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## SYNTHESES AND PROPERTIES OF *cis*- AND *trans*-DIALKYNYL COMPLEXES OF PLATINUM(II)

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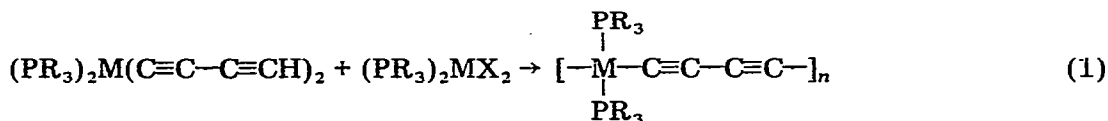
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### Summary

Selective syntheses of *cis*- and *trans*-platinum(II) acetylide complexes of the type  $(R_3P)_2Pt(C\equiv CR')_2$  (where R = Et or n-Bu, R' = H, CH=CH<sub>2</sub>, C≡CH, Ph or *p*-C<sub>6</sub>H<sub>4</sub>C≡CH), and systematic studies on characterization of the *cis*- and *trans*-isomers by spectroscopic methods are reported.

### Introduction

Recently we have reported a convenient method for preparing transition metal- $\sigma$ -alkynyl complexes by the reaction between metal halides and acetylenes using cuprous halides as catalysts [1], and we have applied this method to a synthesis [2,3] of novel poly-yne polymers containing transition metals in the main chain backbone as shown in eq. 1. The poly-yne polymers (I) may be ex-



(I)

pected to have rod-like structures if the transition metals in the main chain have exclusively *trans*-configuration. In order to establish the configuration around the metal, we have attempted to synthesize model complexes of both the *trans*- and the *cis*-isomers of bis(trialkylphosphine)dialkynylplatinum complexes,  $(R_3P)_2Pt(C\equiv CR)_2$ , and to obtain information applicable to discrimination between the configurational isomers. Most of the alkynylplatinum(II) complexes which have appeared in the literature have the *trans* form and very few examples of the *cis* analogs are known [4]. We report here the selective syntheses of

both isomers and a systematic investigation of their physical and spectroscopic properties.

## Experimental

### Apparatus

IR spectra were taken in Nujol mulls with a Hitachi EPI2G or a Hitachi 295 spectrophotometer. Electronic spectra were recorded with a Shimadzu UV202 spectrometer.  $^1\text{H}$  NMR spectra were run on a Hitachi R20 spectrometer in  $\text{CD}_2\text{Cl}_2$ .

### Materials

The starting materials, *cis*- and *trans*-dichlorobis(triethylphosphine)platinum [5] and *cis*- and *trans*-dichlorobis(tri-*n*-butylphosphine)platinum [6] were prepared by standard procedures. Butadiyne [7], monovinylacetylene [8], *p*-diethynylbenzene [9] and their copper(I) derivatives [10] were prepared by literature methods.

### Syntheses of platinum acetylide complexes

All reactions were carried out under a nitrogen atmosphere.

#### Method A

*trans*-Bis(triethylphosphine)diethynylplatinum (Ia). Gaseous acetylene was bubbled into a solution of *trans*-( $\text{Et}_3\text{P}$ ) $_2\text{PtCl}_2$  (250 mg, 0.5 mmol) in 40 ml of diethylamine in the presence of CuI (10 mg), with stirring at room temperature. White, solid diethylammonium chloride immediately began to precipitate. After 30 min, the solvent was evaporated. Water (20 ml) was added to the solid residue and the mixture was extracted with benzene. Purification by chromatography on alumina using a mixture of benzene/hexane (1/1) provided pale yellow product. Recrystallization from *n*-hexane gave pale yellow needles of Ia in 90% yield, m.p. 62°C (lit. [11] m.p. 62–63°C). *trans*-Bis(tri-*n*-butylphosphine)diethynylplatinum (IIa) was prepared in this manner as a pale yellow oil in 90% yield. Purification by repeated chromatography on alumina gave analytically pure product.

*cis*-Bis(triethylphosphine)diethylplatinum (Ib). Gaseous acetylene was passed through a suspension of *cis*-( $\text{Et}_3\text{P}$ ) $_2\text{PtCl}_2$  (1 g, 2 mmol) in 100 ml of diethylamine in the presence of CuI (20 mg) at 0°C for one hour. White, solid diethylammonium chloride separated. After the solvent has been evaporated, water was added to the residue and the mixture was extracted with benzene. Evaporation of the extracts gave the crude product which was chromatographed on alumina. Elution with benzene/hexane (1/1) afforded Ia (7% yield), and elution with benzene/AcOEt (6/4) gave Ib which formed colorless needles (85% yield) from benzene/hexane. *cis*-Bis(tri-*n*-butylphosphine)diethynylplatinum (IIb) was prepared similarly and was isolated as colorless needles from *n*-hexane in 89% yield.

*trans*-Bis(tri-*n*-butylphosphine)dibutadiynylplatinum (IVa). A solution of *trans*-(*n*- $\text{Bu}_3\text{P}$ ) $_2\text{PtCl}_2$  (3.4 g, 5 mmol) in diethylamine (30 ml) was added to a solution of butadiyne (1 g, 20 mmol) in ether (30 ml) in the presence of CuI

(10 mg) at 0°C. After 2 h, evaporation of the solvent and purification of the residue by chromatography on alumina gave the pale yellow product, which was recrystallized from ethanol, affording pale yellow crystals of IVa in 90% yield. *trans*-Bis(tri-*n*-butylphosphine)bis(*p*-ethynylphenylethynyl)platinum (VIIa) was prepared similarly from *trans*-(*n*-Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (3.4 g, 5.0 mmol) and *p*-diethynylbenzene (2.5 g, 20 mmol) in 82% yield, yellow crystals from *n*-hexane.

*cis*-Bis(tri-*n*-butylphosphine)bisbutadiynylplatinum (IVb). To a solution of butadiyne (2 g, 40 mmol) and CuI (10 mg) in a mixture of ether (50 ml) and diethylamine (50 ml), solid *cis*-(*n*-Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (6.7 g, 10 mmol) was added at -78°C. The reaction was allowed to proceed at -20°C for one hour and then at room temperature for 30 min. Evaporation of the solvent and chromatography of the residue on alumina with benzene gave the crude product. Recrystallization from ether afforded colorless needles of IVb in 83% yield. *cis*-Bis(tri-*n*-butylphosphine)bis(*p*-ethynylphenylethynyl)platinum (VIIb) was prepared similarly from *cis*-(*n*-Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (3.4 g, 5 mmol) and *p*-diethynylbenzene (2.5 g, 20 mmol) in 90% yield, pale yellow needles from benzene/hexane.



*trans*-Bis(triethylphosphine)bis(phenylethynyl)platinum (Va). A mixture of *trans*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (502 mg, 1 mmol) and phenylacetylene (224 mg, 2.2 mmol) in diethylamine was allowed to react in the presence of CuI (5 mg) at room temperature for one hour. Evaporation of the solvent and purification of the residue by chromatography on alumina with hexane/benzene (1/1) afforded the pale yellow product. Recrystallization from *n*-hexane gave pale yellow needles of Va in 90% yield, m.p. 187–189°C (dec.) (lit. [11] m.p. 186–187°C (dec.)). *trans*-Bis(tri-*n*-butylphosphine)bis(phenylethynyl)platinum (VIa) was prepared in a similar manner in 87% yield, pale yellow crystals from methanol.

*cis*-Bis(triethylphosphine)bis(phenylethynyl)platinum (Vb). Phenylacetylene (2.2 mmol) was allowed to react with a suspension of *cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (1 mmol) in diethylamine (30 ml) in the presence of CuI (5 mg) at -20°C for one hour and then at 0°C for 2 h. After evaporation of the solvent, the residue was chromatographed on alumina with benzene, giving the colorless solid. Recrystallization from benzene/hexane afforded colorless needles of Vb in 87% yield. *cis*-Bis(tri-*n*-butylphosphine)bis(phenylethynyl)platinum (VIb) was prepared in this manner, colorless needles from *n*-hexane, 85% yield.

#### Method B

*cis*-Bis(triethylphosphine)bis(vinylethynyl)platinum (IIIb). To a mixture of *cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (502 mg, 1 mmol) and cuprous vinylacetylde (240 mg, 2 mmol) in 30 ml of acetone was added *N,N,N',N'*-tetramethylethylenediamine (350 mg) with stirring at room temperature. After a few minutes, the mixture turned from yellow to green. After one hour, the solvent was evaporated and the residue was chromatographed on alumina (benzene/ether), giving the yellow product. Recrystallization from benzene/hexane gave yellow needles of IIIb in 78% yield. Prepared in this manner were: *trans*-bis(triethylphosphine)bis(vinylethynyl)platinum (IIIa) [14] from *trans*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>, yellow crystals, m.p. 46–48°C; *cis*- and *trans*-bis(triethylphosphine)bis(phenylethynyl)platinum (Va and Vb) from the reactions of cuprous phenylacetylde with *cis*- and *trans*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>, respectively.

TABLE 1  
 PROPERTIES AND ANALYTICAL DATA OF NEW COMPOUNDS

Compound	M.p. (°C)	Analysis (Found (calcd.)) (%)			Mol. wt. <sup>a</sup> (Found (calcd.))
		C	H	P	
IIb	<i>cis</i> -(Et <sub>3</sub> P) <sub>2</sub> Pt(C≡CH) <sub>2</sub>	40.02 (39.91)	6.92 (6.71)	12.48 (12.87)	474 (481)
IIa	<i>trans</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡CH) <sub>2</sub>	51.45 (51.76)	8.54 (8.67)	9.00 (9.53)	—
IIb	<i>cis</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡CH) <sub>2</sub>	51.52 (51.76)	8.92 (8.67)	9.23 (9.53)	—
IIIb	<i>cis</i> -(Et <sub>3</sub> P) <sub>2</sub> Pt(C≡C-CH=CH <sub>2</sub> ) <sub>2</sub>	45.01 (45.02)	7.08 (6.80)	11.72 (11.61)	549 (534)
IVa	<i>trans</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡C-C≡CH) <sub>2</sub>	55.00 (55.09)	8.37 (8.09)	9.08 (8.88)	718 (698)
IVb <sub>1</sub>	<i>cis</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡C-C≡CH) <sub>2</sub>	54.89 (55.09)	8.36 (8.09)	8.85 (8.88)	683 (698)
Vb	<i>cis</i> -(Et <sub>3</sub> P) <sub>2</sub> Pt(C≡CPh) <sub>2</sub>	53.25 (53.06)	6.45 (6.38)	9.50 (9.78)	627 (634)
VIIa	<i>trans</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡CPh) <sub>2</sub>	59.73 (59.91)	7.95 (8.04)	7.69 (7.72)	—
VIIb	<i>cis</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡CPh) <sub>2</sub>	59.88 (59.91)	8.26 (8.04)	7.48 (7.72)	—
VIIIa	<i>trans</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡C-  -C≡CH) <sub>2</sub>	61.95 (62.17)	7.81 (7.59)	7.10 (7.29)	838 (850)
VIIIb	<i>cis</i> -(Bu <sub>3</sub> P) <sub>2</sub> Pt(C≡C-  -C≡CH) <sub>2</sub>	62.00 (62.17)	7.88 (7.59)	7.26 (7.29)	865 (850)

<sup>a</sup> By vapor-pressure osmometry in CH<sub>2</sub>Cl<sub>2</sub>.

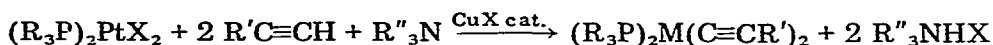
## Results and discussion

### *Selective syntheses of cis- and trans-bis(trialkylphosphine)dialkynylplatinum complexes*

$\sigma$ -Alkynyl derivatives of transition metals generally are prepared by the reaction of metal halides with alkynylating agents such as alkynyl compounds of the alkali metals, magnesium, or copper, or by HX elimination between metal halides and active acetylenes having an electron-withdrawing substituent. However, square-planar transition metal complexes of type  $(R_3P)_2M(C\equiv CR)_2$ , ( $M = Pt, Pd,$  and  $Ni$ ) obtained by the above methods usually have the *trans* structure, regardless of the preparative method and the configuration of starting materials. We have found a new method [1] using cuprous compounds which provides a route to the synthesis of the *cis*-form of the complexes,  $(PR_3)_2Pt-(C\equiv CR)_2$ , in good yields.

Our new method utilizes a cuprous halide as catalyst in the HX elimination between acetylenes and halides such as  $(R_3P)_2PtX_2$  (method A) or cuprous acetylides as stoichiometric alkynylating agents in the presence of  $N,N,N',N'$ -tetramethylethylenediamine (method B). Both methods are easily effected and proceed with retention of the configuration at the transition metal center of the original metal halides.

#### Method A



#### Method B



The procedure simply involves mixing of the platinum halide and an equimolar amount or a slight excess of the acetylenic compound under appropriate conditions. The preparation of the complexes having terminal acetylenic protons may require a large excess of acetylenes to prevent further reaction giving oligomer complexes. In method B, the cuprous acetylides (e.g., cuprous phenylacetylide) are almost insoluble in common organic solvents. However, in the presence of  $N,N,N',N'$ -tetramethylethylenediamine they smoothly dissolve in acetone, affording a green solution which reacts rapidly with the platinum halides. Method A is especially suitable for the preparation of alkynyl complexes derived from gaseous acetylenes such as I, II, III and IV. The new platinum acetylide complexes prepared by methods A or B listed in Table 1, along with their physical data.

Square-planar complexes of the type  $Pt(PR_3)_2X_2$  exhibit *cis-trans*-isomerization in solution. In the case of dialkynylplatinum complexes, slow isomerization of the *cis* to the *trans* form was observed in solutions of diethylamine and tetrahydrofuran at reflux, and we have found that cuprous halides in catalytic quantities accelerate the isomerization [12]. When the reaction of *cis*- $(Bu_3P)_2PtCl_2$  and  $PhC\equiv CH$  was carried out at  $20^\circ C$ , a mixture (ca. 1/1) of *cis*-VIa and the *trans*-VIb was obtained. Therefore, for the preparation of the thermodynamically less stable *cis*-isomers, the reaction should be carried out

at temperatures below  $-20^{\circ}\text{C}$ . Fortunately, the *cis*- and the *trans*-isomers can be separated from each other completely by column chromatography on alumina and the pure isomers are easily obtained. Their purities may be quantitatively checked by liquid chromatography \* using Permaphase-ODS column and methanol/water as a mobile phase.

#### General properties of dialkynylplatinum complexes

All of the *trans*-dialkynylplatinum complexes listed in Table 1 are stable in air in the solid state. The *cis* analogs are somewhat less stable and decompose slowly at room temperature, but they may be stored without decomposition in a refrigerator for several months. The *trans* isomers show higher solubilities than the *cis* isomers and are very soluble in common organic solvents such as hexane, benzene, ether, THF, acetone and dichloromethane.

#### Spectral properties

We have attempted to distinguish between the *cis*- and the *trans*-configurations about the platinum by means of spectroscopic methods. The *trans* isomers containing triethylphosphine were characterized by the typical 1/4/6/4/1 quintet for methyl proton signals [13] in their NMR spectra, while the *cis*-isomers showed the methyl resonance of a doublet of 1/2/1 triplets. Unfortunately, acetylenic protons could not be assigned because they were hidden in the signals for the ethyl or the butyl group on the phosphorus except for the diethynylbenzene derivatives (VIIa and VIIb), which showed acetylenic protons in both cases at  $\delta$  3.14 ppm in  $\text{CD}_2\text{Cl}_2$ . Proton NMR spectroscopy is not generally applied to distinguish configuration, but we successfully performed the configurational analyses by the infrared and the electronic spectra as described below.

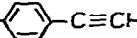
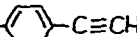
#### Infrared spectra

In IR spectra of organoplatinum  $\sigma$ -complexes the absorption band mainly associated with the stretching mode of the platinum-carbon bond has been observed [4,14] in the region  $500-600\text{ cm}^{-1}$  for alkyl- and alkynyl-platinum complexes. The IR spectra of the dialkynylplatinum complexes are summarized in Table 2. The point group for the *cis*-dialkynyl complex is  $C_{2v}$ , and group theory predicts that there will be two IR active platinum-carbon stretching modes, while only one stretching mode will be IR active for the *trans* isomer which belongs to the point group of  $D_{2h}$ . Thus, for the complex *cis*-( $\text{PBu}_3$ )<sub>2</sub>-Pt[( $\text{C}\equiv\text{C}$ )<sub>2</sub>H]<sub>2</sub> (IVb), we observed two bands at 575 and 557  $\text{cm}^{-1}$  attributed to the Pt-C stretching modes, whereas for the *trans* analog IVa, only one band at 576  $\text{cm}^{-1}$  was observed. Moreover, the *cis* complex showed two  $\nu(\text{C}\equiv\text{C})$  absorptions bands at 2153 and 2145  $\text{cm}^{-1}$  and two  $\nu(\text{C}-\text{H})$  absorptions due to acetylenic hydrogen at 3315 and 3295  $\text{cm}^{-1}$ , while the *trans* isomer showed one  $\nu(\text{C}\equiv\text{C})$  absorption at 2147  $\text{cm}^{-1}$  and one  $\nu(\text{C}-\text{H})$  absorption at 3312  $\text{cm}^{-1}$ . Other complexes also showed similar features, except some cases for which we were unable to assign the  $\nu(\text{Pt}-\text{C})$  absorption owing to their low intensities and/or the complexity of the absorption bands which overlapped with those of the other ligand itself, e.g., phenylethynyl ligand [15].

\* Shimazu-Du Pont Liquid Chromatograph type 840.

TABLE 2

INFRARED SPECTRA OF BIS(TERTIARY PHOSPHINE)DIALKYNYLPLATINUM L<sub>2</sub>PtR<sub>2</sub>

L	R	Configuration	$\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}\equiv\text{CH})$	$\nu(\text{Pt}-\text{C})$	
Ia	PEt <sub>3</sub>	C≡CH	<i>trans</i>	1960	3290	?
Ib	PEt <sub>3</sub>	C≡CH	<i>cis</i>	1977 1985	3270 3290	575 565
IIa	PBu <sub>3</sub>	C≡CH	<i>trans</i>	1974	3300	?
IIb	PBu <sub>3</sub>	C≡CH	<i>cis</i>	1979 1988	3270 3290	575 555
IIIa	PEt <sub>3</sub>	C≡C-CH=CH <sub>2</sub>	<i>trans</i>	2050	—	544
IIIb	PEt <sub>3</sub>	C≡C-CH=CH <sub>2</sub>	<i>cis</i>	2110 2103	—	?
IVa	PBu <sub>3</sub>	C≡C-C≡CH	<i>trans</i>	2147	3312	576
IVb	PBu <sub>3</sub>	C≡C-C≡CH	<i>cis</i>	2153 2145	3315 3295	575 557
Va	PEt <sub>3</sub>	C≡CPh	<i>trans</i>	2107	—	549
Vb	PEt <sub>3</sub>	C≡CPh	<i>cis</i>	2113 2106	—	?
VIa	PBu <sub>3</sub>	C≡CPh	<i>trans</i>	2100	—	547
VIIb	PBu <sub>3</sub>	C≡CPh	<i>cis</i>	2098 2110	—	?
VIIa	PBu <sub>3</sub>	C≡C-  -C≡CH	<i>trans</i>	2098	3280	?
VIIb	PBu <sub>3</sub>	C≡C-  -C≡CH	<i>cis</i>	2120 2130	3265	?

The platinum-phosphorus stretching vibrations often are used for configurational analysis [16]. However, for dialkynylplatinum complexes it is very difficult to assign systematically the absorption bands which appear in the region 400–300 cm<sup>-1</sup>.

## Electronic spectra

There seem to be few systematic studies of the electronic spectra of organo-transition metal complexes involving metal-carbon  $\sigma$ -bonds because of the difficulty in obtaining useful information [17]. For the alkynyl complexes, however, we may expect to obtain significant information concerning inter-

TABLE 3

## ELECTRONIC SPECTRA OF BIS(TERTIARY PHOSPHINE)DIALKYLPLATINUM

Measured in ether (I, III, and V) or in dichloromethane (II, IV, VI, and VII).

Compound <sup>a</sup>	$\lambda_{\text{max}}$ (nm (log $\epsilon$ ))		
Ia	304(3.85)	267(3.81)	258(3.83)
Ib	285(3.84)	246(4.04)	
IIa	302(3.90)	267(4.04)	
IIb	283(3.79)	250(4.13)	
IIIa	323(4.24)	286(4.01)	260(4.38)
IIIb	300(4.16)	264(sh)(4.13)	247(4.45)
IVa	318(4.39)	287(3.95)	268(4.01)
IVb	301(4.19)	276(4.05)	238(4.37)
Va	328(4.22)	288(4.13)	264(4.23)
Vb	309(4.44)	268(4.53)	253(4.57)
VIa	322(4.46)	280(4.48)	263(4.55)
VIIb	307(4.47)	267(4.54)	252(4.58)
VIIa	338(4.73)	297(4.59)	279(sh)(3.38)
VIIb	308(4.75)	287(4.70)	

<sup>a</sup> The symbols, a and b represent *trans*- and *cis*-configurations, respectively (see Table 2).

actions between the metals and the alkynyl groups, as reported previously [2,18]. Table 3 shows the electronic spectra (240–400 nm) of dialkynylplatinum complexes. The intensities of absorption bands are of the order of 4 in the log scale for both isomers, indicating intramolecular charge-transfer transitions [18]. The absorption band due to the lowest energy transition of the *cis* isomers shows a blue shift relative to that of the corresponding *trans* isomers. This may be a result of longer conjugation in the *trans*-form than in the *cis*-form, since the lowest band evidently is due to the charge-transfer transition involved in metal–carbon bonds, i.e., the transition from  $\pi$ -orbitals of the alkynyl groups to the  $\pi^*$ -metal *p*-orbitals [18]. The shift of the lowest band may be interpreted in terms of through-metal conjugation of the two alkynyl groups, since the interaction between the metal and the alkynyl groups involves two *d*-orbitals of the metal,  $d_{xy}$  and  $d_{xz}$  in the *trans*-form, while one metal orbital,  $d_{xy}$ , is involved in the *cis*-form in the square-planar configuration.

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