

Reactions of 1-Ferrocenyl and 1,1'-Ferrocenediyl Platinum Complexes with Copper Acetylide.
Synthesis and Molecular Structure of a Novel 1,1'-Ferrocenediyl Pt₂Cu₃ Acetylide Complex

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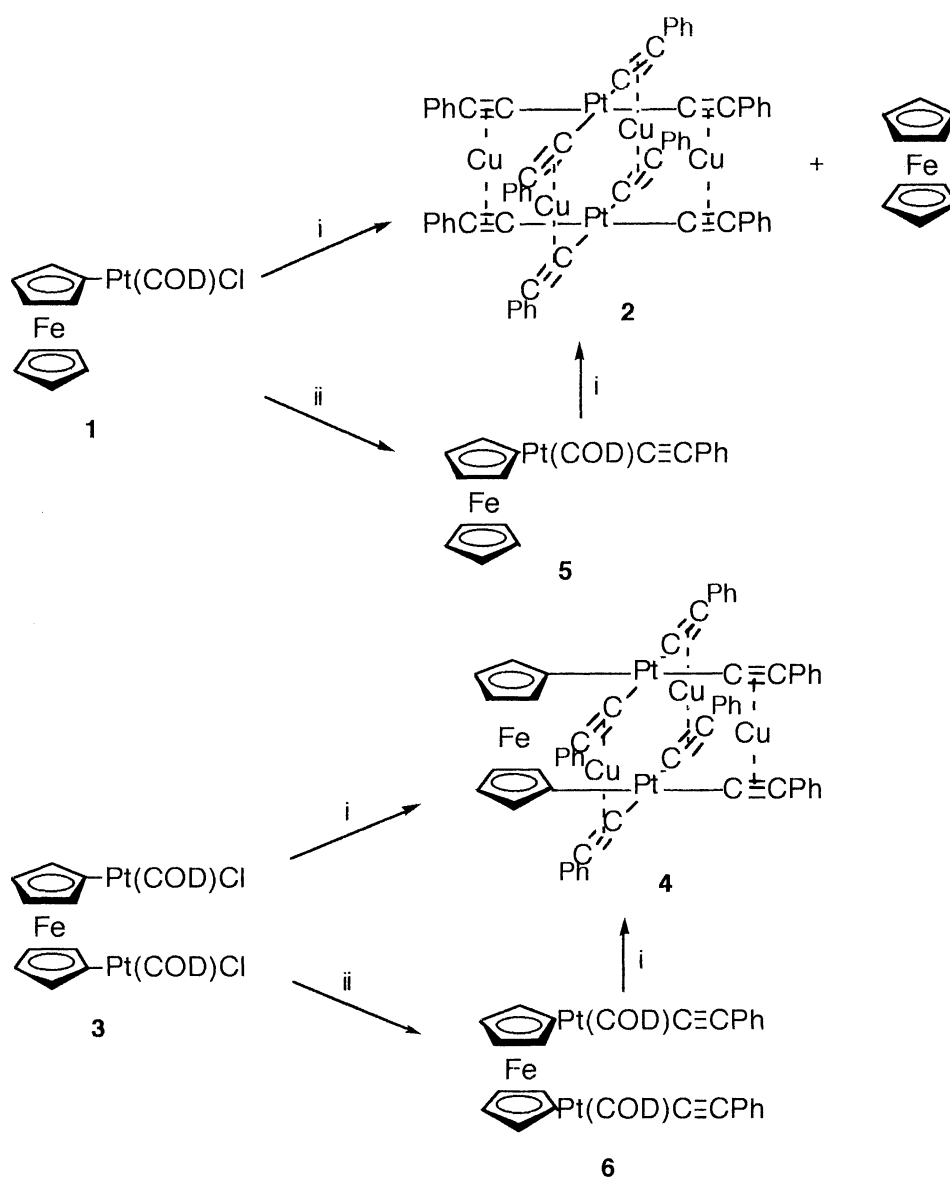
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Treatment of 1,1'-bis{chloro(η^4 -cyclooctadiene)platino}ferrocene with excess phenylacetylene and CuI in diethylamine/acetone results in the formation of a novel 1,1'-ferrocenediyl Pt₂Cu₃ acetylide complex (**4**), of which structure is characterized by an X-ray diffraction analysis. Similar treatment of 1,1'-bis{phenylethynyl(η^4 -cyclooctadiene)platino}ferrocene also gave complex **4**. The reaction of 1-{chloro(η^4 -cyclooctadiene)platino}ferrocene or 1-{phenylethynyl(η^4 -cyclooctadiene)platino}ferrocene affords a Pt₂Cu₄ acetylide complex.

Transition metal complex which has an intramolecular interaction between transition metal and the iron atom of ferrocene has developed a new aspect in the chemistry of ferrocene derivatives.¹⁾ We have been interested in the chemistry of α -metalated ferrocene, in which metal-iron direct or indirect interactions, through the cyclopentadienyl group, are expected. 1,1'-Dimetalated ferrocene may have interactions not only between transition metal and iron but also between two metal atoms. In addition, 1,1'-dimetalated ferrocene can control the distance between two metal atoms by the rotation of cyclopentadienyl rings and may be available for the synthesis of a new type cluster. Thus, we have examined some reactions of 1-ferrocenyl and 1,1'-ferrocenediyl platinum complexes. We wish to describe here the synthesis and the molecular structure of a novel 1,1'-ferrocenediyl Pt₂Cu₃ acetylide complex by the reaction of 1,1'-ferrocenediyl platinum complex with phenylacetylene in the presence of diethylamine and CuI.

On treatment of 1-ferrocenyl platinum complex (**1**)²⁾ with excess phenylacetylene and CuI, which would generate copper acetylide, a red complex (**2**) was isolated in 85% yield and almost quantitative amount of ferrocene was recovered. By the spectral and elemental analyses complex **2** was characterized as a known Pt₂Cu₄ acetylide complex,³⁾ which had been prepared by the reaction of analogous Pt₂Ag₄ acetylide complex with CuCl.⁴⁾

When 1,1'-ferrocenediyl diplatinum complex (**3**)²⁾ was treated with excess phenylacetylene and CuI, the color of the reaction mixture gradually changed from red to green and green precipitates were produced with the progress of the reaction. Purification by column chromatography on alumina using dichloromethane as an eluent followed by recrystallization from dichloroethane led to the isolation of a green crystal (**4**)⁵⁾ and any ferrocene



Scheme 1. Reagents: i, excess PhC≡CCu; ii, PhC≡CH, CuI cat.

was not recovered. The results of ESCA and ICP emission spectroscopy suggested that complex **4** contains platinum, iron and copper atoms. The IR spectrum of **4** showed absorptions at 2023 and 1981 cm^{-1} due to $\nu(\text{C}\equiv\text{C})$, of which wave numbers are close to those of **2** and lower than those of normal acetylide complexes such as **5** and **6** stated below, indicating that Cu atoms coordinate to C-C triple bonds of Pt acetylide. It should be noted that the resonances of ferrocenediyl protons were observed as a broad signal at much lower magnetic field (δ 46 and 25) owing to the paramagnetic property of ferrocene and the signal was detected by ESR.⁶⁾ The ^1H NMR spectrum exhibited two sets of signals for phenyl protons in a 2:1 integral ratio in the range δ 6.67-4.11, which had shifted to higher magnetic field than normal chemical shift of aromatic protons. This phenomenon may be due to the influence of paramagnetic iron atom through cyclopentadienyl group, platinum

atom and C-C triple bond. Thus, in order to determine the structure of complex **4** X-ray diffraction study was carried out and the molecular structure is presented in Figure 1.⁷⁾

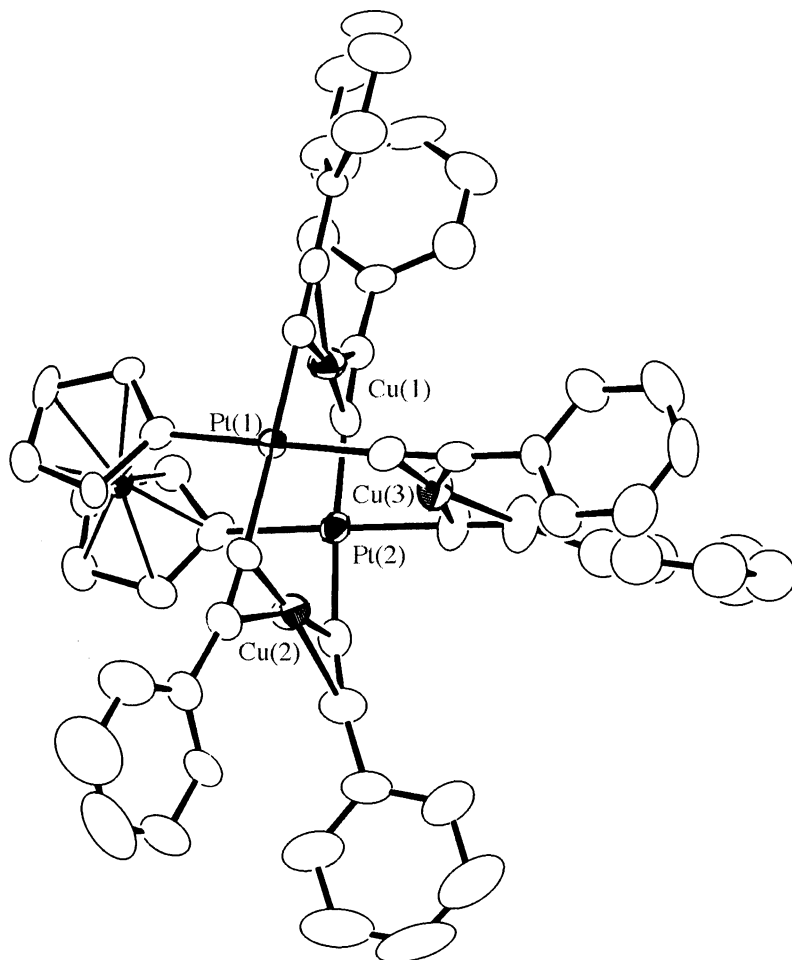


Fig. 1. ORTEP drawing of 1,1'-ferrocenediyl Pt_2Cu_3 complex (**4**). One of the disordered phenyl rings and hydrogen atoms have been omitted for clarity.

The six metal atoms are arranged in slightly irregular octahedron with two platinum atoms mutually *trans* while three copper atoms and one iron atom are in the equatorial plane.⁸⁾ Three phenylethynyl ligands combine to each platinum atom by σ -bond and form π -linkages to each of the copper atoms. The Pt-Cu distances are 2.845(5)-2.975(3) Å and the other M-M distances are more than 3.0 Å, indicating the absence of M-M direct bonds. Two coordination planes of platinum are essentially parallel and the dihedral angles is 4.5°. Each square plane of platinum atom is twisted away from the cyclopentadienyl ring by 7.7° or 7.3°. Ferrocenediyl group has eclipsed conformation and the dihedral angle between the two cyclopentadienyl rings is 7.4°. Copper atoms coordinate to acetylene asymmetrically and the bond lengths are in the range 1.956(10)-1.994(9) Å for Cu- C_α and 2.130(11)-2.253(10) Å for

Cu- C_β , respectively. The C-C bond lengths of acetylene are in the range 1.173(12)-1.216(14) Å. The platinum atom and the three carbon atoms containing acetylenic C_α and C_β are slightly bent, the range of the Pt- C_α - C_β angles is from 172.8(8)° to 176.1(8)° and the range of the C_α - C_β -C angles is from 158(1)° to 174(1)°.

On the other hand, complex **1** was treated with one equivalent of phenylacetylene in the presence of CuI catalyst in diethylamine to give a normal acetylide complex (**5**)¹⁰⁾ in 83% yield.¹¹⁾ Similar treatment of **3** gave a diplatinum acetylide complex (**6**)¹²⁾ in 87% yield. Complex **5** was treated with excess phenylacetylene and CuI to give complex **2**, and the treatment of complex **6** in the similar conditions also afforded complex **4**.

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- 3) mp 225-235 °C (dec. in Ar); IR(KBr): $\nu(\text{C}\equiv\text{C})$ 2026(s), 1983(m) cm^{-1} ; ^1H NMR(CDCl_3): δ 7.32(16H, d, $J=7.3$ Hz, Ph), 7.20(8H, t, $J=7.3$ Hz, Ph), 7.10(16H, t, $J=7.6$ Hz, Ph); ^{13}C NMR(CDCl_3): δ 149.92, 132.30, 128.11, 124.74, 112.41, 91.89.
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- 5) mp 244-254 °C (dec. in Ar); IR(KBr): $\nu(\text{C}\equiv\text{C})$ 2023(s), 1981(m) cm^{-1} ; ^1H NMR(CDCl_3): δ 46(4H, br, Cp), 25(4H, br, Cp), 6.65(2H, t, $J=7.8$ Hz, Ph), 5.86(2H, t, $J=7.1$ Hz, Ph), 5.68(4H, br, Ph), 5.55(1H, t, $J=7.6$ Hz, Ph), 4.76(2H, d, $J=7.8$ Hz, Ph), 4.11(4H, br, Ph); ^{13}C NMR(CDCl_3): δ 143.71, 136.86, 132.29, 130.84, 126.84, 125.66, 123.62, 119.43, 118.55, 108.38.
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- 7) Crystals of complex **6** suitable for X-ray analysis were obtained by slow evaporation of a dichloroethane solution at ambient temperature. Crystal data: $\text{C}_{58}\text{H}_{38}\text{Cu}_3\text{FePt}_2$, $M=1371.6$, space group $\text{P2}_1/\text{c}$, $a=12.151(6)$ Å, $b=23.435(7)$ Å, $c=16.835(5)$ Å, $\beta=103.00(3)^\circ$, $V=4709(3)$ Å³, $Z=4$, $D_c=1.937$ g cm^{-3} . Diffraction data were collected on a Rigaku AFC5R diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation using the ω -2 θ scan mode to a maximum 2θ value of 45° . The structure was solved by Patterson method and refined to $R=0.025$ and $R_w=0.025$ for 547 parameters against 4313 ($F > 3\sigma(F)$) out of 7434 unique reflections. The hydrogen atoms were placed in idealized positions. One of the phenyl rings was disordered, and the C(63)-C(68) and C(73)-C(78) were refined as a rigid group using isotropic thermal parameter.
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- 10) mp 157-158 °C (dec. in Ar); IR(KBr): $\nu(\text{C}\equiv\text{C})$ 2121(m) cm^{-1} ; ^1H NMR(CDCl_3): δ 7.45(2H, d, $J=7.3$ Hz, Ph), 7.26(2H, t, $J=7.6$ Hz, Ph), 7.18(1H, t, $J=7.3$ Hz, Ph), 5.61(2H, br, $^2J_{\text{Pt-H}}=36.6$ Hz, COD), 5.56(2H, br, $^2J_{\text{Pt-H}}=28.8$ Hz, COD), 4.43(2H, s, $^2J_{\text{Pt-H}}=23.2$ Hz, Cp), 4.22(7H, s, Cp), 2.54(8H, br, COD); ^{13}C NMR(CDCl_3): δ 131.43, 127.97, 127.28, 126.04, 107.65, 106.53, 104.45($J_{\text{Pt-C}}=35.5$ Hz), 98.56($J_{\text{Pt-C}}=99.8$ Hz), 78.59, 74.88($J_{\text{Pt-C}}=67.5$ Hz), 69.69($J_{\text{Pt-C}}=60.2$ Hz), 97.97, 30.30, 30.00.
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- 12) mp 133-139 °C (dec. in Ar); IR(KBr): $\nu(\text{C}\equiv\text{C})$ 2119(m) cm^{-1} ; ^1H NMR(CDCl_3): δ 7.43(4H, d, $J=6.7$ Hz, Ph), 7.23(4H, t, $J=7.6$ Hz, Ph), 7.15(2H, t, $J=7.3$ Hz, Ph), 5.60(4H, br, COD), 5.55(4H, br, COD), 4.44(4H, br, Cp), 4.40(4H, br, Cp), 2.56-2.43(16H, m, COD); ^{13}C NMR(CDCl_3): δ 131.49, 127.91, 127.53, 125.90, 108.31, 106.40, 104.15($J_{\text{Pt-C}}=49.9$ Hz), 98.66($J_{\text{Pt-C}}=102.7$ Hz), 79.79, 75.00($J_{\text{Pt-C}}=63.0$ Hz), 65.94($J_{\text{Pt-C}}=60.2$ Hz), 30.24, 30.05.

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