Monoarylplatinum(II) Complexes with a 2-Phenylpyridyl Ligand and Coordinated Solvent, [Pt(Ar)(Phpy)(solv)] (Phpy = 2-phenylpyridyl; solv = $NCCH_3$, dmso). Preparation from $[Pt(Ar)_2(solv)_2]$, Structures, and Chemical Properties

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Diarylplatinum(II) complexes, $[Pt(Ar)_2(dmso)_2]$ (Ar = $C_6H_3Me_2$-3,5 (**1a**), $C_6H_3(CF_3)_2$-3,5 (**1b**), Ph (**1c**); dmso = dimethyl sulfoxide) and $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}_2(NCCH_3)_2]$ (**2b**), were prepared and fully characterized. Heating mixtures of 2-phenylpyridine (PhpyH) with the complexes in solution at 50 °C caused coordination of PhpyH and its cyclometalation accompanied by elimination of arene to produce monoarylplatinum(II) complexes with a solvent ligand, [Pt(Ar)(Phpy)(dmso)] (Ar = $C_6H_3Me_2$-3,5 (**3a**), $C_6H_3(CF_3)_2$-3,5 (**3b**), Ph (**3c**)) and $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}(Phpy)(NCCH_3)]$ (**4b**). The rate of the reactions decreased in the order **1a** > **1c** > **2b** > **1b**. Crystal structures of **3a**,**c** and ^1H NMR spectra of the complexes showed that the aryl ligand and phenyl group of the Phpy ligand occupied cis positions. A diarylplatinum complex with a monodentate phenylpyridyl ligand, $[Pt(C_6H_3Me_2\text{-}3,5)_2(CF_3PhpyH)(dmso)]$ (**5**), was isolated and characterized using X-ray crystallography. The neutral arylplatinum(II) complex **4b** underwent exchange of the acetonitrile ligand more easily than the cationic complex, $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}(bpy)(NCCH_3)]^+$, because of the C-bonded phenyl group of the Phpy ligand had a greater trans effect than the N-bonded pyridyl group of bpy. Oxidative addition of I_2 to **3a**,**b** and **4b** readily gave Pt(IV) dimeric complexes with bridging iodo ligands, $[(Pt(Ar)(Phpy)I)_2(\mu\text{-}I)_2]$ (Ar = $C_6H_3Me_2$-3,5 (**7a**), $C_6H_3(CF_3)_2$-3,5 (**7b**)). The dimeric structure of **7b** was confirmed using X-ray crystallography.

Introduction

Organoplatinum complexes exhibit various reactivities toward fundamental reactions such as C−H activation,[1] oxidative addition,[2] and reductive elimination,[3] depending on the valence of the metal centers and on the supporting ligands. Recently, 2-phenylpyridyl (Phpy) ligands have attracted attention because their Ir complexes show good fluorescent properties.[4] Platinum complexes with the 2-(2′-thienyl)pyridyl (thpy) ligand, Pt(thpy)(CO)(mts) (mts = methylthiosalicylate),[5] PtCl(thpy)(CO),[6] and Pt(thpy)(acac),[7] were prepared. Then their optical properties were studied. Ligands of this type perform as monoanionic bidentate ligands via coordination of nitrogen and cyclometalation of the aryl or thienyl group.

Monoarylplatinum complexes having neutral chelating ligands, such as diene and diamines and labile solvent ligand, contain a cationic metal center. These complexes reportedly show various reactivities such as insertion of unsaturated molecules into the Pt−Ar bond,[8,9] oxidative addition,[9] transmetalation of the aryl ligand,[10] and C−H activation.[11] Monoarylplatinum complexes with a solvent ligand and chelating (2-pyridyl)aryl ligand have a neutral Pt center and exhibit chemical properties different from those with diene and diamine ligands. Such neutral Pt complexes with a solvent ligand, however, have been reported only rarely.[12]

In this study, we attempted to obtain solvated diarylplatinum complexes using a coordinating solvent by direct substitution

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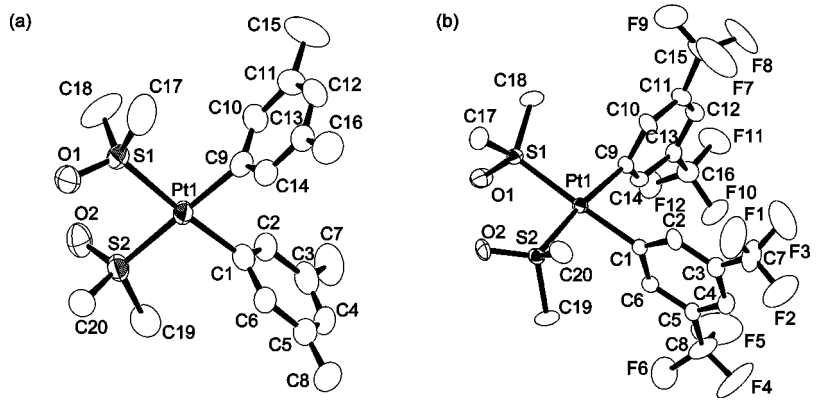
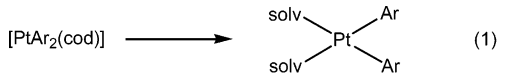


Figure 1. ORTEP drawings of (a) **1a** and (b) **1b** (50% probability).

of cod in $[PtAr_2(cod)]$ with the solvent molecules. We have therefore chosen acetonitrile as the solvent molecule and investigated it for some aryl groups. Reactivities of obtained complexes for cyclometalation with 2-phenylpyridine, which involves oxidative addition and reductive elimination, have been discussed on the basis of the nature of the coordinating solvent and aryl group. In addition, exchange reactions of the coordinating acetonitrile and oxidative addition of I_2 to cyclometalated complexes have been studied.

Results and Discussion

Preparation and Characterization of Solvated Diarylplatinum(II) Complexes. The preparation of $[PtPh_2(dmso)_2]$ was reported by Lanza et al.[13] Analogous reactions of dmso with $PtAr_2(cod)$ produce $[PtAr_2(dmso)_2]$ (Ar = $C_6H_3Me_2$-3,5 (**1a**), $C_6H_3(CF_3)_2$-3,5 (**1b**)) as shown in eq 1. The complex $[PtPh_2(dmso)_2]$ (**1c**) was also used in the following study to compare the reactivities of the complexes depending on the coordinating solvent and the aryl ligands.



(1)

	Ar	solv
1a	$C_6H_3Me_2$-3,5	dmso
1b	$C_6H_3(CF_3)_2$-3,5	dmso
1c	Ph	dmso
2b	$C_6H_3(CF_3)_2$-3,5	CH_3CN

Heating an acetonitrile solution of $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}_2(cod)]$ at 50 °C forms $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}_2(NCCH_3)_2]$ (**2b**) in moderate yield (59.0%). Isolated **2b** is stable both in the solid state and in solution (acetone or acetonitrile) for at least 1 week in the air. However, the reactions with $[Pt(C_6H_3Me_2\text{-}3,5)_2(cod)]$ and with $[PtPh_2(cod)]$ give only small amounts of complexes with $NCCH_3$ ligands, which were confirmed using ^1H NMR spectroscopy in CD_3CN. Attempts at isolation have failed, probably because of decomposition that releases the corresponding biaryl.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1a,b and 5

	1a	1b	5
Pt1−S1	2.316(2)	2.325(2)	2.287(1)
Pt1−S2	2.332(2)	2.310(2)	
Pt1−C1	2.025(8)	2.020(6)	2.033(4)
Pt1−C9	2.034(8)	2.033(6)	2.016(4)
Pt1−N1			2.143(4)
S1−Pt1−S2	90.73(7)	95.58(6)	
S1−Pt1−C1	175.9(2)	172.8(2)	178.6(1)
S1−Pt1−C9	91.2(2)	91.4(2)	91.3(1)
S2−Pt1−C1	93.1(2)	90.2(2)	
S2−Pt1−C9	176.2(2)	172.9(2)	
C1−Pt1−C9	84.9(3)	83.0(3)	89.5(2)
S1−Pt1−N1			88.84(10)
N1−Pt1−C1			90.4(1)
N1−Pt1−C9			178.0(2)

Figure 1 shows crystal structures for **1a**,**b**. The complexes have distorted-square-planar platinum centers that are bonded to two aryl groups and two S-coordinated dmso molecules with a cis configuration. Selected bond lengths and angles are given in Table 1. The Pt−C bond distances are similar among **1a** (2.025(8) and 2.034(8) Å), **1b** (2.020(6) and 2.033(6) Å), and **1c** (2.043(5) and 2.046(6) Å).[14] The Pt−S bond lengths (2.316(2) and 2.332(2) Å for **1a** and 2.325(2) and 2.310(2) Å for **1b**) are longer than those of $[PtCl_2(dmso)_2]$ (2.244(2) and 2.299(2) Å)[15] because of a strong trans influence of the aryl ligands. The ^1H NMR spectra of the complexes in $CDCl_3$ exhibit signals of para and ortho hydrogens of aryl ligands at δ 6.46 and 6.93 (**1a**), at δ 6.81 and 7.29 (**1c**), and at δ 7.41 and 7.77 (**1b**). The peak positions are influenced by the electron-donating Me groups and electron-withdrawing CF_3 groups of the aryl ligand. Positions of CH_3 hydrogens of the dmso ligand are also shifted to lower magnetic field positions in the order **1a** (δ 2.78), **1c** (δ 2.82), and **1b** (δ 2.90). The $^1H-^{195}Pt$ coupling constants observed for the signals of the ortho hydrogens (70−71 Hz) and hydrogens of dmso (14−15 Hz) do not vary in the complexes. The latter coupling constants are reasonable for dmso molecules that are S-coordinated to Pt. Furthermore, **2b** is characterized as the cis complex on the basis of the similarity of the $^1H-^{195}Pt$ coupling constant between the ortho hydrogen and ^{195}Pt (78 Hz) with those of **1a**−**c**.

Reaction of PhpyH with 1a−c and 2b Leading to Cyclometalation. $[PtAr_2(dmso)_2]$ was reported by Lanza et al. to undergo substitution of the dmso ligands.[13] The reaction of 2-phenylpyridine (PhpyH) with these complexes results in

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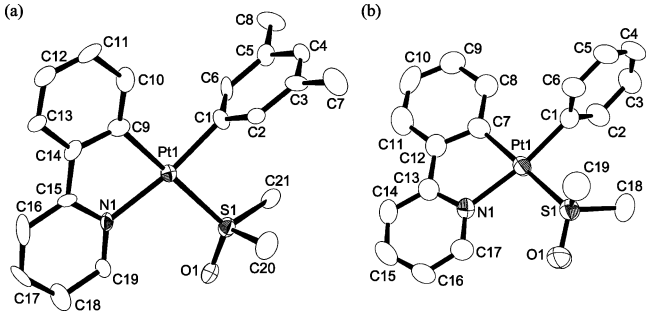


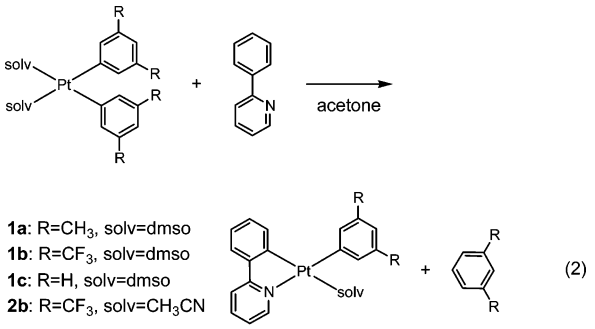
Figure 2. ORTEP drawings of (a) **3a** and (b) **3c** (50% probability).

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3a,c

	3a	3c		3a	3c
Pt1−S1	2.299(4)	2.302(2)	Pt1−C9	2.02(2)	2.019(9)
Pt1−N1	2.12(1)	2.115(7)	O1−C19	3.10(2)	
Pt1−C1	2.03(2)	2.031(9)	O1−C17		3.09(1)
S1−Pt1−N1	99.5(4)	99.5(2)	N1−Pt1−C1	172.2(6)	171.3(3)
S1−Pt1−C1	88.3(5)	89.0(3)	N1−Pt1−C9	80.5(6)	79.6(3)
S1−Pt1−C9	176.6(4)	178.5(2)	C1−Pt1−C9	91.8(7)	91.9(3)

coordination of the ligand with the nitrogen atom of the pyridyl group and the subsequent cyclometalation of the ligand, similar to the reaction of PhpyH with other transition-metal complexes. Few studies of such cyclometalation involving C−H bond activation and formation of a new metal−carbon bond have been reported for the preparation of arylplatinum complexes with solvent ligands.[12]

Adding PhpyH to acetone solutions of **1a**−**c** and **2b** and heating the solutions to 50 °C afford the monoarylplatinum complexes [Pt(Ar)(Phpy)(dmso)] (Ar = $C_6H_3Me_2$-3,5 (**3a**), $C_6H_3(CF_3)_2$-3,5 (**3b**), Ph (**3c**)) and [Pt{$C_6H_3(CF_3)_2$-3,5}(Phpy)-($NCCH_3$)] (**4b**), as shown in eq 2.



The complexes were characterized by X-ray crystallography and NMR spectroscopy. Figure 2 shows the crystal structures of **3a**,**c**. Both complexes have distorted-square-planar platinum centers that are bonded to an aryl group, to the C−N bidentate deprotonated 2-phenylpyridine, and to S-coordinated dmso. Selected bond lengths and angles are given in Table 2. Distances of the Pt−aryl and Pt−S bonds of **3a**,**c** are comparable to those for **1a**,**c**,[14] whereas Pt−C bond lengths of the Phpy ligand (2.02-(2) Å for **3a** and 2.019(9) Å for **3c**) are slightly longer than those of analogous cyclometalated platinum complexes (1.975-

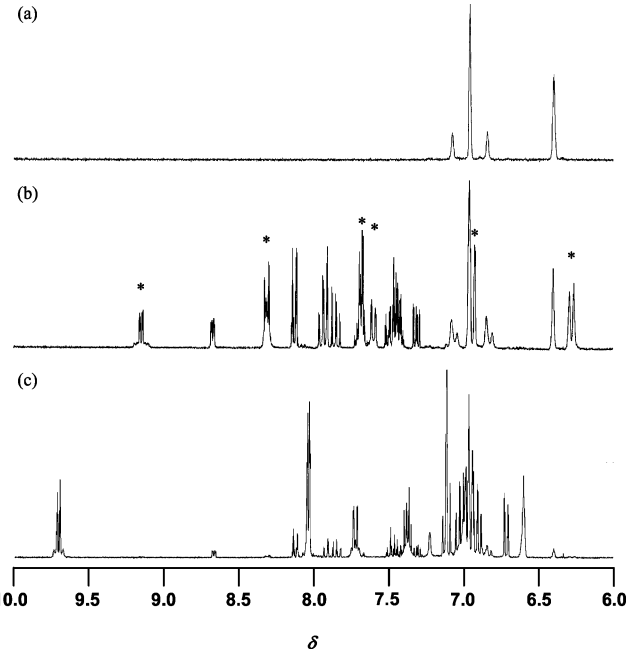


Figure 3. ^{1}H NMR spectra (300 MHz, acetone-d_6) of (a) **1a**, (b) of the solution immediately after mixing **1a** and PhpyH at room temperature, and (c) of the solution in (b) 10 h after reaction at 50 °C. Signals with asterisks are assigned to intermediate complex **A**.

(8)−1.993(7) Å).[16] The Pt−N bonds of **3a** (2.12(1) Å) and **3c** (2.115(7) Å) are similar to that of [PtCl(Phpy)(CO)] (2.114-(19) Å),[16a] in which a nitrogen atom is trans to the CO ligand. These distances are longer than those of other complexes having the C−N cyclometalated ligand (2.011(6)−2.016(5) Å).[16] The strong trans influence of the aryl ligands of **3a**,**c** and of the CO ligand of [PtCl(Phpy)(CO)] lengthens the Pt−N bond trans to the ligand. The N−Pt−C bite angles of the Phpy ligands of **3a** (80.5(6)°) and **3c** (79.6(3)°) are smaller than for the other cyclometalated complexes (80.7(2)−82.1(3)°)[16] because of the elongation of Pt−C and Pt−N bond lengths for **3a**,**c**.

The ^{1}H NMR spectra of **3a**,**b** in acetone-d_6 show signals of para and ortho hydrogens of the aryl ligand at δ 6.59 and 7.10 (**3a**) and at δ 7.62 and 8.15 (**3b**). Higher magnetic field positions for the former complex than for the latter are ascribed to the difference in the electron-donating capabilities of the substituents, CH_3 and CF_3, of the aryl ligands. The ^{1}H−^{195}Pt coupling constants observed in the ^{1}H NMR signals of ortho hydrogens and methyl protons of dmso of **3a** (70 and 17 Hz) are similar to those for **3b** (69 and 16 Hz). The signals of H_6 of Phpy of **3a** (δ 9.70) and **3b** (δ 9.71) are shifted downfield compared to that of **4b** (δ 8.87). Crystal structures of the complexes show a short contact between the O atom of dmso and the CH group adjacent to the N atom of Phpy (**3a**, O1−C19 = 3.10(2) Å; **3c**, O1−C17 = 3.09(1) Å). The presence of a C−H···O interaction is suggested in the solid state. The downfield shift of the ^{1}H NMR signal of that hydrogen described above is attributed to a similar intramolecular interaction in solution.

Reactions of PhpyH with **1a**−**c** and **2b** at 50 °C were monitored using ^{1}H NMR spectroscopy in acetone-d_6. Figure 3 summarizes the change of spectra caused by the reaction of PhpyH with **1a**. The spectrum of an equimolar mixture of **1a** and PhpyH at room temperature (Figure 3b) shows the signal for the hydrogen of the pyridine ring at δ 9.16. The signal is at

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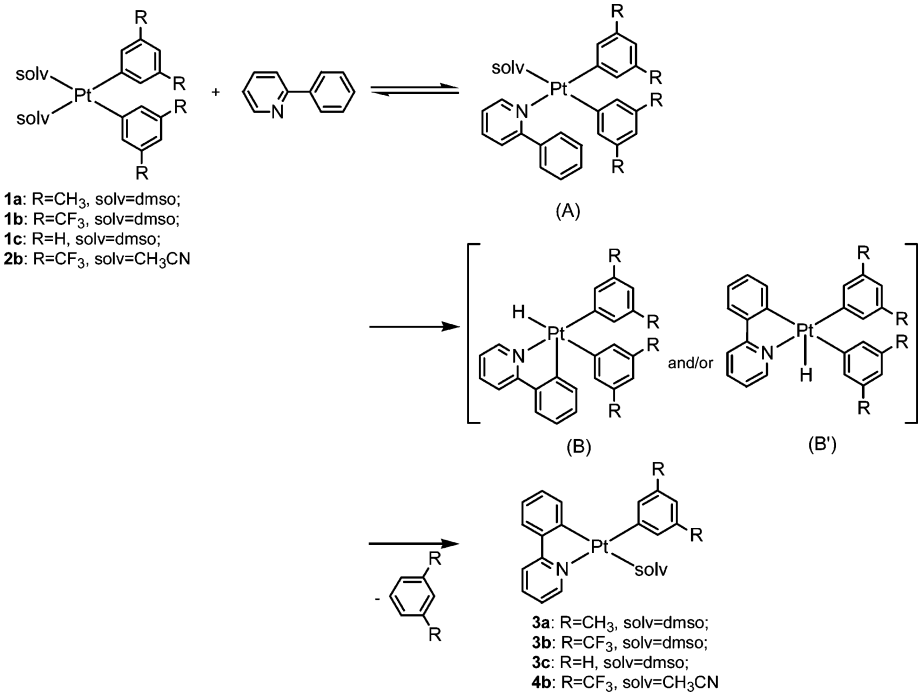
Scheme 1



a much lower field than the corresponding hydrogen of the free ligand, PhpyH (δ 8.68), with accompanying ^{195}Pt satellite signals ($J_{Pt-H} = 20$ Hz). Two signals attributable to para hydrogens of the 3,5-dimethylphenyl groups are observed at δ 6.26 and 6.29, indicating the nonequivalence of the two aryl ligands bonded to Pt. Nonequivalent meta hydrogens (δ 2.01 and 2.07) of the aryl group are also observed. The signals attributable to liberated and coordinated dmso molecules are observed respectively at δ 2.50 and 2.80 ($J_{Pt-H} = 15$ Hz). These signals are assigned to [Pt($C_6H_3Me_2$-3,5)$_2$(PhpyH)(dmso)] (**A**), having the two aryl ligands in cis positions, an N-coordinated PhpyH ligand, and an S-coordinated dmso molecule. The ratio of **A** to **1a** is close to 1:1 immediately after mixing PhpyH and **1a**. The reactions of PhpyH with **1b**,**c** and **2b** also form complexes with similar structures, [PtAr$_2$(PhpyH)(solv)], but the ratios of the complexes with and without the PhpyH ligand are highly dependent on both the aryl ligand and coordinating solvent molecule. In the reaction of **1b**,**c**, the ratio of the intermediate complex to the starting complex is also about 1:1, whereas complex **2b** is almost converted to [Pt{$C_6H_3(CF_3)_2$-3,5}$_2$(PhpyH)($NCCH_3$)] in the reaction mixture, probably because acetonitrile is less donating than dmso. The complexes with a PhpyH ligand are stable at room temperature in solution.

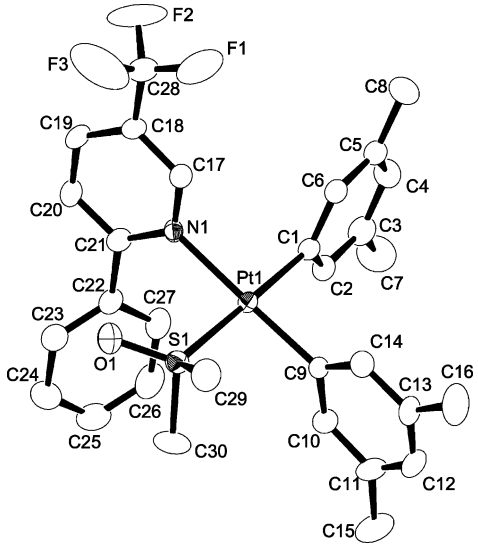


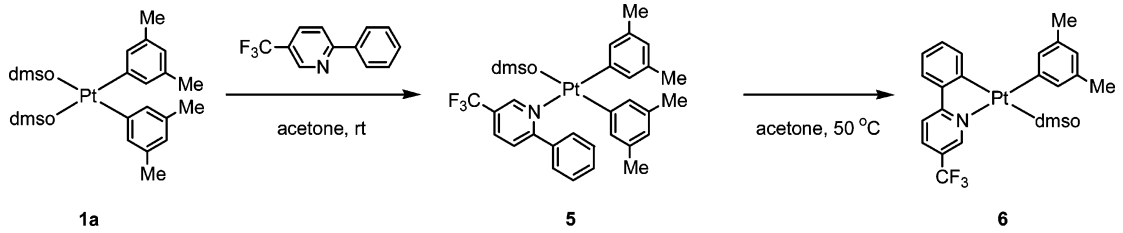
Figure 4. ORTEP drawing of **5** (50% probability).

Figure 3c shows the NMR spectrum after the reaction for 10 h at 50 °C. The signals of **A** are not observed after heating. Newly observed signals at δ 9.73, 6.75, and 6.60 are assigned to complex **3a**. Heating at 50 °C also engenders the formation of **3b**,**c** and **4b** from the reaction mixtures, respectively, using **1b**,**c**, and **2b**.

A plausible mechanism for the total reaction is depicted in Scheme 1. First, one of the coordinated solvent molecules of the diaryl complex is replaced by 2-phenylpyridine, which creates the intermediate complex **A** observed in ^{1}H NMR spectra and in the crystal structure of **5** (vide infra). Then, the remaining solvent molecule probably dissociates from complex **A**; also, oxidative addition of the ligand to the platinum center accompanied by C−H activation gives the platinum(IV) hydride complex **B**. Two possible structures can be inferred for the intermediate **B**. Reductive elimination of hydride and one aryl group proceeds to give the cyclometalated platinum(II) complexes **3a**−**c** and **4b**. It has been reported that this reductive elimination proceeds though the pentacoordinated square-pyramidal species.[12b,17]

The intermediate complexes of the reaction, [Pt(Ar)$_2$(PhpyH)(solv)] (**A**), were characterized using the ^{1}H NMR spectra of the mixtures and assigned to the intermediate complexes for formation of **3a**−**c** and **4b**. Isolation or characterization by X-ray crystallography was not feasible. However, the reaction of 2-phenyl-5-(trifluoromethyl)pyridine ($PhCF_3$pyH) with **1a** produces [Pt($C_6H_3Me_2$-3,5)$_2$($PhCF_3$pyH)(dmso)] (**5**), which was obtained as crystals suitable for X-ray crystallography. Figure 4 shows the molecular structure of the complex. It has a distorted-square-planar platinum center that is bonded to two aryl groups with a cis configuration, a nitrogen atom of $PhCF_3$-pyH, and a sulfur atom of the dmso molecule. Selected bond lengths and angles are given in Table 1. The Pt−C bond

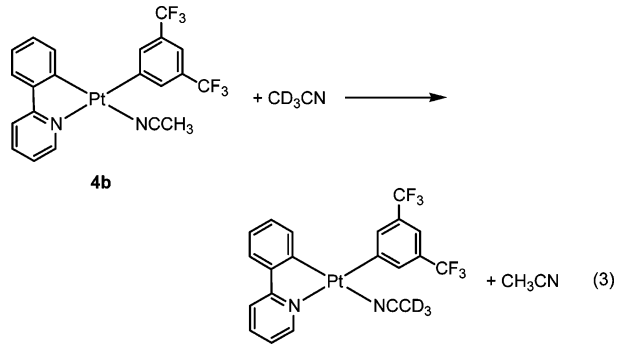
Scheme 2



1a **5** **6**

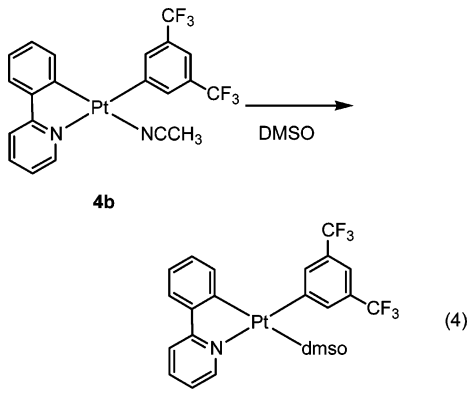
distances (2.033(4) and 2.016(4) Å) and Pt−S1 bond distance (2.287(1) Å), which are longer than those of $[PtCl_2(dmso)_2]$, are similar to the crystallographic results of **1a**. In addition, the Pt−N1 bond (2.143(4) Å) is also extended, as shown in many organoplatinum complexes whose nitrogen atoms are trans to Pt−C bonds. The isolated complex **5** undergoes cyclometalation to give an arylplatinum(II) complex analogue of **3a**, $[Pt(C_6H_3Me_2\text{-}3,5)(PhCF_3py)(dmso)]$ (**6**), in acetone at 50 °C (Scheme 2). Rates of the cyclometalation reactions are very sensitive to the aryl ligand and coordinating solvent. At 50 °C, the reactions of PhpyH with equimolar **1a**,**c** and **2b,** giving **3a**,**c** and **3b**, are completed in 10 h, 1 day, and 3 days, respectively, whereas **1b** is converted into **3b** in about 30% yield after 2 weeks. The formation of **3a**−**c** becomes faster in the order **3a** > **3c** > **3b**, which is related to the cyclometalation of the intermediate complexes $[Pt(Ar)_2(PhpyH)(solv)]$. Complexes having more electron-donating substituents at the aryl group undergo faster cyclometalation. The cyclometalation involves oxidative addition of the C−H bond to the Pt(II) center, which is now common in organoplatinum chemistry, and subsequent reductive elimination of arene via coupling of the formed hydride ligand and an aryl ligand. The different rates of cyclometalation depending on the aryl group are probably attributable to reductive elimination, by which the electron-donating substituent of the aryl ligand enhances the reaction. Complex **2b** with an acetonitrile ligand undergoes much faster ligation and cyclometalation than **1b**, despite having the same aryl ligand. Exchange of the solvent ligand of **2b** with added PhpyH ligand proceeds much more smoothly than that of **1b** because acetonitrile shows a less donating and more labile nature than dmso. To elucidate this matter further, we investigated the reaction of PhpyH with equimolar **2b** in acetonitrile-d_3 at 50 °C. The ^{1}H NMR spectra at the initial stage showed that the ratio of the intermediate complex to the starting complex is about 6:4, with quantitative formation of the intermediate complex in acetone-d_6. The following reaction at 50 °C gave **4b** in 36% yield, even after 2 weeks. The lower yield of **4b** as compared to that in acetone-d_6 is attributable to the stronger affinity of CH_3CN to the platinum center. As an explanation of these solvent effects, we infer that the more strongly donating solvent molecule interrupts the displacement by PhpyH to form the intermediate complex. That molecule also interrupts both the subsequent cyclometalation and the dissociation of the coordinating solvent from the intermediate complex. Thus, the coordinated and free solvents strongly affect the cyclometalation of the solvated diarylplatinum complexes: it is important to choose a less donating and more labile solvent for the reaction. Considering its greater lability and convenience for aftertreatment of acetonitrile, complex **2b** is a good starting material for cyclometalation.

Reactions of Cyclometalated Complexes 3a and 4b. The arylplatinum(II) complexes with the chelating Phpy ligand contain labile solvent ligand. The respective exchange reactions of CH_3CN of **4b** with CD_3CN and dmso were conducted. Dissolution of **4b** in CD_3CN causes exchange of the CH_3CN ligand by CD_3CN within 5 min at 25 °C, to produce $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}(Phpy)(NCCD_3)]$ (**4b-CD$_3$CN**) (eq 3).



To compare the rate of exchange reaction by the isotope dilution method of ^{1}H NMR spectroscopy, $[Pt\{C_6H_3(CF_3)_2\text{-}3,5\}(NCCH_3)(bpy)]^+$ (bpy = 2,2′-bipyridine) was prepared. The signal of CH_3CN bonded to Pt (δ 2.51) decreased, accompanied by the growth of the signal of free CH_3CN (δ 1.95). Completion of the reaction requires 5 h at 25 °C. Consequently, the exchange of the coordinated solvent of **4b** occurs much more rapidly than for the cationic complex with bpy ligand. This rapid exchange is attributable to the strong Pt−C σ-bond of the Phpy ligand of **4b**, which promotes facile dissociation of CH_3CN at the trans position. Acceleration of the exchange reaction, which is caused by the increased number of binding carbon atoms on the metal center, was reported by van Eldik et al. for substitution reactions of platinum complexes.[18]

Although complex **3b** has not been obtained easily from direct cyclometalation of **1b** with the 2-phenylpyridine ligand, it can be prepared independently from the reaction of dmso with **4b,** as shown in eq 4. The substitution of the acetonitrile ligand



takes place at room temperature. As shown in the exchange reaction of eq 3, an arylplatinum complex with a bidentate Phpy

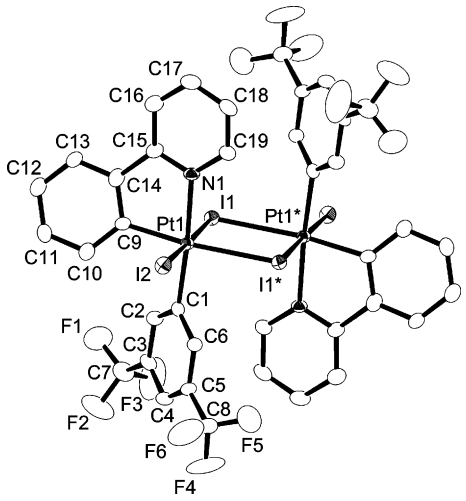


Figure 5. ORTEP drawing of **7b** (50% probability). Atoms with asterisks are crystallographically equivalent to those having the same number without an asterisk.

ligand shows higher reactivity than a cationic Pt complex with a bpy ligand because of the facile dissociation of the ligated solvent.

We examined the reactions of the complexes with high reactivity to oxidative addition of I_2 to Pt(II). The reactions of I_2 with **3a**,**b** and **4b** in acetone-d_6 gave orange precipitates as reaction products and were completed in 1 h at room temperature. Isolated orange precipitates show solubility in general solvent that is too low to be characterized using ^{1}H NMR spectroscopy. However, the reaction of I_2 with **4b** without stirring the reaction mixture gave single crystals of the products suited for X-ray analysis. Figure 5 gives perspective views of the dimeric platinum(IV) complex [(Pt{$C_6H_3(CF_3)_2$-3,5}(Phpy)I)$_2$(μ-I)$_2$] (**7b**), which has C_2 symmetry around the center of the Pt_2I_2 flat four-membered ring. Each platinum center of the molecule has a distorted-octahedral environment and is coordinated to the aryl group, C−N bidentate Phpy ligand, and bridging and nonbridging iodo ligands. The bidentate C−N ligand and the carbon atom of aryl group are oriented in the meridian plane with the same orientation in the square-planar platinum(II) complex **4b**, which implies oxidative addition of I_2 through attack at the apical sites of the coordination plane of the platinum(II) complex, as described for addition of CH_3I.[19] Selected bond distances and angles are given in Table 3. The two Pt−C bond distances have values similar to those of other organoplatinum(IV) complexes,[20] but they are slightly elongated from those of **3a**,**c**. The iodide bridges are asymmetric with Pt−I distances of 2.6680(5) and 2.8232(4) Å, which is probably attributable to the carbon atom having a stronger trans effect than the iodine atom. The structure of the product (**7a**) for the reaction of **3a** is considered to resemble that of **7b** on the basis of elemental analyses and the following results of further reaction with I^-.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 7b

Pt1−N1	2.147(4)	Pt1−I1	2.6680(5)
Pt1−C1	2.066(6)	Pt1−I2	2.6278(5)
Pt1−C9	2.031(6)	Pt1−I1*	2.8232(4)
I1−Pt1−I1*	85.67(1)	I1*−Pt1−C9	174.1(1)
I1−Pt1−I2	177.60(1)	I2−Pt1−N1	90.8(1)
I1−Pt1−N1	86.8(1)	I2−Pt1−C1	91.0(2)
I1−Pt1−C1	91.4(2)	I2−Pt1−C9	88.1(2)
I1−Pt1−C9	91.5(2)	N1−Pt1−C1	174.9(2)
I1*−Pt1−I2	94.46(1)	N1−Pt1−C9	79.5(2)
I1*−Pt1−N1	95.2(1)	C1−Pt1−C9	95.8(2)
I1*−Pt1−C1	89.4(2)	Pt1−I1−Pt1*	94.33(1)

Although complexes **7a**,**b** dissolved little in any of the common solvents we used, the addition of an iodide anion such as Et_4NI or NaI into their acetone solutions brought about their dissolution and gave complexes **8a**,**b**, respectively, which were observed using ^{1}H NMR spectroscopy. Their spectra show signals of the aryl and Phpy ligands, which probably imply the generation of the monomeric complexes $[PtI_3Ar(Phpy)]^-$. Scheme 3 summarizes these reactions.

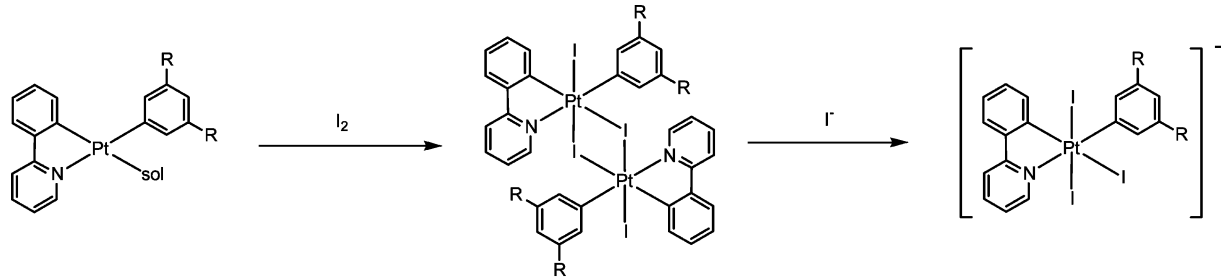
Summary

We prepared the acetonitrile-solvated diarylplatinum(II) complex **2b** through dissolution of [$PtAr_2$(cod)] into acetonitrile when $C_6H_3(CF_3)_2$-3,5 was used as the aromatic ligand. Although **1b**, which has an electron-withdrawing $C_6H_3(CF_3)_2$-3,5 group, is inferior to **1a**, which has an electron-donating group for cyclometalation through the Pt(II)/Pt(IV) system, considering the lability and convenience for aftertreatment of acetonitrile, complex **2b** is a good starting material for cyclometalation. Complex **4b**, resulting from cyclometalation, is very labile for acetonitrile exchange compared to the corresponding cationic arylplatinum(II) complex because it has two strong Pt−C σ bonds. Cyclometalated complexes **3a**,**b** and **4b** are also labile to oxidative addition of I_2 and gave the corresponding iodo-bridged dimeric Pt(IV) complexes.

Experimental Section

General Considerations, Measurement, and Materials. Manipulations of the platinum complexes were carried out in air without noting. Then [$PtAr_2$(cod)] and [PtArI(cod)] (Ar = $C_6H_3Me_2$-3,5 and $C_6H_3(CF_3)_2$-3,5) were prepared by [PtX_2(cod)] (X = Cl, I) with the corresponding Grignard reagents under nitrogen; [$PtPh_2(dmso)_2$] was prepared according to a method described in

Scheme 3



the literature.[13] The other chemicals were commercially available. The ^{1}H NMR spectra were recorded on a Varian 300 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 series II CHNS/O analyzer.

Preparation of Diarylplatinum Complexes with dmso, [PtAr$_2$(dmso)$_2$] (1a,b). The preparation of the complexes was performed according to a modified method of that for [PtPh$_2$(dmso)$_2$]. First, [Pt(C$_6$H$_3$Me$_2$-3,5)$_2$(cod)] (206 mg, 0.401 mmol) was dissolved in 10 mL of dmso and the solution stirred at 80 °C for 1 h. After removal of the solvent under vacuum, recrystallization of the residue from CH_2Cl_2−hexane gave [Pt(C$_6$H$_3$Me$_2$-3,5)$_2$(dmso)$_2$] (**1a**) as a colorless, air-stable powder (200 mg, 88.8%). Single crystals suitable for an X-ray diffraction study were obtained through further recrystallization from CH_2Cl_2−hexane. Anal. Calcd for $C_{20}H_{30}O_2PtS_2$: C, 42.77; H, 5.38. Found: C, 42.87; H, 5.46. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (s, 12H, C*H*$_3$C$_6$H$_3$), 2.78 (s, 12H, CH_3S, $^3J_{H-Pt}$ = 14 Hz), 6.46 (s, 2H, *p*-C$_6$H$_2$*H*), 6.93 (s, 4H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 71 Hz).

Complex **1b** was prepared using a procedure similar to that for **1a**, with [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(cod)] (400 mg, 0.548 mmol) as the starting material. The product (374 mg, 87.8%) was obtained as a colorless, air-stable powder. Single crystals suitable for an X-ray diffraction study were obtained by recrystallization from Et_2O−hexane. Anal. Calcd for $C_{20}H_{18}F_{12}O_2PtS_2$: C, 30.89; H, 2.33. Found: C, 30.95; H, 2.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.90 (s, 12H, CH_3S, $^3J_{H-Pt}$ = 15 Hz), 7.41 (s, 2H, *p*-C$_6$H$_2$*H*), 7.77 (s, 4H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 71 Hz).

Preparation of a Diarylplatinum Complexes with CH_3CN. [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(NCCH$_3$)$_2$] (2b). Preparation of these complexes was also carried out according to a modified method of that for [PtPh$_2$(dmso)$_2$].[13] First, [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(cod)] (376 mg, 0.515 mmol) was dissolved in 100 mL of CH_3CN and the solution stirred at 50 °C overnight. Hexane was added to this solution to extract liberated cod; then the solvent was removed. Crystallization of the residue from Et_2O−hexane gave the complex [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(NCCH$_3$)$_2$] (**2b**) as colorless needlelike crystals (213 mg, 59.0%). Anal. Calcd for $C_{20}H_{12}F_{12}N_2Pt$: C, 34.15; H, 1.72; N, 3.98. Found: C, 34.16; H, 1.71; N, 3.86. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 6H, CH_3CN), 7.37 (s, 2H, *p*-C$_6$H$_2$*H*), 7.61 (s, 4H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 78 Hz).

^{1}H NMR spectra of the mixture using [Pt(C$_6$H$_3$Me$_2$-3,5)$_2$(cod)] or [PtPh$_2$(cod)] showed formation of the corresponding complexes, [PtAr$_2$(NCCH$_3$)$_2$], in small amounts. Isolation of the complexes was not feasible because of their instability in solution.

Preparation of [Pt(C$_6$H$_3$Me$_2$-3,5)(Phpy)(dmso)] (3a). To an acetone (4 mL) solution of [Pt(C$_6$H$_3$Me$_2$-3,5)$_2$(dmso)$_2$] (205 mg, 0.365 mmol) was added Phpy (51.0 μL, 0.357 mmol). The mixture was stirred at 50 °C overnight, and the solvent was removed. Crystallization of the residue from acetone−hexane gave the complex as a yellow powder (163 mg, 83.9%). Anal. Calcd for $C_{21}H_{23}NOPtS$: C, 47.36; H, 4.35; N, 2.63. Found: C, 47.38; H, 4.39; N, 2.57. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.20 (s, 6H, C*H*$_3$C$_6$H$_3$), 2.89 (s, 6H, CH_3S, $^3J_{H-Pt}$ = 17 Hz), 6.59 (s, 1H, *p*-C$_6$H$_2$*H*), 6.70 (dd, 1H, $H_{3'}$, 7 and 1 Hz and $^3J_{H-Pt}$ = 70 Hz), 6.90 (ddd, 1H, $H_{4'}$, 7, 7, and 1 Hz), 7.02 (ddd, 1H, $H_{5'}$, 8, 7, and 1 Hz), 7.10 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 67 Hz), 7.38 (m, 1H, H_5), 7.72 (dd, 1H, $H_{6'}$, 8 and 1 Hz), 8.04−8.06 (m, 2H, H_3 and H_4), 9.70 (dd, 1H, H_6, 6 and 1 Hz).

Preparation of [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}(Phpy)(dmso)] (3b). To an acetone (2 mL) solution of [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}(Phpy)(NCCH$_3$)] (**4b**; 105 mg, 0.174 mmol) was added dmso (12.4 μL, 0.174 mmol). The mixture was stirred at room temperature for 2 h, and the solvent was removed. Crystallization of the residue from Et_2O−hexane gave the complex as a yellow powder (76.0 mg, 68.2%). Anal. Calcd for $C_{21}H_{17}F_6NOPtS$: C, 39.38; H, 2.68; N, 2.19. Found: C, 39.44; H, 2.75; N, 2.03. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.99 (s, 6H, CH_3S, $^3J_{H-Pt}$ = 16 Hz), 6.30 (dd, 1H, $H_{3'}$, 8 and 1 Hz and $^3J_{H-Pt}$ = 65 Hz), 6.93 (ddd, 1H, $H_{4'}$, 8, 8, and 1 Hz), 7.08 (ddd, 1H, $H_{5'}$, 8, 8, and 1 Hz), 7.46 (m, 1H, H_5), 7.62 (s, 1H, *p*-C$_6$H$_2$*H*), 7.79 (dd, 1H, $H_{6'}$, 8 and 1 Hz), 8.11−8.12 (m, 2H, H_3 and H_4), 8.15 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 69 Hz), 9.71 (dd, 1H, H_6, 6 and 1 Hz).

Preparation of [PtPh(Phpy)(dmso)] (3c). To an acetone (30 mL) solution of [PtPh$_2$(dmso)$_2$] (249 mg, 0.493 mmol) was added Phpy (81 mg, 0.52 mmol). The mixture was stirred at 50 °C for 3 h, and the solvent was removed. Yellow precipitate was generated as the reaction proceeded. Crystallization of the crude product from CH_2Cl_2−hexane gave the complex as a yellow powder (186 mg, 74.8%). Anal. Calcd for $C_{19}H_{19}NOPtS$: C, 45.23; H, 3.80; N, 2.78. Found: C, 45.20; H, 3.77; N, 2.74. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.93 (s, 6H, CH_3S, $^3J_{H-Pt}$ = 17 Hz), 6.64 (dd, 1H, $H_{3'}$, 7 and 1 Hz and $^3J_{H-Pt}$ = 68 Hz), 6.98−7.11 (m, 5H, $H_{4'}$, $H_{5'}$, *m*-C$_6$*H*$_2$H$_3$, and *p*-C$_6$H$_4$*H*), 7.25 (ddd, 1H, H_5, 7, 6, and 2 Hz), 7.52 (dd, 2H, *o*-C$_6$*H*$_2$H$_3$, 8 and 1 Hz and $^3J_{H-Pt}$ = 65 Hz), 7.61 (dd, 1H, $H_{6'}$, 8 and 1 Hz), 7.81 (dd, 1H, H_3, 8 and 1 Hz), 7.87 (ddd, 1H, H_4, 8, 7, and 2 Hz), 9.66 (dd, 1H, H_6, 6 and 2 Hz).

Reactions of [PtAr$_2$(solv)$_2$] (1a−c and 2b) with 2-Phenylpyridine in Acetone-d_6 or CD_3CN. A typical method of reactions of [PtAr$_2$(solv)$_2$] with 2-phenylpyridine in acetone-d_6 or CD_3CN is as follows. After the diarylplatinum complex (0.050 mmol) was dissolved in 0.5 mL of the deuterated solvent in the NMR tube, 1 equiv of 2-phenylpyridine (0.050 mmol) was added. The solution was stored at 50 °C, and the reaction was monitored using ^{1}H NMR spectra. In the reactions, no byproduct was formed and the reactions proceeded quantitatively, except for **1b**; thus, the reaction time was determined as the disappearance of the signals for the starting complex or 2-phenylpyridine. Because the reaction of **1b** too so long complete, we decided on conversion to **3b** by the ^{1}H NMR peak area after 2 weeks.

Preparation of [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}(Phpy)(NCCH$_3$)] (4b). To an acetone (2 mL) solution of [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_2$(NCCH$_3$)$_2$] (145 mg, 0.206 mmol) was added Phpy (29.0 μL, 0.206 mmol). The mixture was stirred at 50 °C for 3 days, and the solvent was removed. Crystallization of the residue from Et_2O−hexane gave the complex as a yellow powder (109 mg, 87.7%). Anal. Calcd for $C_{21}H_{14}F_6N_2Pt$: C, 41.80; H, 2.34; N, 4.64. Found: C, 41.62; H, 2.49; N, 4.48. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.52 (s, 3H, CH_3CN), 6.74 (dd, 1H, $H_{3'}$, 7 and 1 Hz, and $^3J_{H-Pt}$ = 68 Hz), 6.91 (ddd, 1H, $H_{4'}$, 7, 7, and 2 Hz), 7.00 (ddd, 1H, $H_{5'}$, 8, 7, and 1 Hz), 7.37 (ddd, 1H, H_5, 7, 5, and 2 Hz), 7.48 (s, 1H, *p*-C$_6$H$_2$*H*), 7.67 (dd, 1H, $H_{6'}$, 8 and 2 Hz), 8.04−8.09 (m, 2H, H_3 and H_4), 8.07 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 68 Hz), 8.87 (dd, 1H, H_6, 5 and 2 Hz).

Preparation of [Pt(C$_6$H$_3$Me$_2$-3,5)$_2$(PhCF$_3$pyH)(dmso)] (5). To an acetone (1 mL) solution of **1a** (40.3 mg, 0.0718 mmol) was added PhCF$_3$pyH (17.5 mg, 0.0784 mmol). The mixture was stirred at room temperature for 30 min. The resultant white precipitates were collected and washed using cold acetone (35.7 mg, 70.3%). Anal. Calcd for $C_{30}H_{32}F_3NOPtS$: C, 50.99; H, 4.56; N, 1.98. Found: C, 50.80; H, 4.49; N, 1.87.

Preparation of [Pt(C$_6$H$_3$Me$_2$-3,5)(PhCF$_3$py)(dmso)] (6). To an acetone (10 mL) solution of **1a** (197 mg, 0.351 mmol) was added PhCF$_3$pyH (82.0 mg, 0.367 mmol). The mixture was stirred at 50 °C for 1 day, and the solvent was removed. Crystallization of the

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residue from Et_2O−hexane gave the complex as a yellow powder (120 mg, 57.0%). Anal. Calcd for $C_{22}H_{22}F_3NOPtS$: C, 44.00; H, 3.69; N, 2.33. Found: C, 43.85; H, 3.86; N, 2.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 6H, C*H*$_3$C$_6$H$_3$), 2.96 (s, 6H, CH$_3$S, $^3J_{H-Pt}$ = 17 Hz), 6.67 (s, 1H, *p*-C$_6$H$_2$*H*), 6.74 (m, 1H, *H*$_{3'}$), 7.07−7.14 (m, 2H, *H*$_{4'}$ and *H*$_{5'}$), 7.12 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 67 Hz), 7.66 (m, 1H, *H*$_{6'}$), 7.91 (d, 1H, *H*$_3$, 9 Hz), 8.08 (dd, 1H, *H*$_4$, 9 and 2 Hz), 10.17 (s, 1H, *H*$_6$). The same complex also formed from the suspension of **5** in acetone by heating to 50 °C.

Preparation of [PtI{C$_6$H$_3$(CF$_3$)$_2$-3,5}(bpy)]. A CH_3CN (40 mL) solution of [PtI{C$_6$H$_3$(CF$_3$)$_2$-3,5}(cod)] (314 mg, 0.488 mmol) and bpy (381 mg, 2.44 mmol) was stirred at room temperature for 3 days. Hexane was added to the solution to extract librated cod; then the solvent was removed. Crystallization of the residue from CH_2Cl_2−hexane gave the complex as a yellow powder (305 mg, 90.4%). Anal. Calcd for $C_{18}H_{11}F_6IN_2Pt$: C, 31.28; H, 1.60; N, 4.05. Found: C, 31.36; H, 1.50; N, 4.01. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.45 (s, 1H, *p*-C$_6$H$_2$*H*), 7.68 (ddd, 1H, *H*$_{5'}$, 8, 6, and 1 Hz), 7.88 (ddd, 1H, *H*$_5$, 8, 5, and 1 Hz), 7.93 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 42 Hz), 8.12 (dd, 1H, *H*$_{6'}$, 6 and 2 Hz and $^3J_{H-Pt}$ = 59 Hz), 8.41 (ddd, 1H, *H*$_4$, 8, 8, and 2 Hz), 8.47 (ddd, 1H, *H*$_{4'}$, 8, 8, and 2 Hz), 8.62−8.68 (m, 2H, *H*$_3$ and *H*$_{3'}$), 9.97 (dd, 1H, *H*$_6$, 5 and 2 Hz).

Preparation of [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}(NCCH$_3$)(bpy)]BF$_4$. A small excess of $AgBF_4$ was added to a solution of [PtI{C$_6$H$_3$(CF$_3$)$_2$-3,5}(bpy)] (85 mg, 0.12 mmol) in dry CH_3CN under argon. The mixture was stirred for 1 min at room temperature; then the resulting precipitate of AgI was filtered off. The crude product obtained by addition of Et_2O to the concentrated filtrate was recrystallized from CH_3CN−Et_2O to give the off-white complex (81 mg, 100%). Anal. Calcd for $C_{20}H_{14}BF_{10}N_3Pt$: C, 34.70; H, 2.04; N, 6.07. Found: C, 34.68; H, 2.22; N, 6.00. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.81 (s, 3H, C*H*$_3$CN), 7.71 (s, 1H, *p*-C$_6$H$_2$*H*), 7.73 (1H, *H*$_{5'}$, overlapping with the signal at δ 7.71), 8.02 (ddd, 1H, *H*$_5$, 8, 5, and 1 Hz), 8.07 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 44 Hz), 8.28 (dd, 1H, *H*$_{6'}$, 6 and 1 Hz, and $^3J_{H-Pt}$ = 57 Hz), 8.50 (ddd, 1H, *H*$_{4'}$, 8, 8, and 1 Hz), 8.55 (ddd, 1H, *H*$_4$, 8, 8, and 2 Hz), 8.72−8.78 (m, 2H, *H*$_3$ and *H*$_{3'}$), 9.21 (dd, 1H, *H*$_6$, 5 and 2 Hz).

Acetonitrile Exchange Reactions of 4b and [Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}(NCCH$_3$)(bpy)]BF$_4$. The sample solution ([Pt complex] = 5.0×10^{-2} mol kg^{-1}) was prepared under a nitrogen atmosphere by dissolution of each complex in CD_3CN that had been distilled before use. Spectral changes for their reactions were monitored at 25.0 °C.

Reactions of I$_2$ with 3a,b and 4b. A sample solution was prepared by dissolution of 0.025 mmol of each complex and 1 equiv of I_2 in acetone-d_6 (0.5 mL). Spectral changes for their reactions were monitored at room temperature.

Preparation of [{Pt(C$_6$H$_3$Me$_2$-3,5)(Phpy)I}$_2$(μ-I)$_2$] (7a). To an acetone (2 mL) solution of **3a** (109 mg, 0.205 mmol) was added iodine (53.4 mg, 0.209 mmol). The mixture was stirred at room temperature for 5 h. The resultant orange precipitates were collected and washed using acetone (41.0 mg, 28.2%). Anal. Calcd for $C_{38}H_{34}I_4N_2Pt_2$: C, 32.22; H, 2.42; N, 1.98. Found: C, 32.32; H, 2.64; N, 1.78.

Preparation of [(Pt{C$_6$H$_3$(CF$_3$)$_2$-3,5}(Phpy)I)$_2$(μ-I)$_2$] (7b). To an acetone (2 mL) solution of **4b** (64.1 mg, 0.100 mmol) was added iodine (31.6 mg, 0.125 mmol). The mixture was stirred at room temperature for 1 h. The resultant orange precipitates were collected and washed using acetone (30.4 mg, 37.2%). Anal. Calcd for $C_{38}H_{22}F_{12}I_4N_2Pt_2$: C, 27.96; H, 1.36; N, 1.72. Found: C, 28.25; H, 1.39; N, 1.59.

Preparation of Et$_4$N[Pt(C$_6$H$_3$Me$_2$-3,5)(Phpy)I$_3$] (8a-Et$_4$N). To an acetone (4 mL) solution of **7a** (33.3 mg, 0.0204 mmol) was added Et_4NI (10.6 mg, 0.0412 mmol). The mixture was stirred at room temperature for 1 day, and the solvent was removed. Crystallization of the residue from acetone−hexane gave the complex as an orange powder (27.5 mg, 69.9%). Anal. Calcd for $C_{27}H_{37}I_3N_2Pt$: C, 33.59; H, 3.86; N, 2.90. Found: C, 33.22; H, 4.04; N, 2.76. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.34 (t, 12H, NCH$_2$C*H*$_3$, 7 Hz), 2.17 (s, 6H, C*H*$_3$C$_6$H$_3$), 3.41 (q, 8H, NC*H*$_2$CH$_3$, 7 Hz), 6.45 (s, 1H, *p*-C$_6$H$_2$*H*), 6.89 (ddd, 1H, *H*$_{5'}$, 8, 7, and 1 Hz), 7.11 (ddd, 1H, *H*$_{4'}$, 7, 7, and 2 Hz), 7.32 (1H, *H*$_5$, overlapping with the signal at δ 7.38), 7.38 (d, 1H, *H*$_{3'}$, 7 Hz, and $^3J_{H-Pt}$ = 36 Hz), 7.85 (dd, 1H, *H*$_{6'}$, 8 and 2 Hz), 7.93 (ddd, 1H, *H*$_4$, 8, 7, and 2 Hz), 8.20 (d, 1H, *H*$_3$, 8 Hz), 8.32 (s, 2H, *o*-C$_6$*H*$_2$H, $^3J_{H-Pt}$ = 39 Hz), 10.52 (d, 1H, *H*$_6$, 6 Hz). The reactions of NaI with **7a** showed similar changes of solutions and analogous ^{1}H NMR spectra, except for the cation part.

Preparation of Et$_4$N[Pt(C$_6$H$_3$Me$_2$-3,5)(Phpy)I$_3$] (8b-Et$_4$N). To an acetone (4 mL) solution of **7b** (20.0 mg, 0.0123 mmol) was added Et_4NI (70.0 mg, 0.270 mmol). The mixture was stirred at room temperature for 3 h, and the solvent was removed. Crystallization of the residue from acetone−hexane gave the complex as an orange powder (18.0 mg, 68.3%). Anal. Calcd for $C_{27}H_{31}F_6I_3N_2Pt$: C, 30.21; H, 2.91; N, 2.61. Found: C, 30.49; H, 3.05; N, 2.47. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.38 (t, 12H, NCH$_2$C*H*$_3$, 7 Hz), 3.49 (q, 8H, NC*H*$_2$CH$_3$, 7 Hz), 6.96 (ddd, 1H, *H*$_{5'}$, 8, 8, and 1 Hz), 7.01 (dd, 1H, *H*$_{3'}$, 8 and 1 Hz, and $^3J_{H-Pt}$ = 36 Hz), 7.19 (ddd, 1H, *H*$_{4'}$, 8, 8, and 2 Hz), 7.41 (ddd, 1H, *H*$_5$, 7, 6, and 1 Hz), 7.45 (s, 1H, *p*-C$_6$H$_2$*H*), 7.92 (dd, 1H, *H*$_{6'}$, 8 and 1 Hz), 8.00 (ddd,

Table 4. Crystallographic Data for Platinum Complexes

	1a	1b	3a	3c	5	7b
chem formula	$C_{20}H_{30}O_2PtS_2$	$C_{20}H_{18}F_{12}O_2PtS_2$	$C_{21}H_{23}NOPtS$	$C_{19}H_{19}NOPtS$	$C_{30}H_{32}F_3NOPtS$	$C_{19}H_{11}F_6I_2NPt$
formula wt	561.67	777.55	532.57	504.52	706.73	816.19
cryst syst	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.117(4)	8.5086(2)	8.699(2)	9.432(5)	8.8977(2)	8.8419(6)
b, Å	9.932(3)	15.8910(7)	19.281(3)	8.630(5)	19.0682(2)	10.2442(7)
c, Å	13.46(1)	19.133(1)	23.397(4)	21.46(1)	17.1095(4)	12.442(1)
α, deg	91.99(6)					103.518(3)
β, deg	97.13(7)			100.75(4)	100.591(1)	105.202(3)
γ, deg	112.58(3)					99.250(1)
V, Å^3	1112(1)	2587.0(2)	3924.2(1)	1715(1)	2853.40(10)	1027.4(1)
Z	2	4	8	4	4	2
μ, cm^{-1}	64.81	56.66	72.37	82.69	50.13	98.66
F(000)	552	1488	2064	968	1392	740
D_{calcd}, g cm^{-3}	1.677	1.996	1.803	1.953	1.645	2.638
cryst size, mm	0.13 × 0.19 × 0.19	0.10 × 0.13 × 0.20	0.02 × 0.02 × 0.10	0.10 × 0.15 × 0.20	0.10 × 0.20 × 0.20	0.04 × 0.10 × 0.10
unique no. of rflns	4487	3335	4500	3451	6493	4498
no. of rflns used ($I > 2.00\ \sigma(I)$)	3719	3029	2522	2304	5334	3439
no. of variables	226	335	226	208	334	262
R1	0.039	0.025	0.066	0.035	0.031	0.027
wR2	0.097	0.055	0.128	0.080	0.080	0.059

1H, H_4, 8, 7, and 2 Hz), 8.26 (d, 1H, H_3, 8 Hz), 9.33 (s, 2H, *o*-C_6H_2H, $^3J_{H-Pt} = 42$ Hz), 10.51 (d, 1H, H_6, 6 Hz). The reactions of NaI with **7b** showed similar changes of solutions and analogous ^{1}H NMR spectra, except for the cation part.

Crystal Structure Determination. Crystals of **1a**,**b** and **3a**,**c** suitable for X-ray diffraction study were obtained respectively by recrystallization from CH_2Cl_2−hexane, Et_2O−hexane, Et_2O−hexane, and CH_2Cl_2−hexane; single crystals of **5** were obtained using the reaction mixture of **1a** with 2-phenyl-5-(trifluoromethyl)pyridine without stirring at room temperature. Single crystals of **7b** were obtained using the reaction mixture of **4b** with I_2 without stirring. Crystallographic and diffraction data were obtained using an Enraf-Nonius CAD4-EXPRESS four-circle diffractometer with graphite-monochromated Mo Kα radiation at room temperature for **1a** and **3c** and using a Rigaku/MSC Mercury CCD with graphite-monochromated Mo Kα radiation at −100 °C for **1b**, **3a**, **5**, and **7b**. All structures were solved using a combination of direct methods and were expanded using the Fourier technique. Atomic scattering factors and anomalous dispersion terms were taken from ref 21. All non-hydrogen atoms were refined using a full-matrix least-squares method with anisotropic displacement parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculations without further refinement of the parameters. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.[22] Crystallographic data and details of the refinement are summarized in Table 4.

Supporting Information Available: CIF files giving crystallographic data for **1a**,**b**, **3a**,**c**, **5**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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