2454 *Organometallics* **1994,** *13,* 2454-2460

Bridging Cyaphide ($C{\equiv}P^-$) and Bridging Aryl Isocyaphide ($C{\equiv}P{-}R$) Ligands: Synthesis and Characterization of $(X)(PEt_3)_2Pt(\mu\text{-}C{\equiv}P)Pt(PEt_3)_2$ and $(X)(PEt_3)Pt(\mu\text{-}C{\equiv}P{-}R)Pt(PEt_3)_2(X)$ (X = Cl, Br; R = 2,4,6-Tri-*tert*-butylphenyl)[†]

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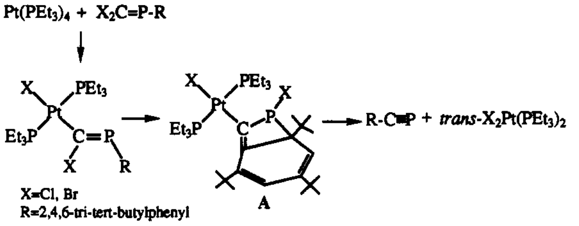
The halophosphaalkene platinum complexes, *trans*-$(X)(PEt_3)_2Pt[C({=}PR)X]$ (**1a**, X = Cl; **1b**, X = Br; R = 2,4,6-tri-*tert*-butylphenyl) react with $Pt(PEt_3)_4$ to yield $(X)(PEt_3)Pt(\mu\text{-}C{\equiv}PR)Pt(PEt_3)_2(X)$ (**3a**, X = Cl; **3b**, X = Br). The molecular structure of **3a** shows that it contains a semibridging isocyaphide (C≡P—R) ligand. The platinum complexes *trans*-$(X)(PEt_3)_2Pt[C({=}PR)X]$ (**1a**, X = Cl; **1b**, X = Br; R = 2,4,6-tri-*tert*-butylphenyl) react with $Pd(PEt_3)_4$ to give $(X)(PEt_3)_2Pt(C{\equiv}P)$ (**4**) and $(X)(PEt_3)_2Pd(R)$ (**5**). Complexes **4**, which are tentatively assigned a structure with a terminal cyaphide ($C{\equiv}P^-$) ligand, react with $Pt(PEt_3)_4$ to give bridging cyaphide diplatinum complexes $(PEt_3)_2Pt(\mu\text{-}C{\equiv}P)Pt(PEt_3)_2(X)$ (**6a**, X = Cl; **6b**, X = Br). The molecular structure of **6a** exhibits a bridging $C{\equiv}P^-$ ligand carbon-bonded to Pt(1) and η^2-bonded to Pt(2). In the structure of **5a**, a methyl group of each of the two *o*-*tert*-butyl groups of the R ligand sits above (and below) the Pd; however, NMR studies suggest there is little if any agostic interaction.

Introduction

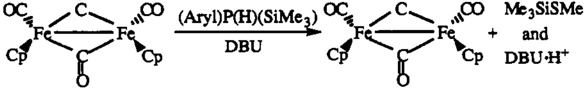
During the past two decades, bulky alkyl and aryl R groups have been used to stabilize compounds with multiple bonds between carbon and phosphorus. As a result, many phosphaalkynes (RC≡P)[1] have been synthesized and subsequently incorporated as ligands into transition metal complexes.[2] According to photoelectron spectroscopic studies,[3] the HOMO of phosphaalkynes is a π-type orbital and the nonbonding (n) electrons are of lower energy; the π–n separation is greater in phosphaalkynes than in the corresponding nitriles (RC≡N), which generally prefer N ligation to metals. The relatively high energy of the C≡P π-bond may explain the preference of RC≡P for side-on π-bonding over P-donor coordination in transition metal phosphaalkyne complexes.

Unlike RC≡P compounds, the isomeric alkyl or aryl isocyaphides (C≡PR)[4] are unknown and are unstable relative to the RC≡P isomer according to ab initio calculations.[5] In fact, these calculations indicate that C≡P—H is 85 kcal/mol less stable than the H—C≡P isomer. Recently, several research groups have proposed free C≡PR (where R = 2,4,6-tri-*tert*-butylphenyl) as a transient intermediate in the conversion of Li(Cl)C=PR to LiCl and RC≡P[6a–d] and in the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PR$ to give $(Cl)_2Pd(PPh_3)_2$ and R—C≡P.[6e] The latter reaction, however, probably does not proceed through free C≡PR; this is suggested by our study[7] of the analogous reaction (eq 1) of $Pt(PEt_3)_4$ with $Cl_2C{=}PR$ or $Br_2C{=}PR$. For this reaction, intermediate **A** has been isolated and characterized by X-ray diffraction studies. Thus, there is no evidence for free C≡PR as a transient intermediate in this reaction.



(1)

While there is no experimental evidence for free alkyl or aryl isocyaphides (C≡PR), we communicated[8] previously the synthesis of a diplatinum complex $(Cl)(PEt_3)Pt(\mu\text{-}C{\equiv}PR)Pt(PEt_3)_2(Cl)$ (**3a**) with a semibridging C≡PR ligand. More recently, Weber and co-workers[9] reported the synthesis (eq 2) of a diiron complex with a bridging



(2)

[†] Dedicated to Professor Helmut Werner, Universität Würzburg, on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

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(4) By analogy with the name aryl isocyanide for C≡NR, we suggest aryl isocyaphide for C≡PR.

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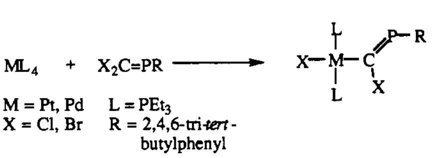
C≡PR ligand. In the present paper, we provide details for the synthesis of **3a** and related derivatives.

In addition to our interest in stabilizing C≡PR ligands in transition metal complexes, we have also sought to prepare complexes with the cyaphide[10] ($C{\equiv}P^-$) ligand, the phosphorus analog of cyanide ($C{\equiv}N^-$), a well-known ligand in transition metal chemistry.[11] Since $C{\equiv}P^-$ has not been detected, little is known about it; however, a MO calculation[12] suggests that its heat of formation is ca. 40 kcal/mol greater than that of $C{\equiv}N^-$. However, as discussed in a communication,[13] we have isolated and characterized crystallographically a diplatinum complex. $(Cl)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$, in which the $C{\equiv}P^-$ is C-bonded to one Pt and π-bonded to the other. Details of the synthesis and characterization of this diplatinum complex are described herein.

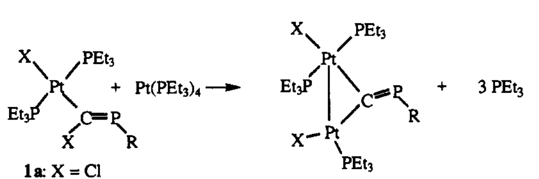
The syntheses of both the semibridging aryl isocyaphide complex $(Cl)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(Cl)$ (**3a**)[8] and the bridging cyaphide complex $(Cl)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ (**6a**)[13] begin with the platinum complexes *trans*-$(X)(PEt_3)_2Pt[C({=}PR)X]$ [X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl), whose preparations (eq 3) were reported previously.[7,8] In this paper, are given details of the syntheses of **3a** and **6a** and related compounds, as well as evidence for the formation of the complexes $(X)(PEt_3)_2Pt(C{\equiv}P)$ (X = Cl, Br) with a terminal cyaphide ($C{\equiv}P^-$) ligand.



(3)

Results and Discussion

Synthesis of Semibridging Isocyaphide Platinum Complexes, $(X)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(X)$ (3a, X = Cl; 3b, X = Br). The first examples of stable aryl isocyaphide metal complexes $(X)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(X)$ (**3a**, X = Cl; **3b**, X = Br) were prepared by the reaction of *trans*-$(X)(PEt_3)_2Pt[C({=}PR)X]$ with $Pt(PEt_3)_4$ in benzene (or in hexanes) solvent at room temperature (eq 4). This oxidative-addition type reaction was complete within 24 h and afforded **3a** or **3b** as the only product, as determined by ^{31}P NMR spectra of the reaction solutions; some $O{=}PEt_3$ impurity was also formed, presumably resulting from the reaction of PEt_3 with adventitious O_2. The reaction leading to the bromo analog **3b** was faster than that to **3a**. But both of these reactions were much slower than those (eq 3) of $X_2C{=}PR$ (X = Cl, Br) with $Pt(PEt_3)_4$ which were complete within minutes in the same solvents (C_6H_6 or hexanes) at room temperature.[7,8] Complexes **3a** and **3b** were isolated in 60–65% yield after recrystallization in hexanes at −78 °C. During recrystallization, red crystals of **3a** or **3b** precipitated after colorless crystals of the $O{=}PEt_3$ impurity formed. Complexes **3a** and **3b** are stable in air for at least 1 month at room temperature and are soluble in organic solvents (C_6H_6, hexanes, acetone, THF, and CH_2Cl_2). Complexes **3a** and **3b** were also prepared by the direct reaction of $X_2C{=}PR$ (X = Cl, Br) with 2 equiv of $Pt(PEt_3)_4$ in benzene (or in hexanes) solvent at room temperature; in this synthesis, both reactions (eqs 3 and 4) occur in the same solution. But the yield (<40%) was much lower than that obtained from the reaction of **1a** with $Pt(PEt_3)_4$ (eq 4).



1a: X = Cl
1b: X = Br

3a: X = Cl
3b: X = Br

(4)

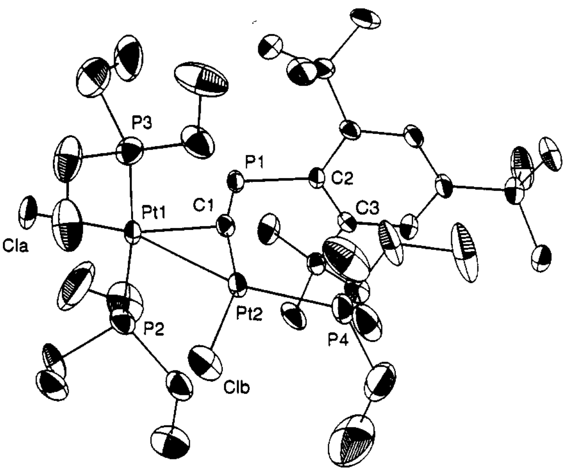


Figure 1. ORTEP drawing of $(Cl)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(Cl)$ (**3a**).

Compounds **3a** and **3b** were characterized by NMR spectroscopy ($^{31}P\{^1H\}$ and ^1H), elemental analysis, and X-ray crystallography (for **3a**). The NMR spectra of both **3a** and **3b** show the same pattern of signals which suggests they have the same structure. And these spectra are consistent with the structure (Figure 1) of **3a** as established crystallographically. The $^{31}P\{^1H\}$ NMR spectrum of **3a** shows three different signals. The peak at 151.3 ppm, assigned to the phosphorus in the C=PR ligand, shows a doublet of triplets with two different Pt satellites, which is consistent with the structure of **3a**; the triplet ($^3J_{PP}$ = 23 Hz) results from coupling of P(1)[14] to the two equivalent PEt_3 ligands on Pt(1) and the doublet ($^3J_{PP}$ = 35 Hz) is caused by coupling to the PEt_3 ligand on Pt(2). Although the two ^{195}Pt—P(1) coupling constants ($^2J_{PtP(1)}$ = 321 Hz, $^2J_{PtP(1)}$ = 110 Hz) to the Pt atoms cannot be assigned unambiguously, we can make a best guess based on previous observations[15] that J_{PtP} coupling constants are larger for complexes with a lower Pt coordination number. Thus, the large J_{PtP} (321 Hz) may be assigned to ^{195}Pt(2)—P(1) and the small value (110 Hz) to ^{195}Pt(1)—P(1). Similarly, the ^{195}Pt—P coupling constant (2428 Hz) for the two PEt_3 ligands on Pt(1) is smaller than that (4814 Hz) for the PEt_3 ligand on Pt(2). The doublet at 19.6 ppm is assigned to the two equivalent PEt_3 ligands on Pt(1), while the other doublet at 22.8 ppm is assigned to the PEt_3 ligand on Pt(2). The chemical shift of the

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[10] By analogy with the name cyanide for $C{\equiv}N^-$, we suggest cyaphide for $C{\equiv}P^-$.

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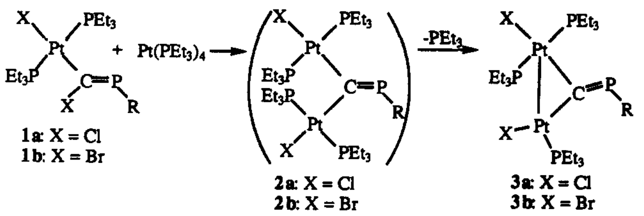
[14] Atom labels used in NMR discussions of the compounds are given in Figures 1–3.

[15] Pidcock, A.; Nixon, J. F. *Annu. Rev. NMR Spectrosc.* **1969**, *2*, 345.

Scheme 1



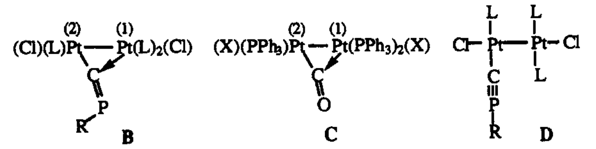
phosphorus in the semibridging isocyaphide ligand (151.3 ppm) is significantly upfield of that for the phosphorus in **1a** (223.3 ppm).

Although no intermediates were observed by ^{31}P NMR spectroscopy during the reaction (eq 4) of **1a** (or **1b**) with Pt(PEt$_3$)$_4$, a possible mechanism for the formation of **3a** (or **3b**) could involve intermediate **2a** (or **2b**) resulting from oxidative addition of the C–X bond to Pt(PEt$_3$)$_4$ (Scheme 1). Loss of PEt$_3$ from this intermediate followed by Pt–Pt bond formation would give the final product **3a** (or **3b**).

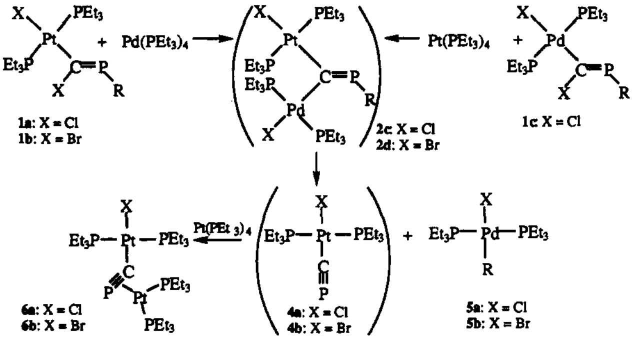
X-ray Crystal Structure of (Cl)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Cl) (3a). The ORTEP drawing of complex **3a** (Figure 1), which was reported briefly in a communication,[8] shows a dinuclear complex with a bridging μ-C=PR ligand. The atoms Cl(a), Pt(1), C(1), P(1), C(2), Pt(2), Cl(b), and P(4) are all coplanar within 0.134 Å; of the coordinated atoms, only P(2) and P(3) are out of this plane, the Pt(1)—P(2) and Pt(1)—P(3) bond vectors being approximately perpendicular to this plane. The C(1)—P(1) distance (1.67(1) Å) in the μ-C=PR ligand is the same as that (1.678(5) Å) in the precursor complex (Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (**1a**)[7] and that (1.67 Å) in Ph(H)C=PR, where R = 2,4,6-tri-*tert*-butylphenyl.[16] The Pt—C distances to the bridging C=PR from the inequivalent Pt atoms are significantly different; Pt(1)—C(1) (2.107(9) Å) is 0.22 Å longer than Pt(2)—C(1) (1.89(1) Å). Also, the Pt—C(1)—P(1) angles are vastly different; the Pt(2)—C(1)—P(1) angle (164.1(6)°) approaches linearity while Pt(1)—C(1)—P(1) (112.0(5)°) is sharply bent.

The geometry of the C=P—R ligand in **3a** is not analogous to symmetrically bridging isocyanide ligands as occurs in compounds such as the triangular Pt$_3$(μ-CNR)$_3$(CNR)$_3$,[17] the dinuclear Cp$_2$Fe$_2$(μ-CNR)$_2$(CNR)$_2$,[18] or the symmetrically bridging isocyaphide ligand in Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-C=P—mesityl) (eq 2).[9] The long nonbonding Pt(1)—P(1) distance (3.15 Å) eliminates the possibility that the C=P—R ligand is a four-electron donor with π-donation from the C=P bond to Pt(1). Therefore, the most reasonable description of μ-C=P—R in this complex is that of a semibridging group, which is strongly coordinated to Pt(2) and interacts more weakly with Pt(1) by accepting at C(1) electron donation from the more electron rich Pt(1) (with two PEt$_3$ donor ligands), as represented in **B** (Chart 1).

Chart 1



Scheme 2



Structure **B** of compound **3a** is very similar to that (**C**) of (X)(PPh$_3$)Pt(μ-CO)Pt(PPh$_3$)$_2$(X) (X = Cl,[19] Br[20]), both of which have been described as containing a semibridging CO ligand. As in **3a**, the Pt(2)—C—O angle (156(1)°) is very open and the Pt(2)—C bond distance (1.901(13) Å) is shorter than that of Pt(1)—C (2.218(13) Å) in (Br)(PPh$_3$)Pt(μ-CO)Pt(PPh$_3$)$_2$(Br).[20] In the absence of a semibridging interaction with Pt(1), the C≡PR ligand in **3a** would be terminal and have structure **D**. It is not clear why the C≡PR ligand in **3a** and the CO in **C** prefer the semibridging structure.

Reaction of (X)(PEt$_3$)$_2$Pt[C(=PR)X] (1a, X = Cl; 1b, X = Br) with Pd(PEt$_3$)$_4$ To Give 4 and 5 and Then with Pt(PEt$_3$)$_4$ To Give (X)(PEt$_3$)Pt(μ-C=P)Pt(PEt$_3$)$_2$ (6a, X = Cl; 6b, X = Br). When the precursor complexes **1a** and **1b** react with Pd(PEt$_3$)$_4$ in benzene (or hexanes) solvent at room temperature, the reaction proceeds in a totally different manner (Scheme 2) than that with Pt(PEt$_3$)$_4$ (eq 4). After stirring the reaction solution of **1a** and Pd(PEt$_3$)$_4$ for 24 h, the two complexes (**4a** and **5a**) were observed as the only products in the ^{31}P{^{1}H} NMR spectrum. These products were quite stable in solution under argon even at room temperature for at least 1 week. Despite this stability, all attempts to separate **4a** by fractional crystallization in hexanes at low temperature (−78 °C) were unsuccessful; however, colorless crystals of **5a** (90% yield) readily separated at an early stage of this recrystallization. Complex **5a** was also separated from the mixture by column chromatography (neutral alumina, hexanes). Complex **4a** decomposed to unidentifiable products during the chromatography even when performed at low temperature (−30 °C). The spectroscopic characterization of **4a** is described below. The reaction of **1b** with Pd(PEt$_3$)$_4$ showed exactly the same reaction pattern and gave the analogous products (**4b** and **5b**).

The ^{1}H and ^{31}P{^{1}H} NMR spectra of **5a** in solution are consistent with its structure as determined by X-ray diffraction (Figure 2). The ^{1}H NMR spectrum of **5a** clearly shows the expected signals, two singlets at δ 1.89 ppm (*o*-*t*-Bu, 18H) and δ 1.34 ppm (*p*-*t*-Bu, 9H) and a doublet at δ 7.42 ppm (2H on Ph), for the supermesityl group; it also exhibits two multiplets at δ 1.68 and 0.88 ppm, for the CH$_2$ and CH$_3$ protons of the PEt$_3$ ligands. The ^{31}P{^{1}H} NMR spectrum of **5a** contains only one singlet at δ −2.75 ppm for the two equivalent PEt$_3$ ligands.

Although we were unable to isolate and fully characterize **4a**, it may be tentatively assigned to the terminal cyaphide structure in Scheme 2 on the basis of its ^{31}P{^{1}H} NMR

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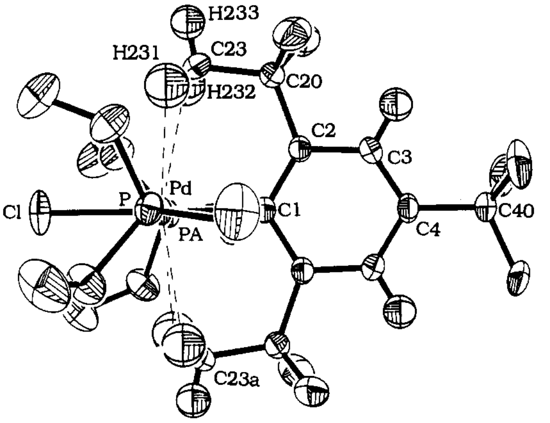

Figure 2. ORTEP drawing of (Cl)$(PEt_3)_2$Pd(2,4,6-tri-*tert*-butylphenyl) (**5a**).

spectrum in the reaction mixture with **5a**. Of the two signals ascribed to **4a**, the one at δ 7.3 ppm is assigned to the PEt_3 ligands because the chemical shift is characteristic of a PEt_3 bound to Pt(II) and the ^{195}Pt—P coupling constant (2871 Hz) is typical of *trans*-$Pt^{II}(PEt_3)_2X_2$[15] complexes; the small J_{PP} (9.2 Hz) is reasonable for coupling to the more distant phosphorus on the $C{\equiv}P^-$ ligand. The signal at δ 68.0 ppm, which we assign to the cyaphide phosphorus, is split (J_{PP} = 9.2 Hz) into a triplet by the equivalent PEt_3 phosphorus atoms, and the ^{195}Pt satellites show a relatively small J_{PtP} (303 Hz) coupling constant.

Although complex **4a** was not isolated, it can be trapped by reaction (Scheme 2) with $Pt(PEt_3)_4$ to give the diplatinum complex **6a**. Complex **6a** formed quickly when $Pt(PEt_3)_4$ was added to a benzene (or hexanes) solution containing the **4a** and **5a** mixture. Complex **6a** was isolated in 80% yield by fractional crystallization over a period of approximately 2 weeks in hexanes at −78 °C. During this recrystallization, impurity O=PEt_3 and complex **5a** precipitated first, and then **6a** crystallized. Pale brown crystals of **6a** are slightly stable in air at room temperature; they may be handled in air for a maximum of 5 min. The synthesis of the bromo analog **6b** proceeded in the same manner.

Complex **6a** was fully characterized by NMR spectroscopy ($^{31}P\{^1H\}$ and ^1H), elemental analysis, and an X-ray crystal structure determination. The analogous complex **6b** was identified by its $^{31}P\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **6a** shows four different signals. The signal at δ 107.0 ppm, assigned to the phosphorus in the bridging C≡P ligand, is a doublet of doublets of triplets with two different ^{195}Pt satellites. The two doublets ($^2J_{P(1)P(4)}$ = 10.7 Hz, $^2J_{P(1)P(5)}$ = 13.7 Hz) result from coupling to the two PEt_3 ligands on Pt(2), and the triplet is due to splitting by the two equivalent PEt_3 ligands on Pt(1). Of the two ^{195}Pt—P coupling constants obtained from the P(1) signal, the one (255 Hz) assigned to $^2J_{Pt(1)P(1)}$ is much smaller than that in *trans*-(Cl)$(PEt_3)_2$Pt[C(=PR)-Cl] (**1a**) (657.7 Hz)[7] but is quite similar to that (303 Hz) in **4a**. The other coupling constant (58 Hz), assigned to $^1J_{Pt(2)P(1)}$, is very similar to that in η^2-(RC≡P)$Pt(PPh_3)_2$ (62 Hz)[21] (where R = *t*-Bu); such small coupling constants are typical for side-on bound R—C≡P ligands in Pt metal complexes. The two signals at δ 18.6 ppm (dd, $^1J_{Pt(2)P(4)}$ = 3619 Hz) and δ 15.0 ppm (ddt, $^1J_{Pt(2)P(5)}$ = 3155 Hz) are assigned to the two PEt_3 ligands on Pt(2) on the basis of their splitting patterns and the $J_{Pt—P}$ values which are typical of η^2-(R-C≡P)$Pt(L)_2$ (J_{PtP} = 3200–3600 Hz).[2] The signal at δ 4.9 ppm (dd, $^1J_{Pt(1)P(2)}$ = 2936 Hz) is assigned to the two equivalent PEt_3 ligands on Pt(1); the ^{195}Pt—P coupling constant is similar to that (2871 Hz) in **4a**, which is typical for *trans*-$X_2Pt(PR_3)_2$ complexes.[20]

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Compound (Cl)(PEt_3)Pt(μ-C=PR)$Pt(PEt_3)_2$ (Cl) (3a), R = 2,4,6-Tri-*tert*-butylphenyl

	Distances (Å)		
Pt(1)–Pt(2)	2.6751(5)	Pt(1)–Cl(a)	2.388(3)
Pt(1)–P(2)	2.338(4)	Pt(2)–Cl(b)	2.398(3)
Pt(1)–C(1)	2.107(9)	Pt(1)–P(3)	2.324(4)
Pt(2)–C(1)	1.89(1)	Pt(2)–P(4)	2.217(3)
P(1)–C(1)	1.67(1)	P(1)–C(2)	1.89(1)
	Angles (deg)		
Pt(2)–Pt(1)–Cl(a)	155.2(1)	Pt(2)–Pt(1)–P(2)	90.34(9)
Pt(2)–Pt(1)–P(3)	90.4(1)	Pt(2)–Pt(1)–C(1)	44.7(2)
Cl(a)–Pt(1)–P(2)	87.8(2)	Cl(a)–Pt(1)–P(3)	86.4(1)
Cl(a)–Pt(1)–C(1)	159.9(3)	P(2)–Pt(1)–P(3)	167.7(1)
P(2)–Pt(1)–C(1)	96.8(2)	P(3)–Pt(1)–C(1)	92.4(2)
Pt(1)–Pt(2)–Cl(b)	104.76(9)	Pt(1)–Pt(2)–P(4)	163.42(9)
Pt(1)–Pt(2)–C(1)	51.5(3)	Cl(b)–Pt(2)–P(4)	91.5(1)
Cl(b)–Pt(2)–C(1)	156.2(3)	P(4)–Pt(2)–C(1)	112.3(3)
C(1)–P(1)–C(2)	110.7(5)	Pt(1)–C(1)–Pt(2)	83.8(4)
P(1)–C(2)–C(3)	122.1(7)	P(1)–C(2)–C(7)	120.6(7)
Pt(1)–C(1)–P(1)	112.0(5)	Pt(2)–C(1)–P(1)	164.1(6)

No intermediates were detected in ^{31}P NMR spectra taken during the reaction (Scheme 2) of **1a** (or **1b**) with $Pd(PEt_3)_4$ to give **4a** (or **4b**) and **5a** (or **5b**). However, we propose that the first step in this reaction is the formation of the mixed Pt—Pd complex **2c** (or **2d**) by oxidative addition of the C—X bond of **1a** (or **1b**) to $Pd(PEt_3)_4$. Subsequent transfer of the R group from P to Pd would give the products **4a** (or **4b**) and **5a** (or **5b**). To test the proposed intermediacy of **2c**, the Pd complex **1c** was reacted with $Pt(PEt_3)_4$ (Scheme 2). If **2c** is an intermediate in this latter reaction, the same products should be obtained as in the reaction of **1a** with $Pd(PEt_3)_4$. Indeed, **1c** reacts with $Pt(PEt_3)_4$ in C_6H_6 (or hexanes) at room temperature for 24 h to give **4a** and **5a** in quantitative yield, as determined by ^{31}P NMR spectra of the product mixture. This experiment not only supports **2c** and **2d** as intermediates in the reaction in Scheme 2 but is also consistent with the suggestion that **2a** and **2b** are intermediates in the reaction in Scheme 1.

X-ray Crystal Structures of (Cl)$(PEt_3)_2$Pd(R) (5a) and (Cl)(PEt_3)Pt(μ-C≡P)$Pt(PEt_3)_2$ (6a). Data collection information, bond distances, angles, and positional parameters for **5a** and bond distances and angles for **6a** are presented in Tables 1–5. The ORTEP drawing of **6a** (Figure 3), which was also reported briefly in a communication,[13] shows that it contains a bridging $C{\equiv}P^-$ ligand carbon-bonded to Pt(1) and η^2-bonded to Pt(2); the Pt atoms are not bonded to each other [Pt(1)—Pt(2) = 3.7868(3) Å]. The atoms Cl, Pt(1), C(1), P(1), Pt(2), P(4), and P(5) are all nearly coplanar (within 0.061 Å), while P(2) and P(3) are 2.292 and 2.279 Å out of this plane. The C(1)—P(1) distance (1.666(6) Å) is longer than those of triple bonds in phosphaalkynes RC≡P [1.52(1) Å for R = 2,4,6-tri-*tert*-butylphenyl[22] and 1.536(2) Å for R = *tert*-butyl][23] but is very similar to that (1.67 (2) Å) in η^2-(RC≡P)$Pt(PPh_3)_2$ (where R = *t*-Bu).[21] The C(1)—P(1)

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Table 2. Crystal and Data Collection Parameters for *trans*-(Cl)(PEt$_3$)$_2$Pd(R) (5a), R = 2,4,6-Tri-*tert*-butylphenyl

Crystal Data	
formula	C$_{30}$H$_{59}$ClP$_2$Pd
fw	623.6
color and habit	yellow, monoclinic
cryst size, mm	0.55 × 0.40 × 0.37
cryst syst	monoclinic
space group	$C2/c$
a, Å	17.580(4)
b, Å	12.945(2)
c, Å	14.877(3)
β, deg	102.99(2)
V, Å^3	3307.4(11)
Z	4
D_{calcd}, g/cm^3	1.252
Data Collection and Refinement	
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα [λ = 0.710 73 Å)
monochromator	highly-oriented graphite crystal
scan type	θ–2θ
2θ range, deg	4.0–50.0
no. of data collcd	6187
no. of unique data	2907 (R_m = 0.029)
no. of unique obsd data	2690; $F > 4.0\sigma(F)$
no. of params refined	186
R,[a] R_w,[b] %	0.0272, 0.0403
goodness-of-fit[c]	1.10

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Goodness-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Compound *trans*-(Cl)(PEt$_3$)$_2$Pd(R) (5a), R = 2,4,6-Tri-*tert*-butylphenyl

atom	*x*	*y*	*z*	*U*(eq)
Pd	5000	1907	2500	23(1)
Cl	5000	58(1)	2500	49(1)
P	4013(1)	1863(1)	3331(1)	30(1)
C(11)	4302(2)	1010(2)	4338(2)	47(1)
C(12)	3710(2)	596(3)	4824(2)	75(1)
C(13)	3764(2)	3103(2)	3794(2)	45(1)
C(14)	3072(2)	3155(2)	4231(3)	64(1)
C(15)	3047(1)	1401(2)	2716(2)	48(1)
C(16)	3018(2)	375(2)	2224(2)	65(1)
C(1)	5000	3483(2)	2500	23(1)
C(2)	4501(1)	4052(1)	1786(1)	25(1)
C(20)	3890(1)	3640(2)	932(1)	32(1)
C(21)	3078(1)	3945(2)	1035(2)	58(1)
C(22)	4042(2)	4150(2)	43(2)	56(1)
C(23)	3880(1)	2483(2)	743(2)	44(1)
C(3)	4516(1)	5128(1)	1817(1)	30(1)
C(4)	5000	5695(2)	2500	30(1)
C(40)	5000	6883(2)	2500	35(1)
C(41)	5244(4)	7287(4)	1675(4)	59(2)
C(42)	5531(4)	7350(3)	3372(3)	58(2)
C(43)	4154(3)	7258(4)	2479(5)	61(2)

Table 4. Selected Bond Distances (Å) and Angles (deg) for the Complex *trans*-(Cl)(PEt$_3$)$_2$Pd(R) (5a), R = 2,4,6-Tri-*tert*-butylphenyl

Distances (Å)			
Pd–Cl	2.394(1)	Pd–C(1)	2.045(3)
Pd–P	2.348(1)	Pd–PA	2.348(1)
Pd–H(231)	2.495	Pd–H(232)	2.795
Angles (deg)			
Cl–Pd–P	88.6(1)	Cl–Pd–C(1)	180.0(1)
P–Pd–C(1)	91.4(1)	Cl–Pd–PA	88.6(1)
P–Pd–PA	177.2(1)	C(1)–Pd–PA	91.4(1)

Table 5. Selected Bond Distances (Å) and Angles (deg) for the Compound (Cl)(PEt$_3$)$_2$Pt(μ-C=P)Pt(PEt$_3$)$_2$ (6a)

Distances (Å)			
Pt(1)–C(1)	1.950(6)	Pt(1)–Cl	2.412(2)
Pt(1)–P(2)	2.302(2)	Pt(1)–P(3)	2.297(2)
Pt(2)–C(1)	2.083(5)	Pt(2)–P(1)	2.337(2)
Pt(2)–P(4)	2.269(2)	Pt(2)–P(5)	2.277(2)
C(1)–P(1)	1.666(6)		
Angles (deg)			
C(1)–Pt(1)–Cl	178.9(2)	C(1)–Pt(1)–P(2)	91.6(2)
C(1)–Pt(1)–P(3)	87.1(2)	Cl–Pt(1)–P(2)	88.05(7)
Cl–Pt(1)–P(3)	93.46(7)	P(2)–Pt(1)–P(3)	168.53(6)
C(1)–Pt(2)–P(1)	43.8(2)	C(1)–Pt(2)–P(4)	146.1(2)
C(1)–Pt(2)–P(5)	109.2(2)	P(1)–Pt(2)–P(4)	102.45(6)
P(1)–Pt(2)–P(5)	152.96(6)	Pt(1)–C(1)–Pt(2)	139.7(3)
Pt(1)–C(1)–P(1)	144.0(3)	Pt(2)–C(1)–P(1)	76.2(2)
Pt(2)–P(1)–C(1)	59.9(2)		

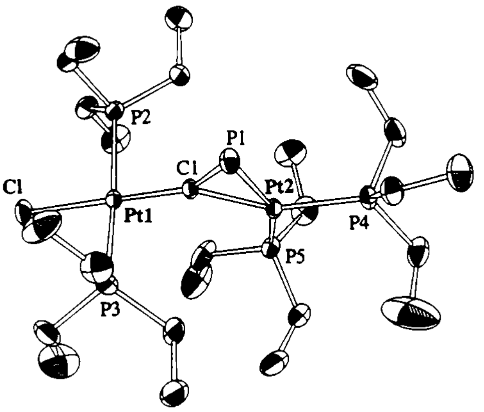

Figure 3. ORTEP drawing of (Cl)(PEt$_3$)$_2$Pt(μ-C=P)Pt(PEt$_3$)$_2$ (**6a**).

distance is also very similar to that of a C=P double bond, as found in Ph(H)C=PR (1.67 Å, where R = 2,4,6-tri-*tert*-butylphenyl).[16]

The ORTEP drawing of complex **5a** (Figure 2) shows that it has essentially a square planar geometry with two PEt$_3$, a Cl, and a C-bonded supermesityl ligand. The atoms Cl, Pd, C(1), C(2), C(3), C(4), and C(40) are all nearly coplanar within 0.009 Å; only P and PA are out of this plane, the Pd–P and Pd–PA bond vectors being approximately perpendicular to this plane. An interesting structural feature of **5a** is the placement of two methyl groups of the two *o-tert*-butyl substituents on the phenyl ring above and below the Pd atom. This geometry suggests that there may be an agostic C–H interaction between the Pd and two H atoms on each CH$_3$ group. As the distances Pd–C(23) (2.992 Å) and Pd–C(23a) (2.992 Å) are much longer than the normal Pd–C bond distance (ca. 2.00 Å), there appears to be no Pd–C bonding. The estimated distances of Pd···H(231) (2.495 Å) and Pd···H(232) (2.795 Å) (assuming 0.96 Å for the methyl C–H distances) are comparable to nonbonding Pd···H distances to the ortho hydrogens of the phenyl rings in the phosphine complexes I$_2$Pd(PPhMe$_2$)$_2$ (2.84–2.85 Å)[24] and Pd(PPh^{t}Bu$_2$)$_2$ (2.6 Å).[25] In (Br)(PPh$_3$)$_2$Pd[C$_4$(CO$_2$Me)$_4$H],[26] the agostic Pd···H (vinyl) distance is only 2.3 Å and the agostic vinyl ^{1}H NMR signal is split into a triplet by coupling to the two PPh$_3$ ligands on Pd. Since ^{1}H and ^{13}C NMR spectra of **5a** in CD$_2$Cl$_2$ solvent show no splitting of the CH$_3$ signal by the PEt$_3$ ligands and all three methyl carbons and all nine hydrogens of the *o-tert*-butyl groups are equivalent even at low temperature (−75 °C), any agostic interaction between the Pd and the protons in the two *o-tert*-butyl groups must be weak or nonexistent.

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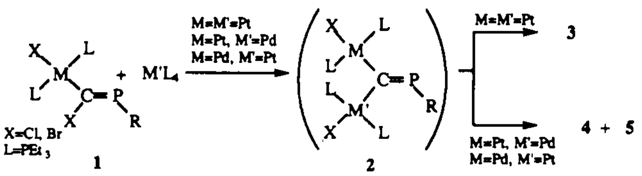
Scheme 3



Conclusion

The remarkable reactions of $(X)(PEt_3)_2Pt[C(=PR)X]$ (**1a**, X = Cl; **1b**, X = Br) with $Pt(PEt_3)_4$ and $Pd(PEt_3)_4$ have yielded the first examples of complexes containing $C\equiv P^-$ and $C\equiv PR$ ligands. In these reactions, the first step (Scheme 3) is presumably oxidative addition of the C—X bond in the $[C(=PR)X]$ ligand to $Pt(PEt_3)_4$ or $Pd(PEt_3)_4$ to give intermediate **2**. If M and M′ are both Pt, Intermediate **2** is converted to products of type **3**; the bridging aryl isocyaphide complexes $(X)(PEt_3)Pt(\mu\text{-}C=PR)Pt(PEt_3)_2(X)$ (**3a** and **3b**) are prepared in this type of reaction. On the other hand, if M is Pt and M′ is Pd, intermediate **2** gives the terminal cyaphide ($C\equiv P^-$) complex *trans*-$(X)(PEt_3)_2Pt(C\equiv P)$ (**4**) and *trans*-$(X)(PEt_3)_2Pd(R)$ (**5**). Thus, the presence of Pd in intermediate **2** yields products that are dramatically different from those obtained when M and M′ in **2** are both Pt. Of additional importance is the reaction of the terminal cyaphide complexes **4** with $Pt(PEt_3)_4$ to give $(X)(PEt_3)_2Pt(\mu\text{-}C=P)Pt(PEt_3)_2$ (**6**), which contains a bridging cyaphide ligand.

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. 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.

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 tetramethylsilane (TMS) (δ 0.00 ppm) as the inernal 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. The complexes $Pt(PEt_3)_4$,[27] $Pd(PEt_3)_4$,[28] *trans*-$(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (**1a**),[7] *trans*-$(Br)(PEt_3)_2Pt[C(=PR)Br]$ (**1b**),[7] and *trans*-$(Cl)(PEt_3)_2Pd[C(=PR)Cl]$ (**1c**),[7] where R = 2,4,6-tri-*tert*-butylphenyl, were prepared by literature methods.

Preparation of $(Cl)(PEt_3)Pt(\mu\text{-}C=PR)Pt(PEt_3)_2(Cl)$ (3a). To a benzene solution (5 mL) of *trans*-$(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (**1a**) (0.395 g, 0.500 mmol) was added a benzene solution (5 mL) of $Pt(PEt_3)_4$ (0.334 g, 0.500 mmol). After the solution was stirred at room temperature under argon for 24 h, the solvent was evaporated to dryness to yield an oily reddish-yellow residue. The residue was extracted with hexanes (30 mL) and filtered by cannula. After reducing the extract to one-fourth of its volume under vacuum, red crystals of **3a** (0.717 g, 65%) were obtained by cooling (−30 °C) the solution. ^1H NMR (C_6D_6): δ 7.46 (s, 2H, R), 2.43 (m, 6H, CH_2), 2.09 (m, 6H, CH_2), 1.49 (m, 6H, CH_2), 1.74 (s, 18H, CH_3 of R), 1.35 (s, 9H, CH_3 of R), 1.26 (m, 18H, CH_3 of Et), 0.82 (m, 9H, CH_3 of Et). ^{31}P NMR (acetone-d_6, 85% H_3PO_4 external standard) (see Figure 1 for atom labels): δ 151.3 (td, $^3J_{P(1)P(2)}$ = 23 Hz, $^3J_{P(1)P(4)}$ = 35 Hz, $^2J_{Pt(1)P(1)}$ = 110 Hz, $^2J_{Pt(2)P(1)}$ = 321 Hz, P(1)), 22.8 (d, $^3J_{P(4)P(1)}$ = 35 Hz, $^1J_{Pt(2)P(4)}$ = 4814 Hz, $^2J_{Pt(1)P(4)}$ = 512 Hz, P(4) in PEt_3), 19.6 (d, $^3J_{P(2)P(1)}$ = 23 Hz, $^1J_{Pt(1)P(2)}$ = 2428 Hz, $^2J_{Pt(2)P(2)}$ = 67 Hz, P(2) and P(3) in PEt_3). Anal. Calcd for $C_{37}H_{74}Cl_2P_4Pt_2$: C, 40.25; H, 6.78. Found: C, 40.36; H, 6.95.

Preparation of $(Br)(PEt_3)Pt(\mu\text{-}C=PR)Pt(PEt_3)_2(Br)$ (3b). Complex **3b** was prepared by the same method as described above using *trans*-$(Br)(PEt_3)_2Pt[C(=PR)Br]$ (**1b**) (0.088 g, 0.10 mmol) and $Pt(PEt_3)_4$ (0.067 g, 0.10 mmol). The product **3b** was obtained as red crystals (0.072 g, 60%). ^1H NMR (C_6D_6): δ 7.47 (s, 2H, R), 2.53 (m, 12H, CH_2 of Et), 2.10 (m, 6H, CH_2 of Et), 1.73 (s, 18H, CH_3 of R), 1.35 (s, 9H, CH_3 of R), 1.25 (m, 18H, CH_3 of Et), 0.82 (m, 9H, CH_3 of Et). ^{31}P NMR (C_6D_6): δ 142.3 (td, $^3J_{P(1)P(2)}$ = 23 Hz, $^3J_{P(1)P(4)}$ = 36 Hz, $^2J_{Pt(1)P(1)}$ = 102 Hz, $^2J_{Pt(2)P(1)}$ = 352 Hz, P(1)), 19.9 (d, $^3J_{P(4)P(1)}$ = 36 Hz, $^1J_{Pt(2)P(4)}$ = 4754 Hz, $^2J_{Pt(1)P(4)}$ = 465 Hz, P(4) in PEt_3), 14.7 (d, $^3J_{P(2)P(1)}$ = 23 Hz, $^1J_{Pt(1)}P_{(2)}$ = 2387 Hz, $^2J_{Pt(2)P(2)}$ = 53 Hz, P(2) and P(3) in PEt_3). Anal. Calcd for $C_{37}H_{74}Br_2P_4Pt_2$: C, 37.27; H, 6.20. Found: C, 37.49; H, 6.26.

Reaction of *trans*-$(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (1a) with $Pd(PEt_3)_4$ To Give 4a and 5a and Then with $Pt(PEt_3)_4$ To Give $(Cl)(PEt_3)_2Pt(\mu\text{-}C=P)Pt(PEt_3)_2$ (6a). To a benzene solution (5 mL) of **1a** (0.395 g, 0.500 mmol) was added a benzene solution (5 mL) of $Pd(PEt_3)_4$ (0.289 g, 0.500 mmol). After the solution was stirred at room temperature under argon for 8 h, only two products, **4a** and **5a**, were generated, as established by a $^{31}P\{^1H\}$ NMR spectrum. To this mixture (in situ) was added a benzene solution (5 mL) of equimolar $Pt(PEt_3)_4$ (0.334 g, 0.500 mmol). After stirring the reaction solution for 30 min at room temperature, the solvent was evaporated to dryness under vacuum. The residue was extracted with hexanes (30 mL) and filtered by cannula. After reducing the hexanes extract to half of its volume, colorless crystals of **5a** (0.279 g, 90%) were obtained after 2–3 days by cooling to −78 °C. After filtering off **5a** by cannula, the volume of the solution was reduced under vacuum to give pale brown crystals of **6a** (0.376 g, 80%) within ca. 2 weeks upon cooling to −78 °C. Data for **4a**: ^{31}P NMR δ 68.0 (t, $^3J_{PP}$ = 9.2 Hz, $^2J_{PtP}$ = 303 Hz, $C\equiv P$), 7.3 (d, $^3J_{PP}$ = 9.2 Hz, $^1J_{PtP}$ = 2871 Hz, PEt_3). For **5a**: ^1H NMR (C_6D_6) δ 7.42 (t, 2H, $^5J_{PH}$ = 0.97 Hz, R), 1.89 (s, 18H, CH_3 of R), 1.68 (tq, 12H, $^3J_{PH}$ = 2.69 Hz, $^3J_{HH}$ = 7.08 Hz, CH_2 of Et), 1.34 (s, 9H, CH_3 of R), 0.88 (m, 18H, $^3J_{HH}$ = 7.08 Hz, CH_3 of Et); ^{31}P NMR (C_6D_6) δ −2.75 (s, PEt_3). Anal. Calcd for $C_{30}H_{59}ClP_2Pd$: C, 57.83; H, 9.73. Found: C, 57.60; H, 9.56. For **6a**: ^{31}P NMR (C_6D_6) δ 107.0 (tdd, $^3J_{P(1)P(2)}$ = 10.7 Hz, $^2J_{P(1)P(4)}$ = 10.7 Hz, $^2J_{P(1)P(5)}$ = 13.7 Hz, $^2J_{Pt(1)P(1)}$ = 255 Hz, $^1J_{Pt(2)P(1)}$ = 58 Hz, $C\equiv P$), 18.6 (dd, $^2J_{P(1)P(4)}$ = 10.7 Hz, $^2J_{P(4)P(5)}$ = 35.1 Hz, $^1J_{Pt(2)P(4)}$ = 3619 Hz, $^3J_{Pt(1)P(4)}$ = 137 Hz, P(4)), 15.0 (dtd, $^2J_{P(5)P(1)}$ = 13.7 Hz, $^4J_{P(5)P(2)}$ = 4.5 Hz, $^2J_{P(5)P(4)}$ = 35.1 Hz, $^1J_{Pt(2)P(5)}$ = 3155 Hz, P(5)), 4.9 (dd, $^3J_{P(2)P(1)}$ = 10.7 Hz, $^4J_{P(2)P(5)}$ = 4.5 Hz, $^1J_{Pt(1)P(2)}$ = 2936 Hz, P(2) and P(3)). Anal. Calcd for $C_{25}H_{60}ClP_5Pt_2$: C, 31.89; H, 6.38. Found: C, 31.72; H, 6.61.

Reaction of *trans*-$(Br)(PEt_3)_2Pt[C(=PR)Br]$ (1b) with $Pd(PEt_3)_4$ To Give 4b and 5b and Then with $Pt(PEt_3)_4$ To Give $(Br)(PEt_3)_2Pt(\mu\text{-}C=P)Pt(PEt_3)_2$ (6b). To a benzene solution (1 mL) of **1b** (0.044 g, 0.050 mmol) was added a benzene solution (1 mL) of $Pd(PEt_3)_4$ (0.029 g, 0.050 mmol). After the solution was stirred at room temperature under argon for 3 h, only two products **4b** and **5b** were observed in the ^{31}P NMR spectrum. To this reaction mixture (in situ) was added a benzene solution (1 mL) of equimolar $Pt(PEt_3)_4$ (0.033 g, 0.050 mmol). After stirring the reaction solution for 30 min at room temperature, only one product **6b** was formed quantitatively; **5b** was also present in the final reaction mixture. ^{31}P NMR (C_6D_6) data: (for **4b**) δ 68.0 (t, $^3J_{PP}$ = 9.6 Hz, $^2J_{PtP}$ = 293 Hz, $C\equiv P$), 3.8 (d, $^3J_{PP}$ = 9.6 Hz, $^1J_{PtP}$ = 2877 Hz, PEt_3); (for **5b**) δ −5.4 (s, PEt_3); (for **6b**) δ 107.0 (tdd, $^3J_{P(1)P(2)}$ = 11.0 Hz, $^2J_{P(1)P(4)}$ = 9.6 Hz, $^2J_{P(1)P(5)}$ = 13.7 Hz, $^2J_{Pt(1)P(1)}$ = 251 Hz, $C\equiv P$), 18.4 (dd, $^2J_{P(1)P(4)}$ = 9.6 Hz, $^2J_{P(4)P(5)}$ = 37.1 Hz, $^1J_{Pt(2)P(4)}$ = 3886 Hz, $^2J_{Pt(2)P(4)}$ = 137 Hz, P(4)), 14.5 (dtd, $^2J_{P(5)P(1)}$ = 13.7 Hz, $^4J_{P(5)P(2)}$ = 4.1 Hz, $^2J_{P(5)P(4)}$ = 37.1 Hz, $^1J_{Pt(2)P(5)}$ = 3194 Hz, P(5)), 1.0 (dd, $^3J_{P(2)P(1)}$ = 11.0 Hz, $^4J_{P(2)P(5)}$ = 4.1 Hz, $^1J_{Pt(1)P(2)}$ = 2950 Hz, P(2) and P(3)).

Reaction of *trans*-$(Cl)(PEt_3)_2Pd[C(=PR)Cl]$ (1c) with 2 equiv of $Pt(PEt_3)_4$ To Give 4a and 5a and Then To Give 6a as the Final Product. To a benzene solution (1 mL) of **1c**

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(28) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187.

(0.070 g, 0.10 mmol) was added a benzene solution (1 mL) of $Pt(PEt_3)_4$ (0.134 g, 0.200 mmol). After the solution was stirred at room temperature for 12 h, only two products, **5a** and **6a**, were found in the reaction mixture. These two products were separated by the same recrystallization procedure as that used in the synthesis of **6a** from the reaction of **1a** with $Pd(PEt_3)_4$ followed by $Pt(PEt_3)_4$. Products **5a** (0.045 g, 72%) and **6a** (0.061 g, 65%) were identified by their ^{31}P NMR spectra.

X-ray Crystal Structure Analyses. Each crystal was attached to the tip of a glass fiber and mounted on the diffractometer for data collection at −50(1) °C. Cell constants were determined from lists of reflections found by an automated search routine. Pertinent data collection and reduction information for **5a** are given in Table 2. Lorentz and polarization corrections were applied. A correction for nonlinear decay[29] in the standard reflections (3.6%) was applied to the data for **5a**. Absorption corrections based on a series of azimuthal scans were applied to the data. The centric space group *C*2/*c* for **5a** was indicated initially by systematic absences and intensity statistics. The structure was solved by direct methods.[29] The space group requires that half of the molecule be unique. All non-hydrogen atoms in **5a** were refined with anisotropic displacement parameters. All hydrogen atoms in **5a** were refined as riding atoms with C–H distances equal to 0.96 Å and individual isotropic thermal parameters, except in the case of methyl groups which were constrained to group isotropic temperature parameters. The *p*-*tert*-butyl group was statistically disordered about the crystallographic 2-fold rotation axis, and these hydrogens were given fixed isotropic temperature factors. All the refinement calculations were performed on a Digital Equipment Micro Vax 3100 computer using the SHELXTL Plus programs[29] for **5a**.

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Supplementary Material Available: Description of the data collection and structure solution, a labeled drawing of **5a**, and tables of crystal data, positional and thermal parameters, and complete bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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[29] SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.