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Reaction of ruthenium complexes containing heterocyclic thiazine–thione ligand

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Abstract

Treatment of the ruthenium complex [Ru]–C=C(Ph)C(=S)N(Ph)C(=NPh)S (**3**, [Ru] = Cp(dppe)Ru) containing a heterocyclic [1,3]-thiazine-4-thione six-membered-ring ligand with various organic halides results in alkylation at the thione sulfur terminus of the ligand to yield [Ru]–C=C(Ph)C(SCH$_2$R)N(Ph)C(=NPh)S][X] (**4a**, R = CN, X = I; **4b**, R = Ph, X = Br; **4c**, R = CH = CH$_2$, X = I, **4d**, R = *p*-C$_6$H$_4$CF$_3$, X = Br). Similarly the reaction of **3** with $HgCl_2$ at room temperature affords [Ru]–C=C(Ph)C(SHgCl)N(Ph)C(=NPh)S][Cl] (**5**). Transformation of **5** to the cationic vinylidene complex {[Ru]=C=C(Ph)C(O)NHPh}$_2$[Hg$_2$Cl$_6$] (**6**) readily occurred in the air. The structures of **4c** and **6** are determined by single crystal X-ray diffraction analysis.

Keywords: Ruthenium; Thiazine–thione; Alkylation

1. Introduction

Recently we reported that the reaction of isocyanates and isothiocyanates with two ruthenium acetylide complexes resulted in sequential additions of the organic substrate to the acetylide ligand to produce novel heterocyclic ligands [1]. Namely, treatment of [Ru]–C≡CPh (**1**, [Ru] = Cp(dppe)Ru) with a 10-fold excess of PhNCS afforded the [2+2] cycloaddition product [Ru]–C=C(Ph)C(=NPh)S (**2**). If the reaction was carried out for 7 days at room temperature, the [2+2+2] cycloaddition product [Ru]–C=C(Ph)C(=S)N(Ph)C(=NPh)S (**3**) could be isolated [1] in moderate yield. In search for new chemical properties of such ruthenium complexes containing heterocyclic ligand, we performed the electrophilic addition reaction of **2** to form the *S*-alkylation and *N*-alkylation vinylidene complexes. Subsequent cyclization reactions of these vinylidene complexes induced by deprotonation generates neutral heterocyclopentenyl complexes [2]. We also reported that the reaction of the ruthenium dihydrofuranyl complex (C$_5$Me$_5$)(dppp)Ru–C=C(Ph)CH(CN)C(CH$_3$)$_2$O with electrophiles, such as XCH$_2$R, H^+ and $HgCl_2$, afforded a series of cationic carbene complexes [3]. Formation of these cationic carbene complexes occurs via selective addition of electrophiles to the nucleophilic β-carbon of the five-membered ring. New reactivity of these ruthenium complexes containing heterocyclic ligand toward electrophiles intrigues us to explore the reactivity of such complexes. One possible site for the electrophilic addition is the sulfur atom of a thioketone group [4–6]. Herein, we report the electrophilic addition of organic halides to the six-membered-ring heterocycles of complex **3**. Addition of electrophiles is found to take place at the thione sulfur terminus to give new cationic six-membered-ring complexes. In the case where $HgCl_2$ is

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used as the electrophile, transformation of the product takes place at room temperature in the presence of excess $HgCl_2$ in the air to give a new cationic vinylidene complex. Structure of two relevant complexes is confirmed by single crystal X-ray diffraction analysis.

2. Results and discussion

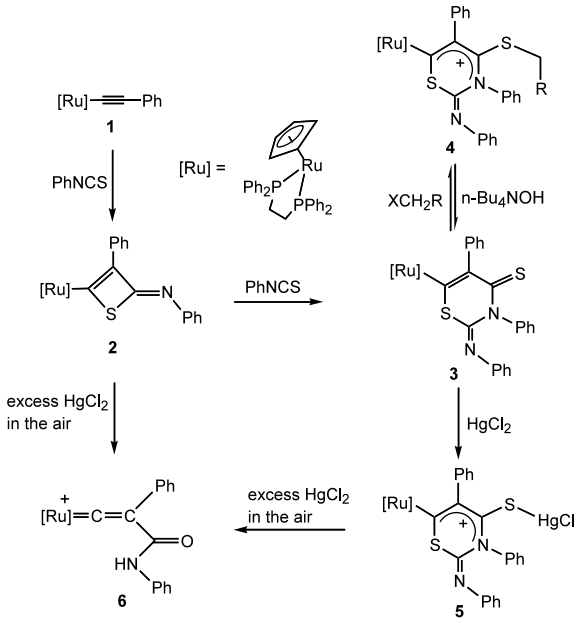
2.1. Electrophilic addition of ruthenium six-membered-ring complex

When treated with ICH_2CN in $CHCl_3$ at room temperature, the orange–yellow solution of **3** changed to purple in 5 min. The reaction finished in 1 h yielding the cationic complex [Ru]–C=C(Ph)C(SCH_2CN)N(Ph)C(=NPh)S][I] (**4a**). The electrophilic addition was found to take place at the thione sulfur terminus of the heterocyclic six-membered ring ligand. Chemical shifts of **3** and **4a** in ^{31}P-NMR spectra differs only slightly. The ^{31}P-NMR resonance of **3** appears at δ 99.27 and the resonance attributed to **4a** appears at δ 99.33. In the ^{1}H-NMR spectrum of **3**, the singlet resonance at δ 3.68 is assigned to the Cp group and multiplet resonance at δ 2.65–2.30 is assigned to dppe. For **4a**, the ^{1}H–Cp resonance shifts to δ 4.04 and the singlet resonance at δ 2.84 is assigned to the CH_2 group. The FAB mass spectrum of **4a** shows a parent peak at $m/z = 976.1$. In the presence of excess NH_4PF_6, the counter ion is replaced by PF_6^-.

Reactions of **3** with other organic halides XCH_2R (R = Ph, X = Br; R = CH=CH_2, X = I; R = p-$C_6H_4CF_3$, X = Br) give [Ru]–C=C(Ph)C(SCH_2R)N(Ph)C(=NPh)S][X] (**4b**, = Ph, X = Br; **4c**, R = CH=CH_2, X = I; **4d**, R = p-$C_6H_4CF_3$, X = Br), respectively, (Scheme 1). The most characteristic spectroscopic data of these cationic six-membered-ring complexes consist of a singlet Cp resonance at δ 4.02 ± 0.03 in ^{1}H-NMR spectra and a singlet resonance at δ 99.0 ± 1.0 in ^{31}P-NMR spectra. Complexes **4a**–**d** are purple solids, stable in the air, soluble in CH_2Cl_2, moderately soluble in methanol and acetone, insoluble in diethyl ether and n-hexane. Reaction of **4a**–**d** with n-Bu_4NOH results in removal of the CH_2R groups and gives back complex **3**. Disappearance of the ^{13}C-NMR data of the thione group in **3** provides useful information of the reaction. The ^{13}C resonance at δ 180 was previously assigned to the thione carbon atom in **3**. Alkylation at the thione group results in appearance of two ^{13}C resonances at δ 152.8, 149.0 assigned to carbon atoms of two NCS groups in the six-membered ring. Alkylation at the thione sulfur atom is also confirmed by an X-ray diffraction analysis of **4c** described below.

Treatment of **3** with excess $HgCl_2$ under nitrogen resulted in a similar electrophilic-addition reaction at the same site and afforded the cationic complex [Ru]–C=C(Ph)C(SHgCl)N(Ph)C(=NPh)S][Cl] (**5**). Upon addition of $HgCl_2$, the orange–yellow solution of **3** also changed to deep-purple immediately. The ^{31}P-NMR resonance of **5** appears at δ 100.53 again shifts only slightly from that of **3** indicating that the addition takes place at the six-membered ring ligand. In the ^{1}H-NMR spectrum of **5**, the Cp resonance appears at δ 3.85. The FAB mass spectrum of **5** shows a parent peak at $m/z = 1173.1$. Like **4a**–**d**, complex **5** is stable in the air, soluble in CH_2Cl_2, moderately soluble in methanol and acetone, insoluble in diethyl ether and n-hexane.

If the solution of complex **5** is stored in the presence of $HgCl_2$ in the air for more than 1 h, color of the solution changed from deep purple to purple-red gradually. The reaction finished in 3 h to yield the red cationic vinylidene complex [Ru]=C=C(Ph)C(O)NHPh]$_2$[Hg_2Cl_6] (**6**) [7]. The ^{31}P-NMR resonance of **6** appears at δ 78.33 significantly shifted from that of **5** at δ 100.53. In the ^{1}H-NMR spectrum of **6**, the Cp resonance at δ 5.58 and two multiple resonances of dppe at δ 3.23 and 3.03 indicate that the ligand environment around the metal should have changed. In the ^{13}C-NMR spectrum, a highly-deshielded triplet resonance at δ 348.7 with $J_{C-P} = 15.4$ Hz shows that **6** is a vinylidene complex and two singlet resonances at δ 190.1 and 93.2 are assigned to the C=O and Cp groups of **6**, respectively. Complex **6** is a red solid, stable in the air, moderately soluble in $CHCl_3$, CH_2Cl_2 and acetone and insoluble in ether and hexane. Re-crystallization of **6** from acetone–diethyl ether (1:2) afforded red single crystals, suitable for X-ray diffraction study. Reaction of **6** with bases such as n-Bu_4NOH, DBU, $NaNH_2$ and



Scheme 1.

$(C_2H_5)_2NH$ resulted in removal of the amido group PhNHCO- and afforded the metal acetylide complex **1** (see Scheme 1).

Complex **6** could also be obtained by the reaction of [Ru]–C≡C(Ph)C(=NPh)S (**2**) with excess $HgCl_2$ in the air. Treatment of **2** with excess $HgCl_2$ in CH_2Cl_2 caused color change of the solution from yellow to purple-red immediately and afforded **6** with high yield. According to our previous report [2], it could afford a cationic vinylidene intermediate [Ru]=C=C(Ph)C(=NPh)-SHgCl][Cl] first, and then the intermediate could then be oxidized in the air to give **6**. The oxidation reaction is fast and the proposed intermediate is observed by NMR spectra.

2.2. Structure determination of *4c* and *6*

The molecular structure of **4c** is determined by an X-ray diffraction study. An ORTEP diagram of **4c** is shown in Fig. 1, crystal and intensity collection data of **4c** are given in Table 1 and selected bond distances and bond angles are listed in Table 2. The final R indices for $I > 2\sigma(I)$ of $R_1 = 0.0951$, $wR_2 = 0.2123$ and R indices of all data of $R_1 = 0.1933$, $wR_2 = 0.2584$ are a little too high. These high values are partly due to poor quality of the crystal and a 30% disorder of the $CH_2CH{=}CH_2$ group, the crystal data can only be used as a reference for the structure of **4c**. The heterocyclic six-membered ring is essentially planar. The Ru–C1 bond length of 2.029(8) Å is typical of a Ru–C single bond, and the C1–C2 bond length of 1.499(11) Å is obviously longer than a typical double bond. The C3–N2 bond length of 1.391(11) Å is between the C4–N1 double bond (1.232(11) Å) and C4–N2 single bond (1.433(11) Å).

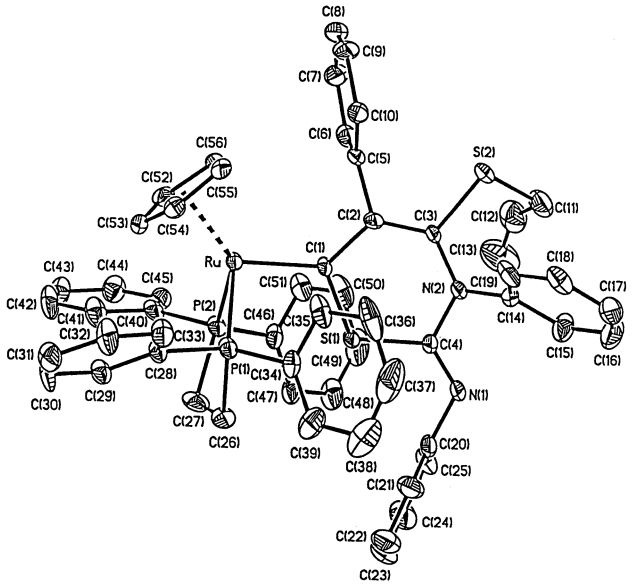


Fig. 1. An ORTEP drawing of **4c** with thermal cllipsoid shown at the 30% probability level.

Table 1
Crystal and intensity collection data for [Cp(dppe)Ru–C≡C(Ph)C(SCH$_2$CH=CH$_2$)N(Ph)C(=NPh)S][PF$_6$] (**4c**) and [Cp(dppe)Ru=C=C(Ph)C(O)NHPh]$_2$[Hg$_2$Cl$_6$] (**6**)

Molecular formula	$C_{57}H_{54}F_6N_2OP_3RuS_2$ (**4c**)	$C_{92}H_{78}Cl_6Hg_2N_2O_2P_2Ru_2$ (**6**)
Space group	$P2_1/c$	$P\bar{1}$
Crystal system	Monoclinic	Triclinic
a (Å)	18.7860(2)	12.7619(1)
b (Å)	13.6014(2)	12.8464(2)
c (Å)	21.15500(10)	13.6499(2)
α (°)	90	90.686(1)
β (°)	92.1340(10)	94.353(1)
γ (°)	90	103.499(1)
V (Å^3)	5401.69(10)	2168.71(5)
Z	4	1
Crystal size (mm)	0.40 × 0.25 × 0.03	0.45 × 0.30 × 0.30
2θ Range (°)	1.08–25.16	1.50–26.37
Total number of reflections	9573	8823
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0951$, $wR_2 = 0.2123$	$R_1 = 0.0286$, $wR_2 = 0.0572$
R indices (all data)	$R_1 = 0.1933$, $wR_2 = 0.2584$	$R_1 = 0.0389$, $wR_2 = 0.0620$

Table 2
Selected bond distances (Å) and angles (°) of [Cp(dppe)Ru–C≡C(Ph)C(SCH$_2$CH=CH$_2$)N(Ph)C(=NPh)S][I] (**4c**)

Ru–P1	2.313(3)	Ru–P2	2.320(2)
Ru–C1	2.032(8)	C1–C2	1.487(12)
C2–C3	1.361(12)	C3–N2	1.398(12)
C4–N2	1.437(12)	S1–C1	1.753(9)
S1–C4	1.755(9)	S2–C3	1.788(9)
S2–C11	1.827(14)	C11–C12	1.52(4)
C12–C13	1.15(5)		
P1–Ru–P2	83.85(10)	Ru–C1–C2	132.7(6)
Ru–C1–S1	114.3(4)	C1–C2–C3	123.6(8)
C2–C3–N2	127.7(8)	N2–C4–S1	122.8(7)
C2–C1–S1	113.0(6)	C3–S2–C11	102.4(5)
S2–C11–C12	109(2)	C11–C12–C13	137(4)
C1–S1–C4	111.9(4)		

The planarity of the six-membered-ring along with these bond distance informations indicates that there should be a conjugation in the cyclic ligand. The C3–S2 single bond in **4c** is 1.787(8) Å, which is comparable with the C1–S1 single bond (1.744(8) Å).

The red single crystals of **6** were obtained by recrystallization of **6** from acetone–diethyl ether (1:2) for 2 days. The structure of **6** is determined by a single-crystal X-ray diffraction analysis. An ORTEP drawing of **6** is shown in Fig. 2. The crystal and intensity collection data of **6** are given in Table 1 and selected bond distances and bond angles are given in Table 3. The presence of the vinylidene ligand is clearly indicated by the fact the Ru–C1 bond length of 1.842(3) Å is typical of a Ru=C double bond, and the bond length of C1–C2 and C2–C3 of 1.323(4) Å and 1.520(4) Å are typical of a

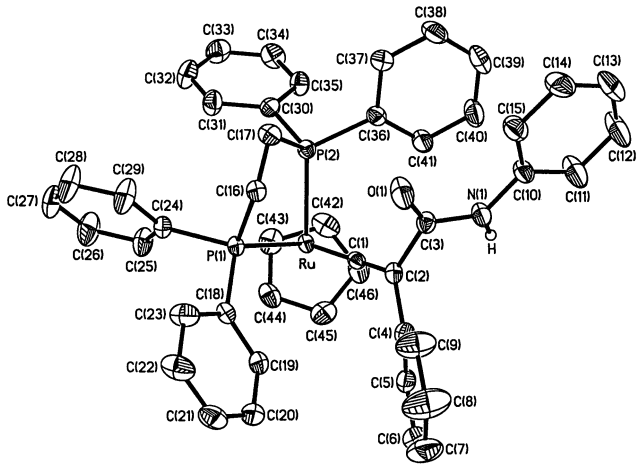


Fig. 2. An ORTEP drawing of **6** with thermal cllipsoid shown at the 30% probability level.

Table 3
Selected bond distances (Å) and angles (°) of [Cp(dppe)Ru=C=C(Ph)C(O)NHPh]$_2$[Hg_2Cl_6] (**6**)

Ru–P1	2.3028(7)	Ru–C1	1.842(3)
Ru–P2	2.3114(8)	O1–C3	1.208(4)
N1–C10	1.417(4)	C2–C4	1.475(4)
N1–C3	1.332(4)	C1–C2	1.323(4)
C2–C3	1.520(4)		
C1–Ru–P1	84.94(9)	C1–Ru–P2	91.70(9)
P1–Ru–P2	81.86(3)	C3–N1–C10	129.2(3)
C2–C1–Ru	179.6(2)	C1–C2–C3	117.7(3)
O1–C3–N1	124.4(3)	N1–C3–C2	114.8(3)
C1–C2–C4	124.6(3)	C4–C2–C3	117.5(3)
O1–C3–C2	120.7(3)		

carbon–carbon double and single bond, respectively. The O1–C3 bond length of 1.208(4) Å is that of a C–O double bond and the bond length of C3–N1 (1.332(4) Å) is shorter than that of a C–N single bond. There should be some delocalization at O1–C3 and C3–N1 bonds. Instead of two Cl^-, the counter anion is $Hg_2Cl_6^{2-}$, which is formed from two chloride anions with excess $HgCl_2$ in CH_2Cl_2 solution. Similar examples were found in other reported literature [8–10].

2.3. Conclusions

Complex **3** containing a heterocyclic [1,3]-thiazine-4-thione six-membered-ring ligand reacted with alkyl halide RCH_2X (X = Br or I; R = CN, CH=CH_2, Ph, *p*-$C_6H_4CF_3$) to afford cationic ruthenium complexes [Ru]–C=C(Ph)C(SCH_2R)N(Ph)C(=NPh)S][X] (**4a**, R = CN, X = I; **4b**, R = C_6H_5, X = Br; **4c**, R = CH=CH_2, X = I, **4d**, R = *p*-$C_6H_4CF_3$, X = Br). The reaction of **3** with $HgCl_2$ afforded [Ru]–C=C(Ph)C(SHgCl)N(Ph)C(=NPh)S][Cl] (**5**), which was oxidized in the air to give the cationic ruthenium vinylidene complex [Ru]=C=C(Ph)C(O)NHPh]$_2$[Hg_2Cl_6] (**6**).

3. Experimental

3.1. General

All manipulations were performed under nitrogen using vacuum-line, dry box, and standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 and diethyl ether and THF from sodium diphenyketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless states otherwise) and are reported in units of δ with residual protons in the solvents as an initial standard ($CDCl_3$, δ 7.24: acetone-d_6, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complexes [Ru]C≡CPh (**1**) [11], **2** and **3** [1,2] were prepared following the methods reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

3.1.1. Synthesis of [Ru]–C=C(Ph)C(SCH_2CN)N(Ph)C(=NPh)S][I] (**4a**)

To a 20 ml CH_2Cl_2 solution of **3** (200.1 mg, 0.214 mmol) ICH_2CN (0.047 ml, 0.642 mmol) was added. The solution was stirred for 2 h, then the solvent was reduced to 5 ml. This mixture was slowly added to 60 ml of a vigorously stirred diethyl ether. Purple-red precipitates, thus, formed were filtered and washed with diethyl ether and hexane and dried under vacuum to give the product **4a** (171.1 mg, 0.175 mmol) in 82% yield. Spectroscopic data of **4a** are as follows: ^{1}H-NMR ($CDCl_3$): δ 7.64–5.92 (m, 35H, Ph), 4.04 (s, 5H, Cp), 2.84 (s, CH_2), 2.92, 2.65 (m, 4H, PCH_2CH_2P). ^{31}P-NMR ($CDCl_3$): δ 99.33. ^{13}C-NMR ($CDCl_3$): δ 152.8, 149.0 (S*C*N), 146.3–120.7 (m, Ph, C_α and C_β), 114.4 (CN), 90.9 (Cp), 30.1 (t, PCH_2CH_2P, J_{C-P} = 19.7 Hz), 20.2 (CH_2). MS (FAB, *m*/*z*): 976.1 [M^+ − I], 565.0 [M^+ − I − CH_2CN − 2PhNCS − CCPh]. Anal. Calc. for $C_{55}H_{46}N_3P_2S_2RuI$ (1102.98): C, 59.89; H, 4.20; N, 3.81. Found: C, 60.10; H, 4.25; N, 3.63%.

Complex [Ru]–C=C(Ph)C(SCH2Ph)N(Ph)C(=NPh)S][Br] (**4b**) (160.3 mg, 0.158 mmol, 74% yield from 200.0 mg of **3**), complex [Ru]–C=C(Ph)C(SCH_2CH=CH_2)N(Ph)C(=NPh)S][I] (**4c**) (156.6 mg, 0.161 mmol, 75% yield from 200.2 mg

of **3**), and complex {[Ru]–C=C(Ph)C[SCH$_2$(*p*-C$_6$H$_4$CF$_3$)]N(Ph)C(=NPh)S}[Br] (**4d**) (191.1 mg, 0.171 mmol, 80% yield from 199.9 mg of **3**) were similarly prepared from BrCH$_2$Ph, ICH$_2$CH=CH$_2$, and BrCH$_2$(*p*-C$_6$H$_4$CF$_3$, respectively. Spectroscopic data of **4b** are as follows: ^{1}H-NMR (CDCl$_3$): δ 7.88–5.97 (m, 35H, Ph), 4.02 (s, 5H, Cp), 3.33 (s, CH$_2$), 2.93, 2.63 (m, 4H, PCH$_2$CH$_2$P). ^{31}P-NMR (CDCl$_3$): δ 99.73. ^{13}C-NMR (CDCl$_3$): δ 146.4, 144.7 (S*C*N), 141.3–120.6 (m, Ph and C$_\alpha$, C$_\beta$), 90.2 (Cp), 40.7 (CH$_2$), 29.9 (t, PCH$_2$CH$_2$P, J_{C-P} = 21.9 Hz). MS (FAB, *m*/*z*): 1027.3 [M$^+$ − Br], 565.1 [M$^+$ − Br − CH$_2$Ph − 2PhNCS − CCPh]. Anal. Calc. for C$_{60}$H$_{51}$N$_2$P$_2$S$_2$BrRu (1107.06): C, 65.09; H, 4.64; N, 2.53. Found: C, 66.02; H, 4.73; N, 2.37%. Spectroscopic data of **4c** are as follows: ^{1}H-NMR (CDCl$_3$): δ 7.57–6.99 (m, 30H, Ph), 5.95 (d, 1H, J_{H-H} = 7.36 Hz, C*H*=CH*H*$_{trans\ to\ H}$), 5.36 (m, 1H, C*H*=CH$_2$), 4.01 (s, 5H, Cp), 4.97 (d, 1H, J_{H-H} = 6.19 Hz, C*H*=CH*H*$_{cis\ to\ H}$), 2.76 (d, 2H, J_{H-H} = 7.01 Hz, CH$_2$), 2.85, 2.65 (m, 4H, PCH$_2$CH$_2$P). ^{31}P-NMR (CDCl$_3$): δ 99.37. ^{13}C-NMR (CDCl$_3$): δ 158.2, 149.7 (S*C*N), 146.4 (*C*H=CH$_2$), 144.8–119.1 (m, Ph and C$_\alpha$, C$_\beta$), 90.2 (Cp), 39.1 (CH$_2$), 29.8 (t, PCH$_2$CH$_2$P, J_{C-P} = 21.9 Hz). MS (FAB, *m*/*z*): 977.1 [M$^+$ − I], 565.0 [M$^+$ − I − CH$_2$CH=CH$_2$ − 2PhNCS − CCPh]. Anal. Calc. for C$_{56}$H$_{49}$N$_2$P$_2$S$_2$RuI (1104.01): C, 60.92; H, 4.47; N, 2.54. Found: C, 61.46; H, 4.55; N, 2.42%. Spectroscopic data of **4d** are as follows: ^{1}H-NMR (CDCl$_3$): δ 7.80–5.91 (m, 35H, Ph), 4.03 (s, 5H, Cp), 4.56 (s, 2H, CH$_2$), 2.86, 2.13 (m, 4H, PCH$_2$CH$_2$P). ^{31}P-NMR (CDCl$_3$): δ 98.87. ^{13}C-NMR (CDCl$_3$): δ 149.1, 146.3 (S*C*N), 145.2–118.4 (m, Ph and C$_\alpha$, C$_\beta$), 90.3 (Cp), 39.4 (CH$_2$), 29.7 (t, PCH$_2$CH$_2$P, J_{C-P} = 22.2 Hz). MS (FAB, *m*/*z*): 1096.3 [M$^+$ − Br], 565.0 [M$^+$ − Br − CH$_2$(*p*-C$_6$H$_4$CF$_3$) − 2PhNCS − CCPh]. Anal. Calc. for C$_{61}$H$_{50}$N$_2$F$_3$P$_2$S$_2$BrRu (1175.06): C, 62.35; H, 4.29; N, 2.38. Found: C, 62.57; H, 4.43; N, 2.22%.

3.2. Synthesis of [Ru]C=C(Ph)C(SHgCl)N(Ph)C(=NPh)S][Cl] (5)

To a 20 ml CH$_2$Cl$_2$ solution of **3** (200.1 mg, 0.214 mmol) was added HgCl$_2$ (174.4 mg, 0.642 mmol). The solution was stirred for 30 min, then the solid HgCl$_2$ was filtered off, and the solvent was reduced to 5 ml. This mixture was slowly added to 30 ml of a vigorously stirred diethyl ether. The purple precipitates, thus, formed were filtered and washed with diethyl ether and hexane and dried under vacuum to give the product **5** (220.7 mg, 0.188 mmol) in 88% yield. Spectroscopic data of **5** are as follows: ^{1}H-NMR (CDCl$_3$): δ 7.72–6.97 (m, 35H, Ph), 3.85 (s, 5H, Cp), 2.80–2.50 (m, 4H, PCH$_2$CH$_2$P). ^{31}P-NMR (CDCl$_3$): δ 100.53. ^{13}C-NMR (CDCl$_3$): δ 173.0, 149.8 (S*C*N), 143.6–120.3 (m, Ph and C$_\alpha$, C$_\beta$), 88.8 (Cp), 31.2 (t, PCH$_2$CH$_2$P, J_{C-P} = 21.0 Hz). MS (FAB, *m*/*z*): 1173.1 [M$^+$ − Cl], 565.1 [M$^+$ − Cl − HgCl − 2PhNCS − CCPh]. Anal. Calc. for C$_{53}$H$_{44}$N$_2$P$_2$S$_2$Cl$_2$RuHg (1207.53): C, 52.71; H, 3.67; N, 2.32. Found: C, 53.05; H, 3.75; N, 2.21%.

3.3. Synthesis of [Ru]=C=C(Ph)C(=O)NHPh]$_2$[Hg$_2$Cl$_6$] (6)

To a 20 ml acetone solution of **3** (100.1 mg, 0.085 mmol) HgCl$_2$ (232.1 mg, 0.85 mmol) was added. The solution was stirred in the air for 3 h, then the solid HgCl$_2$ was filtered off and the solvent was reduced to 5 ml. This mixture was slowly added to 30 ml of a vigorously stirred diethyl ether. The purple-red precipitates, thus, formed were filtered and washed with diethyl ether and dried under vacuum to give the product **6** (71.5 mg, 0.070 mmol) in 82% yield. Spectroscopic data of **6** are as follows: ^{1}H-NMR (CDCl$_3$): δ 7.43–6.71 (m, 35H, Ph), 5.58 (s, 5H, Cp), 3.23, 3.03 (m, 4H, PCH$_2$CH$_2$P). ^{31}P-NMR (CDCl$_3$): δ 78.33. ^{13}C-NMR (CDCl$_3$): δ 348.7 (t, C$_\alpha$, J_{C-P} = 15.4 Hz), 190.1 (C=O), 159.4, 139.0–120.3 (m, Ph, C$_\beta$), 93.2 (Cp), 29.0 (t, PCH$_2$CH$_2$P, J_{C-P} = 23.3 Hz). MS (FAB, *m*/*z*): 786.1 [1/2M$^+$ − Hg$_2$Cl$_6$], 565.1 [M$^+$ − HgCl$_3$ − CCPh − CONHPh]. Anal. Calc. for C$_{92}$H$_{80}$N$_2$O$_2$P$_4$Cl$_6$Ru$_2$Hg$_2$ (2185.51): C, 50.56; H, 3.69; N, 3.06. Found: C, 51.03; H, 3.73; N, 2.93%.

3.4. Single crystal X-ray diffraction analysis of 4c and 6

Single crystals of **6** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.45 × 0.30 × 0.30 mm^3 was glued to a glass fiber and mounted on an SMART CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube molybdenum K$_\alpha$ radiation (T = 295 K). Exposure time was 5 s per frame [12]. SADABS [13] (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL [14] program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (23 926 reflectios) to give R_1 = 0.0286 and wR_2 = 0.0572 [15] for 8823 unique observed reflections ($I > 2\sigma(I)$). Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. The procedure for the structure determination of **4c** was similar to that of **6**. The final R indices of **4c** for $I > 2\sigma(I)$ of R_1 = 0.0951, wR_2 = 0.2123 and R indices of all data of R_1 = 0.1933, wR_2 = 0.2584 are high due to a 30% disorder of the CH$_2$CH=CH$_2$ group. The structure of **4c** is used only for reference only.

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