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Syntheses and Properties of Heterodinuclear μ-Ethynediyl Complexes Containing Palladium and Platinum

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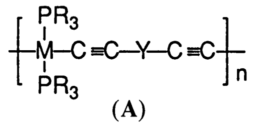
Synopsis. Heterodinuclear μ-ethynediyl complexes $Cl(R_3P)_2MC{\equiv}CM'(PR_3)_2Cl$ (**3**) (M=Pt, M′=Pd; R=Me, Et, *n*-Bu) were prepared by the reactions of chloroethynylbis(trialkylphosphine)platinum (**1**) with dichlorobis(trialkylphosphine)palladium (**2**) in the presence of CuCl catalyst. These complexes were fully characterized by mass, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies.

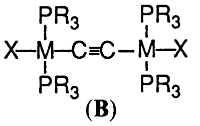
Hydrocarbon-bridged multinuclear transition metal complexes have been of interest as a model of reactive intermediates on heterogeneous catalyst surface.[1] Complexes containing two or more metal atoms in the molecule often exhibit unusual structural and reactivity feature owing to their mutual interaction. Many heteronuclear complexes have been studied with a view of exhibiting unique properties which are different from those of homonuclear complexes.

We previously reported the synthesis and properties of transition metal-poly(yne) polymers (**A**) in which metals are linked by conjugated acetylenic systems.[2] Recently we have also reported the preparation of μ-ethynediyl complexes $X(R_3P)_2MC{\equiv}CM(PR_3)_2X$ (M=Pd, Pt; R=Me, Et, *n*-Bu; X=Cl, I) (**B**) as the first examples of the σ,σ-coordination mode of acetylene,[3] and revealed that μ-ethynediyl dinuclear complexes exhibit a novel reactivity based on the mutual interaction of metals through the conjugated system.[4] Since then the synthesis of some transition metal μ-ethynediyl complexes were reported,[5] however there are few reports on the syntheses of multinuclear complexes in which different metals are linked by just one acetylene unit.[6] Here we wish to present the syntheses of heterodinuclear μ-ethynediyl complexes containing palladium and platinum by the reaction between ethynylplatinum complexes (**1**) and dichloropalladium complexes (**2**) in the presence of CuCl catalyst.



(A)

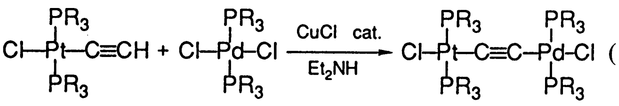
M = Pd, Pt
Y = bond, C_6H_4



(B)

M = Pd, Pt
R = Me, Et, n-Bu
X = Cl, I

Results and Discussion



(1)

(1) (2) (3)

a: R=Et
b: R=Me
c: R=Bu

trans-Chloroethynylbis(triethylphosphine)platinum (**1a**), which was prepared from a proportionation between *trans*-diethynylbis(triethylphosphine)platinum and dichlorobis(triethylphosphine)platinum in the presence of CuCl catalyst under reflux in dioxane, was reacted with *trans*-dichlorobis(triethylphosphine)palladium (**2a**) in the presence of CuCl catalyst in diethylamine at room temperature to give a pale yellow product (**3a**) in good yield. (Eq. 1). Complex **3a** was characterized by spectral analyses and gel permeation chromatography. The FD mass spectrum of **3a** showed the strongest molecular ion peak at m/z=868, and gel permeation chromatography using HSG-20® column, which can separate multinuclear μ-ethynediyl complexes from each other up to tetranuclear species, indicated **3a** to be dinuclear. The $^{31}P\{^1H\}$ NMR spectrum of **3a** exhibited two singlets at 22.8 and 19.6 ppm, of which the latter signal was attended with satellite signals ($^1J_{P\text{-}Pt}$=2518 Hz) due to the coupling of ^{195}Pt nucleus, indicating that both palladium and platinum have *trans*-configuration. Though **3a** has an asymmetrical structure about acetylene, no absorptions attributable to $\nu_{C\equiv C}$ were observed in the IR spectrum, since two metal groups attaching to the acetylene are not so different to each other in their weight. The $^{13}C\{^1H\}$ NMR spectrum exhibited the acetylenic carbon resonances at 94.26 ppm (triplet, $^2J_{C\text{-}P}$=16 Hz) and 88.62 ppm (triplet, $^2J_{C\text{-}P}$=14 Hz) having attendant satellites due to the coupling with ^{195}Pt nucleus. The former has a coupling constant of $^2J_{C\text{-}Pt}$=363 Hz and the latter $^1J_{C\text{-}Pt}$=1339 Hz. Thus the former is assigned to the signal of the carbon bonded to palladium and the latter to that of the carbon bonded to platinum. These spectral data are consistent with the proposed structure **3a** in which palladium and platinum are linked by just one acetylene unit.

A similar reaction of the complexes containing trimethylphosphine and tri-*n*-butylphosphine gave heterodinuclear μ-ethynediyl complexes **3b** and **3c**, respectively (Eq. 1). Preparation of complex **3c** required longer reaction time due to the steric effect of the tributylphosphine ligand bound to the two metals. The spectral data of heterodinuclear μ-ethynediyl complexes **3** are summarized in Table 1.

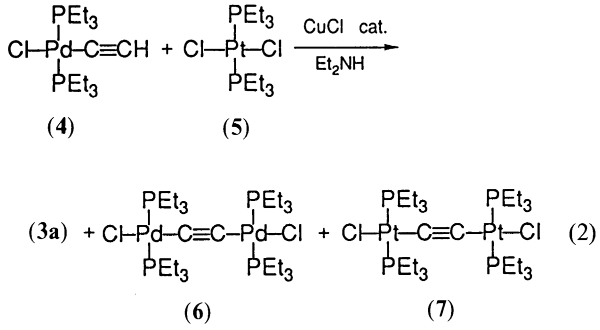
On the other hand, when *trans*-chloroethynylbis(triethylphosphine)palladium (**4a**) was treated with dichlorobis(triethylphosphine)platinum (**5**) under the same conditions, not only heterodinuclear μ-ethynediyl complex **3a** but also μ-ethynediyl dipalladium complex (**6**) were formed along with a small amount of diplatinum complex (**7**) (Eq. 2). This result may be attributable to the higher reactivity of the palladium complexes than the platinum complexes toward ethynyl complexes under such reaction conditions. In fact *trans*-

Table 1. Physical Data for Complexes (**3**)

Complex	$\mathrm{PR_3}$	Mp	^{31}P NMR/ppm		MS (m/z)[a]
		°C	P on Pd	P on Pt	
3a	$\mathrm{PEt_3}$	119—123 (decomp)	22.8	19.6 (J=2518 Hz)	868
3b	$\mathrm{PMe_3}$	242—245 (decomp)	−8.7	−10.3 (J=2444 Hz)	700
3c	$\mathrm{PBu_3}$	130—133 (decomp)	13.8	10.5 (J=2512 Hz)	1204

a) Complexes **3a**—**c** contain several kinds of isotopes such as ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{35}Cl, and ^{37}Cl, thus the values of molecular ions with the strongest intensity are listed. The distributions of molecular ions in the spectra of complexes **3** are in accord with those simulated with JMA-DA5000 system.

chloroethynylbis(triethylphosphine)platinum (**1a**) does not react with dichlorobis(triethylphosphine)platinum (**5**) in diethylamine at room temperature, but in piperidine under reflux to give μ-ethynediyl diplatinum complex (**7**). Thus, in the reaction of Eq. 2, complex **4** reacts with itself as well as **5** to give a mixture of μ-ethynediyl complexes **6** and **7** via a cleavage of the M–C≡ bonds. But in the reaction of Eq. 1 complex **1** reacts selectively with **2** to give heterodinuclear μ-ethynediyl complexes.



$$\mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}CH} + \mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}Cl} \xrightarrow[\mathrm{Et_2NH}]{\mathrm{CuCl\ cat.}}$$

(**4**) (**5**)

$$(\mathbf{3a}) + \mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pd}}{-}Cl} + \mathrm{Cl{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}C{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}Cl} \quad (2)$$

(**6**) (**7**)

Experimental

All the reactions were carried out under nitrogen atmosphere. ^{13}C{^{1}H} NMR (in $\mathrm{CDCl_3}$) was measured on a Bruker AM-360 spectrometer, using $\mathrm{SiMe_4}$ as an internal standard, and ^{31}P{^{1}H} NMR (in $\mathrm{CD_2Cl_2/CH_2Cl_2}$=1/1) spectra on a JEOL FX-100 spectrometer against an external $\mathrm{PPh_3}$ (in $\mathrm{C_6D_6}$) reference. Infrared spectra were recorded on a Hitachi 295 spectrophotometer, and FD mass spectra on a JMS-SX 102 spectrometer. Elemental analyses were performed by Material Analysis Center, ISIR, Osaka University. Gel permiation chromatograms were obtained using a Shimadzu HSG-20® column with THF as a mobile phase.

trans-Diethynylbis(trialkylphosphine)metal complexes, $\mathrm{(R_3P)_2M(C{\equiv}CH)_2}$ (M=Pd, Pt; R=Me, Et, *n*-Bu), were prepared from the reaction of dichlorobis(trialkylphosphine)metal complex, $\mathrm{(R_3P)_2MCl_2}$ (M=Pd, Pt; R=Me, Et, *n*-Bu), with acetylene in the presence of CuCl as catalyst in diethylamine.[7)]

Synthesis of $\mathrm{Cl(Et_3P)_2Pt(C{\equiv}CH)}$ (1a). *trans*-Diethynylbis(triethylphosphine)platinum (723 mg, 1.5 mmol) was treated with dichlorobis(triethylphosphine)platinum (754 mg, 1.5 mmol) in the presence of 5 mg of copper(I) chloride as catalyst in 30 ml of dioxane under reflux. After 7 h the solvent was evaporated under reduced pressure, and the residue was purified by chromatography on alumina with benzene as eluent. Recrystallization from dichloromethane–hexane gave white crystals (1101 mg, 75%). Mp 84—85 °C, IR $\nu_{\equiv\mathrm{C-H}}$ 3250 cm^{-1}, $\nu_{\mathrm{C\equiv C}}$ 1990 cm^{-1}. Found: C, 34.44; H, 6.29; P, 12.33; Cl, 7.46%. Calcd for $\mathrm{C_{14}H_{31}P_2ClPt}$: C, 34.19; H, 6.35; P, 12.59; Cl, 7.21%.

Synthesis of $\mathrm{Cl(Me_3P)_2Pt(C{\equiv}CH)}$ (1b) and $\mathrm{Cl(Bu_3P)_2Pt(C{\equiv}CH)}$ (1c). These complexes were prepared from *trans*-diethynylbis(trialkylphosphine)platinum and dichlorobis(trialkylphosphine)platinum by a similar method. THF was used as the solvent for preparation of **1b**, and recrystallization from dichloromethane–hexane gave white crystals of **1b**. But unfortunately we were not able to obtain analytically pure sample of **1c**, because **1c** is an oily product and it is difficult to separate **1c** from small amounts of concomitant such as diethynylplatinum and μ-ethynediylplatinum complexes. **1b**: Mp 197—199 °C, IR $\nu_{\equiv\mathrm{C-H}}$ 3260 cm^{-1}, $\nu_{\mathrm{C\equiv C}}$ 1985 cm^{-1}. Found: C, 24.02; H, 4.32; P, 15.03; Cl, 8.53%. Calcd for $\mathrm{C_8H_{19}P_2ClPt}$: C, 23.57; H, 4.70; P, 15.19; Cl, 8.70%. **1c**: IR $\nu_{\equiv\mathrm{C-H}}$ 3260 cm^{-1}, $\nu_{\mathrm{C\equiv C}}$ 1985 cm^{-1}.

Synthesis of $\mathrm{Cl(Et_3P)_2PtC{\equiv}CPd(PEt_3)_2Cl}$ (3a). *trans*-Chloroethynylbis(triethylphosphine)platinum (180 mg, 0.37 mmol) was treated with *trans*-dichlorobis(triethylphosphine)palladium (151 mg, 0.37 mmol) in the presence of 5 mg of copper(I) chloride as catalyst in 30 ml of diethylamine at room temperature for 4 h. The solvent was removed in vacuo, and the residue was purified by chromatography on alumina with benzene as eluent. Recrystallization from dichloromethane–hexane gave yellow crystals (279 mg, 88%). Found: C, 35.96; H, 6.72; P, 14.35; Cl, 8.23%. Calcd for $\mathrm{C_{26}H_{60}P_4Cl_2PdPt}$: C, 35.93; H, 6.96; P, 14.26; Cl, 8.16%.

Synthesis of $\mathrm{Cl(Me_3P)_2PtC{\equiv}CPd(PMe_3)_2Cl}$ (3b) and $\mathrm{Cl(Bu_3P)_2PtC{\equiv}CPd(PBu_3)_2Cl}$ (3c). These complexes were prepared by a method similar to that for **3a**, but **3c** needed longer reaction time, that is 24 h. As the eluent for the purification by chromatography on alumina, dichloromethane was used for **3b** and benzene for **3c**. Pure complex **3b** was obtained by recrystallization from dichloromethane–hexane in 54% yield and complex **3c** from hexane in 90% yield. **3b**: Found: C, 23.80; H, 4.84; P, 17.69; Cl, 9.96%. Calcd for $\mathrm{C_{14}H_{36}P_4Cl_2PdPt}$: C, 24.00; H, 5.18; P, 17.68; Cl, 10.12%. **3c**: Found: C, 49.57; H, 9.36; P, 10.52; Cl, 5.78%. Calcd for $\mathrm{C_{50}H_{108}P_4Cl_2PdPt}$: C, 49.84; H, 9.03; P, 10.28; Cl, 5.88%.

Synthesis of $\mathrm{Cl(Et_3P)_2Pd(C{\equiv}CH)}$ (4a). *trans*-Diethynylbis(triethylphosphine)palladium (589 mg, 1.5 mmol) was treated with *trans*-dichlorobis(triethylphosphine)palladium (621 mg, 1.5 mmol) in the presence of 5 mg of copper(I) chloride as catalyst in 50 ml of diethyl ether at room temperature for 12 h. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on alumina with benzene as eluent. Recrystallization from dichloromethane–hexane gave pale yellow crystals (784 mg, 65%). Mp 88—90 °C, IR $\nu_{\equiv\mathrm{C-H}}$ 3240 cm^{-1}, $\nu_{\mathrm{C\equiv C}}$ 1980 cm^{-1}. Found: C, 41.86; H, 7.72; P, 15.16; Cl, 8.89%. Calcd for $\mathrm{C_{14}H_{31}P_2ClPd}$: C, 41.70; H, 7.75; P, 15.36; Cl, 8.79%.

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