Formation of Metallacyclic Complexes by Activation of an Aryl C−H Bond in a Platinum−Safrole Analogue of Zeise's Salt

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*Summary: Potassium trichloro(safrole)platinate(II), K[Pt-(Saf)Cl$_3$] (**1**), reacts with piperidine to give cis-[Pt(Saf-1H)(Piperidine)Cl] (**2**). The interaction of **1** with AgNO$_3$, SnCl$_2$, KOH, and ethanol−water solutions leads to formation of the dinuclear chelate ring complex [Pt$_2$(Saf-1H)$_2$Cl$_2$] (**3**). ^{1}H and ^{13}C NMR spectra and single-crystal X-ray diffraction show that in complexes **2** and **3** deprotonated safrole is bound up with platinum(II) both at a benzene carbon and at the ethylenic double bond of the side chain.*

The activation of a C−H bond promoted by coordination to Pt is a topic of great interest in organometallic chemistry. Many examples of saturated and unsaturated hydrocarbon C−H activation have been seen,[1,2] but relatively few examples of aromatic hydrocarbon C−H activation have been reported.[3] In recent years there has been intense interest in platinum−olefin complexes.[4–6] Among arylolefin ligands, phenylethylene (styrene) and substituted phenylethylenes have been widely studied, but substituted phenylpropylenes (propenylbenzenes) are rare.[7,8] Substituted propenylbenzenes, which are easily available from natural resources, have been used as valuable starting materials in various synthetic processes. In many cases transition metal−olefin complexes are present as key intermediates.[9] This prompted us to synthesize a few series of platinum complexes with natural arylolefins and to find out if there are any activated C−H bonds in the resulting compounds which may be utilized for their functionalization.

Results and Discussion

For the reasons mentioned above, we have prepared potassium trichloro(safrole)platinate(II), K[Pt(Saf)Cl$_3$] (**1**), an analogue of Zeise's salt, where safrole is 4-allyl-1,2-methylenedioxybenzene (see the Experimental Section). The chloro ligand in the position trans to safrole in **1** is readily substituted by an amine (Am) in ethanol−water solution; thus, we obtained *trans*-[Pt(Saf)(Am)Cl$_2$] (Am = ammonia, dimethylamine, *o*-toluidine, *p*-toluidine, *o*-anisidine, *p*-anisidine, pyridine, quinoline).[10]

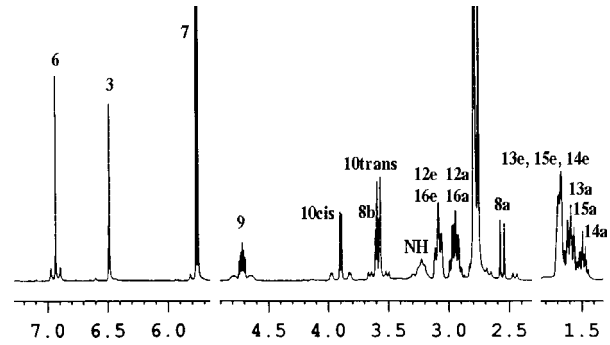

Figure 1. ^{1}H NMR spectrum of **2**.

It was a great surprise that the interaction between piperidine and K[Pt(Saf)Cl$_3$] (**1**) gave no *trans*-[Pt(Saf)(Piperidine)Cl$_2$] but an unexpected metallacyclic complex: compound **2** (see the Experimental Section).

In the ^{1}H NMR spectrum of **2** (Figure 1), there are only two singlets due to two aromatic protons of safrole. This indicates that one aromatic proton of safrole is lost and the coupling constant between the two remaining aromatic protons is equal to 0. The singlet at 6.93 ppm has two singlet satellites with a coupling constant between them of 47 Hz. This value is comparable in magnitude to $^3J_{PtH}$ in many platinum(II) complexes.[11,12] It is worth noting that the coordinated safrole undergoes loss of proton H-5 to form σ-bound (C-5)−Pt.

Furthermore, it is seen that in Figure 1, all signals of η^2-coordinated safrole and N-coordinated piperidine are present. On the basis of the IR and ^{1}H and ^{13}C NMR spectra and elemental analyses, we suggest that the formula of complex **2** is [Pt(Saf-1H)(Piperidine)Cl], corresponding to either **A** (cis form) or **B** (trans form) in Figure 2, where safrole is present as a chelating ligand.

In the NOESY spectrum of **2** there are no cross peaks between H−N, H-12, and H-16 of piperidine and either H-6 or H-3 of safrole. Three cross peaks between H−N, H-12, and H-16 of piperidine and H-10-cis of safrole show that piperidine is cis

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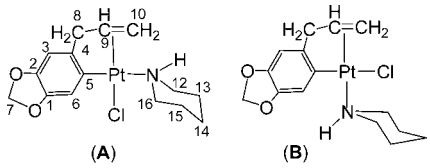

Figure 2. Two possible structures of **2**.

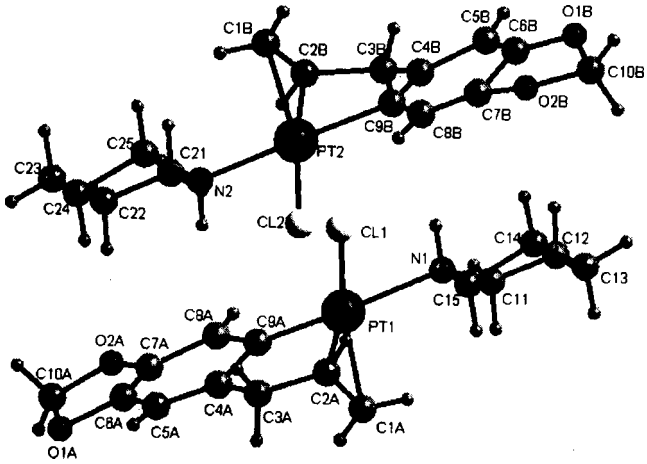

Figure 3. Complex **2**, existing in the crystal lattice as a racemate according to the chemical formula $C_{30}H_{40}Cl_2N_2O_4Pt_2$.

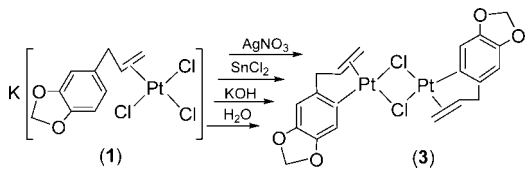

Figure 4. Formation and structure of **3**.

to the ethylenic double bond of safrole. These indicate that **2** have structure **A** (cis form). The single-crystal X-ray diffraction data (see Figure 3 and the Experimental Section) also indicate that **2** has structure **A** (cis form). This brings up the following question: why is the piperidine not trans to the ethylenic double bond (formula **B** in Figure 2) but rather in the cis position (formula **A** in Figure 2)?

We predicted that the formation of the Pt−(C-5) bond precedes the formation of the Pt−N bond: i.e., upon formation of **2**, a deprotonation of H-5 occurs first, and then the replacement of Cl with piperidine takes place. We carried out some reactions of complex **1** with $AgNO_3$ solution, $SnCl_2$ solution, KOH solution, and ethanol−water solution and obtained only one crystalline product: compound **3** (see the Experimental Section).

In the ^{1}H NMR spectrum of **3**, all resonances of coordinated safrole in complex **3** resemble those in complex **2**, suggesting that a chelating safrole is present in both complexes. The molecular mass of **3** (from ESI MS) shows that it associates with a dinuclear complex.

On the basis of the IR and ^{1}H and ^{13}C NMR spectra, ESI MS, and elemental analysis (see the Experimental Section), we suggest that complex **1** underwent a loss of HCl to form the dinuclear compound $[Pt_2(Saf\text{-}1H)_2Cl_2]$ (**3** in Figure 4).

In the formation of compound **3** (Figure 4), $AgNO_3$ and $SnCl_2$ facilitate the elimination of Cl^- from **1** due to generation of a precipitate of AgCl and stable $[SnCl_3]^-$, respectively, and KOH and H_2O facilitate the elimination of H^+ from **1** due to generation of H_2O and solvated H_3O^+, respectively. The reaction of **3** with piperidine afforded the same species as complex **2** (see the Experimental Section); therefore, we suggest that the dinuclear complex **3** is the intermediate compound leading to **2** from complex **1** and piperidine.

It is noted that compounds with transition-metal−C_{aryl} bonds usually obtained by arylation of transition-metal halides, acetates, alkoxides, and so on with aryls of Li, Mg, Zn, Al, Sn, and Hg. The direct substitution of H at the benzene ring by Pt occurs when benzene is coordinated with the metal in very few cases: for instance, in ref 3. It is of interest that, in complex **1**, not allyl C−H but aryl C−H has been activated.

Experimental Section

General Considerations and Instrumentation. The IR spectra were recorded on an IMPACK-410 Nicolet spectrometer with KBr disks in the range 400−4000 cm^{-1}. The NMR spectra were recorded on a Bruker AVANCE 500 MHz instrument, all at 298−300 K, in CD_3COCD_3, with TMS as the internal standard. ESI MS was recorded on an 1100 LC-MSD-Trap-SL instrument. Single-crystal X-ray diffraction data were recorded on a Bruker-AXS diffractometer at the Institute Bio-Nano Technology, Ewha Womans University, Seoul, Korea.

Preparation. K[Pt(Saf)Cl$_3$] (1). To a stirred solution of 3.68 g (10 mmol) of Zeise's salt in 80 mL of ethanol was slowly added a solution of 2.2 mL (15 mmol) of safrole in 20 mL of ethanol. The reaction mixture was stirred at 40−45 °C for 1 h; it was then cooled to room temperature. Yellow crystals were collected, washed with cool water and cool ethanol, and then dried under vacuum at 50 °C for 2 h. The yield was 4.25 g (85%). ^{1}H NMR (δ (ppm), J (Hz)): 7.04 (d, ^4J = 1.5, 1H, H-3), 6.88 (dd, ^3J = 8, ^4J = 1.5, 1H, H-5), 6.76 (d, ^3J = 8, 1H, H-6), 5.94 (s, 2H, H-7), 2.96 (dd, ^2J = 15, ^3J = 8, 1H, H-8a), 3.43 (dd, ^2J = 15, ^3J = 6, 1H, H-8b), 4.98 (m, $^2J_{PtH}$ = 70, 1H, H-9), 4.25 (dd, ^3J = 13, ^4J = 2 and $^2J_{PtH}$ = 65, 1H, H-10-trans), 4.11 (dd, ^3J = 7.5, ^2J = 2, and $^2J_{PtH}$ = 70, 1H, H-10-cis). ^{13}C NMR (δ (ppm)): 147.56 (C-1), 149.11 (C-2), 110.27 (C-3), 134.42 (C-4), 122.88 (C-5), 109.14 (C-6), 102.11 (C-7), 40.32 (C-8), 91.42 (C-9), 65.34 (C-10). Anal. Calcd for $KPtC_{11}H_{14}O_2Cl_3$: Pt + 1/2K_2SO_4, 51.23; C, 23.88; H, 2.01. Found: Pt + 1/2K_2SO_4, 51.55; C, 23.65; H, 2.24. IR (cm^{-1}): 3080, 3017, 2874 (ν_{CH}); 1510, 1486 ($\nu_{C=C}$).

[Pt(Saf-1H)(Piperidine)Cl] (2). Solution A consists of 503 mg (1 mmol) of K[Pt(Saf)Cl$_3$] (**1**) in 20 mL of 60% by volume aqueous EtOH. A solution of 0.6 mL (6 mmol) of piperidine in 8 mL of 25% by volume aqueous EtOH was added to solution A and stirred at 40−45 °C for 4 h. The resulting yellow precipitate was collected, washed with a solution of 0.1 N HCl, cool water, and cool ethanol, and recrystallized from EtOH/$CHCl_3$ (1/2 by volume). The light yellow crystals were dried under vacuum at 50 °C for 2 h. The yield was 100 mg (20%). Crystal data: centric, space group $P\bar{1}$; a = 8.586(2) Å, b = 8.699(2) Å, c = 11.006(3) Å, α = 67.761(4)°, β = 85.046(4)°, γ = 82.433(4)°, V = 753.6(3) Å^3; formula weight 953.72. Important distances (Å) and angles (deg): Pt1−C1A = 2.09, Pt1−C2A = 2.17, Pt1−C9A = 1.84, Pt1−N1 = 2.19, Pt1−Cl1 = 2.339; C9A−Pt1−C1A = 85.6, C9A−Pt1−N1 = 177.2, C9A−Pt1−C2A = 80.0, C1A−Pt1−C2A = 40.9, N1−Pt1−C2A = 101.8, C9A−Pt1−Cl1 = 95.3, C1A−Pt1−Cl1 = 153.9, N1−Pt1−Cl1 = 82.5, C2A−Pt1−Cl1 = 164.7. IR (cm^{-1}): 3225 (ν_{NH}); 3053, 2931, 2863 (ν_{CH}); 1611, 1490 ($\nu_{C=C}$). ^{1}H NMR (δ (ppm), J (Hz)): 6.49 (s, 1H, H-3), 6.93 (s, $^3J_{PtH}$ = 47, 1H, H-6), 5.77 (d, ^2J =1.5, 1H, H-7a), 5.75 (d, ^2J = 1.5, 1H, H-7b), 2.56 (d, ^2J = 17, 1H, H-8a), 3.61 (d, ^2J = 17, 1H, H-8b), 4.72 (m, $^2J_{PtH}$ = 73, 1H, H-9), 3.58 (dd, ^3J = 13, ^4J = 1, $^2J_{PtH}$ = 72, 1H, H-10-trans), 3.90 (d, ^3J = 8, $^2J_{PtH}$ = 76, 1H, H-10-cis), 2.93−3.09 (m, 4H, H-12, H-16), 1.58−1.70 (m, 4H, H-13, H-15), 1.48 (m, 2H, H-14), 3.24 (s, 1H, NH). ^{13}C NMR (δ (ppm)): 143.95 (C-1), 146.13 (C-2), 105.45 (C-3), 141.54 (C-4), 125.08 (C-5), 114.99 (C-6), 100.52 (C-7), 39.53

(C-8), 86.45 (C-9), 60.05 (C-10), 50.23, 49.53 (C-12, C-16), 27.85, 27.76 (C-13, C-15), 24.54 (C-14). Anal. Calcd for $PtC_{15}H_{20}NO_2Cl$: Pt, 40.91; C, 37.77; H, 4.23. Found: Pt, 40.62; C, 37..91; H, 4.56.

Compound **2** was also prepared by addition of a solution of 0.13 mL (1.3 mmol) of piperidine in 15 mL of acetone to a mixture of 392 mg (0.5 mmol) of $[Pt_2(Saf\text{-}1H)_2Cl_2]$ (**3**) and 15 mL of acetone followed by agitation. The yield was 390 mg (80%). IR and ^1H and ^{13}C NMR spectra are the same as those of the product from **1** and piperidine.

$[Pt_2(Saf\text{-}1H)_2Cl_2]$ (3). Solution B consisted of 503 mg (1 mmol) of $K[Pt(Saf)Cl_3]$ in 40 mL of 65% by volume aqueous EtOH.

Variant 1. A solution of $AgNO_3$ (230 mg, 1.35 mmol) in 10 mL of 33% by volume aqueous EtOH was slowly added to solution B and the mixture stirred at 25−30 °C for 1 h. The resulting precipitate was collected and washed with cool water−ethanol. The precipitate was treated with $CHCl_3$, and the AgCl was filtered off. The filtrate was evaporated at room temperature until a yellow precipitate formed. The precipitate was filtered, washed with cool chloroform, and dried under vacuum at 50 °C for 2 h. The yield was 106 mg (27%). IR (cm^{-1}): 3063, 3010, 2888, 2823 (ν_{CH}); 1598, 1455 ($\nu_{C=C}$). ^1H NMR (δ (ppm), J (Hz)): 6.66 (s, 1H, H-3), 6.76 (s, $^3J_{PtH} = 40$, 1H, H-6), 5.83 (s, 1H, H-7a), 5.84 (s, 1H, H-7b), 2.76 (d, $^2J = 17$, 1H, *H*-8a), 3.66 (dd, $^2J = 17$, $^3J = 4.5$, 1H, H-8b), 5.08 (m, $^3J_{PtH} = 75$, 1H, H-9), 3.94 (d, $^3J = 17$, $^3J_{PtH} = 75$, 1H, H-10-trans), 4.30 (d, $^3J = 5.5$, $^3J_{PtH} = 75$, 1H, H-10-cis). ^{13}C NMR (δ (ppm)): 143.03 (C-1), 145.72 (C-2), 105.23 (C-3), 140.54 (C-4), 133.14 (C-5), 112.82 (C-6), 99.84 (C-7), 37.68 (C-8), 95.52 (C-9), 67.42 (C-10). Anal. Calcd for $Pt_2C_{20}H_{18}O_4Cl_2$: Pt, 49.81; C, 30.65; H, 2.30. Found: Pt, 49.62; C, 30..91; H, 2.56.

Variant 2. A solution of 190 mg (1 mmol) of $SnCl_2$ in 40 mL of 10% by volume aqueous EtOH was slowly added to solution B with stirring at 25−30 °C for 3 h. The resulting precipitate was collected, washed with cool water, cool acetone, and cool chloroform, and dried under vacuum at 50 °C for 2 h. The yield was 200 mg (51%). The IR and ^1H NMR spectra are the same as spectra of the product from variant 1.

Variant 3. A 1 mL portion of 0.1 M KOH solution was added dropwise to solution B with stirring at 25−30 °C for 3 h. The resulting precipitate was collected, washed with cool water, cool acetone, and cool chloroform, and dried under vacuum at 50 °C for 2 h. The yield was 75 mg (19%). The IR and ^1H NMR spectra are the same as spectra of the product from variant 1.

Variant 4. $K[Pt(Saf)Cl_3]$ (503 mg, 1 mmol) was dissolved in 60 mL of 10% by volume aqueous EtOH. The solution was stirred at 25−30 °C for 2 h and then at 60−65 °C for an additional 6 h. The resulting precipitate was collected, washed with cool water, cool acetone, and cool chloroform, and dried under vacuum at 50 °C for 2 h. The yield was 251 mg (64%). The IR and ^1H NMR spectra are the same as spectra of the product from variant 1.

Supporting Information Available: A CIF file giving X-ray crystal data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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