Chemical Properties of Cationic Phenylplatinum(II) Complexes with a 2,2′-Bipyridine Ligand. Insertion of CO and Allene into the Pt−C Bond and Oxidative Addition of MeI

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[PtPh(bpy)(solvent)]BF_4 (**1-MeCN**, solvent = MeCN; **1-acetone**, solvent = acetone) are prepared from the reaction of HBF_4 with $PtPh_2$(bpy) or from the reaction of $AgBF_4$ with PtI(Ph)(bpy). The MeCN ligand of **1-MeCN** in a CD_3CN solution undergoes exchange with the solvent in 12 h at room temperature. The coordinated solvent of **1-acetone** is replaced with acetone-d_6 much more rapidly. **1-acetone** reacts easily with H_2O and CO to form **1-OH$_2$** and **1-CO**, respectively. The reaction of phenylallene with **1-acetone** produces the (π-allyl)-platinum complex [Pt(η^3-$CH_2CPhCHPh$)(bpy)]BF_4 (**2**) as a mixture of syn and anti isomers. One of the isomers, **2-*syn***, was isolated by recrystallization of the products and characterized by X-ray crystallography and ^{1}H NMR spectroscopy. The complex reacts with CO (1 atm) at room temperature to form a mixture of [Pt((*Z*)-CH_2CPh=$CHPh$)(bpy)(CO)]BF_4 (**3-*Z***) and [Pt-((*E*)-CH_2CPh=$CHPh$)(bpy)(CO)]BF_4 (**3-*E***). The ratio of **3-*Z*** to **3-*E*** decreases gradually during the reaction to afford an equilibrium mixture ([**3-*Z***]:[**3-*E***] = 35:65) after 26 min. First-order rate constants of the reaction under CO and under argon are similar to each other, indicating that the isomerization occurs via a pentacoordinate intermediate with carbonyl and π-allyl ligands bonded to the Pt center. **1-MeCN** reacts with MeI at 50 °C to produce a mixture of two isomeric cationic Pt(IV) complexes after 9 days. X-ray crystallography of one of the products, [PtI(Me)(Ph)(NCMe)(bpy)]BF_4 (**4**), revealed an octahedral structure having the methyl, iodo, and bipyridine ligands in the same coordination plane.

Introduction

Cationic methylplatinum(II) complexes with auxiliary nitrogen ligands undergo facile C−H bond activation of alkanes and insertion of alkenes into the Pt−Me bond, which is often related to activation and functionalization of methane promoted by Pt complexes and by related Pd complexes.[1,2] In the past decade, analogous cationic arylplatinum(II) complexes having chelating diimine ligands, [PtAr(L_2)(solvent)]$^+$ (L_2 = diimine ligand), have attracted significant attention due to their unique chemical properties, such as facile insertion of unsaturated molecules into the Pt−Ar bond.[3−5] Recently, we reported that the cationic arylpalladium complexes with a labile THF or acetone ligand undergo facile intermolecular coupling of the aryl ligands to afford biaryl or insertion of unsaturated molecules such as alkyne and allene into the Pd−aryl bond.[6] The reactivity of the cationic Pd−MeCN complexes toward the above reactions is lower than the complexes with acetone or THF ligand. Comparison of the chemical properties of cationic arylplatinum complexes with those of the Pd complexes is of interest because the Pt−C bonds are more stable than the Pd−C bonds of similar square-planar complexes and because the arylplatinum complexes are suitable for elucidating the mechanism of their reactions. De Felice et al. reported the preparation of [PtAr-

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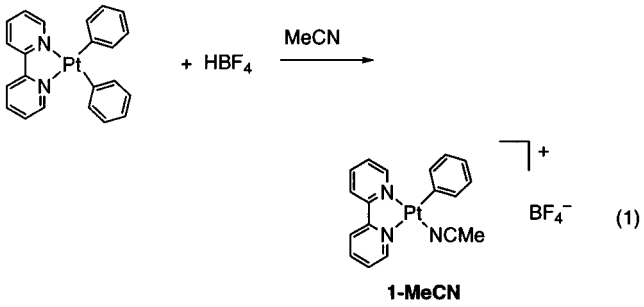
$(L_2)(NCMe)]^+$ (Ar = C_6H_4OMe-4; L_2 = 2,9-dimethylphenanthroline, phenanthroline) and their reaction with CO to cause insertion of CO into the Pt−Ar bond under mild conditions and the reaction with 1,1-dimethylallene to afford a (π-allyl)platinum complex.[3c,d,7] In this paper, we report preparation of the cationic phenylplatinum complex with bipyridine and reactivity of the complex, which differs depending on the solvent coordinated to the metal center. The reaction of allene with the complex to form the (π-allyl)platinum complex and its further reaction with CO are also mentioned.

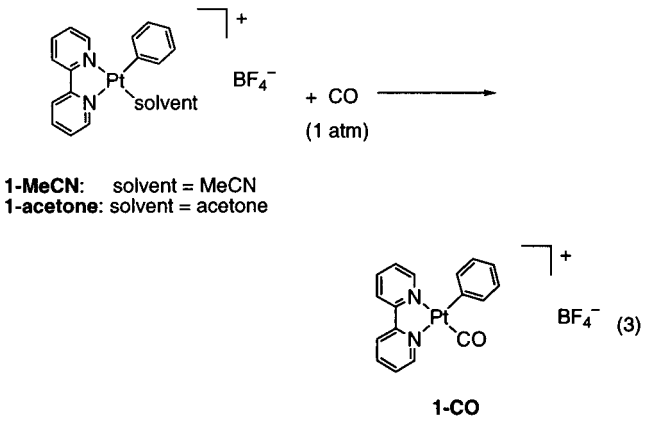
Results and Discussion

Preparation of Cationic Phenylplatinum Complexes with a Bipyridine Ligand. The cationic phenylplatinum complex [PtPh(bpy)(NCMe)]BF_4 (**1-MeCN**) is prepared from an equimolar reaction of HBF_4 with $PtPh_2$(bpy) in MeCN (eq 1) or the reaction of $AgBF_4$ with PtI(Ph)(bpy) in MeCN (eq 2). The reaction of $AgBF_4$ with



PtI(Ph)(bpy) in acetone produces [PtPh(bpy)(acetone)]BF_4 (**1-acetone**) as a colorless solid. Previously, we reported that the reaction of $AgBF_4$ with PdI(Ph)(bpy) in acetone led to formation of the biphenyl species via the initial formation of the cationic palladium complex [PdPh(bpy)(acetone)]BF_4, which was not sufficiently stable to be isolated or fully characterized but, rather, underwent bimolecular coupling of the phenyl ligand. The complex **1-acetone**, however, is stable in acetone solution for 24 h at room temperature. The complexes **1-MeCN** and **1-acetone** were characterized by ^{1}H NMR spectroscopy, although the low solubility of the complexes in organic solvents prevented detailed ^{13}C NMR analyses. ^{1}H NMR signals of ortho phenyl hydrogens of **1-MeCN** and **1-acetone** are observed at δ 7.35 (J(PtH) = 39 Hz) and δ 7.30 (J(PtH) = 33 Hz), respectively. Two pyridyl groups of the bipyridine ligand are observed in the ^{1}H NMR spectra of **1-MeCN** in CD_3CN and of **1-acetone** in acetone-d_6. The ^{1}H NMR signal of the coordinated solvent of **1-MeCN** in CD_3CN appears at δ 2.52 flanked by ^{195}Pt satellite signals (J(PtH) = 14 Hz), whose position is distinguished unambiguously from CHD_2CN contained as an impurity in the solvent (δ 1.93; free CH_3CN δ 1.95). The peak position and the coupling constants are similar to those of cationic Pt complexes with a NCMe ligand.[8] The gradual intensity decrease of the signal of the coordinated MeCN and concomitant growth of the peak at δ 1.95 indicates exchange of the coordinated and uncoordinated MeCN molecules. The spectroscopic change is completed in 12 h at room temperature. On the other hand, **1-acetone** in acetone-d_6 exhibits a single solvent signal at δ 2.08, which suggests rapid exchange of the coordinated and free solvents. Evaporation of a part of acetone from the solution of **1-acetone** under vacuum followed by addition of Et_2O led to crystallization of the cationic phenylplatinum aqua complex [PtPh(bpy)(H_2O)]BF_4 (**1-OH_2**), which was probably formed via exchange of the coordinated solvent with water contained in the solution. [PtPh(D_2O)(bpy)]BF_4 (**1-OD_2**) was prepared also from the reaction with D_2O in acetone-d_6 and showed NMR signals of the aromatic hydrogens at positions different from those of **1-acetone**.

The introduction of carbon monoxide (1 atm) to solutions of **1-MeCN** and of **1-acetone** leads to the formation of the cationic carbonyl complex [PtPh(bpy)(CO)]BF_4 (**1-CO**), as shown in eq 3. The complete



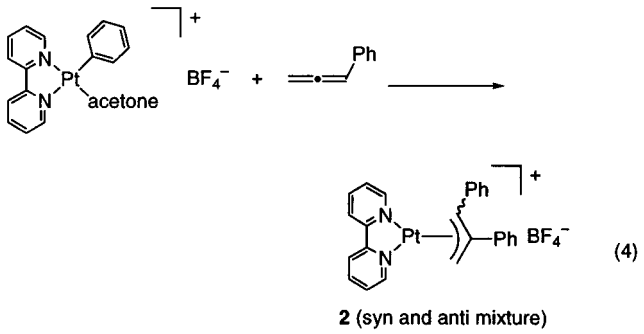
substitution of MeCN of **1-MeCN** with CO requires 7 days, while **1-acetone** undergoes similar ligand exchange within 3 h. **1-CO** is sufficiently stable to be characterized by ^{1}H NMR spectroscopy and elemental analyses. The NMR signals are located at reasonable positions; the ortho hydrogen signal at δ 7.46 is accompanied by ^{195}Pt satellite signals (J(PtH) = 32 Hz). The IR spectrum exhibits a characteristic band due to the carbonyl ligand (ν(CO) = 2120 cm^{-1}). The reaction under CO (1 atm) does not cause insertion of CO into the Pt−Ph bond. This is in contrast with the previous results that PtAr(Cl)(CO)(L_2) (L_2 = 2,9-dimethylphenanthroline) with a labile pentacoordinated metal center reacts with CO to cause facile insertion of CO into the Pt−Ar bond, affording the aroylplatinum(II) complex.[3d]

(7) For analogous reaction of Pt−phosphine complexes, see: Chisholm, M. H.; Johns, W. S. *Inorg. Chem.* **1975**, *14*, 1189.

(8) $[PtCl(NH_3)_2(NCMe)]^+$ showed the ^{1}H NMR signal of the MeCN ligand at δ 2.53 with ^4J(PtH) = 12.7 Hz (Erxleben, A.; Mutikinen, I.; Lippert, B. *J. Chem. Soc., Dalton Trans.* **1994**, 3667). The coupling constants of similar complexes are in the range 10.4−14.4 Hz. See also ref 2.

The reaction of CO with **1-MeCN** at higher pressure (30 atm) produces a mixture of **1-CO** and [Pt(COPh)(bpy)(CO)]BF_4. The mixture shows IR peaks at 2066 and 1647 cm^{-1} of the carbonyl and benzoyl ligands of the latter complex in addition to the peaks of **1-CO**. Isolation of the benzoylplatinum complex, produced via CO insertion into the Pt−Ph bond, was not possible, due to rapid decarbonylation of it during purification. Exposure of the above mixture of the complexes to argon causes regeneration of **1-CO** very quickly at room temperature. The reaction is much faster than the decarbonylation of cationic *trans*-aroylplatinum(II) complexes with two monodentate phosphine ligands[9] and that of pentacoordinated PtCl(COAr)(CO)(L_2) (L_2 = 2,9-dimethylphenanthroline).[3]

Insertion of Allene into the Pt−C Bond. The insertion of allene into the Pd−Me bond was studied in detail.[10,11] Previously, we reported preparation of a (π-allyl)palladium complex from the insertion of a C=C double bond of phenylallene into the Pd−C bond of [Pd($C_6H_3Me_2$-3,5)(bpy)(solvent)]BF_4.[6] [Pt(C_6H_4OMe)(L_2)(MeCN)]BF_4 (L_2 = 2,9-dimethylphenanthroline) was reported to cause similar insertion of 1,1-dimethylallene into the Pt−C bond, affording the corresponding (π-allyl)platinum complex.[3c] The reaction of phenylallene with the platinum complex **1-acetone** also takes place smoothly to produce the (π-allyl)platinum complex [Pt(η^3-$CH_2CPhCHPh$)(bpy)]BF_4 (**2**), as shown in eq 4. The



(4)

2 (syn and anti mixture)

^{1}H NMR spectrum of the reaction mixture shows the existence of syn and anti isomers of **2**. Recrystallization of the product gives single crystals of **2-*syn***, whose phenyl substituent occupies the syn position of the allyl ligand. The molecular structure determined by X-ray crystallography is shown in Figure 1. Despite the unsymmetrical structure of the π-allyl ligand, the two Pt−N bond distances and Pt−C1 and Pt−C3 bond distances are similar within experimental error. The phenyl plane bonded to the central carbon of the ligand

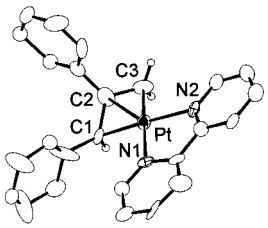


Figure 1. ORTEP drawing of **2-*syn*** (30% probability). Selected bond lengths (Å) and angles (deg): Pt1−N1 = 2.10(2), Pt1−N2 = 2.09(2), Pt1−C1 = 2.12(2), Pt1−C2 = 2.07(7), Pt1−C3 = 2.13(2), C1−C2 = 1.45(3), C2−C3 = 1.47(3); N1−Pt1−N2 = 78.6(8), N1−Pt1−C1 = 109(1), N1−Pt1−C2 = 173.7(9), N1−Pt1−C3 = 106.9(9), N2−Pt1−C1 = 109(1), N2−Pt1−C2 = 137.8(9), N2−Pt1−C3 = 170.2(4), C1−Pt1−C3 = 69.8(9).

is almost perpendicular to the π-allylic plane, while the phenyl group bonded to the terminal carbon of the ligand is coplanar with the π-allyl ligand.

The ^{1}H NMR spectrum of **2-*syn*** contains signals of the three hydrogens of the allyl ligand at δ 3.69, 4.07, and 4.55. The first two signals are coupled with each other (J(HH) = 3 Hz) and are assigned to the two =CH_2 hydrogens of the ligand. The signal at higher magnetic field (δ 3.69) and the signal assigned to benzylidene hydrogen (δ 4.55) show J(PtH) values of 67 and 70 Hz, respectively. The signal at δ 4.07 with a smaller coupling constant (J(PtH) = 23 Hz) is assigned to the hydrogens at the syn position of the π-allylic ligand. Heating the solution of **2-*syn*** at 50 °C caused its isomerization into **2-*anti***, which gave an equilibrated mixture of the syn and anti isomers (52:48) in 8 days. The ^{1}H NMR spectrum of the mixture shows signals of π-allyl hydrogens of **2-*anti*** at δ 3.48 (J(PtH) = 71 Hz), 4.42 (J(PtH) = 23 Hz), and 6.39 (J(PtH) = 42 Hz). The first two signals are assigned to the two =CH_2 hydrogens at anti and syn positions, respectively, on the basis of the peak positions and J(PtH) values. The benzylidene hydrogen signal at the syn position causes its appearance at a lower magnetic field and a smaller coupling constant as compared to those of **2-*syn***. The isomerization between **2-*syn*** and **2-*anti*** occurs much more slowly than for the Pd complex [Pd{η^3-$CH_2C(C_6H_3Me_2$-3,5)CHPh}(bpy)]BF_4, which is obtained as the thermodynamically stable syn isomer soon after the preparation.[6]

Contact of CO (1 atm) with **2-*syn*** in MeCN causes rapid conversion into a (σ-allyl)platinum complex, [Pt(CH_2CPh=$CHPh$)(bpy)(CO)]BF_4. The solution after the reaction with CO for 4 min contains a mixture of the isomer with a *Z* configuration, **3-*Z***, and the *E* isomer, **3-*E***, in a 72:28 ratio. The ratio between the isomers decreases to 35:65 after 26 min and does not change further. These results indicate that the complexes **3-*Z*** and **3-*E*** are in equilibrium under the reaction conditions, as shown in eq 5. The ^{1}H NMR spectrum of the equilibrated mixture shows two singlets of CH_2−Pt hydrogens at δ 3.61 and 3.33 with large J(PtH) values (94 and 112 Hz, respectively). Since the ^{1}H NMR spectrum of an initial reaction mixture of CO with **2-*syn*** shows the signal at δ 3.61 at a higher intensity than that at δ 3.33, these peaks are assigned to **3-*Z*** and **3-*E***, respectively. Complexes **3-*E*** and **3-*Z*** exhibit vinylic hydrogen signals at δ 6.79 and 6.88. The J(PtH) value (22 Hz) of **3-*E*** is larger than that of **3-*Z*** (17 Hz), which

(9) Huang, L.; Ozawa, F.; Osakada, K.; Yamamoto, A. *J. Organomet. Chem*. **1990**, *383*, 587.

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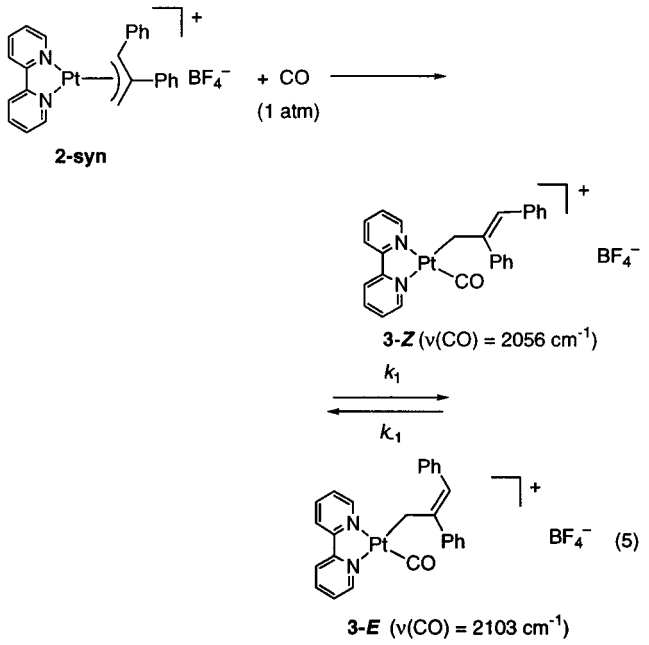
(11) For the related insertion of the C=C double bond of allene into Pd−X and Pt−X bonds (X = R, Cl, etc.), see: Powell, P. Synthesis of η^3-Allyl Complexes. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S. Eds.; Wiley: New York, 1982; pp 355−357. Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. D* **1970**, 598. Stevens, R. R.; Shier, G. D. *J. Organomet. Chem*. **1970**, *21*, 495. Hughes, R. P.; Powell, J. *J. Organomet. Chem*. **1972**, *34*, C51. Hughes, R. P.; Powell, J. *J. Organomet. Chem*. **1973**, *60*, 409. May, C. J.; Powell, J. *J. Organomet. Chem*. **1980**, *184*, 385.



is consistent with the above assignment of the isomers. These results suggest that the (σ-allyl)platinum complex with an *E* configuration is thermodynamically more stable than the *Z* isomer that is initially formed via carbonylation of **2-*syn***. Figure 2a depicts a linear first-order plot of the reaction, indicating that the isomerization obeys the first-order kinetics of the complex. The sum of the rate constants of the forward and reverse reactions, ($k_1 + k_{-1}$ in eq 5) is 2.0×10^{-3} s^{-1} under CO at 22 °C. The reaction under argon at the same temperature occurs at a rate ($k_1 + k_{-1} = 1.7 \times 10^{-3}$ s^{-1}) similar to that in CO. The small difference of the rate constants between the reaction under argon and that under CO is assigned to slow conversion of the (σ-allyl)-platinum complex in part to form **2-*syn*** irreversibly during the reaction under argon.

The structural change between **3-*E*** and **3-*Z*** should involve syn−anti isomerization of a (π-allyl)platinum intermediate, although the square-planar π-allyl complexes **2-*syn*** and **2-*anti*** isomerize with a much slower reaction rate. Scheme 1 depicts a plausible mechanism of the isomerization to account for the above results. Complex **3-*Z***, which is formed from the reaction of CO with **2-*syn***, is equilibrated with an intermediate square-pyramidal (π-allyl)platinum complex containing a carbonyl ligand (**A**), although trigonal-bipyramidal organoplatinum complexes with a 2,9-dimethylphenanthroline ligand were reported.[3] The coexistence of π-allyl and bipyridine ligands in **A** renders the square-planar coordination more stable than the trigonal-bipyramidal structure. The intermediate **A** undergoes the syn−anti isomerization more rapidly than complex **2** with a square-planar coordination. Partial loss of the carbonyl ligand from **A** produces **2-*syn***, which is much slower than the isomerization between **3-*E*** and **3-*Z*** both under argon and under CO.

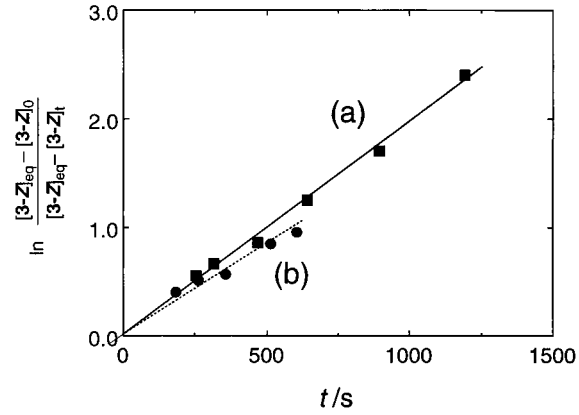
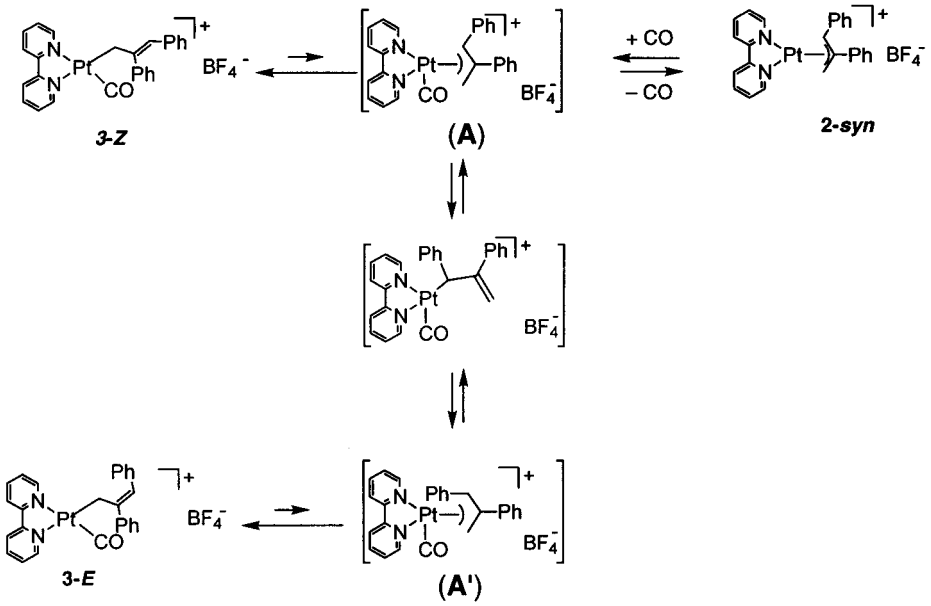


Figure 2. First-order plots of the isomerization of **3-*Z*** to **3-*E*** (a) under CO and (b) under argon. The reaction was carried out in an NMR tube at 22 °C.

Oxidative Addition of MeI to 1. Oxidative addition of MeI to dimethyl- or diphenylplatinum(II) complexes produces octahedral triorganoplatinum(IV) complexes with a halogeno ligand.[1,12−17] They are currently used in the synthesis of organometallic polymers containing Pt centers. The cationic monoorganoplatinum(II) complexes seem to have a more electrophilic metal center

Scheme 1



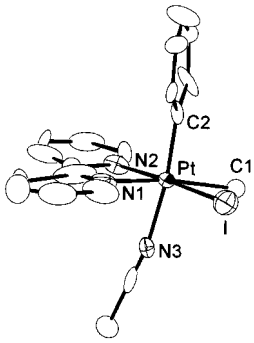
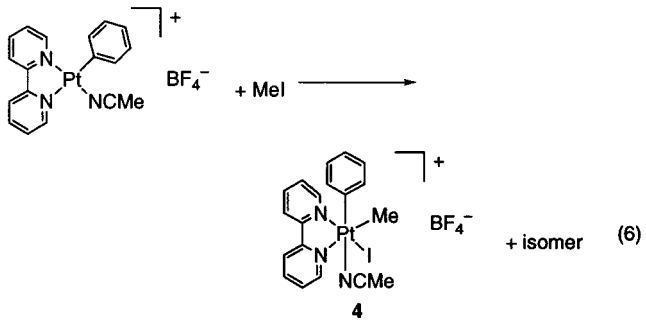


Figure 3. ORTEP drawing of **4** (30% probability). Selected bond lengths (Å) and angles (deg): Pt−I = 2.581(3), Pt−N1 = 2.19(2), Pt−N2 = 2.05(3), Pt−N3 = 2.08(3), Pt−C1 = 2.25(2), Pt−C2 = 2.01(3); I−Pt−N1 = 97.5(7), I−Pt−N2 = 175.8(8), I−Pt−N3 = 94.9(9), I−Pt−C1 = 73.2(4), I−Pt−C2 = 92.4(9), N1−Pt−N2 = 79(1), N1−Pt−C1 = 167.9(7), N2−Pt−C1 = 111.3(9), N3−Pt−C2 = 172(1).

and undergo oxidative addition of MeI less easily than do the neutral diorganoplatinum complexes. The reaction of MeI with **1-MeCN** takes place slowly at room temperature to produce Pt(IV) complexes after 9 days (eq 6). One of the products, complex **4**, was isolated as



single crystals and characterized by X-ray crystallography. The other isomer formed in the reaction mixture was not isolated or characterized unambiguously. Figure 3 depicts the molecular structure of **4** with an octahedral coordination around the Pt center. The phenyl and methyl ligands are situated at cis positions in order to minimize the mutual trans effects. Complex **4** has methyl and iodo ligands at cis positions, which is not consistent with the trans stereochemistry of the oxidative addition of MeI to a late-transition-metal center.[1,12a] This suggests the occurrence of isomerization of the initial product with a labile MeCN ligand into **4**.

In summary, the cationic phenylplatinum(II) complex with 2,2′-bipyridine exhibits different reactivities in insertion of small molecules into the Pt−C bond depending on the coordinated solvent ligands. It undergoes unprecedented oxidative addition of MeI to afford the Pt(IV) complex with phenyl, methyl, and iodo ligands. Allene inserts into the Pt(II)−phenyl bond to form (π-allyl)platinum complexes whose structures are similar to the palladium analogue reported previously. The (π-allyl)platinum complex formed via insertion of allene into the Pt(II)−phenyl bond reacts with CO to afford the (σ-allyl)platinum complex, which undergoes cis−trans isomerization via the (π-allyl)platinum intermediate with a carbonyl ligand.

Experimental Section

General Consideration, Measurement, and Materials. Manipulations of the platinum complexes were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were purified in the usual manner and stored under argon. The other chemicals were commercially available. NMR spectra were recorded on JEOL EX-400 and Varian MERCURY300 spectrometers. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of [PtPh(NCMe)(bpy)]BF_4 (1-MeCN). To a MeCN (2 mL) solution of $PtPh_2$(bpy) (45.4 mg, 0.090 mmol) was added an Et_2O solution of HBF_4 (54 wt % Et_2O solution, 12 μL, 0.087 mmol) dropwise at 0 °C. The reaction mixture was stirred continuously for 1 h. Et_2O (25 mL) was added to the mixture to induce separation of a colorless solid. The solid product was collected by filtration and dried in vacuo to give **1-MeCN** as an off-white solid (35.3 mg, 71%). **1-MeCN** was prepared also from the reaction of PtI(Ph)(bpy) with $AgBF_4$ in MeCN (57%). Anal. Calcd for $C_{18}H_{16}BF_4N_3Pt$: C, 38.87; H, 2.90; N, 7.55. Found: C, 38.89; H, 3.12; N, 7.69. ^{1}H NMR (300 MHz, CD_3CN): δ 2.52 (s, CH_3CN, J(PtH) = 14 Hz), 7.08 (m, 1H, C_6H_5-*p*), 7.15 (m, 2H, C_6H_5-*m*), 7.35 (d, 2H, C_6H_5-*o*, J(HH) = 7 Hz, J(PtH) = 39 Hz), 7.48 (ddd, 1H, H5′-bpy, J(HH) = 8, 6, 2 Hz), 7.82 (ddd, 1H, H5-bpy, J(HH) = 7, 5, 2 Hz), 8.24 (ddd, 1H, H4′-bpy, J(HH) = 8, 8, 2 Hz), 8.29* (1H, H6′-bpy), 8.32* (H3′-bpy), 8.34 (ddd, 1H, H4-bpy, J(HH) = 7, 7, 2 Hz), 8.39 (1H, H3-bpy), 8.89 (d, 1H, H6-bpy, J(HH) = 5 Hz). The peaks with asterisks are overlapped significantly with other signals.

Preparation of [PtPh(acetone)(bpy)]BF_4 (1-acetone). To PtI(Ph)(bpy) (190 mg, 0.34 mmol) dispersed in acetone (1 mL) was slowly added an acetone solution of $AgBF_4$ (equimolar to the Pt complex) to induce dissolution of the Pt complex, a color change from yellow to orange, and separation of AgI. After 5 min of the reaction, insoluble AgI was removed by filtration. Reducing of the solvent under vacuum and subsequent addition of Et_2O to the product caused separation of a yellow solid that was dried in vacuo to give **1-acetone** (141 mg, 72%). ^{1}H NMR (400 MHz, acetone-d_6): δ 2.08 (s, solvent), 7.04 (m, 1H, C_6H_5-*p*), 7.13 (m, 2H, C_6H_5-*m*), 7.30 (m, 2H, C_6H_5-*o*, J(PtH) = 33 Hz), 7.64 (ddd, 1H, H5′-bpy, J(HH) = 8, 6, 2 Hz), 7.91 (ddd, 1H, H5-bpy, J(HH) = 8, 5, 1 Hz), 8.40 (1H, H4′-bpy), 8.42 (1H, H4-bpy), 8.53 (dd, 1H, H3-bpy, J(HH) = 5, 1 Hz), 8.57−8.60 (1H, H6′-bpy), 8.59−62 (1H, H3′-bpy), 8.66 (d, 1H, H6-bpy, J(HH) = 8 Hz).

Attempts to purify **1-acetone** by recrystallization from acetone−Et_2O were not successful, probably due to the exchange of the coordinated acetone with water contained in the acetone during recrystallization and the lower solubility of **1-H_2O** as compared to **1-acetone**. The obtained analytical results suggest the formation of [PtPh(H_2O)(bpy)]BF_4 (**1-H_2O**). Anal. Calcd for $C_{16}H_{15}BF_4N_2OPt$: C, 36.04; H, 2.84; N, 5.25. Found: C, 36.49; H, 3.33; N, 4.92. The reaction of PtI(Ph)(bpy) with $AgBF_4$ in the presence of D_2O produced [PtPh(D_2O)(bpy)]BF_4 (**1-D_2O**), which exhibited the NMR signals at posi-

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tions different from those of **1-acetone**. To PtI(Ph)(bpy) (34.6 mg, 0.0623 mmol) and $AgBF_4$ (16.4 mg, 0.0845 mmol) dispersed in acetone-d_6 (0.7 mL) was added slowly to cause dissolution of the Pt complex and separation of AgI. After 5 min of stirring at room temperature, D_2O (40 μL, 2.0 mmol) was added. Insoluble AgI was removed by filtration before the ^{1}H NMR was measured. ^{1}H NMR (300 MHz, acetone-d_6): δ 6.97 (m, 1H, C_6H_5-*p*), 7.07 (m, 2H, C_6H_5-*m*), 7.39 (m, 2H, C_6H_5-*o*, J(PtH) = 39 Hz), 7.57 (ddd, 1H, H5′-bpy, J(HH) = 8, 6, 2 Hz), 8.00 (ddd, 1H, H5-bpy, J(HH) = 8, 5, 1 Hz), 8.38 (ddd, 1H, H4′-bpy, J(HH) = 8, 8, 2 Hz), 8.43−8.45* (1H, H6′-bpy), 8.46 (ddd, 1H, H4-bpy, J(HH) = 8, 8, 2 Hz), 8.57 (m, 1H, H3-bpy), 8.66 (m, 1H, H3′-bpy), 8.89 (m, 1H, H6-bpy). The peaks with asterisks are overlapped significantly with other signals.

Reaction of CO (1 atm) with 1-CH_3CN and 1-acetone. An acetone (1.5 mL) solution of $AgBF_4$ (31.7 mg, 0.163 mmol) was added to PtI(Ph)(bpy) (87.6 mg, 0.158 mmol) at room temperature, which instantly caused separation of a white solid of AgI. After separation of AgI, CO (1 atm) was introduced to the solution containing **1-acetone**, which caused separation of a dark solid from the yellow solution. The formation of **1-CO** was completed within 3 h, on the basis of the results of ^{1}H NMR analyses of the reaction mixture. After the mixture was stirred continuously for 10 h, the solid product was removed by filtration, and the solvent was reduced under vacuum. Addition of Et_2O (40 mL) to the solution caused separation of a white solid that was dried in vacuo to give **1-CO** (52.6 mg, 61%). The reaction using CH_3CN as a solvent gave the same product in 5 days (55%). At this time, the reaction was not completed. The reaction in an NMR tube caused complete ligand substitution in 7 days. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.29* (1H, C_6H_5-*p*), 7.25−7.29* (2H, C_6H_5-*m*), 7.46 (m, 2H, C_6H_5-*o*, J(PtH) = 32 Hz), 7.55 (ddd, 1H, H5′-bpy, J(HH) = 7, 6, 1 Hz), 7.82−7.87* (1H, H5-bpy), 7.82−7.87* (1H, H6′-bpy), 8.39 (m, 1H, H4-bpy), 8.46 (m, 1H, H4′-bpy), 8.83−8.87* (1H, H3-bpy), 8.83−8.87*(1H, H3′-bpy), 8.83−8.87*(1H, H6-bpy). The peaks with asterisks are overlapped significantly with other signals. IR (KBr): ν(C≡O) 2120 cm^{-1}. Anal. Calcd for $C_{17}H_{13}BF_4N_2OPt$: C, 37.59; H, 2.41; N, 5.16. Found: C, 37.16; H, 2.69; N, 5.20.

Reaction of CO (30 atm) with 1-CH_3CN and 1-acetone. An acetone (10 mL) solution of $AgBF_4$ (53.5 mg, 0.275 mmol) was added to PtI(Ph)(bpy) (149 mg, 0.269 mmol) at room temperature, which instantly caused separation of AgI. After separation of AgI, the solution was stirred under CO (30 atm) for 13 h at room temperature. After the pressure was released, a black solid was generated. The solid was removed by filtration. The solvent was reduced under vacuum. Addition of Et_2O (40 mL) to the solution caused the separation of a white solid that was dried in vacuo to give a mixture of [Pt(COPh)(bpy)(CO)]BF_4 and **1-CO** in an 82:18 molar ratio (59.0 mg). ^{1}H NMR of [Pt(COPh)(bpy)(CO)]BF_4 in the mixture of the complexes (400 MHz, acetone-d_6): δ 7.29 (m, 1H, C_6H_5-*p*), 7.60 (m, 2H, C_6H_5-*m*), 7.97 (m, 1H, H5′-bpy), 8.08 (m, 1H, H5-bpy), 8.48 (d, 2H, C_6H_5-*o*, J(HH) = 7 Hz), 8.48 (d, 1H, H6′-bpy, J(HH) = 7 Hz), 8.59−8.61* (1H, H_4), 8.59−8.61* (1H, $H_{4'}$), 8.85−8.92* (1H, H_3), 8.85−8.92* (1H, $H_{3'}$), 9.19 (dd, 1H, H6-bpy, J(HH) = 5, 2 Hz). The peaks with asterisks are overlapped significantly with other signals. IR (KBr): ν(C≡O) 2066 cm^{-1}, ν(C═O) 1647 cm^{-1}.

Reaction of Phenylallene with 1-acetone. An acetone (3 mL) solution of $AgBF_4$ (133 mg, 0.68 mmol) was added to PtI(Ph)(bpy) (350 mg, 0.63 mmol) at room temperature. The resulting AgI was removed by filtration. To the solution containing **1-acetone** formed in situ was added phenylallene (40 μL, 0.64 mmol). The reaction mixture was stirred for 48 h. Evaporation of the solvent to ca. 1 mL and addition of Et_2O to the solution caused separation of a colorless solid that was collected by filtration and dried in vacuo. The NMR spectrum indicated the presence of syn and anti isomers of [Pt(η^3-CH_2-CPhCHPh)(bpy)]BF_4 (**2**). Anal. Calcd for $C_{25}H_{21}BF_4N_2Pt$: C, 47.56; H, 3.35; N, 4.44. Found: C, 47.29; H, 3.26; N, 4.41. Isolation of **2-*syn*** was carried out by the same reaction without stirring the solution. Allowing the solution of phenylallene with **1-acetone** to stand for 48 h led to the growth of colorless crystals that were collected by filtration and dried in vacuo to give **2-*syn*** (139 mg, 35%). ^{1}H NMR (400 MHz, CD_3CN): δ 3.69 (d, 1H, CH_2, J(HH) = 3 Hz, J(PtH) = 67 Hz), 4.07 (d, 1H, CH_2, J(HH) = 3 Hz, J(PtH) = 23 Hz), 4.55 (s, 1H, CHPh, J(PtH) = 70 Hz), 7.15−7.35* (11H, $2C_6H_5$, H5′-bpy), 7.44 (m, 1H, H6′-bpy, J(PtH) = 33 Hz), 7.80 (ddd, 1H, H5-bpy, J(HH) = 2, 5, 7 Hz), 8.19 (ddd, 1H, H4′-bpy, J(HH) = 2, 8, 8 Hz), 8.39* (1H, H4-bpy), 8.40* (1H, H3′-bpy), 8.46 (m, 1H, H3-bpy), 9.30 (dd, 1H, H6-bpy, J(HH) = 1, 5 Hz, J(PtH) = 35 Hz). The peaks with asterisks are overlapped significantly with other signals.

Thermal Isomerization of 2-*syn*. In an NMR tube was charged a CD_3CN (0.5 mL) solution of **2-*syn*** (12.4 mg, 0.0196 mmol) under Ar. The Pt complex was dissolved. The NMR tube was heated in an oil bath (50 °C) and stored when not being actively monitored. ^{1}H NMR spectra were checked occasionally. After reaction for 8 days, the ^{1}H NMR spectrum showed signals due to **2-*syn*** and **2-*anti*** in a 52:48 peak area ratio. ^{1}H NMR for **2-*anti*** (400 MHz, CD_3CN, obtained from the spectrum of the above mixture of **2-*syn*** and **2-*anti***): δ 3.48 (d, 1H, CH_2, J(HH) = 3 Hz, J(PtH) = 71 Hz), 4.42 (dd, 1H, CH_2, J(PtH) = 23 Hz), 6.39 (s, 1H, CHPh, J(PtH) = 42 Hz), 7.15−7.35* (10H, $2C_6H_5$), 7.41−7.48* (1H), 7.28−7.70* (2H), 7.83 (ddd, 1H, J(HH) = 2, 5, 7 Hz), 8.31 (ddd, 1H, J(HH) = 2, 8, 8 Hz), 8.35−8.45* (1H), 9.20 (m, 1H, J(PtH) = 34 Hz), 9.51 (m, 1H, J(PtH) = 33 Hz). The peaks with asterisks are overlapped significantly with other signals.

Reaction of CO with 2-*syn*. A CD_3CN (5 mL) solution of **2-*syn*** (10.4 mg, 0.017 mmol) in a flask was degassed by a pump-and-thaw cycle. CO (1 atm) was introduced into the flask, and the solution was stirred for ca. 5 min. A part of the deep yellow solution (0.5 mL) was transferred to an NMR tube under CO. The ^{1}H NMR spectrum indicates the formation of **3-*Z*** and **3-*E*** in a 72:28 molar ratio. The mixture of the original solution and that in the NMR tube was kept for 24 h at room temperature. Addition of Et_2O (20 mL) to the solution caused separation of a colorless solid that was isolated by decantation of the solvent. The ^{1}H NMR spectrum showed the existence of a mixture of **3-*Z*** and **3-*E*** in a 34:66 molar ratio. ^{1}H NMR of **3-*Z*** (400 MHz, CD_3CN): δ 3.61 (s, 2H, Pt−CH_2, J(PtH) = 94 Hz), 6.88 (s, 1H, CHPh, J(PtH) = 17 Hz, overlapped partly with aromatic hydrogen peaks). IR (KBr): ν(C≡O) 2056 cm^{-1}. ^{1}H NMR of **3-*E*** (400 MHz, CD_3CN): δ 3.33 (d, 2H, Pt−CH_2, J(HH) = 1 Hz, J(PtH) = 112 Hz), 6.79 (s, 1H, CHPh, J(PtH) = 22 Hz). IR (KBr): ν(C≡O) 2103 cm^{-1}. Isomerization of **3-*Z*** into **3-*E*** was monitored by the NMR measurement of the solution under CO or argon.

Reaction of MeI with 1-MeCN. To **1-MeCN** (38.0 mg, 0.068 mmol) were added MeCN (1 mL) and MeI (3.4 g, 24 mmol), in that order. Stirring the yellow solution for 9 days at room temperature caused separation of a yellow solid that was collected by filtration, washed with Et_2O, and dried in vacuo (20.5 mg). The ^{1}H NMR spectrum analyses of the solid indicated two signals at δ 1.82 (J(PtH) = 77 Hz) and 2.30 (J(PtH) = 67 Hz) due to $PtCH_3$ hydrogens and signals of **1-MeCN**. ^{1}H NMR of the major product (400 MHz, CD_3CN): δ 1.82 (J(PtH) = 77 Hz), 7.15−7.30 (5H, C_6H_5), 7.75 (ddd, 1H, H5′-bpy, J(HH) = 8, 6, 2 Hz), 7.95 (ddd, 1H, H5-bpy, J(HH) = 7, 5, 1 Hz), 8.20 (dd, 1H, H6′-bpy, J(HH) = 6, 1 Hz, J(PtH) = 39 Hz), 8.30−8.35 (1H, H4′-bpy), 8.40 (ddd, 1H, H4-bpy, J(HH) = 10, 8, 2 Hz), 8.54 (d, 1H, H3′-bpy, J(HH) = 8 Hz), 8.61 (d, 1H, H3-bpy, J(HH) = 8 Hz), 9.94 (m, 1H, H6-bpy, J(PtH) = 11 Hz). ^{1}H NMR of the minor product (400 MHz, CD_3CN): δ 8.92 (d, 1H, H6′-bpy, J(HH) = 5 Hz), 10.00 (d, 1H, H6-bpy, J(HH) = 4 Hz, J(PtH) = 38 Hz). Other signals were not assigned due to low intensity and overlapping of the peaks.

Crystal Structure Determination. Crystals of **2-*syn*** and **4** suitable for X-ray diffraction study were obtained by slow

Table 1. Crystallographic Data of 2-*syn* and 4

	2-*syn*	**4**
chem formula	$C_{25}H_{21}BF_4N_2Pt$	$C_{19}H_{19}BF_4IN_3Pt$
fw	631.35	698.18
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	10.276(1)	12.606(3)
b, Å	20.401(5)	9.844(3)
c, Å	12.001(1)	17.836(4)
β, deg	110.697(9)	99.42(2)
V, Å^3	2353.3(6)	2183.3(8)
Z	4	4
μ, mm^{-1}	5.985	7.859
F(000)	1216	1304
D_{calcd}, g cm^{-3}	1.782	2.124
cryst size, mm	0.75 × 0.15 × 0.15	0.25 × 0.15 × 0.15
2θ range, deg	5.0−55.0	5.0−55.0
no. of unique rflns	5574	5304
no. of used rflns ($I > 3.0\sigma(I)$)	2953	1880
no. of variables	298	257
R	0.067	0.079
R_w	0.068	0.057

evaporation of an acetone solution and by recrystallization from MeCN−Et_2O, respectively, and mounted in glass capillary tubes. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation (λ = 0.710 69 Å) and the $\omega-2\theta$ scan method, and an empirical absorption correction (Ψ scan) was applied. Scattering factors were taken from the literature.[18] Calculations were carried out using the program package TEXSAN for Windows. Atomic scattering factors were obtained from the literature. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement of the two complexes are summarized in Table 1.

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Supporting Information Available: Tables of atomic coordinates, isotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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