Pentamethylcyclopentadienyl Ruthenium Complexes with Sulfur- and Selenium-Donor Ligands

Qian-Feng Zhang,† Florence K. M. Cheung,† Wai-Yeung Wong,‡ Ian D. Williams,† and Wa-Hung Leung*,†

Departments of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China, and Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, People's Republic of China

Received January 23, 2001

Treatment of [Cp*Ru(NO)Cl_2] (Cp* = η^5-C_5Me_5) with NaQAr or LiQAr (Q = S, Se, Te; Ar = C_6F_4H or Ph) affords [Cp*Ru(NO)$(QAr)_2$]. Interactions of [Cp*Ru(NO)$(SC_6F_4H)_2$] with PR_3 (R = Ph or Me) give [Cp*Ru$(PR_3)_2(SC_6F_4H)$] via phosphoraminate intermediates. The crystal structures of [Cp*Ru(NO)$(SC_6F_4H)_2$] and [Cp*Ru$(PMe_3)_2(SC_6F_4H)$] have been determined. Treatment of [Cp*Ru$(MeCN)_3$][PF_6] with HN[SeP(*i*-Pr)$_2$]$_2$ affords a novel Cp*Ru(IV) complex, [Cp*Ru{η^2-Se_2P(*i*-Pr)$_2$}{η^2-SeP(*i*-Pr)$_2$}][PF_6], which has been characterized by X-ray crystallography.

Introduction

Metal complexes in chalcogen-rich coordination spheres are of interest due to the important roles of metal chalcogenides in heterogeneous catalysts and biological systems.[1,2] Over the past decade, a large number of ruthenium thiolate complexes, mostly supported by π-accepting ancillary ligands including phosphines, carbonyl, nitrosyl, and cyclopentadienyl ligands, have been synthesized as models for metal sulfide catalysts.[3,4] In particular, Cp*Ru (Cp* = η^5-C_5Me_5) thiolate and sulfide complexes were found to be engaged in many interesting organometallic reactions due to the ability of the Cp*Ru fragment to bind to and activate unsaturated substrates.[5−7] Recently, Hidai and co-workers demonstrated that Cp*Ru thiolate complexes exhibit intriguing reactivities toward alkynes, CO, isocyanides, H_2, and alkyl halides.[8] As part of our continuing effort to explore the potential of Ru chalogenide complexes in homogeneous catalysis,[9] we become interested in high-valent Cp*Ru complexes with chalcogenolate ligands. Two approaches to high-valent Cp*Ru complexes have been attempted: (a) deoxygenation of Ru nitrsoyl complexes with tertiary phosphines[10] and (b) oxidative addition of Cp*Ru(II) species with phosphine chalcogenides. In this paper, we describe the reaction of [Cp*Ru(NO)$(SR)_2$] with tertiary phosphines and the isolation of a novel Cp*Ru(IV) selenolate complex from the reaction of [Cp*Ru$(MeCN)_3$]$^+$ with HN[SeP(*i*-Pr)$_2$]$_2$.

Results and Discussion

Preparation of [Cp*Ru(NO)$(QR)_2$]. [Cp*Ru(NO)$(SR)_2$] have been prepared previously by the reaction of [Cp*Ru(NO)$(OTf)_2$] (OTf = triflate) and RSSR.[7c] We found that [Cp*Ru(NO)$(SR)_2$] could be synthesized directly by the reaction of [Cp*Ru(NO)Cl_2][7b] with NaSR in good yield. Thus, treatment of [Cp*Ru(NO)Cl_2] with $NaSC_6F_4H$ or $Na_2(C_7H_6S_2)$ ($C_7H_6S_2H_2$ = 3,4-dimercaptotoluene) afforded [Cp*Ru(NO)$(SC_6F_4H)_2$] (**1**) or [Cp*Ru(NO)$(C_7H_6S_2)_2$] (**2**), respectively. The analogous chalcogenolate complexes [Cp*Ru(NO)$(QPh)_2$] (Q = Se (**3**) and Te (**4**)) were prepared similarly from [Cp*Ru(NO)Cl_2] and LiQPh and characterized by NMR spectroscopy and microanalysis. The structure of **1** has been established by an X-ray diffraction study (Figure 1). The Ru−N length [1.7558(18) Å], average Ru−S (2.3885 Å), and Ru−Cp*(centroid) (1.907 Å) distances and the Ru−N−O bond angle [168.9(2)°] in **1** are comparable to those for [Cp*Ru(NO)(S-*t*-Bu)$_2$].[7c]

* To whom correspondence should be addressed. E-mail: chleung@ust.hk.
† The Hong Kong University of Science and Technology.
‡ Hong Kong Baptist University.

(1) (a) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460. (b) Sellmann, D.; Fürsattel, A.; Sutter, J. *Coord. Chem. Rev.* **2000**, *200*, 545.

(2) (a) Stiefel, E. I. In *Transition Metal Sulfur Chemistry*, Stiefel, E. I., Matsumoto, K., Eds.; American Chemical Society: Washington, DC, 1996; p 2. (b) Hadai, M.; Kuwata, S.; Mizobe, Y. *Acc. Chem. Res.* **2000**, *33*, 46.

(3) (a) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. (b) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47.

(4) (a) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (b) Rao, K. M.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1992**, *11*, 2303. (c) Olivan M.; Caulton, K. G. *Chem. Commun.* **1997**, 1733. (d) Fan, L.; Einstein, F. W. B.; Sutton, D. *Organometallics* **2000**, *19*, 684.

(5) (a) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725. (b) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601.

(6) (a) Itoh, K.; Masuda, K.; Fikahori, T.; Nakano, K.; Aoki, K.; Nagashima, H. *Organometallics* **1994**, *13*, 1020. (b) Yi, C. S.; Torres-Lubain, J. R.; Liu, N.; Rheingold, A. L.; Guzei, I. A. *Organometallics* **1998**, *17*, 1257.

(7) (a) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298. (b) Hubbard, J. L.; Morneau, A.; Burns, R. M.; Zoch, C. R. *J. Am. Chem. Soc.* **1991**, *115*, 9176. (c) Tagge, C. D.; Bergman, R. G. *Inorg. Chem.* **1996**, *35*, 6908.

(8) (a) Hidai, M.; Mizobe, Y.; Matsuzaka, H. *J. Organomet. Chem.* **1994**, *473*, 1. (b) Hashizume, K.; Mizobe, Y.; Hidai, M. *Organometallics* **1995**, *14*, 5367.

(9) (a) Leung, W.-H.; Zheng, H.; Chim, J. L. C.; Chan, J.; Wong, W.-T.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **2000**, 423. (b) Leung, W.-H.; Lau, K.-K. Zhang, Q.-F.; Wong, W.-T.; Tang, B. *Organometallics* **2000**, *19*, 2084. (c) Zhang, Q.-F.; Zheng, H.; Wong, W.-Y.; Wong, W.-T.; Leung, W.-H. *Inorg. Chem.* **2000**, *39*, 5255.

(10) (a) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417. (b) Dehnicke K.; Strähle, J. *Polyhedron* **1989**, *8*, 707. (c) Demadis, K. D.; Bakir, M.; Klesczewski, B. G.; Williams, D. S.; White, P. S.; Meyer, T. J. *Inorg. Chim. Acta* **1998**, *270*, 511.

10.1021/om010054x CCC: $20.00
Publication on Web 07/25/2001

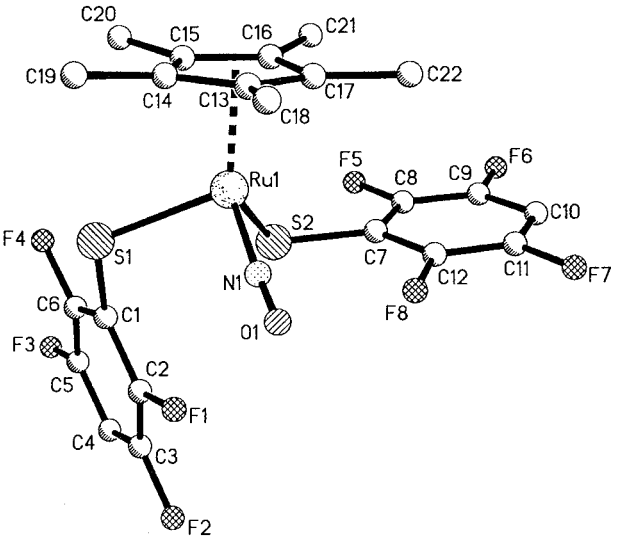


Figure 1. Perspective view of $[Cp^*Ru(NO)(SC_6HF_4)_2]$, **1**. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1), 2.3899(6); Ru(1)−S(2), 2.3880(6); Ru(1)−N(1), 1.17558(18); Ru(1)−Cp*, 1.907; Ru(1)−N(1)−O(1), 168.9(2); S(1)−Ru(1)−S(2), 86.52(2); S(1)−Ru(1)−N(1), 97.27(6); S(2)−Ru(1)−N(1), 101.51(7).

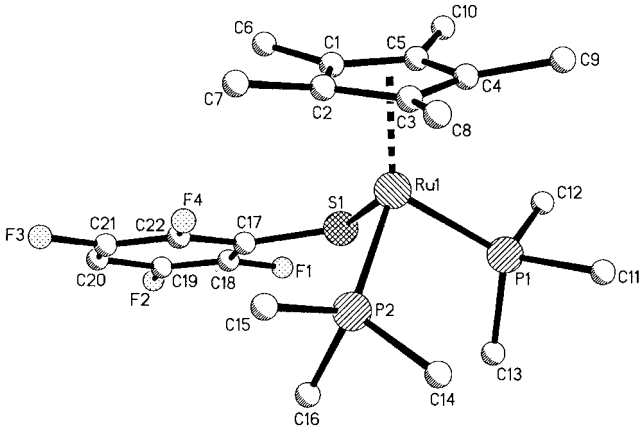
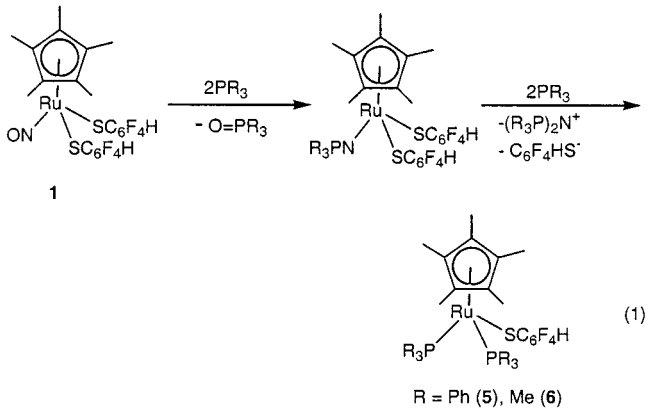


Figure 2. Perspective view of $[Cp^*Ru(PMe_3)_2(SC_6F_4H)]$, **6**. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1), 2.4104(9); Ru(2)−S(2), 2.4156(9); Ru(1)−P(1), 2.3019(10); Ru(1)−P(2), 2.2.2845(10); Ru(2)−P(3), 2.2977(8); Ru(2)−P(4), 2.2958(8); Ru(1)−Cp*, 1.889; Ru(2)−Cp*, 1.889; P(1)−Ru(1)−P(2), 90.92(4); P(1)−Ru(1)−S(1), 81.47(4); P(2)−Ru(1)−S(1), 96.34(4); P(3)−Ru(1)−P(4), 90.60(3); P(3)−Ru(1)−S(2), 83.35(3); P(4)−Ru(1)−S(2), 95.03(3).

Reduction of 1 by Phosphines. It is well known that metal nitrosyls react with phosphines to afford metal phosphoraminate complexes.[10] However, treatment of **1** with PR_3 followed by recrystallization led to isolation of $[Cp^*Ru(PR_3)_2(SC_6HF_4)]$ (R = Ph (**5**), Me (**6**)) along with $O{=}PR_3$. Complex **6** has been characterized by X-ray crystallography (Figure 2). The average Ru−P, Ru−Cp*(centroid), and Ru−S distances in **6** are 2.998, 1.889, and 2.4104 Å, respectively, which are comparable to those for $[Cp^*Ru(PEt_2Ph)_2(S\text{-}t\text{-}Bu)]$.[11] It may be noted that thermolysis of the dialkyl analogues $[Cp^*Ru(NO)(R)(R')]$ with tertiary phosphines resulted in migratory insertion of NO into the Ru−C bond instead of NO deoxygenation.[12] It seems likely that **1** reacted with PR_3 to give initially the phosphoraminate intermediates $[Cp^*Ru(N{=}PPh_3)(SC_6F_4H)_2]$, which were further reduced by phosphines to give the Ru(II) products (eq 1). The organic product for reaction 1 is likely to be $[(Ph_3P)_2N](C_6F_4HS)$ or $(C_6F_4H)_2S_2$.[13]



The reaction between **1** and PMe_3 has been monitored by ^{31}P NMR spectroscopy. Upon addition of a slight excess of PMe_3 to **1** in $CDCl_3$, a singlet at δ −4.60 due to a new species, presumably a Ru phosphoraminate complex, was observed along with the signal for $O{=}PMe_3$ (δ 37.97). After the reaction mixture was left to stand at room temperature for 1 day, the resonance at δ −4.60 gradually decreased in intensity and the signal for **6** (δ −1.55) appeared. The phosphoraminate intermediate, which could be isolated as a crude product from the reaction mixture, was characterized as $[Cp^*Ru(N{=}PMe_3)(SC_6F_4H)_2]$ by mass spectrometry [*m*/*z* 706 (M^+)] and IR spectroscopy [ν_{PN} at 1124 cm^{-1},[10] and the absence of ν_{NO}]. Unfortunately we have not been able to obtain an analytically pure sample of the Ru phosphoraminate complex due to its high solubility and the cocrystallization of $O{=}PMe_3$. Further recrystallization of the crude product resulted in isolation of the Ru(II) product **6**.

Oxidative Addition of $[Cp^*Ru(MeCN)_3]^+$. Our second approach to high-valent Cp*Ru complexes involves oxidative addition of Cp*Ru(II) with phosphine chalcogenides. In particular, the reactions of amidodiphosphinochalcogenides $HN(QPR_2)_2$ (Q = S, Se; R = alkyl or phenyl), which are capable of transferring their chalcogen to transition metals,[9b,14] with $[Cp^*Ru(MeCN)_3]^+$ were studied. Treatment of $[Cp^*Ru(MeCN)_3][PF_6]$ with the $HN(QPPh_2)_2$ afforded paramagnetic species analyzed as $[Cp^*Ru\{N(QPPh_2)_2\}(MeCN)][PF_6]$ (Q = S or Se).[15] Interestingly, reaction of $[Cp^*Ru(MeCN)_3][PF_6]$ with the isopropyl analogue $HN[SeP(i\text{-}Pr)_2]_2$ in THF led

(11) Treichel, P. M.; Schmidt, M. S.; Crane, R. A. *Inorg. Chem*. **1991**, *30*, 379.

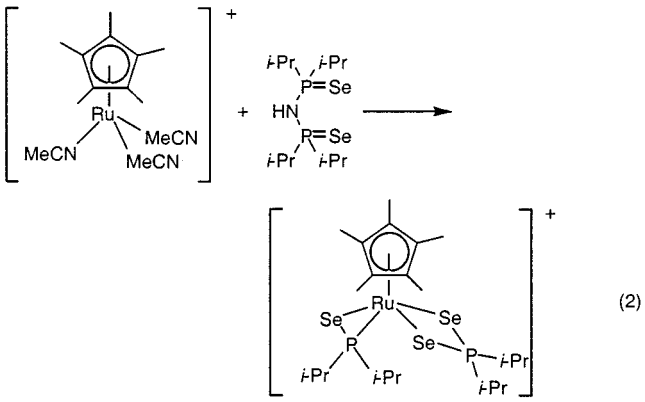
(12) Chang, J.; Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3258.

(13) It was reported that reaction of an Os(IV) phosphoraminate complex with excess PR_3 afforded an Os(II) species along with $R_3P{=}N{=}PR_3^+$ (see ref 10c).

(14) (a) Rossi, R.; Marchi, A.; Marvelli, L. Castellato, U.; Tamburini, S.; Grazinai, R. *J. Chem. Soc., Dalton Trans*. **1991**, 263. (b) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans*. **1995**, 3189. (c) Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans*. **1997**, 1877.

(15) Related Ru and Rh complexes have been synthesized recently: Valderrama, M.; Contreras, R.; Lamata, M. P.; Viguri, F.; Carmona, D.; Lahoz, F. J.; Elipe, S.; Oro, L. A. *J. Organomet. Chem*. **2000**, *607*, 3.

to isolation of a novel ruthenium(IV) complex [Cp*Ru{η^2-$Se_2P(i\text{-}Pr)_2$}{η^2-$SeP(i\text{-}Pr)_2$}][PF_6] (**7**) in 38% yield (eq 2).



(2)

7

The $^{31}P\{^1H\}$ NMR spectrum of **7** shows two doublets at δ 105.54 and 116.06 [$^3J_{PP}$ ca. 5.5 Hz] assignable to the $[Se_2P(i\text{-}Pr)_2]^-$ and $[SeP(i\text{-}Pr)_2]^-$ ligands along with the resonance of $[PF_6]^-$. It appears that the $[Se_2P(i\text{-}Pr)_2]^-$ and $[SeP(i\text{-}Pr)_2]^-$ ligands in **7** were derived from the P−N bond cleavage of $HN[SeP(i\text{-}Pr)_2]_2$. It may be noted that P−N bond cleavage occurs when $NH(PPh_2O)_2$ is hydrolyzed at high temperature.[16] The formation of the $[Se_2P(i\text{-}Pr)_2]^-$ ligand possibly involves the addition of a Se atom extruded from the $HN[SeP(i\text{-}Pr)_2]_2$ chelate[9b,14b] to the $P(Se)(i\text{-}Pr)_2$ group.

The solid-state structure of **7** has been unambiguously characterized by X-ray diffraction and is shown in Figure 3. To our knowledge, **7** is the first example of a Cp*Ru(IV) complex with selenolate ligands. Complex **7** adopts a four-legged piano stool structure, which is commonly encountered for Cp*Ru(IV) complexes such as $[CpRu(H)_2(PPh_3)_2]^+$,[17] and $[Cp^*RuH(SH)(PEt_3)_2]^-$.[18] The Ru−Cp*(centroid) distance is 1.916 Å. The diselenophosphinate $[Se_2P(i\text{-}Pr)_2]^-$ binds to Ru in an approximate symmetric η^2 mode [Ru−Se distances being 2.543(2) and 2.538(2) Å], while the selenophosphinite $[SeP(i\text{-}Pr)_2]^-$ ligand is in an unusual η^2-(Se,P) mode with the P(2)−Ru(1)−Se(3) bite angle of 51.98°. Metal complexes with η^2-selenophosphinite ligands are rather rare.[19] The P−Se(3) bond distance of 2.166(4) Å for **7** is short and comparable to that in $[Mn(CO)_5(\eta^2\text{-}SePCy_2)]$,[19c] indicative of P=Se double bond character. The Ru−P bond [2.320(4) Å] is shorter than that in $[CpRu(H)_2(PPh_3)_2]^+$ [2.412(3) Å].[17] The Ru−Se distances in **7** are in the range of 2.538(2)−2.590(2) Å, which are comparable to those in $[CpRu(PPh_3)_2](Se_2)(OTf)_2$ [2.473(1)−2.556(1) Å][20] and $[Ru_4(\mu\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{HN(PPh_2)_2\}]$ [2.552(2)−2.579(2) Å].[14c] The Ru(1)−Se(3) bond is slightly longer than the Ru(1)−Se(1) and Ru(1)−Se(2) bonds probably due to steric effects.

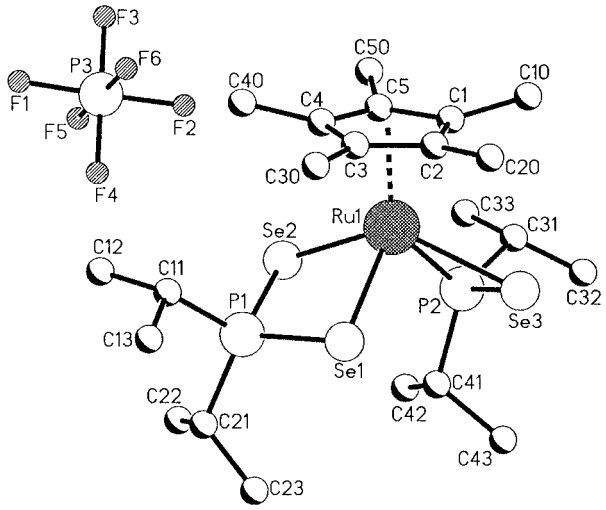


Figure 3. Molecular structure of [Cp*Ru{η^2-$Se_2P(i\text{-}Pr)_2$}{η^2-$SeP(i\text{-}Pr)_2$}][PF_6], **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−P(1), 2.320(4); Ru(1)−Se(1), 2.543(2); Ru(1)−Se(2), 2.538(2); Ru(1)−Se(3), 2.590(2); Ru(1)−Cp*, 1.916; Se(1)−P(1), 2.179(5); Se(2)−P(1), 2.194(4); Se(3)−P(2), 2.166(4); Se(1)−Ru(1)−Se(2), 81.17(6); Se(2)−Ru(1)−Se(3), 130.74(7); Se(1)−Ru(1)−Se(3), 82.85(6); P(1)−Se(1)−Ru(1), 88.38(12); P(1)−Se(2)−Ru(1), 88.38(12); P(1)−Se(3)−Ru(1), 57.56(11); P(2)−Ru(1)−Se(1), 97.37(11); P(2)−Ru(1)−Se(2), 84.46(10); P(2)−Ru(1)−Se(3), 51.98(10); Se(3)−P(2)−Ru(1), 70.46(12).

In summary, we have demonstrated that [Cp*Ru(NO)$(SC_6F_4H)_2$] underwent deoxygenation with PR_3 to give Ru(IV) phosphoraminate species, which were subsequently reduced to $[Cp^*Ru(PR_3)_2(SC_6F_4H)]$. Reaction of $[Cp^*Ru(MeCN)_3]^+$ with $HN[SeP(i\text{-}Pr)_2]_2$ resulted in P−N cleavage of $HN[SeP(i\text{-}Pr)_2]_2$ and the formation of a Cp*Ru(IV) complex containing a η^2-selenophosphinite ligand.

Experimental Section

General Considerations. 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 Bruker ALX 300 spectrometer operating at 300, 121.5, and 282.4 MHz for ^1H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H and ^{13}C) and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, and mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

Materials. LiSePh and LiTePh were obtained from the reactions of *n*-BuLi with Ph_2Se_2 and Ph_2Te_2 in THF, respectively. $[Cp^*Ru(NO)Cl_2]$,[7b] $[Cp^*Ru(MeCN)_3][PF_6]$,[21] and $HN[SeP(i\text{-}Pr)_2]_2$[22] were prepared according to the literature methods. 2,3,5,6-Tetrafluorobenzenethiol, 3,4-dimercaptotoluene, Ph_2Se_2, Ph_2Te_2, and PMe_3 were purchased from Aldrich Ltd.

Preparation of [Cp*Ru(NO)$(SC_6F_4H)_2$] (1). To a solution of $[Cp^*Ru(NO)Cl_2]$ (100 mg, 0.297 mmol) in THF (10 mL) was added a MeOH (5 mL) solution of C_6F_4HSH (108 mg, 0.594 mmol) and NaOMe (35 mg, 0.60 mmol). The solution color

(16) Corbridge, D. E. C. *Phosphorus*: *An Outline of Its Chemistry, Biochemistry, and Technology*, 5th ed.; Elsevier: Amsterdam, The Netherlands, 1995; p 472.

(17) de los Ríos, I.; Jiménez-Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, *15*, 4565.

(18) Coto, A.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4392.

(19) (a) Walther, B. *Coord. Chem. Rev.* **1984**, *60*, 67. (b) Gelmini, L.; Stephan, W. *Organometallics* **1987**, *6*, 1515. (c) Lindner, E.; Bosch, E.; Fawzi, R.; Steimann, M.; Mayer, H. A.; Gierling, K. *Chem. Ber.* **1996**, *129*, 945.

(20) Amarasekera, J.; Houser, E. J.; Rauchfuss, T. B.; Stern, C. L. *Inorg. Chem.* **1992**, *31*, 1614.

(21) Steinmatz, B.; Schenk, W. A. *Organometallics* **1999**, *18*, 943.

Table 1. Crystallographic Data and Experimental Details for 1, 6, and 7

	1	6	7
formula	$C_{22}H_{17}NOF_8S_2Ru$	$C_{22}H_{34}F_4P_2SRu$	$C_{22}H_{43}F_6P_3Se_3Ru$
fw	628.56	569.56	852.42
color, habit	red, prism	orange, slab	dark red, block
cryst dimens, mm	0.34 × 0.32 × 0.27	0.42 × 0.30 × 0.14	0.40 × 0.30 × 0.25
a, Å	22.6486(14)	9.0410(6)	15.373(4)
b, Å	11.2357(7)	15.8143(10)	16.117(5)
c, Å	9.0880(6)	35.550(2)	13.214(3)
β, deg	101.02(2)		
V, Å^3	2312.6(3)	5082.8(6)	3214(2)
Z	4	8	4
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$Pna2_1$	$P2_12_12_1$	$P2_1/c$
D_{calc}, g cm^{-3}	1.805	1.489	1.762
T, °C	23	23	23
λ, Å	0.71073	0.71073	0.71073
scan type	ω	ω	ω
$2\theta_{max}$, deg	54.98	55.00	50.00
μ, mm^{-1}	0.939	0.861	4.081
no. of reflns measured	5156	29 632	5764
no. of reflns obsd ($I>2.0\sigma(I)$)	4866	11 286	5508
R1[a]	0.0186	0.0292	0.0780
wR2[b]	0.0487	0.0785	0.1523
F(000)	1248	2336	1680
GoF[c]	1.003	0.777	1.047

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [(\sum w(F_o^2 - F_c^2)^2/\sum w|F_o^2|^2]^{1/2}$. [c] $GoF = [(\sum w|F_o| - |F_c|)^2/(N_{obs} - N_{param}]^{1/2}$.

changed from deep green to red. After 2 h of vigorous stirring at room temperature, the solvent was pumped off and the residue extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane afforded reddish brown crystals (yield: 115 mg, 62%). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 15H, C_5Me_5), 6.83 (dd, 2H, SC_6F_4H, $^1J_{HF}$ = 19 Hz, $^3J_{HF}$ = 34 Hz). ^{19}F NMR ($CDCl_3$): δ −132, −142. IR (KBr, cm^{-1}): 1789 ν_{NO}. MS (FAB): *m*/*z* 629 (M^+), 599 (M^+ − NO), 448 (M^+ − SC_6F_4H), 418 (M^+ − NO − SC_6F_4H). Anal. Calcd for $C_{22}H_{17}NOF_8S_2Ru$: C, 42.02; H, 2.70; N, 2.20. Found: C, 41.54; H, 2.73; N, 2.19.

Preparation of [Cp*Ru(NO)($S_2C_7H_6$)$_2$] (2). This was prepared similarly to complex **1** using 1 equiv of 3,4-dimercaptotoluene ($H_2S_2C_7H_6$) instead of HSC_6F_4H. Yield: 94 mg, 75%. ^{1}H NMR ($CDCl_3$): δ 1.88 (s, 15H, C_5Me_5), 2.23 (s, 3H, CH_3), 6.62 (d, 1H, J_{HH} = 8 Hz), 7.14 (d, 1H, J_{HH} = 8 Hz), 7.21 (d, 1H, J_{HH} = 8 Hz). IR (KBr, cm^{-1}): 1754 ν_{NO}. MS (FAB): *m*/*z* 421 (M^+), 391 (M^+ − NO). Anal. Calcd for $C_{17}H_{21}NOS_2Ru$: C, 48.55; H, 5.03; N, 3.33. Found: C, 48.63; H, 4.98; N, 3.21.

Preparation of [Cp*Ru(NO)(SePh)$_2$] (3). To a solution of [Cp*Ru(NO)Cl_2] (100 mg, 0.297 mmol) in THF (20 mL) was added LiSePh (97 mg, 0.594 mmol). The mixture was stirred at room temperature for 2 h, during which time the color changed from green to brown. The solvent was pumped off, and the residue was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane afforded reddish brown crystals (yield: 125 mg, 73%). ^{1}H NMR ($CDCl_3$): δ 1.72 (s, 15H, C_5Me_5), 6.91 (vt, 2H, J_{HH} = 7 Hz), 7.23 (vt, 4H, J_{HH} = 7 Hz), 7.52 (d, 4H, J_{HH} = 7 Hz). IR (KBr, cm^{-1}): 1726 ν_{NO}. MS (FAB): *m*/*z* 579 (M^+), 549 (M^+ − NO), 423 (M^+ − SePh), 393 (M^+ − NO − SePh). Anal. Calcd for $C_{22}H_{25}NOSe_2Ru$: C, 45.68; H, 4.36; N, 2.42. Found: C, 45.37; H, 4.25; N, 2.37.

Preparation of [Cp*Ru(NO)(TePh)$_2$] (4). This was prepared similarly as for **3** using LiTePh instead of LiSePh. Yield: 90 mg, 45%. ^{1}H NMR ($CDCl_3$): δ 1.71 (s, 15H, C_5Me_5), 6.94−7.62 (m, 10H, C_6H_5). IR (KBr, cm^{-1}): 1720 ν_{NO}. MS (FAB): *m*/*z* 676 (M^+), 646 (M^+ − NO), 471 (M^+ − TePh), 441 (M^+ − NO − TePh). $E_{1/2}$ (CH_2Cl_2, V vs $Cp_2Fe^{+/0}$): 0.95 [Ru(II/III)]. Anal. Calcd for $C_{22}H_{25}NOTe_2Ru{\cdot}CH_2Cl_2$: C, 36.32; H, 3.58; N, 1.84. Found: C, 35.51; H, 3.44; N, 1.81.

Preparation of [Cp*Ru(PPh_3)$_2$(SC_6F_4H)] (5). An excess of PPh_3 (120 mg, 0.46 mmol) was added to a solution of **1** (75 mg, 0.12 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 1 day. The solvent was removed in vacuo and the residue extracted with CH_2Cl_2/Et_2O (1:3). Cooling at −10 °C overnight resulted in precipitation of the white PPh_3, which was then removed by filtration. The resultant yellow filtrate was evaporated to dryness and extracted with hexane (20 mL). Concentration and cooling at −10 °C afforded a yellow microcrystalline solid characterized as [Cp*Ru(SC_6HF_4)(PPh_3)$_2$] (**5**) (yield: 34 mg, 42%). ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 15H, C_5Me_5), 6.72 (d, 1H, SC_6F_4H, J_{HF} = 16 Hz), 6.97−7.68 (m, 15H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34.2. MS (FAB): *m*/*z* 942 (M^+), 679 (M^+ − PPh_3), 499 (M^+ − PPh_3 − C_6F_4H), 417 (M^+ − 2PPh_3). Anal. Calcd for $C_{52}H_{46}F_4P_2SRu$: C, 66.30; H, 4.92. Found: C, 65.64; H, 4.85.

Preparation of [Cp*Ru(PMe_3)$_2$(SC_6F_4H)] (6). This was prepared similarly as for **5** using PMe_3 instead of PPh_3 and was isolated as yellow crystals in 79% yield. ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 15H, C_5Me_5), 1.52 (d, 18H, PMe_3, J_{HP} = 13 Hz), 6.80 (d, 1H, SC_6F_4H, J_{HF} = 28 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 1.55. MS (FAB): *m*/*z* 570 (M^+), 494 (M^+ − PMe_3), 417 (M^+ − 2PMe_3), 389 (M^+ − PMe_3 − C_6F_4H). Anal. Calcd for $C_{22}H_{34}F_4P_2SRu$: C, 46.39; H, 6.02. Found: C, 45.26; H, 5.87.

Preparation of [Cp*Ru{η^2-$Se_2P(i\text{-}Pr)_2$}{η^2-$SeP(i\text{-}Pr)_2$}][PF_6] (7). To a solution of [Cp*Ru($MeCN)_3$][PF_6] (150 mg, 0.30 mmol) in THF (20 mL) was added 1 equiv of HN[$SeP(i\text{-}Pr)_2)_2$] (122 mg, 0.30 mmol). The mixture was stirred at room temperature for 4 h, during which time the solution color changed from yellow to red brown. The solvent was pumped off, and the residue was washed with hexane. Recrystallization from CH_2Cl_2/hexane gave dark red crystals (yield: 80 mg, 38%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 4H, $CH(CH_3)_2$, J_{HH} = 6 Hz), 1.11−1.54 (m, 24H, $CH(CH_3)_2$), 1.81 (s, 15H, C_5Me_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 105.54 (d, J = 5.8 Hz), 116.06 (d, J = 5.3 Hz), −145.3 (sept, [PF_6]$^-$ J_{PF} = 707 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −74.5 (d, J_{PF} = 707 Hz). MS (FAB): *m*/*z* 709 (M^+ − PF_6). Anal. Calcd for $C_{22}H_{43}F_6P_3Se_3Ru$: C, 31.00; H, 5.08. Found: C, 30.78; H, 5.02.

X-ray Diffraction Measurements. A summary of crystallographic data and experimental details for complexes **1**, **6**, and **7** is provided in Table 1. Intensity data were collected on a Bruker SMART CCD diffractometer for **1** and **6** and a Siemens P4 diffractometer for **7** using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 23 °C. Intensity data were corrected for Lorentz and polarization and absorption effects. The structures were solved by direct methods and refined on F^2 by full matrix least-squares analyses. Hydrogen atoms were placed at the idealized positions (C−H = 0.95 Å).

All calculations were performed using the SHELXL crystallographic software package.[23] Final atomic coordinates are provided as the Supporting Information.

Acknowledgment. The financial support from the Hong Kong University of Science and Technology and the Hong Kong Research Grants Council is gratefully acknowledged. We thank Dr. Zhenyang Lin for helpful discussions.

Supporting Information Available: Listings of final atomic coordinates, anisotropic displacement parameters, and bond lengths and angles of **1**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010054X

(22) Cupertino, D.; Birdsall, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chim. Acta* **1999**, *290*, 1.
(23) Sheldrick, G. M. *SHELXL V5.1 Software Reference Manual*; Bruker AXS Inc.: Madison, WI, 1997.