Journal of Organometallic Chemistry 705 (2012) 34–38

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and characterization of ruthenium complexes with 1-aryl-2-mercaptoimidazole ligands

Ai-Quan Jia [a,*], Qing Ma [a,b], Qun Chen [b], Hua-Tian Shi [a], Wa-Hung Leung [c], Qian-Feng Zhang [a,b,**]

[a] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China
[b] Department of Applied Chemistry, School of Petrochemical Engineering, Changzhou University, Jiangsu 213164, PR China
[c] Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China

ARTICLE INFO

Article history:
Received 26 November 2011
Received in revised form
9 January 2012
Accepted 16 January 2012

Keywords:
Ruthenium
Vinyl
1-Aryl-2-mercaptoimidazole
N–H bond addition
X-ray structure

ABSTRACT

Reactions of the vinyl ruthenium starting material $Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2$ (**1**) with 1-aryl-2-mercaptoimidazole (HLa, aryl = 4-chloro-phenyl; HLb, aryl = 4-methyl-phenyl; HLc, aryl = 4-nitro-phenyl) in the presence of sodium methoxide in dichloromethane and methanol afforded $[Ru(CH{=}CHPh)(\kappa^2\text{-L})(CO)(PPh_3)_2]$ (**2a**–**2c**). Treatment of **1** with HL in THF gave $[RuCl(\kappa^2\text{-L})(CO)(PPh_3)_2]$ (**3a**–**3c**) contaminant with formation of styrene as byproduct. Interactions of **1** with HLa in dichloromethane led to isolation of a novel dinuclear ruthenium complex $[(CO)(PPh_3)(CHNCH_2Ph)Ru(\mu\text{-}Cl)_2(\mu\text{-}S)RuCl(CO)(PPh_3)]$ (**4a**) via N–H bond addition to styryl ligand. Complexes **2a**–**2c**, **3a**–**3c**, and **4a** were characterized by microanalyses, IR, and (^1H, ^{13}C, ^{31}P) NMR spectroscopies. The molecular structures of **3a**–**3c** and **4a** have been determined by single-crystal X-ray diffraction.

1. Introduction

Since the vinyl ruthenium complexes $[Ru(CR^1{=}CHR^2)Cl(CO)(PPh_3)_2]$ were firstly prepared by insertion of the alkyne into the Ru–H bond of $RuHCl(CO)(PPh_3)_3$ [1], considerable effort has been focused on the preparation, reactivity and mechanism study of such complexes [2–15]. Reactions related to vinyl ruthenium complexes mainly include (i) insertion of small molecules, such as CS_2 and CO_2, into ruthenium–alkenyl bond [2], (ii) addition of π-acid ligands such as carbon monoxide and isocyanide to yield coordinatively saturated compounds and subsequent migration of the vinyl group to form acyl complexes [3], (iii) substitution of chloride by bi- or polydentate ligand [12–18].

1-Methyl-2-mercaptoimidazole (also referred to as 1-methylimidazole-2-thiol, methimazole) [19–23], as well as 1-tertbutyl-2-mercaptoimidazole [24], can form stable complexes with a wide range of main group and transition metal ions. It could act as monodentate ligand in the neutral form and bidentate, three-electron S,N-donor ligand after deprotonation. Despite the extensive interest on the coordination chemistry of such mercaptoimidazoles as ligands for metal complexes, there has been little exploration of 1-aryl-2-mercaptoimidazole. Apart from one study [25] in which Mim^{Ph} (Mim^{Ph} = 2-mercapto-1-phenylimidazole) was used to construct a polymetric compound $[Ag_5I_5(Mim^{Ph})_4]_n$. Herein, we report the reactions of vinyl ruthenium complexes with 1-aryl-2-mercaptoimidazole ligands (Scheme 1).

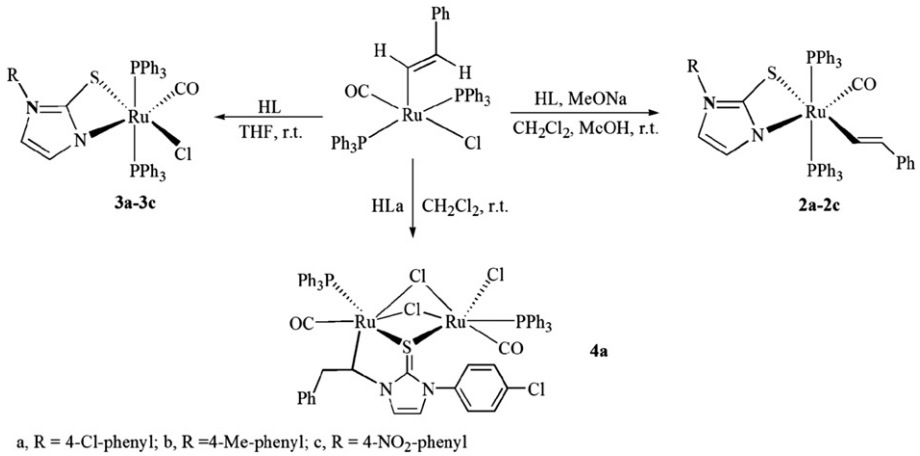
2. Results and discussion

2.1. Synthesis of ruthenium complexes (2a–2c), (3a–3c), and (4a) from vinyl ruthenium complex

It is well known that Wilton-Ely and coworkers have concentrated on the reactivity of alkenyl complexes $Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2$ and $Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole, a labile ligand), toward a series of bi- and tridentate ligands involving carboxylates, dithiocarbamates, dithiophosphinates, nitrogen–sulfur and nitrogen–oxygen mixed donors, polypyrazolylborate, and sulfur macrocycle ([9]aneS$_3$) [12–18]. A remarkable rearrangement of vinyl to sulfur atom was observed based on bulky *N*-heterocyclic carbenes dithiocarboxylate ligands [14]. In the initial experiments we investigated the reactions of 1-aryl-2-mercaptoimidazole (HL) with $Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2$ (**1**) using a slightly

* Corresponding author. Tel./fax: +86 555 2312041.
** Corresponding author. Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China. Tel./fax: +86 555 2312041.
E-mail address: jaiquan@ahut.edu.cn (A.-Q. Jia).

0022-328X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2012.01.010



Scheme 1. Synthesis of Complexes **2a**–**2c**, **3a**–**3c** and **4a**.

modified procedure reported by Wilton-Ely and coworkers [15]. The expected vinyl ruthenium complexes [Ru(CH=CHPh)(κ^2-L)(CO)(PPh$_3$)$_2$] (**2a**–**2c**) were obtained easily. However, treatment of **1** with HL without base in THF at room temperature gave [RuCl(κ^2-L)(CO)(PPh$_3$)$_2$] (**3a**–**3c**) in high yields, the styryl ligand in the starting ruthenium compound was substituted by L$^-$ as a bidentate ligand, releasing styrene. The PhCH=C*H*$_2$ proton signals (5.74 (dd, J = 17.6 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H)) [26] could be clearly observed in the ^{1}H NMR spectra of the crude products of **3a**–**3c**. The recrystallization of **3a**–**3c** from a THF/cyclohexane mixture (1:3) afforded analytically pure crystals suitable for an X-ray diffraction (vide infra), which clearly identified the solid-state structure of this species. In fact, displacement of styryl ligand by benzophenone imine and 2-vinylpyridine on Ru(CH=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$ in refluxing toluene has already been reported [27]. A pure sample of [(CO)(PPh$_3$)(CHNCH$_2$Ph)Ru(μ-Cl)$_2$(μ-S)RuCl(CO)(PPh$_3$)] (**4a**) was obtained only in small quantity from interactions of **1** with HLa in dichloromethane followed by recrystallization of the crude product in CH$_2$Cl$_2$/cyclohexane mixture (1:2). Possibly, substitution of PPh$_3$ by LHa via sulfur atom, followed by addition of N–H bond in HLa to phenylethenyl ligand, and trapping of chloride from dichloromethane solvent took place during the formation of **4a** according to its molecular structure. However, reactions of **1** with HLb and HLc in chloromethane or chloroform led to isolation of **3b** and **3c**, respectively (Scheme 1).

2.2. Single-crystal X-ray diffraction study of complexes (*3a*–*3c*) and (*4a*)

The structures of complexes **3a**–**3c** and **4a** were established by an X-ray diffraction study. The ORTEP representation of the molecular structures of them with selected interatomic distances and angles are shown in Figs. 1–4. Based on the crystallographic data, complexes **3a**–**3c** can be formulated as an 18-electron species with the formally six-coordinate Ru(II) atom. The ruthenium atoms in **3a**–**3c** are coordinated by 1-arylimidazole-2-thiolate, acting as a bidentate N,S-donor. The P–Ru–P angles for complexes **3a**–**3c** with mutually *trans* PPh$_3$ ligands are in the range of 175.21(3)–177.02(34)°. The bond distances of Ru–S in **3a**–**3c** lie in the range of 2.4383(9)–2.4948(8) Å, shorter than that in complex Ru(CH=CHC$_6$H$_4$Me-4)(κ^2-MI)(CO)(PPh$_3$)$_2$] (MI = 1-methylimidazole-2-thiolate, 2.5907(16) Å) [15]. The structure of **4a** clearly shows addition of N–H bond of HLa to the styryl ligand to give a new N(2)–C(1) bond (1.507(6) Å) as an integral part of a five-membered metallacycle. And it is obvious that the original C=C double bond of vinyl turns to be a typical C–C single bond (C(1)–C(2) 1.546(7) Å), inducting of chirality at C1. The terminal Ru(1)–Cl(2) bond length is 2.413(2) Å, shorter than those of bridged Ru–Cl bond distance (2.46–2.53 Å) in **4a**.

2.3. NMR characterization of complexes (*2a*–*2c*), (*3a*–*3c*), and (*4a*)

Complexes **2a**–**2c** were examined by multinuclear NMR spectroscopy and readily identified as vinyl complexes having PhCH=CH moiety compared to related compounds [15]. The ^{1}H NMR spectrum of **2a** showed both vinylic protons and imidazole ring protons (H^4, H^5, Chart 1), appearing at 7.92 (Hα, d, $^3J_{HH}$ = 16.4 Hz), 5.94 (Hβ, d, $^3J_{HH}$ = 16.4 Hz), 6.00 (s, im-H), 6.39 (s, im-H) ppm, respectively. Three low field triplets at 135.0 (t, J_{CP} = 3.6 Hz), 156.3 (t, J_{CP} = 11.0 Hz) and 206.3 ppm (t, J_{CP} = 16.2 Hz) were assigned to the β-carbon of the vinyl, α-carbon of the vinyl and the carbonyl ligand, respectively. The resonances of C^5 (114.7 ppm), C^4

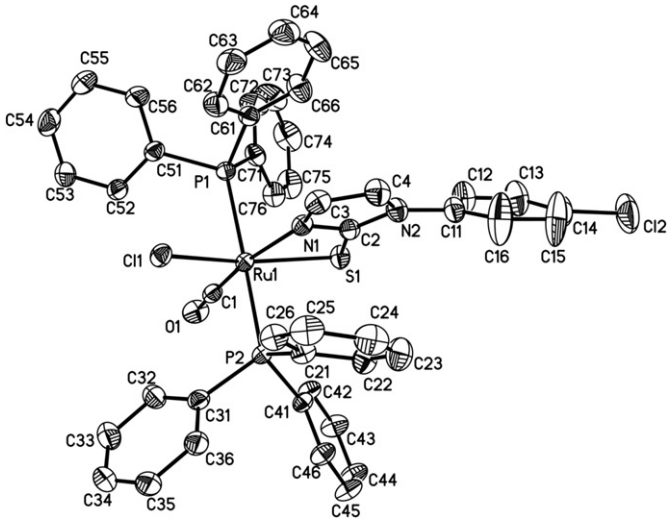


Fig. 1. Molecular structure of **3a**. Hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)–C(1) 1.861(3), Ru(1)–S(1) 2.4948(8), Ru(1)–N(1) 2.164(2), Ru(1)–P(1) 2.3952(8), Ru(1)–P(2) 2.3843(7), Ru(1)–Cl(1) 2.3992(8), S(1)–C(2) 1.714(3), N(1)–C(2) 1.316(3), N(1)–C(3) 1.370(3), N(1)–Ru(1)–S(1) 67.33(6), P(1)–Ru(1)–P(2) 175.43(2), Cl(1)–Ru(1)–S(1) 160.93 (3), C(1)–Ru(1)–N(1) 167.40(10).

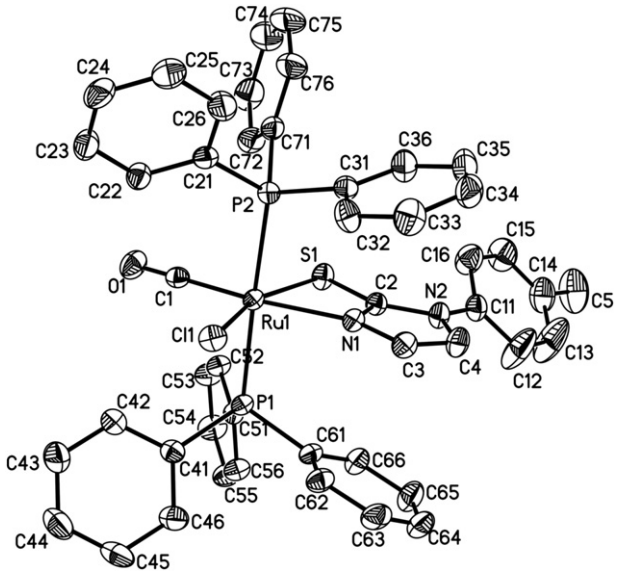


Fig. 2. Molecular structure of **3b**. Hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)–C(1) 1.850(3), Ru(1)–S(1) 2.4545(9), Ru(1)–N(1) 2.165(2), Ru(1)–P(1) 2.3836(8), Ru(1)–P(2) 2.3979(9), Ru(1)–Cl(1) 2.4056(8), S(1)–C(2) 1.723(3), N(1)–C(2) 1.320(4), N(1)–C(3) 1.363(4), N(1)–Ru(1)–S(1) 67.54(7), P(1)–Ru(1)–P(2) 175.21(3), Cl(1)–Ru(1)–S(1) 160.99 (3), C(1)–Ru(1)–N(1) 167.55(12).

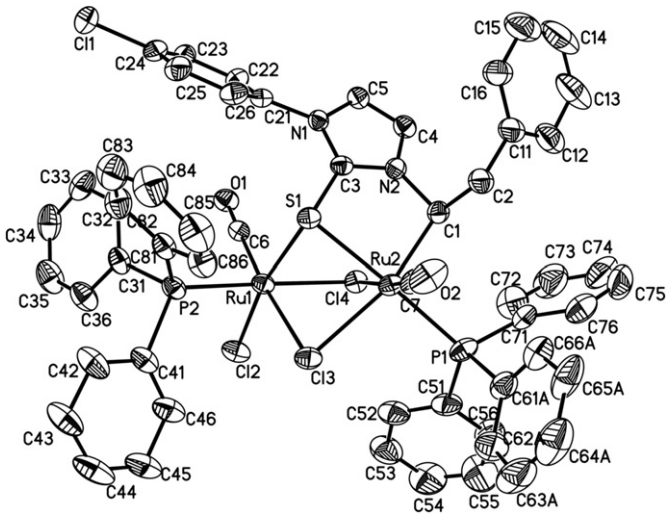


Fig. 4. Molecular structure of **4a**. Hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)–C(6) 1.821(5), Ru(1)–S(1) 2.417(1), Ru(1)–Cl(2) 2.413(2), Ru(1)–Cl(3) 2.506(2), Ru(1)–Cl(4) 2.490(2), Ru(1)–P(2) 2.295(2), Ru(2)–C(7) 1.811(6), Ru(2)–C(1) 2.097(5), Ru(2)–P(1) 2.334(2), Ru(2)–S(1) 2.430(1), Ru(2)–Cl(3) 2.535(2), Ru(2)–Cl(4) 2.465(1), C(1)–C(2) 1.546(7), C(2)–C(11) 1.492(9), C(1)–N(2) 1.507(6), C(3)–N(2) 1.328(6), C(3)–S(1) 1.748(5), Cl(3)–Ru(1)–C(6) 174.4(2), Cl(4)–Ru(1)–P(2) 177.7(5), Cl(2)–Ru(1)–S(1) 167.0(5), S(1)–Ru(2)–P(1) 175.3(5), C(7)–Ru(2)–Cl(4) 174.5(2), Cl(3)–Ru(2)–C(1) 163.3(1), S(1)–Ru(1)–P(2) 96.9(5).

(123.6 ppm) and NCN (153.5 ppm) in the imidazole ring were shown as three singlets. There was one ^{31}P signal at 42.0 ppm in the ^{31}P NMR, indicating *trans*-position of the two phosphine ligands. Similar spectroscopic data were observed for complexes **2b** and **2c**. The NMR data for **3a**–**3c** are in agreement with their crystal structures. One ^{31}P signal, around 38.3 ppm, was observed in their ^{31}P NMR spectra. Three singlets at 114.5, 123.0, and 152.3 ppm were identified as C^5, C^4 and NCN of the imidazole ring, respectively, shift upfield a little compared to those in **2a**. Although complex **4a** could not be obtained in sufficient quantities to allow the complete analytical and spectroscopic characterization, its ^{1}H NMR spectrum was readily assigned based on the comparison with that of **2a**. No resonances due to vinylic α and β-protons were observed. Instead, new resonances at 2.77 and 4.27 ppm were noted, which could be assigned to Ru*CHCH*$_2$Ph protons. The imidazole protons, appearing at 6.76 and 5.52 ppm, shift upfield compared to free ligand (6.84 ppm). There were two ^{31}P signals, appeared at 45.5 (PPh_3) and 42.8 (PPh_3) ppm, in ^{31}P NMR spectrum of **4a**.

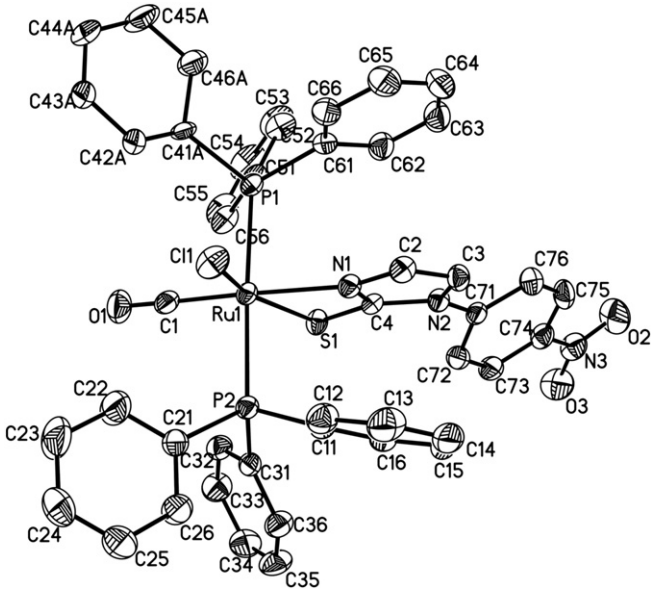


Fig. 3. Molecular structure of **3c**. Hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)–C(1) 1.839(4), Ru(1)–S(1) 2.4383(9), Ru(1)–N(1) 2.158(3), Ru(1)–P(1) 2.3899(9), Ru(1)–P(2) 2.3892(9), Ru(1)–Cl(1) 2.4141(10), S(1)–C(4) 1.720(3), N(1)–C(4) 1.312(4), N(2)–C(4) 1.383(4), N(1)–Ru(1)–S(1) 67.87(7), P(1)–Ru(1)–P(2) 177.02(3), Cl(1)–Ru(1)–S(1) 157.71 (4), C(1)–Ru(1)–N(1) 170.55(13).

3. Experimental

3.1. General comments

All the operations were carried out under pure nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled prior to use, [Ru(CH═CHPh)Cl(CO)(PPh_3)$_2$] [1], and 1-aryl-2-mercaptoimidazole [28] were prepared according to modified literature methods. NMR spectra were recorded on a BrukerALX400 spectrometer operating at 400, 100, and 162 MHz for ^{1}H, ^{13}C and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H), the residual solvent peak (^{13}C) and H_3PO_4 (^{31}P). Infrared spectra (KBr) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer with the use of pressed KBr pellets, and elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer.

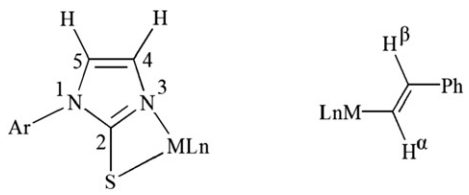


Chart 1. Numbering scheme for the 1-arylimidazole-2-thiolate (L) and styryl ligand.

3.2. Preparation of [Ru(CH=CHPh)(CO)(PPh_3)$_2$(κ^2-L)] (**2a**–**2c**)

To a suspension of [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] (80.0 mg, 0.10 mmol) and 1-aryl-2-mercaptoimidazole (0.10 mmol) in dichloromethane (5 mL) and methanol (2 mL) was added MeONa (6.0 mg, 0.12 mmol) in methanol (3 mL), the mixture was stirred for 1 h at room temperature, the solvent volume was concentrated under reduced pressure until pale yellow-green crystals precipitated. The product was filtered, washed with methanol (5 mL) and hexane (10 mL) and dried. For **2a**, yield: 83.0 mg (86%). IR (KBr): 1924 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$): 42.0 [s, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 5.94 [d, Hβ, 1H, J = 16.4 Hz], 6.00 [br, *im*-CH, 1H], 6.39 [br, *im*-CH, 1H], 6.47 [d, C_6H_4, 2H, J = 7.6 Hz], 6.78 [d, *o*-C_6H_5, 2H, J = 8.4 Hz], 6.88 [t, *p*-C_6H_5, 1H, J_{HH} = 7.2 Hz], 7.16 [t, *m*-C_6H_5, 2H, J_{HH} = 7.2 Hz], 7.20–7.32, 7.46–7.56 [m × 2, PC_6H_5, 30H], 7.92 [d, Hα, 1H, J_{HH} = 16.4 Hz] ppm. ^{13}C NMR ($CDCl_3$): δ 206.3 [t, CO, J_{CP} = 16.2 Hz], 156.3 [t, Cα, J = 11.0 Hz], 153.5 [s, NCN], 141.7 [s, *ipso*-Ph], 135.3 [s, *ipso*-C_6H_4], 135.0 [t, Cβ, J = 3.6 Hz], 134.3 [t, *o*/*m*-PC_6H_5, J_{CP} = 5.4 Hz], 132.9 [t, *ipso*-PC_6H_5, J_{CP} = 21.2 Hz], 131.7 [s, *o*/*m*-C_6H_4], 129.1 [s, *p*-PC_6H_5], 128.8 [s, *o*/*m*-C_6H_4], 127.5 [s, *o*/*m*-Ph], 127.5 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.6 Hz], 124.3 [s, *p*-C_6H_4], 123.6 [s, NC^{4}H], 123.3 [s, *o*/*m*-Ph], 123.3 [s, *p*-Ph], 114.7 [s, NC^{5}H] ppm. Anal. Calc. for $C_{54}H_{43}ClN_2OP_2RuS$: C 67.07; H 4.49; N 2.90; Found: C, 66.99; H, 4.47; N, 2.94. For **2b**, Yield: 80.4 mg (85%). IR (KBr): 1916 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$): 42.0 [s, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 2.25 [s, Me, 3H], 5.97 [d, Hβ, 1H, J = 14.4 Hz], 6.00 [br, *im*-CH, 1H], 6.37 [br, *im*-CH, 1H], 6.48 [d, C_6H_4, 2H, J = 6.8 Hz], 6.69 [d, *o*-C_6H_5, 2H, J = 6.4 Hz], 6.89 [t, *p*-C_6H_5, 1H, J_{HH} = 7.2 Hz], 6.96–7.06 [m, *m*-C_6H_5 + C_6H_4, 4H], 7.01–7.22, 7.45–7.55 [m × 2, PC_6H_5, 30H], 7.94 [d, Hα, 1H, J_{HH} = 14.4 Hz] ppm. ^{13}C NMR ($CDCl_3$): δ 206.4 [t, CO, J_{CP} = 16.0 Hz], 156.7 [t, Cα, J = 10.8 Hz], 153.3 [s, NCN], 141.8[s, *ipso*-Ph], 136.0 [s, *ipso*-C_6H_4], 134.9 [t, Cβ, J = 3.6 Hz], 134.3 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.4 Hz], 134.3 [s, *o*/*m*-C_6H_4], 133.0 [t, *ipso*-PC_6H_5, J_{CP} = 21.1 Hz], 129.2 [s, *o*/*m*-C_6H_4], 129.1 [s, *p*-PC_6H_5], 127.5 [s, *o*/*m*-Ph], 127.4 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.6 Hz], 124.3 [s, *p*-C_6H_4], 123.2 [s, *o*/*m*-Ph], 122.8 [s, *p*-Ph], 122.4 [s, NC^{4}H], 115.1 [s, NC^{5}H], 20.9 [s, Me] ppm. Anal. Calc. for $C_{55}H_{46}N_2OP_2RuS$: C 69.75; H 4.90; N 2.96; Found: C, 69.80; H, 4.88; N 2.99. For **2c**, yield 90.0 mg (92%). IR (KBr): 1918 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$): 42.0 [s, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 5.95 [d, Hβ, 1H, J = 16.4 Hz], 6.10 [br, *im*-CH, 1H], 6.41 [br, *im*-CH, 1H], 6.48 [d, *o*-C_6H_5, 2H, J = 7.6 Hz], 6.90 [t, *p*-C_6H_5, 1H, J_{HH} = 7.2 Hz], 7.02 [t, *m*-C_6H_5, 2H, J_{HH} = 7.2 Hz], 7.16 [d, C_6H_4, 2H, J = 8.8 Hz], 7.20–7.30, 7.48–7.52 [m × 2, PC_6H_5, 30H], 7.91 [dt, Hα, 1H, J_{HH} = 16.4 Hz], 8.08 [d, C_6H_4, 2H, J = 9.2 Hz] ppm. ^{13}C NMR ($CDCl_3$): δ 206.2 [t, CO, J_{CP} = 16.2 Hz], 155.6 [t, Cα, J = 9.9 Hz], 154.4 [s, NCN], 145.0 [s, *ipso*-Ph], 142.0 [s, *ipso*-C_6H_4], 141.5 [s, *p*-C_6H_4], 135.1 [t, Cβ, J = 3.6 Hz], 134.3 [t, *o*/*m*-PC_6H_5, J_{CP} = 5.4 Hz], 132.8 [t, *ipso*-PC_6H_5, J_{CP} = 21.3 Hz], 129.2 [s, *p*-PC_6H_5)], 127.6 [s, *o*/*m*-Ph], 127.5 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.6 Hz], 124.5 [s, *o*/*m*-C_6H_4], 124.3 [s, *o*/*m*-C_6H_4], 124.2 [s, *o*/*m*-Ph], 123.5 [s, *o*/*m*-Ph], 121.7 [s, NC^{4}H], 114.1 [s, NC^{5}H] ppm. Anal. Calc. for $C_{54}H_{43}N_3O_3P_2RuS$: C 66.32; H 4.43; N 4.30; Found: C, 66.38; H, 4.44; N 4.34.

3.3. Preparation of [RuCl(CO)(PPh_3)$_2$(κ^2-L)] (**3a**–**3c**)

To a solution of [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] (40.0 mg, 0.05 mmol) in THF (10 mL) was added 1-aryl-2-mercaptoimidazole (0.05 mmol), the mixture was stirred overnight to yield a yellow or red solution. The solvent was evaporated in vacuum and washed with *n*-hexane. Slow diffusion of cyclohexane to THF solution afforded yellow or red crystals of **3a**–**3c**. For **3a**, yield: 40.5 mg (90%). IR (KBr): 1921 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$): 38.3 [s, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 5.91 [d, *im*-CH, 1H, J = 1.6 Hz], 6.30 [d, *im*-CH, 1H, J = 2.0 Hz], 6.78 [d, C_6H_4, 2H, J = 8.8 Hz], 7.20 [d, C_6H_4, 2H, J = 8.8 Hz], 7.27–7.32, 7.57–7.62 [m × 2, PC_6H_5, 30H] ppm. ^{13}C NMR ($CDCl_3$): δ 206.2 [t, CO, J_{CP} = 16.0 Hz], 152.3 [s, NCN], 135.1 [s, *ipso*-C_6H_4], 134.9 [t, *o*/*m*-PC_6H_5, J_{CP} = 5.5 Hz], 133.0 [t, *ipso*-PC_6H_5, J_{CP} = 21.8 Hz], 132.4 [s, *o*/*m*-C_6H_4], 130.0 [s, *p*-PC_6H_5], 129.7 [s, *o*/*m*-C_6H_4], 128.1 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.6 Hz], 126.1 [s, *p*-C_6H_4], 123.0 [s, NC^{4}H], 114.5 [s, NC^{5}H] ppm. Anal. Calc. for $C_{46}H_{36}Cl_2N_2OP_2RuS$: C 61.47; H 4.04; N 3.12; Found: C, 61.45; H, 4.09; N 3.13. For **3b**, 38.6 mg, yield (88%). IR (KBr): 1919 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$):

Table 1
Crystallographic data and experimental details for complexes (**3a**·**0.5C$_6$H$_{12}$**, **3b**·**0.5C$_6$H$_{12}$**, **3c**·**CH$_2$Cl$_2$**) and (**4a**·**CH$_2$Cl$_2$**).

Complex	**3a**·**0.5C$_6$H$_{12}$**	**3b**·**0.5C$_6$H$_{12}$**	**3c**·**CH$_2$Cl$_2$**	**4a**·**CH$_2$Cl$_2$**
Empirical formula	$C_{49}H_{42}Cl_2N_2OP_2RuS$	$C_{50}H_{45}ClN_2OP_2RuS$	$C_{47}H_{38}Cl_3N_3O_3P_2RuS$	$C_{56}H_{46}N_2O_2Cl_6P_2SRu_2$
Formula weight	940.82	920.40	994.22	1290.31
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	10.885(2)	10.8794(10)	18.862(3)	19.696(2)
b (Å)	14.678(3)	14.6864(13)	14.552(2)	11.0868(12)
c (Å)	27.451(5)	27.565(2)	17.857(3)	26.305(3)
α (°)	90	90	90	90
β (°)	90.887(2)	91.0950	110.342(2)	102.4210(10)
γ (°)	90	90	90	90
V (Å^3)	4385.4(14)	4403.4(7)	4595.6(11)	5609.8(10)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.425	1.388	1.437	1.528
Temperature (K)	296(2)	296(2)	296(2)	296(2)
F(000)	1928	1896	2024	2602
μ(Mo-Kα) (mm^{-1})	0.639	0.576	0.674	0.961
Total refln	26826	27139	28337	34422
Independent refln	9941	10089	10495	12795
R_{int}	0.0288	0.0502	0.0450	0.0525
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0391, 0.1013	0.0423, 0.0919	0.0505, 0.1241	0.0570, 0.1604
*R*1, *wR*2 (all data)	0.0548, 0.1110	0.0770, 0.1058	0.0791, 0.1367	0.1054, 0.1905
Parameter	508	509	596	680
GoF[c]	1.023	0.987	0.981	1.008

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

38.4 [s, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 2.28 [s, Me, 3H], 5.90 [d, *im*-CH, 1H, J = 2.0 Hz], 6.26 [d, *im*-CH, 1H, J = 1.6 Hz], 6.69 [d, C_6H_4, 2H, J = 8.8 Hz], 7.03 [d, C_6H_4, 2H, J = 8.0 Hz], 7.22–7.28, 7.58–7.63 [m × 2, PC_6H_5, 30H] ppm. ^{13}C NMR ($CDCl_3$): δ 206.2 [t, CO, J_{CP} = 15.8 Hz], 152.0 [s, NCN], 136.8 [s, *ipso*-C_6H_4], 134.9 [t, *o*/*m*-PC_6H_5, J_{CP} = 5.5 Hz], 134.1 [s, *o*/*m*-C_6H_4], 133.1 [t, *ipso*-PC_6H_5, J_{CP} = 21.7 Hz], 130.1 [s, *o*/*m*-C_6H_4], 129.9 [s, *p*-PC_6H_5], 128.1 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.8 Hz], 125.6 [s, *p*-C_6H_4], 121.8 [s, NC^4H], 114.9 [s, NC^5H], 21.4 [s, Me] ppm. Anal. Calc. for $C_{47}H_{39}ClN_2OP_2RuS$: C 64.27; H 4.48; N 3.19; Found: C, 64.19; H, 4.44; N, 3.23. For **3c**, 38.6 mg, yield (85%). IR (KBr): 1940 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$): 38.2 [s, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 6.03 [d, *im*-CH, 1H, J = 1.6 Hz], 6.32 [d, *im*-CH, 1H, J = 1.6 Hz], 6.71 [d, C_6H_4, 2H, J = 3.7 Hz], 7.24–7.29, 7.57–7.62 [m × 2, PC_6H_5, 30H], 8.12 [d, C_6H_4, 2H, J = 3.6 Hz] ppm. ^{13}C NMR ($CDCl_3$): δ 205.3 [t, CO, J_{CP} = 15.3 Hz], 152.9 [s, NCN], 145.1 [s, *ipso*-C_6H_4], 141.2 [s, *p*-C_6H_4], 134.4 [t, *o*/*m*-PC_6H_5, J_{CP} = 5.4 Hz], 132.4 [t, *ipso*-PC_6H_5, J_{CP} = 21.9 Hz], 129.6 [s, *p*-PC_6H_5], 127.6 [t, *o*/*m*-PC_6H_5, J_{CP} = 4.8 Hz], 126.3 [s, *o*/*m*-C_6H_4], 124.9 [s, *o*/*m*-C_6H_4], 120.6 [s, NC^4H], 113.4 [s, NC^5H] ppm. Anal. Calc. for $C_{46}H_{36}ClN_3O_3P_2RuS$: C 60.72; H 3.99; N 4.62; Found: C, 60.45; H, 4.03; N, 4.67.

3.4. Preparation of [(CO)(PPh_3)(CHNCH_2Ph)Ru(μ-Cl)$_2$(μ-S)RuCl(CO)(PPh_3)] (**4a**)

To a solution of [Ru(CH═CHPh)Cl(CO)(PPh_3)$_2$] (40.0 mg, 0.05 mmol) in dichloromethane (10 mL) was added 1-4-chlorophenyl-2-mercaptoimidazole (10.5 mg, 0.05 mmol), the mixture was then stirred at room temperature overnight to yield a yellow solution. The solvent was evaporated in vacuum and washed with *n*-hexane. Pure **4a** was obtained by crystallization in dichloromethane/*n*-hexane. Yield: 18.0 mg (30%). IR (KBr): 1918, 1921 ν (CO) cm^{-1}. ^{31}P NMR ($CDCl_3$): 45.5, 42.1 [s × 2, PPh_3] ppm. ^{1}H NMR ($CDCl_3$): 7.98–7.00 [m, Ph + C_6H_4, 36H], 6.76 [d, *im*-CH, 1H, J = 2.0 Hz], 6.28 [d, C_6H_4, 2H, J = 7.2 Hz], 6.22 [m, 1H, Ph], 5.52 [br, *im*-CH, 1H], 4.27 [m, Ru*CH*CH_2Ph, 1H], 2.77 [m, RuCHCH_2Ph, 2H] ppm. Anal. Calc. for $C_{55}H_{44}Cl_4N_2O_2P_2SRu_2$: C 54.92; H 3.69; N 2.33; Found: C, 55.01; H, 3.65; N, 2.37.

3.5. X-ray diffraction measurements

Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT [29]. The data were corrected for absorption using the program SADABS [30]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [31,32]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96, C_{sp2}–H = 0.93), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or oxygen atoms before the final cycle of least-squares refinement. One phenyl in **3c**·CH_2Cl_2 was isotropically refined due to disorder. Crystallographic data and experimental details for **3a**·0.5C_6H_{12}, **3b**·0.5C_6H_{12}, **3c**·CH_2Cl_2 and **4a**·CH_2Cl_2 are given in Table 1.

Acknowledgments

This project was supported by the Natural Science Foundation of China (20771003) and the Hong Kong Research Grants Council (project no. 601708).

Appendix A. Supplementary material

CCDC 854737–854740 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] M.R. Torres, A. Vegas, A. Santos, J. Ros, J. Organomet. Chem. 309 (1986) 169–177.
[2] M.R. Torres, A. Perales, J. Ros, Organometallics 7 (1988) 1223–1224.
[3] H. Loumrhari, J. Ros, M.R. Torres, A. Santos, A.M. Echavarren, J. Organomet. Chem. 411 (1991) 255–261.
[4] B. Gómez-Lor, A. Santos, M. Ruiz, A.M. Echavarren, Eur. J. Inorg. Chem. (2001) 2305–2310.
[5] H. Xia, T.B. Wen, Q.Y. Hu, G. Jia, Organometallics 24 (2005) 562–569.
[6] S.K. Seetharaman, M.-C. Chung, U. Englich, K. Ruhlandt-Senge, M.B. Sponsler, Inorg. Chem. 46 (2007) 561–567.
[7] S. Jung, C.D. Brandt, J. Wolf, H. Werner, Dalton Trans. (2004) 375–383.
[8] D.J. Huang, K.B. Renkema, K.G. Caulton, Polyhedron 25 (2006) 459–468.
[9] M. Pichlmaier, R.F. Winter, M. Zabel, S. Záliš, J. Am. Chem. Soc. 131 (2009) 4892–4903.
[10] X.-H. Wu, J.H. Liang, J.-L. Xia, S. Jin, G.-A. Yu, S.H. Liu, Organometallics 29 (2010) 1150–1156.
[11] Y. Maruyama, K. Yamamura, T. Sagawa, H. Katayama, F. Ozawa, Organometallics 19 (2000) 1308–1318.
[12] A.F. Hill, C.T. Ho, J.D.E.T. Wilton-Ely, Chem. Commun. (1997) 2207–2208.
[13] J.D.E.T. Wilton-Ely, P.J. Pogorzelec, S.J. Honarkhah, D.A. Tocher, Organometallics 24 (2005) 2862–2874.
[14] S. Naeem, A.L. Thompson, L. Delaude, J.D.E.T. Wilton-Ely, Chem. Eur. J. 16 (2010) 10971–10974.
[15] J.D.E.T. Wilton-Ely, S.J. Honarkhah, M. Wang, D.A. Tocher, A.M.Z. Slawin, Dalton Trans. (2005) 1930–1939.
[16] J.C. Green, A.L. Hector, A.F. Hill, S. Lin, J.D.E.T. Wilton-Ely, Organometallics 27 (2008) 5548–5558.
[17] S. Naeem, A.L. Thompson, A.J.P. White, L. Delaudec, J.D.E.T. Wilton-Ely, Dalton Trans. 40 (2011) 3737–3747.
[18] J.D.E.T. Wilton-Ely, M. Wang, S.J. Honarkhah, D.A. Tocher, Inorg. Chim. Acta 358 (2005) 3218–3226.
[19] A. Cingolani, E.F. Marchetti, C. Pettinari, B.W. Skelton, A.H. White, Inorg. Chem. 41 (2002) 1151–1161.
[20] Y. Matsunaga, K. Fujisawa, N. Amir, Y. Miyashita, K.-I. Okamoto, J. Coord. Chem. 58 (2005) 1047–1061.
[21] F. Isaia, M.C. Aragoni, A. Garau, V. Lippolis, A. Pintus, Dalton Trans. 40 (2011) 4505–4513.
[22] R.D. Dewhurst, A.R. Hansen, A.F. Hill, M.K. Smith, Organometallics 25 (2006) 5843–5846.
[23] M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 28 (2009) 2787–2798.
[24] J.G. Melnick, K. Yurkerwich, G. Parkin, Inorg. Chem. 48 (2009) 6763–6772.
[25] A. Beheshti, W. Clegg, R. Khorramdin, V. Nobakht, L. Russo, Dalton Trans. 40 (2011) 2815–2821.
[26] T. Bekele, S.R. Brunette, M.A. Lipton, J. Org. Chem. 68 (2003) 8471–8479.
[27] M.L. Buil, M.A. Esteruelas, E. Goni, M. Oliván, E. Oñate, Organometallics 25 (2006) 3076–3083.
[28] K. Matsuda, I. Yanagisawa, Y. Isomura, Synth. Commun. 27 (1997) 3565–3571.
[29] G.M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
[30] SMART and SAINT+ for Windows NT Version 6.02a, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.
[31] G.M. Sheldrick, SHELXTL Software Reference Manual, Version 5.1, Bruker AXS Inc., Madison, WI, 1997.
[32] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112–122.