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Synthesis, Reactions, and Rearrangement of $X(PR'_3)_2M[C({=}PR)X]$ (M = Pt, Pd; X = Cl, Br; R′ = Et, Ph; R = 2,4,6-Tri-*tert*-butylphenyl): Mechanism of the Transition Metal Promoted Conversion of $X_2C{=}PR$ to $R{-}C{\equiv}P$[†]

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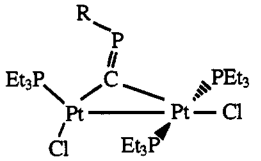
Oxidative addition reactions of $X_2C{=}PR$ (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) with $M(PEt_3)_4$ (M = Pt, Pd) or $(C_2H_4)Pt(PPh_3)_2$ initially yield the *cis* isomer of square planar $(X)(PR'_3)_2M[C({=}PR)X]$ (**II**); these complexes (**IIa–IId**), where PR'_3 is PEt_3, rearrange rapidly in the presence of free PEt_3 to give the *trans* isomers (**Ia–Id**). In contrast, the *cis* isomers (**IIe** and **IIf**), where PR'_3 is PPh_3 and M is Pt, react further to give $R{-}C{\equiv}P$ and *cis*-$X_2Pt(PPh_3)_2$. In polar solvents (CH_2Cl_2 and $CHCl_3$), all the addition products (**I** and **II**) convert to $R{-}C{\equiv}P$ and *cis*- or *trans*-$X_2M(PR'_3)_2$ via the surprising phosphabicyclo intermediate $(X)(PR'_3)_2Pt(X{-}PBC)$ (**III** and **IV**); the structure of **IIIa** was established crystallographically. In the presence of H_2O, $(X)(PEt_3)_2Pt[C({=}PR)X]$ (**Ia** and **Ib** where X = Cl, Br) give the oxophosphabicyclo complex $(X)(PEt_3)_2Pt[(H)O{=}PBC]$ (**Va** and **Vb**) which was characterized by X-ray diffraction. A mechanism for the conversion of $(X)(PR'_3)_2M[C({=}PR)X]$ to $R{-}C{\equiv}P$ and $X_2M(PR'_3)_2$ is proposed.

Introduction

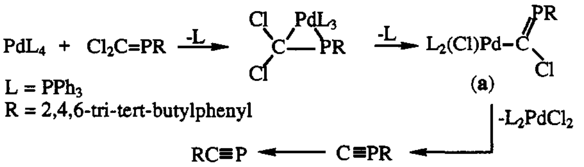
After Gier[1] obtained the first experimental evidence for a compound with a P—M multiple bond in 1961, many stable phosphaalkyne ($R{-}C{\equiv}P$) and phosphaalkene ($R{-}P{=}CR_2$) compounds have been prepared and studied.[2] Despite the inherent reactivity of P≡C and P=C bonds, such compounds have been stabilized with bulky R groups. However, there is still no evidence for phosphorus analogs, $C{\equiv}P{-}R$, of the well-known aryl or alkyl isocyanides $C{\equiv}N{-}R$.[3] In fact, calculations indicate that $C{\equiv}P{-}H$ is 85 kcal/mol less stable than the $H{-}C{\equiv}P$ isomer.[4] Thus, it seems unlikely that free $C{\equiv}P{-}R$ molecules can be prepared. However, we have reported[5] in a preliminary communication that an aryl isocyaphide ($C{\equiv}P{-}R$)[6] can be stabilized as a bridging ligand in $(Cl)(PEt_3)Pt(\mu\text{-}C{=}P{-}R)Pt(PEt_3)_2(Cl)$ (R = 2,4,6-tri-*tert*-butylphenyl) (**A**).



A

Free aryl isocyaphides ($C{\equiv}P{-}R$) have been proposed as intermediates in reactions of phosphaalkenes. Appel and co-workers[7] suggested that the formation of $R{-}C{\equiv}P$ from $(Li)(Cl)C{=}P{-}R$ proceeds by way of an undetected highly reactive $C{\equiv}P{-}R$ which rapidly rearranges to the $R{-}C{\equiv}P$ product (eq 1). Other research groups[8] have also reported in related systems reactions of the type in eq 1. Although no intermediates were observed in these reactions even at the low temperature (−78 °C),[9] $C{\equiv}P{-}R$ was proposed as a transient intermediate.

(1)



(2)

Recently, Romanenko and co-workers[10] reported the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PR$ which gives $R{-}C{\equiv}P$ and $Pd(PPh_3)_2Cl_2$ in greater than 85% yield (eq 2). This reaction involves the overall dechlorination of $Cl_2C{=}PR$

[†] Dedicated to Professor Ekkehard Lindner, Universität Tübingen, on the occasion of his 60th birthday.

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and migration of the supermesityl (R) group from the phosphorus to the carbon. While no intermediates were detected, they proposed (eq 2) that the reaction proceeds by way of initial oxidative addition across a C—Cl bond to give an intermediate (**a**) which is analogous to the complex $Cl(PEt_3)_2Pt[C({=}PR)Cl]$ that we isolated previously[5] from the reaction of $Pt(PEt_3)_4$ with $Cl_2C{=}PR$. Then, L_2PdCl_2 is eliminated from this intermediate (**a**) to give the free aryl isocyaphide $C{\equiv}PR$, which was proposed to rearrange to the $R{-}C{\equiv}P$ product.[2a]

A reaction that is similar to the first steps in eq 2 is the three-fragment oxidative addition of $Cl_2C{=}N{-}R$ to low valent metal complexes.[11] Such reactions give products with terminal isocyanide ligands, as in eq 3. Recently, we attempted to synthesize the phosphorus analog $Cl_2Pt(PEt_3)(C{\equiv}P{-}R)$ of the product in eq 3 by reacting $Cl_2C{=}P{-}R$ (R = 2,4,6-tri-*tert*-butylphenyl) with $Pt(PEt_3)_4$.[5] From those trials, only the two-fragment oxidative-addition product $Cl(PEt_3)_2Pt[C({=}PR)Cl]$ was obtained. While we were able to convert this to $(Cl)(PEt_3)Pt(\mu\text{-}C{=}P{-}R)Pt(PEt_3)_2(Cl)$ (**A**) with a semibridging C=PR group, compounds with terminal $C{\equiv}P{-}R$ ligands have not yet been prepared.

$$Pt(PPh_3)_4 \xrightarrow{Cl_2C{=}NR} Cl_2Pt(PPh_3)(CNR) + Cl_2Pt(PPh_3)_2 \qquad (3)$$

$$R = 2,4,6\text{-tri-}tert\text{-butylphenyl}$$

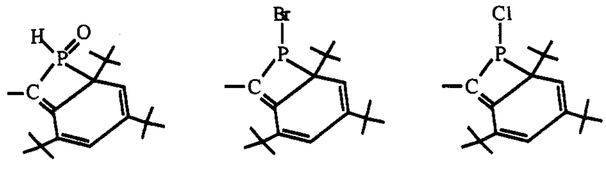
In this paper, we report an expanded study of the syntheses and reactions of the compounds $X(PR'_3)_2M[C({=}PR)X]$ (M = Pt, Pd; X = Cl, Br; R′ = Ph, Et; R = 2,4,6-tri-*tert*-butylphenyl). Also we describe the structure of an unusual intermediate formed in the conversion of $X(PR'_3)_2M[C({=}PR)X]$ to $R{-}C{\equiv}P$ and $X_2M(PR'_3)_2$. Some of these results were reported in a communication.[12]

Experimental Section

General Procedure. All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents under N_2. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while hexanes and dichloromethane (CH_2Cl_2) were distilled from CaH_2. Distilled water was used as the solvent or reagent. Chromatography columns (ca. 30 cm in length and 1 cm in diameter) were packed with silica gel (Davisil 62, Davison Chemical).

The ^1H NMR spectra were recorded in C_6D_6 unless otherwise noted using a Nicolet-NT 300-MHz or Varian VXR 300-MHz spectrometer with TMS (δ 0.00 ppm) as the internal standard. The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer in C_6D_6 using 85% H_3PO_4 (δ 0.00 ppm) as the external standard. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN, or Desert Analytics, Tucson, AZ. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. The complexes $(PPh_3)_2Pt(C_2H_4)$,[13] $Pt(PEt_3)_4$,[14] and $Pd(PEt_3)_4$[15] and compounds $Cl_2C{=}PR$[16] and $Br_2C{=}PR$[17] were prepared by literature methods.

Chart 1



(H)O=PBC Br-PBC Cl-PBC

The products, **Ia–Ic**, **IIa**, **IIIa** and **IIIb**, **Va** and **Vb**, and **VIe** are air stable for at least 1 month. The phosphabicyclo ligands, with abbreviations Cl—PBC, Br—PBC, and (H)O=PBC, in compounds **IIIa**, **IIIb**, **IVa**, **IVe**, **IVf**, **Va**, **Vb**, and **VIe** are shown in Chart I.

Preparation of *trans*-(Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (R = 2,4,6-tri-*tert*-butylphenyl) (Ia). Method A. To a benzene solution (10 mL) of $Pt(PEt_3)_4$ (0.67 g, 1.0 mmol) was added a benzene solution (2 mL) of $Cl_2C{=}PR$ (R = 2,4,6-tri-*tert*-butylphenyl) (0.36 g, 1.0 mmol). After the solution was stirred at room temperature for 1 h, the solvent was evaporated under vacuum to yield an oily yellow residue. The residue was extracted with hexanes (50 mL) and filtered by cannula. After reducing the extract to one-fourth of its volume under vacuum, pale yellow crystals of **Ia** were obtained by cooling the solution to −78 °C (0.67 g, 85%).

Method B. A cold (−78 °C) solution of $(Li)(Cl)C{=}P{-}R^7$ was generated by adding a hexane solution of *n*-BuLi (0.500 mmol) to a THF solution (5 mL) of $Cl_2C{=}P{-}R$ (0.180 g, 0.500 mmol) at −78 °C and then stirring the solution for 30 min at the same temperature. This solution was added over a period of 15 min to a cold (−78 °C) THF (5-mL) solution of *trans*-$Cl_2Pt(PEt_3)_2$ (0.251 g, 0.500 mmol). After 30 min of stirring at −78 °C, the reaction mixture was slowly warmed to room temperature over a period of 2 h. In the reaction mixture, both isomers (**Ia** and **IIa**) were observed in the ^{31}P NMR spectrum. This mixture was evaporated to dryness under vacuum; the residue was extracted into hexanes (30 mL), and the solution was filtered by cannula. This solution was reduced under vacuum to half its volume, whereupon **IIa** began to precipitate. Cooling to −30 °C yielded more **IIa**. Additional amounts of **IIa** and **Ia** were isolated from the mother liquor by reducing the volume of the solution and cooling to −30 °C several times. The overall yields of **IIa** and **Ia** were 0.205 g (52%) and 0.142 g (36%), respectively. ^1H NMR (C_6D_6): δ 7.58 (s, 2H, R), 1.95 (m, 12H, CH_2 of Et), 1.71 (s, 18H, CH_3 of R), 1.35 (s, 9H, CH_3 of R), 1.03 (m, 18H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6, 85% H_3PO_4 external standard): δ 223.3 (t, $^3J_{PP}$ = 25.2 Hz, $^2J_{PtP}$ = 657.7 Hz, $C{=}P{-}R$), 15.0 (d, $^3J_{PP}$ = 25.2 Hz, $^1J_{PtP}$ = 2752.7 Hz, PEt_3), EIMS (70 eV): *m/e* 790 (M^+), 755 ($M^+ - Cl$), 733 ($M^+ - t\text{-Bu}$), 698 ($M^+ - (Cl + t\text{-Bu})$). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.11; H, 7.46. Found: C, 47.54; H, 7.48.

Preparation of *trans*-(Br)(PEt$_3$)$_2$Pt[C(=PR)Br] (Ib). Complex **Ib** was prepared by the same method (**A**) as described above using $Pt(PEt_3)_4$ (0.67 g, 1.0 mmol) and $Br_2C{=}PR$ (0.45 g, 1.0 mmol). The product **Ib** was obtained as pale yellow crystals (0.49 g, 56%). ^1H NMR (C_6D_6): δ 7.50 (s, 2H, R), 2.00 (m, 12H, CH_2 of Et), 1.62 (s, 18H, CH_3 of R), 1.32 (s, 9H, CH_3 of R), 1.00 (m, 18H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 234.2 (t, $^3J_{PP}$ = 25.2 Hz, $^2J_{PtP}$ = 661.2 Hz, $C{=}P{-}R$), 9.5 (d, $^3J_{PP}$ = 24.7 Hz, $^1J_{PtP}$ = 2712.3 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Br_2P_3Pt$: C, 42.35; H, 6.71. Found: C, 42.17; H, 6.83.

Preparation of *trans*-(Cl)(PEt$_3$)$_2$Pd[C(=PR)Cl] (Ic). Complex **Ic** was prepared by method A used for compound **Ia**; the reactants were $Pd(PEt_3)_4$ (0.58 g, 1.0 mmol) and $Cl_2C{=}PR$ (0.36 g, 1.0 mmol). The product **Ic** was obtained as pale yellow crystals (0.55 g, 78%). ^1H NMR (C_6D_6): δ 7.56 (s, 2H, R), 1.86 (m, 12H, CH_2 of Et), 1.69 (s, 18H, CH_3 of R), 1.34 (s, 9H, CH_3 of R), 1.05 (m, 18H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 227.6 (t, $^3J_{PP}$ = 42.7

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Hz, C═PR), 16.1 (d, $^3J_{PP}$ = 42.7 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pd$: C, 53.07; H, 8.41. Found: C, 53.15; H, 8.51.

Conversion of *trans*-(Cl)$(PEt_3)_2$Pd[C(═PR)Cl] (Ic) to R—C≡P and *trans*-$Cl_2Pd(PEt_3)_2$. After complex **Ic** (0.070 g, 0.10 mmol) in 2 mL of dry CH_2Cl_2 was stirred at room temperature under argon for 24 h, the reaction solution was evaporated to dryness. The residue was extracted with hexanes (10 mL) and filtered through a short column of Celite. The crude products were separated by column chromatography (hexanes, silica) under an argon atmosphere to give R—C≡P (0.019 g, 65%) and *trans*-$Cl_2Pd(PEt_3)_2$ (0.015 g, 36%). A $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed that these products were formed in essentially quantitative yield, and no intermediates were observed during the course of the reaction. R—C≡P[10] and *trans*-$Cl_2Pd(PEt_3)_2$[18b] were characterized by their NMR spectra. ^1H NMR (C_6D_6) for R—C≡P: δ 7.16 (d, $^4J_{PH}$ = 1.2 Hz, 2H, on R), 1.72 (s, 18H, CH_3 on R), 1.23 (s, 9H, CH_3 on R). $^{31}P\{^1H\}$ NMR (C_6D_6): (for R—C≡P) δ 33.9 (s); (for *trans*-$Cl_2Pd(PEt_3)_2$) δ 17.5 (s).

Conversion of Br_2C═PR to R—C≡P through the Intermediate *trans*-$(PEt_3)_2$(Br)Pd[C(═PR)Br] (Id). To a CH_2Cl_2 solution (2 mL) of $Pd(PEt_3)_4$ (0.058 g, 0.10 mmol) was added a CH_2Cl_2 solution (1.0 mL) of Br_2C═PR (0.045 g, 0.10 mmol). After the solution was stirred at room temperature for 6 h, the solvent was evaporated under vacuum. The resulting solid was purified by column chromatography (hexanes, silica) under an argon atmosphere to give R—C≡P (0.016 g, 50%) and *trans*-$Br_2Pd(PEt_3)_2$[18e] (0.018 g, 36%). As indicated by a $^{31}P\{^1H\}$ NMR spectrum of the reaction solution, these were the only products of the reaction and **Id** was the only intermediate. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) of **Id**: δ 243.0 (t, $^3J_{PP}$ = 41.2 Hz, C═P—R), 12.5 (d, $^3J_{PP}$ = 41.2 Hz, PEt_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) of *trans*-$Br_2Pd(PEt_3)_2$: δ 14.4 (s).

Preparation of *cis*-(Cl)$(PEt_3)_2$Pt[C(═PR)Cl] (IIa). To a cold (−50 °C) hexanes (10-mL) solution of $Pt(PEt_3)_4$ (0.67 g, 1.0 mmol) was added a hexanes solution (5 mL) of Cl_2C═PR (0.36 g, 1.0 mmol). After being stirred for 5 min at the same temperature and then reducing the reaction solution to half of its volume under vacuum, white crystals of **IIa** precipitated (0.51 g, 65%). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 224.0 (dd, $^3J_{PP}$ = 46.3 Hz, $^3J_{PP}$ = 12.3 Hz, $^2J_{PtP}$ = 365.4 Hz, C═P—R), 6.0 (dd, $^2J_{PP}$ = 15.1 Hz, $^3J_{PP}$ = 12.3 Hz, $^1J_{PtP}$ = 3921.2 Hz, PEt_3), 8.0 (dd, $^2J_{PP}$ = 15.1 Hz, $^3J_{PP}$ = 46.3 Hz, $^1J_{PtP}$ = 2125.4 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.12; H, 7.47. Found: C, 47.06; H, 7.56.

Conversion of *cis*-$(PEt_3)_2$(Cl)Pt[C(═PR)Cl] (IIa) to R—C≡P and *cis*-$(Cl)_2Pt(PEt_3)_2$ through the Intermediate *cis*-$(PEt_3)_2$(Cl)Pt(Cl—PBC) (IVa). After complex **IIa** (0.079 g, 0.10 mmol) in 2 mL of dry CH_2Cl_2 was stirred at room temperature under argon for 24 h, the reaction solution was evaporated to dryness. A $^{31}P\{^1H\}$ NMR spectrum taken during the reaction showed **IVa** as an intermediate. The residue was extracted with hexanes (10 mL) and filtered through a short column of Celite. After reducing the filtrate to one-fourth of its volume under vacuum, white crystals of *cis*-$(Cl)_2Pt(PEt_3)_2$[18a] were obtained upon cooling to −78 °C (0.023 g, 46%). The mother liquor from the crystals was chromatographed (hexanes, silica) under an argon atmosphere to give R—C≡P (0.016 g, 55%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): (for *cis*-$(Cl)_2Pt(PEt_3)_2$) δ 9.3 ($^1J_{PtP}$ = 3509 Hz); (for **IVa**) δ 88.2 (d, $^3J_{PP}$ = 18.3 Hz, $^2J_{PtP}$ = 190.7 Hz, P in Cl—PBC), 9.3 (dd, $^3J_{PP}$ = 18.3 Hz, $^2J_{PP}$ = 18.3 Hz, $^1J_{PtP}$ = 1793.0 Hz, PEt_3), −0.1 (d, $^3J_{PP}$ = 18.3 Hz, $^1J_{PtP}$ = 3970.5 Hz, PEt_3).

Conversion of Cl_2C═PR to R—C≡P through Intermediates *cis*-(Cl)$(PPh_3)_2$Pt[C(═PR)Cl] (IIe) and *cis*-(Cl)$(PPh_3)_2$Pt(Cl—PBC) (IVe). To a CH_2Cl_2 solution (5 mL) of $(PPh_3)_2Pt(C_2H_4)$ (0.075 g, 0.10 mmol) was added a CH_2Cl_2 solution (2 mL) of Cl_2C═PR (0.036 g, 0.10 mmol). After the solution was stirred at room temperature for 12 h, the solvent was evaporated under vacuum to yield an oily yellow residue which was extracted with hexanes. The extract solution was filtered through a short column of Celite. After reducing the filtrate to one-fourth of its volume under vacuum, white crystals of *cis*-$(Cl)_2Pt(PPh_3)_2$[18d] (0.034 g, 43%) were obtained by cooling to −78 °C. The mother liquor from the crystals was chromatographed (hexanes, silica) under an argon atmosphere to give R—C≡P (0.018 g, 62%). During the 12-h course of the reaction, intermediates **IIe** and **IVe** were identified by the $^{31}P\{^1H\}$ NMR spectra, as discussed in the Results. $^{31}P\{^1H\}$ NMR (C_6D_6) data: (for *cis*-$(Cl_2)Pt(PPh_3)_2$) δ 13.5 (s, $^1J_{PtP}$ = 3680 Hz); (for **IIe**) δ 234.6 (dd, $^3J_{PP}$ = 22.5 Hz, $^3J_{PP}$ = 45.4 Hz, $^2J_{PtP}$ = 354.8 Hz, C═P—R), 17.8 (dd, $^3J_{PP}$ = 45.4 Hz, $^2J_{PP}$ = 16.4 Hz, $^1J_{PtP}$ = 1889.8 Hz, PPh_3), 10.4 (dd, $^3J_{PP}$ = 22.5 Hz, $^2J_{PP}$ = 16.4 Hz, $^1J_{PtP}$ = 4203.2 Hz, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) data for **IVe**: δ 80.0 (dd, $^3J_{PP}$ = 19.2 Hz, $^3J_{PP}$ = 5.3 Hz, $^2J_{PtP}$ = 142.0 Hz, P in PBC), 16.5 (dd, $^3J_{PP}$ = 19.2 Hz, $^3J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 1750.0 Hz, PPh_3), 14.2 (dd, $^3J_{PP}$ = 18.1 Hz, $^3J_{PP}$ = 5.3 Hz, $^1J_{PtP}$ = 4150.0 Hz, PPh_3).

Conversion of Br_2C═PR to R—C≡P through the Intermediate *cis*-(Br)$(PPh_3)_2$Pt(Br—PBC) (IVf). In a reaction of Br_2C═PR (0.045 g, 0.10 mmol) and $(PPh_3)_2Pt(C_2H_4)$ (0.075 g, 0.10 mmol) that was carried out as for the reaction directly above, R—C≡P (0.020 g, 69%) was obtained as the final product. The other product *cis*-$Br_2Pt(PPh_3)_2$[18d] was observed by $^{31}P\{^1H\}$ NMR spectrometry in the product mixture. Complex **IVf** was identified as an intermediate by its $^{31}P\{^1H\}$ NMR spectrum obtained during the course of the reaction. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) data: (for *cis*-$Br_2Pt(PPh_3)_2$) δ 12.8 (s, $^1J_{PtP}$ = 3630 Hz); (for **IVf**) δ 88.5 (dd, $^3J_{PP}$ = 19.2 Hz, $^3J_{PP}$ = 6.4 Hz, $^2J_{PtP}$ = 144.1 Hz, P in Br—PBC), 13.1 (dd, $^3J_{PP}$ = 19.2 Hz, $^3J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 1762.8 Hz, PPh_3), 13.8 (dd, $^3J_{PP}$ = 18.1 Hz, $^3J_{PP}$ = 6.4 Hz, $^1J_{PtP}$ = 4204.2 Hz, PPh_3).

Preparation of *trans*-(Cl)$(PEt_3)_2$Pt(Cl—PBC) (IIIa). After a solution of complex **Ia** (0.40 g, 0.50 mmol) in 10 mL of dry CH_2Cl_2 was stirred at room temperature under argon for 24 h, it was evaporated to dryness. The residue was recrystallized from hexanes at −30 °C to give **IIIa** as colorless crystals (0.36 g, 90%). ^1H NMR (C_6D_6): δ 6.11 (d, $^4J_{HH}$ = 1.46 Hz, 1H, on C(6)), 6.04 (dd, $^4J_{HH}$ = 1.46 Hz, $^3J_{PH}$ = 18.80 Hz, 1H, on C(4)), 2.14 (m, 6H, CH_2 of Et), 2.00 (m, 6H, CH_2 of Et), 1.54 (s, 9H, CH_3 of R), 1.10 (s, 9H, CH_3 of R), 1.08 (s, 9H, CH_3 of R), 1.18 (m, 9H, CH_3 of Et), 1.08 (m, 9H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 93.8 (s, $^2J_{PtP}$ = 387.7 Hz, P(3)), 12.9 (s, $^1J_{PtP}$ = 2737.1 Hz, PEt_3), 11.2 (s, $^1J_{PtP}$ = 2632.5 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.11; H, 7.46. Found: C, 47.46; H, 7.61.

Conversion of IIIa to R—C≡P and *trans*-$Cl_2Pt(PEt_3)_2$. A solution of complex **IIIa** (0.016 g, 0.020 mmol) in 0.4 mL of dry C_6H_6 in an NMR tube was monitored by ^{31}P NMR spectroscopy. After 6 h at room temperature, only the two final products R—C≡P[10] and *trans*-$Cl_2Pt(PEt_3)_2$[18a] were observed. $^{31}P\{^1H\}$ NMR (C_6H_6) data for *trans*-$Cl_2Pt(PEt_3)_2$: δ 13.2 (s, $^1J_{PtP}$ = 2405 Hz).

Preparation of *trans*-(Br)$(PEt_3)_2$Pt(Br—PBC) (IIIb). A solution of complex **Ib** (0.44 g, 0.50 mmol) in 10 mL of dry CH_2Cl_2 was stirred at 0 °C under argon for 8 h; then it was evaporated to dryness. The residue was recrystallized from hexanes at −78 °C to give **IIIb** as light yellow crystals (0.35 g, 80%). ^1H NMR (C_6D_6): δ 6.18 (d, $^4J_{HH}$ = 1.46 Hz, 1H on C(6)), 6.07 (dd, $^4J_{HH}$ = 1.46 Hz, $^3J_{PH}$ = 19.04 Hz, 1H on C(4)), 2.30 (m, 6H, CH_2 of Et), 2.08 (m, 6H, CH_2 of Et), 1.55 (s, 9H, CH_3 of R), 1.32 (s, 9H, CH_3 of R), 1.04 (s, 9H, CH_3 of R), 1.14 (m, 9H, CH_3 of Et), 1.01 (m, 9H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 92.1 (s, $^2J_{PtP}$ = 393.8 Hz, P(3)), 7.2 (s, $^1J_{PtP}$ = 2714.6 Hz, PEt_3), 5.3 (s, $^1J_{PtP}$ = 2588.6 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Br_2P_3Pt$: C, 42.35; H, 6.71. Found: C, 42.67; H, 6.77.

Conversion of IIIb to R—C≡P and *trans*-$Br_2Pt(PEt_3)_2$. Complex **IIIb** (0.018 g, 0.020 mmol) in C_6H_6 solvent at room temperature in an NMR tube converted to R—C≡P and *trans*-$Br_2Pt(PEt_3)_2$[18c] during a 3-h period. $^{31}P\{^1H\}$ NMR data for *trans*-$Br_2Pt(PEt_3)_2$: δ 6.9 (s, $^1J_{PtP}$ = 2349 Hz).

Preparation of *trans*-(Cl)$(PEt_3)_2$Pt[(H)O═PBC] (Va). Method A. To a solution of complex **Ia** (0.395 g, 0.500 mmol)

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(18) (a) Grim, S. O.; Keiter, R. L.; McFarland, W. *Inorg. Chem.* **1967**, *6*, 1133. (b) Grim, S. O.; Keiter, R. L. *Inorg. Chim. Acta* **1970**, *4*, 56. (c) Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 2370. (d) Mastin, S. H. *Inorg. Chem.* **1974**, *13*, 1003. (e) Hitchcock, C. H. S.; Mann, F. G. *J. Chem. Soc.* **1958**, 2081.

in 10 mL of dry CH_2Cl_2 was added H_2O (0.009 g, 0.5 mmol). After being stirred at room temperature for 48 h, the solution was evaporated to dryness. The residue was recrystallized from a CH_2Cl_2/hexanes (4:1) solvent mixture at room temperature by slow evaporation to give **Va** as colorless crystals (0.232 g, 60%).

Method B. To a solution of complex **IIIa** (0.040 g, 0.050 mmol) in 2 mL of dry CH_2Cl_2 was added H_2O (0.0009 g, 0.05 mmol). After stirring at room temperature for 24 h, the mixture was evaporated to dryness under vacuum. The residue was recrystallized from the solvent mixture stated above to give **Va** (0.030, 80%). ^1H NMR (C_6D_6): δ 7.3 (d, $^1J_{PH}$ = 435.8 Hz, 1H, on P(3)), 6.1 (d, $^4J_{HH}$ = 1.7 Hz, 1H, on C(6)), 5.9 (dd, $^4J_{HH}$ = 1.7 Hz, $^3J_{PH}$ = 17.3 Hz, 1H, on C(4)), 2.2 (m, CH_2 of Et), 1.8 (m, CH_2 of Et), 1.6 (m, CH_2 of Et), 1.5 (s, 9H, *t*-Bu), 1.3 (s, 9H, *t*-Bu), 1.0 (s, 9H, *t*-Bu), 1.1 (m, 9H, CH_3 of Et), 0.9 (m, 9H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.9 (d, $^3J_{PP}$ = 9.6 Hz, $^2J_{PtP}$ = 147.1 Hz, P in (H)O—PBC), 13.0 (d, $^3J_{PP}$ = 9.6 Hz, $^1J_{PtP}$ = 2680.0 Hz, PEt_3), 11.4 (s, $^1J_{PtP}$ = 2575.0 Hz, PEt_3). Anal. Calcd for $C_{32}H_{62}Cl_3OP_3Pt{\cdot}CH_2Cl_2$: C, 44.86; H, 7.23. Found: C, 45.24; H, 7.56.

Conversion of *trans*-(Br)(PEt_3)$_2$Pt[C(=PR)Br] (Ib) to *trans*-(Br)(PEt_3)$_2$Pt[(H)O=PBC] (Vb). Following method A in the above procedure, complex **Ib** (0.088 g, 0.10) was treated with H_2O (0.018 g, 0.10 mmol) to give complex **Vb** (0.037 g, 45%). Complex **Vb** was identified only by its $^{31}P\{^1H\}$ NMR spectrum. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.5 (d, $^3J_{PP}$ = 12.4 Hz, $^2J_{PtP}$ = 145.7 Hz, P in (H)O=PBC), 10.1 (d, $^3J_{PP}$ = 12.4 Hz, $^1J_{PtP}$ = 2537.7 Hz, PEt_3), 8.2 (s, $^1J_{PtP}$ = 2583.0 Hz, PEt_3).

Reaction of (PPh_3)$_2$Pt(C_2H_4) with $Cl_2C{=}PR$ and H_2O To Give *cis*-(Cl)(PPh_3)$_2$Pt[(H)O=PBC] (VIe) through Intermediates IIe and IVe. To a CH_2Cl_2 solution (5 mL) of (PPh_3)$_2$Pt(C_2H_4) (0.075 g, 0.10 mmol) and $Cl_2C{=}PR$ (0.036 g, 0.10 mmol) was added H_2O (0.0018 g, 0.10 mmol). A series of $^{31}P\{^1H\}$ NMR spectra of the solution indicated that **IIe** formed immediately after the addition (within 1 min); it then slowly converted to **IVe** and finally to **VIe**. After the solution was stirred at room temperature for 12 h, the solvent was evaporated to dryness. The residue was recrystallized from a CH_2Cl_2/hexanes (4:1) solvent mixture at room temperature (slow evaporation) to give **VIe** (0.037 g, 35%). Compound **VIe** was characterized only by its ^{31}P NMR spectrum. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 13.0 (d, $^3J_{PP}$ = 3.2 Hz, $^2J_{PtP}$ = 20 Hz, P in (H)O=PBC), 16.4 (dd, $^3J_{PP}$ = 3.2 Hz, $^2J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 1760 Hz, PPh_3), 12.2 (d, $^2J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 4150 Hz, PPh_3).

R Group Rearrangement from Ia to IIIa in the Presence of (*t*-Bu)$_2$NO. After adding (*t*-Bu)$_2$NO (1 equiv) to a CH_2Cl_2 solution (2 mL) of **Ia** (0.040 g, 0.050 mmol) at room temperature, the solution was stirred for 24 h. Then, the solvent was evaporated to dryness and the residue was recrystallized from hexanes at −78 °C to give **IIIa** (0.030 g, 75%) as the only product.

Conversion of *trans*-(Cl)(PEt_3)$_2$Pt[C(=PR)Cl] (Ia) to *trans*-(Cl)(PEt_3)$_2$Pt[(H)O=PBC] (Va) with Hydrated Ag-BF_4. To a THF solution (2 mL) of **Ia** (0.040 g, 0.050 mmol) was added moist solid $AgBF_4$ (0.0097 g, 0.050 mmol); the mixture was stirred at room temperature for 1 h. A white precipitate formed immediately, and the solution color darkened. After 1 h, the solution was filtered by cannula, and the solvent was removed under vacuum. The residue was recrystallized from hexanes/CH_2Cl_2 (1:1) solvent by slow evaporation at room temperature, giving colorless crystals of **Va** (0.024 g, 60%).

Reactions of *trans*-(Cl)(PEt_3)$_2$Pt[C(=PR)Cl] (Ia) and *trans*-(Cl)(PEt_3)$_2$Pt[Cl—PBC] (IIIa) with Dry $AgBF_4$. To a dry THF solution (2 mL) of **Ia** (0.040 g, 0.050 mmol) was added dry solid $AgBF_4$ (0.0097 g, 0.050 mmol); the solution was stirred at room temperature in a glovebox for 1 h. A white precipitate formed immediately. After 1 h, I was completely converted to a new product, (Cl)(PEt_3)$_2$Pt[BF_4—PBC] (VII). Product **VII** slowly decomposed during attempted recrystallizations at −30 °C in THF. The same product **VII** was also produced quantitatively in the reaction of **IIIa** with dry $AgBF_4$ in dry THF solution. When a drop of H_2O was added to THF solutions of **VII**, **Va** was formed immediately. Due to its instability, **VII** could not be isolated and was only characterized by its ^{31}P NMR spectrum. $^{31}P\{^1H\}$ NMR (THF) of **VII**: δ 139 (dddd, $^3J_{PP}$ = 8.25 Hz, $^3J_{PF}$ = 63.95 Hz, $^1J_{PF}$ = 866.07 Hz, $^1J_{PF}$ = 1055.78 Hz, $^2J_{PtP}$ = 299.68 Hz, P in PBC ligand), 13.3 (d, $^3J_{PP}$ = 8.25 Hz, $^1J_{PtP}$ = 2623 Hz, PEt_3), 10.5 (s, $^1J_{PtP}$ = 2587 Hz, PEt_3).

Table 1. Crystal and Data Collection Parameters for (C1)(PEt_3)$_2$Pt[C(=PR)Cl] (Ia) and (Cl)(PEt_3)$_2$Pt[(H)O=PBC] (Va)

	Ia	Va
formula	$C_{31}H_{59}Cl_2P_3Pt$	$C_{31}H_{60}ClP_3OPt$
fw	790.72	857.17
space group	$P2_1/c$	$P2_12_12_1$
a, Å	13.188(1)	9.183(1)
b, Å	12.106(1)	12.265(2)
c, Å	23.990(2)	34.973(8)
β, deg	105.099(9)	
cell vol, Å^3	3697.8(8)	3939(1)
Z	4	4
D_{calcd}, g cm^{-3}	1.42	1.445
cryst size, mm	0.45 × 0.45 × 0.40	0.50 × 0.35 × 0.35
μ (Mo Kα), cm^{-1}	41.4	39.1
data collcn instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
temp, °C	20(1)	−50(1)
scan method	θ–2θ	θ–2θ
data colcn range, 2θ, deg	4.0–50.0	4.0–50.0
tot. no. of uniq reflec	6820 (R_m = 0.018)	3910
no. of uniq reflec obs	4434 ($I \geq 2\sigma(I)$)	3659 ($I \geq 2\sigma(I)$)
no. of params refined	335	401
trans factors: max, min	0.994, 0.739	0.901, 0.514
refinement	SHELXTL-PLUS[19a]	SHELXL-93[19b]
R^a	0.025	0.038
$R_w{}^b$ or $wR_2{}^c$	0.032 (R_w)	0.101 (wR_2)
quality-of-fit indicator	0.867[d]	1.150[e]
largest shift/esd, final cycle	0.00	0.00
largest peak, e/Å^3	0.88	1.031

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $wR_2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$; $w = q/\{\sigma^2(F_o^2) + (ap)^2 + (bp) + d + (e \sin\theta)\}$; see ref 19b. [d] Quality-of-fit = $\{\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})\}^{1/2}$. [e] Quality-of-fit = $[\sum\{w(F_o^2 - F_c^2)^2/(n-p)\}]^{1/2}$; see ref 19b.

X-ray Crystallographic Analyses of *trans*-Cl(PEt_3)$_2$Pt-[C(=PR)Cl] (Ia) and *trans*-Cl(PEt_3)$_2$Pt[(H)O=PBC] (Va). Diffraction-quality crystals of **Ia** were obtained at −78 °C in hexanes; crystals of **Va** were obtained by slow evaporation of a hexanes/CH_2Cl_2 (1:1) solution of **Va** at room temperature. Data collection and reduction information are given in Table 1. Positional parameters and selected bond distances and bond angles are given in Tables 2–5. Colorless crystals of **Ia** and **Va** were mounted on glass fibers for data collection at 20(1) °C (**Ia**) and −50(1) °C (**Va**) on an Enraf-Nonius CAD4 diffractometer. Cell constants for the data collection were determined from a list of reflections found by an automated search routine. Data collection and reduction information are presented in Table 1. Lorentz and polarization corrections were applied. A correction based on nonlinear decay[19] in the standard reflections was applied to the data. **Ia** decayed 22.4% and **Va** decayed 6.8% over the courses of their respective data collections on the basis of sets of three standard reflections. An absorption correction based on a series of ψ-scans using the semiempirical method was applied. The centric space group $P2_1/C$ (**Ia**) and the acentric space group $P2_12_12_1$ (**Va**) were unambiguously determined by systematic absences. Both structures were solved by direct methods.[19] All non-hydrogen atoms were placed directly from the E map and refined with anisotropic thermal parameters. Hydrogen atom positions were generated with ideal geometries and refined as

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(19) (a) SHELXTL-Plus, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990. (b) Sheldrick, G. M. *J. Appl. Crystallogr.*, in press. (c) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

Table 2. Positional Parameters for Complex (Cl)(PEt$_3$)$_2$Pt[C(=PR)(Cl] (Ia) with Estimated Standard Deviations in Parentheses

	x	*y*	*z*	*B* (Å^2)
Pt	0.58510(1)	0.27816(2)	0.12824(1)	3.496(4)
Cl(a)	0.7142(1)	0.1790(1)	0.24698(5)	4.33(3)
Cl(b)	0.4513(1)	0.2428(2)	0.04228(7)	7.79(4)
P(1)	0.78281(9)	0.4058(1)	0.21715(5)	3.50(3)
P(2)	0.4801(1)	0.4106(1)	0.15474(5)	3.83(3)
P(3)	0.6812(1)	0.1569(1)	0.08771(5)	4.11(3)
C(1)	0.7012(3)	0.2974(4)	0.2009(2)	3.07(9)
C(2)	0.8833(3)	0.3729(4)	0.2861(2)	3.14(9)
C(3)	0.8608(3)	0.3714(4)	0.3429(2)	3.33(9)
C(4)	0.9271(4)	0.3117(5)	0.3856(2)	4.1(1)
C(5)	1.0190(4)	0.2620(4)	0.3811(2)	3.8(1)
C(6)	1.0479(4)	0.2826(4)	0.3303(2)	3.9(1)
C(7)	0.9861(3)	0.3398(4)	0.2836(2)	3.4(1)
C(8)	0.7723(4)	0.4362(4)	0.3577(2)	4.3(1)
C(9)	0.7282(5)	0.5350(5)	0.3178(2)	6.0(1)
C(10)	0.6833(4)	0.3575(5)	0.3620(2)	5.6(1)
C(11)	0.8163(5)	0.4901(5)	0.4182(2)	6.3(2)
C(12)	1.0372(4)	0.3746(4)	0.2348(2)	4.2(1)
C(13)	1.1559(4)	0.3576(6)	0.2522(3)	6.7(2)
C(14)	0.9939(4)	0.3148(6)	0.1781(2)	6.2(1)
C(15)	1.0236(4)	0.5012(5)	0.2256(2)	5.5(1)
C(16)	1.0878(4)	0.1977(4)	0.4322(2)	4.9(1)
C(17)	1.1905(6)	0.1569(7)	0.4201(3)	10.0(2)
C(18)	1.1182(8)	0.2695(6)	0.4841(3)	12.3(3)
C(19)	1.0309(6)	0.0958(6)	0.4425(3)	9.7(2)
C(20)	0.3443(4)	0.4123(5)	0.1104(3)	5.6(1)
C(21)	0.2739(4)	0.5012(6)	0.1233(3)	6.6(2)
C(22)	0.4673(4)	0.4009(5)	0.2290(2)	5.1(1)
C(23)	0.4277(5)	0.2891(6)	0.2422(3)	7.5(2)
C(24)	0.5274(5)	0.5499(5)	0.1500(3)	5.9(1)
C(25)	0.5337(6)	0.5814(7)	0.0891(3)	9.4(2)
C(26)	0.8088(4)	0.1107(4)	0.1311(2)	4.3(1)
C(27)	0.8848(5)	0.0625(6)	0.0993(3)	7.7(2)
C(28)	0.7030(5)	0.2203(5)	0.0223(2)	6.3(1)
(C29)	0.7601(6)	0.3304(7)	0.0332(3)	8.4(2)
C(30)	0.6156(5)	0.0285(5)	0.0608(3)	6.8(2)
C(31)	0.5851(5)	–0.0388(7)	0.1062(4)	9.6(2)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (Ia)^a

	Distances (Å)		
Pt–Cl(b)	2.377(2)	Pt–P(2)	2.313(1)
Pt–P(3)	2.312(1)	Pt–C(1)	2.013(4)
Cl–P(1)	1.678(5)	C(1)–Cl(a)	1.790(5)
P(1)–C(2)	1.874(5)	P(2)–C(20)	1.829(6)
P(2)–C(22)	1.836(6)	P(2)–C(24)	1.812(7)
P(3)–C(26)	1.820(5)	P(3)–C(28)	1.835(7)
P(3)–C(30)	1.814(7)		
	Angles (deg)		
Cl(b)–Pt–P(2)	90.07(5)	Cl(b)–Pt–P(3)	83.39(6)
Cl(b)–Pt–C(1)	176.1(1)	P(2)–Pt–P(3)	171.24(5)
P(2)–Pt–C(1)	93.2(1)	P(3)–Pt–C(1)	93.5(1)
C(1)–P(1)–C(2)	107.6(2)	Pt–C(1)–Cl(a)	111.8(2)
Pt–C(1)–P(1)	126.1(3)	Cl(a)–C(1)–P(1)	122.1(3)

^{a} Numbers in parentheses are estimated standard deviations.

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for (Cl)(PEt$_3$)$_2$Pt[(H)O=PBC] (Va)

atom	*x*	*y*	*z*	*U*(eq), Å^2
Pt	0.7316(1)	0.0725(1)	0.8271(1)	0.031(1)
Cl	0.6879(4)	0.1771(3)	0.7707(1)	0.059(1)
P(3)	0.9539(3)	–0.0653(3)	0.8850(1)	0.034(1)
O	1.0509(9)	–0.1386(7)	0.8613(2)	0.053(2)
C(1)	0.7842(12)	–0.0158(8)	0.8734(3)	0.032(2)
C(2)	0.7333(11)	–0.0456(7)	0.9086(2)	0.026(2)
C(3)	0.8591(12)	–0.1065(8)	0.9284(3)	0.033(2)
C(4)	0.9001(11)	–0.0446(9)	0.9638(3)	0.037(3)
C(5)	0.8050(12)	0.0152(9)	0.9827(3)	0.039(3)
C(6)	0.6523(12)	0.0186(9)	0.9696(3)	0.035(2)
C(7)	0.6090(11)	–0.0141(8)	0.9335(3)	0.033(2)
C(8)	0.8471(13)	–0.2328(9)	0.9363(3)	0.040(3)
C(81)	0.7898(11)	–0.2949(8)	0.9012(3)	0.048(3)
C(82)	0.9980(11)	–0.2774(9)	0.9456(3)	0.063(4)
C(83)	0.7405(15)	–0.2542(9)	0.9696(3)	0.049(3)
C(9)	0.8389(13)	0.0726(12)	1.0202(4)	0.054(3)
C(91)	1.0033(17)	0.0778(17)	1.0276(5)	0.099(7)
C(92)	0.7861(31)	0.1874(12)	1.0192(5)	0.129(10)
C(93)	0.7611(28)	0.0135(14)	1.0537(4)	0.107(8)
C(10)	0.4532(13)	–0.0148(9)	0.9204(3)	0.041(3)
C(101)	0.4255(14)	–0.1202(10)	0.8990(4)	0.054(3)
C(102)	0.3484(12)	–0.0078(12)	0.9536(3)	0.052(3)
C(103)	0.4223(12)	0.0820(12)	0.8944(3)	0.055(3)
P(1)	0.6976(3)	–0.0760(3)	0.7878(1)	0.041(1)
C(111)	0.5229(14)	–0.729(14)	0.7631(3)	0.054(3)
C(112)	0.3915(15)	–0.0639(16)	0.7873(4)	0.080(5)
C(121)	0.7127(18)	–0.2100(9)	0.8086(3)	0.058(4)
C(122)	0.7062(22)	–0.3077(10)	0.7804(4)	0.078(5)
C(131)	0.8340(12)	–0.0724(13)	0.7497(3)	0.051(3)
C(132)	0.9858(19)	–0.0788(22)	0.7629(5)	0.103(7)
P(2)	0.7903(4)	0.2367(2)	0.8550(1)	0.048(1)
C(211)	0.8059(16)	0.2460(9)	0.9069(3)	0.051(3)
C(212)	0.8640(21)	0.3538(11)	0.9227(4)	0.077(5)
C(221)	0.6626(19)	0.3530(10)	0.8424(4)	0.068(4)
C(222)	0.5069(23)	0.3305(16)	0.8488(6)	0.106(7)
C(231)	0.9592(18)	0.2855(14)	0.8360(5)	0.085(5)
C(232)	1.0851(17)	0.2145(15)	0.8456(6)	0.105(7)
Cl(1′)	0.5834(8)	–0.0680(5)	1.1592(2)	0.155(3)
C(1′)	0.7118(19)	–0.1643(11)	1.1715(5)	0.081(5)
Cl(2′)	0.8864(8)	–0.1247(5)	1.1533(2)	0.126(2)

Table 5. Selected Bond Distances (Å) and Angles (deg) for (Cl)(PEt$_3$)$_2$Pt[(H)O=PBC] (Va)^a

	Distances (Å)		
Pt–C(1)	2.006(10)	Pt–P(2)	2.302(3)
Pt–P(1)	2.304(3)	Pt–Cl	2.388(3)
P(3)–O	1.484(8)	P(3)–C(1)	1.776(3)
P(3)–C(3)	1.844(10)	P(3)–C(2)	2.247(10)
C(1)–C(2)	1.369(13)	C(2)–C(7)	1.485(14)
C(2)–C(3)	1.539(14)	C(3)–C(4)	1.500(14)
C(3)–C(8)	1.58(2)	C(5)–C(6)	1.48(2)
C(5)–C(9)	1.52(2)	C(6)–C(7)	1.38(2)
C(7)–C(10)	1.50(2)		
	Angles (deg)		
Cl–Pt–P(1)	84.74(11)	Cl–Pt–P(2)	85.40(11)
P(1)–Pt–P(2)	167.54(11)	C(1)–Pt–P(1)	95.0(3)
C(1)–Pt–P(2)	94.2(3)	O–P(3)–C(1)	126.6(5)
O–P(3)–C(3)	125.1(5)	C(1)–P(3)–C(3)	80.2(5)
C(2)–C(1)–P(3)	90.7(7)	Pt–C(1)–C(2)	142.1(8)
Pt–C(1)–P(3)	126.2(6)	C(1)–C(2)–C(7)	136.0(9)
C(1)–C(2)–C(3)	106.1(8)	C(3)–C(2)–C(7)	116.2(8)
C(2)–C(3)–C(4)	108.2(8)	C(4)–C(3)–C(8)	111.6(8)

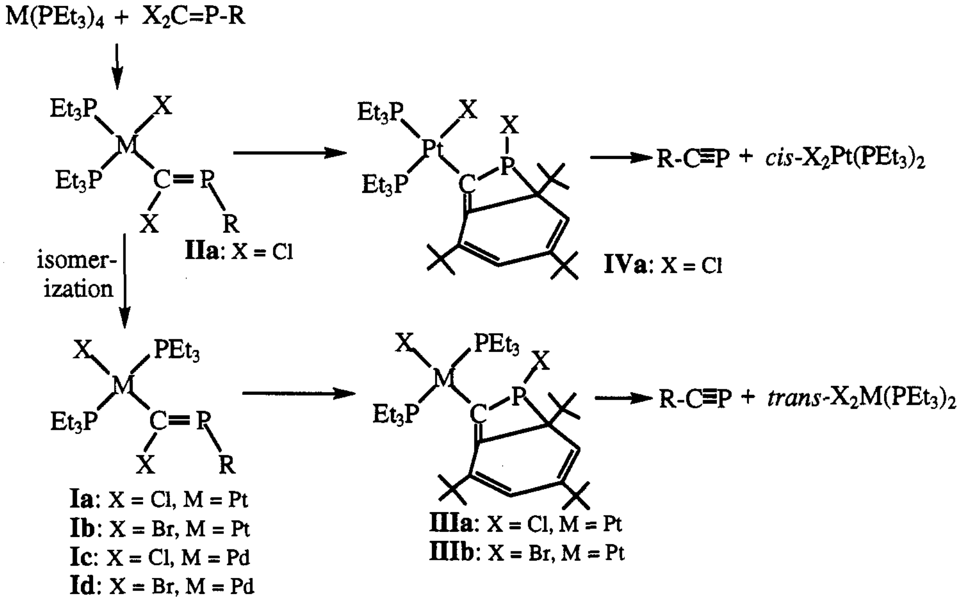
^{a} Numbers in parentheses are estimated standard deviations.

riding, isotropic atoms. One exception was the phosphine–oxo hydrogen atom (H(1)) in **Va**, which was located and refined as an isotropic atom. In addition, it was found necessary to refine **Va** as a racemic twin.[19b] The contribution of the minor component was 14.4(15)%. The Flack X parameter for absolute structure[19c] was determined to be 0.00(2).

Results

Reactions of X$_2$C=P—R (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) with M(PEt$_3$)$_4$ (M = Pt, Pd). The reactions of X$_2$C=P—R (X = Cl, Br) with M(PEt$_3$)$_4$ (M = Pt, Pd) in C$_6$H$_6$ (or hexanes) solvent at room temperature for 1 h gave only the *trans*-(X)(PEt$_3$)$_2$M[C(=PR)X] (**Ia** X = Cl, M = Pt; **Ib** X = Br, M = Pt; **Ic** X = Cl, M = Pd) complexes which were isolated in moderate yield (56%–85%). Complex **Id** was unstable in organic solvents (CH$_2$Cl$_2$, C$_6$H$_6$, and hexanes) and could not be isolated; it reacted further to give the final products R—C≡P and *trans*-Br$_2$Pd(PEt$_3$)$_2$.[18e] But it was sufficiently stable to be observed by ^{31}P{^{1}H} NMR spectroscopy. In the presence

Scheme 1



of free PEt_3, the first product, *cis* isomer **IIa**, slowly isomerized to the *trans* isomer **Ia** even at low temperature (-30 °C).[20] At -50 °C in hexanes, *cis*-(Cl)$(PEt_3)_2$Pt-[C(=P—R)X] (**IIa**) separated as white crystals. At this temperature, any *cis* isomer **IIa** that formed quickly precipitated. When pure isolated **IIa** was allowed to stand in hexanes (or in C_6H_6) in the absence of free PEt_3, no isomerization to **Ia** occurred over a period of 3 days at room temperature. The *cis* isomer **IIb** of **Ib** was also observed but the other *cis* isomers of **Ic** and **Id** were not observed during the reactions at room temperature. Presumably, the rates of isomerization of the *cis* to the *trans* isomers were so fast that the *cis* isomers were not observed under these reaction conditions. The *trans* **I** products (except **Id**) were very stable in nonpolar organic solvents (C_6H_6, hexanes, and CCl_4) and did not undergo further reaction over a period of 1 week at room temperature. But in some polar organic solvents (CH_2Cl_2, $CHCl_3$, and THF), **Ia**, **Ib**, and **IIa** were quantitatively converted to **IIIa**, **IIIb**, and **IVa**, respectively, within 24 h at room temperature. At longer times these complexes reacted further to give the final products, R—C≡P and $X_2Pt(PEt_3)_2$[18a] (X = Cl, Br) (Scheme 1). In the conversion of **Ic** and **Id** to the final products, an intermediate of type **III** was not observed. Isolated **IIIa** was stable in polar solvents (at least 24 h in CH_2Cl_2) but slowly converted to the R—C≡P and *trans*-$Cl_2Pt(PEt_3)_2$ final products in hexanes within 6 h. Intermediate **IIIb** was sufficiently stable to be isolated from polar CH_2Cl_2 but readily converted to the final products in hexanes even at -30 °C. Intermediate **IVa** was too unstable to be isolated in all organic solvents tried (CH_2Cl_2, $CHCl_3$, and THF); it went on to form the final R—C≡P and *cis*-$Cl_2Pt(PEt_3)_2$ products.

The *cis*- and *trans*-(Cl)$(PEt_3)_2$Pt[C(=P—R)Cl] complexes (**Ia** and **IIa**) were also prepared by reaction of *trans*-$Cl_2Pt(PEt_3)_2$ with 1 equiv of Li(Cl)C=P—R[7] in THF at -78 °C. This reaction may provide a more general route for the synthesis of complexes containing the [C(=P—R)-Cl] ligand from the corresponding chloro complexes.

$$trans\text{-}Cl_2Pt(PEt_3)_2 + Li(Cl)C{=}PR \rightarrow \mathbf{Ia} + \mathbf{IIa} \quad (4)$$

Compounds **Ia**–**Ic**, **IIa**, **IIIa**, and **IIIb** were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectrometry and elemental analysis; the structures of **Ia** and **IIIa** were established by X-ray diffraction studies. The very similar $^{31}P\{^1H\}$ NMR chemical shifts and coupling constants for **Ia** and **Ib** indicate that they have the same structures; the J_{PtP} values for the PEt_3 ligands (**Ia**, 2752 Hz; **Ib**, 2759 Hz) are typical of *trans* complexes as in *trans*-$Pt^{II}(PEt_3)_2(R)(X)$.[21] The ^{195}Pt—P coupling constants (**Ia**, 657.7 Hz; **Ib**, 661.2 Hz) of the phosphorus in the [C(=PR)X] ligands are approximately twice the value of that in the *cis* isomer (**IIa**, 365.4 Hz) and in $(PPh_3)_2Pt(\eta^2\text{-}RP{=}CPh_2)$ (319 Hz at -50 °C) (where R = 2,6-dimethylphenyl).[22]

The $^{31}P\{^1H\}$ NMR spectrum of the *cis* isomer **IIa** shows the same pattern as that of **IIe** and **IIf**. Of the three signals for **IIa**, the doublet of doublets at 224.0 ppm, assigned to the phosphorus in the phosphaalkene unit Pt-[C(=PR)Cl], is slightly upfield from $Cl_2C{=}PR$ (232.0 ppm). The ^{195}Pt—P coupling constant (365.4 Hz) of this P is similar to that in **IIe** (354.8 Hz) but almost half the value of that (657.7 Hz) in **Ia**. The other two peaks at 6.0 and 8.0 ppm are assigned to the PEt_3 ligands. The one at 6.0 ppm shows a larger ^{195}Pt—P coupling constant (3921.2 Hz) but a smaller P—P coupling constant ($^3J_{PP}$ = 12.3 Hz) than the other at 8.0 ppm ($^1J_{PtP}$ = 2125.4 Hz, $^3J_{PP}$ = 46.3 Hz). On the basis of their P—P coupling constants to the phosphorus in the Pt[C(=PR)Cl] ligand, the peak at 8.0 ppm can be assigned to the PEt_3 ligand which is *trans* to the Pt[C(=PR)Cl] group and the peak at 6.0 ppm can be assigned to the *cis* PEt_3 ligand. The $^{31}P\{^1H\}$ NMR spectra of **Ic** and **Id** exhibit the same pattern as that of **Ia** and **Ib** except there are no ^{195}Pt satellites. Interestingly, the $^{31}P\{^1H\}$ NMR signals of the phosphorus in the phosphabicyclo ligands of intermediates **IIIa**, **IIIb**, and **IIIc** are not split by coupling to the PEt_3 ligands; in

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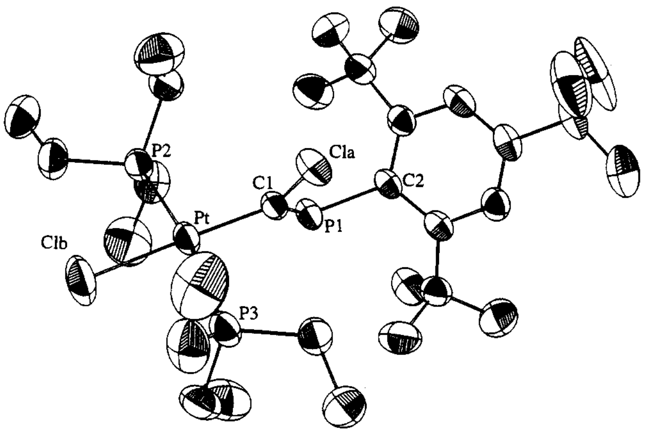


Figure 1. ORTEP drawing of (Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (**Ia**).

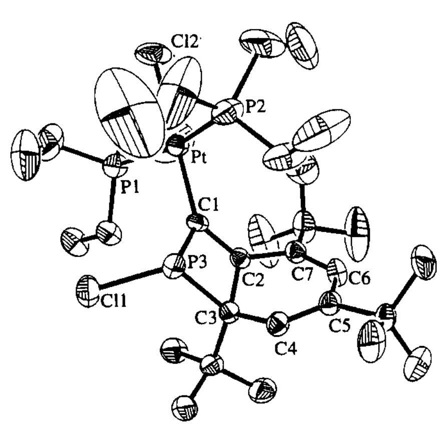
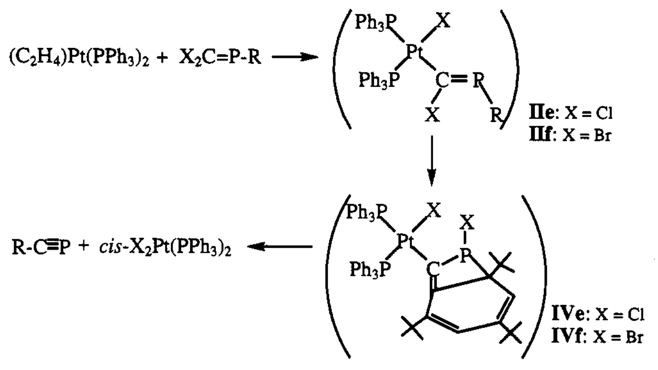


Figure 2. ORTEP drawing of (Cl)(PEt$_3$)$_2$Pt(Cl-PBC) (**IIIa**).

Scheme 2



contrast, this coupling is significant (5–20 Hz) in the *cis* isomers (**IVa**, **IVe**, and **IVf**). Also the two PEt$_3$ ligands in these intermediates (**IIIa**, **IIIb**, and **IIIc**) are not equivalent because they are diastereotopic; but there is no coupling between their phosphorus nuclei.

X-ray Crystal Structures of Ia and IIIa. Bond distances and angles for **Ia** are presented in Table 3. The ORTEP drawing (Figure 1) of complex **Ia** shows that the platinum atom is in a square planar environment which is defined by the two PEt$_3$, Cl, and [C(=PR)Cl] ligands. The atoms Pt, P(2), P(3), Cl(b), and C(1) are all nearly coplanar (within 0.087(1) Å). The C(1)—P(1) distance (1.678(5) Å) is very similar to that of a C=P double bond, e.g., as found in Ph(Me$_3$Si)C=P—R (1.676(6) Å, where R = 2,4,6-tri-*tert*-butylphenyl).[23] The C(1)—P(1) distance is also very similar to that (1.679(4) Å) in the P-bound phosphaalkene in Cr(CO)$_5$(η^1-Mes—P=CPh$_2$),[2d] but it is shorter than that (1.773(8) Å) of the side-on π-bound phosphaalkene in Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$].[24]

The ORTEP drawing of complex **IIIa** (Figure 2), which was reported briefly in a communication,[12] shows that it contains a remarkable phosphabicyclo ligand. The six-membered ring of this ligand is not aromatic but contains double bonds at C(4)–C(5) (1.348(7) Å) and C(6)–C(7) (1.339(8) Å) and single bonds at C(3)–C(4) (1.509(7) Å), C(2)–C(3) (1.533(6) Å), and C(2)–C(7) (1.490(8) Å), while the C(5)–C(6) distance (1.464(8) Å) is characteristic of the central C–C bond of a diene.[25] In the four-membered ring, C(2)–C(3) (1.533(6) Å) is a single bond, whereas C(1)–C(2) (1.389(8) Å) is a somewhat long double bond.[26] The P(3)–C(3) bond (1.911(6) Å) is also longer than a typical P–C single bond (1.85 Å),[25] but the P(3)–C(1) distance (1.802(5) Å) is close to that of a single bond.

A comparison of the isomers **Ia** and **IIIa** shows that the geometries around the Pt and the Pt–P and Pt–Cl distances are very similar in both complexes. However, the P–Pt–P angle in **IIIa** (P(1)–Pt–P(2) = 166.9(1)°) is slightly less linear than that in **Ia** (P(2)–Pt–P(3) = 171.24(5)°), probably due to the bulkiness of the Cl–PBC ligand.

Reactions of X$_2$C=P—R (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) with (PPh$_3$)$_2$Pt(C$_2$H$_4$). The reactions of X$_2$C=P—R with (PPh$_3$)$_2$Pt(C$_2$H$_4$) in organic solvents (C$_6$H$_6$, CH$_2$Cl$_2$, CHCl$_3$, and hexanes for Cl$_2$C=P—R; C$_6$H$_6$ and CH$_2$Cl$_2$ for Br$_2$C=P—R) at room temperature for 12 h gave the final products, R—C≡P (65%–69%) and *cis*-X$_2$Pt(PPh$_3$)$_2$, in moderate yield after workup. These products were identified by comparison of their ^{1}H and ^{31}P{^{1}H} NMR spectra with those reported in the literature[10] for these compounds. In nonpolar organic solvents (C$_6$H$_6$ and hexanes), white crystals of *cis*-X$_2$Pt(PPh$_3$)$_2$ precipitated during the reaction. Interestingly, two types of intermediates (**IIe** and **IIf**, **IVe** and **IVf**) were observed during the reaction in polar solvents (CH$_2$Cl$_2$) by ^{31}P{^{1}H} NMR spectroscopy (Scheme 2). They were not separable even at low temperature (−78 °C), but were sufficiently stable to be observed by ^{31}P{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} NMR spectra (described below) of these intermediates show that they all have a *cis* structure; this is evident from the two PPh$_3$ signals, coupling between the two PPh$_3$ phosphorus nuclei, and the quite different ^{195}Pt–P coupling constants for the PPh$_3$ ligands, all of which are typical of *cis* square planar (PR$_3$)$_2$Pt$^{(II)}$(R)(X) complexes.[21] Thus, these intermediates, as well as the products *cis*-X$_2$Pt(PPh$_3$)$_2$, all have *cis* structures; there was no evidence for *trans* isomers.

The ^{31}P{^{1}H} NMR spectra of **IIe** and **IIf** show the same pattern as that of **IIa**. Of the three signals for **IIe** (X = Cl), the doublet of doublets at 234.6 ppm, assigned to the phosphorus in the phosphaalkene unit Pt[C(=P—R)Cl], is slightly downfield from Cl$_2$C=P—R (232.0 ppm). The

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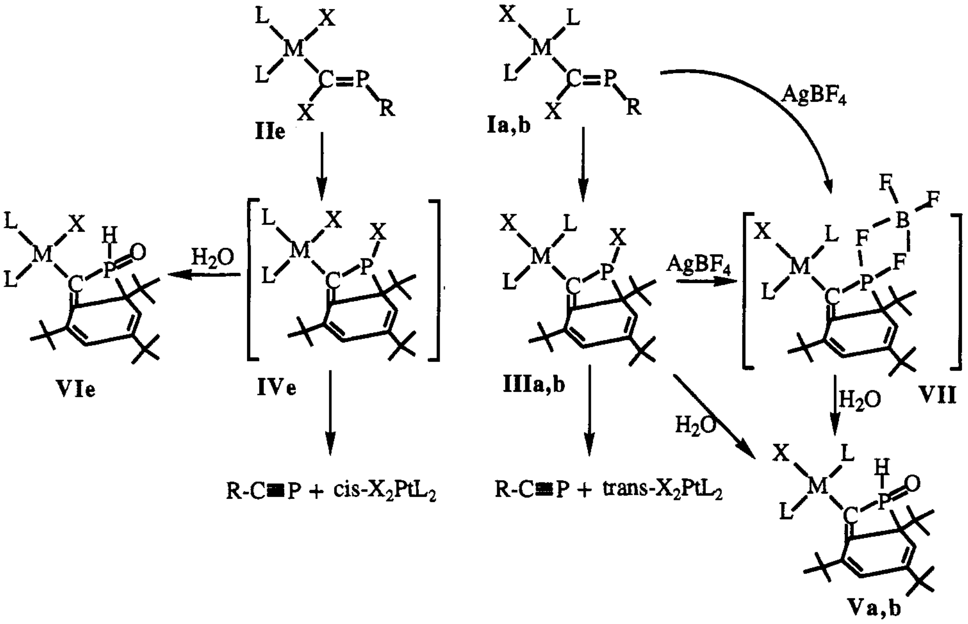
Scheme 3



^{195}Pt—P coupling constant (354.8 Hz) of this P is similar to that in *cis*-(Cl)(PEt$_3$)$_2$Pt[C(=P—R)Cl] (**IIa**) (365.4 Hz) but almost half the value of that (657.7 Hz) in *trans*-(Cl)(PEt$_3$)$_2$Pt[C(=P—R)Cl] (**Ia**). The other two peaks at 17.8 and 10.4 ppm are assigned to the inequivalent PPh$_3$ ligands. The one at 10.4 ppm which is trans to the Cl$^-$ ligand, shows a larger ^{195}Pt—P coupling constant (4203.2 Hz) than the other at 17.8 ppm (1889.8 Hz), which is trans to the [C(=PR)Cl] ligand. The ^{31}P{^{1}H} NMR spectra of **IVe** and **IVf** show almost the same pattern. Of the three signals for intermediate **IVe** (X = Cl), the doublet of doublets at 80.0 ppm assigned to the phosphorus in the phosphabicyclo ligand is upfield of that in $Cl_2C{=}PR$ and also of that in **IIe**. The ^{195}Pt—P coupling constant (142.0 Hz) of the Cl—PBC ligand in **IVe** is significantly smaller than that in **IIe** (354.8 Hz) and that in (Cl)(PEt$_3$)$_2$Pt(Cl—PBC) (**IIIa**) (387.7 Hz). The other two signals (δ 16.5 ppm, $^1J_{PtP}$ = 1750.0 Hz; δ 14.2 ppm, $^1J_{PtP}$ = 4150.0 Hz) assigned to the PPh$_3$ ligands have chemical shifts and ^{195}Pt—P coupling constants very similar to those in **IIe** (δ 17.8 ppm, $^1J_{PtP}$ = 1889.8 Hz; δ 10.4 ppm, $^1J_{PtP}$ = 4203.2 Hz). The analogous Br intermediates, **IIf** and **IVf**, show the same ^{31}P{^{1}H} patterns and similar chemical shifts as those for **IIe** and **IVe** (see Experimental Section).

Reactions of Ia and Ib with H_2O and $AgBF_4$ and Reactions of $(PPh_3)_2Pt(C_2H_4)$ with $Cl_2C{=}P{-}R$ and H_2O. Complexes **Ia** and **Ib** reacted (Scheme 3) with H_2O within 24 h at room temperature under an argon atmosphere in CH_2Cl_2 to give **Va** (X = Cl, L = PEt$_3$) and **Vb** (X = Br, L = PEt$_3$) which were isolated as analytically pure compounds and identified by their ^{1}H and ^{31}P{^{1}H} NMR spectra; the structure of **Va** was established by an X-ray diffraction study. A ^{31}P{^{1}H} NMR study showed that **Ia** and **Ib** converted to **Va** and **Vb** through intermediates **IIIa** and **IIIb** without forming $R{-}C{\equiv}P$ and $X_2Pt(PEt_3)_2$ (X = Cl, Br). Complex **Va** was also synthesized from the direct reaction of **IIIa** with H_2O in CH_2Cl_2 solvent (80% yield). Of the two ^{31}P{^{1}H} NMR signals for the diastereotopic PEt$_3$ ligands in **Va**, only the doublet at 13.0 ($^1J_{PtP}$ = 2680 Hz) is coupled with the phosphorus in the phosphabicyclo ligand ($^3J_{PP}$ = 9.6 Hz). The ^{195}Pt—P coupling constants of the PEt$_3$ ligands (2680 Hz, 2575 Hz) in **Va** are typical of *trans*-Pt^{II} (PEt$_3$)$_2$(X)R complexes.[21] The ^{1}H NMR spectrum of **Va** showed three signals in the 7.3–5.9 ppm range. The doublet at 7.3 ppm is assigned to the proton on the phosphorus in the phosphabicyclo ligand because of the large one bond coupling to the phosphorus ($^1J_{PH}$ = 436 Hz).[27] The other two signals at 6.1 (d, $^4J_{HH}$ = 1.7 Hz) and 5.9 ppm (dd, $^4J_{HH}$ = 1.7 Hz, $^3J_{PH}$ = 17.3 Hz) were assigned to the two protons on the six-membered ring in the phosphabicyclo ligand.

Reaction of **Ia** with AgBF$_4$ in dry THF solution produced (Scheme 3) an immediate precipitate of AgCl and a new complex **VII** in solution; **VII** was also formed in the reaction of **IIIa** with AgBF$_4$ in dry THF solution. Unfortunately, **VII** was not sufficiently stable to be isolated; it decomposed to unidentifiable products within 24 h at −30 °C. The reaction of **VII** with H_2O in THF solution immediately gave **Va**, which was identified by its ^{31}P NMR spectrum. The reaction of **Ia** with AgBF$_4$ in the presence of H_2O gave **Va** as the only product. Since **VII** could not be isolated, it was not possible to establish its structure by X-ray diffraction. However, its ^{31}P NMR spectrum suggests the structure shown in Scheme 3. In this spectrum, the splitting of the peak at 139 ppm (dddd), assigned to the P in the BF$_4$-PBC ligand, shows two relatively large coupling constants (1055.78 and 866.07 Hz), which are typical of one-bond ^{31}P–^{19}F coupling; another coupling constant (63.95 Hz) is typical of three-bond ^{31}P–^{19}F coupling constants.[28] The fourth coupling constant (8.25 Hz) is probably due to coupling with a PEt$_3$ ligand. The ^{195}Pt–P coupling constant (299.68 Hz) of this peak is close to that of **IIIa** (387.7 Hz). These ^{31}P{^{1}H} NMR data are consistent with the structure in Scheme 3 if it is assumed that one of the terminal F atoms does not couple to the phosphorus of the phosphabicyclo ligand. In the absence of further structural characterization, this structural assignment for **VII** must be regarded as tentative.

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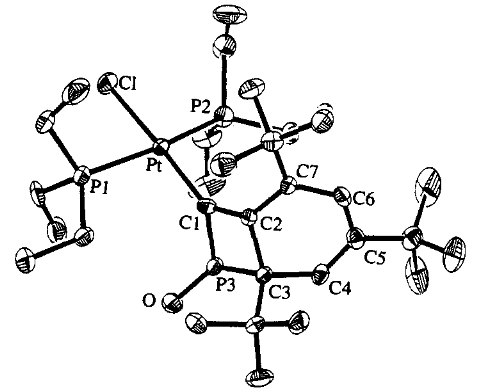


Figure 3. ORTEP drawing of (Cl)$(PEt_3)_2$Pt[(H)O═PBC] (**Va**).

The reaction of $(PPh_3)_2Pt(C_2H_4)$ and Cl_2C═P—R in the presence of a trace amount of H_2O in CH_2Cl_2 solution proceeded in almost the same manner as that of $(PPh_3)_2Pt(C_2H_4)$ with Cl_2C═P—R in dry CH_2Cl_2 (Scheme 3). In both reactions, monitored by $^{31}P\{^1H\}$ NMR spectrometry, **IIe** formed first and this rearranged to intermediate **IVe**, which converted to the final products R—C≡P and *cis*-$Cl_2Pt(PPh_3)_2$ (Schemes 2 and 3); however, the reaction with trace H_2O gave a very small amount of a new product (**VIe**). When an amount of H_2O equivalent to Cl_2C═P—R and $(PPh_3)_2Pt(C_2H_4)$ was used, **VIe** was obtained as the major product together with R—C≡P and *cis*-$Cl_2Pt(PPh_3)_2$ as minor products. The $^{31}P\{^1H\}$ NMR spectrum of **VIe** shows a splitting pattern typical of *cis* square planar (X)(R)$Pt^{II}L_2$ (X = halogen; R = alkyl, aryl; L = phosphine) complexes in which the J_{PtP} of the L that is *trans* to the halogen is much larger than that of the L which is *trans* to the R group.[21] Of the three $^{31}P\{^1H\}$ NMR signals for **VIe**, that at 16.4 ppm (dd, $^3J_{PP}$ = 3.2 Hz, $^2J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 1760 Hz) is assigned to the PPh_3 that is *trans* to the (H)O—PBC ligand while the signal at 12.2 ppm (d, $^2J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 4150 Hz) is assigned to the PPh_3 that is *trans* to the Cl ligand. The remaining signal at 13.0 ppm (d, $^3J_{PP}$ = 3.2 Hz, $^2J_{PtP}$ = 20 Hz) assigned to the phosphorus in the (H)O═PBC ligand was much further upfield than that (80 ppm) in **IVe**. Somewhat unexpected is the observation that the PPh_3 ligand *trans* to the Cl ligand is not split by coupling to the phosphorus in the phosphabicyclo ligand.

In order to explore the possibility that the rearrangement of **Ia** to R—C≡P and *trans*-$Cl_2Pt(PEt_3)_2$ is initiated by radicals, this reaction was performed in the nonpolar solvent CCl_4 which is a better Cl radical source than CH_2Cl_2. However, **Ia** did not rearrange or react in CCl_4 for 1 week at room temperature, which suggests that radicals are not involved in this conversion. Also, the rearrangement of **Ia** to **IIIa** in CH_2Cl_2 solvent with added $(t\text{-}Bu)_2NO$, which is a good radical scavenger, gave the same product (**IIIa**) quantitatively within 24 h at room temperature; thus, $(t\text{-}Bu)_2NO$ had no effect on the product or rate of the reaction.

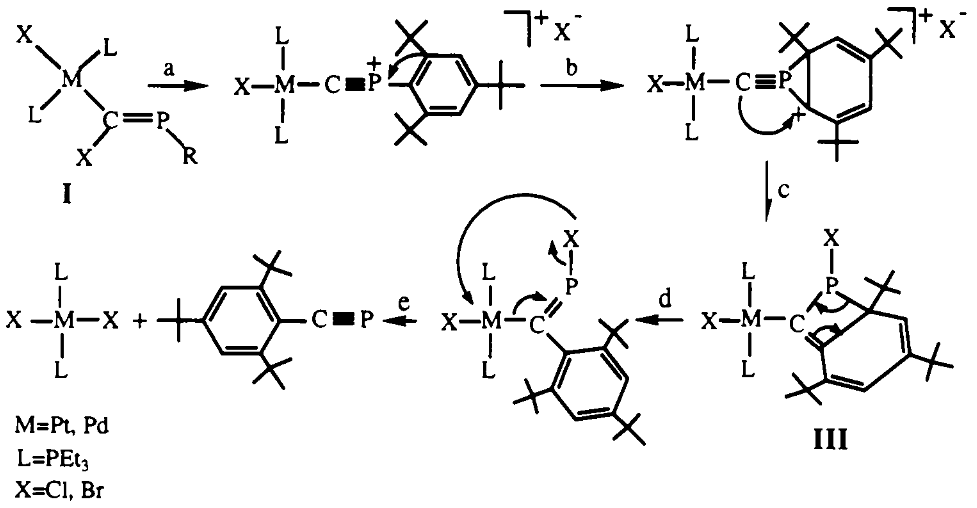
X-ray Crystal Structure of Va. The ORTEP drawing (Figure 3) of complex **Va** shows that it contains the phosphabicyclo ligand with almost the same structure as in **IIIa** (Figure 2) except for the oxygen and hydrogen on the phosphorus instead of C(1). The P(3)—O distance (1.473(7) Å) is very similar to that of a typical P═O double bond in R_3P═O (1.489 Å).[25] A comparison of the **IIIa** and **Va** structures shows that the geometries around the Pt, the single bonds at C(3)—C(4), C(7)—C(2), and C(5)—C(6) in the six-membered ring, and the single bonds at C(2)—C(3) in the four-membered ring are very similar in both complexes. The double bond at C(6)—C(7) (1.38(2) Å) in **Va** appears to be marginally longer than that (1.339(8) Å) in **IIIa**. In the four-membered ring, the C(1)—C(2) bond (1.369(13) Å) is similar to that (1.389(8) Å) in **IIIa**. The P(3)—C(3) bond (1.844(9) Å) is similar to a typical P—C single bond (1.85 Å), whereas the P(3)—C(1) distance (1.766(11) Å) appears to be shorter than that of a single bond and also shorter than that (1.802(5) Å) in **IIIa**.

Discussion

Synthesis and Rearrangement of (X)$(PR_3)_2$M[C(═PR)X] Complexes. Unlike the reactions of $Pt(PPh_3)_4$ with Cl_2C═N—R (R = C_6H_{11}, C_6H_5, *p*-$C_6H_4NO_2$) which give three-fragment oxidative-addition products (eq 3), the reactions of $M(PEt_3)_4$ (M = Pt, Pd) or $(PPh_3)_2Pt(C_2H_4)$ with X_2C═P—R (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) give the *cis* products **II** (Schemes 1 and 2). The *cis* products **IIa**–**IId** rearrange quickly to the *trans* isomers **Ia**–**Id** in the presence of free PEt_3, as occurs in other $(PR_3)_2M^{II}X_2$ (M = Pt, Pd) complexes.[21] The other *cis* products, **IIe** and **IIf**, do not rearrange to the *trans* isomer even in the presence of PPh_3. Instead they go on to form the products, R—C≡P and *cis*-$X_2Pt(PPh_3)_2$. In nonpolar organic solvents (C_6H_6, hexanes, and CCl_4), **Ia**–**Ic** are stable enough to be isolated. Under the same reaction conditions, **Id** reacts further to give the final products, R—C≡P and *trans*-$Br_2Pd(PEt_3)_2$, without evidence (^{31}P NMR) for intermediates (Scheme 1). But in polar organic solvents (CH_2Cl_2, $CHCl_3$, and THF), all reactions of $M(PEt_3)_4$ (M = Pt, Pd) with X_2C═P—R (X = Cl, Br) give the final products R—C≡P and *trans*-$X_2M(PR_3)_2$ (X = Br, Cl, M = Pt, Pd) via intermediates **I** and **III**. Thus, the solvent greatly affects the rate of formation of R—C≡P and *trans*-$X_2M(PR_3)_2$ from complexes **I**.

In addition, the rate of conversion of the type **I** and **II** complexes to form **III** and **IV** depends on the PR_3 ligands, the metal, and the halogen of the X_2C═P—R reactant. In nonpolar solvents (C_6H_6 and hexanes), the *cis* and *trans* isomers of Cl$(PEt_3)_2$Pt[C(═PR)Cl] (**Ia** and **IIa**) do not react further over a period of 72 h, but the *cis*-(X)$(PPh_3)_2$Pt[C(═PR)X] complexes (**IIe** and **IIf**) easily convert to the final products R—C≡P and *cis*-$X_2Pt(PPh_3)_2$ under the same conditions. On the other hand, in the polar solvent CH_2Cl_2 all of the type **II** complexes are unstable and undergo further reactions. Complex **Ia**, which has a relatively poor leaving group (Cl^-) at the carbon in the phosphaalkene ligand, is more stable than **Ib**, which has a better leaving group (Br^-). In general **Ia**, **Ib**, and **IIa**, are more stable than the Pd analogs **Ic** and **Id** in polar solvents. The tendency of polar solvents to promote further reactions of **I** and **II** suggests that X^- (X = Cl, Br) dissociation from the [C(═PR)X] ligand is the initial step in these reactions. This is supported by results of the reaction of Ag^+ with **Ia** which gives **VII** within 1 min (Scheme 3). However, there is no spectroscopic evidence for terminal isocyaphide complexes $XL_2M(C{\equiv}PR)^+X^-$ expected to result from such a X^- dissociation. Presum-

Scheme 4

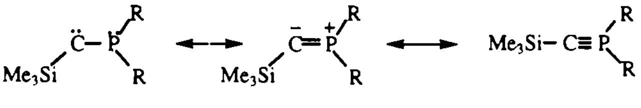


M=Pt, Pd
L=PEt$_3$
X=Cl, Br

ably, they are so reactive that they immediately convert to $XL_2M[X{-}PBC]$. However, the mass spectrum (EI, at 70 ev) of **Ia** shows a fragment peak at *m/e* 755.7 which corresponds to $[M - Cl]^+$. Although the structure of this fragment ion is not known, it could be the terminal isocyaphide complex $[Cl(PEt_3)_2Pt(C{\equiv}P{-}R)]^+$.

The stabilities of intermediates **III** and **IV** also depend on the PR_3 ligands, the halogen on the phosphorus, the structures (*cis* or *trans*), and the solvent. The *cis* type complex **IVa** reacts much more rapidly to give $R{-}C{\equiv}P$ and $Cl_2Pt(PEt_3)_2$ than the *trans* analog **IIIa**. And also **IVa** is more reactive than **IVe**. The trend in increasing reactivity (**IIIa** < **IVe** < **IVa**) follows the trend ($Cl < PPh_3 < PEt_3$) in *trans* influence[29] of the ligand *trans* to the phosphabicyclo ligand. The reactivities of intermediates **III** and **IV** also depend on the halogen which is on the phosphorus. The bromo complexes **IIIb** and **IVf** are more reactive than the Cl analogs **IIIa** and **IVe**.

Proposed Mechanism for the Conversion of Complexes I to $R{-}C{\equiv}P$ and $X_2M(PEt_3)_2$. On the basis of the above reaction studies and the structure of **IIIa**, we propose the mechanism in Scheme 4 for the conversion of **I** to $R{-}C{\equiv}P$ and *trans*-$X_2M(PEt_3)_2$. In step a, X^- dissociates to give a highly reactive aryl isocyaphide ($C{\equiv}P{-}R$) ligand whose positive phosphorus is attacked by an electron-rich carbon on the supermesityl to give a λ^5-phosphaacetylene type transient intermediate (step b). Addition of the isocyaphide carbon (step *c*) to the aryl ring carbon gives complex **III**; the structure of **IIIa** was established crystallographically. The formation of **III** clearly indicates that it is thermodynamically more stable than its isomer **I**. This is surprising since the supermesityl group loses its aromaticity in this isomerization. The aromaticity is restored in the final steps (d) and (e), leading to the final products *trans*-$X_2M(PEt_3)_2$ and $R{-}C{\equiv}P$. Support for the proposed λ^5-phosphaacetylene intermediate formed in step b may be found in recent studies of Bertrand and co-workers,[30] who reported the synthesis and reactions of the λ^5-phosphaacetylene $Me_3Si{-}C{\equiv}PR_2$ (where R = $(i\text{-}Pr)_2N$). On the basis of NMR studies, they suggested that resonance form **C** best represents the compound. The unusual bicyclic ring structure in **III** is also found in a dihydrophetium salt reported recently.[31]



A **B** **C**

On the basis of the evidence for the mechanism in Scheme 4 and the similar reactivities of $Pt(PR_3)_4$ and $Pd(PR_3)_4$, it is likely that the previously reported[10] reaction (eq 2) of $Pd(PPh_3)_4$ with $Cl_2C{=}P{-}R$ to give the analogous products, $R{-}C{\equiv}P$ and $Cl_2Pd(PPh_3)_2$, proceeds by a mechanism that involves initial oxidative addition (as in Schemes 1 and 2) to give $X(PPh_3)_2Pd[C({=}P{-}R)Cl]$; this latter intermediate then reacts according to the mechanism in Scheme 4 to give the products. One might even speculate that the conversion (eq 1) of $Li(Cl)C{=}P{-}R$ to $R{-}C{\equiv}P$ proceeds by a similar mechanism in which lithium plays the role of platinum.

Effect of H_2O on Reactions of I–III. Under conditions where the reactants and solvents are carefully dried, *cis*- and *trans*-$(X)(PR'_3)_2M[C({=}PR)X]$ (**I** and **II**) rearrange (Schemes 1 and 2) to give $R{-}C{\equiv}P$ and $(X)_2(PR'_3)_2M$ through intermediates **III** and **IV**. However, if water is present in the reaction solution (Scheme 3), the major (or sole) products are the $(X)(PR'_3)_2M[(H)O{=}PBC]$ complexes (**V**); very little if any of the $R{-}C{\equiv}P$ and $(X)_2(PR'_3)_2M$ products are observed. Since water reacts with the halo–phosphabicyclo complexes **III** to give **V**, it appears that it is this facile reaction that leads to the formation of **V**. Thus, small amounts of water in this system dramatically change the course of the reaction.

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Supplementary Material Available: Textual description of the data collection and structure solution, fully labeled drawings of **Ia** and **Va**, and tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least squares planes (36 pages). Ordering information is given on any current masthead page.

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