Stoichiometric and Catalytic sp^3 C-H/D_2 Exchange Reactions of *ortho*-Substituted Benzenethiol and Phenols by a Ruthenium(II) Complex. Effect of a Chalcogen Anchor on the Bond Cleavage Reaction

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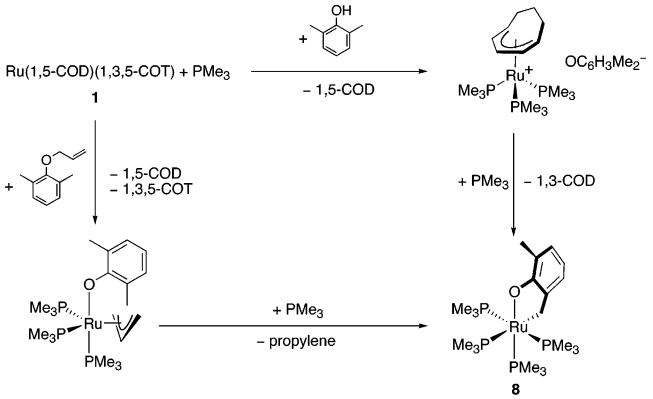
A divalent thiaruthenacycle complex, *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2*S,C*](PMe_3)$_4$ (**3**), is prepared by the treatment of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) with 2,6-dimethylbenzenethiol in the presence of PMe_3 via Ru(η^5-cyclooctadienyl)($SC_6H_3Me_2$-2,6)(PMe_3)$_2$ (**2**). Exposure of **3** in benzene to H_2 (0.1 MPa) leads to the quantitative formation of *cis*-RuH($SC_6H_3Me_2$-2,6)(PMe_3)$_4$ (**4**), which readily turns to **3** at room temperature on evacuation, indicating the reversibility of the reaction. Both forward and backward reactions of this equilibrium are retarded by addition of PMe_3, suggesting prerequisite prior dissociation of PMe_3 for both reactions. Complex **3** catalyzes selective and facile deuteration of the *ortho*-methyl and the mercapto groups in 2,6-dimethylbenzenethiol under D_2.

Introduction[1]

C−H bond cleavage reaction by low-valent ruthenium complexes has attracted considerable attention as one of the promising inlets for direct functionalization of C−H bonds.[2] Recent representative catalyses involve alkylation of aromatic ketones,[3] aryl phosphite,[4] and isocyanide[5] and acylations of pyridine[6] and pyrazoles.[7] Most of these catalytic processes are postulated to involve prior coordination of heteroatoms such as chalcogens, phosphorus, or nitrogen to the ruthenium center followed by the formation of a ruthenacycle intermediate.[8] We previously reported stoichiometric O−C/O−H and sp^3 C−H bond activation of *ortho*-substituents in allyl aryl ether and phenols by Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) in the presence of PMe_3 to give oxaruthenacycle complexes (Scheme 1).[9] In this reaction we have demonstrated prior formation of aryloxo intermediates, whose aryloxo moiety also acts as a powerful anchor to enforce the proximal sp^3 C−H bond close to the ruthenium(II) center. The simplified key step for the C−H bond cleavage reaction is illustrated in Chart 1. Although such aryloxo-promoted activation of a sp^3 C−H bond in *ortho*-substituents in phenol has mainly been documented for early transition metal complexes[10] and group 6 complexes,[11] those studies for ruthenium complexes are unexplored until our previous report.[9]

Scheme 1



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(1) Abbreviation used in this text: COD = cyclooctadiene (C_8H_{12}); COT = cyclooctatriene (C_8H_{10}); DMPE = 1,2-bis(dimethylphenylphosphino)ethane ($Me_2PC_2H_4PMe_2$); DPPM = diphenylphosphinomethane ($Ph_2PCH_2PPh_2$).

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(9) (a) Hirano, M.; Kurata, N.; Marumo, T.; Komiya, S. *Organometallics* **1998**, *17*, 501. (b) Hirano, M.; Kurata, N.; Komiya, S. *J. Organomet. Chem.* **2000**, *607*, 18. (c) Komiya, S.; Hirano, M. *Dalton Trans.* **2003**, 1439. (d) Komiya, S.; Hirano, M. *Activation of Substrates with Polar Single Bonds in Fundamentals of Molecular Catalysis;* Kurosawa, H., Yamamoto, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2003; p 115.

10.1021/om0504598 CCC: $30.25
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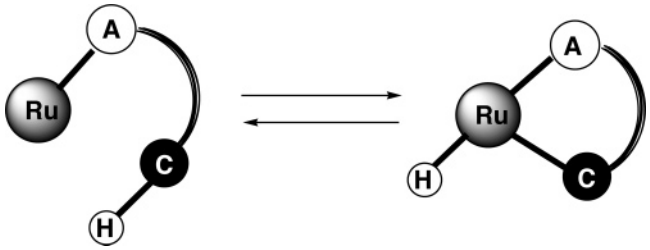
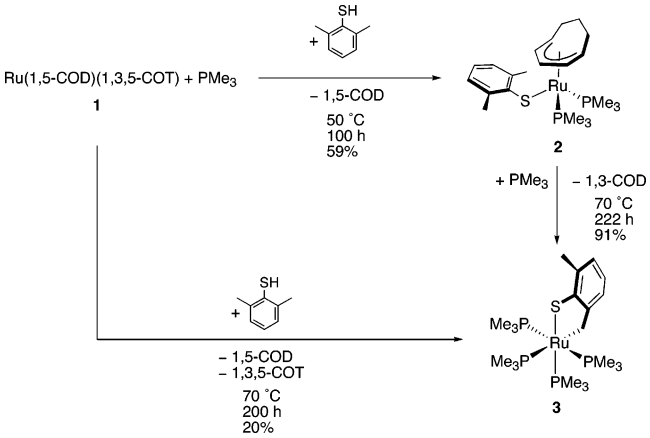
Chart 1



Scheme 2



We now report a full account of the reaction of **1** with 2,6-dimethylbenzenethiol or 2,6-xylenol in the presence of PMe_3, where stoichiometric and catalytic H/D exchange reactions of *ortho*-methyl substituents in 2,6-dimethylbenzenethiol with D_2 are involved.

Results and Discussion

Preparation of Thiaruthenacycle Complex. Treatment of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) with 2,6-dimethylbenzenethiol in the presence of 2 equiv of PMe_3 in benzene resulted in the precipitation of a new thiolate complex, Ru(η^5-C_8H_{11})($SC_6H_3Me_2$-2,6)(PMe_3)$_2$ (**2**), accompanied by liberation of 1,5-COD (Scheme 2). Off-white single crystals of **2** suitable for X-ray analysis were obtained by recrystallization from cold benzene. Two independent molecules having essentially the same structures were found in a unit cell, and the following discussion refers to one of them (named molecules **2**A and **2**B). The ORTEP drawing of molecule **2**A is depicted in Figure 1, and the selected bond distances and angles are tabulated in Table 1.

The molecular structure of **2** is best regarded as a three-legged *chair* form with a thiolato and two PMe_3 ligands. The Ru(1)−S(1) bond [2.476(8) Å] is longer than those in the formally coordinatively unsaturated complex Ru($SC_6H_3Me_2$-2,6)$_2$(η^6-$MeC_6H_4CHMe_2$-4)

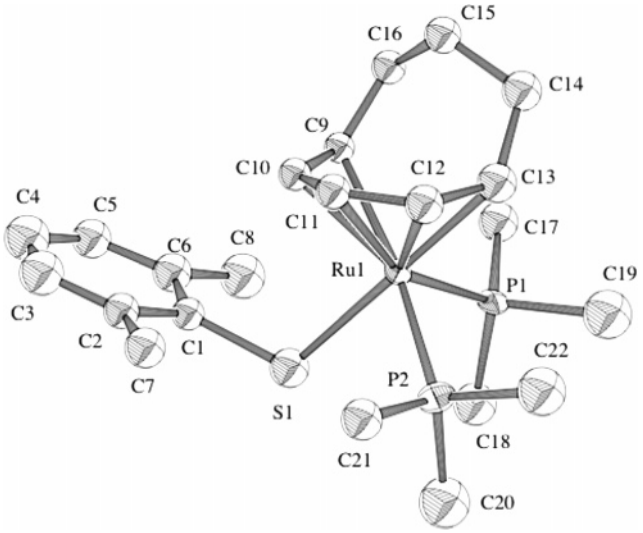


Figure 1. Molecular structure of Ru(η^5-C_8H_{11})($SC_6H_3Me_2$-2,6)(PMe_3)$_2$ (**2**). All hydrogen atoms are omitted for clarity. Elipsoids represent 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Ru(η^5-C_5H_{11})($SC_6H_3Me_2$-2,6)(PMe_3)$_2$ (2) (molecule 2A)

Ru(1)−S(1)	2.476(8)	Ru(1)−P(1)	2.340(3)
Ru(1)−P(2)	2.344(3)	Ru(1)−C(9)	2.28(1)
Ru(1)−C(10)	2.22(1)	Ru(1)−C(11)	2.23(1)
Ru(1)−C(12)	2.12(2)	Ru(1)−C(13)	2.23(3)
S(1)−C(1)	1.79(1)		
S(1)−Ru(1)−P(1)	88.4(2	S(1)−Ru(1)−P(2)	84.2(2)
P(1)−Ru(1)−P(2)	93.7(1)	Ru(1)−S(1)−C(1)	112.2(7)

(2.263−2.311 Å)[12] but comparable to those in saturated thiolato complexes such as Ru(SC_6H_4Me-4)$_2$(CO)$_2$(PPh_3)$_2$ (2.470 Å) and RuH(SC_6H_4Me-4)(CO)$_2$(PPh_3)$_2$ (2.458 Å).[13] The bond distances among Ru(1) and adjacent carbons in the cyclooctadienyl moiety [C(9), −C(10), −C(11), −C(12), and −C(13)] are in the range 2.12−2.28 Å, showing η^5-coordination of the cyclooctadienyl ligand. The bond angles show no anomalies. The $^{31}P\{^1H\}$ NMR spectrum of **2** appeared as an AX pattern due to two diastereotopic PMe_3 ligands attached to the ruthenium center. A similar inequivalency of diastereotopic phosphorus ligands is also reported for RuCl(η^5-C_7H_9)(PPh_3)$_2$[14] and RuCl(η^5-C_8H_9)(PPh_3)$_2$.[15] The ^1H NMR and $^1H-^1H$ COSY spectra of **2** are consistent with the X-ray structure (see Experimental Section). Complex **2** is considered to be formed by protonation of the ruthenium center by 2,6-dimethylbenzenethiol followed by hydride migration to the 1,3,5-COT ligand to form the cyclooctadienyl moiety and final coordination of the thiolato anion,[16] although the pathway involving direct protonation of the COT ligand cannot be ruled out. It is also notable that the neutral η^5-cyclooctadienyl complex **2** is formed in this reaction, while a similar reaction with phenols involving 2,6-xylenol gives the cationic complex [Ru(η^5-cyclooctadienyl)(PMe_3)$_3$]$^+$[OAr]$^-$.[9b] This fact would

(10) C−H bond activations of substituent groups at the *ortho* positions are carried out by early transition metal aryloxides: (a) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. (b) Yu, J. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1990**, *112*, 8171. (c) Visciglio, V. M.; Clark, J. R.; Nguyen, M. T.; Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 3490. (d) Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 4442, and references therein.

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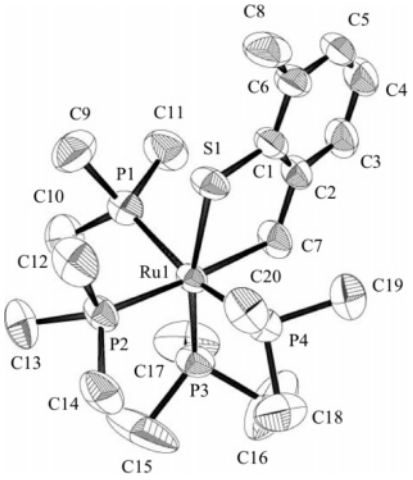


Figure 2. Molecular structure of *cis*-Ru[SC_6H_3(2-CH)(6-Me)-κ^2S,C](PMe_3)$_4$ (**3**). All hydrogen atoms are omitted for clarity. Elipsoids represent 50% probability.

reflect stronger coordination ability of sulfur to ruthenium than oxygen.[17]

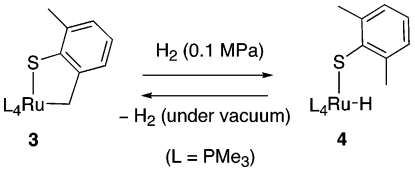
When isolated **2** was heated at 70 °C in the presence of PMe_3, a thiaruthenacycle complex *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2S,C](PMe_3)$_4$ (**3**) was slowly formed in 91% yield in 9 days with concomitant formation of 1,3-COD (91%), indicating that the sp³ C−H bond activation of one of the *ortho*-methyl groups took place, where the η^5-cyclooctadienyl ligand in **2** acted as an acceptor of the cleaved hydrogen. Since complex **3** is also directly formed by the treatment of **1**/PMe_3 with 2,6-dimethylbenzenethiol, **2** is regarded as an intermediate to give **3** (Scheme 2).

Single crystals of **3** were obtained by the recrystallization from a cold hexane solution. The X-ray structure analysis of **3** also reveals the unit cell having two crystallographically independent molecules. Since they are basically isomorphous molecules to each other (named molecules **3**A and **3**B), only the molecular structure of **3**A is shown in Figure 2. The selected bond distances and angles for **3**A are summarized in Table 2. The bond distances Ru(1)−C(7) and Ru(1)−S(1) are 2.193(6) and 2.429(2) Å, respectively, indicating typical single bonds, and the S(1)−Ru(1)−C(7) angle is 82.6-(2)°. Complex **3** is regarded as a five-membered thiaruthenacycle complex having a distorted octahedral geometry. The $^{31}P\{^1H\}$ NMR spectrum of **3** consistently shows a typical AM_2X pattern at δ 0.0 (1P), −8.4 (2P), and −16.8 (1P). The central doublet of doublets at δ −8.4 is assignable to two equivalent mutually *trans* PMe_3 ligands. The two doublets of triplets at δ −16.8 and 0.0 are assignable to the phosphorus nuclei *trans* to the methylene and thiolato groups, respectively, because of the greater *trans* influence of the alkyl ligand than the thiolato ligand.[18] In the ^1H NMR spectrum, two doublets and one virtual triplet at δ 0.99 (9H), 1.11 (9H), and 1.10 (18H) are assignable to the two magnetically inequivalent *cis* PMe_3 and two mutually *trans* PMe_3 ligands, respectively. The most significant feature in the ^1H NMR spectrum is the triplet of doublets of triplets at δ 2.70 (2H) assignable to the *ortho*-methylene protons coupled to the phosphorus nuclei, while the other *ortho*-methyl group appears as a singlet at δ 2.88 (3H). These data are consistent with the molecular structure of **3**.

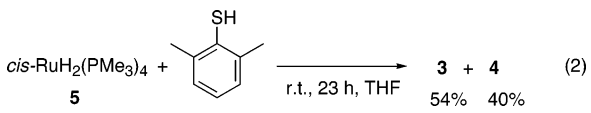
Table 2. Selected Bond Distances (Å) and Angles (deg) for *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)](PMe_3)$_4$ (3) (molecule 3A)

Ru(1)−S(1)	2.429(2)	Ru(1)−P(1)	2.371(2)
Ru(1)−P(2)	2.350(2)	Ru(1)−P(3)	2.302(2)
Ru(1)−P(4)	2.368(2)	Ru(1)−C(7)	2.193(6)
S(1)−C(1)	1.765(7)	C(1)−C(2)	1.393(9)
C(2)−C(7)	1.514(9)	S(1)−Ru(1)−P(1)	84.74(7)
S(1)−Ru(1)−P(2)	94.50(6)	S(1)−Ru(1)−P(3)	167.36(6)
S(1)−Ru(1)−P(4)	81.66(7)	S(1)−Ru(1)−C(7)	82.6(2)
P(1)−Ru(1)−P(2)	90.98(7)	P(1)−Ru(1)−P(3)	96.48(7)
P(1)−Ru(1)−P(4)	166.31(7	P(1)−Ru(1)−C(7)	87.3(2)
P(2)−Ru(1)−C(7)	176.7(2)	P(3)−Ru(1)−C(7)	84.9(2)
P(4)−Ru(1)−C(7)	89.5(2)	Ru(1)−S(1)−C(1)	101.0(2)
S(1)−C(1)−C(2)	119.5(5)	C(1)−C(2)−C(7)	121.1(5)
Ru(1)−C(7)−C(2)	114.8(4)		

Reversible Reaction of Thiaruthenacycle with Hydrogen Giving (Hydrido)(thiolato)ruthenium-(II). Exposure of the thiaruthenacycle complex **3** to hydrogen gas (0.1 MPa) in C_6D_6 led to hydrogenolysis, giving a new (hydrido)(thiolato)ruthenium(II) complex, *cis*-RuH($SC_6H_3Me_2$-2,6)(PMe_3)$_4$ (**4**), in quantitative yield (eq 1). Since complex **4** was difficult to isolate because



it readily gave the starting complex **3** by evacuation of hydrogen gas (vide infra), the characterization was performed spectroscopically under an atmosphere of hydrogen. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows an AM_2X pattern suggesting the *cis* configuration in an octahedral geometry. Consistently, the ^1H NMR shows two doublets and one virtual triplet in 9:9:18 ratio assignable to PMe_3 ligands. A doublet of doublets of triplets at δ −8.63 (1H) is assignable to the hydride group coupled to two magnetically inequivalent and two equivalent phosphorus nuclei. The methylene signal in **3** disappeared, but instead a singlet was observed at δ 3.01 (6H), suggesting conversion of the *ortho*-methylene group in **3** to one of the *ortho*-methyl groups. These facts well fit the proposed structure of **4**. Complex **3** can also be prepared by the treatment of *cis*-$RuH_2(PMe_3)_4$ (**5**) with 2,6-dimethylbenzenethiol, giving a mixture of **4** and **3** in 40% and 54% yield, respectively (eq 2).[19]



(16) Similar protonation reactions of **1** by Brønsted acids giving η^5-cyclooctadienyl complexes are reported as follows. (a) By $HBPh_4$: Vitulli, G.; Pertici, P.; Bigelli, C. *Gazz. Chim. Ital.* **1985**, *115*, 79. (b) By 3-butenoic acid: Osakada, K.; Grohmann, G. A.; Yamamoto, A. *Organometallics* **1990**, *9*, 1990. (c) By HBF_4: Bouachir, F.; Chaudret, B.; Dahan, F.; Agbossou, F.; Tkachenko, I. *Organometallics* **1991**, *10*, 455. (d) By phenols: ref 9b. (e) By methacylic acid: Kanaya, S.; Komine, N.; Hirano, M.; Komiya, S. *Chem. Lett.* **2001**, 1284. (e) By allylic alcohols: Kanaya, S.; Imai, Y.; Komine, N.; Hirano, M.; Komiya, S. *Organometallics* **2005**, *24*, 1059.

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

(18) (a) Yamamoto, A. *Organotransition Metal Chemistry, Fundamenal Concepts and Applications*; Wiley: New York, 1986; p 181.

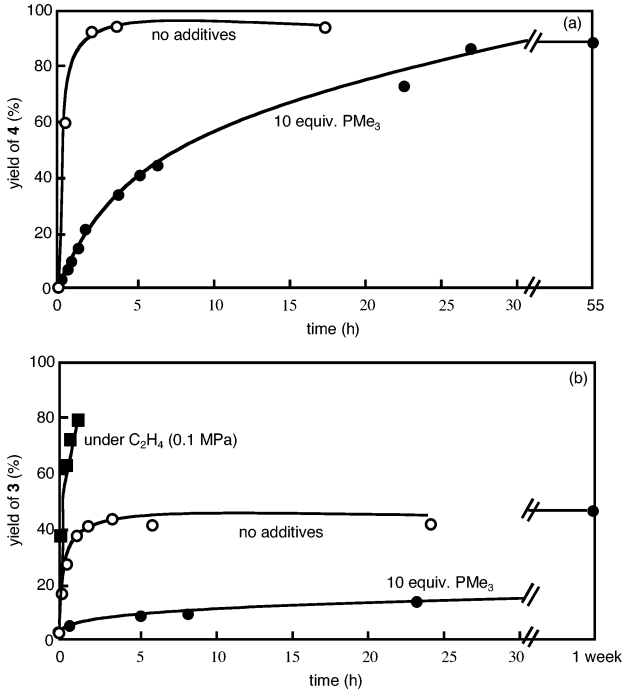
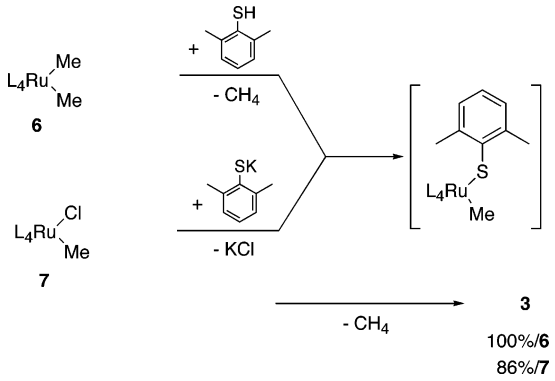


Figure 3. Time−yield curves for (a) the reaction of Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2*S,C*](PMe_3)$_4$ (**3**) with H_2 (0.1 MPa) and (b) the reaction of *cis*-RuH($SC_6H_3Me_2$-2,6)(PMe_3)$_4$ (**4**) under reduced pressure or ethylene atmosphere. Open circles, solid circles, and solid squares indicate reactions without additives, with 10 equiv of PMe_3, and under ethylene (0.1 MPa) atmosphere, respectively.

To shed light on the interconversion mechanism between complexes **3** and **4**, time-course curves for the forward and backward reactions were monitored by NMR spectroscopy (Figure 3 and eq 1). As shown in Figure 3a, when complex **3** was placed under hydrogen (0.1 MPa), **4** was formed in 94% yield within 3 h. A significant retardation effect on the rate was observed when 10 equiv of PMe_3 was added to the reaction solution. The backward reaction was also retarded significantly by the addition of PMe_3 as shown in Figure 3b. These facts indicate that both forward and backward reactions proceed via prior dissociation of PMe_3. In the absence of free PMe_3, an equilibrium mixture of **3** and **4** (4:6) was formed in an hour (Figure 3b) at room temperature. Incomplete conversion of **4** to **3** is due to the presence of hydrogen gas evolved in this process. In fact, when the reaction was carried out in an atmosphere of ethylene, almost complete conversion to **3** from **4** was observed, where effective consumption of hydrogen gas by hydrogenation of ethylene would force the equilibrium to the **3** side.[20]

It is interesting to note that treatments of both *cis*-$RuMe_2(PMe_3)_4$ (**6**) with 2,6-dimethylbenzenethiol and *cis*-RuClMe(PMe_3)$_4$ (**7**) with potassium 2,6-dimethylbenzenethiolate under vacuum cleanly afforded **3** (100% and 86%, respectively) with evolution of methane (169% and 106%, respectively) (Scheme 3). Both reactions are

Scheme 3



considered to involve a common intermediate, *cis*-RuMe($SC_6H_3Me_2$-2,6)(PMe_3)$_4$, from which facile methane elimination is considered to take place to give **3**. Contrary to the formation of **3** from **4**, these reactions were irreversible since no backward reaction is practically possible. These results suggest the importance of a hydrogen acceptor such as hydride and methyl in the C−H bond cleavage process, where the alkyl group acts as a better leaving group than the hydride.[21,22] This effect will be discussed in the next section.

Reaction of Oxaruthenacycle 8 with Hydrogen. We have reported the synthesis of the oxaruthenacycle complex *cis*-Ru[OC_6H_3(2-CH_2)(6-Me)-κ^2*O,C*](PMe_3)$_4$ (**8**) by treatment of either **1**/PMe_3 with allyl 2,6-xylyl ether or **1**/PMe_3 with 2,6-xylenol.[9a,b] Contrary to the thiaruthenacycle **3**, on exposure of the oxaruthenacycle **8** to H_2 under the same conditions, the corresponding (aryloxo)(hydrido)ruthenium(II) complex was not observed at all, but *cis*-dihydridoruthenium(II) complex **5** was quantitatively obtained with liberation of 2,6-xylenol (Scheme 4). On the other hand, treatment of **5** with 2,6-xylenol remained unreacted under an atmosphere of nitrogen. However, when the reaction was carried out in the presence of ethylene or butadiene, oxaruthenacycle **8** was formed in 70% and 40% yield, respectively. As described above, ethylene or butadiene is also considered to act as an effective hydrogen acceptor from a putative (alkyl)(aryloxo)ruthenium intermediate to give **8** (route A in Scheme 4). An alternative route, removal of H_2 from **5** via (alkyl)(hydrido)ruthenium intermediate (route B), is less likely because *cis*-RuH(Et)(PMe_3)$_4$ is thermally stable even at 75 °C in benzene.[23] Thus, under these conditions, route A is more plausible and we can conclude that the equilibrium between **5** and **8** seems to lie far to the

(19) Reaction of **5** with phenol, *p*-cresol, or *p*-cyanophenol was reported to give the corresponding *cis*-(aryloxo)(hydrido)ruthenium(II) complex: Osakada, K.; Oshiro, T.; Yamamoto, A. *Organometallics* **1991**, *10*, 404.

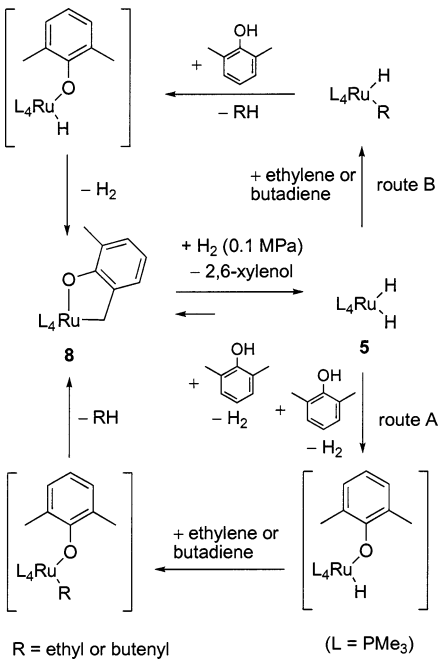
(20) Similar ethylene-promoted sp^2 C−H bond activation by a Ir complex was reported: Hauger, B.; Caulton, K. G. *J. Organomet. Chem.* **1993**, *450*, 253.

(21) Smooth C−H bond cleavage reactions of alkylruthenium complexes may also concern weaker Ru−C than Ru−H bonds. It is reported that the M−C BDEs are normally weaker than M−H by 15−25 kcal/mol. Labinger, J.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926.

(22) Similar sp^2 C−H bond activation by alkyl- and arylruthenium complexes are reported: (a) Statler, J. A.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1731. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (c) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990**, *394*, 417. (d) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404. sp^3 C−H bond activation by alkylruthenium: (e) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3326. (f) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344. (g) McNeill, K.; Andersen, A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11244.

(23) Wong, W.-K.; Chiu. K. W.; Statler, J. A.; Wilkinson, G. Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1984**, 1255.

Scheme 4



dihydride side under hydrogen atmosphere, showing a sharp contrast to the thiaruthenacycle system. Probably, this also reflects the weaker Ru−O than Ru−S bond.[24] Moreover, kinetic factors due to steric hindrance or low acidity of 2,6-xylenol may also discourage the reaction of **5** with 2,6-xylenol, since phenol is reported to react with **5** to give *cis*-RuH(OPh)(PMe_3)$_4$.[19]

H/D Exchange Reaction of the *ortho*-Methyl Groups with D_2. When complex **3** was exposed to D_2 at room temperature, the *ortho*-methyl and methylene protons in **3** and **4** were exclusively deuterated and other protons remained intact. Figure 4 shows the ^{1}H NMR spectra of the hydride, methylene, and *ortho*-methyl regions in the reaction of **3** with D_2. In these experiments, the conversion of **3** and yield of **4** were monitored by the ^{31}P{^{1}H} NMR spectrum, and the deuterium distribution was calculated by the integration in the ^{1}H NMR spectra based on the methine signal in $CHPh_3$ as an internal standard.

Before exposure of **3** to D_2, the methyl and *ortho*-methylene in **3** (0.018 mmol) were exclusively observed (0 min in Figure 4). After exposure to D_2 (1.48 mmol) for 15 min, a new singlet at δ 3.10 and doublet of doublets of triplets at δ −8.6 assignable to the methyl and hydride in **4** grow with concomitant increase of signals due to **3**. At this stage the conversion of **3** and yield of **4** were found to be 23% and 26%, respectively, and the deuterium contents in the *ortho*-methyl and hydride groups in **4** were 16 and 28 atom % D, respectively. It is interesting to note that the *ortho*-methyl and methylene in **3** were also deuterated in 13 and 12 atom % D, respectively. After 30 min, the signals due to **3** almost disappeared and besides the methyl groups in **4** a small but characteristic 1:1:1 triplet and a quintet appeared, being assignable to methyl-d_1 and -d_2 signals, respectively, showing isotopic anisotropy chemical shift. After 120 min, the relative ratio of the methyl-d_2 increased compared to the methyl-d_0 and -d_1, and their total intensities decreased along with an increase in deuteration. After 53 h, the incorporated deuterium in the *ortho*-methyl and hydride in **4** reached 77 and 56 atom % D, respectively. When the reaction was carried out in the presence of 5.6 equiv of PMe_3 at room temperature, the hydrogenolysis of **3** took place to give **4** in 88% yield after 1 day, but the deuterium content in the *ortho*-methyl groups was only 25 atom % D, suggesting that the C−H bond activation process was significantly suppressed. It is notable that the hydride was completely deuterated at this stage in this case. After 10 days the yield of **4** increased up to 95%, but the D content in the *ortho*-methyl groups was still 45 atom % D and that in the hydride was 73 atom % D in **4**.

This experiment shows interesting features of this reaction as follows. (a) If simple hydrogenolysis of **3** by D_2 occurs, *cis*-RuD[$SC_6H_3(CH_2D)$Me-2,6](PMe_3)$_4$ (**4**-d_2) [*ortho*-Me: 17 (= 1/6) atom % D, Ru−H: 100 atom % D] is expected to be formed. The observed distribution of deuterium in the *ortho*-methyl groups in **4** was 16 atom % D at the initial stage, but much less deuterium in the hydride position (28 atom % D) was observed than expected even at the initial stage of the reaction. This

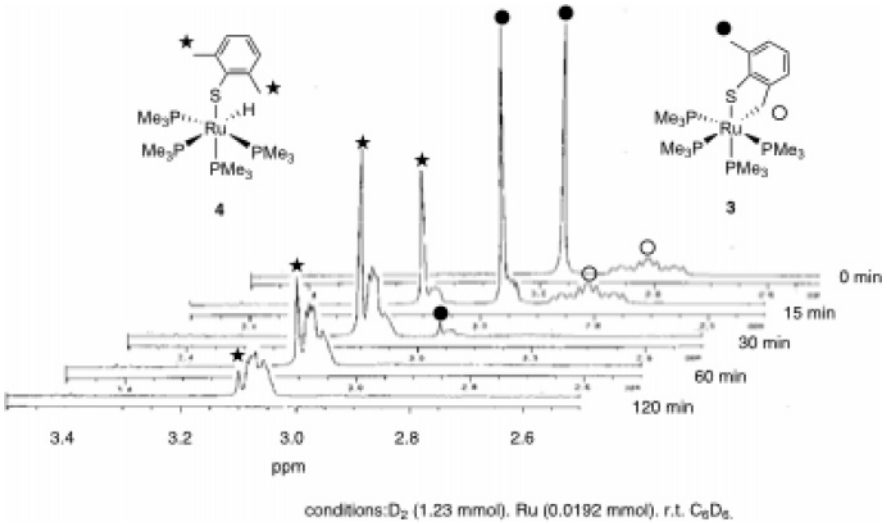
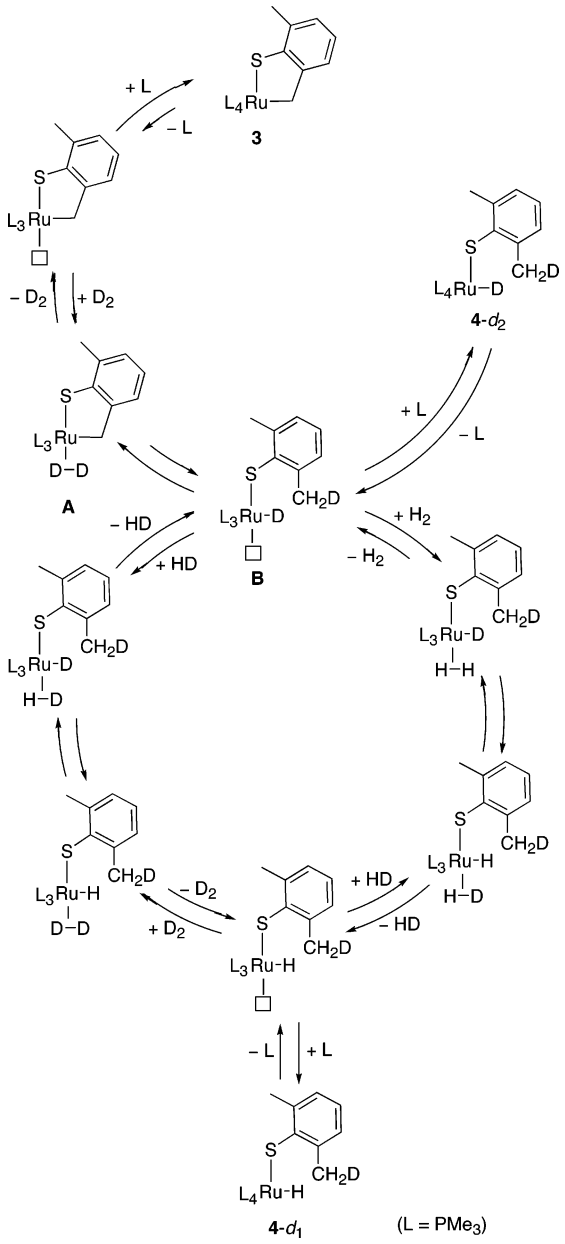


Figure 4. ^{1}H NMR spectra for the reaction of *cis*-Ru(SC_6H_3(2-CH)(6-Me)-κ^2S,C](PMe_3)$_4$ (**3**) with D_2 giving *cis*-RuH(SC_6H_3-Me_2-2,6)(PMe_3)$_4$ (**4**). Open circles, solid circles, and stars indicate *ortho* methylene and methyl protons in **3** and *ortho* methyl protonsin **4**, respectively.

indicates that six hydrogen atoms in the *ortho*-methyl groups are partially deuterated by simple hydrogenolysis of the Ru−C bond in **3**[25] and the deuteride (Ru-D) is replaced by H (vide infra). (b) Even at the initial stage of the reaction of **3** with D_2 (after 15 min), partially deuterated reactant **3**-*d* was observed. This means the presence of rapid equilibrium between **3** and **4**. Although the conversion of **3** was only 23% at this stage, the *ortho*-methyl and methylene in **3** were already deuterated in 13 and 12 atom % D, respectively. This fact indicates that enough of the H atom (0.0087 mmol) is evolved for the formation of hydride in **4** (26% yield; 0.0047 mmol). Thus, the H source in the hydride in **4** is most likely due to evolved H from the partially deuterated *ortho*-methyl and methylene in **3**, and such intermolecular exchange between H and D is considered to be much faster than exchange between the hydride in **4** and D_2 in the gas phase. Proton-mediated hydride/deuteride exchange by incorporated water is another possibility. However, this is less likely because addition of D_2O in hydrogenolysis of **3** by H_2 resulted in no incorporation of deuterium either in **4** or **3** under these conditions. (c) The deuteride/hydride exchange reaction was significantly retarded by the addition of PMe_3, suggesting the dissociative mechanism. (d) At the final stage, the *ortho*-methyl group and the hydride in **4** were deuterated in 77 and 56 atom % D, respectively. Since statistical H/D exchange among the *ortho*-methyl and methylene groups in **3** and D_2 is calculated to be 77% under these conditions, the D content in the *ortho*-methyl group in **4** can be regarded as a result of random H/D distribution. However, the low distribution of deuterium in the hydride site in **4** cannot be explained by the statistical exchange. The present result shows that **4** favors hydride rather than deuteride. This is probably due to the lower free energy of the metal hydride than that of metal deuteride. A similar trend is reported by Berke and co-workers, where the hydrogen atom tends to remain as a hydride and deuterium is enriched in the molecular D_2 ligand in partially deuterated isotopomers of $[RuH(H_2)(PMe_3)_4]^+$.[26] A similar trend that shows affinity toward hydride in preference to deuteride is also proposed in other H/D exchange reactions of transition metal hydride complexes.[27]

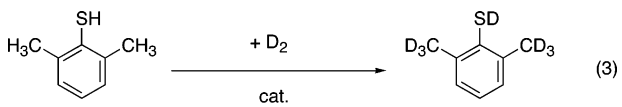
By taking into account of all these matters, the most probable mechanism for the stoichiometric H/D exchange reaction by D_2 can be explained as shown in Scheme 5. First, a PMe_3 ligand in **3** is displaced by D_2 via a dissociative mechanism.[28] The resulting intermediate **A** affords coordinatively unsaturated intermediate **B**, although we do not have any information about a change of metal valency in this process. Finally, coordination of PMe_3 to **B** gives **4**-d_2. Coordination of HD or H_2 to **B** leads to the formation of **4**-d_1. These processes are considered to constitute an equilibria to give **3**-d_1.

Scheme 5



Multiple introduction of deuterium is accomplished by repeating these processes.

Catalytic Deuteration of the *ortho*-Methyl and the Mercapto Groups by D_2. Complex **3** was found to catalyze sp^3 C−H/D_2 and S−H/D_2 exchange reactions of 2,6-dimethylbenzenethiol under an atmosphere of D_2 at room temperature. The deuteration process was monitored by the ^1H NMR spectra, and Figure 5 shows a typical example in the *ortho*-methyl region for 2,6-dimethylbenzenethiol, where besides the *ortho*-methyl resonance at δ 2.13 (s), multiplets assignable to a 1:1:1 triplet centered at δ 2.11 for methyl-d_1 and a 1:3:4:3:1 quintet at δ 2.09 for methyl-d_2 appeared (eq 3).



(3)

Figure 6 shows time-course curves for deuteration of the methyl and mercapto groups in 2,6-dimethylben-

(24) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. *J. Am.Chem. Soc.* **1987**, *109*, 1444. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875.

(25) Theoretical deuterium content in *ortho* methyl groups in RuD-[$SC_6H_3(CH_2D)$Me-2,6]$(PMe_3)_4$ is 17 atom % D.

(26) Gusev, D. G.; Hübener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716.

(27) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403, and references therein.

(28) Although, in Scheme 5, the coordinated D_2 is illustrated as a nonclassical dideuterium form such as intermediate **A**, a classical dideuteride form is also possible.

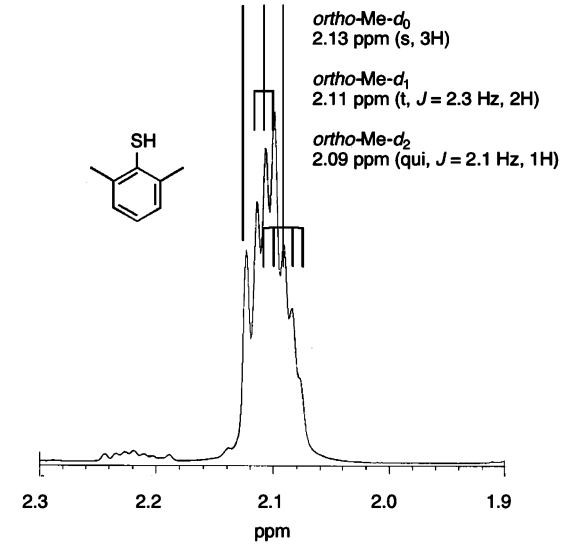


Figure 5. ^{1}H NMR spectrum of partially deuterated 2,6-dimethylbenzenethiol.

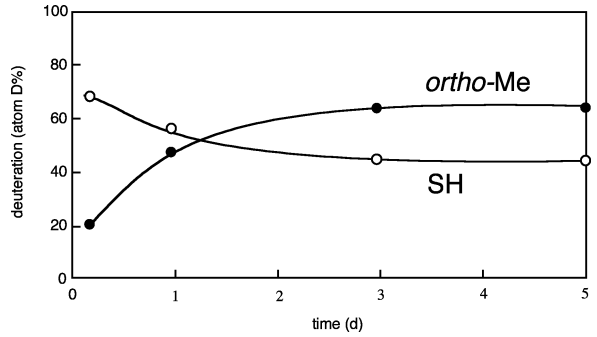
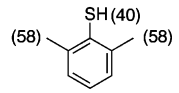
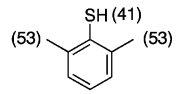
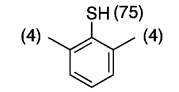
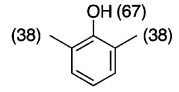
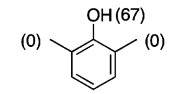
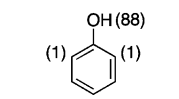
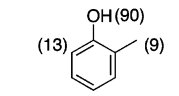


Figure 6. Time−yield curves for deuteration of 2,6-dimethylbenzenethiol by D_2 catalyzed by $Ru[SC_6H_3(2\text{-}CH_2)(6\text{-}Me)](PMe_3)_4$ (**3**) at 25 °C.

zenethiol catalyzed by **3** (5 mol %) under D_2. One of the characteristic features of this catalytic H/D exchange reaction is that deuteration of the mercapto group is a quite rapid process, but the final D content gradually decreased during the reaction. This is probably due to the fact that the exchange between S−H and D_2 is a quite rapid process and the deuterium content in the SH group would reflect the composition of the deuterium in the gas phase. On the other hand, the deuterium content in the *ortho*-methyl groups increased during the reaction and was saturated at 63 atom % D. It is worthwhile to note that the final deuterium contents in the *ortho*-methyl groups (63 atom % D) and mercapto group (44 atom % D) are significantly different. This fact may reflect different thermodynamic stability in C−H/C−D and S−H/S−D bond energies. It is also worth noting that an independent study using C_6H_6 as a solvent monitored by $^2H\{^1H\}$ NMR spectrum shows that the deuteration by D_2 exclusively took place in the *ortho*-methyl and mercapto protons in this catalysis.

Table 3 shows representative results for the catalytic H/D exchange reaction. Thiaruthenacycle complex **3** catalyzed the deuteration reaction of the *ortho*-methyl and mercapto groups (entry 1). Dihydride complex **5** also catalyzed the deuteration in comparable activity (entry 2) and was employed as a catalyst for the following catalyses. In the presence of 11 equiv of PMe_3, significant retardation was observed for the sp³ C−H/D_2 exchange reaction, but no retardation was observed for the S−H/D_2 exchange reaction (entry 3). This fact suggests independent mechanisms are operating for these H/D exchange reactions. It was found that 2,6-xylenol was much less reactive than 2,6-dimethylbenzenethiol (entry 4). The sp³ C−H/D_2 exchange process was also retarded by the addition of PMe_3 (entry 5).[29] When phenol was employed in this catalysis, O−H/D_2 exchange reaction proceeded but the *ortho* sp² C−H bond activation did not occur (entry 6). This is probably due to the fact that a four-membered oxaruthenacycle intermediate is much less favorable than the five-membered one. Interestingly, the sp² C−H bond activation was enhanced for 2-cresol (entry 7). The steric repulsion between the *ortho*-methyl group in the 2-methylphenoxo intermediate and the ancillary ligands would force the *ortho* sp² C−H bond into a position proximal to the ruthenium center. All these data suggest an anchoring effect of the ruthenium center by the sulfur or oxygen atom upon C−H bond cleavage reaction.

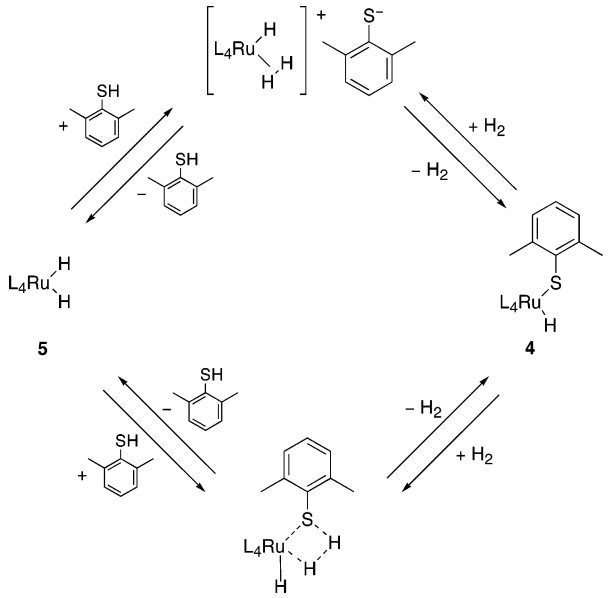
Table 3. Catalytic H/D Exchange Readction of 2,6-Dimethylbenzenethiol and Phenols[a]

entry	catalyst	substrates	additive (equiv./cat.)	products deuterium content (atom D%)
1	**3**		none	
2	**5**		none	
3	**5**		PMe_3 (11)	
4[b]	**5**		none	
5	**5**		PMe_3 (7.9)	
6	**5**		none	
7	**5**		none	

[a] These reactions were carried out in benzene-d_6 at rt for 5 days in the presence of catalyst (5 mol %) under an atmosphere of D_2 (0.1 MPa). [b] Reaction for 7 days.

(29) As shown in Table 3, the addition of PMe_3 to the 2,6-dimethylbenzenthiol/D_2 system had an effect on the D content (entries 2 and 3). By taking into account the time-course curve shown in Figure 6, the added PMe_3 retarded the sp³ C−H/D_2 exchange reaction, but the D content in the mercapto group suggested no retardation effect on the thiolato/thiol exchange reaction. For the 2,6-xylenol system (entries 4 and 5 in Table 3), the addition of PMe_3 also reduced the sp³ C−H/D_2 exchange reaction, but the D content in the hydroxo group remained unchanged. This difference is probably due to the fact that the aryloxo/phenol exchange reaction for the 2,6-xylenol system is a slower process than the thiolato/thiol exchange for the 2,6-dimethylbenzenethiol system.

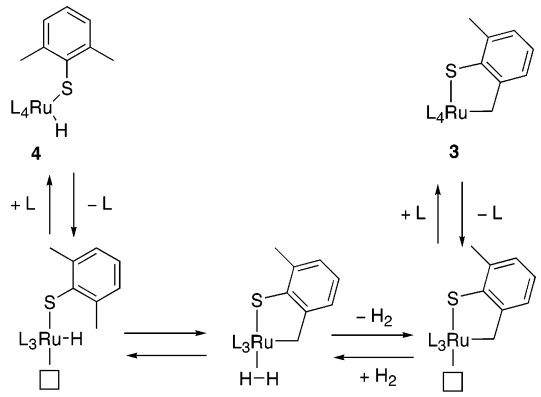
Scheme 6



Possible Mechanism of the Catalysis. The above observations demonstrate that ruthenacycle and (hydrido)(thiolato)ruthenium(II) complexes are viable catalyst precursors for the S−H and sp^3 C−H bond activation. This catalysis consists of two key reactions.

The first key reaction is rapid exchange between the thiolato ligand and external thiol. Since this exchange reaction was not retarded by the addition of PMe_3 at all, this S−H/D_2 exchange reaction would proceed without dissociation of PMe_3 (Scheme 6). There are some related reports that support an ionic mechanism for the reaction of **4** with hydrogen (or deuterium) gas, giving **5** without dissociation of PMe_3. For example, reactions of **5** with phenol and *para*-cresol,[19,24b,30] *trans*-$RuH_2(DMPE)_2$ with thiols,[31] and *trans*-$RuH_2(DPPM)_2$ with phenol[32] are documented to give cationic intermediates. Thus, the S−H/D_2 exchange process may involve similar cationic species *cis*-$[RuH(D_2)(PMe_3)_4]^+[SC_6H_3Me_2\text{-}2,6]^-$, from which $DSC_6H_3Me_2$-2,6 and *cis*-$RuHD(PMe_3)_4$ would be produced. Berke and co-workers revealed that $[RuH_3(PMe_3)_4]^+[BPh_4]^-$ was formulated as the *cis*-hydrido(dihydrogen) structure by a low-temperature NMR study,[26] where η^2-dihydrogen and hydrido ligands in cationic ruthenium(II) were rapidly exchanging. On the other hand, the treatment of the related oxaruthenacycle complex *cis*-$Ru[OC_6H_3(2\text{-}CH_2)(6\text{-}Me)\text{-}\kappa^2O,C](PMe_3)_4$ with H_2 smoothly gives the *cis*-dihydride complex **5** and 2,6-xylenol, indicating the reversibility of the reaction as illustrated in Scheme 6. An ionic mechanism may be favorable, although an alternative metathetical mechanism cannot be ruled out. The exchange reaction between the thiolato/thiol is also a rapid process. Since related alkoxo/alcohol and aryloxo/phenol exchange reactions in late transition metal complexes are well established to proceed through a hydrogen bonding,[19,33] a similar mechanism may also be operating for the present thiolato/thiol exchange process.

Scheme 7



The second step concerns the sp^3 C−H bond activation process as shown in Scheme 7. Since the sp^3 C−H/D_2 exchange reaction is significantly retarded by the addition of PMe_3, this reaction proceeds via prior dissociation of the PMe_3 ligand, suggesting that the cleavage reaction requires a vacant coordination site. Then, bond cleavage of the sp^3 C−H bond takes place as shown in Scheme 7. Although we should await further studies for further details on the C−H bond cleavage step, both oxidative addition[34] and metathetical mechanisms[8c,35] are documented to occur for ruthenium(II) complexes. Then, a rapid exchange reaction between putative coordinated dihydrogen and H_2 gas followed by hydrogenolysis of the Ru−C bond promote the H/D exchange reaction of the *ortho* methyl groups.

Concluding Remarks

This study provides stoichiometric and catalytic sp^3 C−H/D_2 and S−H/D_2 exchange reactions of *ortho*-substituted benzenethiol and phenols by ruthenium complexes. The facile sp^3 C−H/D_2 exchange indicates the importance of a prior anchoring to the ruthenium center through the chalcogen atom, which also enables catalytic H/D exchange reaction of 2,6-dimethylbenzenethiol with D_2 under ambient conditions. Moreover, this system clearly shows the different nature of the catalytic bond cleavage reactions between the sp^3 C−H and S−H bonds, where the former bond cleavage reaction is triggered by dissociation of PMe_3 while the latter proceeds associatively.

Experimental Section

General Procedures. All manipulations and reactions were performed under dry nitrogen using standard Schlenk

(30) Burn, M. J.; Bergman, R. G. *J. Organomet. Chem.* **1994**, *472*, 43.

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(32) Ayllon, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000.

(33) Selected examples for interaction between aryloxo and phenols (or related compounds) are as follows: (a) Ru: Ozawa, F.; Yamagami, I.; Yamamoto, A. *J. Organomet. Chem.* **1994**, *473*, 265. (b) Rh: Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (c) Ni, Pd: Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (d) Pd: (a) Bugno, C. D.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. (b) Kapteijin, G. M.; Dervisi, A.; Grove, D. M.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 10939. (c) Kapteijin, G. M.; Spee, M. P. R.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 1405.

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and vacuum line techniques, unless noted otherwise. Benzene, toluene, THF, and hexane were distilled over sodium/benzophenone ketyl, and these solvents were stored under nitrogen. Pentane was distilled over potassium/benzophenone ketyl and was stored under vacuum. PMe_3 was prepared from $P(OPh)_3$ with MeMgI. Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) was prepared according to literature procedures with magnetic stirring instead of ultrasonic irradiation.[36] *cis*-$RuH_2(PMe_3)_4$ (**5**),[37] *cis*-$RuMe_2(PMe_3)_4$ (**6**),[38] *cis*-RuClMe$(PMe_3)_4$ (**7**),[22a] and *cis*-Ru[OC_6H_4(2-CH_2)(6-Me)-κ^2*O,C*]$(PMe_3)_4$ (**8**)[9b] were prepared by the literature methods. Potassium 2,6-dimethylbenzenethiolate was prepared by the reaction of 2,6-dimethylbenzenethiol with KOH in methanol. Benzene-d_6 was distilled over sodium wires and was stored under vacuum. D_2 gas was purchased from Nippon Sanso and used as received. All other reagents were obtained from commercial suppliers and used as received. Reactions in a NMR tube under vacuum or hydrogen were carried out by use of a 5 mm ϕ Aldrich NMR tube with a Teflon valve, in which benzene-d_6 was introduced by valve-to-valve distillation and H_2 or D_2 gas was introduced by use of mercury manometer. ^{1}H NMR spectra were recorded on a JEOL LA 300 spectrometer (300.4 MHz for ^{1}H). Chemical shifts (δ) are given in ppm, relative to internal TMS for ^{1}H and external 85% H_3PO_3 in deuterated water for ^{31}P. All coupling constants are given in Hz. The deuterium content in the *ortho*-methyl and mercapto groups was estimated on the basis of the relative intensity of 1,4-dioxane as an internal standard. Since the relative signal intensity was found to depend on the pulse delay, the pulse delay was set to 120 s for complete relaxation. Elemental analyses were carried out by a Perkin-Elmer 2400 series II CHNS analyzer. GLC analysis was performed on a Shimazu GC-8A with a FID detector using a Porapak Q column.

Reaction of 1/PMe_3 with 2,6-Dimethylbenzenethiol Giving Ru(1−5-η^5-cyclooctadienyl)($SC_6H_3Me_2$-2,6)$(PMe_3)_2$ (2). Although this compound can be prepared at room temperature in benzene, the following procedure gave the highest yield. Complex **1** (549.5 mg, 1.742 mmol) was placed into a 25 mL Schlenk tube, where benzene (ca. 3 mL) was introduced by valve-to-valve distillation. PMe_3 (450 μL, 3.04 mmol) was added to the solution by a hypodermic microsyringe. The reaction system was stirred at 50 °C for 17 h, and then 2,6-dimethylbenzenethiol (140 μL, 1.05 mmol) was added into the reaction mixture. The reaction mixture was stirred at 50 °C for an additional 100 h. All volatile materials were removed under reduced pressure, and the resulting orange oil was washed with dry hexane (100 mL) to give an analytically pure yellow powder of **2** in 59% yield (294.9 mg, 1.02 mmol). ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.33 (qt, J = 11.6, 2.7 Hz, 1H, *exo*-7-CH_2), 0.91 (d, J = 7 Hz, 9H, PMe_3), 1.05 (m, 1H, *endo*-7-CH_2), 1.26 (m, 2H, *endo*-6- and −8-CH_2), 1.51 (d, J = 8.1 Hz, 9H, PMe_3), 1.85 (m, *exo*-6- and −8-CH_2), 2.15 (br, 1H, 1- or 5-C*H*), 2.24 (br, 1H, 5- or 1-C*H*), 2.62 (s, 6H, $SC_6H_3Me_2$-2,6), 3.21 (m, 1H, 2- or 4-C*H*), 3.31 (m, 1H, 4- or 2-C*H*), 5.67 (br. td, 1H, 3-C*H*), 7.07 (t, J = 7 Hz, 1H, *para*-SC_6H_3), 7.20 (d, J = 7 Hz, 2H, *meta*-SC_6H_3). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ −7.5 (d, J = 32 Hz, 1P, PMe_3), −5.3 (d, J = 32 Hz, 1P, PMe_3). Anal. Found: C, 53.12; H, 7.97; S, 6.77. Calcd for $C_{22}H_{38}P_2RuS$: C, 53.10; H, 7.70; 6.44.

Reaction of 1/PMe_3 with 2,6-Dimethylbenzenethiol Giving *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2*S,C*]$(PMe_3)_4$ (3). Compound **1** (234.3 mg, 0.743 mmol) was placed in a 25 mL Schlenk tube in which benzene (4 mL) was induced via valve-to-valve distillation. PMe_3 (370 μL, 2.86 mmol) and 2,6-dimethylbenzenethiol (120 μL, 0.901 mmol) were added into the solution. The solution was stirred at 70 °C for 200 h. The reaction mixture was then evaporated to dryness, and the resulting white powder was extracted with dry hexane (30 mL). The extract was separated by cannula and was concentrated, and was then kept at −20 °C for a night to give white platelike crystals of **3** in 20% yield (79.6 mg, 0.146 mmol). ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.99 (d, J = 6.6 Hz, 9H, PMe_3), 1.10 (vt, J = 2.7 Hz, 18H, mutually *trans*-PMe_3), 1.11 (d, J = 5.4 Hz, 9H, PMe_3), 2.70 (tdd, J = 13.7, 5.3, 3.7 Hz, 2H, *ortho*-CH_2), 2.88 (s, 3H, *ortho*-SC_6H_3Me), 7.06 (d, J = 4.5 Hz, 2H, *meta*-SC_6H_3), 7.48 (t, J = 4.5 Hz, 1H, *para*-SC_6H_3). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ −16.8 (td, J = 27, 18 Hz, 1P, PMe$_3$ trans to −CH_2−), −8.4 (t, J = 27 Hz, 2P, mutually *trans*-PMe$_3$), 0.0 (td, J = 27, 18 Hz, 1P, PMe$_3$ trans to −S−). Anal. Found: C, 44.06; H, 8.56; S, 6.02. Calcd for $C_{20}H_{44}SP_4Ru$: C, 44.35; H, 8.19; S, 5.92.

Reaction of Ru(1−5-η^5-cyclooctadienyl)($SC_6H_3Me_2$-2,6)$(PMe_3)_2$ (2) with PMe_3. Complex **2** (7.8 mg, 0.016 mmol), a flame shield capillary with PPh_3 and CH_2Cl_2 as internal standard, benzene-d_6 (510 mL), and PMe_3 (15.9 mL, 0.156 mmol) were placed in an NMR tube. Heating at 70 °C for 222 h gave thiaruthenacycle complex **3** in 91% yield.

Reaction of *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2*S,C*]$(PMe_3)_4$ (3) with Hydrogen. Complex **3** (9.9 mg, 0.018 mmol) and triphenylmethane (10.3 mg, 0.0422 mmol) as an internal standard were placed into an Aldrich NMR tube with PTFE screw cap under Ar. The NMR tube was evacuated; then benzene-d_6 was introduced (600 μL). Hydrogen gas (0.1 MPa) was charged into the NMR tube, and the reaction was monitored by NMR. After exposure of **3** to an atmosphere of hydrogen for 10 min, (hydrido)(thiolato)ruthenium(II) complex **4** was detected in 90% yield. Since complex **4** can survive only under hydrogen atmosphere, it was characterized spectroscopically. **4**: ^{1}H NMR (300.4 MHz, C_6D_6): δ −8.63 (ddt, J = 39.6, 13.2, 9.6 Hz, 1H, Ru-*H*), 1.05 (d, J = 7.2 Hz, 9 H, apical PMe_3), 1.25 (vt, J = 3.0 Hz, 18 H, mutually *trans* PMe_3), 1.26 (d, J = 4.5 Hz, 9 H, PMe_3), 3.01 (s, 6H, *ortho*-$SC_6H_3Me_2$), 7.05 (t, J = 7.5 Hz, 1H, *para*-$SC_6H_3Me_2$), 7.20 (d, J = 7.5 Hz, 2H, *meta*-$SC_6H_3Me_2$). ^{31}P{^{1}H} NMR (122.6 MHz, C_6D_6): δ −17.8 (td, J = 27, 16 Hz, 1P, PMe$_3$ *trans* to H), −5.9 (dd, J = 32, 27 Hz, 2P, mutually *trans* PMe$_3$), 6.6 (td, J = 26, 17 Hz, 1P, PMe$_3$ *trans* to S).

The reaction of **3** with D_2 is carried out in the similar manner by using a manometer: **3** (10.3 mg, 0.019 mmol), $CHPh_3$ (10.7 mg, 0.0438 mmol), benzene-d_6 (0.6 mL), D_2 (4.75 mL, 0.199 mmol).

Evacuation of *cis*-RuH($C_6H_3Me_2$-2,6)$(PMe_3)_4$ (4) in Benzene-d_6. A typical experiment was carried out as follows. Complex **3** (9.5 mg, 0.018 mmol) and triphenylmethane (9.3 mg, 0.017 mmol) were placed in an Aldrich NMR tube with PTFE screw cap under Ar. Benzene-d_6 was introduced into the NMR tube by valve-to-valve distillation, and the system was exposed to H_2 (0.1 MPa) for a night at room temperature. Complete formation of **4** was checked by NMR, and then the reaction system was evacuated by freeze−pump−thaw cycles. The NMR study indicates formation of **3** in 40% yield after 24 h at room temperature. Introduction of ethylene (0.1 MPa) into the solution of **4** significantly encourages formation of **3** (95% yield) within 7 h at room temperature.

Reaction of *cis*-Ru[SC_6H_3(2-CH_2)(6-Me)-κ^2*S,C*]$(PMe_3)_4$ (3) with Hydrogen in the Presence of PMe_3. As described above, complex **3** (9.1 mg, 0.017 mmol), triphenylmethane (10.0 mg, 0.0409 mmol), and benzene-d_6 were placed into an NMR tube, and then dry N_2 gas was introduced into the NMR tube. PMe_3 (2.0 μL, 0.19 mmol) was added into the NMR tube, and the NMR spectrum was measured. Then the NMR tube was frozen by liquid N_2 and evacuated to introduce H_2 gas.

Reaction of *cis*-Ru[OC_6H_3(2-CH_2)(6-Me)-κ^2*O,C*]$(PMe_3)_4$ (8) with Hydrogen. Complex **8** (10.5 mg, 0.0200 mmol) was placed in an NMR tube into which benzene-d_6 (0.6 mL) was

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transferred by vacuum distillation. 1,4-Dioxane (1.4 μL, 0.016 mmol) was added to the system by a hypodermic syringe as an internal standard. The reaction system was evacuated by freeze−pump−thaw cycles, and then hydrogen (0.1 MPa) was charged into the tube. After 30 h at room temperature, the hydride complex **5** was formed in 100% yield.

Reaction of *cis*-RuH$_2$(PMe$_3$)$_4$ (5) with 2,6-Dimethylbenzenethiol under Vacuum. Complex **5** (40.0 mg, 0.0982 mmol) was placed in a 50 mL Schlenk tube, where dry THF (ca. 2 mL) was introduced by valve-to-valve distillation. Onto the frozen solution, 2,6-dimethylbenzenethiol (15.7 μL, 0.118 mmol) was added, frozen by using liquid nitrogen, and then evacuated. The reaction temperature was allowed to rise to room temperature, and the mixture was stirred for 23 h. Evolved gas was collected by Toepler pump and was identified as H_2 by GLC (1.2 mL, 0.055 mmol, 56%). On the other hand, the solution was evaporated to dryness and then dried under vacuum. Triphenylmethane (6.6 mg, 0.027 mmol) was added into the Schlenk tube, and benzene-d_6 was introduced into the vessel to dissolve all materials. The ^{1}H NMR analysis revealed formation of a mixture of **3** (0.0530 mmol, 54%) and **4** (0.0388 mmol, 40%).

Reaction of *cis*-RuH$_2$(PMe$_3$)$_4$ (5) with 2,6-Dimethylbenzenethiol under Argon, Ethylene, or Butadiene. (a) Under Ar: In an NMR tube, triphenylmethane (6.9 mg, 0.028 mmol) and **5** (10.8 mg, 0.0265 mmol) were placed and then benzene-d_6 (0.6 mL) was introduced. Under Ar atmosphere, 2,6-dimethylbenzenethiol (8.8 μL, 0.066 mmol) was injected by a hypodermic syringe. The reaction system was heated at 50 °C. After 60 h at 50 °C, formation of **3** (16%) and **4** (55%) was observed by NMR. (b) Under ethylene: The reaction was performed similarly to the above procedure: triphenylmethane (7.0 mg, 0.028 mmol), **5** (10.8 mg, 0.0265 mmol), benzene-d_6 (0.6 μL), 2,6-dimethylbenzenethiol (8.8 μL, 0.066 mmol). Afer 60 h at 50 °C, **3** (72%) and **4** (0%) were formed. (c) Under butadiene: The reaction was performed similarly to the procedure under Ar: triphenylmethane (7.0 mg, 0.028 mmol), **5** (10.9 mg, 0.0265 mmol), benzene-d_6 (0.6 μL), 2,6-dimethylbenzenethiol (8.8 μL, 0.066 mmol). After 60 h at 50 °C, formation of **3** (28%) and **4** (40%) was observed.

Reaction of *cis*-RuMe$_2$(PMe$_3$)$_4$ (6) with 2,6-Dimethylbenzenethiol. Complex **6** (14.8 mg, 0.0340 mmol) was placed in an NMR tube (5 mm φ) into which benzene-d_6 (0.6 mL) was transferred by vacuum distillation. 1,4-Dioxane (1.2 μL, 0.014 mmol) as an internal standard and 2,6-dimethylbenzenethiol (5.2 μL, 0.040 mmol) were added into the system, and then this reaction system was evacuated by freeze−pump−thaw cycles and the reaction mixture was reacted at room temperature. After 5 h, the thiaruthenacycle complex **3** was formed in 100% yield. Then, ethane (1.05 mL) was injected into the NMR tube by a calibrated hypodermic syringe through an Aldrich rubber septum. The GLC analysis shows evolution of methane (0.0575 mmol, 169%).

Reaction of *cis*-RuClMe(PMe$_3$)$_4$ (7) with Potassium Dimethylbenzenethiolate. This reaction was carried out basically similarly to the reaction of **6** with 2,6-dimethylbenzenethiol as described above. A mixture of **7** (2.9 mg, 0.0064 mmol) was placed in an NMR tube into which benzene-d_6 (0.5 mL) was transferred by vacuum distillation. To the frozen mixture was added a slightly excess amount of potassium 2,6-dimethylbenzenethiol under nitrogen atmosphere, and then the system was evacuated. After 2 h at room temperature, the thiaruthenacycle complex **3** was formed in 86% yield with concomitant formation of methane in 106% yield.

Reaction of *cis*-RuH$_2$(PMe$_3$)$_4$ (5) with 2,6-Xylenol under Ethylene or Butadiene. (a) Under ethylene: **5** (14.5 mg, 0.0356 mmol) and 2,6-xylenol (8.1 mg, 0.066 mmol) were placed in an NMR tube. Benzene-d_6 (0.6 μL) was introduced in the NMR tube, and the reaction system was heated at 70 °C. Complex **8** was formed in 70% yield after 4 days. (b) Under butadiene: a similar procedure under butadiene atmosphere was performed: **5** (11.2 mg, 0.0275 mmol), 2,6-xylenol (8.4 mg, 0.069 mmol), under butadiene (0.1 MPa), 70 °C. Complex **8** was formed in 40% yield after 4 days.

Table 4. Crystallographic Data for *cis*-Ru(η^5-C$_8$H$_{11}$)(SC$_6$H$_3$Me$_2$-2,6)(PMe$_3$)$_2$ (2) and *cis*-Ru[SC$_6$H$_3$(2-CH$_2$)(6-Me)](PMe$_3$)$_4$ (3)

	2	**3**
chemical formula	$C_{22}H_{38}P_2SRu$	$C_{20}H_{44}P_4SRu$
fw	497.62	541.59
cryst size (mm)	0.56 × 0.51 × 0.22	0.60 × 0.47 × 0.40
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	14.64(4)	9.566(4)
b (Å)	19.22(5)	16.24(2)
c (Å)	8.59(3)	17.769(4)
α (deg)	98.8(2)	90.01(5)
β (deg)	90.0(3)	105.29(2)
γ (deg)	89.8(2)	89.97(6)
V (Å^3)	2389(12)	2662(2)
Z	4	4
measurement temp (K)	200.2	293.2
radiation type	Mo Kα	Mo Kα
radiation wavelength (Å)	0.7107	0.7107
no. of reflns	4115	12523
total no. of reflns	4103	12129
no. of reflns gt	2979	7589
reflns threshold expression	$F^2 > 3.0\sigma(F^2)$	$F^2 > 3.0\sigma(F^2)$
R^a	0.0747	0.0466
$R_w{}^b$	0.1127	0.0503
goodness of fit	1.247	1.18

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

Stoichiometric Reaction of *cis*-Ru[SC$_6$H$_3$(2-CH$_2$)(6-Me)-κ^2*S,C*](PMe$_3$)$_4$ (3) with D$_2$. A typical example is described as follow. Complex **3** (9.7 mg, 0.018 mmol) was placed in a 50 mL Schlenk tube into which benzene-d_6 (1.5 mL) was transferred by vacuum distillation. 2,6-Dimethylbenzenethiol (50.0 μL, 0.376 mmol) was then added into the solution by a hypodermic syringe. The reaction system was evacuated by freeze−pump−thaw cycles, and deuterium gas (35.8 mL, 1.48 mmol) was charged by use of a mercury manometer. After a certain time period at 30 °C, the solution was moved to a NMR tube through a Teflon cannula to measure the NMR spectrum. This procedure was repeated for each time period.

Catalytic Reaction of *cis*-Ru[SC$_6$H$_3$(2-CH$_2$)(6-Me)-κ^2*S,C*](PMe$_3$)$_4$ (3) with D$_2$. A typical example is described as follow. Complex **3** (10.2 mg, 0.0188 mmol) and triphenylmethane (27.9 mg, 0.114 mmol) were placed in a 50 mL Schlenk tube. Benzene-d_6 and 2,6-dimethylbenzenethiol (50 μL, 0.38 mmol) were added into the solution, and then the reaction system was evacuated by freeze−pump−thaw cycles. D_2 gas (29.63 mL, 1.24 mmol) was introduced into the Schlenk tube by using a manometer, and the reaction mixture was heated at 50 °C for 70 h. A certain amount of the solution (ca. 0.6 mL) was transferred to a NMR tube through a Teflon cannula. This procedure was repeated for each time period.

X-ray Crystallography. 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 in a capillary tube (Glass, 0.7 mm φ), which was sealed by small flame torch, or 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. 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 **2** and **3** are given in Table 4. The data were processed using the teXsan crystal solution package[39] operat-

ing on a SGI O2 workstation. All non-hydrogen atoms were found by using the results of the teXsan direct methods (SIR92). These structures were solved by direct methods (SAPI91). An absorption correction was applied with the program PSI SCAN method. All non-hydrogen atoms were found on difference maps. For complex **2**, Ru(1), Ru(2), S(2), P(1), and P(2) were refined anisotropically. For complex **3**, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the calculated positions. Crystallographic thermal parameters and bond distances and angles have been deposited as Supporting Information.

(39) *teXsan*, Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 and 1999.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters and bond distances and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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