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## Synthesis, Characterization, and Molecular Structure of $\mu$ -Ethyne-diyl Complexes $[X(PR_3)_2MC\equiv CM(PR_3)_2X]$ ( $M = Pd, Pt; R = Me, Et, n\text{-Bu}; X = Cl, I$ )<sup>†</sup>

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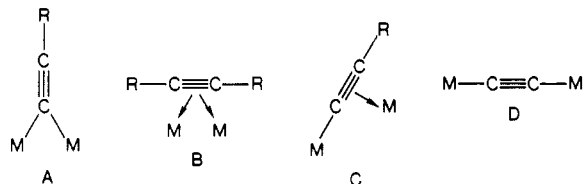
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Dinuclear palladium and platinum complexes,  $[X(PR_3)_2MC\equiv CM(PR_3)_2X]$  ( $M = Pd, Pt; R = Me, Et, n\text{-Bu}; X = Cl, I$ ), have been synthesized as the first examples of group 10 metal- $\mu$ -ethyne-diyl complexes from the reaction of diethynylbis(trialkylphosphine)metal complexes with dichlorobis(trialkylphosphine)metal complexes in the presence of copper(I) chloride in diethylamine. The complexes were characterized by IR, Raman, mass, and <sup>13</sup>C and <sup>31</sup>P NMR spectra. A single-crystal X-ray analysis unequivocally established the structure of  $I Pt(PMe_3)_2C\equiv CPt(PMe_3)_2I$  in which two square planes defined by  $PtP_2IC$  connected perpendicularly. Crystal data: monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 14.133$  (5) Å,  $b = 9.916$  (3) Å,  $c = 21.284$  (7) Å, and  $\beta = 113.51$  (2)°.

### Introduction

There are many possible bonding modes of acetylene ligands in organometallic compounds<sup>1</sup> because acetylene can act as a ligand bridging a pair of metal atoms. Their representative bondings in the dinuclear complexes are A ( $\eta^1(\sigma, \sigma)$ ), B ( $\eta^2(\pi, \pi)$ ), C ( $\eta^2(\sigma, \pi)$ ), and D ( $\eta^2(\sigma, \sigma)$ ). Bonding in an  $\eta^2(\sigma, \sigma)$  fashion (D) is thus one of the principal modes but has not previously been found for group 10 metal compounds,<sup>2</sup> though it is common for elements of group 11 (Cu, Ag, Au), group 2 (Ca, Ba), and group 14 (Si, Sn).



We previously reported the synthesis and properties of metal-poly(yne) polymers (E) in which transition metals are linked by conjugated acetylenes such as buta-1,3-diyne.<sup>3,4</sup> Polymers E provided the first example of organometallic polymers containing transition metals in the main chain through M-C  $\sigma$ -bond. Polymers having

structure F in which transition metals are bound by just one acetylenic unit may be of special interest since they are expected to have unique properties based on the vicinal metals and the rodlike structure. However, as mentioned above  $\mu$ -ethyne-diyl complexes of group 10 metals, which are the fundamental structure of polymer F, have been so far unknown. Hence we have attempted to synthesize the binuclear  $\mu$ -ethyne-diyl complexes (G) as a model subunit of F. In this paper we wish to report the first synthesis of  $\mu$ -ethyne-diyl complexes of palladium and platinum and the molecular structure of 2'a ( $G, M = Pt, R = Me, X = I$ ) as well as their properties.

### Experimental Section

**Materials.** Diethylamine was purchased from Wako Pure Chemical Co. and used without further purification. Tributyl-

(1) See for a review: Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* 1983, 83, 203.

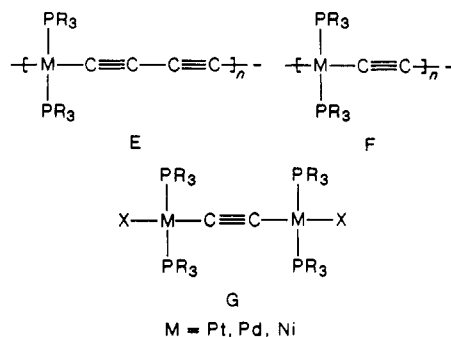
(2) See for a reviews: Holton, J.; Lappart, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* 1983, 83, 135.

(3) (a) Takahashi, S.; Kariya, M.; Yatake, M.; Sonogashira, K.; Hagihara, N. *Macromolecules* 1978, 11, 1064. (b) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Chem., Polym. Chem. Ed.* 1980, 18, 349. (c) Takahashi, S.; Murata, E.; Sonogashira, K.; Hagihara, N. *Ibid.* 1980, 18, 661. (d) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *Ibid.* 1982, 20, 565.

(4) (a) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* 1978, 160, 319. (b) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *Ibid.* 1980, 188, 237.

<sup>†</sup>The preliminary result was presented in ref 12.

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phosphine was obtained commercially. Trimethylphosphine and triethylphosphine were prepared from appropriate alkyl Grignard reagents and triphenyl phosphite.<sup>5</sup> Dichlorobis(trialkylphosphine)metal complexes,  $(\text{PMe}_3)_2\text{PdCl}_2$ ,  $(\text{PEt}_3)_2\text{PdCl}_2$ ,  $(\text{PBu}_3)_2\text{PdCl}_2$ , and *cis*- $(\text{PMe}_3)_2\text{PtCl}_2$ , were prepared by literature methods.<sup>6</sup> Diethynylbis(trialkylphosphine)metal complexes, *trans*- $(\text{PR}_3)_2\text{Pd}(\text{C}\equiv\text{CH})_2$  ( $\text{R} = \text{Me, Et, } n\text{-Bu}$ ) and *trans*- $(\text{PMe}_3)_2\text{Pt}(\text{C}\equiv\text{CH})_2$ , were prepared from the reaction between dichlorobis(trialkylphosphine)metal complexes and acetylene in the presence of copper(I) chloride catalyst in diethylamine as we previously reported.<sup>7</sup>

**Physical Measurements.** Elemental analyses were performed by Material Analysis Center, ISIR, Osaka University. Infrared spectra were recorded on a Hitachi 295 infrared spectrophotometer. Field-desorption mass spectra were obtained on JMS-01SG-2 spectrometer. <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Bruker AM-360 and a JEOL FX-100 spectrometer, respectively. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were measured in CD<sub>2</sub>Cl<sub>2</sub> against an internal Me<sub>4</sub>Si reference and <sup>31</sup>P{<sup>1</sup>H} NMR spectra in CH<sub>2</sub>Cl<sub>2</sub> against an external PPh<sub>3</sub> reference.

**Cl(PMe<sub>3</sub>)<sub>2</sub>PdC≡CPd(PMe<sub>3</sub>)<sub>2</sub>Cl (1a).** *trans*-Diethynylbis(trimethylphosphine)palladium (0.155 g, 0.5 mmol) was treated with 0.495 g (1.5 mmol) of dichlorobis(trimethylphosphine)palladium in the presence of 20 mg of copper(I) chloride as catalyst in 20 mL of diethylamine and stirred for 3 h at room temperature under a nitrogen atmosphere. The yellow suspension became white. The solvent was evaporated in vacuo, and the residue was purified by chromatography on alumina with dichloromethane as the eluent. Recrystallization from dichloromethane-hexane gave pale yellow crystals of complex 1a in 53% yield, decomposition at 181–184 °C. Anal. Calcd for C<sub>14</sub>H<sub>36</sub>P<sub>4</sub>Cl<sub>2</sub>Pd<sub>2</sub>: C, 27.47; H, 5.93; P, 20.24, Cl, 11.58. Found: C, 27.68; H, 6.17, P, 20.47; Cl, 11.74.

This complex is stable in an inert atmosphere at 0 °C but slowly decomposed in air and fast in a solution.

**Cl(PR<sub>3</sub>)<sub>2</sub>PdC≡CPd(PR<sub>3</sub>)<sub>2</sub>Cl (1b, R = Et; 1c, R = *n*-Bu).** These complexes were prepared from the complexes containing triethyl- or tri-*n*-butylphosphine instead of trimethylphosphine by the method similar to that of 1a. The reactions proceeded at room temperature, but they needed longer reaction time, that is, 17 h for 1b and 64 h for 1c. The completion of the reaction was indicated by the disappearance of yellow color of the solution. As the eluent for the purification by chromatography, dichloromethane was used for 1b and benzene for 1c. Recrystallization from toluene-hexane gave lemon yellow crystals of 1b in 70% yield and from *n*-hexane gave lemon yellow crystals of 1c in 64% yield. 1b: mp 111.5–113.0 °C dec. Anal. Calcd for C<sub>26</sub>H<sub>60</sub>P<sub>4</sub>Cl<sub>2</sub>Pd<sub>2</sub>: C, 40.02; H, 7.75; P, 15.88; Cl, 9.09. Found: C, 40.23; H, 7.60; P, 15.83; Cl, 9.15. 1c: mp 122–123 °C dec. Anal. Calcd for C<sub>50</sub>H<sub>108</sub>P<sub>4</sub>Cl<sub>2</sub>Pd<sub>2</sub>: C, 53.76; H, 9.5; P, 11.09; Cl, 6.35. Found: C, 53.51; H, 9.55; P, 10.83; Cl, 6.57. These complexes are stable in an inert atmosphere but decompose gradually in air.

**Cl(PMe<sub>3</sub>)<sub>2</sub>PtC≡Cpt(PMe<sub>3</sub>)<sub>2</sub>Cl (2a).** This complex was prepared by the method similar to that of 1a from the reaction between *trans*- $(\text{PMe}_3)_2\text{Pt}(\text{C}\equiv\text{CH})_2$  and 3 equiv of *cis*-Pt(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, but it needed higher reaction temperature and longer

reaction time, i.e., reflux of diethylamine and the period of 1 week. Purification by chromatography on alumina with dichloromethane and recrystallization from hot methanol gave the colorless needles of 2a in 61% yield, decomposition at 230–234 °C. Anal. Calcd for C<sub>14</sub>H<sub>36</sub>P<sub>4</sub>Cl<sub>2</sub>Pt<sub>2</sub>: C, 21.30; H, 4.60; P, 15.69; Cl, 8.98. Found: C, 21.58; H, 4.49; P, 15.48; Cl, 8.95. This compound is stable in air.

**Cl(PR<sub>3</sub>)<sub>2</sub>PtC≡Cpt(PR<sub>3</sub>)<sub>2</sub>Cl (2b, R = Et; 2c, R = *n*-Bu).** These complexes were prepared from the complexes (PR<sub>3</sub>)<sub>2</sub>Pt(C≡CH)<sub>2</sub> by the method similar to that of 2a with piperidine as a base instead of diethylamine. The reaction was carried out under reflux for 2 days. Pure complex 2b was obtained by recrystallization from toluene and hexane and complex 2c from hexane. 2b: mp 111–113 °C. Anal. Calcd for C<sub>26</sub>H<sub>60</sub>P<sub>4</sub>Cl<sub>2</sub>Pt<sub>2</sub>: C, 32.61; H, 6.31; P, 12.94; Cl, 7.40. Found: C, 32.78; H, 6.23; P, 12.71; Cl, 7.58. 2c: mp 122–123 °C. Anal. Calcd for C<sub>50</sub>H<sub>108</sub>P<sub>4</sub>Cl<sub>2</sub>Pt<sub>2</sub>: C, 46.40; H, 8.41; P, 9.57; Cl, 5.48. Found: C, 46.56; H, 8.32; P, 9.61; Cl, 5.76.

**Conversion of the Chlorides to the Iodides (1 → 1', 2 → 2').** The  $\mu$ -ethynediyl complexes having the terminal chlorine ligands (1a–c, 2a) were treated with 8 times excess of potassium iodide in dichloromethane overnight at room temperature under nitrogen atmosphere. Purification was performed by the method similar to that of the starting materials. 1'a: yield, 72%; decomposition at 166–170 °C. Anal. Calcd for C<sub>14</sub>H<sub>36</sub>P<sub>4</sub>I<sub>2</sub>Pd<sub>2</sub>: C, 21.15; H, 4.56; P, 15.58; I, 31.93. Found: C, 21.36; H, 4.48; P, 15.58; I, 31.79. 1'b: yield, 81%; mp 112–114 °C dec. Anal. Calcd for C<sub>26</sub>H<sub>60</sub>P<sub>4</sub>I<sub>2</sub>Pd<sub>2</sub>: C, 32.42; H, 6.28; P, 12.86; I, 26.35. Found: C, 32.15; H, 6.16; P, 12.68; I, 26.10. 1'c: yield, 78%; mp 121.5–123.5 °C dec. Anal. Calcd for C<sub>50</sub>H<sub>108</sub>P<sub>4</sub>I<sub>2</sub>Pd<sub>2</sub>: C, 46.20; H, 8.37; P, 9.53; I, 19.52. Found: C, 46.35; H, 8.13; P, 9.66; I, 19.59. 2'a: yield, 64%; decomposition at 214–216 °C. Anal. Calcd for C<sub>14</sub>H<sub>36</sub>P<sub>4</sub>I<sub>2</sub>Pt<sub>2</sub>: C, 17.29; H, 3.73; P, 12.74; I, 26.10. Found: C, 17.52; H, 3.50; P, 12.61; I, 26.02. Stabilities of these complexes are substantially unchanged compared with the corresponding chloride complexes.

**(PBu<sub>3</sub>)<sub>2</sub>PdCl(C≡CH) (3).** *trans*-Diethynylbis(tri-*n*-butylphosphine)palladium (0.249 g, 0.444 mmol) was reacted with 0.387 g (0.666 mmol) of dichlorobis(tri-*n*-butylphosphine)palladium in the presence of 10 mg of copper(I) chloride as catalyst in 30 mL of diethylamine and stirred at room temperature under nitrogen atmosphere. After 3 h the solvent was evaporated in vacuo and the residue was purified by chromatography on alumina with benzene/hexane (1/2) as the eluent. The pale yellow, oily product 3 was obtained in 49% yield based on the diethynylmetal complex used.

**Collection of X-ray Diffraction Data and Structure Determination for Complex 2'a.** The preliminary data collection shows the crystal to be monoclinic, with systematic extinctions (*h*0*l*, *l* = 2*n*; 0*k*0, *k* = 2*n*) consistent with the space group *P*2<sub>1</sub>/*c*. Crystal data for C<sub>14</sub>H<sub>36</sub>I<sub>2</sub>P<sub>4</sub>Pt<sub>2</sub> (mol wt 972.3) are *a* = 14.133 (5) Å, *b* = 9.916 (3) Å, *c* = 21.284 (7) Å, β = 113.51 (2)°, *V* = 2735 (2) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 2.36, and *F*(000) = 1768.

The dimensions of the crystal were approximately 0.17 × 0.41 × 0.05 mm. The crystal with six faces of the form [(100), (010), (001), (100), (010), (001)] was mounted such that the *b* axis was nearly parallel to the φ axis of a Rigaku four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation with 2θ < 45° and the ω-2θ (≤30°) and ω (>30°) scan techniques with a scan rate of 4 deg min<sup>-1</sup>. A total of 2965 reflections were measured. The 2127 reflections for which *F*<sub>o</sub> ≥ 5σ(*F*<sub>o</sub>) were used in the calculations. Intensities were corrected for Lorentz and polarization effects. The positions of two Pt atoms were determined by a heavy-atom method, using the UNICS III program system.<sup>8</sup> The other non-hydrogen atomic positions were subsequently found from a series of difference Fourier maps. The positions of non-hydrogen atoms were refined anisotropically by using block-diagonal least-squares methods, minimizing Σw(|*F*<sub>o</sub> - |*F*<sub>c</sub>||<sup>2</sup>). The refinement converged to *R* = Σ(|*F*<sub>o</sub> - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>) and *R*<sub>w</sub> = [Σw(|*F*<sub>o</sub> - |*F*<sub>c</sub>||<sup>2</sup>)/Σ|*F*<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> of 0.1071 and 0.1263, respectively. In this step, an absorption correction was made.<sup>9</sup> The linear absorption coefficient is 12.6 cm<sup>-1</sup>. The calculated transmission factors varied from 0.14 to 0.54. The final *R* and *R*<sub>w</sub> values

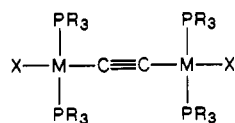
(5) We thank Prof. Masanori Wada for his suggestion of an improved preparation of trialkylphosphines from triphenyl phosphite instead of phosphorus trichloride.

(6) Jensen, K. A. Z. Anorg. Allg. Chem. 1936, 229, 225.

(7) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. J. Organomet. Chem. 1978, 145, 101.

(8) Sakurai, T.; Kobayashi, K. UNICS III System, 1978.

(9) The program BP70 (by T. Ito) used the Gaussian integration method of Busing and Levy.

Table I. Characterization of  $\mu$ -Ethyndiyl Complexes

complex	M	R	X	mp (dec), °C	Raman, $\text{cm}^{-1}$	$^{31}\text{P}$ NMR, <sup>a</sup> ppm ( $J_{\text{Pt-P}}$ , Hz)	MS, m/z
1a	Pd	Me	Cl	181–184°	2008	–9.76	611
1'a	Pd	Me	I	166–170°	2004	–14.39	b
1b	Pd	Et	Cl	111–113		20.02	780
1b'	Pd	Et	I	112–114°		18.82	b
1c	Pd	Bu	Cl	122–123		13.04	1116
1c'	Pd	Bu	I	121–123°		9.86	b
2a	Pt	Me	Cl	230–234°	2024	–9.30 ( $^1J = 2445$ , $^4J = 14.6$ )	787
2'a	Pt	Me	I	214–216°	2022	–17.51 ( $^1J = 2364$ , $^4J = 13.7$ )	b
2b	Pt	Et	Cl	129–133		19.88 ( $^1J = 2520$ , $^4J = 11.7$ )	
2c	Pt	Bu	Cl	142–145°		11.43 ( $^1J = 2507$ )	

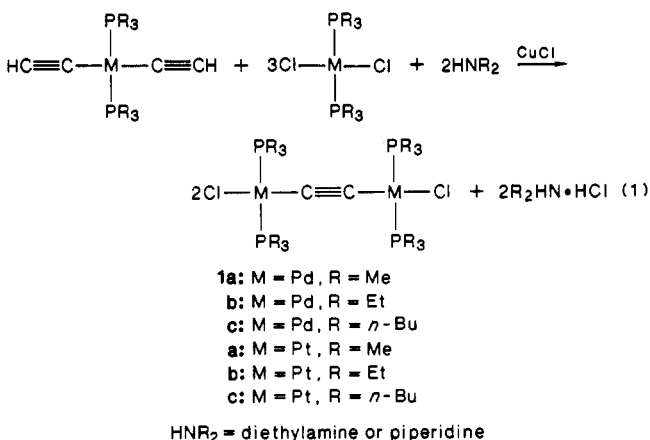
<sup>a</sup>Downfield shifts from external  $\text{PPh}_3$  are positive; in  $\text{CH}_2\text{Cl}_2$ .  
<sup>c</sup>Decomposed without melt.

<sup>b</sup>Molecular ions were not detected by field-desorption mass spectra.

were 0.063 and 0.076 (number of variables refined = 200), respectively, adopting  $w = 0.5$  ( $|F_o| < 50$ ),  $w = 1.0$  ( $50 \leq |F_o| < 200$ ), and  $w = (200/F_o)^2$  ( $F_o \geq 200$ ). The ratio of parameter shift to standard deviation in the parameters in the last cycle was 0.2. A final difference Fourier map showed no residual peaks more than  $2.1 \text{ e } \text{\AA}^{-3}$  around the heavy atoms and did not show any residual peaks greater than  $0.7 \text{ e } \text{\AA}^{-3}$  associated other ligand atoms. No attempt was made to locate the hydrogen atoms. Anomalous dispersion effects were included in the calculation of  $F_c$  by using  $\Delta f'$  and  $\Delta f''$  calculated by Cramer.<sup>10</sup> The atomic scattering factors for Pt, I, P, and C were from the usual tabulation.<sup>11</sup> A list of observed and calculated structure factor is available. The final atomic coordinates parameters are listed in Table III.

## Results and Discussion

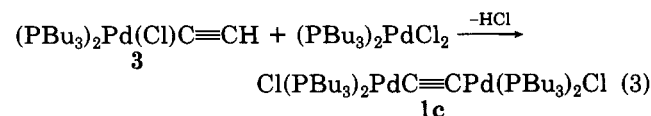
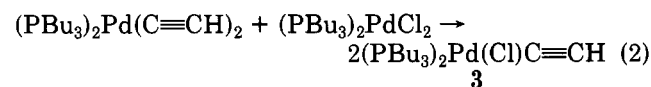
**Synthesis of  $\mu$ -Ethyndiyl Complexes.** The first examples of  $\mu$ -ethyndiyl complexes of group 10 metals are presented. These complexes were synthesized by the direct reaction of diethynylmetal complexes  $(\text{PR}_3)_2\text{M}(\text{C}\equiv\text{CH})_2$  with dichlorometal complexes  $(\text{PR}_3)_2\text{MCl}_2$  in the molar ratio of 1:3 in the presence of copper(I) chloride as a catalyst in diethylamine (eq 1). The amine plays an important role as the acceptor of hydrogen chloride as well as the solvent which dissolves the copper(I) catalyst.



The new  $\mu$ -ethyndiyl complexes were characterized by spectral analyses and gel permeation chromatography. The field-desorption mass spectra showed molecular ions for all the chloride complexes (1a–c, 2a) but none for the iodide complexes. For all of these complexes, no  $\text{C}\equiv\text{C}$  stretching absorption was observed in their IR spectra

because such modes would be symmetry-forbidden. Instead intense Raman scattering peaks were observed around  $2000 \text{ cm}^{-1}$ , indicating these are symmetric acetylene compounds. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1a showed the weak resonance of acetylenic carbon at  $\delta$  101.91 as well as the  $\text{PMe}_3$  ligand resonance at  $\delta$  15.15 (virtual triplet,  $J_{\text{C-P}} = 15.6 \text{ Hz}$ ). The  $^{31}\text{P}$  resonance of palladium complexes (1a–c) appeared as a single peak, indicating that all phosphine ligands are equivalent. For the platinum complex 2a, in addition, the resonances contain satellite peaks by the  $^1J_{\text{Pt-P}}$  and  $^4J_{\text{Pt-P}}$  couplings, 2445 and 14.6 Hz, respectively. Gel permeation chromatography using a SHIMAZU HSG-20 column with tetrahydrofuran as the mobile phase, which can separate multinuclear complexes  $\text{Cl}-[\text{M}(\text{PR}_3)_2\text{C}\equiv\text{C}]_n-\text{M}(\text{PR}_3)_2\text{Cl}$  from each other up to tetranuclear ( $n = 3$ ), indicates that these complexes are all dinuclear. The spectral data are summarized in Table I.

In a previous communication,<sup>12</sup> we reported that a similar reaction of diethynylbis(tri-*n*-butylphosphine)palladium with dichlorobis(tri-*n*-butylphosphine)palladium did not give the  $\mu$ -ethyndiyl complex 1c but yielded the proportionation product *trans*-(chloroethynyl)bis(tri-*n*-butylphosphine)palladium (3), possibly owing to a steric factor due to the bulky tributylphosphine ligand which prevented the further condensation. However, we now believe that additional reaction time resulted in a further reaction of the chloroethynyl complex 3 with the residual dichloro complex giving the  $\mu$ -ethyndiyl complex 1c as the final product. This fact implies that in the copper-catalyzed reaction between the diethynyl complexes and dichloro complexes, the ligand exchange takes place first, followed by a second step of dehydrochlorination to give the  $\mu$ -ethyndiyl complexes. The latter step may be strongly affected by steric factors of the phosphorus ligands attached to the two central metal atoms close to each other.



**Description of Structure.** The molecular structure of 2'a is illustrated in Figure 1. The molecule consists of

(10) Cramer, D. T.; Weber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(11) Cramer, D. T. *Acta Crystallogr.* 1965, 18, 17.

(12) Ogawa, H.; Joh, T.; Takahashi, S.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* 1985, 1220.

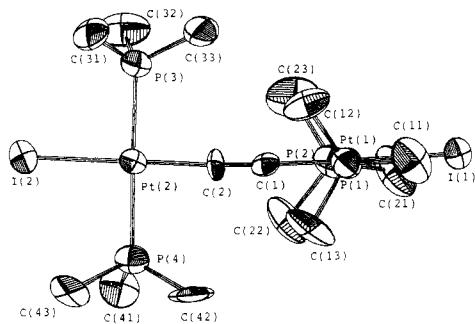


Figure 1. A perspective view of  $\text{IPt}(\text{PMe}_3)_2\text{C}\equiv\text{C}\equiv\text{Pt}(\text{PMe}_3)_2\text{I}$  (**2'a**) showing the atom numbering scheme.

Table II. Positional Parameters ( $\times 10^4$ ) for Complex **2'a**

atom	x	y	z	B(eq), $\text{\AA}^2$
Pt(1)	2783 (1)	6917 (1)	3057 (1)	4.0 (0.0)
Pt(2)	1658 (1)	3487 (1)	1094 (1)	3.5 (0.0)
I(1)	3501 (2)	8586 (3)	4114 (1)	6.3 (0.1)
I(2)	1224 (2)	1446 (3)	217 (1)	5.5 (0.1)
P(1)	2323 (7)	8587 (10)	2254 (5)	4.6 (0.3)
P(2)	3104 (7)	4983 (12)	3713 (5)	5.3 (0.3)
P(3)	3314 (6)	3555 (10)	1135 (5)	4.0 (0.3)
P(4)	-2 (6)	3507 (10)	1040 (5)	4.4 (0.3)
C(1)	2275 (20)	5670 (30)	2270 (14)	2.9 (0.9)
C(2)	2017 (24)	4862 (33)	1826 (18)	4.7 (1.2)
C(11)	2537 (34)	10340 (43)	2519 (24)	7.8 (1.8)
C(12)	2977 (31)	8452 (46)	1664 (20)	6.6 (1.6)
C(13)	940 (24)	8494 (44)	1681 (23)	7.7 (1.6)
C(21)	3461 (37)	5202 (57)	4660 (21)	9.1 (2.0)
C(22)	1980 (32)	3834 (48)	3471 (20)	7.6 (1.6)
C(23)	4086 (35)	3901 (51)	3572 (28)	9.1 (2.2)
C(31)	3380 (30)	3646 (43)	350 (20)	6.0 (1.5)
C(32)	4113 (34)	2145 (56)	1590 (26)	8.6 (2.1)
C(33)	4126 (34)	4910 (51)	1588 (30)	9.4 (2.4)
C(41)	-266 (32)	2105 (38)	1474 (21)	6.2 (1.6)
C(42)	-428 (27)	5026 (49)	1301 (27)	7.9 (2.0)
C(43)	-1037 (24)	3212 (60)	129 (18)	8.5 (1.8)

a geometry in which each vacant site of two  $\text{PtIP}_2$  planes is connected by the ethynediyl group. The ethynediyl group coordinates to two Pt atoms by two sp orbitals; thus, the two platinum and two carbon atoms are colinear. The square planes are twisted away from each other such that angle between the two five-atom least-squares planes is  $89.8 (3)^\circ$ , contrasted with the result that the dihedral angle between  $\text{PtClP}_2\text{C}$  and  $\text{PtP}_2\text{C}_2$  planes is  $2.7^\circ$  in  $\text{Cl}(\text{n-Bu}_3\text{P})_2\text{PtC}\equiv\text{CC}\equiv\text{C}\equiv\text{Pt}(\text{n-Bu}_3\text{P})_2\text{C}\equiv\text{CC}\equiv\text{C}\equiv\text{Pt}(\text{n-Bu}_3\text{P})_2\text{Cl}$  (**4**).<sup>13</sup> From extended Hückel molecular orbital calculations of the model compound  $\text{Cl}(\text{PH}_3)_2\text{PtC}\equiv\text{C}\equiv\text{Pt}(\text{PH}_3)_2\text{Cl}$ , the total energy difference was very small ( $\sim 1$  kcal/mol) between complexes having the eclipsed and staggered geometry. Maybe the result is interpreted by the fact that the p orbitals of acetylenes are cylindrical around the C-C axis. The difference of conformations between these two complexes **2'a** and **4** is attributed to the steric factors of

(13) Aoki, K.; Yamazaki, H., unpublished results.

Table III. Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (deg) for  $\text{IPt}(\text{PMe}_3)_2\text{C}\equiv\text{C}\equiv\text{Pt}(\text{PMe}_3)_2\text{I}$  (**2'a**)

Distances			
Pt(1)-I(1)	2.646 (4)	Pt(1)-C(1)	1.973 (30)
Pt(1)-P(1)	2.280 (11)	Pt(1)-P(2)	2.307 (12)
Pt(2)-I(2)	2.652 (3)	Pt(2)-P(3)	2.308 (10)
Pt(2)-P(4)	2.304 (10)	C(1)-C(2)	1.179 (48)
Pt(2)-C(2)	1.980 (38)		
Angles			
I(1)-Pt(1)-P(1)	94.6 (3)	I(1)-Pt(1)-P(2)	95.2 (3)
I(1)-Pt(1)-C(1)	178.9 (9)	P(1)-Pt(1)-P(2)	170.1 (4)
P(1)-Pt(1)-C(1)	85.4 (9)	P(2)-Pt(1)-C(1)	84.8 (9)
I(2)-Pt(2)-P(3)	89.7 (3)	I(2)-Pt(2)-P(4)	91.5 (3)
I(2)-Pt(2)-C(2)	173.8 (11)	P(3)-Pt(2)-P(4)	177.7 (4)
P(3)-Pt(2)-C(2)	90.7 (11)	P(4)-Pt(2)-C(2)	88.2 (11)
Pt(1)-C(1)-C(2)	175.6 (30)	Pt(2)-C(2)-C(1)	177.1 (33)

phosphine ligand. In the  $-\text{C}\equiv\text{C}$ -bridging complex, for minimization of the repulsive interaction between the phosphine ligands, the staggered structure is adopted. The close distances associated with methyl groups are  $3.87 (6)$   $\text{\AA}$  for  $\text{C}13\cdots\text{C}42$  and  $3.90 (7)$   $\text{\AA}$  for  $\text{C}12\cdots\text{C}33$ , comparable with the sum of the van der Waals radii of the methyl groups ( $2.0$   $\text{\AA}$ ). On the other hand, in the  $-\text{C}\equiv\text{CC}\equiv\text{C}$ -bridging complex no repulsive interaction exists between the phosphine ligands. The eclipsed geometry of complex **4** may also be due to electronic or packing effects.

The  $\text{C}(1)-\text{C}(2)$  bond length is  $1.18 (5)$   $\text{\AA}$ , not significantly different from those in the acetylide complexes. The Pt-P distances ( $2.28$ - $2.31$   $\text{\AA}$ ) are normal as found in the related  $\text{trans-Pt}^{\text{II}}(\text{phosphine})_2$  complexes.<sup>14</sup>

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**Registry No.** **1a**, 101679-96-3; **1'a**, 101809-33-0; **1b**, 115796-33-3; **1'b**, 115796-36-6; **1c**, 115796-34-4; **1'c**, 115796-37-7; **2a**, 101679-97-4; **2'a**, 101771-25-9; **2b**, 115826-41-0; **2c**, 115796-35-5; **3**, 115888-50-1;  $\text{trans}-(\text{PMe}_3)_2\text{Pd}(\text{C}\equiv\text{CH})_2$ , 101679-95-2;  $\text{Pd}(\text{PMe}_3)_2\text{Cl}_2$ , 25892-38-0;  $\text{trans}-(\text{PEt}_3)_2\text{Pd}(\text{C}\equiv\text{CH})_2$ , 34230-57-4;  $\text{trans}[\text{P}(\text{n-Bu})_3]_2\text{Pd}(\text{C}\equiv\text{CH})_2$ , 85477-99-2;  $\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ , 28425-04-9;  $\text{Pd}[\text{P}(\text{n-Bu})_3]_2\text{Cl}_2$ , 14977-08-3;  $\text{trans}-(\text{PMe}_3)_2\text{Pt}(\text{C}\equiv\text{CH})_2$ , 45048-40-6;  $\text{cis-Pt}(\text{PMe}_3)_2\text{Cl}_2$ , 15630-86-1;  $\text{trans}-(\text{PEt}_3)_2\text{Pt}(\text{C}\equiv\text{CH})_2$ , 34230-58-5;  $\text{trans}[\text{P}(\text{n-Bu})_3]_2\text{Pt}(\text{C}\equiv\text{CH})_2$ , 65831-67-6;  $\text{cis-Pt}(\text{PEt}_3)_2\text{Cl}_2$ , 15692-07-6;  $\text{cis-Pt}[\text{P}(\text{n-Bu})_3]_2\text{Cl}_2$ , 15390-92-8.

**Supplementary Material Available:** Listings of molecular planes (Table IV), thermal parameters of non-hydrogen atoms (Table V), and bond distances and angles (Table VII) (3 pages); a listing of structure factors amplitudes (Table VI) (12 pages). Ordering information is given on any current masthead page.

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