DOI: 10.1002/ejic.200800731

Ruthenium η⁶-Hexamethylbenzene Complexes Containing Dichalcogenoimidodiphosphinate Ligands

Wai-Man Cheung,[a] Wai-Hang Chiu,[a] Ian D. Williams,[a] and Wa-Hung Leung*[a]

Keywords: Ruthenium / Arene complexes / Sandwich complexes / Dithiolate ligand

Treatment of $[Ru(\eta^6\text{-}C_6Me_6)Cl_2]_2$ with AgOTf (OTf^- = triflato) followed by $K[N(R_2PQ)_2]$ gave the 16-electron complexes $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(R_2PQ)_2\}][OTf]$ [Q = S, R = Ph (**1**) or *i*Pr (**2**); Q = Se, R = Ph (**3**) or *i*Pr (**4**)] which were isolated as air-stable blue or dark green crystals. For complex **1**, when the crude product was recrystallised from CH_2Cl_2/hexane in air, orange crystals of $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^3\text{-}N(Ph_2PS)_2\}][OTf]$ (**1a**) were isolated as a minor product. The reaction of compound **1** with ammonia, hydrazine hydrate and 4,4′-bipyridyl (4,4′-bpy) gave the 18-electron adducts $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PS)_2\}L][OTf]$ [L = NH_3 (**5**), N_2H_4 (**6**)] and dinuclear $[\{Ru(\eta^6\text{-}C_6Me_6)[\eta^2\text{-}N(Ph_2PS)_2]\}_2(\mu\text{-}4,4'\text{-bpy})][OTf]_2$ (**7**), respectively. Treatment of compound **2** with $Li[BEt_3H]$ and $NaBH_4$ afforded the ethyl $[Ru(\eta^6\text{-}C_6Me_6)\{N(iPr_2PS)_2\}Et]$ (**8**) and hydride $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(iPr_2PS)_2\}H]$ (**9**) compounds, respectively. Formal potentials for $Ru[N(R_2PQ)_2]$ complexes have been determined. The structures for complexes **1**, **1a**, **5**, **6**, **8** and **9** have been established by X-ray crystallography.

Introduction

Coordinatively unsaturated half-sandwich transition metal complexes have attracted much attention due to their interesting reactivity toward small molecules and their applications in organic transformations.[1,2] The most extensively studied 16-electron half-sandwich ruthenium complexes are those of the types [RuCp(L)X] (Cp = $\eta^5\text{-}C_5H_5$, X = monoanionic ligand, L = electron-donating ligands such as phosphanes and *N*-heterocyclic carbenes) and [RuCp(L^L)] (L^L = bidentate phosphane or nitrogen ligand).[1] It has been found that the unsaturation of the $CpRu^{II}$ core can be stabilised by π donation of co-ligands.[3,4] While 16-electron half-sandwich Ru^{II} complexes with *P*-,[1,5,6] *N*-[4,7,8] and *O*-donor[9,10] ligands are well known, analogous complexes with *S*-donor ligands have received relatively less attention.[11] Recently, we have isolated the 16-electron $[RuCp^*\{N(iPr_2PS)_2\}]$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[12] demonstrating the ability of dithioimidodiphosphinato ligands[13] to stabilise the unsaturated Ru^{II} centre. To further explore the chemistry of unsaturated Ru–S complexes, we sought to synthesise Ru π-arene complexes containing dithioimidodiphosphinato ligands.

Unsaturated Ru π-arene complexes with sulfur ligands are more common than their cyclopentadienyl analogues. Examples include those containing thiolato, 1,2-benzenedithiolato,[14] 1,2-dichalcogenolato-*o*-carborane,[15,16] and maleonitriledithiolato[17] ligands. In particular, Ru(arene) complexes with 1,2-dichalcogenolato-*o*-carborane ligands[15,16] have been studied extensively due to their use as building blocks for multinuclear assemblies. The chemistry of Ru π-arene complexes with dithioimidodiphosphinato ligands has not been well developed.[18] Previously, Oro and co-workers reported the synthesis of $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PQ)_2\}py][BF_4]$ (Q = S or Se) from $[Ru(\eta^6\text{-}C_6Me_6)(solvent)_3]^+$ and $HN(Ph_2PQ)_2$ and pyridine (py), presumably through $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PQ)_2\}]^+$ intermediates that have not been isolated.[18] In this paper, we report the synthesis and structures of the 16-electron $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(R_2PS)_2\}][OTf]$ species and their reactivity toward am(m)ines and boron hydrides.

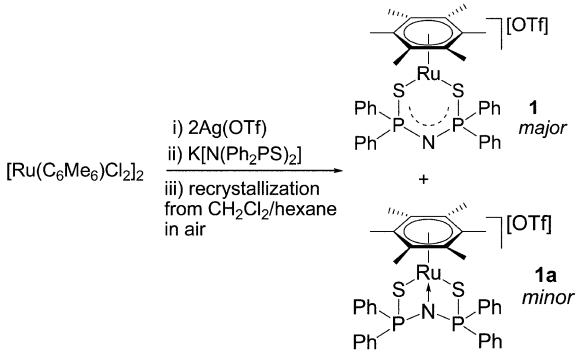
Results and Discussion

Synthesis of $[Ru(C_6Me_6)\{N(R_2PQ)_2\}][OTf]$ (Q = S, Se)

Treatment of $[Ru(\eta^6\text{-}C_6Me_6)Cl_2]_2$ with Ag(OTf) (OTf = triflate) followed by $K[N(R_2PQ)_2]$ afforded the 16-electron cationic complexes $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PQ)_2\}]^+$ [Q = S, R = Ph (**1**) or *i*Pr (**2**); Q = Se, R = Ph (**3**) or *i*Pr (**4**)] which were isolated as air-stable blue or dark green crystals. The blue or dark green colouration is characteristic for 16-electron [RuCp(L)(X)]-type complexes and has been attributed to the LMCT pπ(X)-dπ(Ru) transitions.[1] Consistent with this spectroscopic assignment, the LMCT pπ(*S*)-dπ(Ru) band centred at 651 nm for complex **2** is red-shifted to 663 nm (for **4**) when the ligand donor atom is changed from sulfur to selenium. For comparison, the LMCT pπ(*S*)-dπ(Ru) band for neutral $[Ru(\eta^6\text{-}C_6Me_6)(bdt)]$ (bdt^{2-} = 1,2-benzenedithiolato) was observed at higher energy

[a] Department of Chemistry, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong, China
Fax: +852-2358-1594
E-mail: chleung@ust.hk

(563 nm).[14] Interestingly, when crude **1** was recrystallised from CH_2Cl_2/hexane in air, a small amount of orange crystals identified as the 18-electron complex [Ru(η^6-C_6Me_6){η^3-N($R_2PS)_2$}][OTf] (**1a**) were isolated (Scheme 1) in addition to blue crystals of **1**. No **1a** was obtained when the recrystallisation was carried out strictly under nitrogen. The mechanism for the formation of **1a** (whether it was formed from the reaction of [Ru(η^6-C_6Me_6)$Cl_2]_2$/Ag(OTf) with K[N($Ph_2PS)_2$] or during the crystallisation of the crude product) is not clear. Although complex **1a** is stable in the solid-state, it is not stable in solution. When orange crystals of **1a** were dissolved in $CDCl_3$, a blue solution was formed immediately. The ^1H, $^{31}P\{^1H\}$ NMR and UV/Vis spectra of the orange solution were identical with those of complex **1**, indicating complex **1a** was converted to complex **1** instantaneously and irreversibly in solution. The driving force for the conversion of complex **1a** to **1** is presumably the ring strain of the ruthenacycle in the former, in which the [N($Ph_2PS)_2$]$^-$ binds to Ru in an unusual η^3 mode (see later section). It is unlikely that the two complexes are in equilibrium in solution. We were not able to study the kinetics for the conversion of complex **1a** to **1** because the reaction was too rapid to be followed by NMR or UV/Vis spectroscopy.



Scheme 1. Formation of complexes **1** and **1a**.

Both complexes **1** and **1a** have been characterised by X-ray diffraction studies. Selected bond lengths and angles are listed in Table 1. Figure 1 shows the structure of the cation [Ru(η^5-C_6Me_6){η^2-N($Ph_2PS)_2$}]$^+$ in **1** which features an approximately perpendicular arrangement between the arene ring and the plane defined by the Ru and two sulfur atoms. The pyramidalisation angle,[1] which is defined as the angle of C_6Me_6(centroid)–Ru–RuS_2 centroid for **1**, was determined to be 177.6°. A similar pyramidalisation angle (177.4°) was found for the cyclopentadienyl analogue [RuCp*{η^2-N($Ph_2PS)_2$}].[12] The observed large pyramidalisation angle and relatively short Ru–S distances in **1** [av. 2.3415 Å cf. 2.407(2)–2.4513(8) Å for analogous 18-electron complexes **5** and **6**, see later section] are indicative of Ru–S π interactions. The Ru–C_6Me_6(centroid) distance is similar to that in [Ru(η^6-C_6Me_6)(bdt)] (1.684 Å). Figure 2 shows the structure of the cation [Ru(η^6-C_6Me_6){η^3-N($Ph_2PS)_2$}]$^+$ in **1a** in which the dithioimidodiphosphinato ligand binds to Ru in a tridentate *S*,*N*,*S*′ fashion. While such a tridentate binding mode has been observed in early metal complexes such as [Sm(SePh){η^3-N($Ph_2PSe)_2$}$_2$][19] and [Y{η^3-N($Ph_2PQ)_2$}$_3$] (Q = S, Se),[20] complex **1a** is, to the best of our knowledge, the first example of a late transition metal complex with an η^3-[N($R_2PS)_2$]$^-$ ligand. The Ru–C_6Me_6 (centroid) and Ru–S distances in **1a** are clearly longer than those in **1**. Coordination of the nitrogen in the η^2-[N($Ph_2PS)_2$]$^-$ ligand in **1** to Ru leads to severe distortions of the Ru–S–P–N–P′–S′ metallacycle. The S–Ru–S′, Ru–S–P and S–P–N angles in **1a** are all smaller than those in **1** but no significant difference in the P–N–P′ angle was found

Table 1. Selected bond lengths [Å] and angles [°] for [Ru(η^6-C_6Me_6){η^2-N($Ph_2PS)_2$}][OTf] (**1**) and [Ru(η^6-C_6Me_6){η^3-N(Ph_2-$PS)_2$}][OTf] (**1a**).

	1	**1a**
Ru–S	2.3375(9), 2.3455(9)	2.4574(15), 2.4640(14)
Ru–N	–	2.0378(13)
Ru–C_6Me_6 (centroid)	1.665	1.714
P–S	2.0378(13), 2.0404(12)	2.004(2), 2.005(2)
N–P	1.585(3), 1.594(3)	1.636(4), 1.645(4)
S–Ru–S′	100.90(3)	86.41(5)
Ru–S–P	110.26(4), 106.30(4)	79.22(6), 78.45(6)
S–P–N	117.42(12), 116.49(11)	106.29(17), 106.77(16)
P–N–P′	124.10(18)	125.6(3)

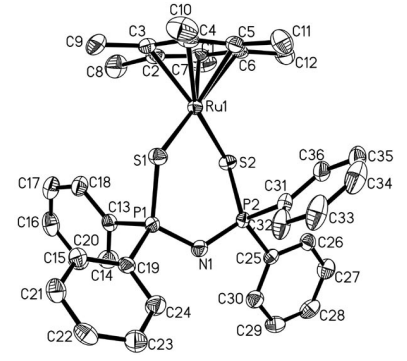


Figure 1. Molecular structure of the cation [Ru(η^6-C_6Me_6){η^2-N($Ph_2PS)_2$}]$^+$ in **1**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level. The Flack parameter is –0.03(2).

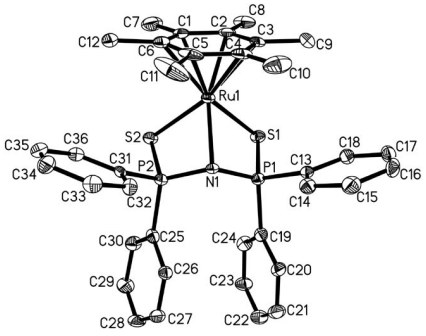
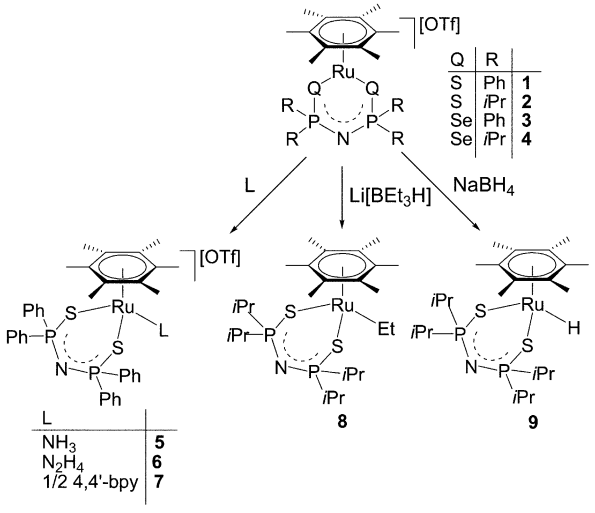


Figure 2. Molecular structure of the cation [Ru(η^6-C_6Me_6){η^3-N($Ph_2PS)_2$}]$^+$ in **1a**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

between the two complexes. The strain in the Ru–S–P–N–P′–S′ metallacycle in **1a** probably leads to the rapid conversion of **1a** to **1** in solution.

Am(m)ine Adducts of 1

Complex **1** is air-stable in both the solid state and solution. No oxidative addition was found when complex **1** was treated with MeI, H_2 or silanes. As previously reported, complex **1** reacts readily with nitrogen ligands to give 18-electron adducts (Scheme 2). For example, treatment of **1** with gaseous NH_3 and hydrazine hydrate afforded the ammine $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PQ)_2\}(NH_3)][OTf]$ (**5**) and hydrazine $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PQ)_2\}(\eta^1\text{-}N_2H_4)][OTf]$ (**6**) complexes, respectively. The ^1H NMR spectrum for **6** displayed two broad peaks at δ = 2.99 and 4.62 ppm due to the NH protons, consistent with the terminal η^1 binding mode of the hydrazine ligand. Contrary to the 1,2-benzenedithiolato analogue that reacted with N_2H_4 to give dinuclear $[Ru(\eta^6\text{-}C_6Me_6)(bdt)]_2(\mu\text{-}\eta^1,\eta^1\text{-}N_2H_4)$,[14] only the mononuclear hydrazine adduct was formed for **1** presumably because of steric effects. Using longer bidentate ligands, it is possible to isolate such dinuclear complexes. For example, treatment of **5** with 4,4′-bipyridyl (4,4′-bpy) led to formation of dinuclear $[\{Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PS)_2\}\}_2(\mu\text{-}4,4'\text{-bpy})][OTf]_2$ (**7**). The ^1H NMR spectrum of **7** showed a singlet at δ = 8.86 ppm due to the pyridyl protons, indicating that the 4,4′-bpy ligand binds to the two Ru atoms symmetrically.



Scheme 2. Reactivity of $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(R_2PS)_2\}][OTf]$.

Figure 3 and Figure 4 show the structures of the cations $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PS)_2\}(L)]^+$ (L = NH_3, N_2H_4) and selected bond lengths and angles are listed in Table 2. The Ru–C_6Me_6 (centroid) and Ru–S distances in both **6** and **7** are longer than those in **1**, indicating that the binding of nitrogen ligands to Ru in **1** results in a weakening of the Ru–C and Ru–S bonds. The Ru–N distance in **6** of 2.1336(18) Å is shorter than that in *trans*-$[Ru\{N(Ph_2PS)_2\}_2(H_2O)(NH_3)]$ [2.142(6) Å].[21] The Ru–N distance [2.151(4) Å] and Ru–N–N′ angle [114.4(3)°] in **7** are similar to those in $[Ru(\eta^6\text{-}C_6H_6)(Sxyl)_2(\eta^1\text{-}N_2H_4)]$ [xyl = 2,6-dimethylphenyl, 2.143(7) Å and 117.9(6)° respectively].[14] It is noteworthy that the N–N distance in the hydrazine ligand in **7** [1.444(5) Å] is closer to that in dinuclear $[Ru(\eta^6\text{-}C_6Me_6)(bdt)]_2(\mu\text{-}N_2H_4)$ [1.454(8) Å] than that in mononuclear $[Ru(\eta^6\text{-}C_6H_6)(Sxyl)_2(\eta^1\text{-}N_2H_4)]$ [1.378(10) Å].[14] The short N–N distance in $[Ru(\eta^6\text{-}C_6H_6)(Sxyl)_2(\eta^1\text{-}N_2H_4)]$ has been attributed to the fact that the σ donation of the nitrogen lone pair of the hydrazine ligand is enforced by further σ donating interactions of the lone pair of the neighbouring nitrogen.[12] However, such an N–N σ donating interaction was not found in complex **7**.

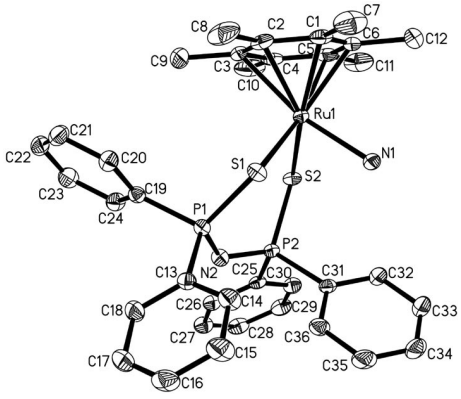


Figure 3. Molecular structure of the cation $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PS)_2\}(NH_3)]^+$ in **5**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

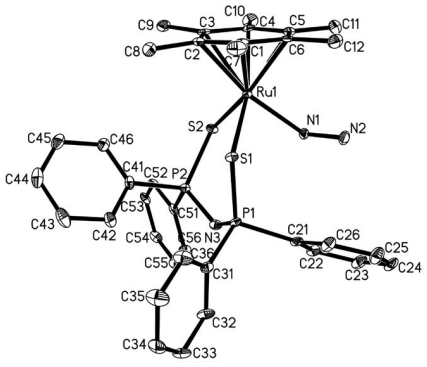


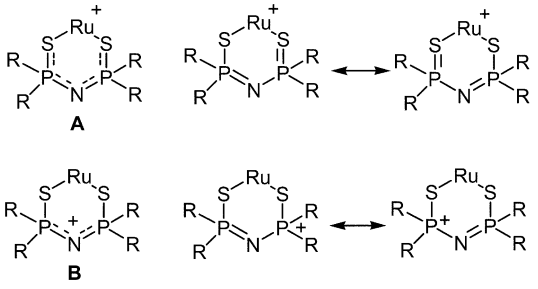
Figure 4. Molecular structure of the cation $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^2\text{-}N(Ph_2PS)_2\}(N_2H_4)]^+$ in **6**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

It is of interest to compare the bonding and structures of the ruthenacycles in unsaturated **1** and the saturated analogues **5** and **6**. Resonance form **A** (Scheme 3) featuring a delocalised S–P–N–P′–S′ framework is normally used to describe bidentate $[N(R_2PS)_2]^-$ ligands (as they are represented in Scheme 1 and Scheme 2). As suggested by one referee, the structures of the ruthenacycles in the Ru-$[N(R_2PS)_2]$ complexes of this work can be described by two resonance forms **A** and **B** (Scheme 3). While extreme **A** is a

Table 2. Selected bond lengths [Å] and angles [°] for [Ru(η⁶-C_6Me_6){N(Ph_2PS)$_2$}(L)][OTf] [L = NH_3 (**5**), N_2H_4 (**6**)].

	5	**6**
Ru–S	2.4351(5), 2.4308(5)	2.4391(12), 2.4043(12)
Ru–C_6Me_6 (centroid)	1.695	1.690
Ru–N	2.1336(18)	2.151(4)
N–N′		1.444(5)
P–S	2.0191(7), 2.0237(7)	2.0236(16), 2.0193(16)
N–P	1.5903(18), 1.5853(19)	1.596(4), 1.594(4)
S–Ru–S′	98.104(18)	98.54(4)
S–Ru–N	81.42(5), 86.99(5)	81.47(10)
Ru–N–N′	–	114.4(3)
S–P–N	118.45(7), 117.33(7)	117.09(15), 117.33(16)
P–N–P	129.11(12)	125.8(2)

suitable description for saturated complexes **5** and **6**, the ruthenacycle in the unsaturated complex is better represented by extreme **B** which allows facile π donation from the lone pair on the S atoms to the unsaturated Ru^{II} centre. Consistent with this proposal, the S–P–N–P′–S′ chelate in unsaturated **1** is less planar (average deviation of atoms from the mean NP_2S_2 plane = 0.358 Å, average torsion angle between the S–P and N–P units = 33.1°). In comparison, more planar arrangements were found for the S–P–N–P′–S′ chelate in saturated complexes **5** (0.2974 Å and 26.6°, respectively) and **6** (0.2916 Å and 25.9°, respectively). Also, the average P–S distance in complex **1** (2.0391 Å) is longer than those in complexes **5** and **6** (2.0214 and 2.0215 Å, respectively). In addition, the observation of a relative downfield ^{31}P chemical shift for unsaturated **1** (δ = 47.49 ppm cf. 31.97–32.11 ppm for saturated complexes **5**–**7**) is consistent with the structure of extreme **B** which contains a partial positive charge on the phosphorus atom.



Scheme 3. Structures of two resonance forms, **A** and **B**, for the ruthenacycles in Ru-[$N(R_2PS)_2$] complexes.

Reaction of 2 with Boron Hydrides

In attempts to synthesise Ru hydride species, reactions of **2** with boron hydrides were studied (Scheme 2). Treatment of **2** with Li[BEt_3H] led to isolation of the ethyl complex [Ru(η⁶-C_6Me_6){η²-N(iPr$_2$PS)$_2$}(Et)] (**8**). Thus, transmetallation of the ethyl group instead of the hydride in [BEt_3H]⁻ occurred. The ^1H NMR spectrum of **8** displayed a triplet and a quartet at δ = 2.08 and 2.71 ppm which can be assigned to the methylene and methyl protons of the ethyl group, respectively. In order to prepare a Ru hydride species, $NaBH_4$ was used as the hydride source. Treatment of **2** with $NaBH_4$ led to formation of the hydride compound [Ru(η⁶-C_6Me_6){η²-N(iPr$_2$PS)$_2$}(H)] (**9**). The ^1H NMR spectrum displayed an upfield resonance at δ = –7.12 ppm due to the hydride ligand. It was unexpected that reaction of complex **2** with superhydride gave an ethyl compound whereas that with a less reactive hydride source, BH_4^-, afforded a hydride compound. No reaction was found between complex **9** and BEt_3 in tetrahydrofuran, suggesting that the ethyl complex **8** was not generated from a hydride intermediate. The reason why [BEt_3H]⁻ underwent ethyl instead of hydride transfer with Ru is not clear. Both complexes **8** and **9** are air-sensitive in solution. No reactions were observed when complex **9** was treated with alkenes such as C_2H_4 or phenylacetylene.

Complexes **8** and **9** have been characterised by X-ray crystallography. Figure 5 and Figure 6 show the molecular structures of **8** and **9**, respectively. Selected bond lengths and angles are listed in Table 3. Unlike **8**, the Ru–S–P–N–P′–S′ ring in **9** is found to flip toward the normal of the C_6Me_6 ring with the C_6Me_6(centroid)–Ru–N angle of 178.6°. Such an orientation of the [N(iPr$_2$PS)$_2$]⁻ chelate is apparently a consequence of the small steric demand of the hydride ligand and results in relatively short Ru–S (av.

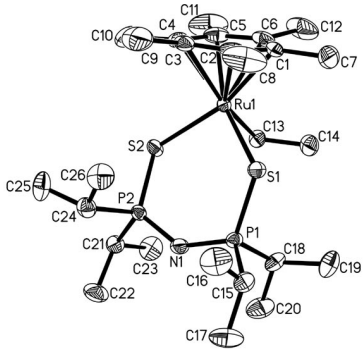


Figure 5. Molecular structure of [Ru(η⁶-C_6Me_6){η²-N(iPr$_2$PS)$_2$}-(Et)] (**8**). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

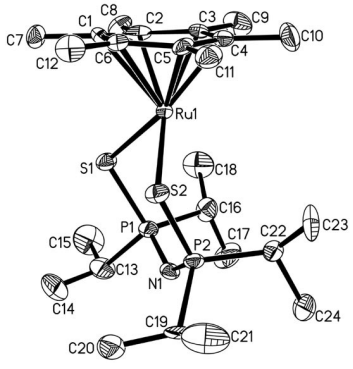


Figure 6. Molecular structure of [Ru(η⁶-C_6Me_6){η²-N(iPr$_2$PS)$_2$}-(H)] (**9**). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

2.410 Å) and Ru–C_6Me_6(centroid) (1.708 Å) distances and a small S–Ru–S′ angle [89.88(7)°] in **9** [cf. av. 2.4428 and 1.729 Å and 98.07(3)°, respectively, in **8**].

Table 3. Selected bond lengths [Å] and angles [°] for [Ru(η^6-C_6Me_6){η^2-N(iPr$_2$PS)$_2$}X] [X = Et (**8**), H (**9**)].

	8	**9**
Ru–S	2.4342(9), 2.4513(8)	2.412(2), 2.407(2)
Ru–C_6Me_6 (centroid)	1.729	1.708
Ru–C	2.133(3)	–
P–S	2.0150(12), 2.0101(12)	2.020(3), 2.014(3)
N–P	1.580(3), 1.575(3)	1.589(6), 1.586(6)
S–Ru–S′	98.07(3)	89.88(7)
S–Ru–C	89.00(10), 82.70(9)	–
P–N–P′	137.33(19)	130.9(4)
Ru–S–P	117.26(4), 117.05(4)	105.5(1), 105.67(10)
S–P–N	117.72(11), 120.12(11)	118.1(2), 118.2(2)

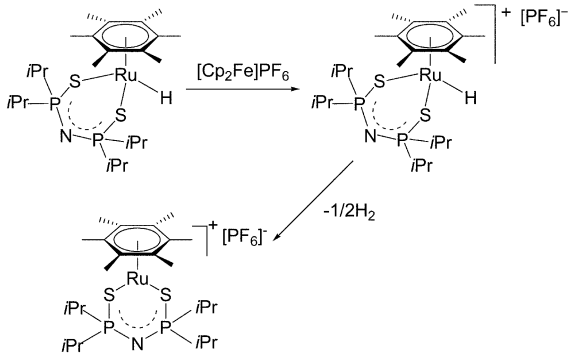
Electrochemistry

Formal potentials of half-sandwich Ru dithioimidodiphosphinato complexes have been determined by cyclic voltammetry (Table 4). Complex **1** was found to decompose to an unknown yellow species in a supporting electrolyte (0.1 M [nBu$_4$N][PF_6] in CH_2Cl_2) and therefore its reduction potential could not be determined. The cyclic voltammogram (CV) of the reported chloride compound [Ru(η^6-C_6Me_6){η^2-N(Ph$_2$PS)$_2$}Cl][22] exhibited a reversible couple at 0.26 V which was assigned as the Ru^{III}–Ru^{II} couple. For comparison, the Ru^{III}–Ru^{II} couple for the pentamethylcyclopentadienyl analogue [RuCp*{η^2-N(Ph$_2$PS)$_2$}Cl] was found at –0.48 V.[12] The Ru^{III}–Ru^{II} potential for [Ru(η^6-C_6Me_6){η^2-N(Ph$_2$PSe)$_2$}Cl] (0.18 V) is slightly more cathodic than that for [Ru(η^6-C_6Me_6){η^2-N(Ph$_2$PS)$_2$}Cl], suggesting that the diselenido ligand is a better donor that the sulfido analogue. The CV for the 4,4′-bpy-bridged dinuclear compound **7** exhibited a single oxidation couple at 0.74 V (tentatively assigned as the $Ru^{III,III}$–$Ru^{II,II}$ couple) which is similar to that of the ammine complex **5**. This result suggests the absence of electronic communication between the two Ru centres in **7**. Unlike the ethyl compound **8**, for which the oxidation is irreversible, the hydride compound **9** exhibited a reversible oxidation couple at –0.46 V, tentatively assigned to the Ru^{III}–Ru^{II} couple. The observation of a low oxidation potential led us to study the chemical oxidation of **9**. Treatment of **9** in CH_2Cl_2 with 1 equiv. of [Cp_2Fe][PF_6] at 0 °C resulted in formation of a purple solution from which [Ru(η^6-C_6Me_6){η^2-N(iPr$_2$PS)$_2$}][PF_6] was isolated in good yield. It seems likely that oxidation of **9** initially gave a transient cationic Ru^{III} hydride species which underwent bimolecular reductive elimination of H_2 to give the 16-electron [Ru(η^6-C_6Me_6){η^2-N(iPr$_2$PS)$_2$}]$^+$ (Scheme 4).

Table 4. Formal potentials ($E_{1/2}$) for [Ru(η^6-C_6Me_6){N(R$_2$PQ)$_2$}X] complexes.[a]

Complex	$E_{1/2}$ / V vs. $Cp_2Fe^{+/0}$
[Ru(η^6-C_6Me_6){η^2-N(Ph$_2$PS)$_2$}Cl][b]	0.26
[Ru(η^6-C_6Me_6){η^2-N(Ph$_2$PSe)$_2$}Cl]	0.18
[Ru(η^6-C_6Me_6){η^2-N(Ph$_2$PS)$_2$}(NH$_3$)][OTf] (**5**)	0.71
[{Ru(η^6-C_6Me_6)[η^2-N(Ph$_2$PS)$_2$]}$_2$(μ-4,4′-bpy)][OTf]$_2$ (**7**)	0.74
[Ru(η^6-C_6Me_6){η^2-N(iPr$_2$PS)$_2$}(Et)] (**8**)	–0.19[c]
[Ru(η^6-C_6Me_6){η^2-N(iPr$_2$PS)$_2$}(H)] (**9**)	–0.46

[a] Potentials measured at a glassy carbon electrode in CH_2Cl_2 solutions with 0.1 M [nBu$_4$N][PF_6] as a supporting electrolyte; scan rate 100 mV s^{-1}. [b] Ref.[22]. [c] Irreversible, E_{pa} value.



Scheme 4. Oxidation of complex **9** with [Cp_2Fe][PF_6].

Conclusions

The syntheses of 16-electron half-sandwich Ru^{II} π-arene complexes containing dithioimidodiphosphinato ligands are described. These unsaturated Ru^{II} complexes react with am(m)ine ligands to give 18-electron adducts but do not undergo oxidative addition with hydrogen, methyl iodide or silanes. Reaction of **2** with [BEt_3H]$^-$ and [BH_4]$^-$ leads to the formation of Ru^{II} ethyl and hydride compounds, respectively. The study of the reactivity of unsaturated Ru dithioimidodiphosphinato compounds is underway.

Experimental Section

General Remarks: All manipulations were performed under nitrogen by using standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operated at 300 (^{1}H) and 121.5 (^{31}P) MHz. ^{1}H and ^{31}P chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0 ppm) and H_3PO_4 (δ = 0 ppm), respectively. Cyclic voltammetry was performed with a Princeton Applied Research model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag/$AgNO_3$ (0.1 M in MeCN) electrodes, respectively. Potentials were reported with reference to ferrocenium-ferrocene ($Cp_2Fe^{+/0}$) couple. Elemental analyses were performed by Medac Ltd., Surrey, UK. The ligands K[N(R$_2$PQ)$_2$] (R = Ph or iPr, Q = S or Se)[23] and [Ru(η^6-C_6Me_6)Cl$_2$]$_2$[24] were prepared according to literature methods.

Preparation of [Ru(η^6-C_6Me_6){η^2-N(R$_2$PS)$_2$}][OTf] [R = Ph (1), iPr (2)]: To a suspension of [Ru(η^6-C_6Me_6)Cl$_2$]$_2$ (67 mg, 0.10 mmol) in CH_2Cl_2 (8 mL) was added 4 equiv. of silver triflate (103 mg, 0.40 mmol) and the reaction mixture was stirred for 1 h and filtered. The solvent was pumped off and the residue was redissolved in tetrahydrofuran (10 mL). To this solution was added 2 equiv. of

K[N(R_2PS)$_2$] [R = Ph (97 mg), *i*Pr (70 mg)]. The orange solution turned dark green (**1**) or blue (**2**) immediately. The reaction mixture was stirred for a further 0.5 h and the solvent was pumped off. The residue was washed with hexane, Et_2O and then extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/Et_2O/hexane afforded blue (**1**) or purple crystals (**2**). Interestingly, when recrystallisation of **1** was carried out in air, in addition to blue crystals of the major product and depending upon crystallisation conditions, a small amount of orange crystals identified as [Ru(η^6-C_6Me_6){η^3-N(Ph_2PS)$_2$}][OTf] (**1a**) were also isolated. In $CDCl_3$ solution, complex **1a** was found to convert to **1** rapidly, as evidenced by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

1: Yield 146 mg, 85%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.88 (s, 18 H, C_6Me_6), 7.40–7.72 (m, 20 H, Ph) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 47.49 (s) ppm. ^{19}F{^{1}H} NMR (300 MHz, $CDCl_3$, 298 K): δ = –79.3 (s) ppm. $C_{37}H_{38}F_3NO_3P_2RuS_3$ (860.91): calcd. C 51.62, H 4.45, N 1.63; found C 51.57, H 4.46, N 1.22.

2: Yield 108 mg, 73%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.06 [m, 24 H, $(CH_3)_2$C], 2.01 (m, 4 H, CH), 2.15 (s, 18 H, C_6Me_6) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 56.41 (s) ppm. ^{19}F{^{1}H} NMR (300 MHz, $CDCl_3$, 298 K): δ = –79.3 (s) ppm. $C_{25}H_{46}F_3NO_3P_2RuS_3$ (725.11): calcd. C 41.43, H 6.40, N 1.93; found C 41.77, H 6.42, N 2.12.

Preparation of [Ru(η^6-C_6Me_6){η^2-N(R_2PSe)$_2$}][OTf] [R = Ph (3), *i*Pr (4)]: These complexes were prepared similarly to the sulfide analogues **1** and **2** using K[N(R_2PSe)$_2$] [R = Ph (116 mg), *i*Pr (89 mg)] in place of K[N(R_2PS)$_2$].

3: Yield 148 mg, 77%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.96 (s, 18 H, C_6Me_6), 7.41–7.74 (m, 20 H, Ph) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 24.54 (s) ppm. ^{19}F{^{1}H} NMR (300 MHz, $CDCl_3$, 298 K): δ = –79.8 (s) ppm. $C_{37}H_{38}F_3NO_3P_2RuSSe_2$ (956.94): calcd. C 46.55, H 4.01, N 1.47; found C 46.33, H 4.02, N 1.70.

4: Yield 111 mg, 68%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.14 [m, 24 H, $(CH_3)_2$C], 2.08 (m, 4 H, CH), 2.15 (s, 18 H, C_6Me_6) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 49.19 (s) ppm. ^{19}F{^{1}H} NMR (300 MHz, $CDCl_3$, 298 K): δ = –79.3 (s) ppm. $C_{25}H_{46}F_3NO_3P_2RuSSe_2$ (821): calcd. C 36.68, H 5.66, N 1.71; found C 36.51, H 5.63, N 1.41.

Preparation of [Ru(η^6-C_6Me_6){η^2-N(Ph_2PS)$_2$}(NH_3)][OTf] (5): NH_3 gas was bubbled into a solution of **1** (30 mg, 0.035 mmol) in CH_2Cl_2 (10 mL) for 15 s. The greenish brown solution turned to yellow immediately. The solvent was removed and the yellow residue was washed with hexane. Recrystallisation from CH_2Cl_2/Et_2O/hexane afforded orange crystals. Yield 27 mg, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.86 (s, 18 H, C_6Me_6), 1.98 (br., 3 H, NH_3), 7.43 (m, 12 H, Ph), 7.81 (m, 8 H, Ph) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 31.97 (s) ppm. ^{19}F{^{1}H} NMR (300 MHz, $CDCl_3$, 298 K): δ = –79.4 (s) ppm. $C_{37}H_{41}F_3N_2O_3P_2RuS_3$ (877.94): calcd. C 50.62, H 4.71, N 3.19; found C 50.37, H 4.70, N 3.05.

Preparation of [Ru(η^6-C_6Me_6){η^2-N(Ph_2PS)$_2$}(η^1-N_2H_4)][OTf] (6): To a solution of **1** (30 mg, 0.035 mmol) in tetrahydrofuran (10 mL) was added excess hydrazine monohydrate at 0 °C. The greenish-brown solution turned to orange immediately. The reaction mixture was stirred at room temperature for 15 min. The solvent was pumped off and the residue washed with hexane. Recrystallisation from CH_2Cl_2/Et_2O/hexane afforded orange crystals. Yield 21 mg, 79%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.89 (s, 18 H, C_6Me_6), 2.99 (br. s, 2 H, NH_2), 4.62 (br. s, 2 H, NH_2), 7.43 (m, 12 H, Ph), 7.78 (m, 8 H, Ph) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 32.11 (s) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$): δ = –79.3 (s) ppm. $C_{37}H_{42}F_3N_3O_3P_2RuS_3$ (892.08): calcd. C 49.77, H 4.74, N 4.70; found C 49.76, H 4.71, N 4.56.

Table 5. Crystallographic data and experimental details for [Ru(η^6-C_6Me_6){η^2-N(Ph_2PS)$_2$}][OTf]·CH_2Cl_2 (**1**·CH_2Cl_2), [Ru(η^6-C_6Me_6){η^3-N(Ph_2PS)$_2$}][OTf]·0.25C_6H_{14} (**1a**·0.25C_6H_{14}) [Ru(η^6-C_6Me_6){η^2-N(Ph_2PS)$_2$}(NH_3)][OTf] (**5**), [Ru(η^6-C_6Me_6){η^2-N(Ph_2PS)$_2$}(η^1-N_2H_4)][OTf] (**6**), [Ru(η^6-C_6Me_6){η^2-N(*i*Pr_2PS)$_2$}(Et)] (**8**) and [Ru(η^6-C_6Me_6){N(*i*Pr_2PS)$_2$}(H)] (**9**).

	1·CH_2Cl_2	**1a**·0.25C_6H_{14}	**5**	**6**	**8**	**9**
Empirical formula	$C_{38}H_{40}Cl_2F_3NO_3P_2RuS_3$	$C_{38.5}H_{41.5}F_3NO_3P_2RuS_3$	$C_{37}H_{41}F_3N_2O_3P_2RuS_3$	$C_{37}H_{42}F_3N_3O_3P_2RuS_3$	$C_{26}H_{51}NP_2RuS_2$	$C_{24}H_{47}NP_2RuS_2$
Formula weight	945.80	885.95	877.91	892.93	604.81	567.76
Crystal system	orthorhombic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a / Å	12.132(2)	10.6392(14)	12.6268(10)	15.8944(8)	10.9756(8)	10.0769(18)
b / Å	15.396(3)	11.0952(3)	12.8350(10)	13.1362(7)	16.0161(12)	14.052(3)
c / Å	22.182(4)	16.966(3)	13.7451(11)	19.3898(11)	17.7244(13)	20.060(4)
α / °		84.465(7)	72.938(1)			
β / °		89.238(3)	65.534(1)	102.099(1)	106.2119(10)	90.687(4)
γ / °		82.054(2)	70.663(1)			
V / Å^3	4143.2(12)	1974.3(5)	1929.1(3)	3958.5(4)	2991.8(4)	2840.4(9)
Z	4	2	2	4	4	4
$\rho_{calcd.}$ / gcm^{-1}	1.516	1.490	1.511	1.498	1.343	1.349
T / K	253(2)	173(2)	298(2)	100(2)	298(2)	298(2)
F(000)	1928	912	900	1832	1280	1216
μ(Mo-K_α) / mm^{-1}	0.786	5.900	0.705	0.689	0.785	0.824
Total reflections	40356	13790	15554	19503	14693	10748
Independent reflections	9908	7131	6650	6905	5185	4731
R_{int}	0.0449	0.0588	0.0153	0.0325	0.0269	0.0817
GoF[a]	1.017	0.996	1.032	1.036	1.023	0.924
R_1[b], wR_2[c] [$I > 2\sigma(I)$]	0.0406, 0.0822	0.0497, 0.0927	0.0267, 0.0721	0.0565, 0.1097	0.0369, 0.0830	0.0688, 0.1062
R_1, wR_2 (all data)	0.0525, 0.0871	0.0870, 0.0995	0.0305, 0.0741	0.0617, 0.1121	0.0475, 0.0867	0.1247, 0.1183
CCDC numbers	691206	691207	691208	691209	691210	691211

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

Preparation of [{Ru(η⁶-C_6Me_6)[η²-N($Ph_2PS)_2$]}₂(μ-4,4′-bpy)][OTf]₂ (7): To a solution of **1** (36 mg, 0.050 mmol) in CH_2Cl_2 (10 mL) was added 0.5 equiv. of 4,4′-bipyridyl (4 mg, 0.025 mmol) in CH_2Cl_2 (3 mL) dropwise. The resultant orange mixture was stirred at room temperature for 1 h and the solvents evaporated in vacuo. Recrystallisation from CH_2Cl_2/Et_2O/hexane afforded orange crystals. Yield 34 mg, 73%. ^{1}H NMR (300 MHz, [D_6]acetone, 298 K): δ = 2.04 (s, 36 H, C_6Me_6), 7.36 (d, J = 6.6 Hz, 4 H, 4,4′-bpy), 7.46 (m, 24 H, Ph), 7.83 (m, 16 H, Ph), 8.86 (d, J = 6.6 Hz, 4 H, 4,4′-bpy) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [D_6]acetone, 298 K): δ = 35.52 (s) ppm. $C_{84}H_{86}F_6N_4O_6P_4Ru_2S_6$ (1880.02): calcd. C 53.67, H 4.61, N 2.98; found C 53.66, H 4.49, N 2.74.

Preparation of [Ru(η⁶-C_6Me_6){η²-N(*i*$Pr_2PS)_2$}(Et)] (8): To a solution of **2** (36 mg, 0.050 mmol) in THF (10 mL) was added excess Li[BEt_3H] (1 M solution in THF, 0.13 mmol) at –78 °C. The orange mixture was slowly warmed to room temperature at which point it was stirred for further 2 h. The solvent was removed and the residue was extracted with hexane. Concentration and cooling at –10 °C afforded orange crystals, yield 31 mg, 82%. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.55 [m, 24 H, $(CH_3)_2C$], 2.02 (s, 18 H, C_6Me_6), 2.08 (t, J = 7.5 Hz, 3 H, CH_3), 2.32 (m, 4 H, CH), 2.71 (q, J = 7.5 Hz, 2 H, CH_2) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ = 56.56 (s) ppm. $C_{26}H_{51}NP_2RuS_2$ (604.84): calcd. C 51.63, H 8.50, N 2.31; found C 51.42, H 8.53, N 2.13.

Preparation of [Ru(η⁶-C_6Me_6){η²-N(*i*$Pr_2PS)_2$}(H)] (9): This compound was prepared in a similar way to **8** using $NaBH_4$ (3 mg, 0.08 mmol) in place of Li[BEt_3H]. Yield 28 mg, 78%. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = –7.12 (s, 1 H, RuH), 1.55 [m, 24 H, $(CH_3)_2C$], 2.87 (m, 4 H, CH) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ = 68.91 (s) ppm. $C_{24}H_{47}NP_2RuS_2$ (576.78): calcd. C 49.98, H 8.22, N 2.43; found C 50.21, H 8.22, N 2.15.

Reaction of Complex 9 with [Cp_2Fe][PF_6]: To a solution of complex **9** in Et_2O (10 mL) at 0 °C was added 1 equiv. of [Cp_2Fe][PF_6]. The mixture was stirred at 0 °C for 30 min and the solvents evaporated. Recrystallisation from CH_2Cl_2/hexane afforded a purple powder in ca. 70% yield which was characterised as [Ru(η⁶-C_6Me_6){η²-N($Ph_2PS)_2$}][PF_6] by NMR spectroscopy.

X-ray Crystallography: Crystallographic data and structure refinement parameters for compounds **1**, **1a**, **5**, **6**, **8** and **9** are summarised in Table 5. Intensity data were collected with a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data was corrected for absorption by using the program SADABS.[25] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[26] Selected bond lengths and angles for complexes **1**, **1a**, **5**, **6**, **8** and **9** are listed in Tables 1–3.

The CCDC numbers given in Table 5 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank Dr. Herman H. Y. Sung for solving the crystal structures. The financial support from the Hong Kong Research Grants Council (project no. 601705) is gratefully acknowledged. We thank the referees for useful suggestions.

[1] M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *Eur. J. Inorg. Chem.* **2004**, 17–32 and references cited therein.
[2] H. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara, K. Kirchner, *Coord. Chem. Rev.* **2003**, *245*, 177–190.
[3] Y. Yamaguchi, H. Nagashima, *Organometallics* **2000**, *19*, 725–727.
[4] K. G. Caulton, *New J. Chem.* **1994**, *18*, 25–41.
[5] B. K. Campion, R. H. Heyn, T. D. Tilley, *J. Chem. Soc., Chem. Commun.* **1988**, 278–280.
[6] T. Arliguie, C. Border, B. Chaudret, J. Devillers, R. Poilblanc, *Organometallics* **1989**, *8*, 1308–1314.
[7] C. Gemel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 5601–5603.
[8] H. Huang, R. P. Hughes, A. L. Rheingold, *Polyhedron* **2008**, *27*, 734–738.
[9] a) T. J. Johnson, K. Folting, W. E. Streib, J. D. Martin, J. C. Huffman, S. A. Jackson, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1995**, *34*, 488–499; b) U. Kölle, J. Kossakowski, *J. Chem. Soc., Chem. Commun.* **1988**, 549; c) U. Kölle, J. Kossakowski, G. Raabe, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 773–774.
[10] M. A. Rankin, D. F. MacLean, G. Schatte, R. MacDonald, M. Stradiotto, *J. Am. Chem. Soc.* **2007**, *129*, 15855–15864.
[11] Y. Ohki, H. Sadohara, Y. Takikawa, K. Tatsumi, *Angew. Chem. Int. Ed.* **2004**, *43*, 2290–2293.
[12] W.-M. Cheung, Q.-F. Zhang, I. D. Williams, W.-H. Leung, *Inorg. Chim. Acta* **2006**, *359*, 782–788.
[13] a) I. Haiduc in: *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), vol. 1, p. 323; b) T. Q. Ly, J. D. Woollins, *Coord. Chem. Rev.* **1998**, *176*, 451–481; c) C. Silvestru, J. E. Drake, *Coord. Chem. Rev.* **2001**, *223*, 117–216.
[14] a) K. Mashima, S.-i. Kaneko, K. Tani, H. Kaneyoshi, A. Nakamura, *J. Organomet. Chem.* **1997**, *545–546*, 345; b) K. Mashima, H. Kaneyoshi, S.-i. Kaneko, K. Tani, A. Nakamura, *Chem. Lett.* **1997**, *6*, 569–570; c) K. Mashima, H. Kaneyoshi, S.-i. Kaneko, A. Mikami, K. Tani, A. Nakamura, *Organometallics* **1997**, *16*, 1016–1025.
[15] a) S. Liu, G.-L. Huang, G.-X. Jin, *Dalton Trans.* **2008**, 425–432; b) S. Liu, Y. F. Han, G.-X. Jin, *Chem. Soc. Rev.* **2007**, *36*, 1543–1560.
[16] D.-H. Wu, B.-H. Xu, Y.-Z. Li, H. Yan, *Organometallics* **2007**, *26*, 6300–6306.
[17] W.-G. Jia, Y.-F. Han, J.-S. Zhang, G.-X. Jin, *Inorg. Chem. Commun.* **2007**, *10*, 1222–1225.
[18] M. Valderrama, R. Contreras, M. P. Lamata, F. Viguri, D. Carmona, F. J. Lahoz, S. Elipe, L. A. Oro, *J. Organomet. Chem.* **2000**, *607*, 3–11.
[19] M. Geissenger, J. Magull, *Z. Anorg. Allg. Chem.* **1997**, *623*, 755–761.
[20] a) C. G. Perrin, J. A. Ibers, *Inorg. Chem.* **2000**, *39*, 1222–1226; b) C. G. Perrin, J. A. Ibers, *Inorg. Chem.* **2000**, *39*, 1216–1221; c) C. G. Perrin, J. A. Ibers, *Inorg. Chem.* **1999**, *38*, 5478–5483.
[21] Q.-F. Zhang, H. Zheng, W.-Y. Wong, W.-T. Wong, W.-H. Leung, *Inorg. Chem.* **2000**, *39*, 5255–5264.
[22] P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, *J. Chem. Soc., Dalton Trans.* **1998**, 2467–2476.
[23] D. Cupertino, R. Keyte, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Inorg. Chem.* **1996**, *35*, 2695–2697.
[24] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1982**, *21*, 74.
[25] *SMART* and *SAINT*+ for Windows NT V6.02a. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1998**.
[26] G. M. Sheldrick, *SHELXTL-Plus* V5.1 Software Reference Manual, Bruker AXS Inc., Madison, Wisconsin, USA, **1997**.

Received: July 24, 2008
Published Online: January 14, 2009

