Syntheses and Properties of Ferrocenylethynyl Transition Metal Complexes of Platinum, Palladium, and Nickel

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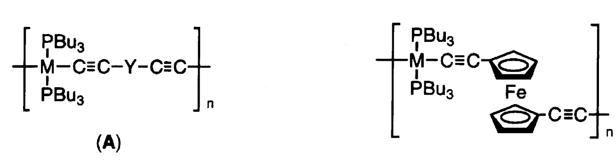
Synopsis. Square planar ferrocenylethynyl transition metal complexes $M(C\equiv CFc)_2(PR_3)_2$ (M = Pt, Pd, Ni; Fc = $(C_5H_4)Fe(C_5H_5)$) were prepared by the reaction of $MCl_2(PR_3)_2$ with ethynylferrocene in the presence of a CuI catalyst in diethylamine, and characterized by spectral analyses. An interaction between transition metals and an iron atom was studied by using electronic spectroscopy.

Organometallic polymers, in which transition metal moieties are linked together by π-conjugated systems, have attracted much attention.[1] In particular, transition metal polyyne polymers are of interest because of their liquid crystal and nonlinear optical properties.[2—4] We recently prepared polyyne polymers (**A**) containing silicon and transition metals in the main chain.[5] We have designed a new type of polymer (**B**) containing transition metals and ferrocenes in the main chain; accordingly, it is important to know about interactions between transition metals and iron atoms through acetylenic bonds and cyclopentadienyl groups. Hence, our initial study focused on the basic model, a ferrocenylethynyl complex. In this paper we wish to report on the syntheses of ferrocenylethynyl transition metal complexes of platinum, palladium, and nickel as well as their properties (Chart 1).

We previously reported a conventional method for the preparation of transition metal acetylide complexes by dehydrohalogenation between a metal halide and a terminal acetylene using a CuI catalyst in amine.[6] This method has been successively applied to the syntheses of ferrocenylethynyl complexes.

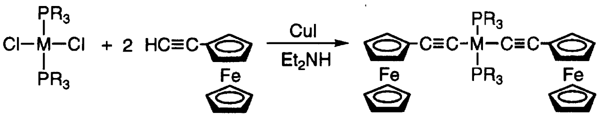
The treatment of *trans*-dichlorobis(tributylphosphine)platinum with two equivalents of ethynylferrocene in the presence of a CuI catalyst in diethylamine gave orange crystals (**1**), which are stable to air and soluble in common organic solvents (Eq. 1). Although analogous complex **2** having a *cis* configuration was obtained by a similar reaction between *cis*-dichlorobis(tributylphosphine)platinum and ethynylferrocene, this reaction was carried out at 0 °C to avoid isomerization into a *trans* complex **1** (Eq. 2). It was confirmed by ^{13}C NMR that complex **2** keeps a *cis* configuration. While the signal of the acetylenic carbon σ-bonded to platinum atom was observed at $\delta = 103.05$ as a triplet in the ^{13}C NMR spectrum of **1**, that of **2** was detected at $\delta = 99.92$ as a double-doublet.



(A)
M = Pt, Pd, Ni
Y=SiMe$_2$, SiMe$_2$SiMe$_2$, SiMe$_2$OSiMe$_2$

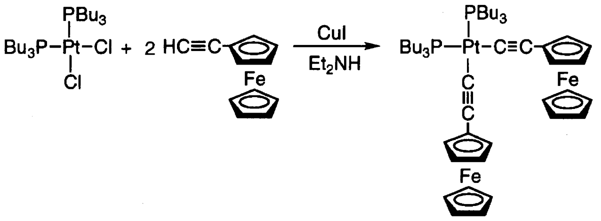
(B)
M = Pt, Pd, Ni

Chart 1.



(**1**): M=Pt; R=Bu
(**3**): M=Pd; R=Bu
(**4**): M=Pd; R=Et

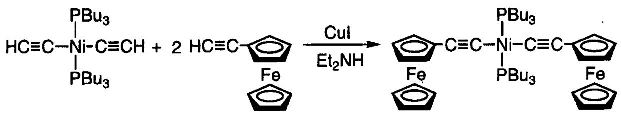
(1)



(**2**)

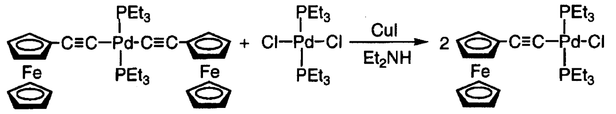
(2)

Although bis(ferrocenylethynyl)palladium complexes **3** and **4** were prepared by a similar method (Eq. 1), the method could not be applied for the nickel analogue, because dichlorobis(phosphine)nickel reacts with amine. Thus, the alkynyl ligand exchange reaction between *trans*-diethynylbis(tributylphosphine)nickel, which was prepared by the reaction of dibromobis(tributylphosphine)nickel with lithium acetylide, and ethynylferrocene was adopted for the synthesis of **5** (Eq. 3).[7] When bis(ferrocenylethynyl)palladium complex **4** was treated with *trans*-dichlorobis(triethylphosphine)palladium, a proportionation reaction occurred to afford a monoferrocenylethynyl complex **6** (Eq. 4).[8]



(**5**)

(3)



(**6**)

(4)

Table 1. Electronic Spectra

Complex	$\lambda_{\max}$/nm (ε)
1[a]	252 (2.5×10^4), 260 (2.6×10^4), 301 (7.9×10^3), 339 (3.1×10^4), 384 (4.7×10^2), 444 (1.3×10^3)
2[a]	296 (1.3×10^4), 313 (2.0×10^4), 383 (2.5×10^2), 444 (8.1×10^2)
3[a]	279 (1.2×10^4), 300 (2.3×10^4), 380 (2.7×10^2), 445 (7.8×10^2)
4[b]	285 (1.6×10^4), 306 (1.9×10^4), 382 (2.1×10^2), 448 (8.1×10^2)
5[a]	256 (2.2×10^4), 272 (2.5×10^4), 304 (8.2×10^3), 347 (2.0×10^4)
6[b]	271 (2.6×10^4), 447 (4.0×10^2)

a) In cyclohexane. b) In dichloromethane.

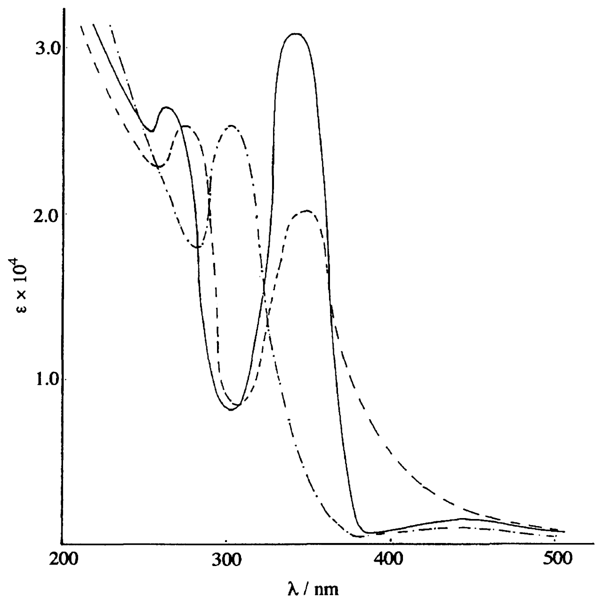


Fig. 1. Electronic Spectra of *trans*-Pt($C\equiv CFc$)$_2$(PBu_3)$_2$ (**1**) (——), *trans*-Pd($C\equiv CFc$)$_2$(PBu_3)$_2$ (**3**) (–·–), and *trans*-Ni($C\equiv CFc$)$_2$(PBu_3)$_2$ (**5**) (- - -) (in cyclohexane).

The electronic spectra of the above-mentional complexes showed absorptions in the 300—350 nm region assigned to the metal-to-ligand charge transfer (MLCT) band of an acetylide complex,[9] and at about 450 nm due to $d_\pi\rightarrow\sigma^*$, which is characteristic to ferrocene.[10] The spectral data are summarized in Table 1, and the electronic spectra of *trans*-M($C\equiv CFc$)$_2$(PBu_3)$_2$ **1**, **3**, and **5** are shown in Fig. 1, where the $\lambda_{\max}$ values of acetylide MLCT bands increase according to Ni>Pt>Pd, the same order as that found in those of *trans*-M($C\equiv CPh$)$_2$(PEt_3)$_2$[9] and [–*trans*-M(PBu_3)$_2$–C≡C–C≡C–]$_n$.[7] The ε value of the lowest energy band of **1** is larger than that of **3**, although the lowest energy band of **5** is not clear due to an overlap of the acetylide MLCT band. The MLCT band of **2** shows a hypsochromic shift relative to that of **1**, which is explained by the *trans* influence of the tributylphosphine and ferrocenylethynyl group; a hypochromic effect is observed in the lowest energy band of **2** relative to that of **1**. The difference in the energy transitions between **4** and **6** is also dependent on the *trans* influence. These results may suggest an interaction between transition metals and an iron atom through the C≡C triple bond and the cyclopentadienyl group.

Experimental

All of the reactions were carried out under a nitrogen atmosphere, and the workup was carried out in air. ^{1}H and ^{13}C NMR (in $CDCl_3$) were measured on a JEOL GX 400 spectrometer using $SiMe_4$ as an internal standard. IR spectra were recorded on a JASCO A-202 Infrared Spectrophotometer, and electronic spectra (in cyclohexane or dichloromethane) on a Shimadzu UV-160A Spectrophotometer. Diethylamine was purchased from Wako Pure Chemical Ltd., and used as received. Ethynylferrocene was prepared by literature method.[11]

***trans*-Bis(ferrocenylethynyl)bis(tributylphosphine)platinum (1).** *trans*-Dichlorobis(tributylphosphine)platinum (168 mg, 0.25 mmol) was treated with ethynylferrocene (105 mg, 0.5 mmol) in 20 ml of diethylamine in the presence of a catalytic amount of CuI at room temperature for 1 h. After removal of the solvent under reduced pressure, water was added to the residue, and the mixture was extracted with benzene. The organic layer was dried over $MgSO_4$ and the solvent was evaporated again. The crude product was obtained by column chromatography on alumina using benzene as an eluent, and recrystallization from hexane gave pure red crystals (170 mg, 67%). Mp 104—105 °C; IR (KBr) ν(C≡C) 2100 cm^{-1}; ^{1}H NMR δ=4.20 (4H, t, J=1.8 Hz, C_5H_4), 4.13 (10H, s, C_5H_5), 4.03 (4H, t, J=1.8 Hz, C_5H_4), 2.16—2.11 (12H, m, CH_2), 1.62—1.59 (12H, m, CH_2), 1.55—1.46 (12H, m, CH_2), 0.98 (18H, t, J=7.3 Hz, CH_3); ^{13}C NMR δ=103.90 (s, J_{Pt-C}=272.9 Hz, acetylene), 103.05 (t, J_{P-C}=14.7, J_{Pt-C}=965.4 Hz, acetylene), 73.28 (s, C_5H_4), 70.17 (s, C_5H_4), 69.40 (s, C_5H_5), 66.87 (s, C_5H_4), 26.40 (s, CH_2), 24.44 (vt, J=6.6 Hz, CH_2), 23.80 (vt, J=16.9 Hz, CH_2), 13.95 (s, CH_3). Anal. Found: C, 56.37; H, 7.18; P, 6.03%. Calcd for $C_{48}H_{72}P_2Fe_2Pt$: C, 56.64; H, 7.13; P, 6.09%.

***cis*-Bis(ferrocenylethynyl)bis(tributylphosphine)platinum (2).** This reaction was carried out by a method similar to that of **1** using *cis*-dichlorobis(tributylphosphine)platinum (134 mg, 0.2 mmol) and ethynylferrocene (84 mg, 0.4 mmol) at 0 °C to give red crystals (140 mg, 69%). Mp 111—112 °C; IR (KBr) ν(C≡C) 2100 cm^{-1}; ^{1}H NMR δ=4.32 (4H, t, J=1.8 Hz, C_5H_4), 4.18 (10H, s, C_5H_5), 4.00 (4H, t, J=1.8 Hz, C_5H_4), 2.02—1.99 (12H, m, CH_2), 1.50—1.40 (24H, m, CH_2), 0.95 (18H, t, J=7.0 Hz, CH_3); ^{13}C NMR δ=102.08 (t, J_{P-C}=16.9 Hz, acetylene), 99.92 (dd, J_{P-C}=145.3, J_{P-C}=22.1 Hz, acetylene), 72.58 (s, C_5H_4), 70.58 (s, C_5H_4), 69.46 (s, C_5H_5), 66.78 (s, C_5H_4), 26.56 (s, CH_2), 24.91 (vt, J=16.9 Hz, CH_2), 24.52 (vt, J=6.7 Hz, CH_2), 13.83 (s, CH_3). Anal. Found: C, 56.23; H, 7.18; P, 5.88%.

Calcd for $C_{48}H_{72}P_2Fe_2Pt$: C, 56.64; H, 7.13; P, 6.09%.

***trans*- Bis (ferrocenylethynyl) bis (tributylphosphine)palladium (3).** A treatment similar to that of **1** using *trans*-dichlorobis(tributylphosphine)palladium (1.176 g, 2.0 mmol) and ethynylferrocene (0.850 g, 4.0 mmol) afforded orange crystals (1.389 g, 74%). Mp 93—95 °C; IR (KBr) ν(C≡C) 2100 cm^{-1}; ^1HNMR δ=4.20 (4H, t, J=1.8 Hz, C_5H_4), 4.13 (10H, s, C_5H_5), 4.03 (4H, t, J=1.8 Hz, C_5H_4), 2.05—2.01 (12H, m, CH_2), 1.62—1.59 (12H, m, CH_2), 1.54—1.48 (12H, m, CH_2), 0.96 (18H, t, J=7.3 Hz, CH_3); ^{13}CNMR δ=106.73 (t, J_{P-C}=17.6 Hz, acetylene), 105.56 (s, acetylene), 72.71 (s, C_5H_4), 70.29 (s, C_5H_4), 69.44 (s, C_5H_5), 66.92 (s, C_5H_4), 26.72 (s, CH_2), 24.71 (vt, J=13.2 Hz, CH_2), 24.60 (s, CH_2), 13.98 (s, CH_3). Anal. Found: C, 61.83; H, 7.95; P, 6.47%. Calcd for $C_{48}H_{72}P_2Fe_2Pd$: C, 62.05; H, 7.81; P, 6.67%.

***trans*- Bis (ferrocenylethynyl) bis (triethylphosphine)palladium (4).** A reaction of *trans*-dichlorobis(triethylphosphine)palladium (413 mg, 1.0 mmol) and ethynylferrocene (420 mg, 2.0 mmol) gave orange crystals (565 mg, 74%), which were recrystallized from dichloromethane-hexane. Mp 139—143 °C; IR (KBr) ν(C≡C) 2100 cm^{-1}; ^1HNMR δ=4.22 (4H, t, J=1.8 Hz, C_5H_4), 4.13 (10H, s, C_5H_5), 4.03 (4H, t, J=1.8 Hz, C_5H_4), 2.10—2.03 (12H, m, CH_2), 1.33—1.22 (18H, m, CH_3); ^{13}CNMR δ=106.31 (s, acetylene), 105.93 (t, J_{P-C}=16.9 Hz, acetylene), 72.49 (s, C_5H_4), 70.23 (s, C_5H_4), 69.32 (s, C_5H_5), 66.90 (s, C_5H_4), 17.20 (vt, J=14.7 Hz, CH_2), 8.67 (s, CH_3). Anal. Found: C, 56.84; H, 6.11; P, 8.04%. Calcd for $C_{36}H_{48}P_2Fe_2Pd$: C, 56.83; H, 6.36; P, 8.14%.

***trans*- Bis (ferrocenylethynyl) bis (tributylphosphine)nickel (5).** To a diethylamine solution of *trans*-diethynylbis(tributylphosphine)nickel (117 mg, 0.23 mmol) and ethynylferrocene (96 mg, 0.46 mmol) was added a catalytic amount of CuI; the reaction mixture was stirred for 30 min at room temperature. After a workup similar to that in the synthesis of **1**, orange crystals (125 mg, 62%) were obtained. Mp 86—88 °C; IR (KBr) ν(C≡C) 2100 cm^{-1}; ^1HNMR δ=4.16 (4H, s, C_5H_4), 4.12 (10H, s, C_5H_5), 4.03 (4H, s, C_5H_4), 1.97—1.93 (12H, m, CH_2), 1.66—1.64 (12H, m, CH_2), 1.58—1.50 (12H, m, CH_2), 0.99 (18H, t, J=7.3 Hz, CH_3); ^{13}CNMR δ=114.67 (s, acetylene), 117.46 (t, J_{P-C}=40.2 Hz, acetylene), 72.87 (s, C_5H_4), 70.10 (s, C_5H_4), 69.41 (s, C_5H_5), 66.99 (s, C_5H_4), 26.82 (s, CH_2), 24.81 (vt, J=5.9 Hz, CH_2), 24.58 (vt, J=14.0 Hz, CH_2), 14.02 (s, CH_3). Anal. Found: C, 65.46; H, 8.45; P, 7.01%. Calcd for $C_{48}H_{72}P_2Fe_2Ni$: C, 65.41; H, 8.23; P, 7.03%.

***trans*-Chloro(ferrocenylethynyl)bis(triethylphosphine)palladium (6).** *trans*-Bis(ferrocenylethynyl)-bis(triethylphosphine)palladium (41 mg, 0.054 mmol) and *trans*-dichlorobis(triethylphosphine)palladium (23 mg, 0.056 mmol) were dissolved in 20 ml of diethylamine, and a catalytic amount of CuI was added. After being stirred for 3 h the solvent was removed under reduced pressure; the residue was purified by column chromatography on alumina with benzene-hexane (3 : 1) followed by recrystallization from dichloromethane-hexane to give orange crystals (47 mg, 74%). Mp 75—77 °C; IR (KBr) ν(C≡C) 2110, 2100 cm^{-1}; ^1HNMR δ=4.21 (2H, t, J=1.8 Hz, C_5H_4), 4.13 (5H, s, C_5H_5), 4.07 (2H, t, J=1.8 Hz, C_5H_4), 2.03—1.95 (12H, m, CH_2), 1.27—1.19 (18H, m, CH_3); ^{13}CNMR δ=102.37 (t, J_{P-C}=5.2 Hz, acetylene), 89.14 (t, J_{P-C}=16.2 Hz, acetylene), 71.53 (s, C_5H_4), 70.23 (s, C_5H_4), 69.38 (s, C_5H_5), 67.25 (s, C_5H_4), 15.47 (vt, J=13.9 Hz, CH_2), 8.37 (s, CH_3). Anal. Found: C, 49.09; H, 6.74; Cl, 6.24; P, 10.71%. Calcd for $C_{24}H_{39}ClP_2Fe_2Pd$: C, 49.09; H, 6.69; Cl, 6.04; P, 10.55%.

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