C-H Bond Activation of the Ferrocenyl Group in the Reaction of σ-Ferrocenylplatinum Complex with Dimethyl or Diethyl Acetylenedicarboxylate

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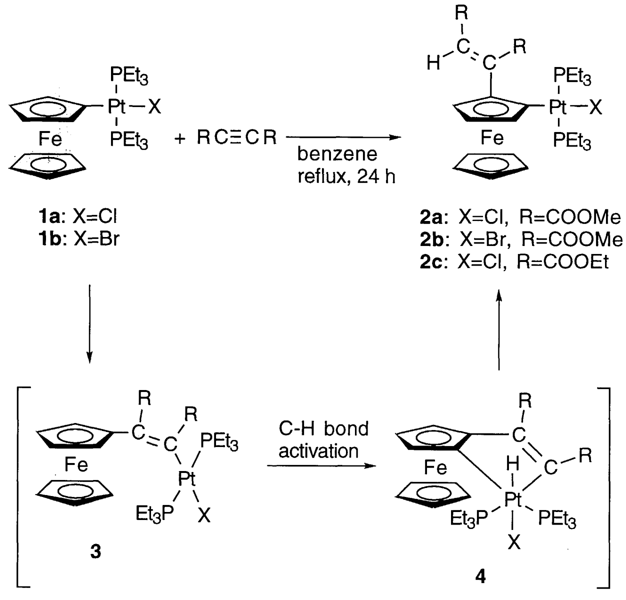
The treatment of σ-ferrocenylplatinum complex with dimethyl or diethyl acetylenedicarboxylate results in the formal insertion of acetylene into the C-H bond at the 2-position of the ferrocenyl group to yield a racemic mixture of σ-(2-ethenyl)ferrocenylplatinum complex (**2**). Characterization of complex **2** was performed by spectroscopic and X-ray diffraction analyses.

The activation of C-H bond using transition metal is a quite interesting area in organometallic chemistry and successfully used in organic synthesis.[1] Especially there are a lot of reports on the intramolecular cyclometallation of the palladium or platinum complexes.[2,3] In those reactions a metal atom having +II oxidation state makes an electrophilic attack to the carbon atom and the hydrogen atom dissociates as a proton with an anionic ligand on the metal. In the course of our study on the σ-ferrocenylplatinum complexes,[4] we found the formal insertion of dimethyl or diethyl acetylenedicarboxylate into the C-H bond at the 2-position of the ferrocenyl group.

On treatment of complex **1a** with an equimolar amount of dimethyl acetylenedicarboxylate in refluxing benzene for 24 h red crystals of **2a** were isolated in 25% yield.[5] Similar treatment of **1b** with dimethyl acetylenedicarboxylate gave **2b** in 21% yield[6] and the reaction of **1a** with diethyl acetylenedicarboxylate afforded **2c** in 19% yield,[7] respectively. However, in the reaction of **1a** with methyl propiolate or methyl 2-butynoate no insertion product was detected. It should be noted that dimethyl acetylenedicarboxylate did not insert into the Pt-C bond of an analogous phenylplatinum complex *trans*-PhPt(PBu$_3$)$_2$Cl and the unreacted starting complex was recovered, suggesting that the reactivity of ferrocenylplatinum complex toward acetylene is higher than that of phenylplatinum complex.



The IR spectrum of **2a** exhibited an absorption assignable to ν(C=C) at 1600 cm^{-1} along with two ν(C=O) absorptions at 1735 and 1705 cm^{-1}, respectively. The ^{1}H NMR spectrum showed three resonances at δ 4.55, 4.45 and 4.09 corresponding to the protons of the substituted cyclopentadienyl ring and a signal of the olefin proton at δ 7.93. In the ^{13}C NMR spectrum of **2a** two signals characteristic of the olefin carbon were detected at δ 155.1 and 112.2, and five resonances attributed to the substituted cyclopentadienyl carbons were observed at δ 84.3, 79.6, 78.8, 70.0 and 68.9, respectively. These data suggest that the acetylene inserts into the C-H bond of the cyclopentadienyl group instead of the Pt-C bond. The ^{31}P NMR exhibited an AB quartet at δ 16.37 ($^1J_{\mathrm{PtP}}$=2631, $^2J_{\mathrm{PP}}$=421 Hz) and 13.41 ($^1J_{\mathrm{PP}}$=2708, $^2J_{\mathrm{PP}}$=421 Hz), indicating that two magnetically unequivalent phosphine ligands coordinate to the platinum atom in mutually *trans* configuration.

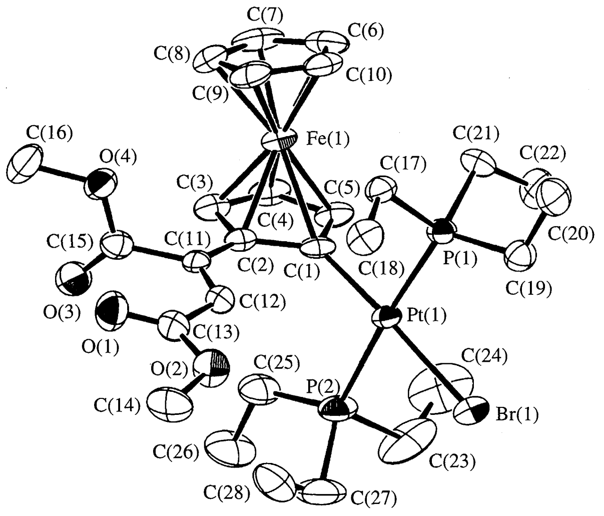


Figure 1. Perspective view of complex **2b**; selected bond distances (Å) and angles (°): Pt(1)-Br(1) 2.509(1), Pt(1)-P(1) 2.285(2), Pt(1)-P(2) 2.318(2), Pt(1)-C(1) 2.056(7), Fe(1)-C(1) 2.163(6), Fe(1)-C(2) 2.048(7), Fe(1)-C(3) 2.000(8), Fe(1)-C(4) 2.019(7), Fe(1)-C(5) 2.074(7), Br(1)-Pt(1)-P(1) 91.58(6), Br(1)-Pt(1)-P(2) 85.44(7), Br(1)-Pt(1)-C(1) 173.8(2), P(1)-Pt(1)-P(2) 176.20(9), P(1)-Pt(1)-C(1) 93.5(2), P(1)-Pt(1)-C(2) 89.3(2).

In order to determine the structure of **2b**, an X-ray crystallography was carried out and the molecular structure is shown in Figure 1.[8] The alkenyl group having two carbomethoxy groups at mutually *cis* position is linked to the α-

carbon of cyclopentadienyl group with relative to the platinum moiety which has a square-planer geometry. Therefore, the rotation around the Pt-C bond is inhibited by the steric hindrance and the two phosphorous atoms are not magnetically equivalent as observed in ^{31}P NMR. Although the molecule possessing the disubstituted π-cyclopentadienyl ligand has planar chirality, both enantiomers are present in the centrosymmetric unit cell of **2b**. The Pt(1)-C(1) bond length is 2.056(7) Å, which is slightly longer than those of the other σ-ferrocenylplatinum complexes[9] but comparable to that of $\{C_5H_4Pt(COD)Cl\}Mn(CO)_3$.[10] The coordination plane around the Pt atom is almost perpendicular to the coordinated cyclopentadienyl ring. The plane of the alkenyl group is essentially coplanar with the cyclopentadienyl ring consisting of C(1)-C(5) and the plane of a carbonyl group containing C(12), C(13), O(1) and O(2), but the plane of the other carbonyl group composed of C(11), C(15), O(3) and O(4) has a perpendicular conformation with respect to the olefin plane owing to the steric hindrance between the two carbonyl groups. The tilt angle between the two cyclopentadienyl rings of 1,2-ferrocenediyl group is 13.7°, which is larger than those of the other σ-ferrocenylplatinum complexes[9]. Various Fe-C bond distances were observed in the substituted cyclopentadienyl ring and the largest one is the Fe(1)-C(1) length of 2.163(6) Å, while the Fe(1)-C bond lengths of non-substituted cyclopentadienyl group lie in the range of 2.029(8)-2.046(8) Å. These phenomena are due to the steric effect of the bulky platinum moiety.

We believe that in the first step of the reaction described here, the acetylene inserts into the Pt-C bond to produce an (alkenyl)-ferrocenylplatinum complex (**3**). Then the C-H bond activation of the ferrocenyl group causes the formation of a five membered platinacycle (**4**) followed by the reductive elimination of the alkenyl group and the hydride to yield **2**. Though it was recently reported that the similar C-H bond activation of the phenyl ring in the cationic phenyl-palladium or -ruthenium complexes with norbornene or diphenylacetylene,[11] there is no instance of the C-H activation of analogous platinum complexes. Furthermore in most of the cyclometallation of the platinum metals, the substrate coordinate to the metal by a hetero atom such as nitrogen, and the metallacycle containing hetero atoms was produced by the intramolecular C-H bond activation. But in our system the ferrocenyl group, of which C-H bond is activated, is linked to platinum by a M-C σ-bond; the high electron density of cyclopentadienyl group may enable the electrophilic attack by a platinum atom. Complex **2** still has a M-C σ-bond, thus we are going to examine further reaction of **2** with acetylene.

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References and Notes

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5 Spectroscopic data for **2a**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H, =CH), 4.55 (t, J=2 Hz, 1H, C_5H_3), 4,45 (s, 1H, C_5H_3), 4.09 (s, J_{PtH}=35 Hz, C_5H_3), 4.00 (s, 5H, C_5H_5), 3.96 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.61-2.15 (m, 6H, CH_2), 1.46-1.35 (m, 6H, CH_2), 1.35-1.24 (m, 9H, CH_3), 0.94-0.86 (m, 9H, CH_3); ^{13}C NMR (100 MHz, C_6D_6): δ 169.5 (s, CO), 166.3 (s, CO), 155.1 (s, =C), 112.2 (s, =CH), 84.3 (t, J_{PC}=9 Hz, ipso C of C_5H_3 bound to Pt), 79.7 (s, J_{PtC}=32 Hz, ipso C of C_5H_3 bound to -C=C), 78.8 (s, J_{PtC}=54 Hz, C_5H_3), 71.1 (s, C_5H_5), 70.0 (s, J_{PtC}=69 Hz, C_5H_3), 68.9 (s, J_{PtC}=43 Hz, C_5H_3), 52.1 (s, OCH_3), 51.0 (s, OCH_3), 13.6 (dd, $^1J_{PC}$=22 Hz, $^3J_{PC}$=12 Hz, CH_2), 12.9 (dd, $^1J_{PC}$=22 Hz, $^3J_{PC}$=12 Hz, CH_2), 7.8 (s, CH_3), 7.7 (s, CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, H_3PO_4 reference): δ 16.37 (d, $^1J_{PtP}$=2631 Hz, $^2J_{PP}$=421 Hz), 13.41 (d, $^1J_{PtP}$= 2708 Hz, $^2J_{PP}$=421 Hz). Anal. Found: C, 42.59; H, 5.68; Cl, 4.57; P, 7.72%. Calcd for $C_{28}H_{45}ClFeO_4P_2Pt$: C, 42.36; H, 5.71; Cl, 4.47; P, 7.80%.

6 Spectroscopic data for **2b**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H, =CH), 4.57 (t, J=2 Hz, 1H, C_5H_3), 4,47 (s, 1H, C_5H_3), 4.09 (s, J_{PtH}=33 Hz, 1H, C_5H_3), 4.01 (s, 5H, C_5H_5), 3.96 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.70-2.20 (m, 6H, CH_2), 1.52-1.39 (m, 6H, CH_2), 1.31-1.23 (m, 9H, CH_3), 0.93-0.85 (m, 9H, CH_3); ^{13}C NMR (100 MHz, C_6D_6): δ 169.4 (s, CO), 166.3 (s, CO), 154.8 (s, =C), 112.2 (s, =CH), 87.2 (t, J_{PtC}=10 Hz, ipso C of C_5H_3 bound to Pt), 79.9 (s, J_{PtC}=40 Hz, ipso C of C_5H_3 bound to -C=C), 78.6 (s, J_{PtC}=56 Hz, C_5H_3), 71.2 (s, C_5H_5), 69.8 (s, J_{PtC}=69 Hz, C_5H_3), 68.9 (s, J_{PtC}=46 Hz, C_5H_3), 52.1 (s, OCH_3), 51.1 (s, OCH_3), 14.2 (dd, $^1J_{PC}$=22 Hz, $^3J_{PC}$=12 Hz, CH_2), 13.7 (dd, $^1J_{PC}$=23 Hz, $^3J_{PC}$=12 Hz, CH_2), 7.9 (s, CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, H_3PO_4 reference): δ 13.76 (d, $^1J_{PtP}$=2613 Hz, $^2J_{PP}$=415 Hz), 10.79 (d, $^1J_{PtP}$=2678 Hz, $^2J_{PP}$=415 Hz). Anal. Found: C, 40.25; H, 5.48; Br, 9.46; P, 7.19%. Calcd for $C_{28}H_{45}BrFeO_4P_2Pt$: C, 40.11; H, 5.41; Br, 9.53; P, 7.39%.

7 Spectroscopic data for **2c**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H, =CH), 4.53 (t, J=2 Hz, 1H, C_5H_3), 4,48 (s, 1H, C_5H_3), 4.42 (quartet, J=7 Hz, 2H, OCH_2), 4.14 (quartet, J=7 Hz, 2H, OCH_2), 4.08 (s, 1H, C_5H_3), 4.01 (s, 5H, C_5H_5), 2.60-2.19 (m, 6H, PCH_2), 1.43 (t, J=7 Hz, 3H, OCH_2CH_3), 1.40-1.35 (m, 6H, PCH_2) 1.32-1.25 (m, 9H, PCH_2CH_3), 1.23 (t, J=7 Hz, 3H, OCH_2CH_3), 0.94-0.88 (m, 9H, PCH_2CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, H_3PO_4 reference): δ 16.56 (d, $^1J_{PtP}$=2637 Hz, $^2J_{PP}$=421 Hz), 13.44 (d, $^1J_{PtP}$=2720 Hz, $^2J_{PP}$=421 Hz). Anal. Found: C, 44.05; H, 5.90; Cl, 4.55; P, 7.35%. Calcd for $C_{30}H_{49}ClFeO_4P_2Pt$: C, 43.83; H, 6.01; Cl, 4.31; P, 7.54%.

8 Crystal data for **2b**: $C_{28}H_{45}BrFeO_4P_2Pt$, space group $P\overline{1}$, a=11.670(2) Å, b=14.187(2) Å, c=10.040(2) Å, α= 102.12(2) °, β=98.32(2)°, γ=92.53(2) °, V=1603.2(5) Å^3, Z=2, D_c=1.737 gcm^{-3}, $\mu(MoK_\alpha)$ = 62.18 cm^{-1}, ω-2θ scan, $2\theta_{max}$ =50.1°, R=0.023 and R_w=0.021 for 334 parameters against 2744 reflections (I>9σ(I)) out of 5688 unique reflections.

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