## **Unprecedented Promoting Effect of a Ferrocenyl Group** for the Oxidatively Induced Reductive Elimination in cis-Aryl(ferrocenyl acetylide)platinum(II) Complexes

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Summary: cis-Aryl(ferrocenyl acetylide)platinum(II) complexes very easily undergo oxidatively induced reductive elimination, which is induced by the oxidation of the ferrocenyl moiety and is promoted by the electrondonating substituent on the aryl ligand.

Reductive elimination is one of the key organometallic reactions for carbon-carbon bond formation.<sup>1</sup> It has been confirmed theoretically that a concerted reductive elimination from the cis-diorgano complexes MR<sub>2</sub>L<sub>2</sub> of  $d^8$  metals is allowed, while that from the trans isomer is forbidden.<sup>2</sup> Oxidatively induced reductive eliminations are now commonly encountered because an increase in oxidation state of a metal center is apt to make reductive elimination susceptible. The oxidation activation is stimulated by the addition of a  $\pi$ -acid.<sup>3</sup> oxidative addition of allyl halides,<sup>4</sup> or electron transfer.<sup>5-8</sup> Organoplatinum complexes are extremely stable toward reductive elimination.<sup>9</sup> Recently cis-[PtMe(SiPh<sub>3</sub>)-(PMePh<sub>2</sub>)<sub>2</sub>] has been reported to undergo reductive elimination easily in the presence of  $\pi$ -acids,<sup>10</sup> but the oxidation of a cis-dialkyl Pt(II) complex has been reported not to bring about reductive elimination.<sup>11</sup> We report here a fine example of oxidatively induced reductive elimination of Pt(II) complexes promoted by a ferrocenyl group.

cis-[Pt(C<sub>6</sub>H<sub>5</sub>)(C=CFc)(dppe)] (2a) was prepared from the reaction of trans-[Pt(C<sub>6</sub>H<sub>5</sub>)(C=CFc)(Ph<sub>3</sub>P)<sub>2</sub>] (1a)<sup>12</sup> with dppe in  $CH_2Cl_2$  in 95% yield (dppe = 1,2-bis-(diphenylphosphino)ethane; Fc = ferrocenyl).<sup>13</sup> In a similar manner, p-MeC<sub>6</sub>H<sub>4</sub>- (2b), p-ClC<sub>6</sub>H<sub>4</sub>- (2c),

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p-MeOC<sub>6</sub>H<sub>4</sub>- (2d), p-EtOCOC<sub>6</sub>H<sub>4</sub>- (2e), and p-MeCOC<sub>6</sub>H<sub>4</sub> analogs (2f) were prepared in good yield.<sup>14</sup> The <sup>31</sup>P NMR spectrum of 2a, for example, showed two singlets accompanied by the Pt satellite at  $\delta$  38.13 ( $^{1}J_{\text{PtP}} = 1531$ Hz) and 44.19 ( ${}^{1}J_{PtP} = 2535$  Hz), suggesting the squareplanar cis configuration of the Pt atom in 2a. This assignment was confirmed by the single-crystal analysis of 2e (Figure 1).<sup>15</sup> The ferrocenyl acetylide ligand is located cis to the phenyl ligand around the Pt(II) atom. The Pt-P distance (2.301(2) Å) trans to the acetylide ligand is somewhat longer than that  $(2.271(2) \text{ \AA})$  trans to the phenyl group, which may reflect the different  $\sigma$ -donating abilities of both ligands. Other bond dis-

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<sup>(13)</sup> trans-[Pt(C=CFc)(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (1a; 50 mg, 0.05 mmol) was stirred with dppe (40 mg, 0.1 mmol) in  $CH_2Cl_2$  (10 mL) at room temperature for 20 min. After the solvent was evaporated, the crude products were chromatographed on  $Al_2O_3$  by elution of  $CH_2Cl_2/hexane$  to give *cis*-[Pt(C=CFc)(C<sub>6</sub>H<sub>5</sub>)(dppe)] (**2a**) as orange crystals (38 mg, 95%).

<sup>(14)</sup> **2a**: orange crystals; mp 187–189 °C; IR (KBr)  $\nu$ (C=C) 2124, 2109 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.14–2.58 (m, 4H, CH<sub>2</sub>), 3.89 (s, 5H, 2109 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.14–2.58 (m, 4H, CH<sub>2</sub>), 3.89 (s, 5H, Cp-unsub), 3.92 (t, J = 1.7 Hz, 2H, Cp- $\beta$ ), 4.13 (t, J = 1.8 Hz, 2H, Cp- $\alpha$ ), 6.73–6.88 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.30–8.12 (m, 23H, C<sub>6</sub>H<sub>5</sub>, Ph<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 26.76 (dd,  $J_{P-C} = 31.5$ , 12.4 Hz, CH<sub>2</sub>), 30.25 (dd,  $J_{P-C} = 35.3$ , 16.6 Hz, CH<sub>2</sub>), 66.70 (s, Cp- $\beta$ ), 69.37 (s, Cp-unsub), 70.57 (s, Cp- $\alpha$ ), 72.40 (s, Cp-ipso), 107.20 (d,  $J_{P-C} = 34.6$  Hz, C=C), 108.70 (dd,  $J_{P-C} = 146.5$ , 15.2 Hz, C=C), 122.06 (s, C<sub>6</sub>H<sub>5</sub>), 126.96 (d,  $J_{P-C} = 7.6$  Hz, C<sub>6</sub>H<sub>5</sub>), 138.71 (s, C<sub>6</sub>H<sub>5</sub>), 153.31 (dd,  $J_{P-C} = 113.3$ , 8.0 Hz, C<sub>6</sub>H<sub>5</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  38.13 (s,  $J_{P-P} = 1531$  Hz, trans to Ar), 44.19 (s,  $J_{P-P} = 2535$  Hz, trans to C=C); <sup>195</sup>Pt NMR (CDCl<sub>3</sub>) –3091.97 (dd,  $J_{P-P} = 2535$ , 1545 Hz). Anal. Found: C, 60.11; H. 4.36. Calcd for  $G_{P-P1} = 2535$ , 1545 H2). Anal. Found: C, 60.11; H, 4.36. Calcd for  $C_{44}H_{38}P_2FePt$ : C, 60.08; H, 4.36. Other products are similarly assigned by the spectroscopic data and satisfactory elemental analyses.



Figure 1. Crystal structure of 2a. Selected bond distances (Å) and angles (deg): Pt-P(1) = 2.301(2), Pt-P(2) = 2.271(2), Pt-C(1) = 2.029(7), Pt-C(3) = 2.089(8), C(1)-C(2) = 1.185(10); P(1)-Pt-P(2) = 85.2(1), C(1)-Pt-C(3) = 86.1(3), Pt-C(1)-C(2) = 175.6(7).

tances and bond angles of 2e are similar to those in trans-[PtH(C=CFc)(PPh<sub>3</sub>)<sub>2</sub>]<sup>16</sup> and cis-[Pt(CCFc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>].<sup>17</sup> In the cyclic voltammogram, trans isomer 1a showed a quasi-reversible wave at  $-0.16 V (Fe^{II}/Fe^{III})$  and an irreversible wave at +0.90 V (PtII/PtIV).18 On the other hand, cis isomer 2a showed one quasi-reversible wave at -0.07 V and one irreversible wave at +0.88 V. Also, an additional redox wave was observed at +0.10 V. whose redox potential is coincident with that of the coupling product 3a. This wave appeared even when the scan turned back at +0.40 V and increased when the scan rate was decreased. Cyclic voltammograms of 2a-d are shown in Figure 2. As seen clearly, the more electron-releasing the substituent, the larger the new wave appears, the potential of which is coincident with that of the corresponding coupling product. Such electrochemical behavior suggests that the one-electronoxidized species of the cis complexes are unstable and are followed by a fast chemical reaction, producing the coupling product.

Complexes  $2\mathbf{a}-\mathbf{f}$  reacted smoothly with 1 equiv of DDQ or AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature to give

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(18) Cyclic voltammograms of 2a-f(1 mM) were measured in CH<sub>2</sub>-Cl<sub>2</sub> solution containing 0.1 M (*n*-Bu)<sub>4</sub>NClO<sub>4</sub> at a Pt electrode and a sweep rate of 100 mV s<sup>-1</sup> at 25 °C. The potential is referred to FcH<sup>+</sup>/ FcH. The waves were assigned in comparison with the reference compounds (+0.12 V for *p*-MeC<sub>6</sub>H<sub>4</sub>C≡CFc and +0.61 V for *trans*-[Pt(C<sub>6</sub>H<sub>4</sub>OMe-p)(C≡CPh)(Ph<sub>3</sub>P)<sub>2</sub>]).



Figure 2. Cyclic voltammograms for 2a-d (1 mM) in 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> at a Pt electrode and a sweep rate of 0.1 V s<sup>-1</sup>.

the corresponding coupling complexes p-XC<sub>6</sub>H<sub>4</sub>C $\equiv$ CFc (**3a**-**f**), in excellent yield.<sup>19</sup> The facile conversion of

<sup>(15)</sup> Crystal structure data for **2a**: C<sub>44</sub>H<sub>38</sub>P<sub>2</sub>FePt-C<sub>6</sub>H<sub>61</sub> fw = 957.75, triclinic, space group  $P\bar{1}$ , a = 17.320(1) Å, b = 11.774(5) Å, c = 10.723. (4) Å,  $\alpha = 97.57(3)^{\circ}$ ,  $\beta = 74.37(4)^{\circ}$ ,  $\gamma = 89.57(5)^{\circ}$ , V = 2086(2) Å<sup>3</sup>, Z = 2,  $\varrho_{calcd} = 1.53$  g cm<sup>-3</sup>,  $\mu = 38.406$  cm<sup>-1</sup>, Mo Ka radiation,  $\lambda = 0.710$  73 Å. Intensity data were collected on a Mac Science MXC18K diffractometer. Of 10 332 reflections collected, 9576 were unique, 7926 of which with  $I > 3.0\sigma(I)$  were used for refinement. The structure was solved by direct methods and refined by a full-matrix least-squares procedure. Absorption correction by the  $\psi$ -scan method and anisotropic refinement for non-hydrogen atoms were carried out. R = 0.046 and  $R_w = 0.053$ .

<sup>(19)</sup> The electrochemical oxidation of **2a** also proceeded smoothly at 0.4 V to give the coupling product **3a**.

Scheme 2



2a-f to the coupling product under the oxidative conditions is in striking contrast to the fact that the corresponding trans isomers 1a-f give the stable oneelectron-oxidized products under similar conditions in good yield.<sup>12</sup> That is, the oxidatively induced reductive elimination takes place only in the cis isomers. This fact is in good agreement with the theoretical prediction.<sup>3</sup> When 2d was refluxed in chloroform for 8 h without the oxidant, only a trace amount of 3d was obtained. The reactions scarcely proceed in the presence of a catalytic amount of the oxidant. These indicate a remarkable oxidative activation by an equimolar amount of DDQ or AgBF<sub>4</sub> in the reductive elimination for the Pt(II) complexes 2a-f. The electronic spectrum of 2e immediately after the addition of 1 equiv of DDQ is, for example, different from that of 2e and is guite similar to that of the one-electron-oxidized complex of the trans isomer 1e. This suggests that the one-electron-oxidized species very rapidly formed on the addition of the oxidant, followed by its slow degradation to the coupling product. The decomposition of 2a-f under oxidative conditions adopted first-order kinetics in CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>20</sup> The observed first-order rate constants ( $k_{obs}$ ; s<sup>-1</sup> at 0 °C) decreased in the following order:  $\, \textbf{2d} \, (8.9 \times 10^{-2}) \,$ > 2b  $(3.3 \times 10^{-2})$  > 2a  $(1.9 \times 10^{-2})$  > 2c  $(2.6 \times 10^{-3})$  > **2e,f** (1.3  $\times$  10<sup>-3</sup>). Curiously, the reaction is retarded by the electron-attracting substituent on the aryl ligand. The rate constants correlate with the substituent constant  $(\sigma_{\rm p})$  of the substituent on the aryl ligand in **2a**-**f** (r = 0.96). A similar but small substituent effect is observed in the AuMe<sub>2</sub>Ar(PPh<sub>3</sub>) complexes.<sup>21</sup> The theo-

retical calculation suggests that the better the  $\sigma$ -donating capability of the leaving groups is, the more readily the elimination reaction proceeds.<sup>3a</sup> A similar reaction of cis-[Pt(p-MeC<sub>6</sub>H<sub>4</sub>)(C=CPh)(dppe)] with DDQ does not proceed successfully; instead, reaction occurs with Ag- $BF_4$  or  $FcHPF_6$  in refluxing  $CH_2Cl_2$  to give only a small yield of the coupling product. These results, along with the CV measurements, indicate a notable stimulating effect of the ferrocenyl group for the oxidatively induced reductive coupling in the Pt(II) complexes. The effect may be explained as follows (Scheme 3): the ferrocenyl part is first oxidized with a mild oxidant such as DDQ, which is not enough to oxidize the Pt(II) part, to give the one-electron-oxidized species A. Then, an electron transfer from the Pt(II) part through the C=C bond produces the species  $\mathbf{B}$ , in which the electron density on the Pt(II) atom is diminished. In this stage, the reductive elimination takes place rapidly, because the decrease of the electron density on the metal atom is known to accelerate the reductive elimination. A species such as A is confirmed to be predominant in the one-electron-oxidized species of the trans isomer,<sup>12</sup> and therefore the contribution of species **B** may be enhanced by the increase of electron density on the Pt(II) atom, so that the oxidatively induced reductive elimination in complexes 2a-f is likely accelerated by the electronreleasing substituents on the aryl group. This seems to be a rare example which the chemical reaction is initiated by the metal-metal interaction.

Supporting Information Available: Text giving characterization data for 2a-f and details of the X-ray crystal structure determination of 2e, including tables of crystal data and data collection and refinement details, positional and thermal parameters, bond distances and angles, torsion angles, nonbonded distances, and least-squares planes and deviations therefrom and a figure giving the full atom-labeling scheme (50 pages). Ordering information is given on any current masthead page.

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<sup>(20)</sup> The reaction was monitored spectroscopically. The spectrum of **2e**, for example, had three isosbestic points at 340, 360, and 400 nm. The reaction rate was followed up by the decrease of the peak near 460 nm, which was perhaps due to the charge-transfer band in the one-electron-oxidized species owing to the observation also in the corresponding trans isomer. The initial concentration of **2a**-e was 0.1 mmol with 2 equiv of DDQ. The rate was independent of the concentration of DDQ in the presence of more than 1 equiv of DDQ. (21) Komiya, S.; Ozaki, S.; Shibue, A. J. Chem. Soc., Chem. Commun. **1986**, 1555.