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Reactions at the Ru–S Bonds of Coordinatively Unsaturated Ruthenium Complexes with Tethered 2,6-Dimesitylphenyl Thiolate

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Coordinatively unsaturated ruthenium complexes with a tethered SDmp (Dmp = 2,6-dimesitylphenyl) ligand, $[(DmpS)Ru(PR_3)][BAr^F_4]$ (**3a**: R = Et; **3b**: R = Ph; Ar^F = 3,5-$(CF_3)_2C_6H_3$), were synthesized by the reactions of $[\{(p\text{-cymene})RuCl\}_2(\mu\text{-}Cl)_2]$, LiSDmp, phosphines, and $NaBAr^F_4$. The Ru–S bonds in **3a** and **3b** were found to serve as the polarized reactive site in reactions with alkyl halides, diazoalkanes, (*p*-tosyliminoiodo)-benzene, phenylacetylene, and H_2. Alkylation of **3a** and **3b** with methyl iodide or ethyl bromide occurred instantaneously to give the thioether complexes $[(DmpSR')RuX(PR_3)][BAr^F_4]$ (**4a**: R = Et, R′ = Me, X = I; **4b**: R = R′ = Et, X = Br; **4c**: R = Ph, R′ = Me, X = I; **4d**: R = Ph, R′ = Et, X = Br). Treatment of **3a** with diazoalkanes N_2CHR (R = CO_2Et, $SiMe_3$) led to the cycloaddition of carbenes to the Ru–S bond to form $[DmpS(CHR)Ru(PEt_3)][BAr^F_4]$ (**5a**: R = CO_2Et; **5b**: R = $SiMe_3$), whereas the reaction with (*p*-tosyliminoiodo)benzene gave rise to $[DmpS\{NS(O)(C_6H_4\text{-}4\text{-}CH_3)O\}Ru(PEt_3)][BAr^F_4]$ (**6**), which contains a five-membered ruthenacycle of RuSNSO. Addition of phenylacetylene to the Ru–S bond occurred reversibly to produce the vinyl sulfide complexes $[DmpS(PhCCH)Ru(PR_3)][BAr^F_4]$ (**7a**: R = Et; **7b**: R = Ph). On the other hand, the phenylacetylene at ruthenium slowly isomerized to vinylidene and bridged Ru and S in the products, $[DmpS\{C(CHPh)\}Ru(PR_3)][BAr^F_4]$ (**8a**: R = Et; **8b**: R = Ph). Complex **3a** catalyzed the hydrogenation of acetophenone, in which the heterolytic H–H splitting at the Ru–S site is suggested to be involved in the mechanism.

Keywords: hydrogenation · ruthenium · tethered ligands · thiolates · transition-metal complexes

Introduction

It has been postulated that coordinatively unsaturated transition-metal complexes with amide, alkoxide, and hydroxide ligands utilize the polar metal–heteroatom bonds to activate small molecules.[1] A topical class of such complexes may be the diamide complexes of ruthenium, [(arene)Ru(κ^2-*N*,*N*′-TsNCHPhCHPhNH)] (Ts = *p*-toluenesulfonyl), which catalyze the transfer hydrogenation of ketones and imines very efficiently.[2] As demonstrated in catalytic reactions and relevant studies of ruthenium– and iridium–amide complexes,[3] the amide nitrogen atom can serve as a basic site. This is also the case for metal–alkoxide and –hydroxide complexes, and Ir–OR (R = Me, H) and Ru–OH complexes appear to mediate the C–H bond cleavage of benzene, in which σ-bond metathesis is thought to occur between a benzene C–H bond and the metal–alkoxide (hydroxide) bond.[4]

As found in the reactions of amide and alkoxide complexes, metal–sulfur bonds of thiolate complexes are also capable of serving as polar reaction sites. Incidentally, there are metalloenzymes that are postulated to use their metal–sulfur bonds in the activation of substrates. For instance, heterolysis of H_2 was proposed to occur at the Ni–S(Cys) bond of the active site of [NiFe] hydrogenase,[5] and the function of acetyl CoA synthase probably involves the formation and cleavage of the Ni–S(CoA) bond.[6] Thus, an important clue to the understanding of the functions of such metalloenzymes may be derived from studying metal–thio-

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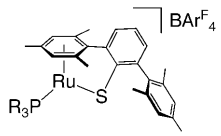
late complexes, in which both metal center and sulfur atoms take part in the reactions. Upon carrying out such a study, the following two factors need to be considered. One is the generation of a coordinatively unsaturated metal center, and the other is to have a terminal thiolate ligand, which is expected to be more nucleophilic than bridging thiolates. Whereas thiolates tend to bridge coordinatively unsaturated metal sites, bulky thiolate ligands may retard the sulfur bridge. For example, SDmp (Dmp = 2,6-(mesityl)$_2$C$_6$H$_3$) has been proven to stabilize low-coordination transition-metal complexes,[7] and we have in fact synthesized coordinatively unsaturated complexes of SDmp.[8] The ruthenium complex [Cp*Ru(SDmp)] (Cp* = 1,2,3,4,5-pentamethylcyclohexadienyl) was found to mediate the trimerization of phenylacetylene to afford the cationic arene complex [Cp*Ru(η^6-C$_6$H$_3$Ph$_3$)](SDmp), in which SDmp is liberated as the counteranion.[8a] We extended our study of coordinatively unsaturated ruthenium complexes to those with a tethered SDmp ligand, [(DmpS)Ru(PR$_3$)][BAr$^F_4$] (**3a**: R = Et; **3b**: R = Ph; Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$). With an additional interaction between ruthenium and the mesityl group, the thiolate sulfur atom is expected to stay within the coordination sphere during reactions with substrates. The tethered coordination mode of the SDmp ligand has a precedent in a homoleptic molybdenum complex.[9] Herein we report the synthesis of **3a** and **3b**, their reactions with alkyl halides, diazoalkanes, and alkynes, and the hydrogenation of acetophenone catalyzed by **3a**.

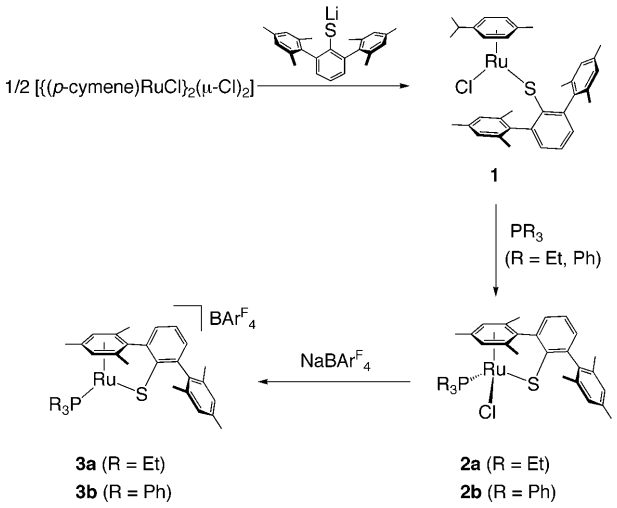


3a (R = Et)
3b (R = Ph)

Results and Discussion

Synthesis of [(DmpS)Ru(PR$_3$)][BAr$^F_4$] (3a: R = Et; 3b: R = Ph)

The coordinatively unsaturated ruthenium complexes **3a** and **3b** were prepared from sequential reactions of a ruthenium chloride complex with a bulky thiolate, PR$_3$ (R = Et or Ph), and borate (Scheme 1). Treatment of [{(*p*-cymene)RuCl}$_2$(μ-Cl)$_2$] with LiSDmp in THF resulted in the formation of a deep-blue solution, from which the thiolate complex [(*p*-cymene)RuCl(SDmp)] (**1**) was isolated in 80% yield as an air-sensitive deep-blue powder. Its deep-blue color and air sensitivity are indicative of coordinative unsaturation at the ruthenium center, as in the case of the previously reported thiolate complexes [(η^6-arene)Ru(SAr)$_2$] (Ar = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-*i*Pr$_3$C$_6$H$_2$).[10] X-ray diffraction confirmed the mononuclear half-sandwich structure of **1** with chloride and SDmp ligands (Figure 1). Complex **1** is formally a 16-electron system, and the Ru–S bond length of 2.2703(9) Å is shorter than those of electronically saturated thiolate complexes (2.38–2.47 Å),[11] because the π electrons are donated from an occupied sulfur p$_\pi$ orbital to ease the electron deficiency of the metal center.



Scheme 1. Synthesis of coordinatively unsaturated ruthenium complexes **3a** and **3b**.

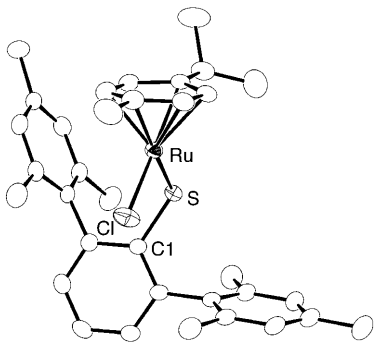


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–Cl 2.3372(8), Ru–S 2.2703(9), S–C1 1.789(2); Cl–Ru–S 94.37(3), Ru–S–C1 112.18(10).

Addition of 1 equivalent of PR$_3$ (R = Et or Ph) to a solution of **1** in toluene caused an immediate color change from deep blue to red. Coordination of phosphine to the vacant ruthenium site was followed by replacement of the *p*-cymene ligand with one of the mesityl groups in the SDmp ligand to give rise to [(DmpS)RuCl(PR$_3$)] (**2a**: R = Et; **2b**: R = Ph). Complexes **2a** and **2b** were isolated as air-stable red crystals and were characterized by means of spectroscopic and crystallographic analysis. The ruthenium atom serves as the chiral center; therefore, the SDmp ligand gave six methyl signals in the ^{1}H NMR spectrum. On the other hand, single crystals of **2a** and **2b** revealed centrosymmetric space groups ($P2_1/n$ for **2a**, $P2_1/a$ for **2b**) as a result of the formation of a racemic couple. Owing to the electron-rich ruthenium center with a bulky thiolate ligand, the Ru–S bond lengths (2.3876(14) and 2.3840(9) Å) are longer than that in **1** (2.2703(9) Å).

The chloride ligands in **2a** and **2b** were selectively displaced upon treatment with NaBAr$^F_4$.[12] This reaction af-

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forded cationic, coordinatively unsaturated complexes **3a** and **3b**, which were isolated as air-sensitive green solids. The ^{1}H NMR spectrum of **3a** indicates its C_s symmetry in solution; four methyl signals for the SDmp ligand were exhibited at $\delta = 2.08$ (3H), 1.92 (6H), 1.46 (3H), and 1.19 ppm (6H). The molecular structures of **3a** and **3b** were determined by X-ray crystallography. The solid-state structure of the cationic part of **3a** is shown in Figure 2, along with selected bond lengths and angles. One of the mesityl groups of the SDmp ligand covers the ruthenium center as an η^6-arene ligand, and the other hinders the sulfur atom from linking to other ruthenium centers. The tethered coordination mode of the SDmp ligand also produces a fixed and bare Ru–S bond, thus enabling it to interact with external substrates. The bond lengths and angles around ruthenium in **3a** are almost identical with those in **3b** except for the Ru–S bond lengths, which are 2.2117(9) and 2.2469(9) Å in **3a** and **3b**, respectively. The plane that consists of ruthenium, sulfur, and phosphorus is almost perpendicular to the η^6-mesityl ring (92.55(9)° for **3a**, 108.6(1)° for **3b**), as seen in coordinatively unsaturated half-sandwich complexes with two terminal ligands.[13]

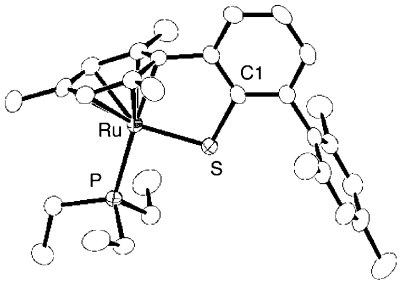
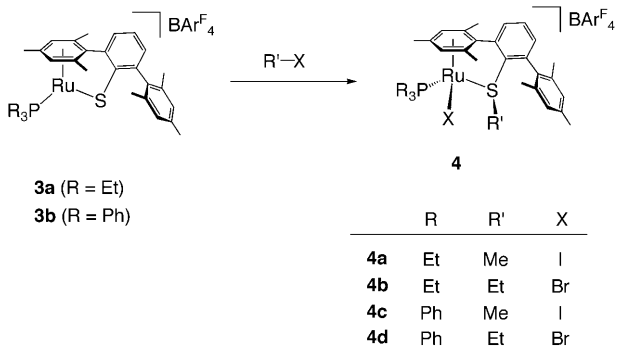


Figure 2. Structure of the complex cation of **3a** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–S 2.2117(9), Ru–P 2.3833(10), S–C1 1.791(3); Ru–S–C1 101.38(12), S–Ru–P 89.29(3).

Reactions of 3a and 3b with Alkyl Halides

Considering the coordinative unsaturation of **3a** and **3b**, we investigated their reactivity towards organic substrates. The reactions of **3a** and **3b** with alkyl halides were first examined to verify the nucleophilicity of the SDmp ligand. When **3a** was treated with methyl iodide or ethyl bromide, alkylation of the thiolate ligand[14] occurred smoothly to give the thioether complexes **4a** or **4b**, respectively (Scheme 2). Their triphenylphosphine analogues **4c** and **4d** were also obtained in a similar manner. As a result of alkylation, the ruthenium centers in **4a–d** became the chiral centers; thus, six ^{1}H NMR signals were observed for the methyl groups of the SDmp ligand. The ESI mass spectra of **4a–d** exhibited cationic signals, whose isotope patterns fit with those calculated. The molecular structures of **4a–c** were determined by X-ray diffraction studies. A perspective view of the cationic part of **4a** is shown in Figure 3, and selected bond lengths and angles of **4a–c** are listed in Table 1. The structures clearly reveal the *cis* addition of alkyl halides across the Ru–S bond. The Ru–S bond lengths in **4a–c** are in the range 2.3793(9)–2.3866(9) Å, which are longer than those found in the coordinatively unsaturated complexes **1**, **3a**, and **3b** (2.2117(9)–2.2703(9) Å). On the other hand, these Ru–S(thioether) bond lengths are comparable to the Ru–S(thiolate) bond lengths in **2a** and **2b** (2.3876(14) and 2.3840(9) Å), which indicates that the tethered coordination mode of SDmp brings the sulfur atom close to the ruthenium center in **4a–c**.



	R	R'	X
4a	Et	Me	I
4b	Et	Et	Br
4c	Ph	Me	I
4d	Ph	Et	Br

Scheme 2. Preparation of thioether complexes **4**.

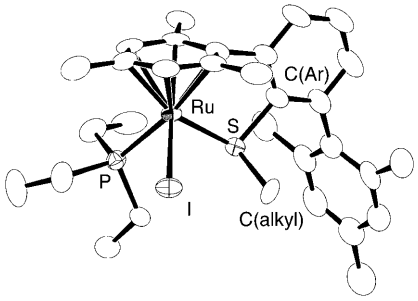


Figure 3. Structure of the complex cation of **4a** with thermal ellipsoids at the 50% probability level.

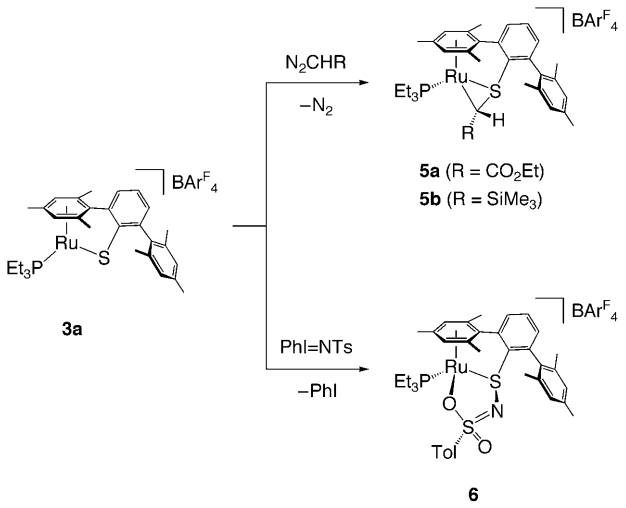
Table 1. Selected bond lengths (Å) and angles (°) for complexes **4a–c**.

	4a	**4b**	**4c**
Ru–X[a]	2.6935(5)	2.5203(4)	2.6930(5)
Ru–S	2.3801(15)	2.3793(9)	2.3866(9)
Ru–P	2.3805(16)	2.3728(10)	2.3812(16)
S–C(Ar)	1.808(6)	1.801(4)	1.797(6)
S–C(alkyl)	1.818(6)	1.836(4)	1.810(5)
Ru–S–C(Ar)	102.7(2)	102.51(14)	102.78(12)
Ru–S–C(alkyl)	112.8(2)	114.27(15)	114.74(19)

[a] X = I (**4a** and **4c**) or Br (**4b**).

Cycloaddition of Carbenes and *N*-Tosylimide to the Ru–S Bond

The structures of **3a** and **3b** indicate that the electron deficiency at ruthenium is alleviated by π donation from sulfur, and that some multiple-bond character is present in the Ru–S bond. Indeed, cycloaddition of carbenes[15] to the Ru–S bond of **3a** was found to occur. Treatment of a solution of **3a** in CH_2Cl_2 with diazoalkane N_2CHR (R = CO_2Et, $SiMe_3$) led to the formation of a yellow solution, from which the carbene adduct **5a** or **5b** was isolated as crystals (Scheme 3). The crystals were subjected to X-ray analysis to



Scheme 3. Cycloaddition of carbenes and *N*-tosylimide to **3a** to give **5** and **6**, respectively. Tol = *p*-tolyl.

confirm the molecular structures, and Figure 4 shows an ORTEP drawing of **5b**. The stereochemistry at the ruthenium center is a distorted three-legged piano stool with a three-membered metallacycle. The strain in the metallacycle leads to closer contact between ruthenium and sulfur; thus, the Ru–S bond lengths in **5a** and **5b** (2.3110(12) and 2.3057(11) Å) are shorter than those in complexes **2a**, **2b**, and **4a–c** (2.3793(9)–2.3876(14) Å). The CO_2Et and $SiMe_3$ groups are located at the *anti* position with respect to the Dmp group on sulfur, probably due to steric hindrance. The metallacycle group of **5b** exhibited ^{1}H NMR signals at $\delta = -0.27$ ($SiMe_3$) and 2.26 ppm (methine proton), whereas a pair of diastereotopic $CO_2CH_2CH_3$ signals for **5a** appeared at $\delta = 3.77$ and 3.59 ppm.

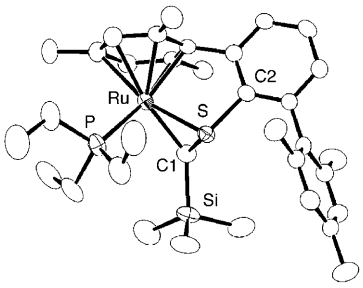


Figure 4. Structure of the complex cation of **5b** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–S 2.3057(11), Ru–P 2.3444(12), Ru–C1 2.169(4), S–C1 1.791(4), S–C2 1.810(3); Ru–S–C1 62.46(15), Ru–C1–S 70.47(15), S–Ru–C1 47.06(11), S–Ru–P 94.42(4).

The *N*-tosylimide (NTs) moiety, generated from (*p*-tosyliminoiodo)benzene (PhI=NTs), also appeared to be captured by **3a**. The reaction of **3a** with PhI=NTs resulted in the formation of **6**, in which the inorganic five-membered metallacycle consists of ruthenium, nitrogen, oxygen, and two sulfur atoms (Scheme 3). Although there is another possible isomer for a ruthenacycle with an Ru–N=S–O–S linkage, NMR spectroscopy indicates the selective formation of one isomer. Owing to the chirality present in the molecule, the ^{1}H NMR spectrum exhibited seven methyl signals for the tosyl and mesityl groups at $\delta = 2.21$, 2.02, 2.01, 2.00, 1.78, 1.56, and 1.04 ppm. The structure of **6** was identified by means of X-ray crystallography (Figure 5). As found in **5a**

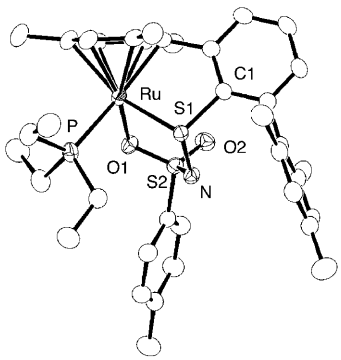


Figure 5. Structure of the complex cation of **6** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–S1 2.3494(9), Ru–P 2.3785(8), Ru–O1 2.124(2), S1–N 1.675(2), S2–O1 1.507(2), S2–O2 1.445(2), S2–N 1.578(3); S1–Ru–P 91.10(3), S1–Ru–O1 81.50(7), P–Ru–O1 82.94(6).

and **5b**, the *p*-tolyl group on S2 is oriented toward the *anti* position with respect to the Dmp group on S1 to avoid steric repulsion. Whereas the S1–N–S2–O1 array in the ruthenacycle may be alternatively interpreted as S1–O1–S2–N linkage, the observed electron density indicates that S1–N–S2–O1 is more appropriate. Consistent with this, the S2–N bond length (1.578(3) Å) is comparable to the S=N double bonds of *S*,*S*-disubstituted sulfimides (1.57–1.59 Å),[16] and the S2–O1 bond length (1.507(2) Å) is significantly longer than the S=O double bond (S2–O2: 1.445(2) Å).

Reversible Insertion of Phenylacetylene and Cycloaddition of Vinylidene to the Ru–S Bond

The insertion of an alkyne into a metal–thiolate bond is known as the key step for alkyne hydrothiolation and carbothiolation,[17] which are efficient methods for the formation

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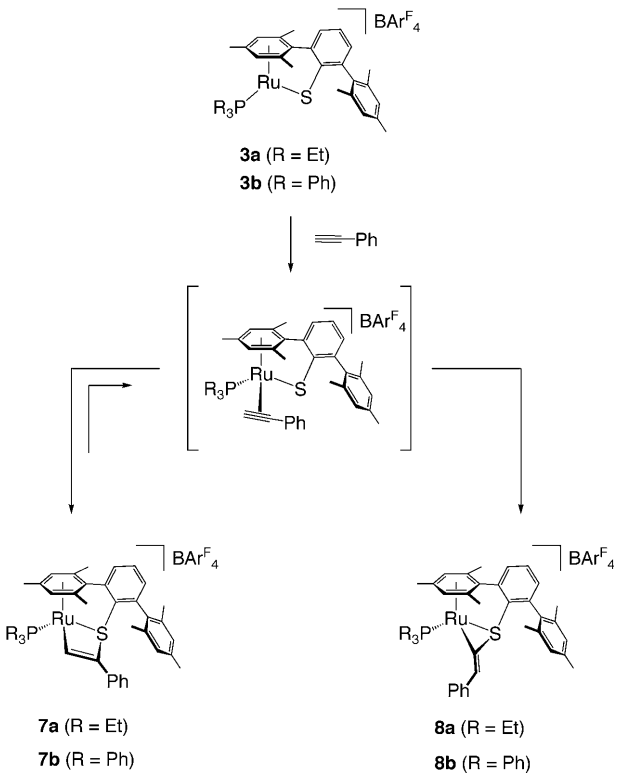
of vinyl sulfides. The electron-deficient ruthenium center and the nucleophilic sulfur atom in **3b** smoothly promoted the reaction with phenylacetylene at room temperature to afford the vinyl sulfide complex **7b** (Scheme 4). The formation of the vinyl sulfide group was indicated by the ^{1}H NMR signal of the vinylic RuC*H*=C(Ph)SDmp proton, which appeared at $\delta = 8.40$ ppm. X-ray structure determination confirmed this composition and gave structural details as shown in Figure 6. Consistent with the typical regioselectivity in hydrothiolation reactions, the insertion occurred in a Markovnikov manner. The Ru–S bond length in the four-membered ring (2.3803(8) Å) is comparable to those in coordinatively saturated complexes. The C1–C2 bond length (1.306(5) Å) is intermediate between C–C double and triple bonds, and the S–C2 bond (1.851(3) Å) is slightly longer than a typical S–C-(sp^2) bond (1.77–1.80 Å), which indicate that phenylacetylene interacts weakly with the Ru–S site. Indeed, addition of phenylacetylene to the Ru−S bond appeared to be reversible. Monitoring of a solution of **7b** and excess PhC≡CD in CD_2Cl_2 by ^{1}H NMR spectroscopy indicated gradual disappearance of the signal for the vinylic RuC*H*=C(Ph)SDmp proton (Figure 7), whereas other signals were retained. This exchange probably occurs via the η^2-alkyne intermediate, which is the initial product in the reaction of **3b** with phenylacetylene.



Scheme 4. Reaction of phenylacetylene with **3** to give **7** and **8**.

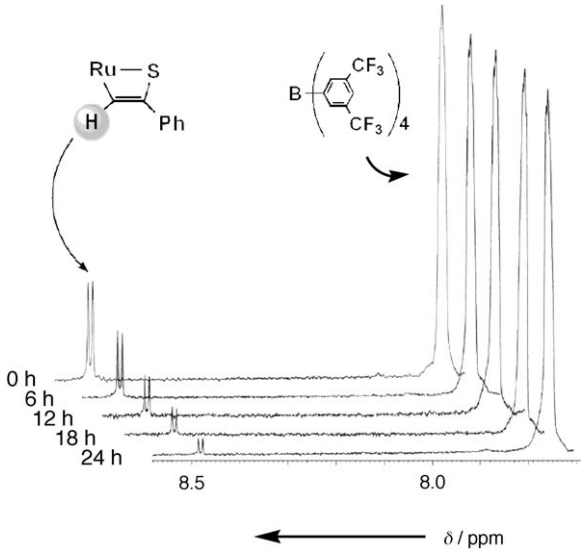


Figure 7. Disappearance of the ^{1}H NMR signal for the vinylic RuC*H*C(Ph)SDmp proton in the reaction of **7b** with PhC≡CD.

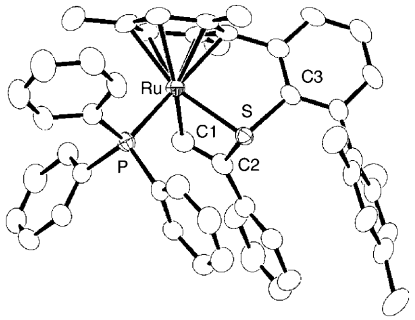


Figure 6. Structure of the complex cation of **7b** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–S 2.3803(8), Ru–P 2.3379(9), Ru–C1 2.059(3), S–C2 1.851(3), S–C3 1.817(3), C1–C2 1.306(5); S–Ru–P 92.07(3), S–Ru–C1 67.80(10), P–Ru–C1 84.71(10), Ru–C1–C2 108.5(2), S–C2–C1 102.8(2).

Cycloaddition of vinylidene to the Ru–S bond was also found to proceed at elevated temperatures. When a solution of **7b** in toluene was heated at 80 °C, it gradually turned from yellow to orange to provide the vinylidene adduct **8b**. The analogous complex **8a**, which has a PEt_3 ligand, was obtained from the reaction of **3a** with phenylacetylene at room temperature. In this reaction, the initial formation of vinyl sulfide complex **7a** was indicated by ^{1}H NMR spectroscopy, in which the signal for the vinylic RuC*H*=C(Ph)SDmp proton was observed at $\delta = 8.15$ ppm. Thus, addition of alkyne across the Ru−S bond is kinetically favored over the formation of **8**. The molecular structure of **8b** was determined by X-ray crystallography (Figure 8). Complexes **8a** and **8b** were presumably formed via the Ru=C=CHPh vinylidene intermediate, in which the electrophilic α-carbon atom interacts with sulfur to produce the Ru–C–S three-membered ring. Tautomerization between η^2-alkyne and vinylidene is known to occur by 1,2-hydrogen shift for Ru^{II}-coordinated alkynes,[18] and the formation of a vinylidene intermediate is supported by the short Ru–C1 bond length

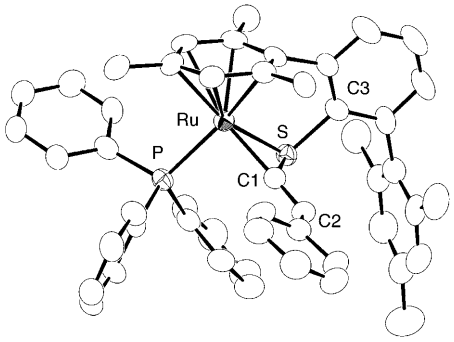
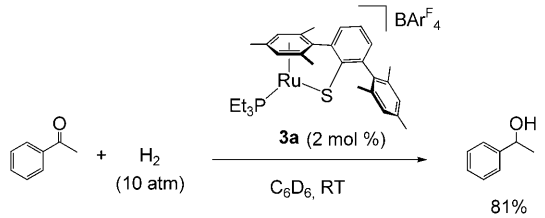


Figure 8. Structure of the complex cation of **8b** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ru–S 2.3426(13), Ru–P 2.3480(13), Ru–C1 2.014(5), S–C1 1.784(4), C1–C2 1.328(8); Ru–S–C1 56.50(19), Ru–C1–S 75.9(2), Ru–C1–C2 158.4(4), S–C1–C2 124.5(4).

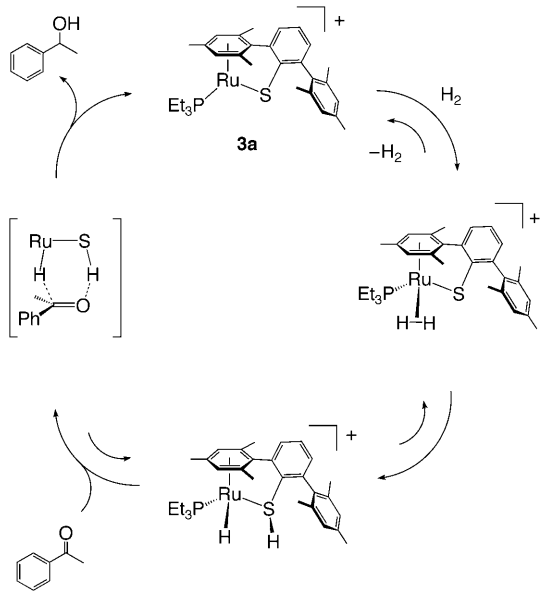
(2.014(5) Å) and the wide Ru–C1–C2 angle (158.4(4)°) of **8b**, which are indicative of some vinylidene character. The formation of a three-membered ring results in the short Ru–S and S–C1 bond lengths (2.3426(13) and 1.784(4) Å) relative to those in **7b**.

Hydrogenation of Acetophenone Catalyzed by 3a

Heterolytic cleavage of H_2 by a metal–sulfur bond, which results in the formation of metal–H and S−H bonds, is postulated as a key function of [NiFe] hydrogenases.[19,20] Although H_2 heterolysis has been demonstrated by some metal–thiolate complexes,[21] these are not catalytically applicable. Considering the relevance between **3a** and (arene)Ru–diamide hydrogenation catalysts,[2] we anticipated catalytic hydrogenation reactions by **3a** in which the heterolytic cleavage of H_2 is induced by the Ru–S site. In the presence of a catalytic amount of **3a** (2 mol%), hydrogenation of acetophenone occurred at room temperature under 10 atm of H_2 to give 1-phenylethanol in 81% yield (Scheme 5). The catalytic hydrogenation presumably proceeds by way of the initial coordination of H_2 at the vacant ruthenium site followed by heterolysis to produce the Ru–H/S–H intermediate, which may transfer both hydride and proton to acetophenone in a concerted manner, as proposed for hydrogenation mediated by Noyori ruthenium catalysts[2] (Scheme 6). The color of the solution did not change from that of **3a** (dark green) during catalysis, which indicates the facile recovery of **3a** by dissociation of H_2 from its adduct.



Scheme 5. Hydrogenation of acetophenone to 1-phenylethanol catalyzed by **3a**.



Scheme 6. Possible reaction pathway for the hydrogenation of acetophenone.

Neither the H_2 adduct of **3a** nor the Ru–H/S–H species was observed when the reaction of **3a** with 1 atm of H_2 was monitored by ^{1}H NMR spectroscopy.

Whereas **3a** serves as a hydrogenation catalyst for acetophenone, addition of a large excess (>200 equiv) of substrate resulted in the degradation of **3a** into a catalytically inactive mixture, from which crystals of **9** and **10** were obtained (Figure 9). The bis(phosphine) complex **9** was alternatively prepared from the reaction of **3a** with PEt_3. The formation of catalytically inert complexes **9** and **10** as degradation products indicates that both coordinative unsaturation and the reactive Ru–S site are crucial for the activation of H_2, and that heterolytic H–H splitting at the Ru–S site is key for hydrogenation.

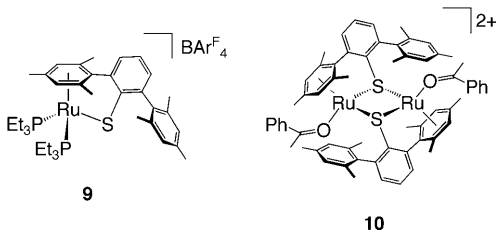


Figure 9. Degradation products of **3a**.

Conclusions

The coordinatively unsaturated ruthenium centers in **3a** and **3b** were found to be stabilized by the tethered SDmp ligand. The tethered coordination mode of SDmp also allows the reactive Ru−S bond to be retained during reactions with substrates. The polar Ru−S bond, which comprises electrophilic ruthenium and nucleophilic sulfur atoms, fa-

cilitated the reaction of **3a** and **3b** with alkyl halides to give the corresponding thioether complexes, and the insertion of phenylacetylene into the Ru–S bond occurred in a Markovnikov manner. Multiple-bond character of the Ru–S bond was indicated by the addition of carbenes and the *N*-tosylimide group. The polarized Ru–S bond also mediates the heterolysis of H_2 during the catalytic hydrogenation of acetophenone, which is relevant to the function of hydrogenases. The fact that the metal–sulfur site activates various incoming substrates suggests the possibility of using metal–sulfur complexes to promote unique catalytic reactions that have not been achieved by metal–amide or metal–alkoxide complexes.

Experimental Section

General Procedures

All reactions were carried out with standard Schlenk techniques and a glove box under nitrogen or argon atmosphere. Toluene, diethyl ether, THF, hexane, pentane, hexamethyldisiloxane (HMDSO), dimethoxyethane (DME), acetonitrile, and CH_2Cl_2 were purified by the method of Grubbs, in which the solvents were passed over columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Degassed and distilled solvents from sodium benzophenone ketyl or CaH_2 were also used. The deuterated solvents C_6D_6, CD_3CN, $CDCl_3$, CD_2Cl_2, and [D_8]THF were vacuum-transferred from sodium or CaH_2 prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were acquired on a JEOL ECA-600 or a Varian INOVA500 spectrometer. ^1H NMR signals were referenced to the residual proton peak of the deuterated solvent. ^{13}C NMR chemical shifts were referenced to the carbon signals for the deuterated solvents. A sample of 85% H_3PO_4 was used as the external reference for the ^{31}P NMR signals. IR spectra were recorded on a JASCO A3 spectrometer. ESI-TOF mass spectra were recorded on a Micromass LCT TOF-MS spectrometer. Elemental analysis was performed on a LECO-CHNS-932 elemental analyzer, in which the crystalline samples were sealed in silver capsules under nitrogen. X-ray diffraction data were collected on a Rigaku AFC7R, a Rigaku AFC8, or a Rigaku RA-Micro7 diffractometer equipped with a CCD area detector by using graphite-monochromated $Mo_{K\alpha}$ radiation. HSDmp[7] and $NaBAr^F_4$[12] were prepared according to literature procedures.

We were unable to obtain satisfactory elemental analyses of **3b** and **5a**. Single crystals of diffraction quality always gave low values for carbon and sulfur. We believe that the compounds were analytically pure and that either their thermal lability or incomplete combustion was responsible for the unsatisfactory analysis.

Syntheses

1: A solution of LiSDmp was prepared by the reaction of a solution of HSDmp (970 mg, 2.80 mmol) in THF (25 mL) with a solution of *n*BuLi (1.58 M, 2.80 mmol) in hexane (1.77 mL). The resultant solution was added dropwise to a solution of [{(*p*-cymene)RuCl}$_2$(μ-Cl)$_2$] (860 mg, 1.40 mmol) in THF (25 mL) at 0 °C. Upon warming to room temperature, the reaction mixture was stirred for 3 days and then evaporated to dryness under reduced pressure. The residue was extracted with toluene (25 mL) and centrifuged to remove LiCl. The solution was evaporated, and the resultant solid was washed with hexane (2×5 mL) to give **1** (1.32 g, 2.14 mmol, 77%) as a deep-blue powder. Single crystals for X-ray analysis were obtained from a cooled solution in toluene. ^1H NMR (C_6D_6): δ = 7.14 (t, J = 7.5 Hz, 1H, SDmp), 7.03 (d, J = 7.5 Hz, 2H, SDmp), 6.83 (s, 4H, SDmp), 4.67 (d, J = 5.5 Hz, 2H, cymene), 4.56 (d, J = 5.5 Hz, 2H, cymene), 2.41 (s, 12H, SDmp), 2.20 (s, 6H, SDmp), 2.19 (sept, J = 6.5 Hz, 1H, *i*Pr of cymene), 1.56 (s, 3H, cymene), 0.89 ppm (d, J = 6.5 Hz, 6H, *i*Pr of cymene); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 147.4, 143.7, 140.5, 137.1, 135.2, 129.2, 126.6 (SDmp and cymene), 78.7 (cymene), 76.5 (cymene), 31.0 (*i*Pr of cymene), 22.4 (cymene), 21.8 (cymene), 21.4 (SDmp), 18.7 ppm (SDmp); elemental analysis: calcd for $C_{34}H_{39}SClRu$: C 66.26, H 6.38, S 5.20; found: C 66.56, H 6.56, S 5.14.

2a: A solution of PEt_3 (0.17 g mL^{-1}, 2.24 mmol) in toluene (1.56 mL) was added to a solution of **1** (925 mg, 1.50 mmol) in toluene (30 mL) at room temperature. After the mixture was stirred at 65 °C for 24 h, the solvent and unreacted PEt_3 were removed under reduced pressure. The residue was washed with a mixture of toluene (5 mL) and hexane (5 mL) to give **2a** (717 mg, 1.19 mmol, 80%) as a red powder. Single crystals for X-ray analysis were obtained from a solution in CH_2Cl_2 layered by hexane. ^1H NMR (C_6D_6): δ = 6.97 (br s, 1H, SDmp), 6.96–6.03 (m, 3H, SDmp), 6.81 (m, 1H, SDmp), 5.16 (s, 1H, SDmp), 4.30 (d, $J_{H,P}$ = 4.5 Hz, 1H, SDmp), 2.10 (d, $J_{H,P}$ = 3.0 Hz, 3H, SDmp), 2.40, 2.27, 2.20, 1.77, 1.48 (s, 3H each, SDmp), 1.70–1.60 (m, 3H, PEt_3), 1.52–1.40 (m, 3H, PEt_3), 0.75 ppm (dt, J = 14.5, 7.5 Hz, 9H, PEt_3); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 22.3 ppm; elemental analysis: calcd for $C_{30}H_{40}PSClRu$: C 60.35, H 6.72, S 5.01; found: C 60.02, H 6.72, S 5.34.

2b: PPh_3 (370 mg, 1.41 mmol) was added to a solution of **1** (580 mg, 0.94 mmol) in toluene (20 mL) at room temperature. After the mixture was stirred at 65 °C for 2 days, the solvent was removed under reduced pressure. The residue was washed twice with a mixture of toluene (5 mL) and hexane (5 mL) to give **2b** (640 mg, 0.86 mmol, 92%) as a red powder. Single crystals for X-ray analysis were obtained from a solution in toluene layered by hexane. ^1H NMR (C_6D_6): δ = 7.83–7.79 (m, 6H, Ar), 7.20–6.94 (m, 3H, Ar), 6.91–6.88 (m, 9H, Ar), 6.84 (dd, J = 7.0, 6.0 Hz, 1H, SDmp), 6.77 (br s, 2H, SDmp), 5.12 (s, 1H, SDmp), 3.62 (d, J = 5.0 Hz, 1H, SDmp), 2.15 (d, J = 3.5 Hz, 3H, SDmp), 2.42, 2.23, 2.22, 1.50, 1.20 ppm (s, 3H each, SDmp); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 29.4 ppm; elemental analysis: calcd for $C_{42}H_{40}PSClRu$: C 67.77, H 5.42, S 4.31; found: C 67.75, H 5.83, S 3.93.

3a: $NaBAr^F_4$ (380 mg, 0.43 mmol) was added to a solution of **2a** (258 mg, 0.42 mmol) in CH_2Cl_2 (20 mL) at room temperature. After the reaction mixture was stirred for 3 h, it was centrifuged to remove NaCl, and the solution was evaporated under reduced pressure. The residue was washed with HMDSO (3×10 mL) to give **3a** (543 mg, 0.38 mmol, 89%) as a green powder. Single crystals for X-ray analysis were obtained from a solution in diethyl ether layered by hexane. ^1H NMR (C_6D_6): δ = 8.34 (s, 8H, BAr^F_4), 7.66 (s, 4H, BAr^F_4), 7.20 (t, J = 7.5 Hz, 1H, SDmp), 7.07 (d, J = 7.5 Hz, 1H, SDmp), 6.94 (d, J = 7.5 Hz, 1H, SDmp), 6.80 (s, 2H, SDmp), 3.75 (s, 2H, SDmp), 2.08 (s, 3H, SDmp), 1.92 (s, 6H, SDmp), 1.46 (s, 3H, SDmp), 1.19 (s, 6H, SDmp), 0.98 (dq, J = 8.0, 7.8 Hz, 6H, PEt_3), 0.27 ppm (dt, J = 17.0, 7.8 Hz, 9H, PEt_3); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 23.2 ppm; MS (ESI-TOF; diethyl ether): m/z = 565.4 $[M]^+$; elemental analysis: calcd for $C_{62}H_{52}BF_{24}PSRu$: C 52.15, H 3.67, S 2.25; found: C 51.66, H 4.05, S 2.17.

3b: $NaBAr^F_4$ (166 mg, 0.19 mmol) was added to a solution of **2b** (139 mg, 0.19 mmol) in CH_2Cl_2 (30 mL) at room temperature. After the reaction mixture was stirred for 1 h, it was centrifuged to remove NaCl, and the solution was evaporated under reduced pressure. The residue was washed with hexane (3×10 mL) to give **3b** (262 mg, 0.17 mmol, 88%) as a green powder. Single crystals for X-ray analysis were obtained from a solution in CH_2Cl_2 layered by HMDSO. ^1H NMR (C_6D_6): δ = 8.35 (s, 8H, BAr^F_4), 7.62 (s, 4H, BAr^F_4), 7.23 (t, J = 7.3 Hz, 1H, SDmp), 7.12 (br s, 1H, SDmp), 7.11 (br s, 1H, SDmp), 7.01–6.86 (m, 15H, Ar), 6.67 (s, 2H, SDmp), 3.80 (s, 2H, SDmp), 2.11 (s, 3H, SDmp), 1.78 (s, 6H, SDmp), 1.30 (s, 6H, SDmp), 0.87 ppm (s, 3H, SDmp); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 32.0 ppm; MS (ESI-TOF; diethyl ether): m/z = 709.2 $[M]^+$.

4a: MeI (10 μL, 0.07 mmol) was added to a stirred solution of **3a** (120 mg, 0.07 mmol) in toluene (5 mL) at room temperature. After the mixture was stirred for 14 h, a red precipitate was noticed. The solvent was removed with a syringe, and the red solid was washed with hexane (3×7 mL) and dried to give **4a** (75 mg, 0.048 mmol, 68%) as a red powder. Single crystals for X-ray analysis were obtained from a cooled solution in diethyl ether. ^1H NMR (CD_3CN): δ = 7.79 (t, 1H, J = 7.5 Hz, SDmp), 7.73 (dd, 1H, J = 1.5, 7.5 Hz, SDmp), 7.70 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 7.39 (dd, J = 1.5, 7.5 Hz, 1H, SDmp), 7.05 (br s, 2H, SDmp), 6.40 (s, 1H, SDmp), 6.09 (d, $J_{H,P}$ = 4.5 Hz, 1H, SDmp), 2.51 (s, 3H, SCH_3), 2.33 (s, 3H, SDmp), 2.25 (s, 3H, SDmp), 2.14 (d, $J_{H,P}$ = 2.5 Hz,

3H, SDmp), 2.13 (s, 3H, SDmp), 2.12 (m, 6H, PEt_3), 1.97 (s, 3H, SDmp), 1.82 (s, 3H, SDmp), 1.05 ppm (dt, $J_{H,P}=15.0$, $J_{H,H}=7.5$ Hz, 9H, PEt_3); $^{31}P\{^1H\}$ NMR (CD_3CN): $\delta=20.9$ ppm; MS (ESI-TOF; CH_3CN): $m/z=$ 707.1 $[M]^+$; elemental analysis: calcd for $C_{63}H_{55}BF_{24}IPRuS$: C 48.20, H 3.53, S 2.04; found: C 47.96, H 3.84, S 1.97.

4b: EtBr (330 μL, 4.42 mmol) was added to a stirred solution of **3a** (109 mg, 0.076 mmol) in toluene (1 mL) at room temperature. After the mixture was stirred for 2 days, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2 mL) and centrifuged. The orange solution was layered by HMDSO to give **4b** (43 mg, 0.028 mmol, 37%) as orange crystals. ^1H NMR (CD_3CN): $\delta=7.77$ (t, 1H, $J=7.5$ Hz, SDmp), 7.73 (d, 1H, SDmp; obscured by the signal for BAr^F_4), 7.71 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 7.43 (dd, $J=7.5$, 1.5 Hz, 1H, SDmp), 7.08 (s, 1H, SDmp), 7.06 (s, 1H, SDmp), 6.16 (s, 1H, SDmp), 6.12 (d, $J_{H,P}=4.0$ Hz, 1H, SDmp), 3.65 (dq, $J=13.0$, 7.2 Hz, 1H, SCH_2CH_3), 2.63 (dq, $J=13.0$, 7.2 Hz, 1H, SCH_2CH_3), 2.33 (s, 3H, SDmp), 2.22 (s, 1H, SDmp), 2.11 (d, $J_{H,P}=3.0$ Hz, 3H, SDmp), 2.07 (m, 6H, PCH_2CH_3), 2.06 (s, 3H, SDmp), 1.98 (s, 3H, SDmp), 1.81 (s, 3H, SDmp), 1.06 (dt, $J_{H,P}=15.0$ Hz, $J_{H,H}=7.5$ Hz, 9H, PCH_2CH_3), 0.49 ppm (t, $J=7.2$ Hz, 3H, SCH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_3CN): $\delta=23.1$ ppm; MS (ESI-TOF; CH_3CN): $m/z=675.2$ $[M]^+$; elemental analysis: calcd for $C_{64}H_{57}BBrF_{24}PRuS$: C 50.02, H 3.74, S 2.09; found: C 49.56, H 3.73, S 1.99.

4c: A similar procedure to that used for **4a** was followed. The reaction of **3b** (147 mg, 0.094 mmol) with a solution of MeI (1 mL, 0.16 mmol) in toluene gave an orange solid, which was washed with HMDSO to afford **4c** (140 mg, 0.081 mmol, 87%) as an orange powder. Single crystals for X-ray analysis were obtained from a solution in diethyl ether layered by pentane. ^1H NMR (CD_3CN): $\delta=7.77$ (t, $J=7.6$ Hz, 1H, SDmp), 7.75 (s, 8H, BAr^F_4), 7.58 (s, 4H, BAr^F_4), 7.44 (br d, $J=7.6$ Hz, 2H, SDmp), 7.52–7.46 (m, 15H, PPh_3), 7.00 (br s, 1H, SDmp), 6.97 (s, 1H, SDmp), 6.39 (br s, 1H, SDmp), 4.72 (br s, 1H, SDmp), 2.36 (s, 6H, SDmp), 2.10 (br s, 3H, SDmp or SMe), 2.03 (br s, 6H, SDmp), 2.00 (br s, 3H, SDmp or SMe), 1.32 ppm (br s, 3H, SDmp or SMe); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta=$ 25.0 ppm; elemental analysis: calcd for $C_{75}H_{55}BF_{24}IPRuS$: C 54.29, H 3.43, S 1.79; found: C 54.52, H 3.40, S 1.91.

4d: EtBr (530 μL, 5.64 mmol) was added to a stirred solution of **3b** (116 mg, 0.074 mmol) in toluene (2 mL) at room temperature. After the mixture was stirred for 2 days at 40 °C, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (1.5 mL) and centrifuged. The orange solution was layered by HMDSO to give **4d** (94 mg, 0.056 mmol, 76%) as orange crystals. ^1H NMR ($CDCl_3$): $\delta=7.77$ (t, $J=$ 7.6 Hz, 1H, SDmp), 7.73 (d, $J=7.6$ Hz, 1H, SDmp), 7.68 (s, 8H, BAr^F_4), 7.48 (s, 4H, BAr^F_4), 7.40–7.48 (m, 10H, PPh_3 and SDmp), 7.32–7.40 (m, 10H, PPh_3 and SDmp), 6.98 (br s, 1H, SDmp), 6.93 (br s, 1H, SDmp), 6.03 (br s, 1H, SDmp), 4.69 (br s, 1H, SDmp), 3.08 (br s, 1H, SCH_2CH_3), 2.32 (s, 3H, SDmp), 2.31 (dq, 1H, SCH_2CH_3; obscured by the mesityl signal), 2.14 (d, $J_{H,P}=3.7$ Hz, 3H, SDmp), 2.02 (s, 6H, SDmp), 1.97 (s, 3H, SDmp), 1.12 (br s, 3H, SDmp), 0.23 ppm (br s, 3H, SCH_2CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=24.8$ ppm; MS (ESI-TOF; CH_3CN): $m/z=$ 819.4 $[M]^+$; elemental analysis: calcd for $C_{76}H_{57}BBrF_{24}PRuS$: C 54.30, H 3.42, S 1.91; found: C 53.84, H 3.56, S 1.87.

5a: Ethyl diazoacetate (N_2CHCO_2Et; 16 μL, 0.15 mmol) was added to a solution of **3a** (164 mg, 0.11 mmol) in CH_2Cl_2 (10 ml), and the mixture was stirred at room temperature for 10 min. After the solvent was evaporated under reduced pressure, the yellowish-orange residue was washed with HMDSO (3×10 mL) to give **5a** as yellowish-orange oil. Single crystals for X-ray analysis (92.6 mg, 0.061 mmol, 53%) were obtained from a solution in CH_2Cl_2 layered by hexane. ^1H NMR (C_6D_6): $\delta=8.37$ (s, 8H, BAr^F_4), 7.67 (s, 4H, BAr^F_4), 6.99 (t, $J=7.6$ Hz, 1H, SDmp), 6.81 (dd, $J=$ 7.6, 1.0 Hz, 1H, SDmp), 6.77 (s, 1H, SDmp), 6.74 (s, 1H, SDmp), 6.66 (dd, $J=7.6$, 1.4 Hz, 1H, SDmp), 4.95 (s, 1H, SDmp), 4.58 (s, 1H, SDmp), 3.77 (dq, $J=10.7$, 7.1 Hz, 1H, $CO_2CH_2CH_3$), 3.62 (s, 1H, $CHCO_2Et$), 3.59 (dq, $J=10.7$, 7.1 Hz, 1H, $CO_2CH_2CH_3$), 1.97 (s, 3H, SDmp), 1.80 (s, 3H, SDmp), 1.79 (s, 3H, SDmp), 1.52 (s, 3H, SDmp), 1.51 (s, 3H, SDmp), 1.17 (s, 3H, SDmp), 1.02 (m, 3H, PCH_2CH_3), 0.91 (m, 3H, PCH_2CH_3), 0.89 (t, $J=7.1$ Hz, 3H, $CO_2CH_2CH_3$), 0.44 ppm (dq, $J_{H,P}=16.5$ Hz, $J_{H,H}=$ 7.6 Hz, 9H, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=27.9$ ppm.

5b: A solution of trimethylsilyldiazomethane ($N_2CHSiMe_3$) in diethyl ether (2 M, 102 μL, 0.20 mmol) was added to a solution of **3a** (224 mg, 0.16 mmol) in CH_2Cl_2 (10 ml), and the mixture was stirred at room temperature for 1 h. After the solvent was evaporated under reduced pressure, the yellow residue was washed with hexane (3×3 mL) to give **5b** (145 mg, 0.10 mmol, 61%) as a yellow powder. Single crystals for X-ray analysis were obtained from a solution in CH_2Cl_2 layered by hexane. ^1H NMR (C_6D_6): $\delta=8.38$ (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 6.97 (t, $J=$ 7.6 Hz, 1H, SDmp), 6.82 (s, 1H, SDmp), 6.78 (s, 1H, SDmp), 6.76 (dd, $J=7.6$, 1.4 Hz, 1H, SDmp), 6.67 (dd, $J=7.6$, 1.4 Hz, 1H, SDmp), 5.02 (s, 1H, SDmp), 4.55 (d, $J_{H,P}=2.7$ Hz, 1H, SDmp), 2.26 (d, $J_{H,P}=2.7$ Hz, 1H, $CHSiMe_3$), 2.10 (s, 3H, SDmp), 1.87 (s, 3H, SDmp), 1.75 (s, 3H, SDmp), 1.54 (s, 3H, SDmp), 1.54 (s, 3H, SDmp), 1.06 (d, $J_{H,P}=1.4$ Hz, 3H, SDmp), 0.89 (m, 3H, PCH_2CH_3), 0.83 (m, 3H, PCH_2CH_3), 0.48 (dq, $J_{H,P}=15.8$ Hz, $J_{H,H}=7.6$ Hz, 9H, PCH_2CH_3), −0.27 ppm (s, 9H, $SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=24.2$ ppm; elemental analysis: calcd for $C_{66}H_{62}BF_{24}PRuSSi$: C 52.35, H 4.13, S 2.12; found: C 52.50, H 4.26, S 2.07.

6: (*p*-Tosyliminoiodo)benzene (PhI=NTs; 26 mg, 0.070 mmol) was added to a solution of **3a** (98 mg, 0.069 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred at room temperature for 3 h. After the solvent was evaporated under reduced pressure, the yellow residue was washed with hexane (3×3 mL) to give **6** as a yellow oil. Single crystals for X-ray analysis (48.2 mg, 0.030 mmol, 44%) were obtained from a solution in DME layered by HMDSO. ^1H NMR (C_6D_6): $\delta=8.37$ (s, 8H, BAr^F_4), 7.65 (s, 4H, BAr^F_4), 7.47 (d, $J=8.2$ Hz, 2H, Ts), 7.13 (t, $J=7.6$ Hz, 1H, SDmp), 6.91 (d, $J=7.9$ Hz, 1H, SDmp), 6.63 (d, $J=8.2$ Hz, 2H, Ts), 6.87 (s, 1H, SDmp), 6.86 (d, $J=7.2$ Hz, 1H, SDmp), 6.83 (s, 1H, SDmp), 5.02 (s, 1H, SDmp), 4.05 (d, $J_{H,P}=4.5$ Hz, 1H, SDmp), 2.21 (s, 3H, CH_3 of SDmp or Ts), 2.02 (s, 3H, CH_3 of SDmp or Ts), 2.01 (s, 3H, CH_3 of SDmp or Ts), 2.00 (d, $J=1.4$ Hz, 3H, SDmp), 1.78 (s, 3H, SDmp), 1.56 (s, 3H, SDmp), 1.04 (s, 3H, SDmp), 1.03 (m, 3H, PCH_2CH_3), 0.90 (m, 3H, PCH_2CH_3), 0.37 ppm (dq, $J_{H,P}=16.5$ Hz, $J_{H,H}=7.6$ Hz, 9H, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=27.7$ ppm; elemental analysis: calcd for $C_{69}H_{59}BF_{24}NO_2PRuS_2$: C 51.89, H 3.72, N 0.88, S 4.02; found: C 51.56, H 3.90, N 1.02, S 4.06.

7b: Phenylacetylene (PhC≡CH; 7 μL, 0.064 mmol) was added to a solution of **3b** (100 mg, 0.064 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred at room temperature for 2 h. After the solvent was evaporated under reduced pressure, the yellow residue was washed with hexane (3× 3 mL) to give **7b** as a yellow oil. Single crystals for X-ray analysis (85 mg, 0.051 mmol, 79%) were obtained from a solution in CH_2Cl_2 layered by HMDSO. ^1H NMR ($CDCl_3$): $\delta=8.40$ (d, $J_{H,P}=5.5$ Hz, 1H, *H*CCPh), 7.71 (s, 8H, BAr^F_4), 7.51 (s, 4H, BAr^F_4), 7.55 (t, $J=7.5$ Hz, 1H, SDmp), 7.43–7.46 (m, 3H, SDmp, HCC*Ph*, and PPh_3), 7.30–7.38 (m, 15H, SDmp, HCC*Ph*, and PPh_3), 7.14 (d, $J=7.5$ Hz, 1H, SDmp), 7.10 (t, $J=7.5$ Hz, 1H, HCC*Ph*), 6.86 (d, $J=7.5$ Hz, 2H, HCC*Ph*), 6.85 (s, 1H, SDmp), 6.58 (s, 1H, SDmp), 6.03 (d, $J=8.5$ Hz, 2H, HCC*Ph*), 5.78 (s, 1H, SDmp), 4.78 (s, 1H, SDmp), 2.36 (s, 3H, SDmp), 2.09 (d, $J_{H,P}=1.0$ Hz, 3H, SDmp), 1.94 (s, 3H, SDmp), 1.90 (s, 3H, SDmp), 1.54 (s, 3H, SDmp), 0.97 ppm (s, 3H, SDmp); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=43.4$ ppm; elemental analysis: calcd for $C_{82}H_{58}BF_{24}PRuS$: C 58.83, H 3.49, S 1.92; found: C 58.96, H 3.41, S 1.87.

Observation of **7a** in the reaction of **3a** with phenylacetylene: Phenylacetylene (1 μL, 15 μmol) was added to a solution of **3a** (7.3 mg, 5.0 μmol) in C_6D_6 (0.6 ml). The mixture was kept standing for 10 min before NMR spectroscopy was performed. Although isolation of **7a** was not successful, the NMR spectra indicated the clean conversion of **3a** into **7a**. ^1H NMR (C_6D_6): $\delta=8.39$ (s, 8H, BAr^F_4), 8.15 (d, $J_{H,P}=5.5$ Hz, 1H, *H*CCPh), 7.68 (s, 4H, BAr^F_4), 6.84 (t, $J=7.6$ Hz, 1H, SDmp), 6.79 (s, 1H, SDmp), 6.65 (d, $J=7.6$ Hz, 1H, SDmp), 6.50 (s, 1H, SDmp), 6.42 (d, $J=7.3$ Hz, 1H, SDmp), 4.71 (s, 1H, SDmp), 4.64 (s, 1H, SDmp), 2.12 (s, 3H, SDmp), 1.93 (s, 3H, SDmp), 1.48 (s, 3H, SDmp), 1.37 (s, 3H, SDmp), 1.33 (s, 3H, SDmp), 1.01 (s, 3H, SDmp), 0.99 (m, 3H, PCH_2CH_3), 0.87 (m, 3H, PCH_2CH_3), 0.40 ppm (dq, $J_{H,P}=16.2$ Hz, $J_{H,H}=7.6$ Hz, 9H, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=32.2$ ppm.

8a: Phenylacetylene (23 μL, 0.21 mmol) was added to a solution of **3a** (152 mg, 0.11 mmol) in toluene (20 ml), and the mixture was stirred at room temperature for 12 h. After the solvent was evaporated under re-

Table 2. Crystal data for complexes **1**–**4c**, **5**, **6**, **7b**, **8b**, **9**, and **10**.

	1·C_7H_8	**2a**·$^1/_2$ C_6H_{14}	**2b**·$^1/_2$ C_7H_8	**3a**	**3b**·$(C_2H_5)_2O$
Formula	$C_{34}H_{39}SClRu·C_7H_8$	$C_{30}H_{40}PSClRu·^1/_2\,C_6H_{14}$	$C_{42}H_{40}PSClRu·^1/_2\,C_7H_8$	$C_{62}H_{52}BF_{24}PSRu$	$C_{74}H_{52}BF_{24}PSRu·(C_2H_5)_2O$
M_r [g mol^{-1}]	708.41	643.29	790.40	1427.97	1646.22
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/a$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a [Å]	16.3297(5)	10.867(5)	16.1260(9)	12.341(2)	10.2526(11)
b [Å]	15.538(2)	23.055(9)	11.3663(14)	15.670(2)	19.241(3)
c [Å]	16.0363(14)	13.974(6)	21.5588(5)	16.291(3)	20.392(2)
α [°]				92.180(4)	101.935(4)
β [°]	118.7305(5)	112.411(4)	105.0067(7)	93.308(3)	104.481(4)
γ [°]				92.908(3)	91.581(6)
V [Å^3]	3568.0(6)	3237(2)	3816.8(5)	3138.3(9)	3797.3(8)
Z	4	4	4	2	2
ρ_{calcd} [g cm^{-3}]	1.319	1.320	1.375	1.511	1.440
$\mu(Mo_{K\alpha})$ [cm^{-1}]	6.00	7.01	6.09	4.19	3.58
$2\theta_{max}$ [°]	55.1	54.9	55.1	55.0	55.0
No. of measured reflections	8169	25508	8748	25695	31166
No. of observed reflections	8169	7221	8748	13788	16698
No. of variables	398	336	452	833	940
$R1$[a]	0.048	0.079	0.064	0.067	0.075
$wR2$[b]	0.157	0.219	0.177	0.202	0.234
GOF[c]	1.29	1.60	1.38	1.43	1.75

	4a	**4b**	**4c**·$^1/_2$ C_5H_{12}	**5a**	**5b**
Formula	$C_{63}H_{55}BF_{24}PSRuI$	$C_{64}H_{57}BF_{24}PSBrRu$	$C_{75}H_{55}BF_{24}PSRuI·^1/_2\,C_5H_{12}$	$C_{66}H_{58}O_2BF_{24}PSRu$	$C_{66}H_{62}BF_{24}SiPSRu$
M_r [g mol^{-1}]	1569.91	1536.93	1751.12	1514.06	1514.18
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a [Å]	12.2263(13)	12.285(3)	14.8859(17)	12.869(4)	12.879(3)
b [Å]	29.392(4)	29.226(5)	15.2778(17)	24.401(7)	24.720(5)
c [Å]	18.1350(3)	18.009(4)	18.7982(19)	22.427(7)	22.065(4)
α [°]			111.396(6)		
β [°]	97.1323(4)	96.381(3)	100.438(6)	104.052(4)	100.785(4)
γ [°]			106.289(7)		
V [Å^3]	6466.5(11)	6426(2)	3623.4(7)	6832(3)	6900(2)
Z	4	4	2	4	4
ρ_{calcd} [g cm^{-3}]	1.612	1.589	1.605	1.472	1.456
$\mu(Mo_{K\alpha})$ [cm^{-1}]	8.86	10.35	8.00	3.91	4.02
$2\theta_{max}$ [°]	55.1	55.0	55.0	55.0	55.0
No. of measured reflections	14728	51079	29518	53556	56169
No. of observed reflections	14728	14714	15939	15301	15411
No. of variables	821	836	913	848	852
$R1$[a]	0.072	0.064	0.074	0.091	0.083
$wR2$[b]	0.202	0.200	0.240	0.250	0.229
GOF[c]	1.25	1.33	1.87	1.58	1.41

	6	**7b**	**8b**·C_7H_8	**9**	**10**·$2C_6H_5COCH_3·2CH_2Cl_2$
Formula	$C_{69}H_{59}BF_{24}NO_2PS_2Ru$	$C_{82}H_{58}BF_{24}PSRu$	$C_{82}H_{58}BF_{24}PSRu·C_7H_8$	$C_{68}H_{67}BF_{24}P_2SRu$	$C_{73}H_{55}O_2BF_{24}SCl_2Ru·C_6H_5COCH_3·CH_2Cl_2$
M_r [g mol^{-1}]	1597.17	1674.24	1766.38	1546.13	1635.05
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P2_1/a$ (#14)	$P\bar{1}$ (#2)
a [Å]	10.2294(18)	18.366(4)	14.278(2)	18.302(4)	16.297(6)
b [Å]	17.185(3)	22.177(4)	24.836(4)	21.174(4)	17.089(7)
c [Å]	21.577(4)	18.454(4)	23.994(4)	18.251(4)	17.347(7)
α [°]	106.701(3)				111.178(4)
β [°]	102.9540(17)	91.835(3)	105.055(2)	103.679(4)	103.767(4)
γ [°]	94.6270(19)				109.1500(5)
V [Å^3]	3497.7(11)	7513(3)	8216.7(22)	6872(3)	3891.4(25)
Z	2	4	4	4	2
ρ_{calcd} [g cm^{-3}]	1.516	1.588	1.428	1.494	1.395
$\mu(Mo_{K\alpha})$ [cm^{-1}]	4.52	3.74	3.35	4.11	3.96
$2\theta_{max}$ [°]	55.0	55.1	55.0	55.0	55.0
No. of measured reflections	28410	59733	67014	55387	30738
No. of observed reflections	15343	16853	18628	15725	17004
No. of variables	918	992	1044	863	929

Table 2. (Continued)

	6	7b	8b·C_7H_8	9	10·2$C_6H_5COCH_3$·2CH_2Cl_2
$R1$[a]	0.067	0.066	0.097	0.074	0.118
$wR2$[b]	0.218	0.194	0.249	0.241	0.292
GOF[c]	1.78	1.20	1.30	1.94	0.92

[a] $I>2\sigma(I)$, $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR=[\{\Sigma w(F_o^2-F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$. [c] GOF$=[\{\Sigma w(F_o^2-F_c^2)^2\}/(N_o-N_p)]^{1/2}$, in which N_o and N_p denote the number of data and parameters.

duced pressure, the yellow residue was washed with hexane (3×3 mL) to give **8a** as a yellow oil. Crystals of **8a** (37 mg, 0.024 mmol, 23%) were obtained from a solution in toluene layered by HMDSO. ^{1}H NMR (C_6D_6): δ=8.38 (s, 8H, BAr^F_4), 7.67 (s, 4H, BAr^F_4), 7.08 (d, J=7.5 Hz, 1H, SDmp), 6.97 (t, J=7.6 Hz, 1H, SDmp), 6.92 (s, 1H, SDmp), 6.86 (s, 1H, SDmp), 6.70 (d, J=7.3 Hz, 1H, SDmp), 4.92 (s, 1H, SDmp), 4.86 (s, 1H, SDmp), 2.10 (s, 3H, SDmp), 1.93 (s, 3H, SDmp), 1.87 (s, 3H, SDmp), 1.62 (s, 3H, SDmp), 1.55 (s, 3H, SDmp), 1.31 (s, 3H, SDmp), 0.72 (m, 6H, PCH_2CH$_3$), 0.34 ppm (dq, $J_{H,P}$=16.5 Hz, $J_{H,H}$=7.6 Hz, 9H, PCH$_2$CH_3); the characteristic Ru–C=C*H*Ph signal was not identified in the ^{1}H NMR spectrum probably because of overlap with aromatic signals; ^{31}P{^{1}H} NMR (C_6D_6): δ=26.3 ppm; elemental analysis: calcd for $C_{70}H_{58}BF_{24}PRuS$: C 54.95, H 3.82, S 2.10; found: C 55.19, H 3.99, S 2.14.

8b: A solution of **7b** (38 mg, 0.0024 mmol) in toluene (5 ml) was heated at 80°C for 24 h and then concentrated to half its volume. The orange solution was cooled at −30°C to afford **8b** (11.5 mg, 0.007 mmol, 30%) as orange crystals. ^{1}H NMR ([D$_8$]toluene): δ=8.32 (s, 8H, BAr^F_4), 7.65 (s, 4H, BAr^F_4), 7.39 (d, J=7.6 Hz, 1H, SDmp, HCC*Ph*, or PPh$_3$), 6.89–7.19 (m, SDmp, HCC*Ph*, and PPh$_3$), 6.83 (d, J=7.6 Hz, 2H, SDmp, HCC*Ph*, and PPh$_3$), 6.78 (d, J=11 Hz, 2H, SDmp, HCC*Ph*, and PPh$_3$), 6.73 (d, J=7.6 Hz, 1H, SDmp, HCC*Ph*, and PPh$_3$), 6.68 (s, 1H, SDmp), 6.37 (d, J=7.6 Hz, 1H, SDmp), 5.17 (s, 1H, SDmp), 4.57 (s, 1H, SDmp), 2.20 (s, 3H, SDmp), 1.82 (s, 3H, SDmp), 1.80 (s, 3H, SDmp), 1.75 (s, 3H, SDmp), 1.41 (s, 3H, SDmp), 1.23 ppm (s, 3H, SDmp); the characteristic Ru–C=C*H*Ph signal was not identified in the ^{1}H NMR spectrum probably because of overlap with aromatic signals; ^{31}P{^{1}H} NMR (C_6D_6): δ=39.6 ppm; elemental analysis: calcd for $C_{82}H_{58}BF_{24}PRuS$: C 58.83, H 3.49, S 1.92; found: C 58.75, H 3.98, S 2.02.

Hydrogenation of acetophenone catalyzed by **3a**: In a glove box, a glass autoclave equipped with a stirrer bar was charged with a solution of **3a** (50 mg, 34.7 μmol), mesitylene (81 μL, 0.58 mmol, as internal standard), and acetophenone (0.20 mL, 1.74 mmol) in C_6D_6 (2.5 mL). The atmosphere of the reaction vessel was replaced with 10 atm of H_2, and the reaction mixture was vigorously stirred at room temperature for 24 h. After careful venting of hydrogen, the yield of 1-phenylethanol was determined to be 81% by ^{1}H NMR spectroscopic analysis.

9: A solution of triethylphosphine (92 mg, 0.16 mmol, 20 wt%) in toluene was added to a solution of **3a** (149 mg, 0.10 mmol) in toluene (20 ml), and the mixture was stirred at room temperature for 12 h. After the solvent was evaporated under reduced pressure, the yellow residue was washed with hexane (3×3 mL) to give **9** (151 mg, 0.098 mmol, 94%) as an orange powder. Single crystals for X-ray analysis were obtained from a solution in toluene layered by HMDSO. ^{1}H NMR (C_6D_6): δ=8.37 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 6.91 (t, J=7.6 Hz, 1H, SDmp), 6.89 (s, 2H, SDmp), 6.80 (dd, J=7.6, 1.0 Hz, 1H, SDmp), 6.70 (dd, J=7.2, 1.4 Hz, 1H, SDmp), 4.76 (s, 2H, SDmp), 2.07 (s, 6H, SDmp), 2.06 (s, 3H, SDmp), 1.51 (s, 3H, SDmp), 1.48 (s, 6H, SDmp), 1.18 (m, 6H, PCH_2CH$_3$), 1.01 (m, 6H, PCH_2CH$_3$), 0.50 ppm (m, 18H, PCH$_2$CH_3); ^{31}P{^{1}H} NMR (C_6D_6): δ=20.9 ppm; elemental analysis: calcd for $C_{68}H_{67}BF_{24}P_2RuS$: C 52.82, H 4.37, S 2.07; found: C 53.24, H 4.51, S 2.11.

Reaction of **3a** with excess acetophenone: Complex **3a** (102 mg, 0.071 mmol) was dissolved in acetophenone (2 mL, 17.1 mmol), and the mixture was stirred overnight. After concentration under reduced pressure, the dark-orange oil was dissolved in CH_2Cl_2 (2 mL), and the mixture was centrifuged. Layering of hexane onto the solution yielded trace amounts of **9** and **10** as orange crystals. These complexes were manually separated and characterized by means of X-ray crystallography.

X-ray Crystal-Structure Determination

Crystal data and refinement parameters for complexes **1**–**4c**, **5**, **6**, **7b**, **8b**, **9**, and **10** are summarized in Table 2. Single crystals were coated with oil (immersion oil, type B: Code 1248, Cargille Laboratories, Inc.) and mounted on loops. Diffraction data were collected at −100°C under a cold nitrogen stream on a Rigaku AFC7R diffractometer equipped with an ADSC Quantum1 CCD detector, on a Rigaku AFC8 diffractometer equipped with a Saturn70 CCD detector, or on a Rigaku AFC7R diffractometer equipped with a Mercury CCD detector, with graphite-monochromated $Mo_{K\alpha}$ radiation (λ=0.710690 Å). Six preliminary data frames were acquired at 0.5° increments of ω to assess the crystal quality and preliminary unit-cell parameters. Intensity images were also recorded at 0.5° intervals of ω. Frame data were integrated with the CrystalClear program package, and data sets were corrected for absorption with the REQAB program. Calculations were performed with the TEXSAN or CrystalStructure program packages. All structures were solved by direct methods and refined by full-matrix least squares. Anisotropic refinement was applied to all non-hydrogen atoms except for solvents of crystallization and disordered CF_3 groups of the BAr^F_4 anion (refined isotropically), and all hydrogen atoms were placed at calculated positions. The solvent of crystallization (hexane) in **2a**·$^1/_2$ C_6H_{14} was disordered over three positions, with occupancy factors of 30:30:40. The solvents of crystallization, toluene in **2b**·$^1/_2$ C_7H_8, pentane in **4c**·$^1/_2$ C_5H_{12}, and dichloromethane in **10**·2 $C_6H_5COCH_3$·2 CH_2Cl_2, were disordered over two positions, with occupancy factors of 50:50. Three of the CF_3 groups in **3a**, **4a**, **5b**, **6**, and **10**·2 $C_6H_5COCH_3$·2 CH_2Cl_2, one in **4b**, four in **4c**·$^1/_2$ C_5H_{12} and **9**, six in **5b**, and two in **8b**·C_7H_8 were disordered over two positions. One of the CF_3 groups in **5b** and **6** were disordered over three positions. CCDC-679589–679603 (**1**–**4c**, **5**, **6**, **7b**, **8b**, **9**, and **10**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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