Carbene Ligands

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The Generation of a Metallocene-Fused Imidazol-2-ylidene and Its Mercury Complex**

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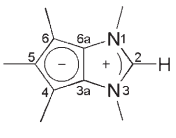
Imidazolium salts and imidazol-2-thiones have been widely used as precursors for the synthesis of stable imidazol-2-ylidene.[1] We recently reported successful methodologies for the synthesis of the first directly annulated imidazolium cyclopentadienide zwitterion (**1**) and its ferrocenyl bis(thione) derivative (**2**).[2] These structures provide an entry into a new class of metallocene-fused imidazole-2-ylidenes. This new architecture for carbenes allows the incorporation of two or more metal centers into a molecule through a combination of σ and π bonding that is tightly coupled through the annulated ligand.



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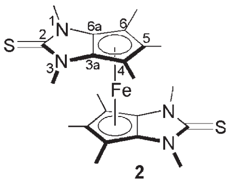

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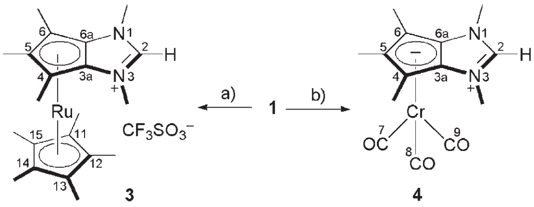
The ruthenocene **3**, a yellow solid that melts at 240–242 °C, was produced in 91 % yield from **1** and [Cp*Ru(CH$_3$CN)$_3$][CF$_3$SO$_3$] (a Cp*Ru transfer source; Cp* = pentamethyl cyclopentadienyl;[3] Scheme 1). A single crystal of **3** suitable for X-ray crystallographic measurements was grown by recrystallization from THF (selected bond lengths and angles are given in Table 1). The 3D structure of **3** is depicted by the KANVAS[4] drawing in Figure 1. Ruthenocene **3** crystallizes in the triclinic space group $P\bar{1}$, and the two π-ligands (**1** and Cp*) are bound to the ruthenium center in a η^5-fashion. The planes of the two cyclopentadienyl ligands are essentially parallel ($\phi = 1.13°$) and adopt an eclipsed conformation. The average Ru−C(ring) length of 219.78(4) pm in **1** is slightly longer than the average Ru−Cp*(ring) length of 218.08(4) pm. This small difference is consistent with the more extensive π delocalization of the zwitterion. The N1-C2-N3 angle of 112.7(3)° is 2.33° greater than that found in **1** and also larger than those found in typical imidazolium ions.[5]



Scheme 1. Reactions of **1**. a) [Cp*Ru(CH$_3$CN)$_3$][CF$_3$SO$_3$]; b) [Cr(CH$_3$CN)$_3$(CO)$_3$].

Metalation of **1** with chromium can be accomplished by treatment of **1** with tris(acetonitrile)tricarbonylchromium(0). The half-sandwich chromium complex **4** was obtained in almost quantitative yield (Scheme 1) as an orange solid which melts at 286–288 °C. Complex **4** is not soluble in nonpolar or halogenated solvents, but it is sparingly soluble in acetonitrile and readily soluble in dimethyl sulfoxide (DMSO).

The molecular structure of **4** was determined by X-ray crystallographic studies. Quality crystals were grown by slow diffusion of petroleum ether into a saturated solution of **4** in acetonitrile. The X-ray crystal structure of **4** is illustrated by the KANVAS[4] drawing in Figure 2, and selected bond lengths and angles in **4** are presented in Table 1. Compound **4** crystallizes in the monoclinic space group $P2_1/n$. The chromium atom is η^5-coordinated to the cyclopentadienyl ring with an average Cr−C(ring) length of 221.84 pm. The average Cr−CO and C−O lengths are 181.5 and 117.3 pm, respectively.

Generation of the free, stable carbenes in solution by deprotonation of **3** or **4** has proved problematic. These carbenes may be too electron-rich (nucleophilic) to allow easy isolation, or alternatively the in situ generated carbene is capable of reaction with the other electrophilic centers in the complex (e.g., ruthenium, chromium, or carbonyl centers). Carbene generation in the presence of electrophiles (metals or main-group elements) has, however, allowed the isolation of various carbene adducts.

A benchmark reaction[6] of the imidazol-2-ylidene with sulfur produced imidazole-2-thione **5** in almost quantitative yield (Scheme 2). The ruthenocene-substituted thione was isolated as an air-stable colorless solid that melts at 282–284 °C. An analogous reaction allowed a clean conversion of imidazolium salt **4** to thione **6**, which was characterized by NMR spectroscopy of the reaction mixture (Scheme 2).

Cooling a saturated solution of **5** in THF/petroleum ether allowed crystals suitable for X-ray structure determination to be grown. Thione **5** crystallizes in the monoclinic space group $P21/n$, and the asymmetric unit contains two unique molecules. The crystal structure is depicted as a KANVAS[4] drawing in Figure 3, and selected bond lengths and angles are presented in Table 1. The Cp* rings exhibit large axial positional variance. (A second position for the Cp* ring could not be refined rotationally along the metal−Cp* centroid, but prolate thermal ellipsoids (with the longest axis tangential to the Cp−ring) provided the best model. No hydrogen atoms

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Table 1: Selected bond lengths [pm] and angles [°] for **1**–**5** and **7**.

Property	**1**	**2**	**3**	**4**	**5**	**7**
r(C2–N1(3))	133.6(3)	136.9(2)	133.3(5)	132.7(3)	136.9(5)	135.3(3)
	134.0(3)	136.9(2)	132.4(5)	133.3(3)	137.5(4)	134.9(3)
r(N1(3)–C6a(3a))	139.6(3)	140.2(2)	140.9(5)	139.9(2)	139.8(4)	140.5(3)
	140.3(3)	140.2(2)	141.0(5)	140.0(2)	139.2(4)	140.3(3)
r(C3a–C6a)	140.3(3)	140.3(3)	141.4(5)	139.7(3)	139.1(5)	141.1(4)
r(C3a(6a)–C4(6))	140.7(3)	142.7(2)	142.7(5)	142.8(3)	143.5(4)	143.6(3)
	140.9(3)	142.7(3)	142.7(5)	142.0(3)	143.9(5)	143.8(3)
r(C4(6)–C5)	141.9(3)	145.0(3)	144.7(5)	144.0(3)	143.7(5)	145.2(4)
	141.6(3)	144.9(3)	145.4(6)	143.9(3)	145.0(5)	145.4(4)
r_{av}(C–C)Cp*	–	–	144.92	–	136.92	143.44
r_{av}(M–C3a–6a)	–	205.8	219.78	221.84	214.8	219.86
r_{av}(M–CCp*)	–	–	218.08	–	218.86	217.72
r_{av}(M–CO)	–	–	–	181.5	–	–
r_{av}(C–O)	–	–	–	117.3	–	–
r(C2–E) (E = S, Hg)	–	167.7(19)	–	–	167.3(3)	208.5(2)
θ(N1-C2-N3)	110.37(19)	108.25(16)	112.7(3)	111.59(18)	107.9(3)	109.4(2)
θ(C2-N1(3)-C6a(3a))	108.53(19)	108.96(15)	107.2(3)	107.59(16)	108.8(3)	108.7(2)
	108.11(18)	108.92(15)	107.2(3)	107.50(16)	108.6(3)	109.0(2)
θ(N1(3)-C6a(3a)-C3a(6a))	106.52(19)	106.89(15)	106.3(3)	106.73(16)	107.0(3)	106.5(2)
	106.45(18)	106.96(15)	106.6(3)	106.58(16)	107.5(3)	106.4(2)
θ(C3a(6a)-C6a(3a)-C6(4))	109.67(18)	109.79(16)	110.6(3)	110.20(17)	110.0(3)	109.8(2)
	109.95(19)	110.14(15)	109.6(3)	110.18(17)	109.9(3)	110.1(2)
θ(C3a(6a)-C4(6)-C5)	103.84(19)	104.83(16)	104.6(3)	103.82(17)	105.1(3)	104.7(2)
	104.04(18)	105.04(16)	103.8(3)	104.19(17)	104.5(3)	104.7(2)
θ(C4-C5-C6)	112.50(18)	110.18(16)	111.3(3)	111.55(17)	110.5(3)	110.6(2)
θ_{av}(C-C-C)^{Cp*}	–	–	108	–	107.98	108.02

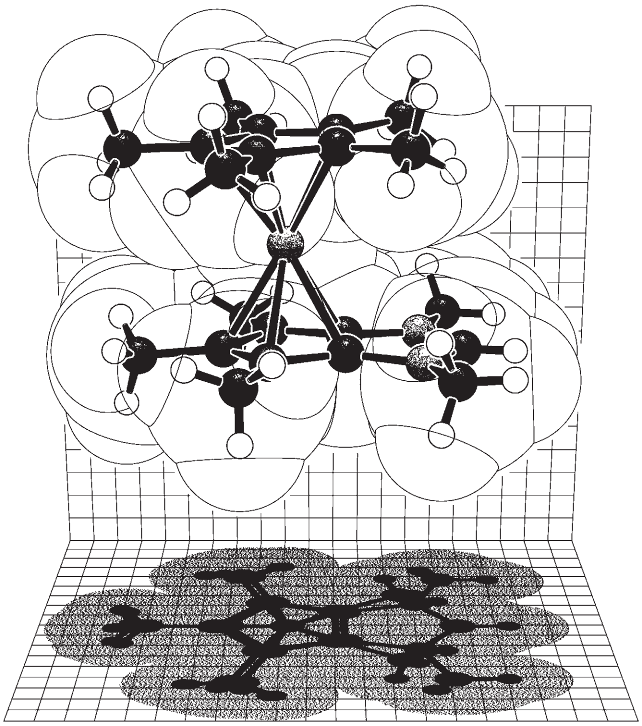


Figure 1. KANVAS[4] drawing of the X-ray structure of **3**.

were affixed to these atoms because of the large thermal motions. The C=S bond of 167.3(3) pm is comparable to that in our previously reported bis(thione) substituted ferrocene **2** (167.7(19) pm.)[2a]

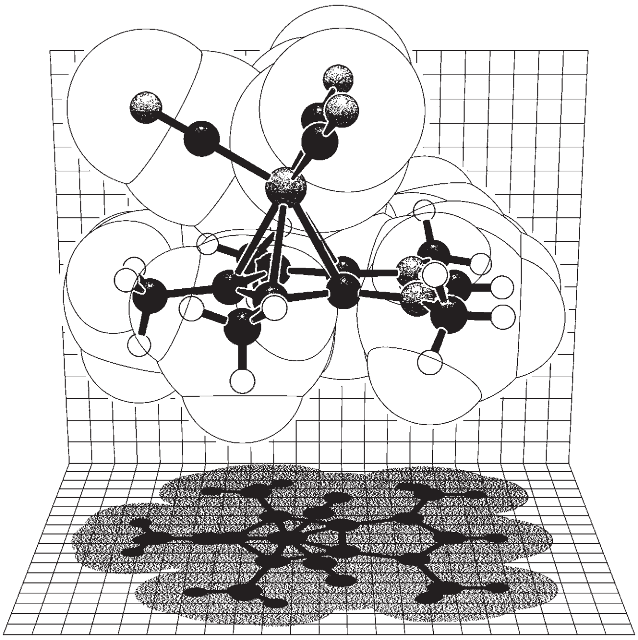
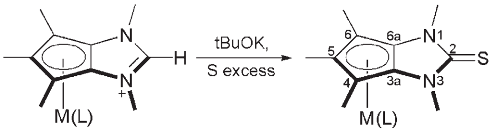


Figure 2. KANVAS[4] drawing of **4**.



3: M = Ru, L = Cp*
4: M = Cr, L = (CO)$_3$
5: M = Ru, L = Cp*
6: M = Cr, L = (CO)$_3$

Scheme 2. The synthesis of **5** and **6**.

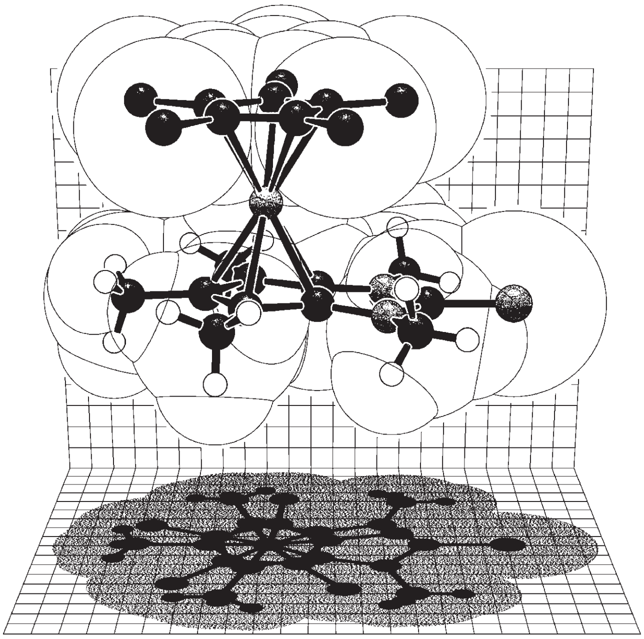
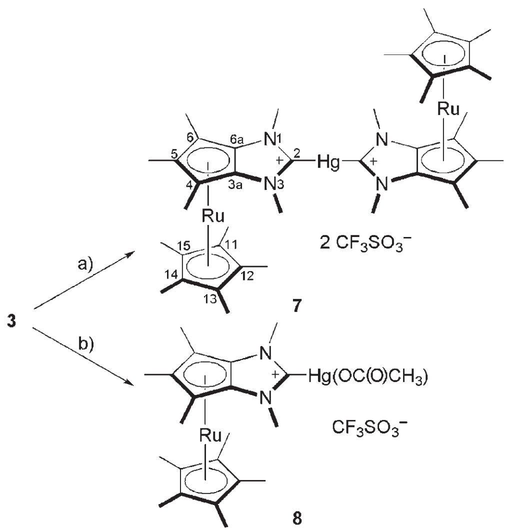


Figure 3. KANVAS[4] drawing of **5**.

The first example of metalation of the carbene center in **3** was accomplished by mercuration. The imidazolium salt **3** reacted slowly with mercury acetate in different stoichiometries. When 0.5 equivalents of mercury acetate were employed in the reaction, after 20 days of stirring at 60 °C, 38 % conversion into the disubstituted mercury complex **7** was observed. No further conversion was observed after longer reaction times. A 1:1 stoichiometry led to a mixture of the mono- and disubstituted mercury complexes **8** and **7**. When a large excess of mercury acetate was used, the monosubstituted mercury complex **8** could be isolated as the only product of the reaction after 2 days at 60 °C (Scheme 3).



Scheme 3. Reactions of **3**. Reagents: a) 0.5 equivalents of $Hg(OAc)_2$, b) excess of $Hg(OAc)_2$.

Mercury bis(carbene) complex **7** is a yellow crystalline solid that is poorly soluble in most organic solvents except acetonitrile and DMSO. Crystals of **7** of suitable quality for X-ray crystallographic studies were obtained by recrystallization from acetonitrile. Figure 4 shows a KANVAS[4] drawing, and selected bond lengths and angles are given in Table 1.

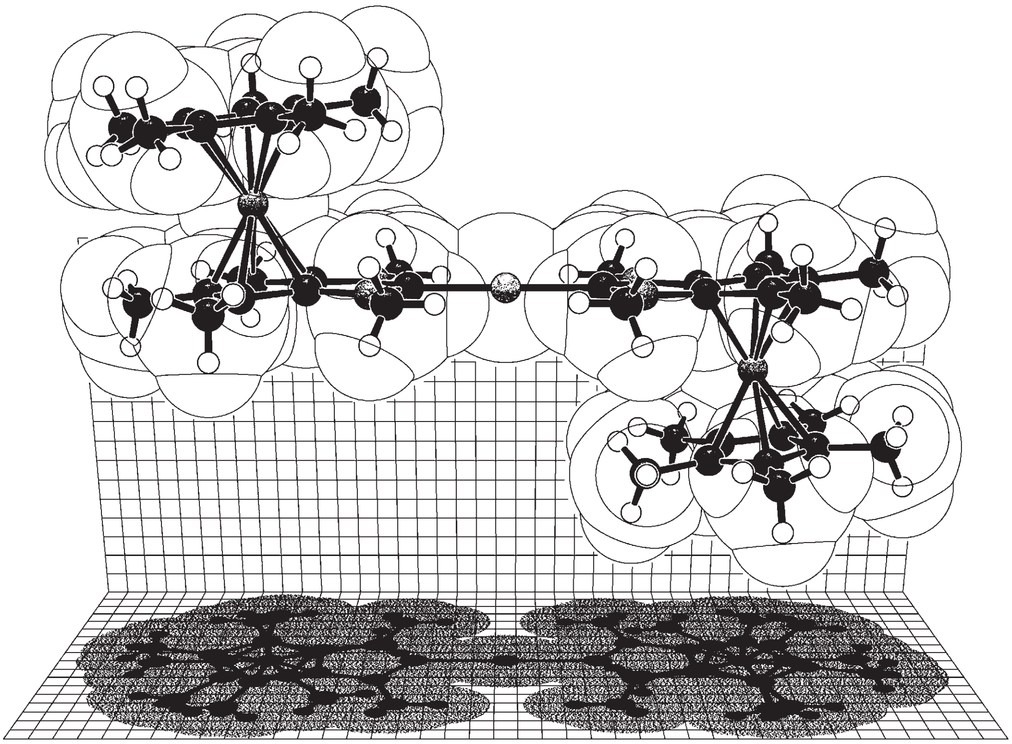


Figure 4. KANVAS[4] drawing of the X-ray structure of **7** (the triflate counterions are omitted for clarity).

Complex **7** crystallizes in the triclinic space group $P\bar{1}$, with an asymmetric unit that contains half of a molecule, a triflate counterion, and an acetonitrile molecule. The ruthenocene fragments are oriented in an antiperiplanar conformation with a C2-Hg-C22 bond angle of 180°. The internal ring angle at the carbene center of 109.4(2)° is larger than that in typical imidazol-2-ylidene/mercury complexes.[7] The larger angle might be the result of strain that arises from fusion of the two five-membered rings.

A comparative analysis of the bond lengths and angles for the zwitterion fragments in all of the studied compounds reveals certain trends among this new class of organometallic compound. The lengths of the C2−N1(3) bonds are greater for thiones **2** and **5** and mercury complex **7** than those found in imidazolium salts **1**, **3**, and **4**. The N-C-N angle is smaller in **2**, **5**, and **7** relative to the corresponding angle in **1**, **3**, and **4**. These changes suggest diminished π delocalization in **2**, **5**, and **7** relative to the imidazolium salts and may reflect a tendency of π-bond fixation when the substituent at C2 is capable of p–π or d–π backdonation.

In summary, a new carbene (imidazol-2-ylidene) architecture has been realized that allows the incorporation of multiple metal and/or main-group element centers in a combination of σ- and π-bonding motifs. Zwitterion **1** combines these two major bonding concepts in organometallic chemistry in a single ligand, in which there is tight electronic coupling between the ligated centers. This investigation has reported the first bi- and trimetallic complexes of this ligand. Future reports will detail electronic interactions in these systems and their influence on structure, chemistry, and catalysis.

Experimental Section

The reactions were carried out in an atmosphere of dry nitrogen using Schlenk techniques or a dry box. Solvents were dried by using standard procedures.[8] The NMR spectra were recorded on a Bruker AMX 360 spectrometer. Melting points were obtained on a MEL-TEMP II apparatus (Laboratory Devices, USA) and were not corrected. Elemental analysis was performed by Atlantic Microlab, Inc., GA. The ruthenium-transfer reagent was prepared according to a reported procedure.[3] All other chemicals were purchased from commercial sources and used as received.

3: A solution of **1**[2b] (0.090 g, 0.51 mmol) in THF (5 mL) was added dropwise to a solution of pentamethylcyclopentadienylruthenium(tris(acetonitrile)) triflate (0.259 g, 0.51 mmol) in THF (25 mL). The reaction mixture was stirred overnight. After evaporation of volatiles, the resulting yellow solid was dissolved in dichloromethane (1 mL) and reprecipitated with diethyl ether (20 mL). After filtration and drying, a yellow product was obtained (0.259 g, 91% yield). M.p. 240–242 °C; ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 9.26$ (s, 1H), 3.79 (s, 6H), 2.02(s, 6H), 1.67(s, 15H), 1.63 ppm (s, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) $\delta = 147.89$, 101.18, 88.16, 85.31, 67.44, 34.24, 10.43, 10.35, 9.52 ppm; elemental analysis (%) calcd for $C_{22}H_{31}N_2RuF_3SO_3$: C 47.05, H 5.56, N 4.99; found: C 46.96, H 5.53, N 5.09.

4: A solution of **1** (0.100 g, 0.56 mmol) in THF (5 mL) was added dropwise to a solution of tris(acetonitrile)tricarbonylchromium(0) (0.147 g, 0.56 mmol) in THF (10 mL), on which a yellow precipitate formed immediately. After stirring of the reaction mixture overnight, the volatiles were evaporated to obtain a yellow product (0.176 g, 99.4% yield). Crystals of suitable quality for X-ray crystallographic studies were obtained by slow diffusion of diethyl ether into a saturated solution of **4** in acetonitrile. M.p. 286–288 °C; ^{1}H NMR (360 MHz, [D$_6$]DMSO): $\delta = 8.57$ (s, 1H), 3.82 (s, 6H), 2.19(s, 6H), 1.77 ppm (s, 3H); ^{13}C NMR (90 MHz, [D$_6$]DMSO): $\delta = 222.25$, 144.77, 108.37, 99.42, 74.20, 33.92, 11.45, 10.23 ppm; elemental analysis (%) calcd for $C_{14}H_{16}N_2CrO_3$: C 53.85, H 5.16, N 8.97; found: C 53.76, H 5.13, N 8.88.

5: A 50-mL round-bottomed flask was charged with **3** (95.7 mg, 0.17 mmol), sulfur (18 mg, 0.56 mmol), and THF (10 mL), and a solution of potassium *tert*-butoxide (20 mg, 0.17 mmol) in THF (6 mL) was added dropwise. The reaction mixture was stirred for 40 min and then the volatiles were evaporated. The resulting residue was extracted with toluene (40 mL), and after filtration and evaporation of toluene, the product as obtained as a white solid (73 mg, 97% yield). Crystals of suitable quality for X-ray crystallographic studies were obtained by cooling a solution of **5** in THF/petroleum ether. M.p. 282–284 °C (decomp); ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 3.56$ (s, 6H), 1.96 (s, 6H), 1.70(s, 15H), 1.57 ppm (s, 3H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 175.23$, 100.57, 84.85, 82.55, 64.99, 32.49, 11.11, 10.39, 9.91 ppm; elemental analysis (%) calcd for $C_{21}H_{30}N_2RuS$: C 56.86, H 6.82, N 6.31; found: C 56.88, H 6.85, N 6.34.

6: A solution of potassium *tert*-butoxide (15 mg, 0.128 mmol) in THF (1 mL) was added to a mixture of **4** (40 mg, 0.128 mmol), sulfur (10 mg, 0.25 mmol), and THF (12 mL). The reaction mixture was stirred for 3 h and then concentrated under vacuum. ^{1}H NMR (360 MHz, [D$_6$]DMSO): $\delta = 3.35$ (s, 6H), 2.18 (s, 6H), 1.85 ppm (s, 3H); ^{13}C NMR (90 MHz, [D$_6$]DMSO): $\delta = 200.59$, 173.43, 112.21, 94.10, 76.53, 32.18, 25.03, 11.09 ppm.

7: A sealed bomb was charged with **3** (150 mg, 0.267 mmol), $Hg(OAc)_2$ (43 mg, 0.135 mmol) and DMSO (2 mL). The reaction mixture was stirred at 60 °C for 20 days. The volatiles were evaporated, and the crude reaction mixture was dissolved in acetonitrile (2 mL) and filtered through celite. This solution was allowed to stand overnight at −22 °C to induce crystallization. The crystalline product was collected by filtration and dried under vacuum to afford the product (68 mg, 39%; the mother liquor contained starting material). M.p. 325–326 °C decomp; ^{1}H NMR (360 MHz, CD_3CN): $\delta = 3.83$ (s, 6H), 2.06 (s, 6H), 1.69(s, 15H), 1.65 ppm (s, 3H; ^{13}C NMR (90 MHz, CD_3CN) $\delta = 186.97$, 104.55, 89.21, 85.59, 68.20, 37.44, 10.62, 10.42, 9.64 ppm; ^{19}F NMR: $\delta = -78.73$ ppm; elemental analysis (%) calcd for $C_{44}H_{60}N_4Ru_2HgF_6S_2O_6$: C 39.98, H 4.57, N 4.23; found: C 39.79, H 4.65, N 4.24.

8: A sealed bomb was charged with **3** (159 mg, 0.283 mmol), $Hg(OAc)_2$ (210 mg, 0.658 mmol), and DMSO (5 mL). The reaction mixture was stirred at 60 °C for 48 h. The volatiles were evaporated and the resulting brown oil contained only the desired complex **8** and excess mercury acetate. The crude reaction mixture was dissolved in $CHCl_3$ and filtered through celite. Further purification of the product was difficult because the monosubstituted complex converts into the disubstituted complex over time. ^{1}H NMR (360 MHz, CD_3Cl): $\delta =$ 3.88 (s, 6H), 2.06 (s, 3H), 2.01 (s, 6H) 1.64 (s, 15H), 1.62 ppm (s, 3H); ^{13}C NMR (90 MHz, CD_3CN): $\delta = 177.60$, 174.06, 104.11, 89.08, 85.57, 68.38, 36.92, 22.08, 10.58, 10.32, 9.58 ppm; ^{19}F NMR: $\delta = -78.73$ ppm; elemental analysis (%) calcd for $C_{24}H_{33}N_2RuHgF_3SO_5$: C 35.14, H 4.06, N 3.42; found: C 33.74, H 3.77, N 3.36.

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