS)_2]^-$ are summarized in Scheme 2.

Treatment of $[Cp^*RuCl_2]_x$ with K[N($R_2PS)_2$] afforded the mononuclear Ru(III) complex [Cp*Ru{N(R_2PS)}Cl] (**1**). Complex **1** is air stable in both the solid state and solution. Reduction of **1** with Li[BEt_3H] in THF afforded the 16-electron Ru(II) complex [Cp*Ru{N($Ph_2PS)_2$}] (**2**). Alternatively, complex **2** could be prepared by reaction of $[Cp^*RuCl]_4$ [24] with K[N($Ph_2PS)_2$]. Complex **2** is highly air sensitive in both the solid state and solution. In the ^1H NMR spectrum of **2**, the Cp* protons appears as a singlet at δ 1.27 ppm. The ^{31}P {^1H} NMR spectrum displays a singlet at δ 29.33 ppm that is more downfield than that for K[N($Ph_2PS)_2$] (δ 37.2 ppm).

Complexes **1** and **2** have been characterized by X-ray crystallography; selected bond lengths and angles are collected in Table 2. Fig. 1 shows a perspective view of **1**. The structure of **1** is similar to that of [Cp*Ir{N($Ph_2PS)_2$}Cl] [19] showing a boat-like conformation

Table 1
Crystallographic data for [Cp*Ru{N($Ph_2PS)_2$}Cl] (**1**), [Cp*Ru{N($Ph_2PS)_2$}] (**2**), and [Cp*Ru($S_2CNMe_2)_2$][N($Ph_2PS)_2$] · 1/2H_2O (**6** · 1/2H_2O)

Compound	**1**	**2**	**6** · 1/2H_2O
Empirical formula	$C_{34}H_{35}ClNP_2RuS_2$	$C_{34}H_{35}NP_2RuS_2$	$C_{40}H_{48}N_3O_{0.50}P_2RuS_6$
Formula weight	720.21	684.76	934.18
Crystal system	monoclinic	monoclinic	triclinic
Unit cell dimensions			
a (Å)	17.261(1)	8.835(1)	14.675(1)
b (Å)	10.485(1)	13.032(1)	17.575(1)
c (Å)	17.626(1)	28.308(2)	18.103(1)
α (°)			71.411(1)
β (°)	99.199(1)	91.049(1)	89.411(1)
γ (°)			77.119(1)
V (Å^3)	3149.0(3)	3258.8(4)	4304.7(4)
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	4	4	4
D_{calc} (g cm^{-3})	1.519	1.396	1.441
Temperature (K)	100(2)	100(2)	100(2)
$F_{(000)}$	1476	1408	1932
μ(Mo Kα) (mm^{-1})	0.843	0.731	0.764
Total reflection	17057	16590	22410
Independent reflection	6106	5712	14831
R_{int}	0.0202	0.0215	0.0266
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0263, 0.0638	0.0418, 0.1140	0.0525, 0.1228
R_1, wR_2 (all data)	0.0289, 0.0651	0.0487, 0.1178	0.0721, 0.1310
Goodness-of-fit[c]	1.054	1.053	1.008

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

[c] $\mathrm{GoF} = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 2
Selected bond lengths and angles for [Cp*Ru{N(Ph$_2$PS)$_2$}Cl] (**1**) and [Cp*Ru{N(Ph$_2$PS)$_2$}] (**2**)

	1	**2**
Bond length (Å)		
Ru(1)–Cp*[a]	1.827	1.739
Ru–S(1)	2.3888(5)	2.370(1)
Ru–S(2)	2.3778(5)	2.388(1)
Ru–Cl(1)	2.3990(5)	
P(1)–S(1)	2.0261(7)	2.020(1)
P(2)–S(2)	2.0270(7)	2.007(1)
P(1)–N(1)	1.582(2)	1.588(3)
P(2)–N(1)	1.580(2)	1.593(3)
Bond angle (°)		
S(1)–Ru(1)–S(2)	97.28(2)	103.46(3)
S(1)–Ru(1)–Cl(1)	93.18(2)	
S(2)–Ru(1)–Cl(1)	92.87(2)	
P(1)–N(1)–P(2)	136.7(1)	126.0(2)
α[b]		177.4

[a] Ru–Cp* (centroid) distance.

[b] Pyramidalization angle is the angle between the centroid of the Cp* ring, Ru, and the centroid of the S–Ru–S moiety [1].

for the (Ru–S–P–N–P′–S′) ring (Fig. 2). The Ru–Cp*(centroid) distance is 1.827 Å. The Ru–Cl distance of 2.3990(5) Å is comparable to those in Cp*Ru(III) complexes (e.g., 2.366 Å for [Cp*RuCl$_2$]$_2$ [25]). The average Ru–S distance of 2.3833(5) Å is slightly shorter than that in [Ru{N(Ph$_2$PS)$_2$}$_3$] (2.414 Å) [16]. Similar to other dithioimidophosphinate complexes, the average P–S distance (2.0266(7) Å) in **1** is longer than that for HN(Ph$_2$PS)$_2$ (average 1.944 Å) whereas the average P–N distance (1.581(2) Å) is shorter than that of the latter (1.678 Å).

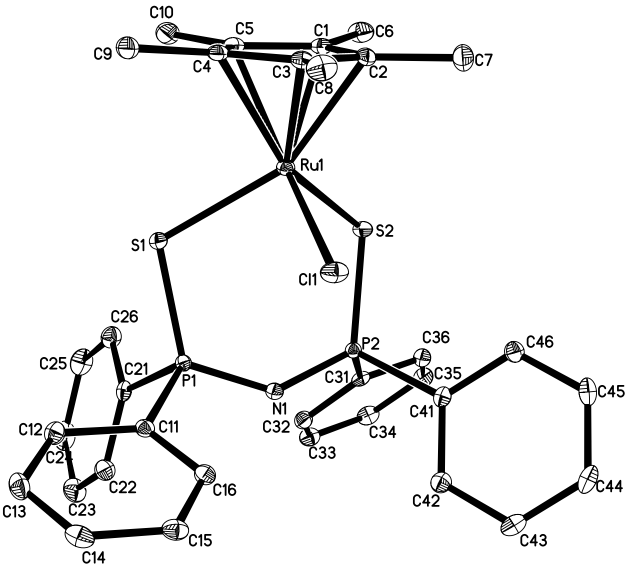


Fig. 1. Molecular structure of [Cp*Ru{N(Ph$_2$PS)$_2$}Cl] (**1**).

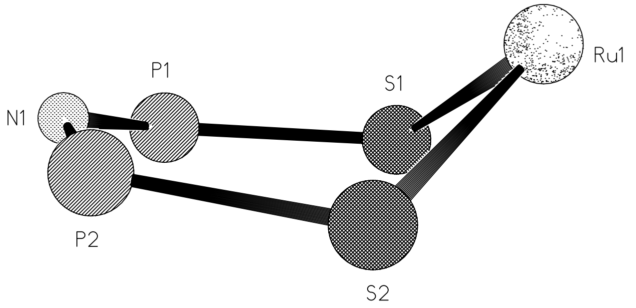
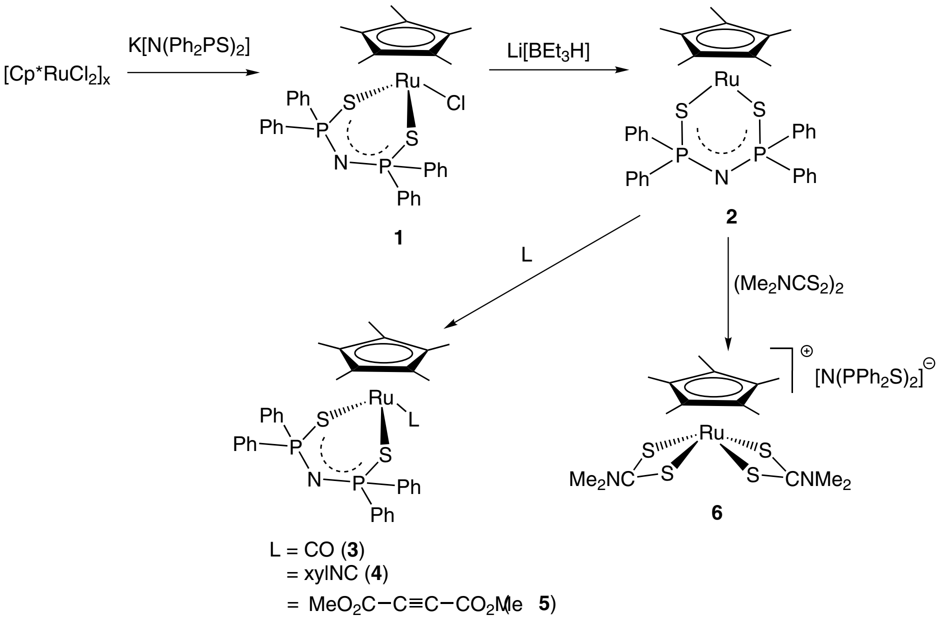


Fig. 2. A view of the Ru–S–P–N–P′–S′ ring in **1** showing the boat-like conformation.



Scheme 2.

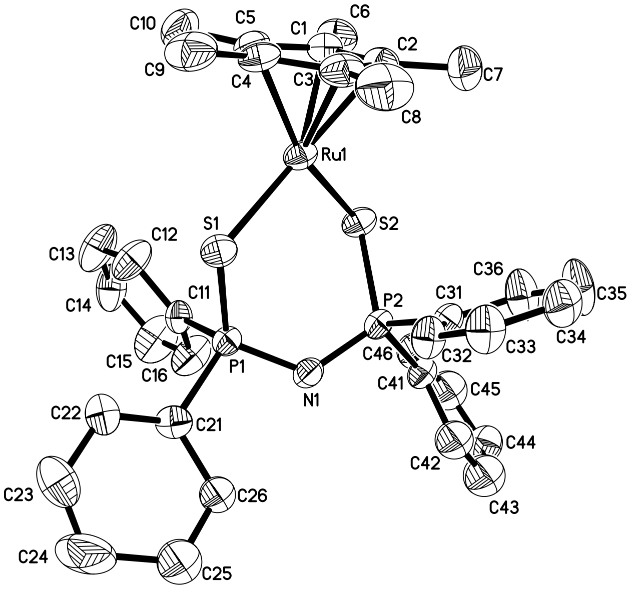


Fig. 3. Molecular structure of [Cp*Ru{N($Ph_2PS)_2$}] (**2**).

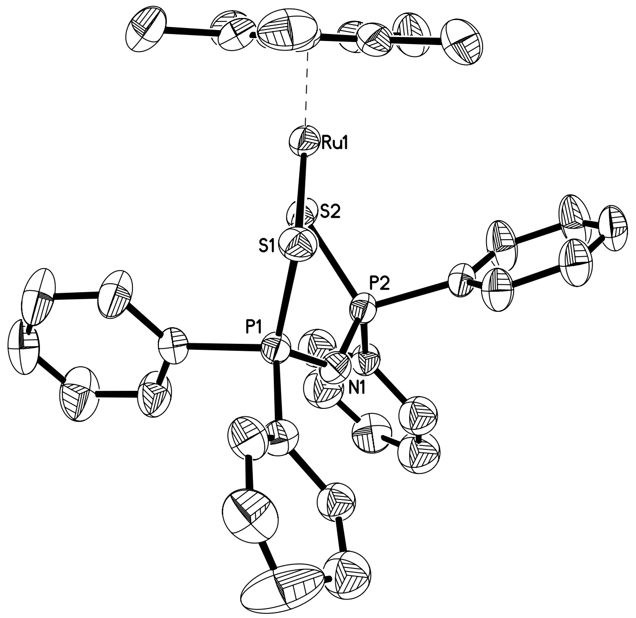


Fig. 4. Side view of **2**.

The molecular structure of **2** is shown in Fig. 3. Although 16-electron half-sandwich $[CpRu(LL)]^n$ (L = N- or P-donor ligand, n = + or 0) as well as [(η^6-arene)Ru$(SR)_2$] [26] have been isolated, to our knowledge, **2** is the first unsaturated Cp*Ru(II) complex supported a bidentate sulfur ligand. Complex **2** exhibits a 2-legged piano-stool structure with an approximate perpendicular arrangement between the Cp* ring and the plane defined by the Ru and two sulfur atoms (Fig. 4). The pyramidization angle (α), which is defined as the angle of Cp*(centroid)–Ru–RuS_2 centroid [1], for **2** is 177.4°, indicative of the σ and π donation by the sulfur ligand that mitigates the coordinative unsaturation of the complex [1,3]. A similar structure has been found for the isoelectronic Ir(III) analogue $[Cp^*Ir\{N(Ph_2S)_2\}]^+$ [19]. The Ru–Cp*(centroid) distance of 1.739 Å in **2** is apparently shorter than that in **1**. The average Ru–S distance of 2.379(1) Å is similar to that **1** but is slightly shorter than that in [Ru{N($Ph_2PS)_2\}_2(PPh_3)$] (average 2.400 Å) [16]. The S–Ru–S angle in **2** (103.46(3)°) is larger than **1** (97.28(2)°) whereas the P–N–P angle in the former (126.0(2)°) is smaller than that in the latter (136.7(1)°).

3.2. Adduct formation of 2

Complex **2** reacted readily with 2-electron ligands to give 18-electron adducts, as evidenced by the ^{31}P {^1H} NMR spectroscopy. The N-donor adducts [Cp*Ru{N($Ph_2PS)_2$}(L)] (L = N-donor ligand, e.g., MeCN) were found to be air sensitive. More stable adducts were obtained with strong π acid ligands such as CO and isocyanides. Thus, treatment of **2** with CO afforded air-stable [Cp*Ru{N($Ph_2PS)_2$}(CO)] (**3**). The IR spectrum of **3** shows the CO band at 1929 cm^{-1}, which is higher than that in [Cp*Ru{PhC($NBu^t)_2$}] (1888 cm^{-1}) [4], indicating that $[N(Ph_2PS)_2]^-$ is a weaker donor than the amidinate. The ^{31}P {^1H} NMR spectrum of **3** displays a singlet at δ 37.18 ppm that is more downfield that that for **2**. Similarly, treatment of **2** with 2,6-dimethylphenyl isocyanide (xylNC) afforded air-stable [Cp*Ru{N(Ph_2-PS$)_2$}(xylNC)] (**4**) that exhibits IR ν(CN) at 2045 cm^{-1}. Similar to **3**, the ^{31}P NMR resonance for **4** (δ = 32.03 ppm) is more downfield than that of **2**. Treatment of **2** with dimethyl maleate afforded the alkyne complex [Cp*Ru{N($Ph_2PS)_2$}(Me$CO_2C\equiv C$-CO_2Me)] (**5**) that exhibits a resonance at δ 38 ppm in the ^{31}P NMR spectrum. The IR spectrum of **5** shows $\nu(C\equiv C)$ at 1887 cm^{-1}, indicative of Ru-to-alkyne backbonding.

3.3. Electrochemistry

Formal potentials of the Ru complexes have been determined by cyclic voltammetry. The cyclic voltammogram of **1** at a glassy carbon electrode in CH_2Cl_2 exhibits reversible couples at 0.08 and −0.48 V vs. $Cp_2Fe^{+/0}$, which are tentatively assigned as the Ru(IV/III) and Ru(III/II) couples, respectively. However, we do not rule out the ligand contributions in these couples given the non-innocent nature of sulfur ligands. Despite the low observed oxidation potential of **1**, attempts to synthesize the Ru(IV) species by oxidation of **1** with Ag(CF_3SO_3) or I_2 were unsuccessful. The Ru(III/II) couples for **3** and **4** were observed at considerably higher potentials (0.79 and 0.53 V, respectively) due to the π-acceptor property of carbonyl and isocyanide. The oxidation of the alkyne complex **5** at ca. 0.24 V is irreversible. The observed Ru(III/II) redox potentials for

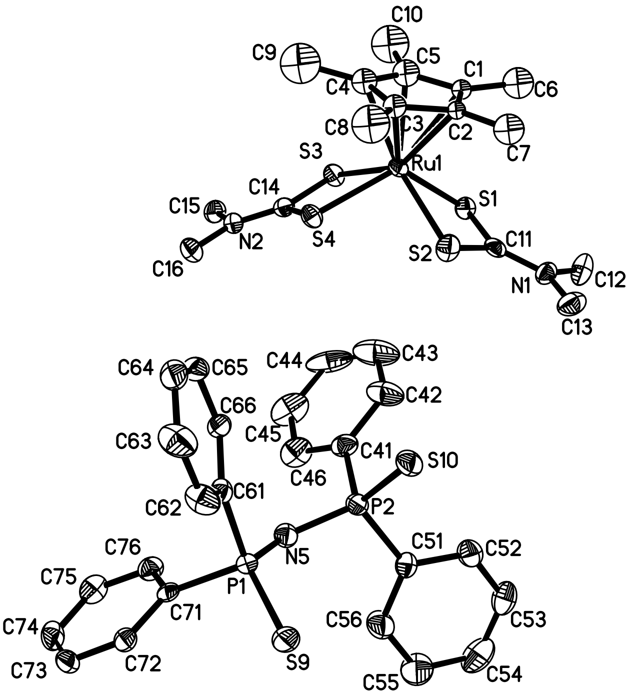


Fig. 5. Molecular structure of $[Cp^*Ru(S_2CNMe_2)_2][N(Ph_2PS)_2]$ (**6**).

Table 3
Selected bond lengths and angles for $[Cp^*Ru(S_2CNMe_2)][N(PSPh_2)_2]$ (**6**).

Bond length (Å)	
Ru–Cp*[a]	1.897
Ru(1)–S(1)	2.391(1)
Ru(1)–S(2)	2.388(1)
Ru(1)–S(3)	2.387(1)
Ru(1)–S(4)	2.378(1)
Ru(2)–S(5)	2.393(1)
Ru(2)–S(6)	2.383(1)
Ru(2)–S(7)	2.378(1)
Ru(2)–S(8)	2.396(1)
Bond angle (°)	
S(1)–Ru(1)–S(2)	71.07(4)
S(1)–Ru(1)–S(4)	124.45(4)
S(1)–Ru(1)–S(3)	84.71(4)
S(3)–Ru(1)–S(4)	71.54(4)
S(2)–Ru(1)–S(3)	126.24(5)
S(2)–Ru(1)–S(4)	83.71(4)
S(7)–Ru(2)–S(5)	128.52(5)
S(6)–Ru(2)–S(5)	70.76(4)
S(7)–Ru(2)–S(8)	71.14(5)
S(6)–Ru(2)–S(8)	121.67(5)
S(5)–Ru(2)–S(8)	86.17(5)
S(7)–Ru(2)–S(6)	82.77(5)

[a] Average Ru–Cp*(centroid) distance.

$[Cp^*Ru\{N(Ph_2PS)_2\}L]$ is consistent with the order of π acidity CO > xylNC > $MeCO_2C{\equiv}CCO_2Me$. For **3**, a reversible reduction couple at −0.04 V was also observed. This reduction couple is possibly ligand-centered because the reduction of Ru(II) is expected to occur at a more negative potential.

3.4. Oxidation of 2

Complex **2** is readily air oxidized in solutions to give an uncharacterized dark red species. Oxidation of **2** with $Ag(CF_3SO_3)$ afforded a brown solid that has not been characterized. No oxidative addition was found when **2** was reacted with H_2, MeI, or silanes. Complex **2** was also oxidized by disulfides. Treatment of with 4-tolyl disulfide afforded a paramagnetic red species, possibly a Ru(III) species, which has not yet been obtained in pure form. Interestingly, treatment of **2** with tetramethylthiuram disulfide gave a diamagnetic compound characterized as $[Cp^*Ru(S_2CNMe_2)_2][N(Ph_2PS)_2]$ (**6**). The $^{31}P\ \{^1H\}$ NMR spectrum of **6** displays a singlet at δ 35.82 ppm due to the $[N(Ph_2PS)_2]^-$ anion. It seems likely that the formation of **6** involves the oxidation of **2** by tetramethylthiuram disulfide and subsequent substitution of $[Me_2NCS_2]^-$ for the $[N(Ph_2PS)_2]^-$ ligand.

The solid-state structure of **6** has been established by X-ray crystallography. Crystals of $\mathbf{6} \cdot 1/2H_2O$ contains two independent molecules in the asymmetric unit. The structure of one of the two crystallographically independent molecules is shown in Fig. 5; selected bond lengths and angles are listed in Table 3. Complex **6** exhibits a 4-legged piano-stool structure typical for Ru(IV) mono cyclopentadienyl complexes. It should be noted that non-hydrido Ru(IV) cyclopentadienyl complexes are rather rare. Previously, the Cp*Ru(IV) selenoate complex $[Cp^*Ru(\eta^2\text{-}Se_2PPr^i_2)(\eta^2\text{-}SePPr^i_2)][PF_6]$ has been synthesized from $[Cp^*Ru(MeCN)_3][PF_6]$ and $K[N(Pr^i_2PSe)_2]$ [27]. The Ru–Cp*(centroid) distance of 1.897 Å is similar to that in $[Cp^*Ru(\eta^2\text{-}Se_2PPr^i_2)\ (\eta^2\text{-}SePPr^i_2)]^+$ (1.916 Å) [27]. It should be noted that the Ru–Cp*(centroid) distances in the Cp*Ru complexes described in this work were found to decrease in the order Ru(IV) (**6**) > Ru(III) (**1**) > Ru(II) (**2**), as the formal coordination number of the complexes decreases from 7 to 5. The average Ru–S distance (2.387(1) Å) for **6** is shorter than that in $[Ru(S_2CNMe_2)_3Cl]$ (Ru–S_{eq} 2.416 Å) [28].

4. Conclusions

In summary, we have synthesized and structurally characterized the first 16-electron Cp*Ru(II) dithioimidophosphinate complex, which exhibits an approximately perpendicular arrangement between the Cp* ring and the Ru–S–S′ plane. $[Cp^*Ru\{N(Ph_2PS)_2\}]$ reacted with 2-electron ligands including CO, $2,6\text{-}Me_2C_6H_4NC$, and dimethyl maleate to give the corresponding 18-electron adducts. Oxidation of $[Cp^*Ru\{N(Ph_2PS)_2\}]$ with tetramethylthiuram disulfide afforded a novel Cp*Ru(IV) dithiocarbamate complex $[Cp^*Ru(S_2CNMe_2)_2][N(Ph_2PS)_2]$. The study of the reactivity of Cp*Ru dithioimidodiphosphinate complexes toward unsaturated organic substrates is underway.

5. Supplementary material

Crystallographic data for [$Cp^*Ru\{N(Ph_2PS)_2\}Cl$] (**1**), [$Cp^*Ru\{N(Ph_2PS)_2\}$] (**2**), and [$Cp^*Ru(S_2CNMe_2)_2$]-[$N(Ph_2PS)_2$] · 1/2H_2O (**6** · 1/2H_2O) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 263955–263957, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk.

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