ORGANOMETALLICS

ARTICLE

pubs.acs.org/Organometallics

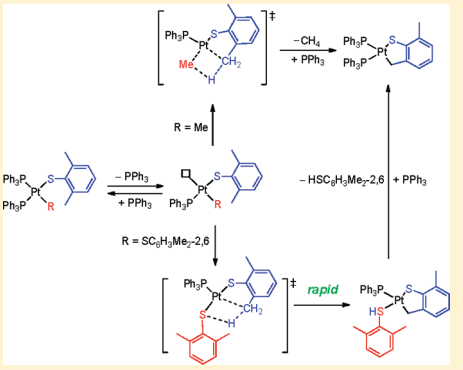
Carbon−Hydrogen Bond Cleavage Reaction in Four-Coordinate (2,6-Dimethylbenzenethiolato)platinum(II) Complexes. Dramatic Acceleration by Thiolato Hydrogen Acceptor†

Masafumi Hirano,* Shin-ya Tatesawa, Minoru Yabukami, Yoko Ishihara, Yusuke Hara, Nobuyuki Komine, and Sanshiro Komiya*

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-26 Nakacho, Koganei, Tokyo 184-8588, Japan

Supporting Information

ABSTRACT: The (2,6-dimethylbenzenethiolato)platinum(II) complexes PtR($SC_6H_3Me_2$-2,6-κ^1S)L_2 (R = Me, L = PMe_3 (**1a**), PPh_3 (**1c**), L_2 = dppe (**1d**), dppp (**1e**); R = Et, L = PPh_3 (**2c**); R = CH_2CMe_3, L = PPh_3 (**3c**)) and Pt($SC_6H_3Me_2$-2,6-κ^1S)$_2L_2$ (L = PMe_3 (**4a**), PEt_3 (**4b**), PPh_3 (**4c**), L_2 = dppe (**4d**), dppp (**4e**), dppb (**4f**)) have been prepared. Heating of these compounds results in an internal sp^3 C−H bond cleavage reaction, giving the thiaplatinacycle complexes Pt[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C]L_2 (L = PMe_3 (**5a**), PEt_3 (**5b**), PPh_3 (**5c**), L_2 = dppe (**5d**), dppp (**5e**), dppb (**5f**)) in moderate to quantitative yields. The reactions of **1c** and **4c** proceed via prior dissociation of PPh_3, and a concerted mechanism is proposed. Of particular interest is the sp^3 C−H bond activation step, whose observed rate constant for **4c** is no less than 10^4-fold faster than that for **1c**. The arenethiolato group is expected to enhance the C−H bond cleavage step as a hydrogen acceptor.



INTRODUCTION

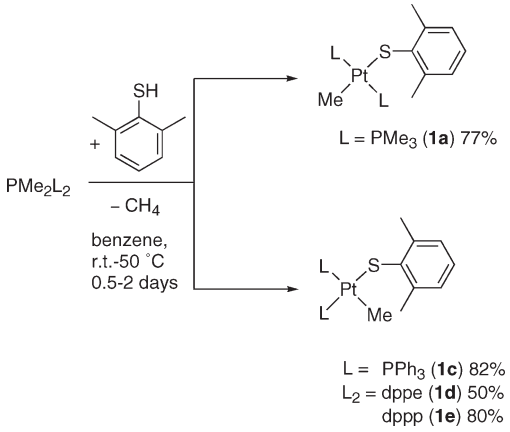
The cleavage of sp^3 carbon−hydrogen bonds at Pt(II) centers has attracted continuing interest since the pioneering discoveries of methane activation by Shilov. For example, Shilov found catalytic activation of methane by K_2PtCl_4 (and also K_2PtCl_6) to give methanol or chloromethane.[1,2] In an improvement on the Shilov approach, Periana developed a remarkable catalysis for the formation of methyl sulfate.[3] On the basis of the principle of microscopic reversibility, many Pt−Me σ-bond cleavage reactions have been studied, since they represent the reverse reactions of the methane activation reaction.[4] On the other hand, Whitesides reported an internal γ-C−H bond cleavage reaction of the alkyl group in Pt(CH_2CMe_3)$_2L_2$, giving platinacyclic compounds.[5] In this pioneering example, the neopentyl group brings the sp^3 C−H bond in proximity to the Pt(II) center and it also acts as a hydrogen acceptor. The neopentyl complex Pt(CH_2CMe_3)$_2L_2$ is also reported to show high activity toward the intermolecular sp^3 C−H bond activations of toluene[6] and methane,[7] giving tolyl- and methylplatinum(II) compounds, respectively. Mechanistic investigations reported for bis(alkyl)platinum(II)[8] and (alkyl)(enolato-η^1C)platinum(II) phosphine complexes reveal a pathway involving initial dissociation of an ancillary phosphine for β-hydride elimination of the alkyl group.

We have documented systematic internal sp^3 C−H bond cleavage reactions of (2,6-dimethylphenoxo)-[9] and (2,6-dimethylbenzenethiolato)ruthenium(II)[10] complexes to give oxa- and thiaruthenacyclic compounds, where the sp^3 C−H bond in the *o*-methyl groups in the aryloxo and thiolato anchoring ligands are brought in proximity to the Ru(II) center. Consequently, the following sp^3 C−H bond cleavage reactions proceeded easily. More recently, we have revealed the mechanism for a rapid and reversible sp^3 C−H bond cleavage reaction in bis(2,6-dimethylbenzenethiolato)ruthenium(II) compounds, where a five-coordinate species is an active compound for the sp^3 C−H bond cleavage reaction.[10b]

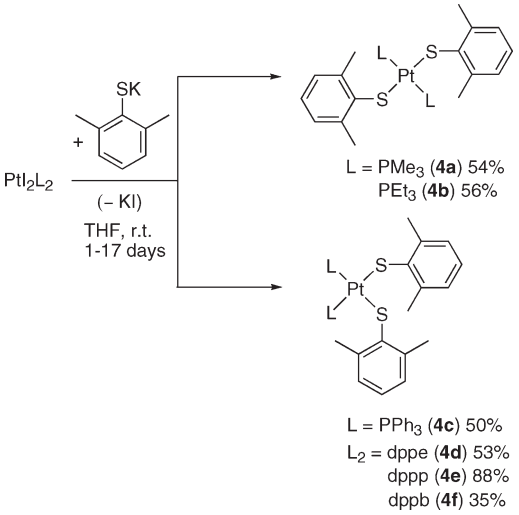
As an extension of this chemistry, we are interested in the internal sp^3 C−H bond cleavage reactions of (2,6-dimethylbenzenethiolato)platinum(II) compounds, where the Pt−S anchoring bond is expected to bring the *o*-methyl group to the square-planar Pt(II) center. Such thiolato-promoted sp^3 C−H bond cleavage reaction at Pt(II) is unexplored, and only one pioneering example has been documented for the sp^2 C−H bond cleavage reaction by *cis*-PtH(triptycylthiolato)$(PPh_3)_2$ under severe conditions (10 h in refluxing toluene).[11] We have conducted a study of the internal sp^3 C−H bond cleavage reactions in four-coordinate (alkyl)(2,6-dimethylbenzenethiolato)platinum(II) and bis(2,6-dimethylbenzenethiolato)platinum(II) complexes, giving thiaplatinacyclic compounds. In this article we disclose that both *cis*-PtMe($SC_6H_3Me_2$-2,6-κ^1S)$(PPh_3)_2$ (**1c**) and *cis*-Pt($SC_6H_3Me_2$-2,6-κ^1S)$_2(PPh_3)_2$ (**4c**) quantitatively give the corresponding thiaplatinacycle Pt[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S, C]$(PPh_3)_2$ (**5c**) with evolution of methane and 2,6-dimethylbenzenethiol, respectively. Interestingly, **4c** produced **5c** much more

Received: April 22, 2011
Published: September 12, 2011

Scheme 1



Scheme 2



quickly than **1c** and this significant enhancement effect on the sp^3 C−H bond cleavage reaction was ascribed to the arenethiolato group as a hydrogen acceptor.

RESULTS AND DISCUSSION

1. Preparation of (2,6-Dimethylbenzenethiolato)platinum(II) Compounds. *1.1. Preparation of (Alkyl)(2,6-dimethylbenzenethiolato)platinum(II).* The series of (methyl)(2,6-dimethylbenzenethiolato)platinum(II) compounds PtMe($SC_6H_3Me_2$-2,6-κ^1S)L_2 (L = PMe_3 (**1a**), PPh_3 (**1c**), dppe (**1d**), dppp (**1e**)) were prepared by protonolysis of *cis*-$PtMe_2L_2$ with 1 equiv of 2,6-dimethylbenzenethiol in 50−82% yields (Scheme 1).[12]

These compounds were characterized by ^{1}H and $^{31}P\{^1H\}$ NMR and elemental analysis. Compound **1a** has a trans configuration, but the other compounds **1c**−**e** have cis configurations in a square-planar geometry. For example, the ^{1}H NMR spectrum of **1c** shows a characteristic resonance at δ −0.42 (t, 3H) possessing a Pt satellite ($^2J_{H-Pt}$ = 30 Hz). This signal is therefore assigned as the Pt−*Me* group in **1c**. In addition, resonances at δ 2.44 (s, 6H), 6.81 (t, 1H), 6.97 (d, 2H), and 7.1−7.6 (m, 30H) are assignable to the $SC_6H_3Me_2$-2,6, para and meta aromatic protons in $SC_6H_3Me_2$-2,6, and P*Ph*$_3$, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ 24.6 (d, $^2J_{P-P}$ = 7.3 Hz, $^1J_{P-Pt}$ = 3310 Hz, 1P) and 29.5 (d, $^2J_{P-P}$ = 7.3 Hz, $^1J_{P-Pt}$ = 1968 Hz, 1P), suggesting the cis configuration. The former and latter resonances are assigned as the PPh_3 ligand trans to the thiolato and methyl groups because of the characteristic $^1J_{P-Pt}$ value based on the trans influence of the arenethiolato ligand being weaker than that of the methyl group.[13] These NMR data are consistent with *cis*-**1c**. The pyridine-promoted cis to trans one-way transformation is reported for $PtCl(SAr)(PR_3)_2$, suggesting the trans form is more thermodynamically stable.[14] $PtH(SAr)(PPh_3)_2$ is also reported to be a trans complex.[15] However, compound **1c** favors the cis configuration probably because of the steric repulsion between the 2,6-dimethylbenzenethiolato group and the PPh_3 ligand.

Similarly, *cis*-PtEt($SC_6H_3Me_2$-2,6-κ^1S)$(PPh_3)_2$ (**2c**) and *cis*-Pt(CH_2CMe_3)($SC_6H_3Me_2$-2,6-κ^1S)$(PPh_3)_2$ (**3c**) were also prepared by the metathetical reaction of corresponding (alkyl)(chlorido)platinum(II) complex with $KSC_6H_3Me_2$-2,6 in 58% and 41% yields, respectively.

1.2. Preparation of Bis(2,6-dimethylbenzenethiolato)platinum(II). The series of bis(2,6-dimethylbenzenethiolato)platinum(II) complexes Pt($SC_6H_3Me_2$-2,6-κ^1S)$_2L_2$ (L = PMe_3 (**4a**), PEt_3 (**4b**), PPh_3 (**4c**); L_2 = dppe (**4d**), dppp (**4e**), dppb (**4f**)) were prepared by the conventional metathetical reaction of PtI_2L_2 with 2 equiv of $KSC_6H_3Me_2$-2,6 in THF at room temperature (Scheme 2).[16]

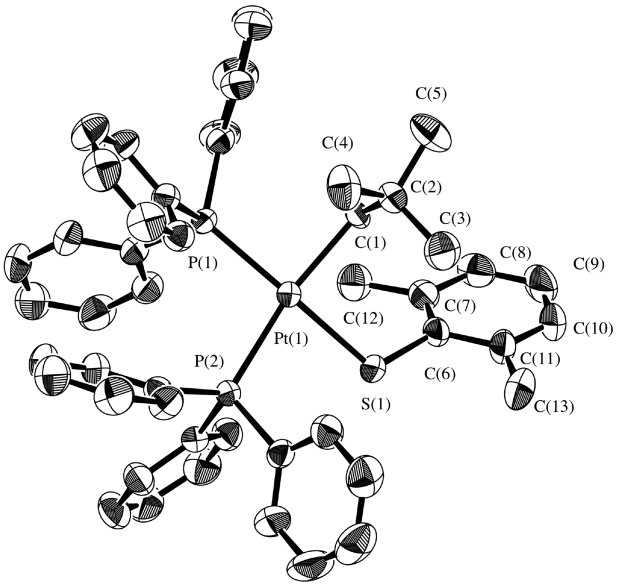
For example, *cis*-Pt($SC_6H_3Me_2$-2,6-κ^1S)$_2(PPh_3)_2$ (**4c**) was prepared by the treatment of $PtI_2(PPh_3)_2$ with $KSC_6H_3Me_2$-2,6 (2.5 equiv) in 50% yield. This compound was characterized by NMR and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 shows a singlet at δ 18.5 ($^1J_{P-Pt}$ = 3043 Hz), and the ^{1}H NMR indicates a singlet at δ 2.17 (12H) and multiplets at δ 6.58−6.65 (6H) with aromatic protons at δ 7.13−7.53 (30H), assignable to the 2,6-dimethyl groups, aromatic protons in arenethiolato groups, and P*Ph*$_3$, respectively. Although it is difficult to determine the cis/trans configuration of **4c** by the NMR data alone,[17] we believe **4c** has the cis configuration in solution because the X-ray analysis reveals the cis configuration.

The other analogues **4a**,**b**,**d**−**f** were also prepared by a similar protocol and the dppe, dppp, and dppb analogues **4d**−**f** were isolated as cis forms, which were also characterized by spectroscopic methods and X-ray structure analyses. The PMe_3 complex **4a** was found to exist in a trans configuration. The X-ray structure of **4a** unambiguously showed the trans configuration, and the PMe_3 resonance was observed as a virtual triplet in the ^{1}H NMR spectrum in CD_2Cl_2. The PEt_3 complex **4b** was also characterized to have a trans configuration by the X-ray analysis.

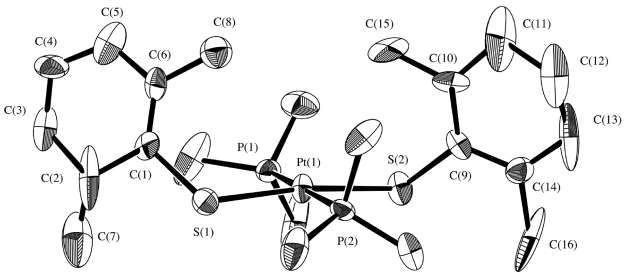
2. Molecular Structures of (2,6-Dimethylbenzenethiolato)platinum(II) Compounds. The molecular structures of (2,6-dimethylbenzenethiolato)(neopentyl)platinum(II) (**3c**) and bis(2,6-dimethylbenzenethiolato)platinum(II) (**4a**−**f**) are shown in Figure 1, and selected metric data for the bis(arenethiolato) complexes **4** are given in Table 1. These complexes adopt a slightly distorted square-planar geometry containing 2,6-dimethylbenzenethiolato ligand(s). These structure determinations confirm the stereochemical conclusions drawn from the NMR spectra.

As expected, the PMe_3 complex **4a** shows a trans configuration in a square-planar geometry. Consistently, the angles S(1)−Pt(1)−S(2) (173.01(5)°) and P(1)−Pt(1)−P(2) (175.53(5)°) are slightly smaller than but close to 180°. Two thiolato groups are on the same side on the square plane.

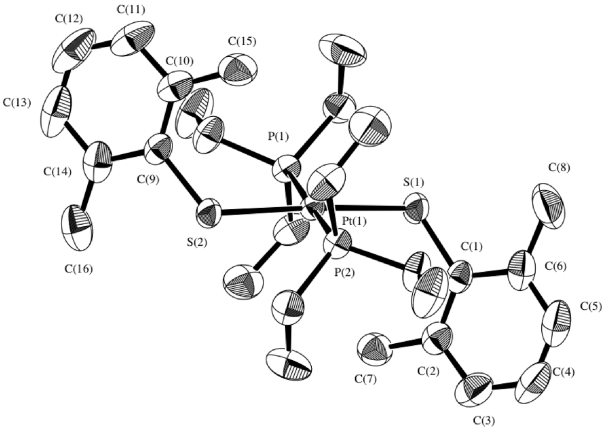
dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122



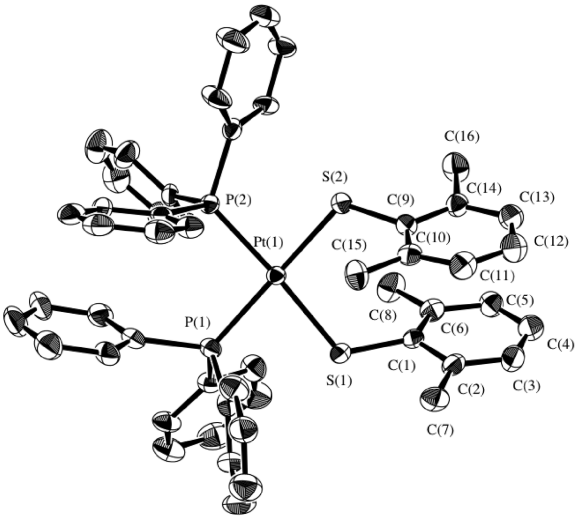
3c



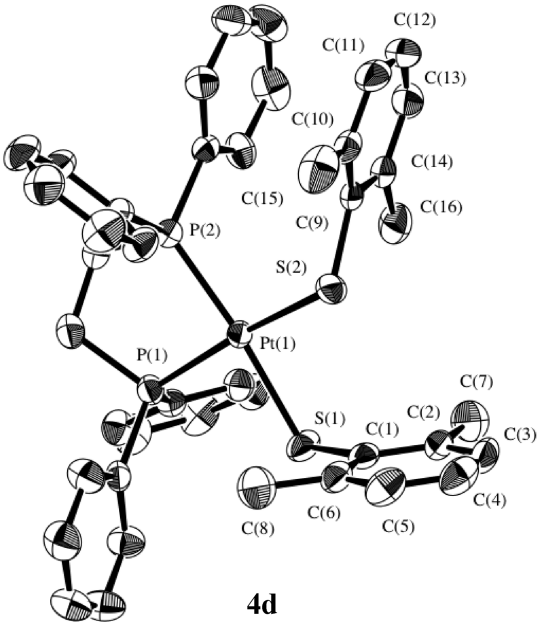
4a



4b



4c



4d

Figure 1. Continued

dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122

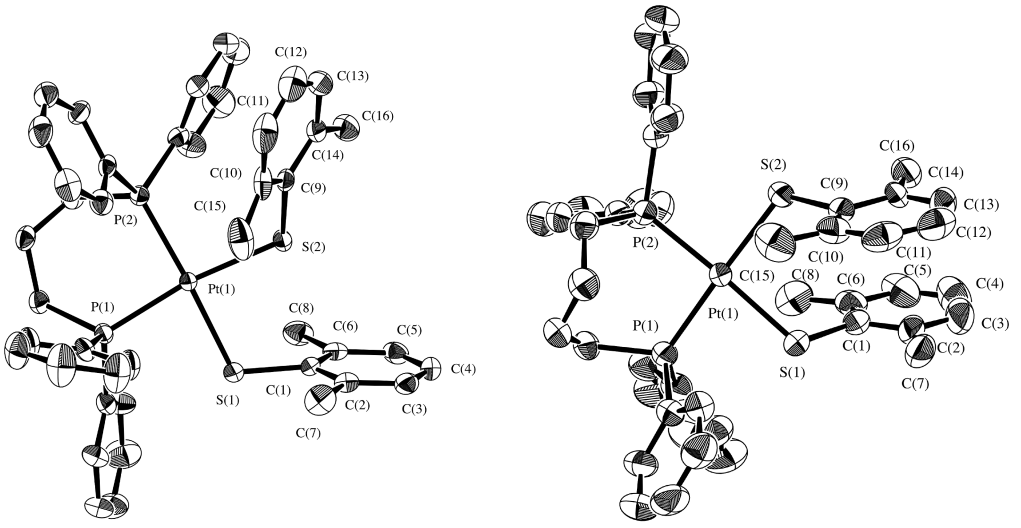


Figure 1. Molecular structures of *cis*-Pt(CH_2CMe_3)($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (**3c**), *trans*-Pt($SC_6H_3Me_2$-κ^1S)$_2$(PMe_3)$_2$ (**4a**), *trans*-Pt($SC_6H_3Me_2$-κ^1S)$_2$(PEt_3)$_2$ (**4b**), *cis*-Pt($SC_6H_3Me_2$-κ^1S)$_2$(PPh_3)$_2$ (**4c**), *cis*-Pt($SC_6H_3Me_2$-κ^1S)$_2$(dppe) (**4d**), *cis*-Pt($SC_6H_3Me_2$-κ^1S)$_2$(dppp) (**4e**), and *cis*-Pt($SC_6H_3Me_2$-κ^1S)(dppb) (**4f**) with selected numbering schemes. All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 4a−f

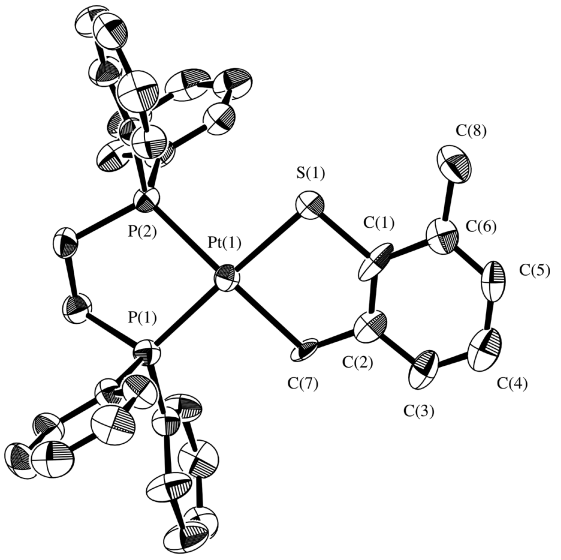
	4a	4b	4c	4d	4e	4f
Pt(1)−S(1)	2.3331(14)	2.3593(10)	2.366(2)	2.3627(11)	2.3601(12)	2.3756(17)
Pt(1)−S(2)	2.3531(13)	2.3493(9)	2.341(2)	2.3636(9)	2.3675(10)	2.3541(16)
Pt(1)−P(1)	2.3171(16)	2.3347(10)	2.319(2)	2.2493(11)	2.2772(8)	2.2884(16)
Pt(1)−P(2)	2.3082(15)	2.3360(10)	2.286(2)	2.2626(11)	2.2688(11)	2.2854(15)
S(1)−C(1)	1.770(7)	1.764(4)	1.771(9)	1.762(4)	1.773(4)	1.777(7)
S(2)−C(9)	1.779(5)	1.771(4)	1.751(8)	1.768(3)	1.773(4)	1.777(7)
S(1)−Pt(1)−S(2)	173.01(5)	176.67(4)	98.55(8)	89.98(3)	87.69(3)	94.57(6)
P(1)−Pt(1)−P(2)	175.53(5)	178.29(3)	95.16(9)	85.64(3)	92.07(3)	93.42(6)
Pt(1)−S(1)−C(1)	115.06(18)	114.66(13)	118.4(3)	110.09(13)	112.66(14)	112.8(2)
Pt(1)−S(2)−C(9)	116.78(17)	117.83(13)	116.6(3)	114.09(12)	113.33(13)	113.0(2)

Though the *o*-methyl groups, C(8) and C(15), seem to interact with the platinum center at first sight, the two bond distances Pt(1)−C(8) and Pt(1)−C(15) are actually 3.523(6) and 3.534(2) Å, respectively, suggesting no strong interaction among these atoms. Similarly, the PEt_3 complex **4b** also has the trans configuration. In contrast to **4a**, the two arenethiolato fragments in **4b** are arranged one above the other with respect to the square plane. This may be due to the crystal packing, where the difference in cavities around the Pt(II) center formed by the alkylphosphines results in a conformational change for the arenethiolato ligand during formation of the crystals. The PPh_3 complex **4c** shows a cis configuration with a parallel alignment of two 2,6-dimethylbenzenethiolato groups. Although they are actually not fully overlapping but twisted with respect to each other in the front and back directions, the distances between these aromatic rings (C(1)−C(9) = 3.162(13) Å, C(2)−C(10) = 3.433(15) Å, C(3)−C(12) = 3.441(15) Å, C(4)−C(13) = 3.457(16) Å, C(5)−C(14) = 3.497(15) Å, C(6)−C(14) = 3.393(13) Å) suggest partial stacking by the $\pi-\pi$ interaction.[18] A similar parallel alignment is observed for the dppb complex **4f**. The bite angles P(1)−Pt(1)−P(2) in **4c**−**f** taken from the molecular structure analysis vary from 85.64(3)° (**4d**, dppe) to 92.07(3)° (**4e**, dppp), 93.42(6)° (**4f**, dppb), and 95.16(9)° (**4c**, PPh_3),[19] and the S(1)−Pt(1)−S(2) angles are in the order of 87.69(3)° (**4e**, dppp), 89.98(3)° (**4d**, dppe), 94.57(6)° (**4f**, dppb), and 98.55(8)° (**4c**, PPh_3).

The structure of (2,6-dimethylbenzenethiolato)(neopentyl) platinum(II) (**3c**) is shown to have the cis configuration. The P(1)−Pt(1)−P(2) and S(1)−Pt(1)−C(1) angles are 98.63(4) and 90.29(10)°, and no significant contact around the arenethiolato and neopentyl groups and Pt are observed (see the Supporting Information).

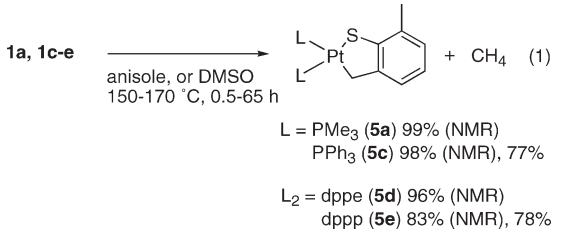
3. Internal sp^3 Carbon−Hydrogen Bond Cleavage Reaction in Four-Coordinate Platinum(II) Compounds. *3.1. Internal sp^3 C−H Bond Cleavage Reaction from (Alkyl)(2,6-dimethylbenzenethiolato)platinum(II) Compounds.* The products obtained by heating the (methyl)(2,6-dimethylbenzenethiolato) platinum(II) compounds are shown in eq 1, and all examples produce thiaplatinacycles **5** in high yields. For example, heating of *cis*-PtMe($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (**1c**) at 150 °C in

dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122



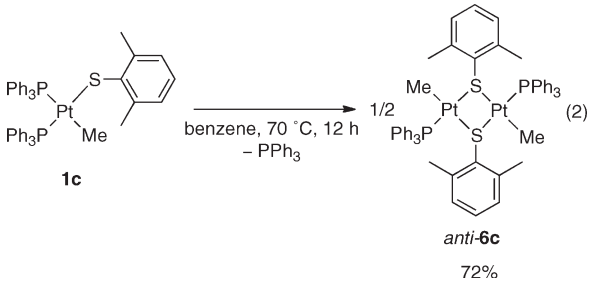
5d

Figure 2. Molecular structure of Pt[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C]-(dppe) (**5d**) with selected numbering schemes. All hydrogen atoms and the incorporated toluene molecule are omitted for clarity. Ellipsoids represent 50% probability.



anisole for 1.5 h produced thiaplatinacycle **5c** in 98% yield based on the internal standard by NMR. Qualitative analysis of the gas phase by GLC indicated the formation of methane.

Thiaplatinacycle **5c** was characterized by NMR and elemental analysis. In the $^{31}P\{^1H\}$ NMR in CD_2Cl_2, two doublets are observed at δ 22.1 ($^2J_{P-P}$ = 19 Hz, $^1J_{P-Pt}$ = 1881 Hz) and δ 24.8 ($^2J_{P-P}$ = 18 Hz, $^1J_{P-Pt}$ = 3250 Hz). This observation shows that two phosphorus ligands resonate inequivalently, suggesting a cis configuration. The small J_{P-Pt} value for the resonance at δ 22.1 reflects a strong trans influence, suggesting that this phosphorus is trans to the carbon atom in the thiaplatinacycle.[14] In the ^1H NMR spectrum, a 3H singlet at δ 2.09, 1H doublets at δ 6.49 and δ 6.62, and a 1H triplet at δ 6.54 are assignable to the one of the *o*-methyl groups, two inequivalent meta aromatic protons, and the para proton in an aromatic ring adjacent to the thiaplatinacycle, respectively. The most significant feature in this ^1H NMR

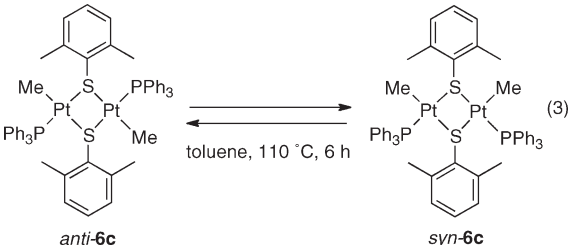


spectrum is a 2H triplet resonance at δ 2.85 with Pt satellites. This signal clearly indicates formation of the Pt−CH_2 bond, whose methylene protons couple to the cis and trans phosphorus ligands with coincidentally the same coupling constant. These NMR data unambiguously support the structure of **5c**.[20]

The formation of **5c** from **1c** evolves methane as a side product. This is also attractive for the methane activation from the viewpoint of microscopic reversibility. To determine whether the evolution of methane is a reversible process, *cis*-Pt(CD_3)-($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (**1c**-d_3: up to 99 atom % D) has been prepared. By heating of **1c**-d_3 at 110 °C in toluene-d_8 for 13 h, **5c** was formed in 91% yield and neither the methylene nor the *o*-methyl groups in **5c** contained deuterium atoms at all. Evolution of methane-d_3 was observed by ^1H NMR (δ 0.14 (sept. $^2J_{H-D}$ = 1.8 Hz)) and GLC.[21] This fact suggests irreversible formation of methane under these conditions.

For the thiaplatinacycle **5d** having a dppe ligand, the molecular structure has been revealed by an X-ray structure analysis, and the ORTEP diagram is depicted in Figure 2.

The bond distance Pt(1)−C(7) in **5d** is in the range of 2.119(6) Å, consistent with a typical Pt−C σ−bond. The bond distance Pt(1)−S(1) (2.2994(16) Å) and the bond angle Pt(1)−S(1)−C(1) (98.1(3)°) in **5d** are shorter and narrower than those in **4d** (2.3627(11) Å and 110.09(13)°), which would dispel the distortion in the formation of five-membered thiaplatinacycles.



Similar treatment of the the (ethyl)(2,6-dimethylbenzenethiolato)platinum(II) species **2c** in anisole at 130 °C for 4 h produced the thiaplatinacycle **5c** in 78% yield, during which time ethane (43%) and ethylene (45%) were evolved. Heating of the (2,6-dimethylbenzenethiolato)(neopentyl)platinum(II) complex **3c** at 150 °C for 0.2 h quantitatively produced **5c** with evolution of neopentane.

3.2. Formation of Dimeric μ-Sulfido Compounds from (alkyl)(2,6-dimethylbenzenethiolato)platinum(II). During the course of the reaction of **1c** to give **5c**, a new dimeric compound of (methyl)(2,6-dimethylbenzenethiolato)platinum(II) was observed with liberation of PPh_3. Upon heating of **1c** at 70 °C for 12 h in a nonpolar benzene solvent, *anti*-**6c** deposited, which was recrystallized from cold THF in 72% yield (eq 2).

anti-**6c** was characterized by NMR. In the $^{31}P\{^1H\}$ NMR in toluene-d_8, a singlet was observed at δ 27.8 ($^1J_{P-Pt}$ = 3861 Hz). In ^1H NMR, a 6H doublet was observed at δ 0.13 ($^3J_{H-P}$ = 4.5 Hz) with a broad Pt satellite ($^2J_{H-Pt}$ = 76 Hz). This signal is assignable to the two equivalent Pt−*Me* groups. A singlet at δ 3.13 (s, 12H) and multiplets at δ 6.6−6.7 (6H) are assigned as two equivalent thiolato groups. Aromatic protons assignable to PPh_3 are observed at δ 6.8 (18H) and δ 7.5 (12H). The most significant feature in this NMR is that all *o*-methyl groups are equivalent. According to the molecular symmetry deduced from the NMR spectrum, this compound is consistent with the dimeric species *anti*-**6c** having C_{2h} symmetry.[22,23]

Upon heating of *anti*-**6c** at 110 °C in toluene, new resonances assignable to *syn*-**6c** were observed by NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8, a singlet peak was observed at δ 25.3 ($^1J_{P-Pt}$ = 3918 Hz). In the ^1H NMR spectrum, a new 6H doublet at δ 0.16 ($^3J_{H-P}$ = 4.8 Hz) was observed, which was assigned to the two magnetically equivalent Pt−*Me* groups.[24] On the other hand, two 6H singlets were observed at δ 2.48 and δ 3.55, assignable to the *o*-methyl groups in the 2,6-dimethylbenzenethiolato groups. These spectroscopic features, two arenethiolato groups being inequivalent while two Pt−*Me* and PPh_3 ligands are equivalent, suggest the C_{2v} symmetry that is consistent with the structure of *syn*-**6c**. We therefore assigned this compound as *syn*-**6c**. The final ratio *anti*-**6c**/*syn*-**6c** was estimated to be 2/1 under these conditions based on ^1H NMR (eq 3).

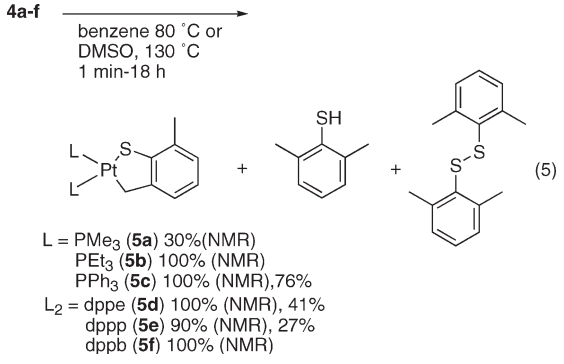
In toluene-d_8 solution, we found that **1c**, *anti*-**6c**, *syn*-**6c**, and PPh_3 constituted an equilibrium in the range of 80−100 °C (eq 4).

$$2\mathbf{1c} \overset{K_1}{\rightleftarrows} [\textit{anti}\text{-}\mathbf{6c} \rightleftarrows \textit{syn}\text{-}\mathbf{6c}] + 2PPh_3 \quad (4)$$

From the van't Hoff plot based on the variable-temperature NMR spectra in toluene-d_8, thermodynamic parameters between **1c** and total amounts of *anti*- and *syn*-**6c** were estimated: K_1 (373 K) = 0.542 M, ΔH = 74.0 ± 3.5 kJ mol^{-1}, ΔG(298 K) = 15 ± 6 kJ mol^{-1}, and ΔS = 197 ± 10 J mol^{-1} K^{-1}. The positive ΔG value shows the forward reaction of this equilibrium (K_1) to be slightly endothermic, and the large positive ΔS value is consistent with the liberation of PPh_3. As noted in section 3.3, a mixture of *anti*- and *syn*-**6c** was observed during the formation of the thiaplatinacycle **5c** from **1c**. Moreover, treatment of the isolated *anti*-**6c** with PPh_3 at 110 °C in toluene produced the thiaplatinacycle **5c**. These facts support the dimeric compound **6c** as being either an intermediate or a resting state in the formation of **5c**.

The (ethyl)(2,6-dimethylbenzenethiolato)platinum(II) complex **2c** also gave a 1/4 mixture of *anti*- and *syn*-[PtEt($SC_6H_3Me_2$-2,6-μ_2S)(PPh_3)]$_2$ (**7c**) in 73% yield by heating of **2c** in benzene at 70 °C. Similar treatment of the (2,6-dimethylbenzenethiolato)(neopentyl)platinum(II) complex **3c** produced a white precipitate with liberation of 1 equiv of PPh_3. Although this white precipitate was thought to be a similar dimeric compound, the low solubility of the precipitate toward most of the solvents prevented a detailed characterization.

3.3. Bis(2,6-dimethylbenzenethiolato)platinum(II) Compounds. The *cis*-bis(2,6-dimethylbenzenethiolato)platinum(II) compounds **4a**−**f** also produced thiaplatinacyclic complexes **5a**−**f** by an sp^3 C−H bond cleavage reaction. As a typical example, heating of a DMSO solution of **4c** at 130 °C yielded the thiaplatinacycle Pt[$SC_6H_3(CH_2$-2)(Me-6)-κ^2S,C](PPh_3)$_2$ (**5c**) in 76% yield in 1 min (eq 5).



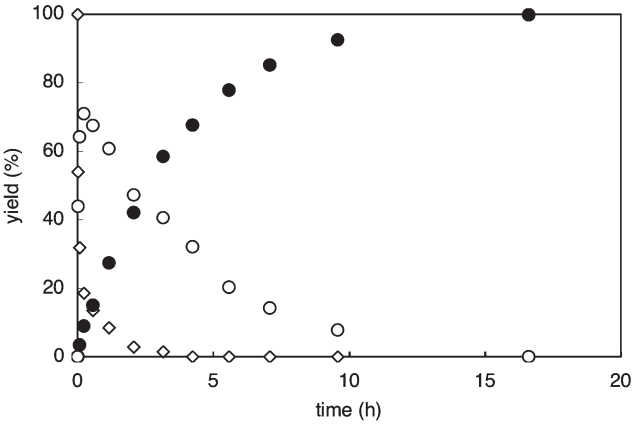


Figure 3. Time-course curves of **1c** giving **5c** at 110 °C in DMF: (◇) **1c**; (○) total amount of *syn*- and *anti*-**6c** based on Pt atom; (●) **5c**. Initial concentration of **1c**: 0.011 M.

Table 2. Effect of Solvent on the Formation Rate Constant of 5c from 1c and 4c[a]

entry	compd	solvent	ε^{27}	temp (°C)	$10^5 k_{obs}$ (s^{-1})
1	**1c**	toluene	2.38	110	2.1 ± 0.2
2	**1c**	anisole	4.33	110	2.81 ± 0.22
3	**1c**	chlorobenzene	5.62	110	3.47 ± 0.53
4	**1c**	DMF	36.7	110	7.4 ± 0.1
5[b]	**1c**	DMF	36.7	110	9.4 ± 0.4
6	**4c**	benzene	2.28	50	16 ± 1
7	**4c**	toluene	2.38	50	15 ± 1
8	**4c**	chloroform	4.70	50	24 ± 1
9	**4c**	THF	7.32	50	36 ± 2
10	**4c**	acetone	20.7	50	13 ± 1
11	**4c**	DMF	36.7	50	17 ± 1
12[c]	**4c**	DMF	36.7	50	17 ± 1

[a] Initial concentration of **1c** or **4c**: 0.0080−0.010 M. [b] Galvinoxyl (0.3 mM) added. [c] Galvinoxyl (0.08 M) added.

In this reaction, 2,6-dimethylbenzenethiol and the corresponding disulfide were observed as side products. The disulfide was confirmed by comparison with an authentic sample, and we believe the disulfide to be formed by spontaneous oxidation of 2,6-dimethylbenzenethiol by DMSO used as the solvent, because sulfoxide is reported to oxidize arenethiols to the corresponding disulfide.[25] In this reaction the starting compound **4c** was completely consumed and the product **5c** was quantitatively yielded. In the meantime, no intermediate or resting state species was observed by NMR spectroscopy. The straightforward formation of **5c** from **4c** shows a sharp contrast to the system starting from **1c**, where **6c** is observed during the course of the reaction.

In order to confirm the reversibility for the formation of the thiaplatinacycle from the bis(arenethiolato) complex, the thiaplatinacycle **5c** was treated with 11 equiv of 2,6-dimethylbenzenethiol in DMF at 50 °C. This treatment gave a complex mixture but the bis(arenethiolato) compound **4c** was undetected.[26] Thus, compound **5c** must be produced from **4c** by an irreversible C−H bond cleavage process.

It is worth noting that while the (methyl)(thiolato)platinum(II) complex **1c** does not yield **5c** at 50 °C in DMF for 5 h, the bis(thiolato)platinum(II) complex **4c** quantitatively

dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122

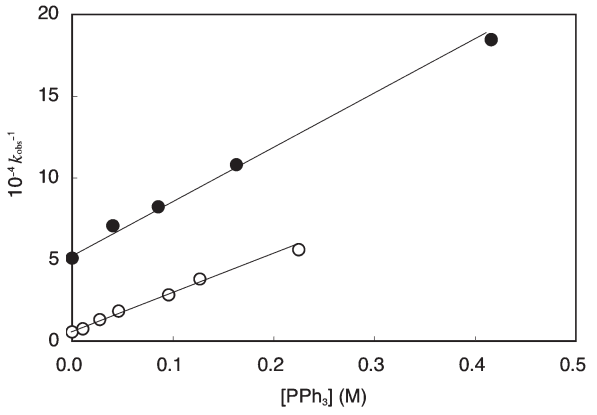


Figure 4. Effect of added PPh_3 on the observed rate constant k_{obs} for **1c** and **4c**: (●) **1c**; (○) **4c**. Conditions: solvent toluene-d_8 for **1c** and DMF for **4c**, temperature 110 °C for **1c** and 50 °C for **4c**, initial [**1c**] = 0.013−0.0170 M, [**4c**] = 0.00846−0.00953 M, [PPh_3] = 0.00−0.416 M.

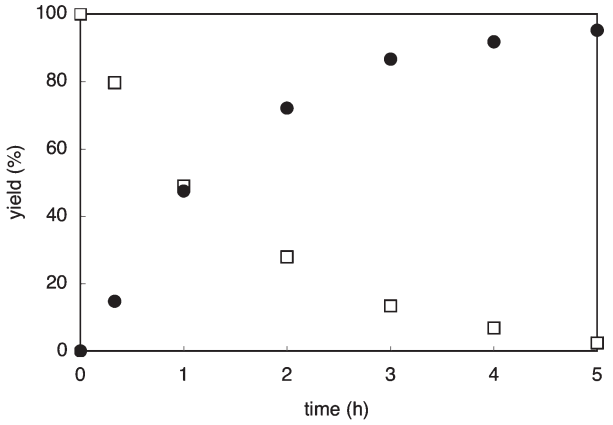


Figure 5. Time-yield curves of **4c**, giving **5c** at 50 °C in DMF: (□) **4c**; (●) **5c**. Initial concentration of **4c**: 0.011 M.

gives **5c** under the same conditions. This sharp contrast in reactivity shows the high activity of the thiolato group toward the sp^3 C−H bond cleavage reaction.

4. Kinetic Studies for the Formation of Thiaplatinacycles. *4.1. (Methyl)(2,6-dimethylbenzenethiolato)platinum(II) Complex* ***1***. The isolated (methyl)(2,6-dimethylbenzenethiolato) platinum(II) compound **1c** was heated at 110 °C in DMF, and the reaction profile was followed by $^{31}P\{^1H\}$ NMR spectroscopy. The time-course curves are shown in Figure 3. Complex **1c** immediately decreased with increase of a mixture of *syn*- and *anti*-**6c**, which finally was converted into the thiaplatinacycle **5c** quantitatively (Figure 3).

The starting compound **1c** and *syn*- and *anti*-**6c** decreased with time at 110 °C in DMF, and the reaction was first-order in the concentration of the sum total of [**1c**] and 2[**6c**]. The observed rate constant for the total consumption of **1c** and **6c** was estimated as $(7.4 \pm 0.3) \times 10^{-5}\ s^{-1}$ in DMF at 110 °C, which is identical with the formation rate constant of thiaplatinacycle **5c** ($(7.4 \pm 0.1) \times 10^{-5}\ s^{-1}$) (Table 2, entry 4). This is consistent with our assumption where **1c** rapidly constitutes rapid pre-equilibrium between **1c** and **6c** by releasing a PPh_3 ligand under the conditions from which thiaplatinacycle **5c** is slowly produced. When this reaction was performed at 70 °C in DMF, the thiaplatinacycle **5c** was not formed at all, and the reaction system reached an equilibrium between **1c** (50%) and **6c** (50%/Pt) in 5.5 h. Thus, the following sp^3 C−H bond cleavage process giving **5c** must be the rate-determining step.

The formation of thiaplatinacycle **5c** from **1c** was significantly retarded by the addition of PPh_3. The dependence of k_{obs}^{-1} (the reciprocal observed formation rate constant of **5c**) on the concentration of added PPh_3 is shown in Figure 4. These data indicate that the reaction is inverse first order in phosphine concentration. This order in added PPh_3 ligand demonstrates that reversible dissociation of PPh_3 occurs before the rate-determining step.

On the basis of these kinetic data, the experimental rate equation can be expressed as shown in eq 6

$$-\frac{d[Pt]}{dt} = k_{obs}[Pt] = \frac{[Pt]}{a[PPh_3] + b} \qquad (6)$$

where [Pt] = [**1c**] + 2[**6c**], $a = (32 \pm 1) \times 10^4\ s\ M^{-1}$, and $b = (5.5 \pm 0.2) \times 10^3$ s at 110 °C.

As shown in Table 2, the formation rate constant of **5c** does not show significant dependence on the dielectric constants of the solvents, excluding a polarized transition state in the rate-determining step (entries 1−4). Some alkylplatinum(II) complexes are reported to involve a radical process in C−H[6,7] and C−X[28] bond cleavage reactions. In the present case, the rate constant is not affected significantly by the addition of galvinoxyl (entry 5). Although the slight increase of the observed rate constant by the addition of galvinoxyl is not clear so far, this result excludes a free radical chain process. Although it is difficult to completely exclude any radical processes from these experiments, we believe a radical process to be less probable.

The transformation of (methyl)(2,6-dimethylbenzenethiolato)platinum(II) complexes with a bidentate ligand to the thiaplatinacycle **5** proceeded much more slowly and required high temperature. At 170 °C in DMSO, the dppp complex **1e** produced the thiaruthenacycle **5e** in 43% yield after 1.8 h and in 83% yield after 8 h. Under the same conditions, the depe complex **1d** produced **5d** in 10% yield after 4.5 h and 98% yield after 65 h. Among (methyl)(2,6-dimethylbenzenethiolato)platinum(II) complexes **1**, the relative formation rate was estimated to be in the order **1c** (PPh_3) > **1e** (dppp) > **1d** (dppe). Thus, the formation rate seems to reflect the order of bite angle of these tertiary phosphines. Such relations between the reactivities of the complexes and the bite angles of the phosphines employed have been widely studied. For example, bidentate ligands with wide bite angles are known to accelerate the reductive elimination from the square-planar compounds[29] on the basis of the Thorpe−Ingold effect.[30] On the other hand, wide bite angles are also reported to induce flexibility and facile half-dissociation of the ligand.[31] In fact, the reaction of the dppp complex **1e** to give **5e** was retarded by the addition of dppp ligand. For example, after 1.8 h at 170 °C, the yields of **5e** were as follows: 43% (0 equiv of dppp), 11% (0.1 equiv of dppp), and 0% (3 equiv of dppp). Thus, the facile half-dissociation property of the phosphorus ligand probably accelerates the reaction.

4.2. Bis(2,6-dimethylbenzenethiolato)platinum(II) Complex. Bis(2,6-dimethylbenzenethiolato)platinum(II) complex **4** also produced thiaplatinacycle **5**, and notably, this reaction proceeded under conditions much milder than those starting from **1**. For example, the reaction of **4c** to give **5c** proceeded in DMF even at 50 °C. In contrast to the case for **1c**, only **4c** and **5c** are the observed platinum species during the course of the reaction (Figure 5), and the reaction was first order in the concentration of **4c**.

dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122

The observed rate constant k_{obs} for the consumption of **4c** at 50 °C was estimated as $(1.8 \pm 0.1) \times 10^{-4}$ s^{-1}, which is comparable to the formation rate constant of **5c** ($(1.7 \pm 0.1) \times 10^{-4}$ s^{-1}) (Table 2, entry 11). This reaction was not retarded by the addition of a radical scavenger (Table 2, entry 12).

The formation of **5c** from **4c** is also retarded significantly by the addition of PPh_3. In the presence of an excess amount of PPh_3, the reaction obeyed first-order kinetics in the concentration of **4c** and the reciprocal observed rate constant was proportional to the concentration of added PPh_3 with an intercept, suggesting prior reversible dissociation of PPh_3 in the formation of **5c** (Figure 4). According to these kinetic experiments, the experimental rate for the conversion of **4c** into **5c** is expressed as shown in eq 7.

$$-\frac{d[\mathbf{4c}]}{dt} = k_{obs}[\mathbf{4c}] = \frac{[\mathbf{4c}]}{c[PPh_3] + d} \quad (7)$$

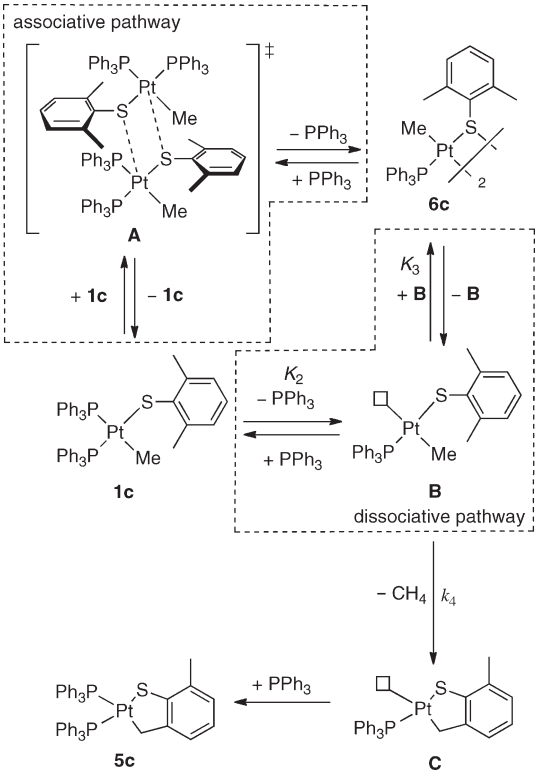
where $c = (23 \pm 1) \times 10^4$ s M^{-1} and $d = (6.7 \pm 0.9) \times 10^{-1}$ s at 50 °C.

The time-course curves for the other bis(2,6-dimethylbenzenethiolato)platinum(II) complexes **4a**,**b**,**d**−**f** showed complex reaction profiles. Heating of the PMe_3 complex **4a** at 110 °C in DMF also produced the thiaplatinacycle **5a**, but the time-course curves monitored by NMR showed an induction period of 1.5 h. Compound **4a** finally produced **5a** in 39% yield for 30 h. Meantime, the starting compound **4a** also produced an unknown product, which may be assigned to the cis analogue of **4a**, and the total conversion of **4a** was estimated to be 66%. Further heating of this system at 110 °C for an additional 22 h did not change the composition. Similar treatment of the PEt_3 complex **4b** at 110 °C in DMF also showed an induction period of 20 min, and **4b** finally produced the thiaplatinacycle **5b** in 73% yield after 20 h with 97% conversion of **4b**. The time-yield curves for the dppe complex **5d** and the dppp complex **5e** starting from **4d** and **4e** showed sigmoid curves at 110 °C in DMF, and their final yields were 73% (260 h) and 90% (14 h), respectively. In contrast to these dithiolato complexes, the time-yield curve of the dppb complex **4f** to give **5f** at 110 °C in DMF showed an almost linear decrease of **4f** with increase of **5f**, and the reaction was complete within 3 h to give a quantitative amount of **5f**. Because of the complex nature of these reaction profiles, we abandoned detailed kinetic analyses for them.

5. Possible Mechanism for the Formation of Thiaplatinacycle. *5.1. Formation Pathway of Thiaplatinacycle from (methyl)(2,6-dimethylbenzenethiolato)platinum(II)* ***1c***. For the (methyl)(2,6-dimethylbenzenethiolato)platinum(II) complex **1c**, the present thermodynamic and kinetic studies described in section 4.1 are consistent with the pathway shown in Scheme 3. This process can be accounted for by the prerequisite rapid equilibrium among **1c** and a mixture of *syn*- and *anti*-**6c**. Although the dimer **6c** is produced by either an associative (through **A**) or dissociative (through **B**) pathway, the associative pathway can be ruled out because the formation rate of **6c** is first order in the concentration of **1c**. In this reaction the methyl group may induce facile liberation of the PPh_3 ligand because of the great trans effect.[32]

At relatively low temperature (80−100 °C) in toluene, a closed equilibrium system between **1c** and **6c** was constituted, as described in section 3.2. In this equilibrium the 14-electron species **B** must be involved, from which the C−H bond cleavage reaction occurs to give **5c** as the rate-determining step. Thus, the equilibrium constant K_1 ($K_1 = [\mathbf{6c}]/([\mathbf{1c}]^2[PPh_3]^2)$) can be

Scheme 3



divided into the two equilibria K_2 ($K_2 = [\mathbf{B}][PPh_3]/[\mathbf{1c}]$) and K_3 ($K_3 = [\mathbf{6c}]/[\mathbf{B}]^2$). The total concentrations of the monophosphine reactants $[PtP_1]$ can be expressed as shown in eq 8.

$$[PtP_1] = \frac{K_2[\mathbf{1c}]}{[PPh_3]} \quad (8)$$

where $[PtP_1] = [\mathbf{B}] + 2[\mathbf{6c}]$.

By assuming an equilibrium between **B** and **6c** much faster than the following C−H bond activation step k_4 and instant formation of **5c** from **C**, the formation rate of **5c** can be defined as proportional to $[PtP_1]$ regardless of the equilibrium constant K_3 (eq 9).

$$\frac{d[\mathbf{5c}]}{dt} = k_4[PtP_1] \quad (9)$$

On the other hand, the total concentration of the reactive Pt species is expressed as [Pt] ($[Pt] = [\mathbf{1c}] + [PtP_1]$). By transformation of eqs 8 and 9, the rate for the formation of **5c** can be expressed by the term [Pt], as shown in eq 10.

$$-\frac{d[Pt]}{dt} = \frac{d[\mathbf{5c}]}{dt} = \frac{[Pt]}{(k_4K_2)^{-1}[PPh_3] + k_4^{-1}} \quad (10)$$

where $[Pt] = [\mathbf{1c}] + [PtP_1]$.

Equation 10 is consistent with the present experimental rate equation (eq 6) because the concentration of [**B**] is very small. The rate constant for the sp^3 C−H bond cleavage reaction k_4 is estimated to be $(1.8 \pm 0.1) \times 10^{-4}$ s^{-1} and the equilibrium constant K_2 to be $(1.7 \pm 0.2) \times 10^{-2}$ M at 110 °C in toluene for **1c**.

In the reaction of the (ethyl)(2,6-dimethylbenzenethiolato)platinum(II) complex **2c** to give the thiaplatinacycle **5c**, we observed evolution of ethane and ethylene (section 3.1).

dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122

Scheme 4

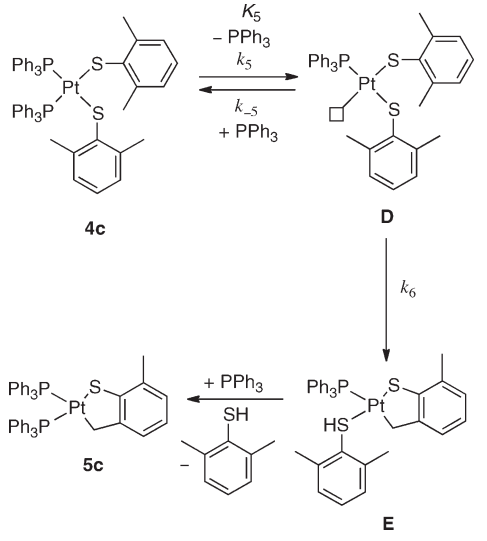
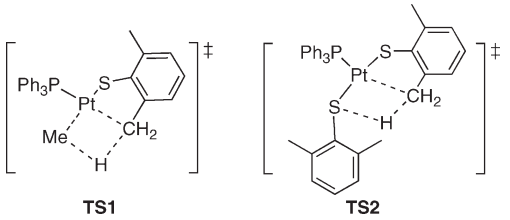


Chart 1



Since facile β-hydride elimination was reported from the three-coordinate species, the C−H bond cleavage reaction in the *o*-methyl groups would compete with β-hydride elimination of the ethyl group. Thus, the formation of ethylene would support prior dissociation of PPh_3 for the C−H bond cleavage reaction.[33]

5.2. Formation Pathway of Thiaplatinacycle from Bis(2,6-dimethylbenzenethiolato)platinum(II) ***4c***. Although no observable intermediate (or the resting state) has been detected during the course of the reaction, the mechanistic features for **4c** are basically similar to those for **1c**: first-order kinetics in the concentration of **4c**, reciprocal first-order kinetics in the concentration of PPh_3, no significant solvent effect on the rate constant, and no retardation by the addition of a radical scavenger. The present results also support the prior dissociation of PPh_3 for the formation of thiaplatinacycle **5c**, and the possible pathway is depicted in Scheme 4.

In this mechanism, we can assume that the equilibrium K_5 lies far to the **4c** side. The sp^3 C−H bond cleavage reaction in **D** occurs to give **E**, from which **5c** is eventually produced by quick displacement of the arenethiol ligand by PPh_3. The rate-determining step is either the dissociation of PPh_3 from **4c** to give **D** (k_5) or the sp^3 C−H bond cleavage reaction from **D** to **E** (k_6). In the case of phosphine dissociation as the rate-determining step, we can apply a steady-state approximation to the concentration of **D**, and the rate equation is derived as shown in eq 11.

$$-\frac{d[\mathbf{4c}]}{dt} = \frac{d[\mathbf{5c}]}{dt} = \frac{[\mathbf{4c}]}{(k_5k_6/k_{-5})^{-1}[PPh_3] + k_5^{-1}} \qquad (11)$$

Alternatively, eq 12 would be derived if we assume the C−H bond activation process to be the rate-determining step.

$$-\frac{d[Pt]}{dt} = \frac{d[\mathbf{5c}]}{dt} = \frac{[Pt]}{(k_6K_5)^{-1}[PPh_3] + k_6^{-1}} \qquad (12)$$

where $[Pt] = [\mathbf{4c}] + [\mathbf{D}]$.

If we apply an assumption for the rate-determining step to be the phosphine dissociation (k_5), the intermediate **D** must immediately convert into **5c**, and k_6 would be greater than $k_{-5}[PPh_3]$. However, in this assumption (eq 11), the experimental result showed a very modest k_6/k_{-5} value: $(2.9 \pm 0.5) \times 10^{-6}$ M. Since the present experiments obeyed first-order kinetics even in the presence of 0.225 M of PPh_3, the $k_6/(k_{-5}[PPh_3])$ value was estimated to be around 10^{-5} under these conditions. This is inconsistent with the large $k_6/(k_{-5}[PPh_3])$ assumption. Thus, we believe the sp^3 C−H bond cleavage reaction is the rate-determining step. With agreement, the rate equation is given by eq 12, and K_5 ($(2.9 \pm 0.5) \times 10^{-6}$ M) and k_6 (1.5 ± 0.2 s^{-1}) are estimated from the experimental data at 50 °C. Despite the the fact that the kinetic experiments of **4c** were measured under conditions (at 50 °C) much milder than those for **1c** (at 110 °C), the estimated rate for the sp^3 C−H bond activation of **4c** (k_6) was no less than 10^4-fold faster than the corresponding rate for **1c** (k_4). The equilibrium concerning phosphine dissociation (K_5) is much smaller than K_2 ($(1.7 \pm 0.2) \times 10^{-2}$ M at 110 °C). This is probably because the thiolato ligand has a much weaker trans effect than the methyl group.[34] In addition to this fact, formation of the dimeric species **6** would stabilize the monophosphine spices. However, no dimeric intermediate was observed in the case of **4c**, probably due to steric repulsion.

5.3. Mechanistic Insights for the sp^3 C−H Bond Cleavage Reaction from ***1c*** *and* ***4c***. In the present article, we have employed the methyl and arenethiolato groups as hydrogen acceptors in the C−H bond cleavage reaction of the *o*-methyl group. Of particular interest is the great acceleration of the C−H bond cleavage step by the arenethiolato acceptor. Although the large difference in the reaction rates makes direct comparison between these species difficult, the arenethiolato acceptor induces a great leap forward effect (*more than 10^4-fold*) on the rate of the sp^3 C−H bond activation step. Such a dramatic change might arise from the mechanistic difference in transition states. In both cases, the experimental results support sp^3 C−H bond activation from the three-coordinate species by a concerted mechanism.

One of the possible transition states for **1c** concerning release of methane is the four-center mechanism (**TS1** in Chart 1). Although the successive oxidative addition/reductive elimination sequence cannot be ruled out, this may be a higher energy process because a five-coordinate Pt(IV) intermediate is involved. Therefore, we believe **TS1** is the most probable transition state for the present C−H bond activation process.

For the arenethiolato complex **4c**, the arenethiol is considered to remain coordinated after the C−H bond cleavage step (intermediate **E** in Scheme 3), as shown for the five-coordinate bis(2,6-dimethylbenzenethiolato)ruthenium(II) compound.[10b] Thus, the transition state for the sp^3 C−H bond cleavage reaction is most consistent with **TS2**, as depicted in Chart 1. Although further investigations are required, **TS2** may show an electrophilic substitution mechanism[35,36] because a hydrogen atom in the *o*-methyl group finally becomes a proton in the arenethiolato moiety. Therefore, we believe that a lone pair at the sulfur atom plays a key role in the significant acceleration of the sp^3 C−H bond activation process.

dx.doi.org/10.1021/om200345h |*Organometallics* 2011, 30, 5110–5122

EXPERIMENTAL SECTION

General Procedure. All procedures described in this paper were carried out under a 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 and dichloromethane were dried over Drierite and distilled under nitrogen. DMF was dried over molecular sieves 4A and then was distilled under reduced pressure. 2,6-Dimethylbenzenethiol was purchased from Aldrich and was stored and used under a nitrogen atmosphere. PMe_3 and PEt_3 were prepared by the reaction of $P(OPh)_3$ with the corresponding Grignard reagent and were stored under a N_2 atmosphere.[37] Other tertiary phosphines were purchased from commercial suppliers. The potassium salt of 2,6-dimethylbenzenethiol was prepared by the treatment of 2,6-dimethylbenzenethiol with KOH in methanol. The diiodoplatinum(II) complexes PtI_2L_2 were prepared by the treatment of $PtI_2(\eta^4\text{-}1,5\text{-COD})$[38] with the corresponding tertiary phosphine ligands. $PtMe_2L_2$ complexes were prepared by the reaction of $PtMe_2(\eta^4\text{-}1,5\text{-COD})$ with the corresponding phosphine ligands.

^1H and $^{31}P\{^1H\}$ NMR spectra were measured on a JEOL LA300 or a JEOL ECX400P spectrometer. The IR spectra were measured on a JASCO FT/IR410 or FT/IR4100 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer. Compounds without elemental analysis were characterized by spectroscopic methods. For thermodynamic and kinetic analyses, reliability intervals indicate 95% probability.

***trans*-PtMe($SC_6H_3Me_2$-2,6-κ^1S)(PMe_3)$_2$ (1a).** To a suspension of $PtMe_2(PMe_3)_2$ (0.320 g, 0.850 mmol) in benzene (15 mL) was added 2,6-dimethylbenzenethiol (124 μL, 0.935 mmol) by a hypodermic syringe. After the mixture was stirred for 34 h at room temperature, all volatile material was removed under reduced pressure. The resulting pale yellow solid was recrystallized from cold dichloromethane/hexane at −30 °C to give pale yellow microcrystals of **1a** in 77% yield (0.330 mg, 0.661 mmol). ^1H NMR (300 MHz, C_6D_6, room temperature): δ 0.52 (t, $^3J_{H-P}$ = 7.2 Hz, $^2J_{H-Pt}$ = 29 Hz, 3H, Pt*Me*), 1.03 (vt, $^2J_{H-P} = {}^4J_{H-P}$ = 3.0 Hz, 18H, P*Me*$_3$), 3.01 (s, 6H, $SC_6H_3Me_2$), 6.94 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, $SC_6H_3Me_2$), 7.13 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, $SC_6H_3Me_2$). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6, room temperature): δ −16.7 (s, $^1J_{P-Pt}$ = 2779 Hz). Anal. Calcd for $C_{15}H_{30}P_2PtS$: C, 36.07; H, 6.05. Found: C, 36.17; H, 6.47.

The following (methyl)(2,6-dimethylbenzenethiolato)platinum(II) compounds were prepared by a similar method.

***cis*-PtMe($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (1c).** Greenish yellow crystals, 52% yield. ^1H NMR (300 MHz, CD_2Cl_2, room temperature): δ −0.42 (t, $^3J_{H-P}$ = 6.3 Hz, $^2J_{H-Pt}$ = 30 Hz, 3H, Pt*Me*), 2.44 (s, 6H, $SC_6H_3Me_2$), 6.81 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, $SC_6H_3Me_2$), 6.97 (d, $^3J_{H-H}$ = 7.2 Hz, $SC_6H_3Me_2$), 7.1−7.6 (m, 30H, P*Ph*$_3$). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, room temperature): δ 24.6 (d, $^2J_{P-P}$ = 7.3 Hz, $^1J_{P-Pt}$ = 3310 Hz, 1P, *P*Ph$_3$ trans to S), 29.5 (d, $^2J_{P-P}$ = 7.3 Hz, $^1J_{P-Pt}$ = 1968 Hz, 1P, *P*Ph$_3$ trans to C). Anal. Calcd for $C_{45}H_{42}P_2PtS$: C, 61.99; H, 4.86. Found: C, 61.62; H, 4.87.

***cis*-Pt(CD_3)($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (1c-*d*$_3$).** CD_3Li (0.59 M) was prepared by the reaction of lithium (246 mg, 35.6 mmol) with CD_3I (975 μL, 15.3 mmol) in Et_2O at room temperature for 2 h. **1c-*d*$_3$** was prepared by the reaction of $Pt(CD_3)_2(PPh_3)_2$ (385 mg, 0.509 mmol), which was derived from PtI_2(1,5-COD) with CD_3Li followed by the addition of PPh_3 with 2,6-dimethylbenzenethiol (74 μL, 0.56 mmol) in benzene at room temperature for 1 day in 42% yield (186 mg, 0.213 mmol). No incorporation of H in the CD_3 group in **1c-*d*$_3$** was observed during the course of the reaction.

***cis*-PtMe($SC_6H_3Me_2$-2,6-κ^1S)(dppe) (1d).** Colorless crystals, 50% yield. ^1H NMR (300 MHz, DMSO-*d*$_6$, room temperature): δ −0.42 (t, $^3J_{H-P}$ = 6.0 Hz, $^2J_{H-Pt}$ = 60 Hz, 3H, Pt*Me*), 2.2−2.5 (m, 4H, PC_2H_4P), 2.36 (s, 6H, $SC_6H_3Me_2$), 6.75 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, $SC_6H_3Me_2$), 6.94 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, $SC_6H_3Me_2$), 7.4−7.7 (m, 16H, P*Ph*$_2$), 7.8−8.1 (m, 4H, P*Ph*$_2$). $^{31}P\{^1H\}$ NMR (122 MHz, DMSO-*d*$_6$, room temperature): δ 45.0 (s, $^1J_{P-Pt}$ = 1813 Hz, 1P, *P*Ph$_2$ trans to C), 46.0 (d, $^1J_{P-Pt}$ = 3157 Hz, 1P, *P*Ph$_2$ trans to S). Anal. Calcd for $C_{35}H_{36}P_2PtS$: C, 56.37; H, 4.87. Found: C, 55.66; H, 4.82.

***cis*-PtMe($SC_6H_3Me_2$-2,6-κ^1S)(dppp) (1e).** Colorless crystals, 80% yield. ^1H NMR (300 MHz, DMSO-*d*$_6$, room temperature): δ −0.69 (t, $^3J_{H-P}$ = 6.3 Hz, $^2J_{H-Pt}$ = 61 Hz, 3H, Pt*Me*), 1.5−1.9 (m, 2H, $PCH_2CH_2CH_2P$), 2.27 (s, 6H, $SC_6H_3Me_2$), 2.6−2.7 (m, 4H, $PCH_2CH_2CH_2P$), 6.70 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, $SC_6H_3Me_2$), 6.87 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, $SC_6H_3Me_2$), 7.3−7.6 (m, 16H, P*Ph*$_2$), 7.7−8.9 (m, 4H, P*Ph*$_2$). $^{31}P\{^1H\}$ NMR (122 MHz, DMSO-*d*$_6$, room temperature): δ 5.23 (d, $^2J_{P-P}$ = 26 Hz, $^1J_{P-Pt}$ = 1813 Hz, 1P, *P*Ph$_2$ trans to C), 46.0 (d, $^2J_{P-P}$ = 26 Hz, $^1J_{P-Pt}$ = 3157 Hz, 1P, *P*Ph$_2$ trans to S). Anal. Calcd for $C_{36}H_{38}P_2PtS$: C, 56.91; H, 5.04. Found: C, 57.25; H, 5.88.

***cis*-PtEt($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (2c).** Pale yellow prisms, 58% yield. ^1H NMR (400 MHz, CD_2Cl_2, room temperature): δ 0.24−0.41 (m, 3H, CH_2CH_3), 0.43−0.66 (m, 2H, CH_2CH_3), 2.52 (s, 6H, $SC_6H_3Me_2$), 6.84 (t, $^3J_{H-H}$ = 7.3 Hz, 1H $SC_6H_3Me_2$), 6.96 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, $SC_6H_3Me_2$), 709−7.60 (m, 30H, P*Ph*$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ 26.87 (d, $^2J_{P-P}$ = 14 Hz, $^1J_{P-Pt}$ = 3568 Hz, 1P, *P*Ph$_3$ trans to Et), 27.95 (d, $^2J_{H-H}$ = 14 Hz, $^1J_{P-Pt}$ = 1645 Hz, 1P, *P*Ph$_3$ trans to S). Anal. Calcd for $C_{46}H_{44}P_2PtS\cdot 0.5CD_2Cl_2$: C, 57.39; H, 4.74. Found: C, 57.09; H, 4.66.

***cis*-Pt(CH_2CMe_3)($SC_6H_3Me_2$-2,6-κ^1S)(PPh_3)$_2$ (3c).** Pale yellow prisms, 41% yield. ^1H NMR (400 MHz, CD_2Cl_2, room temperature): δ 0.57 (s, 9H, CH_2CMe_3), 0.98 (dd, $^3J_{H-P}$ = 9.3, 5.3 Hz, $^2J_{H-Pt}$ = 71 Hz, 2H, CH_2CMe_3), 2.54 (s, 6H, $SC_6H_3Me_2$), 6.77 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, $SC_6H_3Me_2$), 6.90 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, $SC_6H_3Me_2$), 7.10−7.75 (m, 30H, P*Ph*$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ 20.61 (d, $^2J_{P-P}$ = 16.3 Hz, $^1J_{P-Pt}$ = 1368 Hz, 1P, *P*Ph$_3$ trans to S), 23.74 (d, $^2J_{P-P}$ = 16.3 Hz, $^1J_{P-Pt}$ = 3706 Hz, 1P, trans to C). Anal. Calcd for $C_{49}H_{50}P_2PtS\cdot 0.7$(toluene): C, 65.93; H, 5.63. Found: C, 64.68; H, 5.69.

***trans*-Pt($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PMe_3)$_2$ (4a).** *Method A.* To a mixture of $PtI_2(PMe_3)_2$ (0.2161 g, 0.3995 mmol) and potassium 2,6-dimethylbenzenethiolate (0.1796 g, 1.019 mmol) was added THF (8 mL). The resulting suspension was stirred for 2 days at room temperature. After the reaction, all volatile material was removed under reduced pressure to give a yellow solid, which was extracted with benzene. The extract was evaporated, and the resulting yellow solid was recrystallized from cold dichloromethane/hexane at −30 °C to give yellow prisms of **4a** in 54% yield (0.1348 g, 0.2400 mmol). ^1H NMR (300 MHz, CD_2Cl_2, room temperature): δ 1.24 (vt, $^2J_{H-P} = {}^4J_{H-P}$ = 3.6 Hz, $^3J_{H-Pt}$ = 24.9 Hz, 18H, P*Me*$_3$), 2.64 (s, 12H, $SC_6H_3Me_2$), 6.82 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, $SC_6H_3Me_2$), 6.95 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, $SC_6H_3Me_2$). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, room temperature): δ −18.21 (s, $^1J_{P-Pt}$ = 2622 Hz). Anal. Calcd. for $C_{22}H_{36}P_2PtS_2$: C, 42.50; H, 5.84. Found: C, 42.58; H, 5.91.

Method B. Treatment of $PtMe_2(PMe_3)_2$ (0.397 g, 0.105 mmol) with 2,6-dimethylbenzenethiol (343 μL, 2.58 mmol) at room temperature for 2 days followed by removal of all volatile material produced a yellow solid. Recrystallization from cold dichloromethane/hexane at −30 °C gave yellow prisms of **1a** in 79% yield (0.514 g, 0.827 mmol). Anal. Calcd for $C_{22}H_{36}P_2PtS_2$: C, 42.50; H, 5.84. Found: C, 42.63; H, 5.72.

The following bis(2,6-dimethylbenzenethiolato)platinum(II) compounds were prepared by a similar method.

***trans*-Pt($SC_6H_3Me_2$-2,6-κ^1S)$_2$(PEt_3)$_2$ (4b).** Pale yellow needles, 56% yield. ^1H NMR (300 MHz, C_6D_6, room temperature): δ 0.80 (dt, $^3J_{H-H}$ = 7.7 Hz, $^3J_{H-P}$ = 15.4 Hz, 18H, PCH_2Me), 1.6−1.8 (m, 12H, PCH_2Me), 2.67 (s, 12H, $SC_6H_3Me_2$), 6.9−7.2 (m, 6H, $SC_6H_3Me_2$). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6, room temperature): δ 6.83 (s, $^1J_{P-Pt}$ = 2809 Hz).

Anal. Calcd for $C_{28}H_{48}P_2PtS_2$: C, 47.65; H, 6.85. Found: C, 48.53; H, 6.84.

***cis*-Pt(SC$_6$H$_3$Me$_2$-2,6-κ^1*S*)$_2$(PPh$_3$)$_2$ (4c).** Light orange prisms, 50% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 2.17 (s, 12H, $SC_6H_3Me_2$), 6.58−6.65 (m, 6H, $SC_6H_3Me_2$), 7.13−7.53 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ 18.52 (s, $^1J_{P-Pt}$ = 3043 Hz). Anal. Calcd. for $C_{52}H_{48}P_2PtS_2$: C, 62.83; H, 4.87. Found: C, 63.73; H, 4.83.

***cis*-Pt(SC$_6$H$_3$Me$_2$-2,6-κ^1*S*)$_2$(dppe) (4d).** Pale yellow needles, 53% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 2.14 (s, 12H, $SC_6H_3Me_2$), 2.0−2.3 (m, 4H, PC_2H_4P), 6.53−6.61 (m, 6H, $SC_6H_3Me_2$), 7.4−7.7 (m, 20H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ 44.78 (s, $^1J_{P-Pt}$ = 2908 Hz). Anal. Calcd for $C_{42}H_{42}P_2PtS_2$: C, 58.12; H, 4.88. Found: C, 57.56; H, 5.08.

***cis*-Pt(SC$_6$H$_3$Me$_2$-2,6-κ^1*S*)$_2$(dppp) (4e).** Pale yellow prisms, 74% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 2.09 (s, 12H, $SC_6H_3Me_2$), 1.92−2.12 (m, 2H, $PCH_2CH_2CH_2P$), 2.44−2.61 (m, 4H, $PCH_2CH_2CH_2P$), 6.57 (s, 6H, $SC_6H_3Me_2$), 7.3−7.7 (m, 20H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ −2.64 (s, $^1J_{P-Pt}$ = 2908 Hz). Anal. Calcd for $C_{43}H_{44}P_2PtS_2$: C, 58.56; H, 5.03. Found: C, 58.05; H, 5.32.

***cis*-Pt(SC$_6$H$_3$Me$_2$-2,6-κ^1*S*)$_2$(dppb) (4f).** Pale yellow needles, 35% yield. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature): δ 1.75 (br s, 4H, PC_4H_8P), 1.85 (s, 12H, $SC_6H_3Me_2$), 2.70 (br s, 4H, PC_4H_8P), 6.48−6.55 (m, 6H, $SC_6H_3Me_2$), 7.3−7.7 (m, 20H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, room temperature): δ 12.78 (s, $^1J_{P-Pt}$ = 2832 Hz).

Pt[SC$_6$H$_3$(CH$_2$-2)(Me-6)-κ^2*S,C*](PMe$_3$)$_2$ (5a). In an NMR tube were placed complex **4a** (0.0089 g, 0.016 mmol) and triphenylmethane as an internal standard (0.0127 g, 0.0520 mmol), DMSO-d_6 (600 μL) was added, and then the reaction system was heated at 130 °C for 10 min to give **5a** (30% yield). ^{1}H NMR (300 MHz, DMSO-d_6, room temperature): δ 1.5−1.6 (m, 18H, PMe_3), 2.17 (s, 3H, SC_6H_3(2-CH_2)(6-*Me*)), 3.00 (t, $^3J_{H-P}$ = 6.6 Hz, $^2J_{H-Pt}$ = 54.4 Hz, 2H, SC_6H_3(2-CH_2)(6-Me)), 6.5−6.7 (m, 3H, SC_6H_3(2-CH_2)(6-Me)). $^{31}P\{^1H\}$ NMR (122 MHz, DMSO-d_6, room temperature): δ −25.4 (d, $^2J_{P-P}$ = 22 Hz, $^1J_{P-Pt}$ = 1770 Hz, 1P, PMe_3 trans to C), −24.21 (d, $^2J_{P-P}$ = 22 Hz, $^1J_{P-Pt}$ = 3017 Hz, 1P, PMe_3 trans to S).

Pt[SC$_6$H$_3$(CH$_2$-2)(Me-6)-κ^2*S,C*](PEt$_3$)$_2$ (5b). Similar to the case for **5a**, the formation of **5b** was confirmed by NMR experiments (100% yield). ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.63−0.98 (m, 18H, PCH_2Me), 1.33−1.79 (m, 12H, PCH_2Me), 2.84 (s, 3H, SC_6H_3(2-CH_2)(6-*Me*)), 3.43 (t, $^3J_{H-P}$ = 6.6 Hz, $^2J_{H-Pt}$ = 55.0 Hz, 2H, SC_6H_3(2-CH_2)(6-Me)), 7.04−7.27 (m, 3H, SC_6H_3(2-CH_2)(6-Me)). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, room temperature): δ 6.80 (d, $^2J_{P-P}$ = 20 Hz, $^1J_{P-Pt}$ = 1771 Hz, 1P, PMe_3 trans to C), 8.48 (d, $^2J_{P-P}$ = 20 Hz, $^1J_{P-Pt}$ = 3054 Hz, 1P, PMe_2 trans to S).

Pt[SC$_6$H$_3$(CH$_2$-2)(Me-6)-κ^2*S,C*](PPh$_3$)$_2$ (5c). Complex **4c** (0.149 g, 1.72 mmol) was heated in DMSO (5 mL) for 2 h at 180 °C. After removal of all volatile material under reduced pressure, the resulting solid was washed with hexane and Et_2O. The resulting solid was recrystallized from cold dichloromethane/hexane at −30 °C to give colorless crystals of **5c** in 77% yield (0.114 g, 0.132 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 2.09 (s, 3H, SC_6H_3(2-CH_2)(6-*Me*)), 2.85 (t, $^3J_{H-P}$ = 7.2 Hz, $^2J_{H-Pt}$ = 56.3 Hz, 2H, SC_6H_3(2-CH_2)(6-Me)), 6.49 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, SC_6H_3(2-CH_2)-(6-Me)), 6.54 (t, $^3J_{H-H}$ = 7.1 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 6.62 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 7.15−7.47 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ 22.1 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{P-Pt}$ = 1881 Hz, 1P), 24.8 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{P-Pt}$ = 3250 Hz, 1P). ^{1}H NMR (300 MHz, DMSO-d_6, room temperature): δ 1.93 (s, 3H, SC_6H_3(2-CH_2)(6-*Me*)), 2.70 (t, $^3J_{H-P}$ = 6.9 Hz, $^2J_{H-Pt}$ = 57.0 Hz, 2H, SC_6H_3(2-CH_2)(6-Me)), 6.35 (d, $^3J_{H-P}$ = 3.6 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 6.47 (t, $^3J_{H-P}$ = 3.6 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 6.58 (d, $^3J_{H-P}$ = 3.6 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 7.2−7.4 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR (122 MHz, DMSO-d_6, room temperature): δ 22.2 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{P-Pt}$ = 1893 Hz, 1P, PMe_3 trans to C), 24.7 (d, $^2J_{P-P}$ = 19 Hz, $^1J_{P-Pt}$ = 3234 Hz, 1P, PMe_2 trans to S). Anal. Calcd for $C_{45}H_{40}P_2PtS$: C, 57.45; H, 4.29. Found: C,57.96; H, 4.75.

Pt[SC$_6$H$_3$(CH$_2$-2)(Me-6)-κ^2*S,C*](dppe) (5d). Similar to the case for **5a**, the formation of **5d** was confirmed by NMR studies (100%) and X-ray analysis. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 2.24−2.51 (m, 4H, PC_2H_4P), 2.82 (dd, $^3J_{H-P}$ = 7.6, 4.8 Hz, $^2J_{H-Pt}$ = 53.8 Hz, 2H, SC_6H_3(2-CH_2)(6-Me)), 6.64 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 6.72 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, SC_6H_3(2-CH_2)-(6-Me)), 6.83 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, SC_6H_3(2-CH_2)(6-Me)), 7.12−7.26 (m, 4H, PPh_2), 7.43−7.90 (m, 16H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ 45.97 (d, $^2J_{P-P}$ = 5 Hz, $^1J_{P-Pt}$ = 3069 Hz, 1P, PMe_3 trans to S), 46.17 (d, $^2J_{P-P}$ = 5 Hz, $^1J_{P-Pt}$ = 1810 Hz, 1P, PMe_2 trans to C).

Pt[SC$_6$H$_3$(CH$_2$-2)(Me-6)-κ^2*S,C*](dppp) (5e). Colorless crystals, 78% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 1.89−2.06 (m, 2H, $PCH_2CH_2CH_2P$), 2.17 (s, 3H, SC_6H_3(2-CH_2)(6-*Me*)), 2.50−2.60 (m, 2H, SC_6H_3(2-CH_2)(6-Me)), 2.64−2.80 (m, 4H, $PCH_2CH_2CH_2P$), 6.53−6.63 (m, 3H, SC_6H_3(2-CH_2)(6-Me)), 7.33−7.74 (m, 20H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, room temperature): δ −2.19 (d, $^2J_{P-P}$ = 30 Hz, $^1J_{P-Pt}$ = 1740 Hz, 1P, PMe_3 trans to C), 2.96 (d, $^2J_{P-P}$ = 30 Hz, $^1J_{P-Pt}$ = 3026 Hz, 1P, PMe_2 trans to S).

Pt[SC$_6$H$_3$(CH$_2$-2)(Me-6)-κ^2*S,C*](dppb) (5f). Similar to the case for **5a**, the formation of **5f** was confirmed by NMR experiments. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature): δ 1.57−1.70 (m, 4H, PC_4H_8P), 1.98 (s, 3H, SC_6H_3(2-CH_2)(6-*Me*)), 2.5 (obscured by the undeuterated DMSO in DMSO-d_6, SC_6H_3(2-CH_2)(6-Me)) 2.6 (br s, 2H, PC_4H_8P), 2.8 (br s, 2H, PC_4H_8P), 6.38−6.56 (m, 3H, SC_6H_3(2-CH_2)(6-Me)), 7.4−7.7 (m, 20H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, room temperature): δ 12.63 (d, $^2J_{P-P}$ = 22 Hz, $^1J_{P-Pt}$ = 1822 Hz, 1P, PMe_3 trans to C), 20.37 (d, $^2J_{P-P}$ = 22 Hz, $^1J_{P-Pt}$ = 3144 Hz, 1P, PMe_2 trans to S).

***anti*-[PtMe(SC$_6$H$_3$Me$_2$-2,6-κ*S*)(PPh$_3$)]$_2$ (*anti*-6c).** Complex **1c** (0.273 g, 0.313 mmol) was heated in benzene (20 mL) at 70 °C. After removal of all volatile material, the resulting colorless powder was recrystallized from cold dichloromethane/hexane at −30 °C to give a white powder of pure *anti*-**6c** in 72%/Pt yield (0.138 mg, 0.113 mmol). ^{1}H NMR (300 MHz, toluene-d_8, 20 °C): δ 0.13 (d, $^3J_{H-P}$ = 4.5 Hz, $^2J_{H-Pt}$ = 76 Hz, 6H, Pt*Me*), 3.13 (s, 12H, $SC_6H_3Me_2$), 6.6−6.7 (m, 6H, $SC_6H_3Me_2$), 6.8 (m, 18H, PPh_3), 7.5 (m, 12H, PPh_3). $^{31}P\{^1H\}$ NMR (122 MHz, toluene-d_8, 20 °C): δ 27.8 (s, $^1J_{P-Pt}$ = 3861 Hz, 1P, PPh_3).

***syn*-[PtMe(SC$_6$H$_3$Me$_2$-2,6-κ*S*)(PPh$_3$)]$_2$ (*syn*-6c).** Heating of a toluene-d_8 solution of *anti*-**6c** at 110 °C for 6 h produced a 2/1 *anti*-**6c**/*syn*-**6c** mixture. *syn*-**6c**: ^{1}H NMR (300 MHz, toluene-d_8, 20 °C) δ 0.16 (d, $^3J_{H-P}$ = 4.8 Hz, $^2J_{H-Pt}$ coupling value was obscured because of the adjacent *anti*-**6c** resonances, 6H, Pt*Me*), 2.48 (s, 6H, $SC_6H_3Me_2$), 3.55 (s, 6H, $SC_6H_3Me_2$), 6.6−6.7 (m, 6H, $SC_6H_3Me_2$), 6.9−7.0 (m, 18H, PPh_3), 7.5 (m, 12H, PPh_3); $^{31}P\{^1H\}$ NMR (122 MHz, toluene-d_8, 20 °C) δ 25.3 (s, $^1J_{P-Pt}$ = 3918 Hz, 1P, PPh_3).

***anti*-[PtEt(SC$_6$H$_3$Me$_2$-2,6-κ*S*)(PPh$_3$)]$_2$ (*anti*-7c).** Heating of a benzene solution (5 mL) of **2c** (108.2 mg, 0.1221 mmol) at 70 °C for 15 min produced a white precipitate. After removal of the solution, the resulting powder was washed with hexane and dried under reduced pressure to give a 1/4 *anti*-**7c**/*syn*-**7c** mixture. Yield: 73% (55.6 mg, 0.0446 mmol). *anti*-**7c**: ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ 0.05−0.22 (m, 6H, CH_2Me), 0.23−0.28 (m, 4H, CH_2Me), 2.75 (s, 12H, $SC_6H_3Me_2$), 6.75 (s, 6H, $SC_6H_3Me_2$), 7.49−7.67 (m, 30H, PPh_3); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, room temperature): δ 28.06 (s).

***syn*-[PtEt(SC$_6$H$_3$Me$_2$-2,6-κS)(PPh$_3$)]$_2$ (*syn*-7c).** ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.06−0.22 (m, 6H, CH$_2$*Me*), 2.00 (s, 6H, SC$_6$H$_3$*Me*$_2$), 3.24 (s, 6H, SC$_6$H$_3$*Me*$_2$), 6.41 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, SC$_6$*H*$_3$Me$_2$), 6.55 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, SC$_6$*H*$_3$Me$_2$), 6.99 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, SC$_6$*H*$_3$Me$_2$), 7.09 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, SC$_6$*H*$_3$Me$_2$), 7.49−7.67 (m, 30H, P*Ph*$_3$). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, room temperature): δ 27.42 (s).

[Pt(CH$_2$CMe$_3$)(SC$_6$H$_3$Me$_2$-2,6-κS)(PPh$_3$)]$_2$. A DMF solution (5 mL) of **3c** (96.2 mg, 0.104 mmol) at room temperature for 10 min produced a white precipitate. After removal of the solution, the resulting powder was washed with benzene and hexane and dried under reduced pressure to give a white precipitate. This precipitate has low solubility in most organic solvents, but it slightly dissolved in DMSO and was assigned as [Pt(CH$_2$CMe$_3$)(SC$_6$H$_3$Me$_2$-2,6-κS)(PPh$_3$)]$_2$. Yield: 70% (48.5 mg, 0.0364 mmol). ^{1}H NMR (400 MHz, DMSO-d_6, room temperature): δ 0.90 (s, 18H, CH$_2$C*Me*$_3$), 2.54 (s, 12H, SC$_6$H$_3$*Me*$_2$), 2.61 (d, $^3J_{H-P}$ = 5.5 Hz, 4H, C*H*$_2$CMe$_3$), 6.33 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, SC$_6$*H*$_3$Me$_2$), 6.53 (t, $^3J_{H-H}$ = 7.3 Hz, 2H, SC$_6$*H*$_3$Me$_2$), 6.88 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, SC$_6$*H*$_3$Me$_2$), 7.49−7.67 (m, 30H, P*Ph*$_3$). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, room temperature): δ 28.10 (s, $^1J_{P-Pt}$ = 3327 Hz).

Preparation of 5c from 1c-d_3. Compound **1c**-d_3 was heated at 110 °C in toluene-d_8 for 13 h gave **5c** in 91% yield. No incorporation of D in **5c** was observed. Formation of CD$_3$H was observed by ^{1}H NMR at δ 0.140 (sept, $^2J_{H-D}$ = 1.8 Hz, CD$_3$*H*).

Preparation of 5c from 2c. Compound **2c** (26.8 mg, 0.0303 mmol) was placed in a sample tube, into which anisole (2.00 mL) was added by a hypodermic syringe. After heating at 130 °C for 4.3 h, ethylene (0.0135 mmol, 45%) and ethane (0.0131 mmol, 43%) were evolved (GLC, methane as an internal standard). Formation of **5c** was checked by the ^{31}P{^{1}H} NMR spectrum by use of a flame-sealed capillary involving C$_6$D$_6$ (**5c**, 78.4% yield).

Equilibrium among 1c, *syn*-6c, and *anti*-6c. Compound **1c** (9.3 mg, 0.012 mmol) and PPh$_3$ (6.6 mg, 0.025 mmol) were heated in the range 80−100 °C in toluene-d_8 in the presence of triphenylmethane (12.8 mg, 0.0524 mmol) as an internal standard.

Effect of Added PPh$_3$ on the Observed Rate Constant from 4c. Compound **4c** (5.5 mg, 0.0055 mmol) with 1.1 equiv of PPh$_3$ (1.6 mg, 0.0061 mmol), DMF (600 μL), and a flame-sealed capillary of P(O)(C$_6$H$_4$OMe-4)$_3$/DMSO-d_6 as an external standard were added into an NMR tube. The rate was estimated from the ^{31}P{^{1}H} NMR spectrum. Similarly, independent experiments with 3.0, 5.0, 10, 15, and 25 equiv of PPh$_3$ were performed. The rate constant from **1c** was also measured similarly.

Effect of Free Radical Scavenger on the Formation Rate of 5c from 1c. Compound **1c** (6.4 mg, 0.0067 mmol), DMF (600 μL), and a flame-sealed capillary of P(O)(C$_6$H$_4$OMe-4)$_3$/DMSO-d_6 as an external standard were added into an NMR tube. Then, a DMF solution of garvinoxyl (0.0400 M, 5.00 μL) was added into the NMR tube. The solution was heated at 110 °C, and the rate was estimated from the ^{31}P{^{1}H} NMR spectrum.

Effect of Free Radical Scavenger on the Formation Rate of 5c from 4c. Similar to the reaction of **1c** with garvinoxyl, compound **4c** (5.7 mg, 0.0057 mmol), DMF (600 μL), and a DMF solution of garvinoxyl (2.4 mg, 0.0057 mmol) were added into the NMR tube. The solution was heated at 50 °C, and the rate was estimated from the ^{31}P{^{1}H} NMR spectrum.

Effect of Added Potassium 2,6-Dimethylbenzenethiolate on the Formation Rate of 5c from 4c. Compound **4c** (5.8 mg, 0.0058 mmol), DMF (600 μL), and 10 equiv of potassium 2,6-dimethylbenzenethiolate (10.5 mg, 0.0596 mmol) were added into an NMR tube, along with a flame-sealed capillary of P(O)(C$_6$H$_4$OMe-4)$_3$/DMSO-d_6 as an external standard. The solution was heated at 50 °C, and the rate was estimated from the ^{31}P{^{1}H} NMR spectrum.

Effect of Added 2,6-Dimethylbenzenethiol on the Formation Rate of 5c from 4c. Compound **4c** (5.2 mg, 0.0052 mmol), DMF (600 μL), and 9.8 equiv of 2,6-dimethylbenzenethiol (7.2 μL, 0.051 mmol) were added into an NMR tube along, with a flame-sealed capillary of P(O)(C$_6$H$_4$OMe-4)$_3$/DMSO-d_6 as an external standard. The solution was heated at 50 °C, and the formation rate was estimated from the ^{31}P{^{1}H} NMR spectrum.

Kinetic Parameters for the Formation of 5c from 1c or 4c. Similar to the above experiments, the rate was estimated by the ^{31}P{^{1}H} NMR spectrum on the basis of an external standard of P(O)(C$_6$H$_4$O-Me-4)$_3$. The rates from **1c** were measured in the range 100−125 °C. Those from **4c** were measured in the range 35−60 °C.

X-ray Crystallography. Crystallographic data were measured on a Rigaku RASA-7R Mercury II diffractometer using Mo Kα radiation with a graphite crystal monochromator. A single crystal was selected by use of a polarized microscope and mounted on a glass capillary with Paratone N oil. The crystallographic data and details associated with data collection for **3c**, **4a**−**f**, and **5d** are given in the Supporting Information. The R (R_w) values of these crystals are as follows: **3c**, 0.0358 (0.0938); **4a**, 0.0367 (0.1107); **4b**, 0.0303 (0.0884); **4c**, 0.0536 (0.1593); **4d**, 0.0284 (0.0795); **4e**, 0.0300 (0.0725); **4f**, 0.0510 (0.1569); **5d**, 0.0500 (0.1238). The data were processed using CrystalStructure (version 3.8 or 4.0) package software.[39] All non-hydrogen atoms were found by using the results of direct methods (SIR92[40] for **3c** and **4a**,**d**−**f** or SHELXL-97[41] for **5d**) or PATTY for **4c**. All non-hydrogen atoms were found on difference maps. All hydrogen atoms were located in calculated positions. The crystal of **5d** contained a toluene molecule, which was solved anisotropically. Crystallographic thermal parameters and bond distances and angles have been deposited as Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information. Tables and CIF files giving kinetic data for Figures 3−5 and X-ray crystallographic data for **3c**, **4a**−**f**, and **5d**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel and fax: +81 423 88 7044. E-mail: hrc@cc.tuat.ac.jp (M.H.); komiya@cc.tuat.ac.jp (S.K.).

■ ACKNOWLEDGMENT

We are grateful for financial support by a Grant-in-Aid for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" from the Ministry of Education, Culture, Science and Technology of Japan. We thank Ms. S. Kiyota for elemental analysis.

■ DEDICATION

†This paper is dedicated to Prof. Christian Bruneau on the occasion of his 60th birthday.

■ ABBREVIATIONS

dppe = 1,2-bis(diphenylphosphino)ethane (Ph$_2$PC$_2$H$_4$PPh$_2$); dppp = 1,3-bis(diphenylphosphino)propane (Ph$_2$PC$_3$H$_6$PPh$_2$); dppb = 1,4-bis(diphenylphosphino)butane (Ph$_2$PC$_4$H$_8$PPh$_2$); DMF = dimethylformamide (Me$_2$NCHO); COD = cyclooctadiene

REFERENCES

(1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879 and references cited therein.

(2) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180.

(3) Periana, R. A. *Adv. Chem. Ser.* **1997**, *253*, 61.

(4) For examples, see: (a) Aya, K. T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518. (b) Goldberg, K. I.; Yan, J.-Y.; Winter, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 1573. (c) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739. (d) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116. (e) Zhang, F.; Prokopchuk, E. M.; Broczkowski, M. E.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2006**, *25*, 1583. (f) Romeo, R.; D'Amico, G. *Organometallics* **2006**, *25*, 3435.

(5) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732.

(6) Miyashita, A.; Hotta, M.; Saida, Y. *J. Organomet. Chem.* **1994**, *473*, 353.

(7) Miyashita, A.; Saida, Y. *Chem. Lett.* **1994**, 2263.

(8) (a) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528. (b) Whitesides, G. M. *Pure Appl. Chem.* **1981**, *53*, 287.

(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) Hirano, M.; Sato, H.; Kurata, N.; Komine, N.; Komiya, S. *Organometallics* **2007**, *26*, 2007. (d) Hirano, M.; Izhab, I. B.; Kurata, N.; Koizumi, K.; Komine, N.; Komiya, S. *Dalton Trans.* **2009**, 3270.

(10) (a) Hirano, M.; Sakaguchi, Y.; Yajima, T.; Kurata, N.; Komine, N.; Komiya, S. *Organometallics* **2005**, *24*, 4799. (b) Hirano, M.; Togashi, S.; Ito, M.; Sakaguchi, Y.; Komine, N.; Komiya, S. *Organometallics* **2010**, *29*, 3146.

(11) Nakata, N.; Yamamoto, S.; Hashina, W.; Ishii, A. *Chem. Lett.* **2009**, *38*, 400.

(12) Formation of the related (phenoxo)platinum(II) compound *cis*-PtMe(OPh)$(PMe_3)_2$ by the reaction of *cis*-$PtMe_2(PMe_3)_2$ with phenol was documented: Osakada, K.; Kim, Y.-J.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *382*, 303.

(13) Yamamoto, A. In *Organotransition Metal Chemistry: Fundamental Concepts and Applications*; Wiley: New York, 1986; p 179.

(14) Yamashita, F.; Kuniyasu, H.; Terao, J.; Kambe, N. *Inorg. Chem.* **2006**, *45*, 1399.

(15) Keskinen, A. E.; Senoff, C. V. *J. Organomet. Chem.* **1972**, *37*, 201.

(16) Preparation of the related compound, a cis/trans mixture of $Pt(SC_6H_4Me\text{-}4\text{-}\kappa^1S)_2(PPh_3)_2$, by the oxidative addition of disulfide $(SC_6H_4Me\text{-}4)_2$ to $Pt(PPh_3)_4$ has been reported: Kuniyasu, H.; Sugoh, K.; Su, M.-S.; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669.

(17) Kuniyasu and co-workers reported no significant difference in either the chemical shifts or the $^1J_{P-Pt}$ values for *cis*- and *trans*-$Pt(SPh)_2(PPh_3)_2$.[15,16]

(18) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(19) Reported natural bite angles: dppe (85°), dppp (95°), and dppb (99°): van Haaren, R. J.; Oevering, H.; Coussens, B. B.; van Strijdonck, G. P. F.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1999**, 1237.

(20) Quite recently, similar oxaplatinacycles such as $Pt[OC_6H_4\text{-}(2\text{-}CH_2)\text{-}\kappa^2O,C](PPh_3)_2$ have been reported by the oxidative addition of 2-hydroxybenzyl sulfide via O−H and C−S bond cleavage reactions: Nakata, N.; Furukawa, N.; Toda, T.; Ishii, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 5784.

(21) The resonance of methane-d_0 was reported to appear at δ 0.14 in toluene-d_8: Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

(22) A similar dimeric (μ-thiolato)palladium(II) species, $[PdPh(SC_6H_3Me_2\text{-}2,6\text{-}\mu_2\text{-}\kappa^1S)]_2$, was reported: Mann, G.; Baranano, D.; Hartwing, J. F.; Rheingold, L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205.

(23) We assume free rotation of these C−S bonds.

(24) The J_{H-Pt} coupling constant for *cis*-**6c** was obscured because of overlapping with the signals due to *trans*-**6c**.

(25) Walles, T. J. *J. Am. Chem. Soc.* **1964**, *86*, 2018.

(26) Although treatment of **5c** with 11 equiv of 2,6-dimethylbenzenethiol in DMF at 50 °C did not give the bis(2,6-dimethylbenzenethiolato)platinum(II) complex **4c** at all, **5c** converted into unidentified species after 277 h at 50 °C with 53% conversion.

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

(28) Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218.

(29) Marcone, J. E.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 8527.

(30) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc. Trans* **1915**, *107*, 1080.

(31) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.

(32) Yamamoto, A. In *Organotransition Metal Chemistry: Fundamental Concepts and Applications*; Wiley: New York, 1986; p 199.

(33) One of the reviewers recommended checking the formation of ethylene from the ethyl complex **2c** to support the three-coordinate intermediate **B**. We are grateful to this reviewer for the suggestion.

(34) Although a direct comparison of the trans effect between thiolato and methyl groups has not been documented to the best of our knowledge, the thiolato ligand is reported to have weaker trans effect than PR_3 in refs 34a,34b and PR_3 is reported to have a weaker trans effect than the methyl group in ref 34c. Therefore, the thiolato group is considered to have a weaker trans effect than the methyl group. (a) Tu, T.; Zhou, Y.-G.; Hou, X.-L.; Dai, L.-X.; Dong, X.-C.; Yu, Y.-H.; Sun, J. *Organometallics* **2003**, *22*, 1255. (b) Kuniyasu, H.; Takekawa, K.; Yamashita, F.; Miyafuji, K.; Asano, S.; Takai, Y.; Ohtaka, A.; Tanaka, A.; Sugoh, K.; Kurosawa, H.; Kambe, N. *Organometallics* **2008**, *27*, 4788. (c) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(35) (a) Bischof, S. M.; Ess, D. H.; Meier, S. K.; Oxgaard, J.; Nielsen, R. J.; Bhalla, G.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2010**, *29*, 742. (b) Oxgaard, J.; Tenn, W. J., III; Nielsen, R. J.; Periana, R. A.; Goddard, W. A., III *Organometallics* **2007**, *26*, 1565. (c) Cundari, T. R.; Grimes, T. V.; Gunnoe, T. B. *J. Am. Chem. Soc.* **207**, *129*, 13172. (d) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (e) Davies, D. L.; Donald, S. M. A.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *125*, 13754.

(36) Recently, a computational study showing a strong dependence of the mechanism on the leaving group in the C−H bond cleavage reaction has been documented: Ess, D. H.; Gunnoe, T. B.; Cundari, T. R.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2010**, *29*, 6801.

(37) Kosolapoff, G. M.; Maier, L. In *Organic Phosphorus Compounds*; Wiley: New York, 1972; Vol. 1, p 32.

(38) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 47.

(39) *CrystalStructure (Version 3.8): Single Crystal Structure Analysis Software*; Rigaku Americas and Rigaku Corporation, 2007.

(40) Altomare, A.; Casacarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

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