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Article

Carbon−Hydrogen Bond Cleavage Reaction in 5-Coordinate Bis(2,6-dimethylbenzenethiolato)ruthenium(II) Complexes

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A series of bis(2,6-dimethylbenzenethiolato)ruthenium(II) complexes, Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$-(TRIPHOS-κ^3P,P',P'') (**2a**), Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(TDPME-κ^3P,P',P'') (**2b**), *trans*-Ru(SC_6H_3-Me_2-2,6-κ^1S)$_2$(DPPE-κ^2P,P')$_2$ (**3c**) and Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PMe_3)$_3$ (**2d**) are prepared. Treatment of **2a** with PMe_3 in benzene at 50 °C results in the sp^3 C−H bond cleavage reaction of the *ortho* methyl in thiolato group to give a stereochemical mixture of thiaruthenacycle complex Ru[SC_6H_3-(CH_2-2)(Me-6)-κ^2S,C](TRIPHOS-κ^3P,P',P'')(PMe_3) (**1a**) in 70% yield ([(*OC*-6−34)-**1a**]/[(*OC*-6−25)-**1a**] = 80/20) with concomitant liberation of 2,6-dimethylbenzenethiol. Similar treatment of **2d** with PMe_3 in benzene at room temperature rapidly produced *cis*-Ru[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S, C](PMe_3)$_4$ (**1d**) quantitatively. Treatment of **2b** with PMe_3 results in the formation of **1d** by the C−H bond cleavage reaction and ligand displacement reaction. The C−H bond cleavage reaction does not occur from **3c** under these conditions. Treatment of **2d** with PMe_3 in methanol does not give **1d** at all but yields *cis*-Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PMe_3)$_4$ (**3d**), which is not responsible for formation of **1d**, suggesting importance of coordinative unsaturation for the C−H bond cleavage reaction. The kinetic study suggests that present C−H bond cleavage reaction proceeds by a concerted mechanism.

Introduction

Since Chatt and Davidson reported the first C−H bond cleavage reaction by a zerovalent ruthenium complex,[1] activation of C−H bond by low valent ruthenium complexes has been of long-standing interest because of the potential applications of the process for direct functionalization of inactive organic compounds.[2] One of the key factors in such bond activation processes is how to bring a C−H bond in proximity to the ruthenium center.[3] In fact, the C−H bond cleavage reactions of phosphates,[4] isonitrile,[5] carbonyls,[6] alcohols,[7] phenols,[8] carboxylic acids,[9] amines,[10] and pyridines[11] are documented and these reactions are considered to involve prior coordination (or covalent bond formation) step before the C−H bond cleavage reactions. In addition, the C−H bond cleavage reactions by cleaving the covalent metal−chalcogen bond such as σ bond metathesis and electrophilic substitution currently attract a great deal of interest as new potential pathways for molecular transformation.[12−17,44]

We are interested in the bond cleavage reactions of *ortho* substituents in (aryloxo)- and (arenethiolato)ruthenium(II)[18] complexes, where the chalcogen anchor effectively brings the *ortho* substituent in proximity to the ruthenium center.

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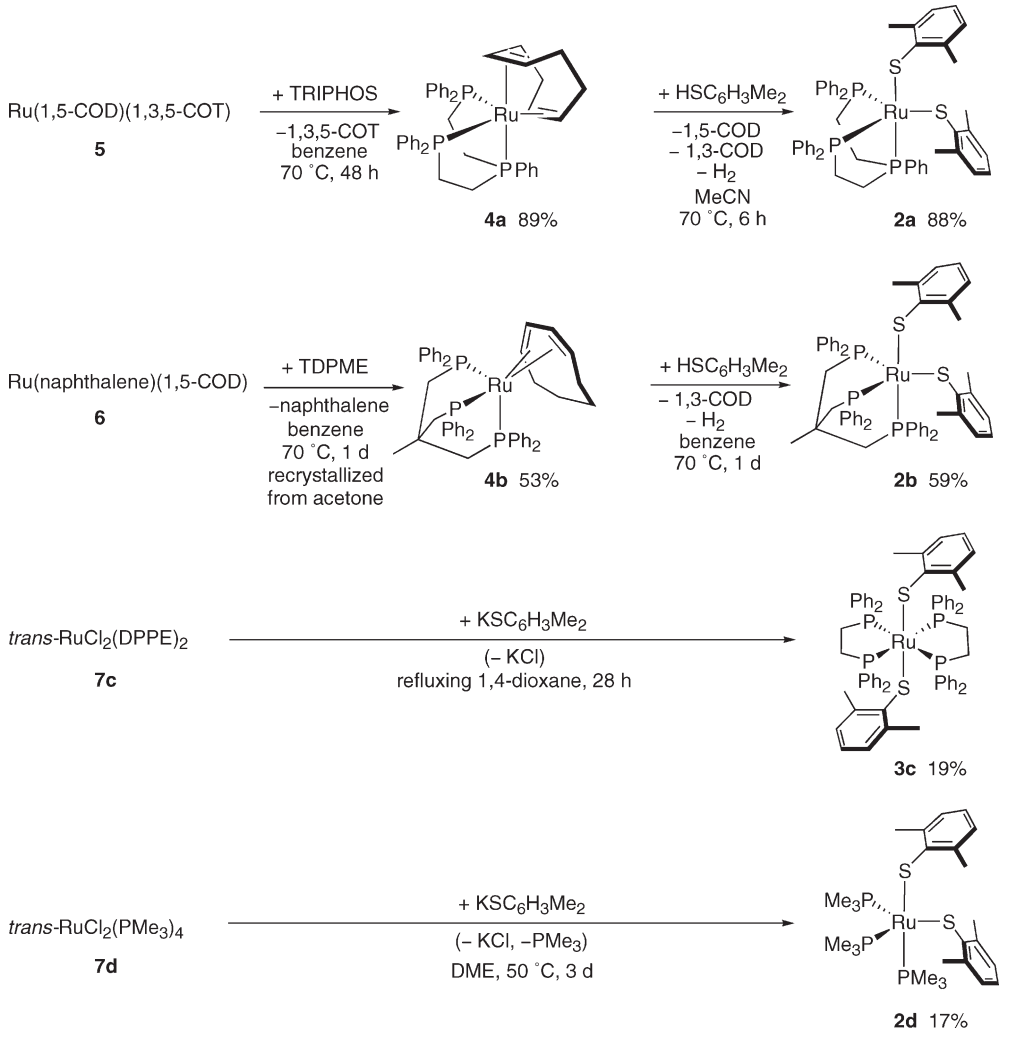
Scheme 1



Of particular interest is the sp^3 C−H bond cleavage reaction of the *ortho* methyl groups in *cis*-RuH($SC_6H_3Me_2$-2,6-κ^1S)-(PMe_3)$_4$, where the C−H bond in the *ortho* methyl group is cleaved only by removing evolved hydrogen gas by evacuation of the reaction system to form a thiaruthenacycle complex Ru[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C](PMe_3)$_4$ (**1d**) at room temperature.[18] This finding prompted us to study the synthesis and reactions of a series of (2,6-dimethylbenzenethiolato)-ruthenium(II) complexes. In this article, we describe the preparation of a series of bis(2,6-dimethylbenzenethiolato)-ruthenium(II) complexes with tri-, bi-, and monodentate tertiary phosphine ligands, and the mechanism for the sp^3 C−H bond cleavage process giving thiaruthenacycle complexes.

Results and Discussion

1. Preparation of Bis(2,6-dimethylbenzenethiolato)ruthenium-(II) Complexes. A series of bis(2,6-dimethylbenzenethiolato)-ruthenium(II) complexes containing tri-, bi-, and monodentate phosphine ligands were prepared by direct reaction of a zero-valent complex with thiol or metathetical reaction of the corresponding dichlorido complex with thiolate anion. The feasible synthetic pathways were summarized in Scheme 1.

1.1. Tridentate Phosphine Complexes. A TRIPHOS [($Ph_2PC_2H_4$)$_2$PPh] complex was prepared by the following manner. Reaction of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**5**) with TRIPHOS in benzene at 70 °C for 48 h yielded Ru(η^4-1,5-COD)(TRIPHOS-κ^3P,P',P'') (**4a**) as analytically pure yellow plates from cold toluene/hexane in 89% yield. The overall molecular structure of **4a** displays a distorted trigonal bipyramidal complex with an η^4-1,5-COD and a κ^3P,P',P''-TRIPHOS ligand on Ru(0) center, where the P(2) and the center between C(5) and C(6) locate on the axial positions [the angle P(2)−Ru(1)−the center between C(5) and C(6) is

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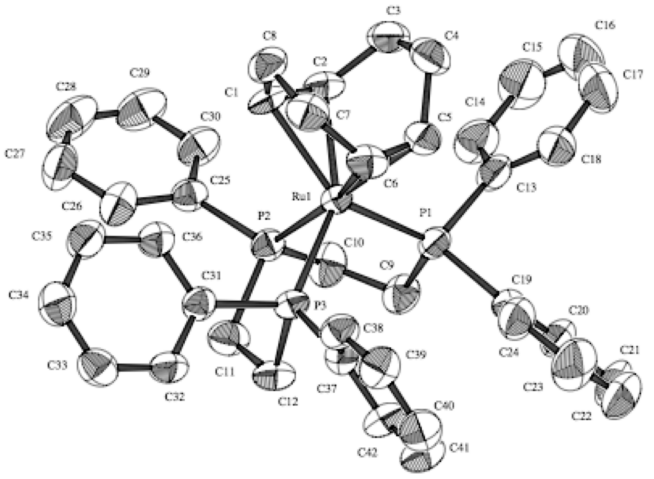


Figure 1. Molecular structure of Ru(η^4-1,5-COD)(TRIPHOS-κ^3P,P',P'') (**4a**) with numbering schemes. All hydrogen atoms and incorporated toluene molecule were omitted for clarity. Ellipsoids represent 50% probability.

179.6(15)°], and P(1), P(3), and the center between C(1) and C(2) constitute a trigonal plane (mean square deviation: 0.1236 Å) (Figure 1).

The $^{31}P\{^1H\}$ NMR spectrum of **4a** at room temperature in benzene-d_6 shows a sharp AX_2 pattern at δ 102.8 (t, 1P) and δ 75.8 (d, 2P), suggesting two of three phosphorus atoms being equivalent. In the ^1H NMR spectrum of **4a** in toluene-d_8, the methylene protons in the COD ligand appear as a slightly broad signal at δ 2.2 (8H) and the methine protons are almost merged into the baseline around δ 2.7−4.0 (4H) at 20 °C. At 100 °C, the methine signal appears at δ 3.2 as a broad peak, which separates into two broad signals at δ 4.3 (2H) and δ 2.6 (2H) at −70 °C. During the variable temperature ^1H NMR experiment, no significant change was observed for the other resonances and the $^{31}P\{^1H\}$ NMR signals remained sharp as an AX_2 pattern over the entire temperature range (−70 to 100 °C). This fluxionality shows "apparent rotation" of the η^4-1,5-COD ligand on the 5-coordinate Ru center either by Berry's pseudo rotation or turnstile rotation mechanism.[19]

Treatment of **4a** with 5 equiv of 2,6-dimethylbenzenethiol in acetonitrile at 70 °C for 6 h gave a 5-coordinate bis(2,6-dimethylbenzenethiolato)ruthenium(II) complex, Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(TRIPHOS-κ^3P,P',P'') (**2a**) in 88% yield as analytically pure dark-purple crystals, whose molecular structure was revealed by the X-ray analysis (vide infra). In the $^{31}P\{^1H\}$ NMR spectrum of **2a**, the TRIPHOS ligand is observed as an AX_2 pattern at δ 88.7 (t, 1P) and 81.5 (d, 2P) in CD_2Cl_2. In the ^1H NMR spectrum of **2a** in CD_2Cl_2 at room temperature, two broad peaks are observed at δ 2.1 (12H) and 6.4 (6H) assignable to the *ortho* methyl groups and aromatic protons in the 2,6-dimethylbenzenethiolato fragments. On cooling the solution, the *ortho* methyl and aromatic resonances gradually collapsed and then at −20 °C new signals appeared at δ 2.0 (s, 6H), 2.2 (s, 6H), 6.2 (d, 2H), and 6.3 (t, 1H). Remaining one set of aromatic protons (3H) in the thiolato group may be obscured by overlapping with the TRIPHOS signals at δ 6.6. The $^{31}P\{^1H\}$ NMR resonances are remained sharp as an AX_2 pattern in this temperature range. These variable temperature NMR data suggest apparent exchange between two thiolato groups, probably by a pseudorotation mechanism.

The reaction of **5** with TDPME [$MeC(CH_2PPh_2)_3$] was sluggish and gave a very complex mixture. When Ru(η^6-naphthalene)(η^4-1,5-COD) (**6**) was employed as a starting compound in benzene at 70 °C for 1 day, Ru(η^4-1,3-COD)-(TDPME-κ^3P,P',P'') (**4b**) was obtained in 53% yield after recrystallization from cold acetone. The $^{31}P\{^1H\}$ NMR spectrum of **4b** in benzene-d_6 shows a singlet at δ 31.2 that indicates all phosphorus atoms being equivalent. In the ^1H NMR spectrum in benzene-d_6, the COD fragment is observed at δ 1.76 (br, 2H), 1.89 (br, 2H), 2.47 (br, 2H), 2.59 (br, 2H), 3.14 (m, 2H), and 5.25 (d, 2H). The spin correlations observed by the $^1H-^1H$ COSY spectrum suggest isomerization of the 1,5-COD fragment to η^4-1,3-COD.[20] Treatment of **4b** with 5 equiv of 2,6-dimethylbenzenethiol in benzene at 70 °C for 1 day led to the formation of a 5-coordinate complex Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(TDPME-κ^3P,P',P'') (**2b**) in 59% yield. The $^{31}P\{^1H\}$ NMR spectrum of **2b** in benzene-d_6 at room temperature shows a sharp singlet at δ 40.5, suggesting that all phosphorus atoms are equivalent. The ^1H NMR spectrum shows sharp resonances at δ 1.06 (s, 3H) and 2.18 (s, 6H) for the methyl and methylene protons in the TDPME ligand and a singlet at δ 2.46 (s, 12H) assigned as the methyl resonances of two thiolato groups. This feature indicates the two thiolato groups to be equivalent at room temperature, suggesting rapid apparent exchange between two thiolato groups.

1.2. Bidentate Phosphine Complexes. When $RuCl_2$-(DPPE-κ^2P,P')$_2$ (**7c**) was treated with 3 equiv of potassium 2,6-dimethylbenzenethiolate in refluxing 1,4-dioxane for 28 h, a 6-coordinate complex *trans*-Ru(SC_6H_3Me-2,6-κ^1S)$_2$-(DPPE-κ^2P,P')$_2$ (**3c**) was obtained as yellow powder in 19% yield.[21] The $^{31}P\{^1H\}$ NMR of **3c** in CD_2Cl_2 shows a sharp singlet at δ 44.99, suggesting the *trans* configuration of the dithiolato ligands. ^1H NMR spectrum of **3c** in CD_2Cl_2 shows a broad signal at δ 2.74 (br, 8H), a sharp singlet at δ 3.65 (s, 12H) ,and multiplet in the range δ 7.02−7.25 (m, 46H). These resonances are assignable to the methylene protons in DPPE, the *ortho* methyl protons in the thiolato group, and the aromatic protons in DPPE and in the thiolato groups, respectively. It is notable that the *ortho* methyl groups (δ 3.65) resonate at lower magnetic field than **2a** (δ 2.11), **2b** (δ 2.46), **2d** (δ 2.55), and free 2,6-dimethylbenzenethiol (δ 2.48). This downfield shift may be explained by deshielding effect caused by the equatorial phenyl groups in **3c**.

1.3. Monodentate Phosphine Complexes. An analytically pure 5-coordinate trimethylphosphine complex of bis(2,6-dimethylbenzenethiolato)ruthenium(II) Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PMe_3)$_3$ (**2d**) was prepared and isolated by the metathetical reaction of *trans*-$RuCl_2(PMe_3)_4$ (**7d**) with potassium 2,6-dimethylbenzenethiolate in DME at 50 °C for 3 days. The product yield of **2d** was poor (17%) due to concomitant

(19) Yamamoto, A. in *Organotransition Metal Chemistry, Fundamental Concepts and Applications*; Wiley: New York, 1986, pp 190.

(20) The isomerization to 1,3-COD from 1,5-COD proceeded in this reaction. Although detailed mechanism for this isomerization was not clear to date, it occurred during the purification process in acetone because the reaction of **5** with TDPME in C_6D_6 monitored by the NMR suggests dominant formation of Ru(η^4-1,5-COD)(TDPME) (**4b′**). One of the reasonable explanations is that a protic species catalyzes the isomerization from 1,5-COD to the more stable 1,3-COD Hirano, M.; Shibasaki, T.; Komiya, S.; Bennett, M. A. *Organometallics* **2002**, *21*, 5738.

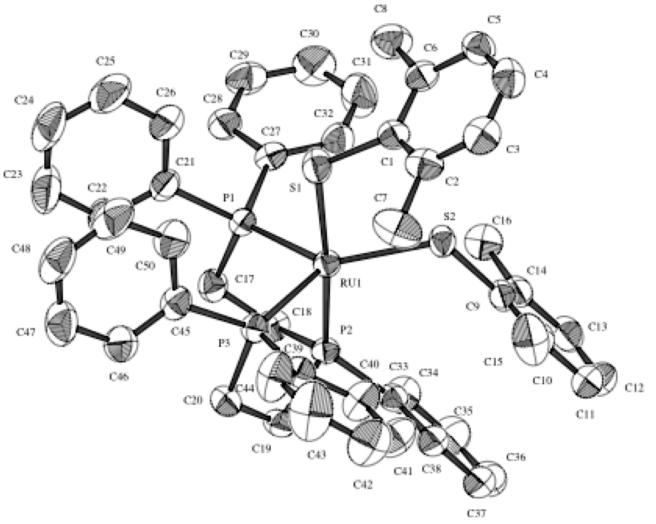
(21) Similar *trans*- and *cis*-Ru(SPh)$_2$(DMPE-κ^2P,P')$_2$ were reported Field, L. D.; Hmbley, T. W.; Ya, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009.

formation of a thiaruthenacycle complex *cis*-Ru[SC_6H_3-(2-CH_2)(6-Me)-$\kappa^2 S,C$](PMe_3)$_4$ (**1d**)[18] (69%) and *cis*-Ru-($SC_6H_3Me_2$-2,6-$\kappa^1 S$)$_2$(PMe_3)$_3$(OH_2) (**3e**) (9%) whose formation processes are discussed later. Complex **2d** was characterized by NMR, elemental analysis and the chemical reactions, and the unambiguous molecular structure was finally determined by the X-ray analysis (vide infra). One PMe_3 has been lost during the formation of **2d** from **7d**. Probably, the initial tetrakis-phosphine product Ru($SC_6H_3Me_2$-2,6-$\kappa^1 S$)Cl(PMe_3)$_4$, or more likely Ru($SC_6H_3Me_2$-2,6-$\kappa^1 S$)$_2$-(PMe_3)$_4$, would favor liberation of one PMe_3 under these conditions because of donation of lone pair electrons in the thiolato group.

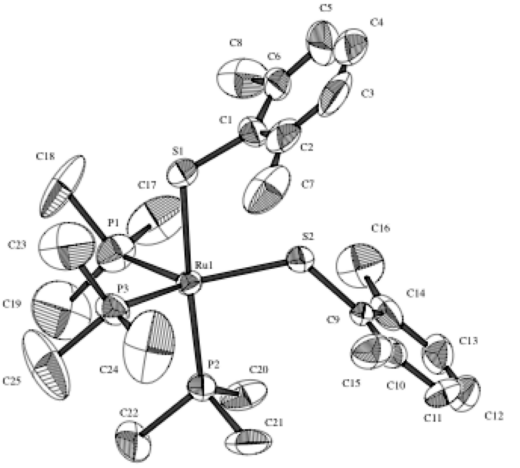
The $^{31}P\{^1H\}$ NMR spectrum of **2d** shows a sharp singlet at δ 16.6 at room temperature, suggesting magnetically equivalence of three phosphorus atoms. The ^1H NMR spectrum contains a slightly broad multiplet at δ 1.13 (27H) assignable to three equivalent PMe_3 protons, and all 2,6-dimethylbenzenethiolato signals also resonate equivalently at δ 2.55 (s, 12H), 6.97 (t, 2H), and 7.08 (d, 4H). No significant change was observed in both variable temperature ^1H and $^{31}P\{^1H\}$ NMR spectra in the range of 20 to −70 °C. These features show rapid fluxionality of **2d** in solution as frequently observed for 5-coordinate compounds.[22] When complex **2d** was treated with dry HCl gas in CD_2Cl_2, 2 equiv of 2,6-dimethylbenzenethiol were liberated, suggesting the presence of two thiolato groups in **2d**.

2. Molecular Structures of Bis(2,6-dimethylbenzenethiolato)-ruthenium(II) Complexes. On cooling of a refluxing acetonitrile solution of **2a** to room temperature were produced dark-purple plates suitable for X-ray analysis. Complex **2d** showed higher solubility toward most of organic solvents, and the single crystals were obtained by the recrystallization from cold toluene. These molecular structures are shown in Figure 2.

The overall molecular structures of **2a** and **2d** are 5-coordinate bis(2,6-dimethylbenzenethiolato)ruthenium(II) complex with three phosphorus donors. The axial thiolato S(1) and a phosphorus ligand P(2) are placed linearly [S(1)−Ru(1)−P(2): 173.3(1)° (**2a**), 176.76(11)° (**2d**)]. Meantime, while angles S(1)−Ru(1)−P(1), S(1)−Ru(1)−P(3), S(1)−Ru(1)−S(2), P-(1)−Ru(1)−P(2), and P(1)−Ru(1)−P(3) are nearly 90°, respectively [**2a**, 83.8−94.97°; **2d**, 81.92−95.24°], both angles P(1)−Ru(1)−S(2) [**2a**, 134.0(6)°; **2d**, 127.99(11)°] and P-(3)−Ru(1)−S(2) [**2a**, 134.4(4)°; **2d**, 137.02(12)°] are significantly larger than 120°.[23] Eisenstein and her co-workers reported theoretical considerations for the structures of electron-deficient 5-coordinate d^6 complexes (Chart 1), where the electronic nature of the ligand X played an important role to determine their structures by perturbing the d_{xy} and d_{x2-y2} orbital:[24] i.e. (i) a strong σ donor and good π acceptor ligand favors square-pyramidal, (ii) a weak σ donor and good π donor ligand favors distorted trigonal bipyramidal geometry where the rest of equatorial ligands are squeezed each other, and the L−M−L angle (α) in the *xy* plane inferiors to only around 80°, and (iii) the role of the ligand perpendicular to the equatorial plane (on *z* axis) has been shown to be negligible.



2a



2d

Figure 2. Molecular structures of Ru($SC_6H_3Me_2$-2,6-$\kappa^1 S$)$_2$-(TRIPHOS-$\kappa^3 P,P',P''$) (**2a**) and Ru($SC_6H_3Me_2$-2,6-$\kappa^1 S$)$_2$(PMe_3)$_3$ (**2d**). Ellipsoids represent 50% probability. All hydrogen atoms are omitted for clarity.

In the present case, one of the thiolato groups is placed in the equatorial position and they are generally regarded as a weak σ donor and good π donor ligand.[25] In fact, the bond distance Ru(1)−S(2) [**2a**, 2.34(2) Å; **2d**, 2.343(2) Å] in the equatorial position is significantly shorter than Ru(1)−S(1) [**2a**, 2.447(1) Å; **2d**, 2.438(2) Å] in the axial position and the angle Ru(1)−S(2)−C(9) [**2a**, 121.2(6)°; **2d**, 125.0(3)°] is larger than Ru(1)−S(1)−C(1) [**2a**, 115.7(5)°; **2d**, 118.9(3)°]. These features suggest contribution of a sp^2 hybridization of the S(2) atom.[26] The dihedral angles among S(1)−Ru(1)−S(2)−C(9) [**2a**, 174.8(2)°; **2d**, 178.2(4)°] and P(2)−Ru(1)−S(2)−C(9) [**2a**, −9.7(2)°; **2d**, −0.9(4)°] show the S(1), Ru(1), P(2), S(2), and C(9) atoms being placed in almost the same *xz* plane (Chart 2).

(22) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd Ed.; Wiley: New York, 2001; pp 268. (b) Yamamoto, A. *Organotransition Metal Chemistry, Fundamental Concepts and Applications*; Wiley: New York, 1986; pp 189.

(23) The P(1)−Ru(1)−S(2) angle is slightly smaller than the P(3)−Ru(1)−S(2) angle for **2d**, while they are comparable for **2a**. The reason for the favor of S(2) in **2d** to be such biased position is not clear so far.

(24) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

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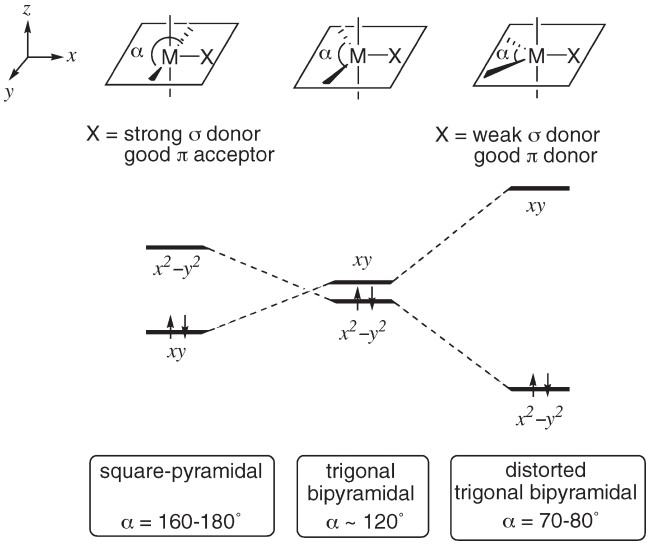
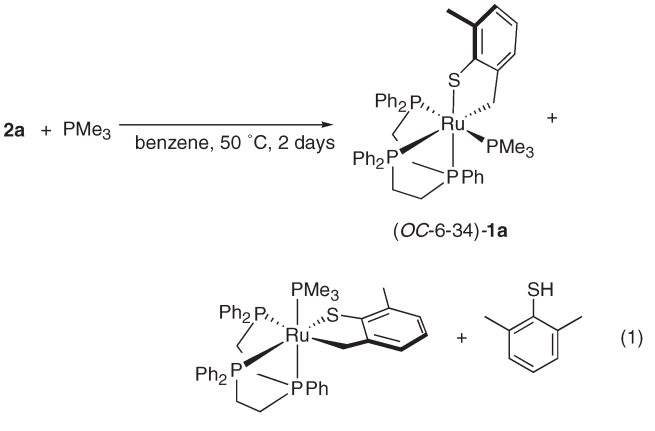
Chart 1. The Geometries of 5-Coordinate d^6 Complexes and the Energy Diagram



These facts mean that the occupied p_y orbital of the S(2) atom is settled in the *xy* plane, and such orientation can be explained by the interaction between the occupied p_y and the empty d_{xy} orbital in the *xy* plane, making a partial Ru−S double-bond character. The corresponding α angles for **2a** (91.4(3)°) and **2d** (92.47(13)°) are consistent with the electronic feature of the thiolato ligand.

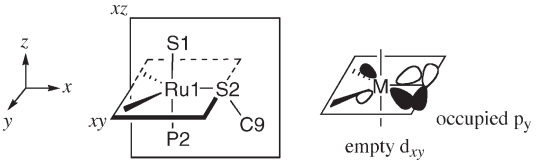
3. C−H Bond Cleavage Reaction of *ortho* Methyl Group. 3.1. Phosphine Induced C−H Bond Cleavage Reaction of Bis(2,6-dimethylbenzenethiolato)ruthenium(II) Having a Tridentate or Bidentate Ligand. The TRIPHOS complex **2a** is formally a 16e coordinatively unsaturated compound and is therefore expected to accept a 2-electron donor. Interestingly, treatment of **2a** with PMe_3 does not give simple adduct of a PMe_3 ligand but produces thiaruthenacycle complexes by the sp^3 C−H bond cleavage reaction, which consist of two stereochemical isomers of Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2C,S]-(TRIPHOS-κ^3P,P',P'')(PMe_3) (**1a**) in 70% NMR yield as shown in eq 1 ([(*OC*-6−34)-**1a**]/[(*OC*-6−25)-**1a**] = 80/20).[27]

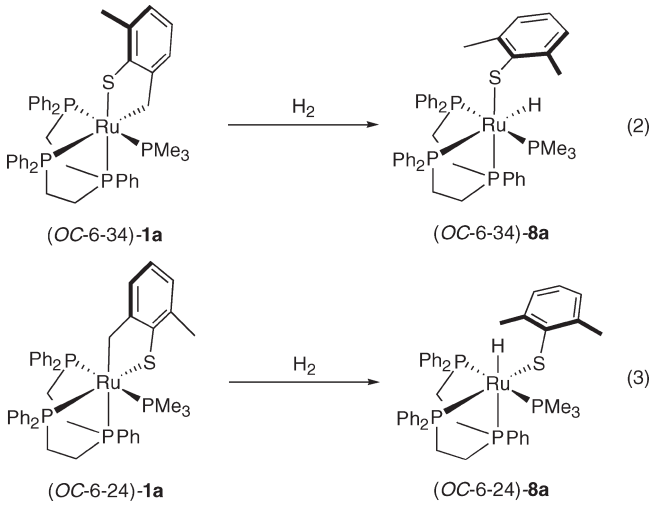


(1)

They were isolated as an analytically pure isomeric mixture in 51% yield, whose separation was unsuccessful by recrystallization. The $^{31}P\{^1H\}$ NMR spectrum of the major species shows four correlated resonances at δ −10.0 (ddd, J = 349, 27, 23 Hz, 1P), 39.9 (ddd, J = 349, 19, 12 Hz, 1P), 47.1 (dd, J = 23, 12 Hz, 1P), and 90.2 (dd, J = 27, 19 Hz) in C_6D_6. The signal appeared at the highest magnetic field at δ −10.0 is assignable to the PMe_3 ligand, and the large coupling constant indicates the PMe_3 locates *trans* to one of the phosphorus atoms in TRIPHOS at δ 39.9. The lowest resonance at δ 90.2 is assigned as the central *P*Ph group based on the analogy of **2a** (δ 88.7).[28] Therefore, the PMe_3 and one of the terminal PPh_2 groups in TRIPHOS are considered to be mutually trans. In the ^1H NMR spectrum and COSY of the major species has two partly overlapped multiplets at δ 2.5−2.6 (1H) and δ 2.88 (1H), assigned as diastereotopic *ortho* methylene protons in the thiaruthenacycle moiety. These data show this thiaruthenacycle compound to be either (*OC*-6−34)-**1a** or (*OC*-6−24)-**1a** (cf. starting compounds in eqs 2 and 3). Although the stereochemical configuration of this compound cannot be specified on the basis of the spectroscopic data alone, we characterize the major compound as (*OC*-6−34)-**1a** on the basis of the following chemical reaction. Namely, hydrogenolysis of this mixture by H_2 (0.1 MPa) in benzene at 50 °C for 1 day produced a corresponding (hydrido)(2,6-dimethylbenzenethiolato)ruthenium(II) complex **8a** in 60% yield whose structure was characterized as described below.[29]

Chart 2. Preferred Orientation of the p_y Orbital





(2)

(3)

The hydrogenolysis product shows a resonance at δ −6.81 (dddd, J = 95.8, 34.8, 19.2, 14.4 Hz, 1H) and a singlet at δ 3.03 (s, 6H) assignable to the hydrido and two equivalent

(26) A similar trend has been seen in the Ru−S bond distance in a formally unsaturated complex Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(η^6-MeC_6H_4-$CHMe_2$-4) (2.263 and 2.311 Å) [ref 26a]. One the other hand, the Ru−S bonds in saturated complexes are relatively longer (2.429−2.476 Å): Ru(SC_6H_4Me-4-κ^1S)$_2$(CO)$_2$(PPh_3)$_2$ (2.470 Å) [refs 26b and 26c], RuH-(SC_6H_4Me-4-κ^1S)(CO)$_2$(PPh_3)$_2$ (2.458 Å) [ref 16], Ru(η^5-C_8H_{11})-($SC_6H_3Me_2$-κ^1S)(PMe_3)$_2$ (2.476 Å), and **1a** (2.429 Å) [ref 12]. (a) Mashima, K.; Mikami, A.; Nakamura, A. *Chem. Lett.* **1992**, 1473. (b) Jessop, P. G.; Rettig, S. L.; James, B. R. *J. Chem. Soc. Chem. Commun.* **1991**, 773. (c) Jessop, P. G.; Rettig, S. L.; Lee., C.-L.; James, B. R. *Inorg. Chem.* **1991**, *30*, 4617.

ortho methyl groups in the ^{1}H NMR spectrum, suggesting formation of a (hydrido)(2,6-dimethylbenzenethiolato)ruthenium(II) complex. In the $^{31}P\{^1H\}$ NMR spectrum, four resonances are observed at δ −7.9 (dt, J = 283, 27 Hz, 1P), 35.3 (m, 1P), 64.2 (ddd, J = 283, 17, 5 Hz, 1P), and 105.7 (dd, J = 29, 19 Hz, 1P), assignable to the PMe_3, and PPh_2, PPh_2 and PPh fragments in the TRIPHOS ligand, respectively, by the analogy of **1a** and **4a**. The large coupling constant between the PMe_3 and one of the PPh_2 fragments suggests mutually trans configuration of these phosphorus atoms. The other PPh_2 fragment at (δ 35.3) shows characteristic upfield shift compared with the corresponding resonance of the starting thiaruthenacycle **1a** (δ 47.1), although the other signals shift to the downfield. Because the hydrido ligand is generally known to show strong trans influence,[30] this upfield shift strongly suggests this PPh_2 fragment being settled in trans to the hydrido. Therefore, this product is considered to be (*OC*-6−34)-**8a**, suggesting the starting compound as (*OC*-6−34)-**1a** ((eq 2).

On the other hand, the minor species (*OC*-6−25)-**1a** can be characterized as follows. The $^{31}P\{^1H\}$ NMR spectrum of minor thiaruthenacycle **1a** has correlated resonances at δ −16.6 (ddd, J = 360, 24, 22 Hz, 1P), 50.9 (ddd, J = 22, 10, 5 Hz, 1P), 73.6 (m, 1P), and 89.9 (ddd, J = 360, 30, 10 Hz, 1P). The signals at δ −16.6 and 89.9 are assignable to the PMe_3 and the central *P*Ph moiety in TRIPHOS, respectively, and their large coupling constant suggests that they are mutually *trans*. Therefore, we characterized the minor thiaruthenacycle species to be (*OC*-6−25)-**1a**.

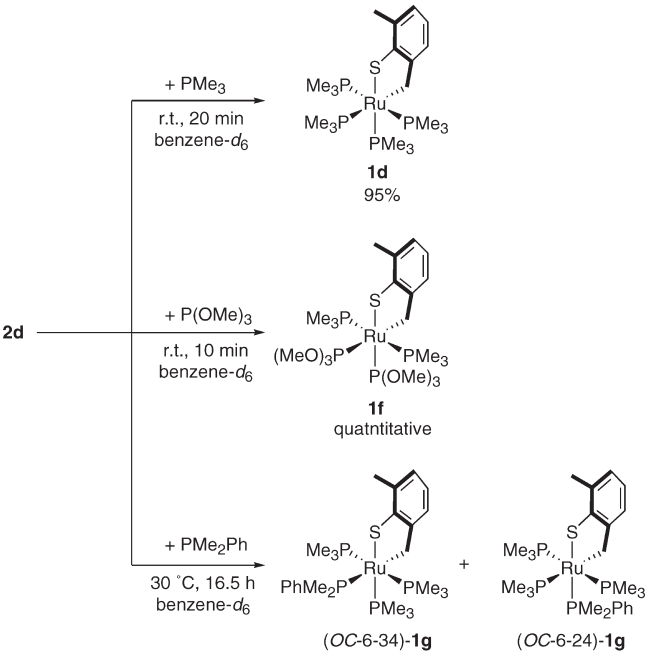
Contrary to PMe_3, neither PPh_3 nor PBu_3 reacted with **2a** under the similar conditions. This is probably due to steric congestions around the ruthenium center.

The reaction of a TDPME complex **2b** with 5 equiv of PMe_3 in C_6D_6 at 50 °C resulted in the displacement of the TDPME ligand to PMe_3, giving *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2C,S](PMe_3)$_4$ (**1d**) (54%) with concomitant formation of 2,6-dimethylbenzenethiol (71%) and free TDPME (70%). Such phosphine exchange reaction also proceeded even in the reaction of **2b** with 1 equiv of PMe_3 to give **1d** in 10% yield.

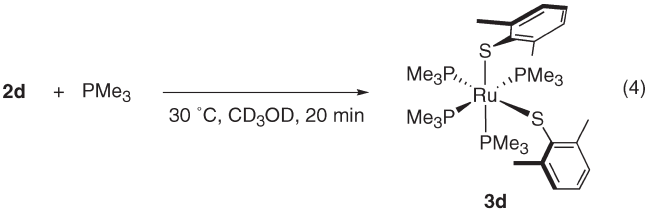
On the other hand, no reaction took place when a bidentate DPPE complex **3c** was treated with 10 equiv of PMe_3 in DMSO-d_6 at 70 °C for 32 h. This is probably because complex **3c** is a coordinatively saturated compound and two 2,6-dimethylbenzenethiolato groups are mutually *trans*. Both factors may discourage the C−H bond cleavage process from **3c**.

3.2. Reactions of Bis(2,6-dimethylbenzenethiolato)ruthenium(II) Having PMe_3 Ligands. Complex **2d** shows more facile sp^3 C−H bond cleavage in the *ortho* methyl group than **2a**. In fact, the reaction of **2d** with PMe_3 proceeded within 20 min in benzene even at room temperature to give **1d** in 95% yield with concomitant formation of 2,6-dimethylbenzenethiol (91%) (Scheme 2).

Scheme 2



Quantitative formation of **1d** was also observed in THF and acetone. Interestingly, when methanol was employed as a solvent in this reaction, a bis(2,6-dimethylbenzenethiolato)tetrakis(phosphine)ruthenium(II) complex, *cis*-Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PMe_3)$_4$ (**3d**) was exclusively produced instead of **1d** (eq 4). It is notable that **3d** never causes C−H bond cleavage reaction to give **1d** in methanol at all. All attempts to isolate **3d** from the methanol solution resulted in failure but gave **2d**, suggesting facile dissociation of PMe_3 from **3d**. Probably, one of the PMe_3 ligands in **3d** was removed during the isolation process. Complex **3d** was therefore characterized by the spectroscopic methods as follows.



In the $^{31}P\{^1H\}$ NMR spectrum of **3d** in methanol-d_4, two triplets are observed at δ 15.67 (t, J = 29 Hz, 2P) and −10.79 (t, J = 29 Hz, 2P), suggesting an A_2X_2 spin system due to presence of two equivalent ligands in *cis* fashion in the octahedral geometry. The ^{1}H NMR spectrum involves a virtual triplet at δ 1.61 (18H) and a slightly broad singlet at δ 1.52 (18H) assignable to the mutually trans PMe_3 and PMe_3 trans to S, respectively. The *ortho* methyl groups in 2,6-dimethylbenzenethiolato groups appear at δ 1.57 (s, 6H) and 2.40 (s, 6H) with resonances due to two different aromatic

(27) The stereochemical description is based on the 1990 IUPAC Inorganic Rules : Block, B. P.; Powell, W. H.; Ernelius, W. C. *Inorganic Chemical Nomenclature: Principles and Practice, ACS Professional Reference Book*; American Chemical Society, Washington, DC, 1990; pp 143.

(28) This assignment is made based on the chemical shift comparisons to the starting compounds **2a** and **4a** because the central *P*Ph fragment was observed in characteristic low field. Although this trend is general feature in the $^{31}P\{^1H\}$ NMR spectra of the octahedral TRIPHOS complexes, we cannot rule out unexpected upfield shift of the central *P*Ph in **1a**. cf. George, T. A.; Tisdale, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 5157.

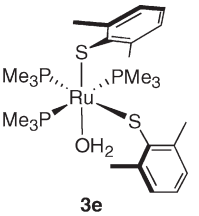
(29) Because separation of these stereochemical isomers was difficult, the isomeric mixture was employed for the hydrogenolysis reaction. The reaction completely proceeded but the hydride species corresponding to the minor species was not observed at all.

(30) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd Ed.; Wiley: New York, 2001; pp 6.

groups.[31] Introduction of dry HCl gas to **3d** in methanol liberated 2,6-dimethylbenzenethiol in 203% yield, clearly indicating presence of two 2,6-dimethylbenzenethiolato groups. It is noteworthy that **3d** has never been observed by the treatment of **2d** with PMe_3 in benzene. High polarity and/or hydrogen bonding may stabilize **3d** in methanol. To know the relation between the employed solvent and the product, we studied the reaction of **2d** with PMe_3 in several polar solvents. In dichloromethane, addition of PMe_3 to **2d** gave both **1d** (15%) and **3d** (69%) in 90% conversion of **2d** at 30 °C for 10 min. These yields were not changed when the mixture was left for 20 h. A similar result was also obtained in chloroform, where the treatment of **2d** with PMe_3 produced both **1d** (48%) and **3d** (10%). Right after addition of 3 equiv of PMe_3 to **2d** at 30 °C in DMSO, a mixture of **2d** (34%), **3d** (42%), and **1d** (13%) was obtained. Then, **2d** and **3d** slowly decreased with increase of **1d** and 2,6-dimethylbenzenethiol. After 11 h at 30 °C, the reaction system constituted of a steady state mixture of **2d** (4%), **3d** (10%), **1d** (73%), and 2,6-dimethylbenzenethiol (88%).

Several two-electron donors were added to a benzene solution of **2d** in order to understand the effect of ligand on the formation of **1d** (Scheme 2). When $P(OMe)_3$ was added to **2d**, a thiaruthenacycle complex, *cis*,*trans*,*cis*-Ru[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C]$(PMe_3)_2[P(OMe)_3]_2$ (**1f**) was produced in quantitative yield. An AMX_2 pattern at δ 156.8 (1P, *P*$(OMe)_3$), 100.7 (1P, *P*$(OMe)_3$) and 3.5 (2P, *P*Me_3) in the $^{31}P\{^1H\}$ NMR and a virtual triplet at δ 1.47 (18H) in the ^1H NMR support this configuration, and a broad peak at δ 2.5 (2H) and a singlet at δ 1.86 (3H) in the ^1H NMR suggest formation of thiaruthenacycle **1f**. Similarly, addition of PMe_2Ph to **2d** gave a 6:4 mixture of regioisomers of *mer*-Ru[SC_6H_3-$(CH_2$-2)(Me-6)-κ^2S,C]$(PMe_3)_3(PMe_2Ph)$ (**1g**) in 31% yield with concomitant formation of 2,6-dimethylbenzenethiol in 36% yield. The major isomer shows an AM_2X pattern at δ 0.16 (1P, *P*Me_2Ph), −8.32 (2P, *P*Me_3), and −16.7 (1P, *P*Me_3) in the $^{31}P\{^1H\}$ NMR and an overlapped signals at δ 2.9 and a triplet of triplets at δ 2.75 (2H) in the ^1H NMR assignable to the *ortho* methyl and methylene groups, respectively, suggesting formation of a thiaruthenacycle **1g**. Similarly, the minor isomer shows an AM_2X pattern at δ 9.35 (1P, *P*Me_2Ph), −9.62 (2P, *P*Me_3), and −17.60 (1P, *P*Me_3) in the $^{31}P\{^1H\}$ NMR and a triplet of triplets at δ 3.11 (2H) and an overlapped signal at δ 2.9 (3H) in the ^1H NMR, assignable to the *ortho* methylene and methyl groups, respectively, suggesting formation of thiaruthenacycle **1g**. In these $^{31}P\{^1H\}$ NMR spectra, the PMe_2Ph in the major isomer resonates at the higher magnetic field (δ 0.16) than that in the minor isomer (δ 9.35), strongly suggesting that the PMe_2Ph ligand is placed *trans* to the carbon ligand with strong *trans* influence. Therefore, we characterize the major species to be (*OC*-6−34)-**1g** (the PMe_2Ph *trans* to methylene) and the minor species to be (*OC*-6−24)-**1g** (the PMe_2Ph *trans* to S). Treatment of **2d** with PCy_3 gave a mixture involving *cis*,*mer*-Ru$(SC_6H_3Me_2$-$\kappa^1S)_2(PMe_3)_3(OH_2)$ (**3e**) (48%). An AX_2 pattern at δ 39.68 (1P) and −3.58 (2P) in the $^{31}P\{^1H\}$ NMR and a virtual triplet

Chart 3



3e

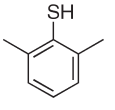
at δ 1.20 (18H) in the ^1H NMR spectrum suggest the meridional geometry of **3e** (Chart 3).

The ^1H NMR spectrum also shows a broad singlet around δ 2.45−2.50 (12H) and a broad peak at δ 11.5 (2H), assignable to the four *ortho* methyl groups and an aqua ligand, respectively. These data support the formation of **3e**. The aqua ligand probably comes from contaminated water in this system. Similar treatment of **2d** with PEt_3 produced a complex mixture involving **1d** (17%) and **3e** (5%) with concomitant formation of 2,6-dimethylbenzenethiol. In this reaction, a PMe_3 ligand probably came from another **2d** by disproportionation reaction to give **1d**. It seems that addition of compact phosphorus ligands to **2d** leads to the C−H bond cleavage reaction to give thiaruthenacycle complexes.[32] On the other hand, exposure of **2d** to CO (0.1 MPa) quickly produced an analytically pure carbonyl complex *cis*,*cis*,*cis*-Ru$(SC_6H_3Me_2$-2,6-$\kappa^1S)_2(PMe_3)_2(CO)_2$ (*cis*,*cis*,*cis*-**3h**) in 93% yield as a kinetic product, which finally gave an equilibrium mixture between *cis*,*cis*,*cis*-**3h** and *trans*,*trans*,*trans*-**3h** (K_{eq} = [*trans*,*trans*,*trans*-**3h**]/[*cis*,*cis*,*cis*-**3h**] = 9.9 at 50 °C in benzene) (Scheme 3).

The stereochemistry of these isomers was determined by the NMR data, where *cis*,*cis*,*cis*-**3h** showed two magnetically inequivalent 2,6-dimethylbenzenethiolato moieties in the ^1H NMR and an AX pattern appeared at δ −16.09 (d) and −11.46 (d) in the $^{31}P\{^1H\}$ NMR, and *trans*,*trans*,*trans*-**3h** gave a sole 2,6-dimethylbenzenethiolato resonance and a virtual triplet at δ1.08 (vt, 18H) assignable to the PMe_3 in the ^1H NMR, and a single resonance δ −14.81 in the $^{31}P\{^1H\}$ NMR. These spectroscopic data suggests proposed structures of **3h**.

3.3. Reversibility of the C−H Bond Cleavage Reaction. Treatment of a mixture of thiaruthenacycle complexes (*OC*-6−34)-**1a** and (*OC*-6−25)-**1a**, with 2 equiv of 2,6-dimethylbenzenethiol in benzene at 70 °C for 3 days gave a bis(2,6-dimethylbenzenethiolato)ruthenium(II) complex **2a** in 83% yield (eq 5).

(*OC*-6-34)-**1a** + (*OC*-6-25)-**1a** +



benzene, 70 °C, 3 d
− PMe_3

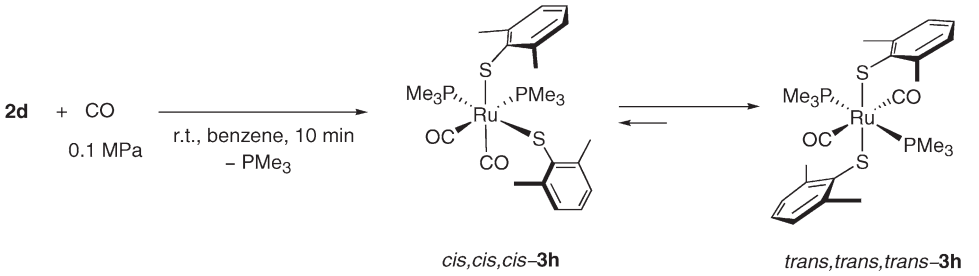
2a 83% (5)

Similarly, the reaction of **1d** with 5 equiv of 2,6-dimethylbenzenethiol in acetone at room temperature for 15 h produced **2d**, which was isolated as analytically pure dark-red needles in 32% yield after recrystallization from cold toluene. With 15 equiv of 2,6-dimethylbenzenethiol in acetone, **2d** was formed in 57% in 30 min (Scheme 4). When similar treatment was performed in benzene, **2d** was formed

(31) One of the *ortho* methyl resonances in **9d** appears in significantly high field at δ 1.57, while another *ortho* methyl group resonates at the comparable region to the related *cis*-bis(2,6-dimethylbenzenethiolato)ruthenium(II) complexes such as **2a** (δ 2.11), **2b** (δ 2.46), **2d** (δ 2.55), and free 2,6-dimethylbenzenethiol (δ 2.48). Because **9d** is a coordinatively unsaturated complex, this fact may be caused by the lone pair electrons on the S atom attached to the saturated Ru center, or the ring current effect of the aromatic ring.

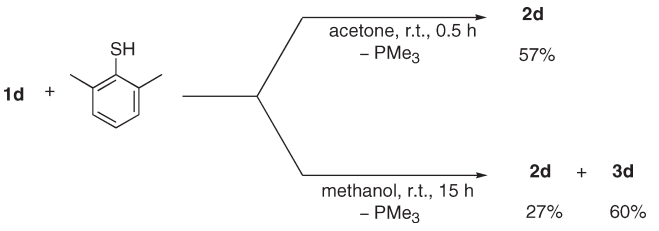
(32) Cone angles: $P(OMe)_3$ (107°), PMe_3 (118°), PMe_2Ph (122°), PEt_3 (132°), PPh_3 (145°) and PCy_3 (170°). Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Scheme 3



cis,cis,cis–**3h** *trans,trans,trans*–**3h**

Scheme 4



in only 12% yield. In methanol, **3d** was produced in 60% yield as a major product along with **2d** in 27% yield. These results show reversibility of the present C−H bond cleavage reaction but the reaction strongly depends on the solvent.

4. Kinetic Study for the C−H Bond Cleavage Reaction. Complex **2d** shows an absorption band at 518 nm (ε = 2530 M^{-1} cm^{-1}) in benzene. When excess PMe_3 was added, the band gradually decreased and finally gave the absorption spectrum identical to **1d**. Though isosbestic points were not observed, the absorption band homogeneously decreased with time and the reaction was first-order on the concentration of **2d**. The observed rate constant k_{obs} was estimated as $2.63 \pm 0.03 \times 10^{-3}$ s^{-1} in the presence of 45 equiv of PMe_3 at 30 °C, and the estimated first-order rate constant was independent from the concentration of PMe_3 (Figure 3).

Therefore, the rate for the conversion of **2d** into **1d** is expressed as shown in eq 6.

$$-\frac{d[\mathbf{2d}]}{dt} = k_{obs}[\mathbf{2d}] = k_1[PMe_3]^0[\mathbf{2d}] \qquad (6)$$

Conversion of **2d** into **1d** was also confirmed by the ^1H NMR spectra in C_6D_6 in the presence of 3 equiv of PMe_3 at 30 °C and the estimated first-order rate constant was k_{obs} = 2.7×10^{-3} s^{-1}, which was comparable to that monitored by the UV−vis spectra. The estimated rate constant depends on the employed solvent and decreased in the order benzene: $(2.78 \pm 2) \times 10^{-3}$ s^{-1} > THF: $(1.10 \pm 1) \times 10^{-3}$ s^{-1} > acetone: $(3.67 \pm 0.5) \times 10^{-4}$ s^{-1}. Therefore, the rate constant is considered to decrease with increase of dielectric constant of the used solvent: benzene (ε = 2.28) < THF (ε = 7.32) < acetone (ε = 20.7).[33] This reaction was not affected by the addition of galvinoxyl and potassium 2,6-dimethylbenzenethiolate.

For the bis(2,6-dimethylbenzenethiolato)ruthenium(II) complex with a tridentate phosphine ligand **2a**, the absorption maximum was at 573 nm (ε = 1690 $M^{-1}cm^{-1}$) in THF whose intensity also decreased after addition of PMe_3, suggesting formation of **1a**. The rate of disappearance of **2a** also showed a good linearity in the first-order rate plot in THF for more than 3 half-lives, although this reaction produced two stereoisomers (*OC*-6−34)-**1a** and (*OC*-6−25)-**1a**. This reaction also depends on neither concentration of added PMe_3 nor potassium 2,6-dimethylbenzenethiolate. The reaction rate in THF [$(1.68 \pm 0.02) \times 10^{-5}$ s^{-1}] is also slower than that in nonpolar toluene [$(6.16 \pm 0.06) \times 10^{-5}$ s^{-1}].

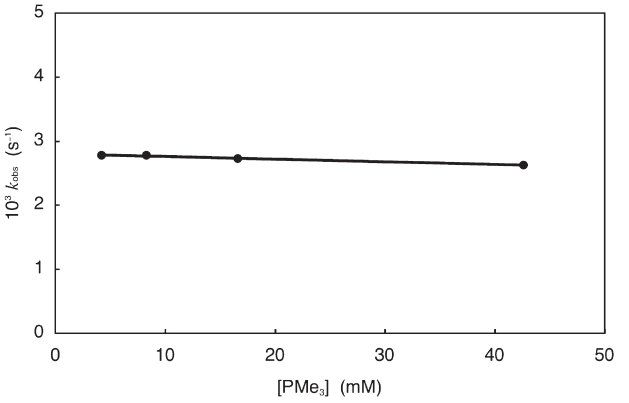
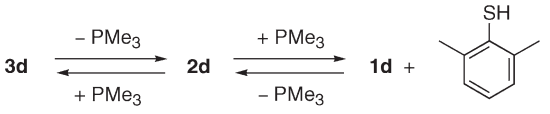


Figure 3. Effect of added PMe_3 on the first-order rate constant k_{obs} monitored by the UV−vis spectral change at 518 nm for conversion of **2d** into **1d** in benzene at 30.0 ± 0.5 °C. Conditions: [**2d**] = 0.94 mM.

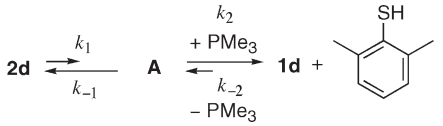
Tris(trimethylphosphine) complex of bis(2,6-dimethylbenzenethiolato)ruthenium(II) **2d** was shown to produce corresponding tetrakis(trimethylphosphine) complex **3d** quantitatively by addition of PMe_3 in methanol, while such treatment in benzene led to the C−H bond cleavage reaction, giving a thiaruthenacycle complex **1d**, exclusively. To clarify the potential ability of the coordinatively saturated complex **3d** for the C−H bond cleavage reaction to give the ruthenacycle, time-course for the formation of the ruthenacycle **1d** was monitored in DMSO-d_6 by NMR at 30 °C in the presence of PMe_3 because **3d** was obtained along with **1d** by the treatment of **2d** with PMe_3 in DMSO (vide supra). After mixing **1d** and 1, 3, and 10 equiv of PMe_3 at 30 °C, the ratios of **2d**/**3d** reached 61%/23%, 34%/42%, and 15%/73%, respectively. The half-lives at 30 °C increased as follows: $t_{1/2}$ = 0.64 h (1 equiv PMe_3), 1.4 h (3 equiv PMe_3), 2.2 h (10 equiv PMe_3). This feature suggests the rate for the formation of **1d**, becoming slower along with increase of concentration of **3d**, although quantitative kinetic studies have not been performed. Therefore, **3d** is considered to be inert to the C−H bond cleavage reaction. The most probable scenario is that the C−H bond cleavage reaction from **2d** competes the formation of **3d** in the presence of PMe_3 in DMSO, and the C−H bond cleavage reaction takes place only from **2d** (Scheme 5). Probably, polar and apolar solvents favor to give **3d** and **1d** in this reaction, respectively. The present consideration also suggests importance of

(33) Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*; Wiley: New York, 1972; pp 6.

Scheme 5



Scheme 6



5-coordinate formally unsaturated compounds for the C−H bond cleavage reaction in Ru(II).

As described above, **2d** is responsible for the C−H bond cleavage reaction to give **1d**. Although this reaction requires addition of PMe_3, present kinetic data suggests the formation rate constant of **1d** is independent of the concentration of PMe_3. We therefore proposed a tris(trimethylphosphine) complex **A** as an intermediate to which PMe_3 coordinated rapidly to give **1d**. (Scheme 6).

Because such an intermediate **A** has never been detected during the formation of **1d**, we apply the steady state approximation to the concentration of **A**, giving the rate equation expressed as shown in eq 7.

$$-(\mathrm{d}[\mathbf{2d}])/(\mathrm{d}t) = (k_1k_2[\mathbf{2d}][\mathrm{PMe_3}] - k_{-1}k_{-2}[\mathbf{1d}][\mathrm{HSC_6H_3Me_2-2,6}][\mathrm{PMe_3}])/(k_{-1}+k_2[\mathrm{PMe_3}]) \quad (7)$$

On the basis of the experimental results, we assumed that (i) the pre-equilibrium between **2d** and **A** in Scheme 6 lay far to the **2d** side, (ii) formation of **A** was the rate-determining step, and (iii) the back reaction from **1d** with 2,6-dimethylbenzenethiol was a slow process. Then, eq 7 is simplified as eq 8, which is consistent with the experimental rate equation (eq 6).

$$-\frac{\mathrm{d}[\mathbf{2d}]}{\mathrm{d}t} = k_1[\mathbf{2d}] \quad (8)$$

5. Proposed Mechanism for the C−H Bond Cleavage Reaction. To get information of the transition state, the kinetic parameters for **2d** are estimated by the Eyring plot for the reaction in benzene in the range of 30−50 °C (Figure 4): $\Delta H^{\ddagger} = 57 \pm 16$ kJ mol^{-1}, $\Delta G^{\ddagger}_{298} = 89 \pm 31$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -107 \pm 51$ J mol^{-1} K^{-1}.

Similarly, the kinetic activation parameters of **2a** in THF are as follows: $\Delta H^{\ddagger} = 87 \pm 14$ kJ mol^{-1}, $\Delta G^{\ddagger}_{298} = 70 \pm 27$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -58 \pm 42$ J mol^{-1} K^{-1}. Those of **2a** in toluene show similar parameters of activation: $\Delta H^{\ddagger} = 85 \pm 5$ kJ mol^{-1}, $\Delta G^{\ddagger}_{298} = 104 \pm 10$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -65 \pm 14$ J mol^{-1} K^{-1}.

Results of reactivities of bis(2,6-dimethylbenzenethiolato)-ruthenium(II) complexes and kinetic studies for the formation process of thiaruthenacycle complexes **1** are summarized as follows: (i) neither *cis*-Ru(SC_6H_3Me-2,6-κ^1S)$_2$(PMe_3)$_4$ (**3d**) nor *trans*-Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(dppe)$_2$ (**3c**) converts into the thiaruthenacycle **1**, suggesting the importance of coordinative unsaturation for the C−H bond cleavage reaction, (ii) the first-order dependence of the rate on the concentration of **2** that rules out a C−H bond cleavage via bimolecular process, (iii) the zero-order dependence of the PMe_3 concentration on the rate suggests that formation of **A** in Scheme 6 is considered to be the rate-determining, (iv) the rate-determining step in the formation of **1d** favors nonpolar solvents, suggesting the less polar transition state than the ground state, (v) a radical scavenger such as galvinoxyl does not retard this process that rules out a free radical process, (vi) because no significant difference in the rate is observed in the presence of 2,6-dimethylbenzenethiolate anion, neither prerequisite dissociation of thiolato anion nor proton abstraction by thiolato anion is a favorable process, and (vii) the large negative entropy of activation suggests a distorted transition state.

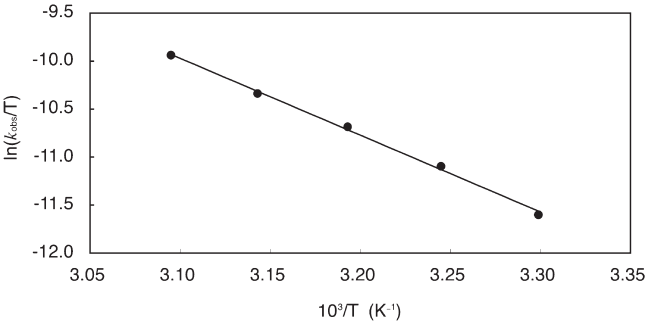


Figure 4. Eyring plot for the intramolecular C−H bond cleavage reaction of **2d** to give **1d** in benzene.

From these facts, the rate-determining step in the present reaction would therefore be the C−H bond cleavage step by concerted mechanisms as shown in Scheme 7.

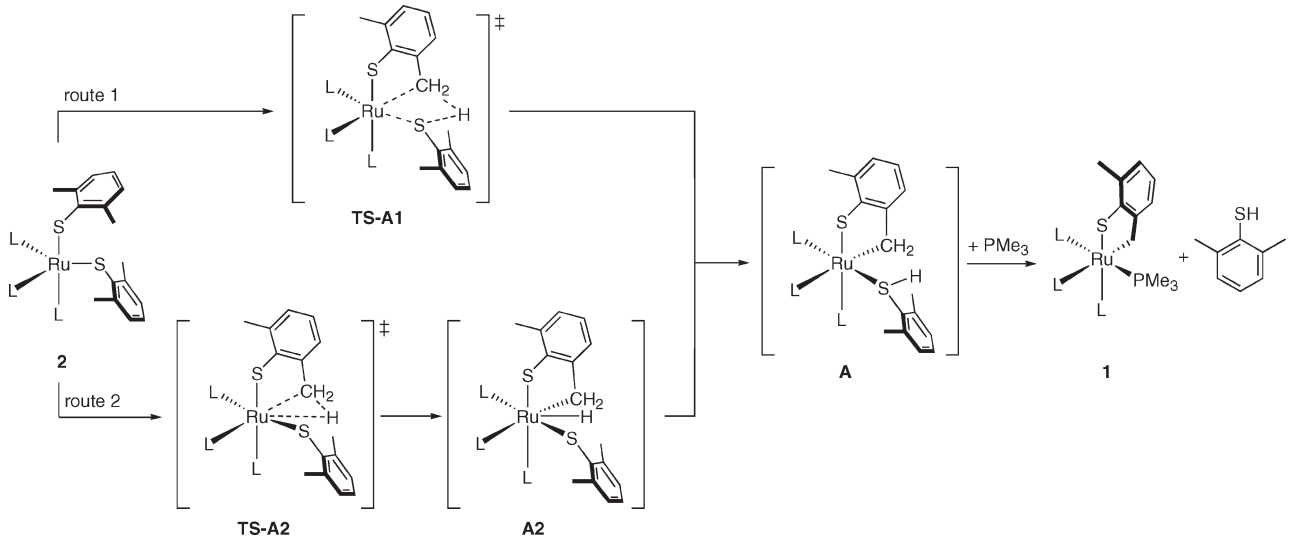
Route 1 involves a four-centered transition state either via a σ-bond metathesis or an internal electrophilic substitution. Because they closely resemble each other and it is difficult to experimentally differentiate these mechanisms, we summarize these two mechanism into a four-centered concerted mechanism. Route 2 involves a three-centered transition state that is so-called the C−H bond oxidative addition mechanism followed by the reductive elimination between the thiolato and hydrido ligands. Although we do not have definitive evidence in support of either mechanism yet, we believe that the reaction through route 1 is the favorable scenario because route 2 requires a 7-coordinate Ru(IV) intermediate **A2**, which is expected to be a high-energy process.[34] In route 1 in Scheme 7, it is reasonable to postulate an equilibrium between **2** and intermediate **A**. An alternative structure of intermediate **A** is a 5-coordinate species Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2S,C](PMe_3)$_3$. However, the large negative entropy of activation suggests the thiol moiety remaining intact on the ruthenium center. Thus intermediate **A** is considered to be a thiaruthenacycle with a 2,6-dimethylbenzenethiol ligand, from which the thiol ligand is rapidly displaced by PMe_3 to give **1**.

Concluding Remarks

We have reported synthesis of 5-coordinate bis(2,6-dimethylbenzenethiolato)ruthenium(II) complexes, which readily give corresponding thiaruthenacycle complexes by addition of PMe_3 ligand. The sp^3 C−H bond cleavage reaction from bis(2,6-dimethylbenzenethiolato)ruthenium-(II) complexes **2** proceeds by the concerted mechanism and

(34) We have found Brønsted acid promote the C−H bond cleavage reaction in aryloxoruthenium(II) complex. The present C−H bond cleavage reaction from **2** in the presence of Brønsted acid will be reported elsewhere. Hirano, M.; Kuga, T.; Kitamura, M.; Kanaya, S.; Komine, N.; Komiya, S. *Organometallics* **2008**, *27*, 3635.

Scheme 7



the coordinative unsaturation is an intrinsic factor for present C−H bond cleavage reaction. It is also notable that the activation energy for the present sp^3 C−H bond cleavage reaction is approximately one-fourth of the bond dissociation energy for the sp^3 C−H bond in toluene.[35] This fact suggests the methyl group C−H bond in bis(2,6-dimethylbenzenethiolato)ruthenium(II) complex being activated probably due to the interaction with the sulfur atom in the arenethiolato group, which also acts as a good acceptor of the cleaved proton.

Experimental Section

General Procedure. All procedures described in this paper were carried out under nitrogen or argon atmosphere by use of Schlenk and vacuum line techniques. Benzene, hexane, toluene, and Et_2O were dried over dry calcium chloride and were distilled over sodium wire under nitrogen using benzophenone ketyl as an indicator. THF was distilled over sodium wire under nitrogen in the presence of benzophenone. Acetone was dried over Drierite and distilled under nitrogen. Methanol was dried over molecular sieves 4A and then was distilled over magnesium methoxide. 2,6-Dimethylbenzenethiol was purchased from Aldrich and was stored and used under nitrogen atmosphere. PMe_3 was prepared by the reaction of $P(OPh)_3$ with MeMgI and was distilled under vacuum.[36] *cis*-Ru[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C]$(PMe_3)_4$ (**1d**) was prepared as reported previously.[18] Ru(1,5-COD)(1,3,5-COT) (**5**),[37] Ru(η^6-naphthalene)(η^4-1,5-COD) (**6**),[38] $RuCl_2(PPh_3)_3$,[39] *trans*-$RuCl_2(DPPE)_2$ (**7c**),[40] and *trans*-$RuCl_2(PMe_3)_4$ (**7d**),[41] were prepared according to the literature methods. Potassium salt of 2,6-dimethylbenzenethiol was prepared by the treatment of 2,6-dimethylbenzenethiol with KOH in methanol. ^1H and $^{31}P\{^1H\}$ NMR spectra were measured on a JEOL LA300 and a JEOL ECX400 spectrometers. The IR spectra were measured on a JASCO FT/IR410 spectrometer. UV−vis spectra were measured on a Shimadzu UV-Spec 1500 photodiode array spectrometer using a thermostatted Schlenk type quartz cell. Elemental analyses were performed on Perkin-Elmer 2400 series II CHN analyzer. The compounds without the elemental analysis were characterized by the spectroscopic methods. For thermodynamic and kinetic analyses, reliability intervals indicate 95% probability.

Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(TRIPHOS-κ^3P,P',P'') (2a). Complex **5** (371.6 mg, 1.18 mmol) was treated with TRIPHOS (621.7 mg, 1.163 mmol) in benzene (22 mL) for 2 days at room temperature. All volatile matters were removed under reduced pressure. Recrystallization of the resulting solid from refluxing toluene gave yellow plates of Ru(η^4-1,5-COD)(TRIPHOS-κ^3P,P',P'')·C_6H_5Me (**4a**·C_6H_5Me) in 89% yield (777.6 mg, 1.045 mmol). **4a**: ^1H NMR (300 MHz, C_6D_6) δ 1.0−1.2 (br m, 2H, CH_2 in TRIPHOS), 1.6−2.0 (m, 4H, CH_2 in TRIPHOS), 2.2 (br s, 8H, COD), 2.4 (m, 1H, CH_2 in TRIPHOS), 2.5 (m, 1H, CH_2 in TRIPHOS), 2.7−4.0 (very broad, COD, 4H), 6.8−7.3 (m, 24H, *Ph*), 7.39 (t, $^3J_{H-H}$ = 7 Hz, 4H, *Ph*), 7.82 (t, $^3J_{H-H}$ = 7 Hz, 4H, *Ph*). $^{13}C\{^1H\}$ (100.5 MHz, C_6D_6) δ 31.0−31.5 (br m, TRIPHOS), 32.9−33.9 (br m, TRIPHOS), 125.6 (s, TRIPHOS), 128.6 (s, ^1J = 143 Hz, TRIPHOS), 129.3 (s, TRIPHOS), 130.8 (d, $^1J_{C-P}$ = 8 Hz, TRIPHOS), 132.7 (q, $^1J_{C-P}$ = $^3J_{C-P}$ = 7 Hz, TRIPHOS), 137.8 (s, TRIPHOS), 141.6 (s, TRIPHOS), 147.1 (s, TRIPHOS) signals due to the 1,5-COD ligand were obscure. $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ 75.8 (d, J = 24 Hz, 2P), 102.8 (t, J = 24 Hz, 1P). Anal. Calcd for $C_{42}H_{45}P_3Ru\cdot C_7H_8$: C, 70.04; H, 6.39. Found: C, 70.75; H, 6.85. **4a**·C_6H_5Me (324.5 mg, 0.4363 mmol) was treated with 2,6-dimethylbenzenethiol (300 μL, 2.25 mmol) in acetonitrile (15 mL) at 70 °C for 6 h. On cooling the solution to room temperature, dark-purple plates of **2a** deposited. Yield: 88% (347.8 mg, 0.382 mmol). ^1H NMR (300 MHz, CD_2Cl_2) δ 1.61 (m, 2H, CH_2 in TRIPHOS), 1.85 (m, 2H, CH_2 in TRIPHOS), 2.11 (overlapped, br, 12H, *ortho-Me*), 2.18 (overlapped, m, 2H, CH_2 in TRIPHOS), 2.49 (m, 2H, CH_2 in TRIPHOS), 6.43 (br, 6H, aromatic protons), 6.8−8.1 (m, 25H, aromatic protons). $^{31}P\{^1H\}$ (122 MHz, CD_2Cl_2) δ 81.5 (d, J = 15 Hz, 2P), 88.7 (t, J = 15 Hz, 1P). Anal. Calcd for $C_{50}H_{51}P_3RuS_2$: C, 65.99; H, 5.65; S, 7.05. Found: C, 65.59; H, 5.77; S, 7.61. UV−vis (THF): λ_{max} = 573 nm (ε = 1690).

Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(TDPME-κ^3P,P',P'') (2b). Complex **6** (65.4 mg, 0.194 mmol) and TDPME (120 mg, 0.192 mmol) were placed in an Schlenk tube (25 mL). Benzene (3 mL) was added into the Schlenk tube, and the solution was heated at

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70 °C for 2 days. After removal of benzene, the free naphthalene was removed by use of an oil diffusion pump. The resulting solid was washed with acetone and then it was recrystallized from cold toluene to give a yellow powder of Ru(η^4-1,3-COD)-(TDPME-κ^3P,P',P'') (**4b**) in 53% yield (85.5 mg, 0.103 mmol). ^{1}H NMR (300 MHz, C_6D_6) δ 1.11 (s, 3H, *Me* in TDPME), 1.7 (br, 2H, 1,3-COD), 1.8 (br, 2H, 1,3-COD), 2.11 (s, 6H, CH_2 in TDPME), 2.4 (br, 2H, 1,3-COD), 2.6 (br, 2H, 1,3-COD), 3.14 (br, 2H, 1,3-COD), 5.25 (t, J = 11 Hz, 2H, 1,3-COD), 6.8−7.2 (m, 30H, *Ph*). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6) δ 31.2 (s). Anal. Calcd for $C_{49}H_{51}P_3Ru$: C, 70.57; H, 6.16. Found: C, 70.02; H, 6.24. It is notable that the 1,3-COD ligand is produced from 1,5-COD by isomerization during the isolation process because the NMR spectra of crude product are assigned as Ru(η^4-1,5-COD)(TDPME) (**4b′**). **4b′**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.06 (s, 3H, *Me* in TDPME), 2.18 (s, 8H, CH_2 in 1,5-COD), 2.62 (d, J = 8.2 Hz, 3H, CH_2 in TDPME), 2.8 (d, J = 8.2 Hz, 3H, CH_2 in TDPME), 3.41 (s, 4H, C*H* in 1,5-COD), 6.8−7.4(m, Ph, 30H). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6) δ 32.1 (s). **4b** (110.4 mg, 0.1324 mmol) was treated with 2,6-dimethylbenzenethiol (90 μL, 0.68 mmol) in benzene at 70 °C for 24 h. Then, all volatile matter was removed under reduced pressure and the resulting solid was recrystallized from refluxing toluene to give **2b** as black needles in 53% yield (70.0 mg, 0.0702 mmol). ^{1}H NMR (300 MHz, C_6D_6) δ 1.06 (s, 3H, *Me* in TDPME), 2.18 (s, 6H, CH_2 in TDPME), 2.46 (s, 12H, *ortho-Me*), 6.7−7.0 (m, 24H, aromatic protons), 7.53 (s, 12H, aromatic protons). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6) δ 40.5 (s). Anal. Calcd for $C_{57}H_{57}P_3RuS_2$: C, 68.45; H, 5.74; S, 6.41. Found: C, 68.47; H, 5.74; S, 6.24. UV−vis (THF): λ_{max} = 432 nm (ε = 2990), 620 nm (ε = 1650).

***trans*-Ru(SC$_6$H$_3$Me$_2$-2,6-κ^1S)$_2$(DPPE)$_2$ (3c).** Complex **7c** (183.4 mg, 0.1893 mmol) and potassium salt of 2,6-dimethylbenzenethiol (97.9 mg, 0.555 mmol) were placed in a 50 mL Schlenk tube. Into the Schlenk tube, 1,4-dioxane (30 mL) was added by a syringe. After the reaction in a refluxing solution for 28.5 h, yellow precipitate deposited. The precipitate was separated, washed with 1,4-dioxane and then hexane, and dried under vacuum to give **3c** as yellow powder in 19% yield (49.5 mg, 0.0363 mmol). This compound was characterized by NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.74 (br, 8H, DPPE), 3.65 (s, 12H, *ortho*-Me), 7.02−7.25 (m, 46H, aromatic protons). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2) δ 44.99 (s).

Ru(SC$_6$H$_3$Me$_2$-2,6-κ^1S)$_2$(PMe$_3$)$_3$ (2d). Complex **7d** (14.6 mg, 0.0307 mmol) was treated with potassium 2,6-dimethylbenzenethiolate (17.8 mg, 0.101 mmol) in DME at 50 °C for 3 days. After removal of all volatile matters, the resulting solid was extracted with C_6D_6 and 1,4-dioxane was added as an internal standard. Complex **2d** was obtained in 17% yield as burgundy crystals with concomitant formation of **1d** (69%) and **7d** (9%). ^{1}H NMR (300 MHz, C_6D_6) δ 1.13 (m, 27H, PMe_3), 2.55 (s, 12H, $C_6H_3Me_2$), 6.97 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-$C_6H_3Me_2$), 7.08 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-$C_6H_3Me_2$). ^{13}C NMR (100.5 MHz, C_6D_6) δ 21.6−21.9 (m, PMe_3), 24.4 (s, $^1J_{C-H}$ = 125 Hz, $C_6H_3Me_2$), 123.4 (s, $^1J_{C-H}$ = 158 Hz, $C_6H_3Me_2$), 127.2 (s, $^1J_{C-H}$ = 151 Hz, $C_6H_3Me_2$), 141.7 (s, $C_6H_3Me_2$), 147.7 (s, $C_6H_3Me_2$). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6, 20 °C) δ 16.6 (s). Anal. Calcd for $C_{25}H_{45}P_3RuS_2$: C, 49.73; H, 7.51; S, 10.62%. Found: C, 49.66; H, 8.01; S, 10.69%.

Protonolysis of 2d with HCl Gas. Complex **2d** (4.6 mg, 0.0076 mmol) was placed in a NMR tube into which a dichloromethane-d_2 solution (0.6 mL) was introduced. Triphenylmethane (3.3 mg, 0.014 mmol) was added into the solution. Right after introduction of excess dry HCl gas into the solution at room temperature, the red solution turned yellow. NMR measurement of the solution indicated formation of 2,6-dimethylbenzenethiol (0.0155 mmol) in 205% yield. The other products could not be characterized.

Treatment of 2d with PMe$_3$ in Benzene-d_6. Complex **2d** (9.9 mg, 0.015 mmol) was placed in a NMR tube into which C_6D_6 (0.6 mL) was introduced by vacuum transfer. 1,4-Dioxane (1.6 μL, 0.19 mmol) was added as an internal standard, and then PMe_3 (1.3 μL, 0.015 mmol) was added by a hypodermic syringe. After 50 min, **1d** was produced in 98% yield.

Treatment of 2d with PMe$_3$ in Methanol-d_4. Complex **2d** (6.3 mg, 0.010 mmol) was placed in a NMR tube into which CD_3OD (600 μL) was introduced by a hypodermic syringe. PMe_3 (2.9 μL, 0.028 mmol) was added into the solution by a hypodermic syringe. The time-course of the reaction was monitored by the NMR spectra at 30 °C. After 20 min, **2d** was completely consumed and *cis*-Ru(SC$_6$H$_3$Me$_2$-2,6-κ^1S)$_2$(PMe$_3$)$_4$ (**3d**) was produced in 100% yield. Complex **3d** could not be isolated because during the isolation process; **3d** converted to **2d**, probably due to facile dissociation/evaporation of a PMe_3 ligand. Therefore **3d** was characterized spectroscopic methods. **3d**: ^{1}H NMR (300 MHz, CD_3OD, 30 °C) δ 1.52 (br s, 18H, PMe_3), 1.57 (s, 6H, *ortho-Me*), 1.61 (vt, $^2J_{H-P}$ = $^4J_{H-P}$ = 3.6 Hz, 18H, PMe_3), 2.40 (s, 6H, *ortho-Me*), 6.58 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, *para*-$C_6H_3Me_2$), 6.79 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, *para*-$C_6H_3Me_2$), 6.84 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, *meta*-$C_6H_3Me_2$), 6.92 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, *meta*-$C_6H_3Me_2$). ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, 30 °C) δ −10.79 (t, $^2J_{P-P}$ = 29 Hz, 2P, mutually *trans* *P*Me$_3$), 15.67 (t, $^2J_{P-P}$ = 29 Hz, 2P, *P*Me$_3$ *trans* to S).

Protonolysis of 3d with Dry HCl. Because complex **3d** was not isolable compound, this reaction was carried out by use of in situ formed **3d** in an NMR tube. Treatment of **2d** (6.8 mg, 0.011 mmol) with 3 equiv of PMe_3 (3.5 μL, 0.034 mmol) in methanol-d_4 produced **3d** quantitatively, which was confirmed by the NMR spectra. The reaction system was exposed to dry HCl to give 2,6-dimethylbenzenethiol in 203% yield (0.023 mmol).

Treatment of 2d with PMe$_3$ in Dimethylsulfoxide-d_6. Complex **2d** (5.5 mg, 0.0091 mmol) and a flame-sealed ampule containing $P(OPh)_3$ in C_6D_6 as an standard were placed in an NMR tube into which DMSO-d_6 (600 μL) was introduced by a hypodermic syringe. Triphenylmethane (2.7 mg, 0.011 mmol) was added as an internal standard. PMe_3 (2.5 μL, 0.024 mmol) was added into the NMR tube by a hypodermic syringe, and the reaction profile was monitored at 30 °C by NMR. After 11 h, **1d** (0.0066 mmol, 73%), **3d** (0.0009 mmol, 10%), and 2,6-dimethylbenzenethiol (0.0080 mmol, 88%) were observed in 96% conversion of **2d**. **1d**: ^{1}H NMR (300 MHz, DMSO-d_6, 30 °C) δ 1.16 (vt, $^2J_{H-P}$ = $^4J_{H-P}$ = 2.1 Hz, 18H, mutually *trans*-PMe$_3$), 1.33 (d, $^2J_{H-P}$ = 10.2 Hz, 9H, PMe_3), 1.36 (d, $^2J_{H-P}$ = 6.3 Hz, 9H, PMe_3), 2.28 (s, 3H, SC_6H_3Me-6), 2.39 (tt, $^3J_{H-P}$ = 9.0, $^3J_{H-P}$ = 4.5 Hz, 2H, $SC_6H_3(CH_2$-2)), 6.76 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, SC_6H_3), 6.89 (t, $^3J_{H-H}$ = 7.5 Hz, 1H, SC_6H_3), 7.01 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, SC_6H_3). ^{31}P{^{1}H} NMR (122 MHz, DMSO-d_6, 30 °C) δ −15.5 (td, $^2J_{P-P}$ = 31, $^2J_{P-P}$ = 20 Hz, 1P, *P*Me$_3$ *trans* to CH_2), −6.58 (t, $^2J_{P-P}$ = 31 Hz, 2P, mutually *trans*-*P*Me$_3$), 1.95 (td, $^2J_{P-P}$ = 31, $^2J_{P-P}$ = 20 Hz, 1P, *P*Me$_3$ *trans* to S). **2d**: ^{1}H NMR (300 MHz, DMSO-d_6, 30 °C) δ 1.48 (br s, 18H, PMe_3), 2.17 (s, 12H, *ortho-Me*), 6.66 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, *para*-$C_6H_3Me_2$), 6.78 (d, $^3J_{H-H}$ = 7.5 Hz, 4H, *meta*-$C_6H_3Me_2$). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 30 °C) 20.37 (s). **3d**: ^{1}H NMR (300 MHz, DMSO-d_6, 30 °C) δ 1.5 (overlapped with signal due to PMe_3 resonances in **1d** and **2d**, 24H, PMe_3 and $SC_6H_3Me_2$), 1.6 (br s, 18H, PMe_3), 2.22 (s, 6H, $SC_6H_3Me_2$), 6.75−6.90 (br., overlapped with signal due to aromatic H in **2d**, $C_6H_3Me_2$). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 30 °C) δ −9.45 (t, $^2J_{P-P}$ = 32 Hz, 2P, mutually *trans* *P*Me$_3$), 16.63 (t, $^2J_{P-P}$ = 32 Hz, 2P, *P*Me$_3$ *trans* to S).

Treatment of 2d with PMe$_3$ in Chloroform-d_1. Complex **2d** (5.2 mg, 0.0086 mmol) and a flame-sealed ampule containing P-$(OPh)_3$ in C_6D_6 as a standard were placed in an NMR tube into which $CDCl_3$ (0.6 mL) was introduced by vacuum distillation. Triphenylmethane (3.3 mg, 0.014 mmol) was added into the solution as an internal standard. Then, PMe_3 (2.4 μL, 0.023 mmol) was added by a hypodermic syringe. The reaction was monitored at 30 °C by NMR. After 1.5 h, **1d** (0.0041 mmol, 48%) and **3d** (0.00086 mmol, 10%) were observed in 99% conversion of **2d**. **1d**: ^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) δ

1.21 (vt, $^2J_{H-P} = {}^4J_{H-P} = 2.7$ Hz, 18H, mutually *trans*-P*Me*$_3$), 1.32 (d, $^2J_{H-P} = 6.6$ Hz, 9H, P*Me*$_3$), 1.40 (d, $^2J_{H-P} = 5.1$ Hz, 9H, P*Me*$_3$), 2.37 (s. 3H, SC_6H_3*Me*), 2.47 (tt, $^3J_{H-P} = 12.6$, $^3J_{H-P} = 4.5$ Hz, 2H, $SC_6H_3CH_2$), 6.89 (br. t, $^3J_{H-H} = 7$ Hz, 1H, SC_6H_3), 7.03 (br d, $^3J_{H-H} = 7$ Hz, 2H, SC_6H_3). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, 24 °C) δ −16.26 (td, $^2J_{P-P} = 31$, $^2J_{P-P} = 18$ Hz, 1P, *P*Me$_3$, *trans* to CH_2), −7.72 (t, $^2J_{P-P} = 31$ Hz, 2P, mutually *trans*-*P*Me$_3$), 1.53 (td, $^2J_{P-P} = 31$, $^2J_{P-P} = 18$ Hz, 1P, *P*Me$_3$ *trans* to S). **2d**: ^1H NMR (300 MHz, $CDCl_3$, 23 °C) δ 1.51 (m, 27H, P*Me*$_3$), 2.22 (s, 12H, SC_6H_3*Me*$_2$), 6.71 (t, $^3J_{H-H} = 7$ Hz, 1H, $SC_6H_3Me_2$), 6.98 (d, $^2J_{H-H} = 7$ Hz, 2H, $SC_6H_3Me_2$). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, 24 °C) δ 17.69 (s). **3d**: ^1H NMR (300 MHz, $CDCl_3$, 30 °C) δ 1.46 (br.m, 18H, P*Me*$_3$), 1.52 (s, 6H, *ortho*-*Me*), 1.59 (vt, $^2J_{H-P} = {}^4J_{H-P} = 3.3$ Hz, 18H, P*Me*$_3$), 2.35 (overlapped with *ortho*-Me groups in free 2,6-dimethylbenzenethiol, *ortho*-*Me*), 6.57 (t, $^3J_{H-H} = 7$ Hz, 1H, *para*-$C_6H_3Me_2$), 6.68 (d, $^3J_{H-H} = 7$ Hz, 1H, *para*-$C_6H_3Me_2$), 6.8−7.0 overlapped with aromatic protons. $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, 24 °C) δ −9.77 (t, $^2J_{P-P} = 33$ Hz, 2P, mutually *trans* *P*Me$_3$), 12.08 (t, $^2J_{H-H} = 33$ Hz, 2P, *P*Me$_3$ *trans* to S).

Treatment of 2d with PMe_3 in Dichloromethane-d_2. Complex **2d** (5.1 mg, 0.0084 mmol) was placed in an NMR tube into which CD_2Cl_2 (0.6 mL) was introduced by vacuum distillation. Triphenylmethane (2.9 mg, 0.012 mmol) was added as an internal standard and then PMe_3 (2.3 μL, 0.022 mmol) was added by a hypodermic syringe. The reaction was monitored at 30 °C by NMR. After 10 min, **1d** (0.0013 mmol, 15%) and **3d** (0.0058 mmol, 69%) were observed in 90% conversion of **2d**. **1d**: ^1H NMR (300 MHz, CD_2Cl_2, 19 °C) δ 1.19 (vt, $^2J_{H-P} = {}^4J_{H-P} = 2.7$ Hz, 18H, mutually *trans*-P*Me*$_3$), 1.34 (d, $^2J_{H-P} = 7.5$ Hz, 9H, P*Me*$_3$), 1.39 (d, $^2J_{H-P} = 5.7$ Hz, 9H, P*Me*$_3$), 2.28 (s. 3H, SC_6H_3*Me*), 2.45−2.50 (m, 2H, $SC_6H_3CH_2$), 6.9−7.0 (m, overlapped with other aromatic signals, SC_6H_3). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, 19 °C) δ −16.3 (td, $^2J_{P-P} = 31$, $^2J_{P-P} = 18$ Hz, 1P, *P*Me$_3$, *trans* to CH_2), −7.9 (t, $^2J_{P-P} = 31$ Hz, 2P, mutually *trans*-*P*Me$_3$), 1.5 (td, $^2J_{P-P} = 31$, $^2J_{P-P} = 18$ Hz, 1P, *P*Me$_3$ *trans* to S). **3d**: ^1H NMR (300 MHz, CD_2Cl_2, 30 °C) δ 1.45 (m, 18H, P*Me*$_3$), 1.52 (vt, $^2J_{H-P} = {}^4J_{H-P} = 3.3$ Hz, 18H, P*Me*$_3$), 2.56 (s, 12H, SC_6H_3*Me*$_2$), 7.14−7.23 (m, 6H, $SC_6H_3Me_2$). $^{31}P\{^1H\}$ (122 MHz, CD_2Cl_2, 30 °C) δ −10.01 (t, $^2J_{P-P} = 33$ Hz, 2P, mutually *trans* *P*Me$_3$), 11.62 (t, $^2J_{H-H} = 33$ Hz, 2P, *P*Me$_3$ *trans* to S).

Treatment of 2d with H_2O. Complex **2d** (9.7 mmol, 0.014 mmol) was placed in a NMR tube into which C_6D_6 (600 μL) was introduced by vacuum transfer. 1,4-Dioxane (1.4 μL, 0.16 mmol) was added as an internal standard. Degassed deionized water (5.0 μL, 0.28 mmol) was added by a hypodermic syringe. After 3 days at room temperature, *cis*,*mer*-Ru($SC_6H_3Me_2$-2,6)$_2$(PMe_3)$_3$(OH_2) (**3e**) was produced in 62% yield. **3e**: ^1H NMR (300 MHz, C_6D_6) δ 1.12−1.15 (m, 9H, P*Me*$_3$ *trans* to S), 1.20 (vt, $^2J_{H-P} = {}^4J_{H-P} = 2.7$ Hz, 18H, mutually *trans*-P*Me*$_3$), 2.45−2.50 (br s, 12H, SC_6H_3*Me*$_2$), 6.95 (t, $^3J_{H-H} = 7$ Hz, 2H, $SC_6H_3Me_2$), 7.03 (br d, $^3J_{H-H} = 7$ Hz, 4H, $SC_6H_3Me_2$), 11.5 (br, 2H, OH_2). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ −3.58 (d, $^2J_{P-P} = 36$ Hz, 2P, mutually *trans* *P*Me$_2$), 39.68 (t, $^2J_{P-P} = 36$ Hz, 1P, *P*Me$_3$ *trans* to S).

Treatment of 2d with $P(OMe)_3$. Complex **2d** (5.6 mg, 0.0093 mmol) was placed in an NMR tube into which triphenylmethane (5.5 mg, 0.0225 mmol) was added as an internal standard. Trimethylphosphite (1.2 μL, 0.01 mmol) was added into the solution. After 10 min at room temperature, **2d** was completely converted into *cis*,*trans*,*cis*-Ru[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C](PMe_3)$_2$[$P(OMe)_3$]$_2$ (**1f**) in 100% yield. Complex **1f** was characterized by spectroscopic methods. **1f**: ^1H NMR (300 MHz, C_6D_6) δ 1.47 (vt, $^2J_{H-P} = {}^4J_{H-P} = 4$ Hz, 18H, mutually *trans* P*Me*$_3$), 1.86 (s, 3H, C_6H_3*Me*), 2.5 (br, 2H, $C_6H_3CH_2$), 3.27 (d, $^3J_{H-P} = 11$ Hz, 9H, P(O*Me*)$_3$), 3.33 (d, $^3J_{H-P} = 10$ Hz, 9H, P(O*Me*)$_3$), 7.0−7.2 (partly overlapped with undeuterated benzene in C_6D_6, C_6H_3). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ 3.5 (dd, $^2J_{P-P} = 43$, $^2J_{P-P} = 39$ Hz, 2P, mutually *trans*-*P*Me$_3$), 100.7 (dt, $^2J_{P-P} = 86$, $^2J_{P-P} = 39$ Hz, 1P, $P(OMe)_3$ *trans* to CH_2), 156.8 (dt, $^2J_{P-P} = 86$, $^2J_{P-P} = 43$ Hz, 1P, $P(OMe)_3$ *trans* to S).

Treatment of 2d with PMe_2Ph. Complex **2d** (7.0 mg, 0.012 mmol) was placed in an NMR tube into which C_6D_6 (0.6 mL) was introduced by vacuum distillation. Then PMe_2Ph (1.6 μL, 0.011 mmol) was added into the NMR tube by a hypodermic syringe. The reaction system was monitored at 30 °C for 16.5 h by NMR, then tripheylmethane (4.4 mg, 0.018 mmol) was added to the reaction mixture as an internal standard. The conversion of **2d** was 99%, and unidentified products were formed in which a 4:6 mixture of (*OC*-6−34)-Ru[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C](PMe_3)$_3$(PMe_2Ph) (*OC*-6−34)-**1g** and (*OC*-6−24)-**1g** was produced in 31% yield with concomitant formation of 2,6-dimethylbenzenethiol in 36% yield. (*OC*-6−34)-**1g**: ^1H (300 MHz, C_6D_6, 19 °C) δ 0.98−1.12 (m, overlapped, P*Me*$_3$ and P*Me*$_2$Ph), 2.75 (tt, $^3J_{H-P} = 13.5$, $^3J_{H-P} = 4.5$ Hz, 2H, $SC_6H_3CH_2$), 2.9 (overlapped with *ortho* Me in (*OC*-6−24)-**1g**, SC_6H_3*Me*), 6.9−7.25 (overlapped with other aromatic protons, SC_6H_3 and PMe_2*Ph*). 7.3−7.4 (overlapped with other aromatic protons, PMe_2*Ph*). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ −16.7 (td, $^2J_{P-P} = 28$, $^2J_{P-P} = 19$ Hz, 1P, *P*Me$_2$Ph *trans* to CH_2), −8.32 (t, $^2J_{P-P} = 28$ Hz, 2P, mutually *trans* *P*Me$_3$), 0.16 (td, $^2J_{P-P} = 28$, 19 Hz, 1P, *P*Me$_3$ *trans* to S). (*OC*-6−24)-**1g**: ^1H (300 MHz, C_6D_6, 19 °C) δ 0.98−1.12 (m, overlapped, P*Me*$_3$ and P*Me*$_2$Ph), 2.9 (overlapped with *ortho* Me in (*OC*-6−34)-**1g**, SC_6H_3*Me*), 3.11 (tt, $^3J_{H-P} = 13.5$, $^3J_{H-P} = 4.5$ Hz, 2H, $SC_6H_3CH_2$), 6.9−7.25 (overlapped with other aromatic protons, SC_6H_3 and PMe_2*Ph*). 7.3−7.4 (overlapped with other aromatic protons, PMe_2*Ph*). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ −17.60 (td, $^2J_{P-P} = 28$, $^2J_{P-P} = 19$ Hz, 1P, *P*Me$_3$ *trans* to CH_2), −9.62 (t, $^2J_{P-P} = 28$ Hz, 2P, mutually *trans* *P*Me$_3$), 9.35 (td, $^2J_{P-P} = 28$, 19 Hz, 1P, *P*Me$_2$Ph *trans* to S).

Treatment of 2d with CO. Complex **3h** (17.6 mg, 0.0259 mmol) was placed in a Schlenk tube into which benzene (5 mL) was added. After cooling of the reaction mixture with liquid nitrogen, the reaction system was evacuated. Carbon monoxide (0.1 MPa) was then introduced to the Schlenk tube. Right after exposure of **2d** to CO, the red solution turned to yellow. After 10 min, all volatile matters were removed under reduced pressure to give yellow powder, which was repeatedly washed with hexane. After drying of the resulting yellow powder under reduced pressure, *cis*,*cis*,*cis*-Ru($SC_6H_3Me_2$-2,6)$_2$(PMe_3)$_2$(CO)$_2$ (*cis*,*cis*,*cis*-**3h**) was obtained in 93% yield (12.5 mg, 0.024 mmol). At 50 °C in benzene, **3h** constitutes an equilibrium mixture between *cis*,*cis*,*cis*-**3h** and *trans*,*trans*,*trans*-**3h** (K_{eq} = [*trans*,*trans*,*trans*-**3h**][*cis*,*cis*,*cis*-**3h**] = 9.9 at 50 °C). *cis*,*cis*,*cis*-**3h**: ^1H NMR (300 MHz, C_6D_6) δ 0.95 (d, $^2J_{H-P} = 9$ Hz, 9H, P*Me*$_3$), 1.31 (d, $^2J_{H-P} = 9$ Hz, 9H, P*Me*$_3$), 2.54 (s, 6H, *ortho*-SC_6H_3*Me*$_2$), 2.90 (s, 6H, *ortho*-SC_6H_3*Me*$_2$), 6.96 (t, $^3J_{H-H} = 7$ Hz, 1H, *para*-$SC_6H_3Me_2$), 7.08 (t, $^3J_{H-H} = 7$ Hz, 1H, *para*-$SC_6H_3Me_2$), 7.12 (d, $^3J_{H-H} = 7$ Hz, 2H, *meta*-$SC_6H_3Me_2$), 7.26 (d, $^3J_{H-H} = 7$ Hz, 2H, *meta*-$SC_6H_3Me_2$). $^{31}P\{^1H\}$ (122 MHz, C_6D_6) δ −16.09 (d, $^2J_{P-P} = 35$ Hz, 1P, *P*Me$_3$), −11.46 (d, $^2J_{P-P} = 35$ Hz, 1P, *P*Me$_3$). IR (KBr, cm^{-1}) 3041(w), 2963(w), 2913(w), 2036(s). 1973(vs), 1458(w), 1424(w), 1365(w), 1312(w), 1291(w), 1160(w), 1054(w), 960(m), 946(m), 849(w), 763(m), 740(w), 719(w), 585(w), 561(m). Anal. Calcd for $C_{24}H_{36}O_2P_2RuS_2$: C, 49.39; H, 6.22%. Found: C, 49.38; H, 6.75%. *trans*,*trans*,*trans*-**3h**: ^1H NMR (300 MHz, C_6D_6) δ 1.08 (vt, $^2J_{H-P} = {}^4J_{H-P} = 3.7$ Hz, 18H, mutually *trans* P*Me*$_3$), 2.89 (s, 12H, SC_6H_3*Me*$_2$), 6.96 (t, $^3J_{H-H} = 7$ Hz, 2H, *para*-$SC_6H_3Me_2$), 7.07 (d, $^3J_{H-H} = 7$ Hz, 4H, *meta*-$SC_6H_3Me_2$). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) δ −14.81 (s).

Treatment of 2a with PMe_3. Complex **2a** (324.5 mg, 0.4030 mmol) was dissolved in a THF solution (16 mL) into which PMe_3 (120 μL, 1.16 mmol) was added by use of a hypodermic syringe. The reaction mixture was warmed at 50 °C for 2 days. Then, all volatile matters were removed under reduced pressure and the resulting solid was dissolved with acetone. Hexane was added into the acetone solution to deposit unreacted **2a**. The

Table 1. Crystallographic Data for Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(TRIPHOS-κ^3P,P',P'') (2a), Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PMe_3)$_3$ (2d), and Ru($SC_6H_3Me_2$-2,6-κ^1S)$_2$(η^4-1,5-COD) (4a)

	2a	2d	4a·0.5MePh
chemical formula	$C_{50}H_{51}P_3RuS_2$	$C_{25}H_{45}P_3RuS_2$	$C_{45.5}H_{49}P_3Ru$
formula weight	910.06	603.74	789.88
cryst size (mm)	0.20 × 0.20 × 0.10	0.30 × 0.25 × 0.10	0.30 × 0.20 × 0.10
cryst syst	*monoclinic*	*orthorhombic*	*orthorhombic*
space group	$P2_1/n$	$P2_12_12_1$	*P*bca
a (Å)	13.2(2)	16.183(3)	17.822(12)
b (Å)	24.1(3)	18.546(2)	17.854(13)
c (Å)	14.8(2)	10.144(4)	25.904(9)
β (deg)	107(1)		
V (Å^3)	8242(6)	3044.7(13)	8242(9)
Z	4	4	8
measurement temp (K)	270.2	200.0	293.1
radiation type	Mo Kα	Mo Kα	Mo Kα
radiation wavelength (Å)	0.71069	0.71069	0.71069
total no. of reflns	11081	4387	9448
no. of reflns gt	7487	3228	4395
reflns threshold expression	$I > 3.0\ \sigma(I)$	$F^2 > 2.0\ \sigma(F^2)$	$F^2 > 2.0\ \sigma(F^2)$
R^a	0.047	0.0420	0.0555
$R_w{}^b$	0.072	0.0962	0.2060
goodness of fit	1.118	0.713	1.001

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

precipitate was filtered off, and the resulting solution was evaporated to dryness. The solid was recrystallized from cold acetone to give yellow crystals of **1a** in 51% yield (154.7 mg, 0.2055 mmol). These crystals were found to be an 80/20 mixture of (*OC*-6−34)-**1a** and (*OC*-6−25)-**1a**. (*OC*-6−34)-**1a**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.46 (d, J = 7.2 Hz, 9H, P*Me*$_3$), 1.4−2.6 (overlapped, C*H*$_2$ in TRIPHOS), 2.5−2.6 (m, 1H, *ortho*-C*H*$_2$), 2.88 (m, 1H, *ortho*-C*H*$_2$), 3.15 (s, 3H, *ortho-Me*), 6.5−8.1 (m, 28H, aromatic protons). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6) δ −10.0 (ddd, J = 349, 27, 23 Hz, 1P), 39.9 (ddd, J = 349, 19, 12 Hz, 1P), 47.1 (dd, J = 23, 12 Hz, 1P) and 90.2 (dd, J = 27, 19 Hz). (*OC*-6−25)-**1a**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.37 (d, J = 6.3 Hz, 9H, P*Me*$_3$), 1.4−2.6 (overlapped, C*H*$_2$ in TRIPHOS), 2.60 (s, 3H, *ortho-Me*), the methylene protons in the *ortho*-C*H*$_2$ were obscured. 6.5−8.1 (m, 28H, aromatic protons). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6) δ −16.6 (ddd, J = 360, 24, 22 Hz, 1P), 50.9 (ddd, J = 22, 10, 5 Hz, 1P), 73.6 (m, 1P) and 89.9 (ddd, J = 360, 30, 10 Hz, 1P). The ^{13}C{^{1}H} NMR spectrum was measured as a mixture of isomers: ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6) δ 14.3 (s), 16.2 (d, $^1J_{C-P}$ = 24 Hz, P*Me*$_3$), 18.9 (d, $^1J_{C-P}$ = 24 Hz, P*Me*$_3$), 22.1 (s), 23.0 (s), 23.4 (s), 24.8 (d, J_{C-P} = 25 Hz, TRIPHOS), 25.1 (d, J_{C-P} = 25 Hz, TRIPHOS), 27.0 (d, J_{C-P} = 23 Hz, TRIPHOS), 27.2 (d, J_{C-P} = 23 Hz, TRIPHOS), 28.6 (d, J_{C-P} = 25 Hz, TRIPHOS), 28.8 (d, J_{C-P} = 25 Hz, TRIPHOS), 31.7 (d, J_{C-P} = 25 Hz, TRIPHOS), 31.8 (d, J_{C-P} = 25 Hz, TRIPHOS), 31.9 (s), 124.0 (s), 124.7 (s), 126.7 (d, J_{C-P} = 8 Hz, TRIPHOS), 127.0−129.5 (obscured by overlapping with the C_6D_6 resonance), 130.2 (d, J_{C-P} = 9 Hz, TRIPHOS), 130.6 (d, J_{C-P} = 10 Hz, TRIPHOS), 131.1 (d, J_{C-P} = 6 Hz, TRIPHOS), 131.4 (d, J_{C-P} = 7 Hz, TRIPHOS), 131.9 (s), 132.0 (s), 132.2 (d, J_{C-P} = 10 Hz, TRIPHOS), 132.8 (d, J_{C-P} = 10 Hz, TRIPHOS), 134.6 (d, J_{C-P} = 10 Hz, TRIPHOS), 135.6 (s), 136.4 (s), 137.4 (d, J_{C-P} = 34 Hz, TRIPHOS), 139.1 (d, J_{C-P} = 33 Hz, TRIPHOS), 140.3 (d, J_{C-P} = 29 Hz, TRIPHOS), 141.6 (d, J_{C-P} = 23 Hz, TRIPHOS), 144.9 (d, J_{C-P} = 22 Hz, TRIPHOS), 151.6 (d, J_{C-P} = 8 Hz, TRIPHOS), 155.7 (d, J_{C-P} = 13 Hz, TRIPHOS). The elemental analysis was measured as a mixture of regioisomers. Anal. Calcd for $C_{47}H_{56}P_4RuS$: C, 64.30; H, 6.43. Found: C, 64.67; H, 6.78.

Variable Temperature NMR Spectra of 2d. Complex **2d** (4.6 mg, 0.010 mmol) was placed in a NMR tube into which toluene-d_8 (0.6 mL) was introduced by vacuum distillation. ^{1}H and ^{31}P{^{1}H} NMR spectra were measured in the range 283−203 K. The ^{31}P{^{1}H} NMR data slightly shifted to the lower magnetic field by cooling as follows: δ 16.6 (s) at 283 K, δ 16.8 (s) at 273 K, δ 16.9 (s) at 263 K, δ 17.0 (s) at 253 K, δ 17.3 (s) at 243 K, δ 17.5 (s) at 233 K, δ 17.6 (s) at 223 K, δ 17.8 (s) at 213 K, δ 18.0 (s) at 203 K, δ 17.6 (s) at 223 K, δ 17.4 (s) at 233 K, δ 17.3 (s) at 243 K, δ 17.1 (s) at 253 K, δ 16.6 (s) at 283 K. The *ortho* Me resonance in the ^{1}H NMR spectra also slightly shifted to the lower magnetic field by cooling as follows: δ 2.48 (s, 12H) at 283 K, δ 2.49 (s, 12H) at 273 K, δ 2.50 (s, 12H) at 263 K, δ 2.52 (s, 12H) at 253 K, δ 2.53 (s, 12H) at 243 K, δ 2.54 (s, 12H) at 233 K, δ 2.56 (s, 12H) at 223 K, δ 2.58 (s, 12H) at 213 K, δ 2.59 (s, 12H) at 203 K, δ 2.56 (s, 12H) at 223 K, δ 2.53 (s, 12H) at 233 K, δ 2.53 (s, 12H) at 243 K, δ 2.52 (s, 12H) at 253 K, δ 2.51 (s, 12H) at 283 K. No apparent change in the other signals in the ^{1}H NMR spectra was observed.

Treatment of a Mixture of (*OC*-6−34)-1a and (*OC*-6−25)-1a with 2,6-Dimethylbenzenethiol. A mixture of (*OC*-6−34)-**1a** and (*OC*-6−25)-**1a** (12.8 mg, 0.0151 mmol) was placed in an NMR tube into which benzene-d_6 (ca. 0.6 mL) was transferred by vacuum distillation. 2,6-Dimethylbenzenethiol (4.0 μL, 0.030 mmol) was added into the solution by a hypodermic syringe. The reaction mixture was heated at 70 °C, and the reaction was monitored by the NMR. After 3 days, complex **2a** was produced in 83% yield based on the internal standard.

Treatment of a Mixture of (*OC*-6−34)-1a and (*OC*-6−25)-1a with Hydrogen. A mixture of (*OC*-6−34)-**1a** and (*OC*-6−25)-**1a** (14.1 mg, 0.0166 mmol) was placed in an NMR tube. After evacuation of the NMR tube, benzene-d_6 (ca. 0.6 mL) was transferred by vacuum distillation. Diphenylmethane (4.0 μL, 0.024 mmol) was added into the solution as an internal standard. After evacuation of the system, hydrogen gas (0.1 MPa) was introduced into the solution and the reaction system was heated at 50 °C for 1 day. Both ^{1}H and ^{31}P{^{1}H} NMR spectra suggested exclusive formation of (*OC*-6−34)-**8a** (60% yield, 0.010 mmol). ^{1}H NMR (300 MHz, C_6D_6) δ −6.81 (dddd, $^2J_{H-P}$ = 95.8, 34.8, 19.2, 14.4 Hz, 1H, Ru−*H*), 0.51 (d, $^2J_{H-P}$ = 7.2 Hz, 9H, P*Me*$_3$), 3.03 (s, 6H, $C_6H_3Me_2$), 6.8−7.2 (overlapped with diphenylmethane resonances), 7.56 (t, J = 7.2 Hz, 4H, TRIPHOS), 7.95 (q, J = 7.2 Hz, 4H, TRIPHOS), 8.34 (t, J = 8.4 Hz, 2H, TRIPHOS). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6) δ −7.87 (dt, J = 283, 27 Hz, 1P, *P*Me$_3$), 35.3 (m, 1P, *P*Ph$_2$), 64.2 (ddd, J = 283, 17, 5 Hz, 1P, *P*Ph$_2$), 105.7 (dd, J = 29, 19 Hz, 1P, *P*Ph). Anal. Calcd for $C_{45}H_{52}P_4RuS$: C, 63.59; H, 6.17. Found: C, 64.21; H, 6.55.

Treatment of 1d with 2,6-Dimethylbenzenethiol. Complex **1d** (197.7 mg, 0.3643 mmol) was placed in a 50 mL Schlenk tube into which 9 mL of acetone was added. 2,6-Dimethylbenzenethiol (242.0 μL, 1.817 mmol) was added to the solution by a

hypodermic syringe, and the reaction mixture was stirred for 15 h at room temperature. All volatile matters were removed off under vacuum, and resulting red solid was recrystallized from toluene to give red crystals of **2d** in 32% yield (70.5 mg, 0.104 mmol).

Kinetic Study for the Reaction of 2d with PMe_3. A typical example is as follows. A benzene solution of **2d** (5.00 mL, 9.44×10^{-4} M, 0.00472 mmol) was added into a Schlenk type quartz UV cell by a measuring pipet. Then, PMe_3 (4.3 μL, 0.042 mmol) was added into the cell by a hypodermic syringe. The time-course of the reaction was monitored by the absorption maximum in benzene at 518 nm. During measurement of the reaction, the cell temperature was set up at 30.0 °C by a thermostatted UV cell holder and the deviation of the temperature was less than ±0.5 °C.

Effect of Added Potassium 2,6-Dimethylbenzenethiolate on the Conversion Rate of 2d to 1d. A THF solution of **2d** (3.00 mL, 1.57×10^{-4} M, 0.00471 mmol) and a THF solution of potassium 2,6-dimethylbenzenethiol (2.00 mL, 4.80×10^{-2} M, 0.0960 mmol) were added into a Schlenk type quartz UV cell by a measuring pipet. Then, PMe_3 (4.3 μL, 0.042 mmol) was added into the cell by a hypodermic syringe. The time-course of the reaction was monitored by the absorption maximum 30 ± 0.5 °C in THF at 511 nm.

Effect of Added Galvinoxyl on the Conversion Rate of 2d to 1d. A benzene solution of **2d** and galvinoxyl (5.00 mL, **2d**: 9.4×10^{-4} M, 0.0047 mmol; galvinoxyl: 3.4×10^{-4} M, 0.0031 mmol) were added into a Schlenk type quartz UV cell by a measuring pipet. Then, PMe_3 (4.3 μL, 0.042 mmol) was added into the cell by a hypodermic syringe. The time-course of the reaction was monitored at 30 ± 0.5 °C by the absorption maximum in benzene at 518 nm.

X-ray Crystallography of 2a, 2d, and 3a. The crystallographic data were measured on a Rigaku RASA-7R four-circle diffractometer using Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator. A single crystal was selected by use of a polarized microscope and mounted onto a glass capillary with Paraton N oil. The unit cell dimensions were obtained by a least-squares fit of 20 centered reflections. Intensity data were collected using the $\omega-2\theta$ technique to a maximum 2θ of 55.0°. The scan rates were 16.0 deg min^{-1}. Three standard reflections were monitored in every 150 reflections. Intensities were corrected for Lorentz and polarization effects. The crystallographic data and details associated with data collection for **2a**, **2d**, and **4a** are given in Table 1. The data were processed using a teXsan software for **2a** and CrystalStructure package software for **2d** and **4a**.[42] All non-hydrogen atoms were found by using the results of the Direct methods (DIRDIF-94 for **2a**, SHELXL-97[43] for **4a**) and PATTY (DIRDIF-99) (**2d**). An absorption correction was applied with the program PSI SCAN method. All non-hydrogen atoms were found on difference maps. All hydrogen atoms were located in the calculated positions. The crystal of **4a** contained 0.5 MePh molecule, which was solved isotropically. Crystallographic thermal parameters and bond distances and angles have been deposited as Supporting Information.

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Supporting Information Available: Tables of atomic coordinates and equivalent anisotropic displacement parameters and bond distances and angles for **2a**, **2d**, and **4a**, typical first-order rate plots for **2a** and **2d**, and first-order rate constants for conversion of **2a** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

(42) Rigaku Americas and Rigaku Corporation. *CrystalStructure* (*Version 3.8*). *Single Crystal Structure Analysis Software*; Rigaku Americas: 9009 TX, USA 77381-5209 ; Rigaku: Tokyo 196−8666, Japan, 2007.

(43) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.

(44) Abbreviations used in this text: COD, cyclooctadiene (C_8H_{12}); COT, cyclooctatriene (C_8H_{10}); DMF, dimethylformamide (Me_2NCHO); DMSO, dimethylsulfoxide (Me_2SO); DPPE, 1,2-bis(diphenylphosphino)-ethane ($Ph_2PC_2H_4PPh_2$); TDPM, tris(diphenylphosphino)methane [$HC(CH_2PPh_2)_3$]; TDPME, tris(diphenylphsphinomethyl)ethane [$MeC-(CH_2PPh_2)_3$]; TRIPHOS, bis[2-(diphenylphosphino)ethyl]phenylphosphine ($Ph_2C_2H_4PPhC_2H_4Ph$).