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Functionalization of η^1,η^2-Bridging Cyaphide $(C\equiv P)^-$ Ligands: Trinuclear η^1,η^1,η^2-Bridging Cyaphide and Dinuclear Bridging Isocyaphide (C≡PR) Complexes of Platinum[†]

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The oxidative addition reaction of $Pt(PEt_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$ at low temperature (−50 °C) forms the η^1-phosphavinyl complex *cis*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ **(Ia)**, which isomerizes to the *trans*-isomer **(Ib)** upon warming to 0 °C; the structure of **Ib** was determined by X-ray diffraction studies. Complex **Ib** reacts with $Pt(PEt_3)_2Cl_2$ in the presence of 3 equiv of sodium benzophenone to generate the bridging, dinuclear η^1,η^2-cyaphide complex $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** in good yield, providing a much simpler and higher yield preparation of **II**, which was synthesized and characterized previously by a more circuitous route. Compound **II** reacts with 0.5 equiv of $[Cl_2Pt(PEt_3)]_2$ or with 1 equiv of $W(CO)_5(THF)$ to generate the trinuclear metal−cyaphide complexes $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{Pt(PEt_3)(Cl)_2\}]Pt(PEt_3)_2$ **(III)** and $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ **(IV)**, respectively, in which the lone pair of electrons on the C≡P phosphorus atom is coordinated to a $Pt(PEt_3)(Cl)_2$ fragment in the former and to a $W(CO)_5$ fragment in the latter; the structure of **IV** was determined by X-ray diffraction studies. Compound **II** also reacts with MeI to form the methyl isocyaphide complex $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)$ **(Vc)**, in which the cyaphide $(C\equiv P^-)$ ligand is converted to a methyl isocyaphide (C≡PMe) ligand in a semibridging coordination mode. When compound **II** is reacted with MeOTf, the product is the cationic isocyaphide complex $[(Cl)(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}PMe)Pt(PEt_3)_2](OTf)$ **(Va)**, which is likely coordinated in an η^1,η^2-bridging mode. Compound **Va** reacts with NaI to form **Vc**, which suggests that **Va** forms as an intermediate before **Vc** in the reaction of **II** with MeI.

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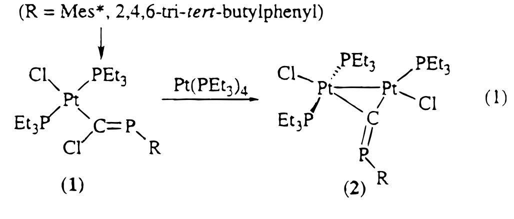
Introduction

Studies involving phosphorus analogues of common organic ligands have evolved at a very rapid pace recently, and coordination compounds of C−P analogues of almost all C−C multiple bond ligands are now known, including phosphaalkenes, phosphaalkynes, phosphaallyls, phosphaallenes, phosphabutadienes, phosphacyclopropenes, phosphacyclobutadienes, phosphacyclopentadienyls, and phosphaarenes.[1−6] However, phosphorus analogues of the well-studied cyanide $(C\equiv N)^-$ and isocyanide (C≡NR) ligands have been limited.[7−9] These phosphorus compounds have been calculated to be high energy species; the heat of formation of $(C\equiv P)^-$ (cyaphide anion) is calculated to be ca. 40 kcal/mol less exothermic than that of $(C\equiv N)^-$,[10] and C≡PH (isocyaphide) is calculated to be 85 kcal/mol less stable than its isomer H−C≡P (phosphaalkyne).[11] Nevertheless, we recently succeeded in preparing the first example of a coordinated isocyaphide ligand by oxidative addition of the C−Cl bond in the phosphavinyl complex **1** (eq 1) to generate a diplatinum complex $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PR)\text{-}Pt(PEt_3)_2(Cl)]$ (**2**), in which the isocyaphide ligand exhibits a semibridging coordination mode.[9] However, this preparation was limited by the few examples of dichlorophosphaalkenes that are available and by the



[†] Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

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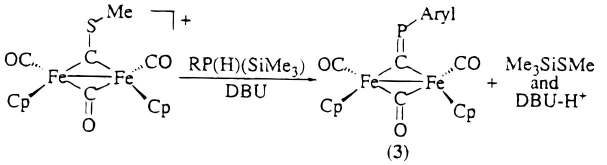
bulky R-groups that are incorporated in these reagents. More recently, Weber and co-workers reported the synthesis (eq 2) of some diiron complexes containing symmetrically bridged isocyaphide ligands (**3**) by a different route.[7] In these reactions, the isocyaphide products were stable only when bulky R-groups were present on phosphorus. We also obtained the first example of a cyaphide complex $(Et_3P)_2ClPt(C{\equiv}P)$ **(4)** from a reaction (eq 3) of the phosphavinyl complex **(1)** with $Pd(PEt_3)_4$, in which the Mes* group was transferred from phosphorus to palladium forming $(Et_3P)_2(Cl)Pd(Mes^*)$ as a side product.[9] Compound **4** could only be characterized by NMR spectroscopy but reacted (eq 3) with $Pt(PEt_3)_4$ to generate the bridging, dinuclear η^1,η^2-cyaphide complex $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)**, which was characterized by X-ray diffraction studies.



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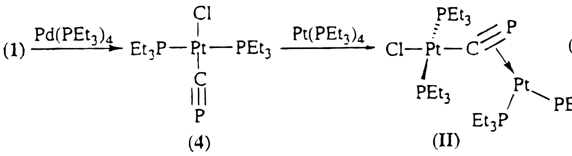
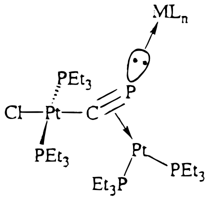


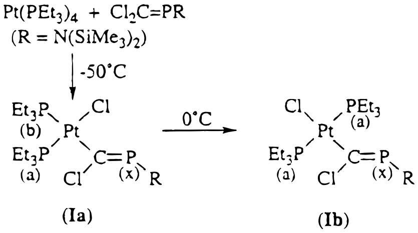
(3)

We describe in the present paper a high-yield preparation of complex **II** utilizing a one-step reaction from the phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ **(Ib)**, which has much different reactivity than the analogous phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$ **(1)**.[12] We also investigate functionalization of the cyaphide ligand in complex **II** by reaction of the accessible lone pair of electrons on the C≡P phosphorus atom. During the course of these studies, we have isolated the first examples of trinuclear metal−cyaphide compounds **(A)** that were formed by coordinating the C≡P phosphorus atom in **II** to other transition metal fragments. We have also found that the cyaphide ligand in **II** can be easily converted to an alkyl isocyaphide ligand by reaction with alkylating agents, constituting the first examples of cyaphide−isocyaphide conversions and demonstrating that isocyaphide ligands with less bulky alkyl R-groups can be stabilized on transition metals.



(A)

Results and Discussion



(4)

Synthesis of *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (Ib). The reaction (eq 4) of $Pt(PEt_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$ in THF or hexanes at −50 °C immediately and quantitatively forms the η^1-phosphavinyl complex *cis*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ **(Ia)** by oxidative addition of one of the C−Cl bonds; upon warming the solution to 0 °C, the *cis*-isomer completely rearranges to the *trans*-isomer **(Ib)**. Some formation of $Pt(PEt_3)_2Cl_2$ also occurs during this reaction. This *cis*−*trans* isomerization is quite similar to that in the analogous phosphavinyl complex $Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$, in which both the *cis*- and *trans*-isomers were isolated and characterized.[12] The structure and ^{31}P NMR spectrum of **Ib** are very similar to those of *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$ **(1)**, but they differ in reactivity. For instance, compound **1** rearranges to $Mes^*C{\equiv}P$ and $Pt(PEt_3)_2Cl_2$ after 24 h in THF at room temperature, whereas **Ib** is stable in THF for weeks at room temperature, although a small amount of $Pt(PEt_3)_2Cl_2$ does form in this time. Further, compound **1** undergoes a second C−Cl oxidative addition reaction (eq 1) with $Pt(PEt_3)_4$ in 24 h at room temperature to form the isocyaphide complex $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMes^*)Pt(PEt_3)_2(Cl)]$ **(2)**; a similar reaction between **Ib** and $Pt(PEt_3)_4$ does not form the $N(SiMe_3)_2$ analogue of compound **2**, but results in decomposition to a complex mixture of unidentified products.

Compound **Ia** was characterized by ^{31}P and $^{31}P\{^1H\}$ NMR spectra; compound **Ib** was characterized by ^{31}P and $^{31}P\{^1H\}$ NMR spectra, elemental analysis, electrospray mass spectrometry, and X-ray diffraction studies. The signals corresponding to P(x) in the ^{31}P NMR spectra of **Ia** and **Ib** were assigned by their characteristic downfield chemical shifts of 225.1 and 222.3 ppm, respectively, and by their proton-coupled ^{31}P NMR spectra, in which these signals do not show any proton coupling, while the signals corresponding to the PEt_3 groups are greatly broadened. The P(x) peak in **Ia** is split into a doublet of doublets ($^3J_{P(x)P(a)} = 8.3$ Hz, $^3J_{P(x)P(b)} = 33.0$ Hz) by the two inequivalent PEt_3 groups and exhibits platinum satellites with $^2J_{P(x)Pt} = 410$ Hz. The P(x) peak in **Ib** is split into a triplet ($^3J_{P(x)P(a)} = 20.0$ Hz) by the two equiv PEt_3 groups and exhibits a larger $^{195}Pt{-}P$ coupling constant ($^2J_{P(x)Pt} = 676$ Hz) than in **Ia**. In **Ia**, the PEt_3 ligand that is *trans* to the $C(Cl){=}PN(SiMe_3)_2$ group is assigned to P(b) at δ 10.1 ppm and the *cis* PEt_3 ligand is assigned to P(a) at δ 5.6 ppm based on the larger coupling constant $^3J_{P(x)P(b)} = 33.0$ Hz between P(x) in the $C(Cl){=}PN(SiMe_3)_2$ group and the *trans* PEt_3 group P(b). These ^{31}P NMR data are analogous to those[12] obtained for *cis*-$Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$ (δ(P(x)): 224.0 (dd, $^3J_{P(x)P(a)} = 12.3$ Hz, $^3J_{P(x)P(b)} = 46.3$ Hz, $^2J_{P(x)Pt} = 365.4$ Hz) and *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$ **(1)** (δ(P(x)): 223.3 (t, $^3J_{P(x)P(a)} = 25.2$ Hz, $^2J_{P(x)Pt} = 657.7$ Hz), which indicates that the compounds are isostructural and that the $N(SiMe_3)_2$ group does not impart dramatic differences in the bonding compared with the Mes* group. However, to more thoroughly

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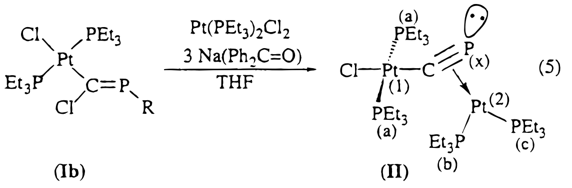
compare the bonding properties in these complexes, the structure of **Ib** was determined by X-ray diffraction studies and compared with the previously determined structure of compound **1**.[12]

X-ray Crystal Structure of *trans*-Cl(Et$_3$P)$_2$Pt-[C(Cl)=PN(SiMe$_3$)$_2$] (Ib). A thermal ellipsoid drawing of **Ib** (Figure 1) shows that the complex is isostructural with the previously characterized compound *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PMes*] **(1)**. The platinum atom is in a square-planar environment as defined by the two PEt$_3$, Cl, and [C(Cl)=PR] ligands; the sum of angles around the platinum atom is 360.0°. The C(1)−P(1) distance of 1.690(7) Å is the same as that (1.678(5) Å) in compound **1** and the C=P distance (1.685(2) Å) in the free phosphaalkene Cl$_2$C=PN(SiMe$_3$)$_2$.[13] The Pt−C(1) distance in **Ib** (1.990(7) Å) is slightly shorter than the corresponding distance (2.013 (4) Å) in **1**.[12] The nitrogen atom in **Ib** is in a trigonal planar environment, and the P(1)−N(1)−Si(1)−Si(2) plane is almost orthogonal (96.4°) to the plane defined by Pt, Cl(1), C(1), P(1), and N(1). This orthogonality rules out any conjugative effects from the nitrogen lone pair; in a series of X-ray-determined structures of phosphaalkenes containing NR$_2$ groups on phosphorus, orthogonal NR$_2$ groups were found to show no conjugative effects with the C=P double bond.[14] If the [C(Cl)=PR] ligands in **1** and **Ib** were significantly different, the bond lengths between platinum and the *trans* ligands (Cl(2)) would be affected by this difference. However, the Pt−Cl(2) length in **Ib** (2.373(2) Å) is the same within error as that (2.377(2) Å) in **1**. Thus, a comparison of the structures of **1** and **Ib** indicates that the N(SiMe$_3$)$_2$ and Mes* groups show similar structural effects in phosphavinyl complexes of the type *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PR].

Preparation of Cl(Et$_3$P)$_2$Pt(μ-η^1,η^2-C≡P)Pt(PEt$_3$)$_2$ (II). The reaction (eq 5) of 1.05 equiv of *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PN(SiMe$_3$)$_2$] **(Ib)** and 1 equiv of Pt(PEt$_3$)$_2$Cl$_2$ with 3 equiv of sodium benzophenone ketyl in THF forms the bridging, dinuclear cyaphide complex Cl(Et$_3$P)$_2$Pt(μ-η^1,η^2-C≡P)Pt(PEt$_3$)$_2$ **(II)** in good yield (79%).



(5)

This preparation is much simpler than that (eq 3) originally reported. Furthermore, this reaction can be done on a several gram scale and gives excellent yields of complex **II** in pure, crystalline form.

To gain an understanding of how this reaction proceeds, several different stoichiometries of the reagents were investigated, as was the order of addition. The use of 3 equiv of the Na/benzophenone ketyl reducing agent was found to be optimum, as more equiv caused decomposition, while fewer resulted in incomplete reaction, which suggests that the two chlorides from Pt(PEt$_3$)$_2$Cl$_2$ and one chloride from **Ib** are removed as NaCl. The N(SiMe$_3$)$_2$ group is possibly removed as (SiMe$_3$)$_2$N−N(SiMe$_3$)$_2$, although this was not investigated. The reaction of *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PMes*] **(1)** with Pt(PEt$_3$)$_2$Cl$_2$ and 3 equiv of sodium benzophenone ketyl also resulted in the formation of **II**, but it produced impurities that could not be separated. To investigate the role of the reducing agent, a reaction was attempted between **Ib** and Na/benzophenone ketyl without any Pt(PEt$_3$)$_2$Cl$_2$ present; no reaction was apparent after 6 h. Also, if Pt(PEt$_3$)$_2$Cl$_2$ is first combined with Na/benzophenone ketyl followed by addition of **Ib**, a ^{31}P NMR spectrum shows that **Ib** is unreacted in solution. Evidently, both **Ib** and Pt(PEt$_3$)$_2$Cl$_2$ must be present during the addition of the reducing agent for this reaction to occur. The reduction of Pt(PEt$_3$)$_2$Cl$_2$ in the presence of ethylene is known to produce Pt(PEt$_3$)$_2$(C$_2$H$_4$),[15] and it has been reported that if a suitable ligand is not present in solution, Pt(PEt$_3$)$_2$ fragments tend to oligomerize into Pt(0) clusters.[16] It is possible that the Pt(PEt$_3$)$_2$ fragment that is generated in eq 5 coordinates to the C=P double bond of **Ib** and activates the carbon-bound Cl toward reduction by a third equiv of Na/benzophenone ketyl, while in the absence of **Ib** the Pt(PEt$_3$)$_2$ oligomerizes and does not react with **Ib**. Reactions similar to that in eq 5 were attempted between **Ib** and Pt(PPh$_3$)$_2$Cl$_2$, Pt(Pi-Pr$_3$)$_2$Cl$_2$, Pt(PCy$_3$)$_2$Cl$_2$, and Pt(depe)Cl$_2$; in all cases, compound **Ib** remained unreacted in solution, indicating that this reaction is not general for other phosphines.

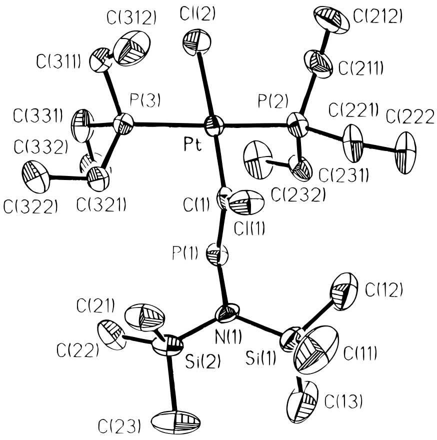
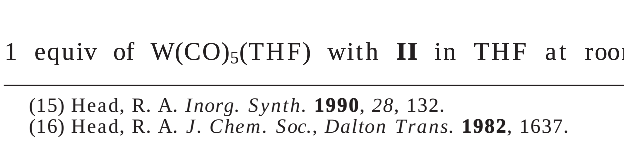


Figure 1. Thermal ellipsoid drawing of *trans*-Cl(Et$_3$P)$_2$-Pt[C(Cl)=PN(SiMe$_3$)$_2$] (**Ib**).

Preparation of Trinuclear Metal−Cyaphide Complexes. The cyaphide ligand that is coordinated to two platinum centers in complex **II** contains a lone pair of electrons on the C≡P phosphorus atom that is a potential site for further coordination. Accordingly, the reactions (eq 6) of either 0.5 equiv of [Pt(Cl)$_2$(PEt$_3$)]$_2$ or 1 equiv of W(CO)$_5$(THF) with **II** in THF at room



(6)

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Table 1. Comparison of ^{31}P NMR Data (THF) for $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (II) with Those of the Complexes $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{ML_n\}]Pt(PEt_3)_2$, Where ML_n = $Pt(Cl)_2(PEt_3)$ (III), $W(CO)_5$ (IV), Me^+ (Va)[a]

cmpd	δ P(x) (ppm)	δ P(c) (ppm)	δ P(b) (ppm)	δ P(a) (ppm)	$^3J_{(x)-(a)}$ (Hz)	$^2J_{(x)-(b)}$ (Hz)	$^2J_{(x)-(c)}$ (Hz)	$^2J_{(b)-(c)}$ (Hz)	$^1J_{Pt-(a)}$ (Hz)	$^1J_{Pt-(b)}$ (Hz)	$^1J_{Pt-(c)}$ (Hz)
II	107.0	18.6	15.0	4.9	10.7	13.7	10.7	35.1	2936	3155	3619
III	111.2	17.2	15.9	5.0	21.4	148.0	42.5	8.7	2829	3601	2926
IV	41.4	13.9	16.6	3.1	18.9	152.9	38.7	9.1	2818	3568	2917
Va	34.7	20.1	18.7	8.1	20.6	148.9	23.8	10.2	2662	3641	2441

[a] See eqs 5, 6 and Scheme 1 for atom labels.

temperature afford the first examples of trinuclear metal–cyaphide complexes $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{Pt(PEt_3)(Cl)_2\}]Pt(PEt_3)_2$ **(III)** and $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ **(IV)**, respectively. Complex **III** forms immediately after the addition of $[Pt(Cl)_2(PEt_3)]_2$ to **II** and a ^{31}P NMR spectrum of the reaction mixture showed practically quantitative conversion to **III** with a small amount of $Pt(PEt_3)_2Cl_2$ formed as a byproduct; complex **III** could not be isolated in pure form, as it decomposes under vacuum to unidentified materials, presumably through loss of PEt_3. In the reaction of $W(CO)_5(THF)$ with **II**, the formation of complex **IV** is complete after 1 h, and a small amount of $W(CO)_5(PEt_3)$ forms as a byproduct that is easily separated. These reactions are similar to those of the η^2-coordinated phosphaalkyne complexes $(R_3P)_2Pt(\eta^2\text{-}R{-}C{\equiv}P)$, in which η^2-coordination of the phosphaalkyne to the platinum fragment enhances the coordinating ability of the lone pair of electrons on phosphorus.[3,17]

Compounds **III** and **IV** were characterized by ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy, and the structure of complex **IV** was determined by X-ray diffraction studies. The ^{31}P NMR data for these compounds are compared in Table 1 along with the starting cyaphide complex **(II)** and the methyl isocyaphide complex **(Va)**, which is a cationic complex of similar structure (see below). In all of these complexes, the peaks corresponding to P(x) are conveniently assigned by proton-coupled ^{31}P NMR spectroscopy, in which the P(x) signals remain sharp, while the PEt_3 signals are broadened by coupling to the ethyl protons. Complex **III** exhibits five distinct signals in its ^{31}P NMR spectrum; peaks corresponding to P(x) at δ 111.2, P(a) at δ 5.0, P(b) at δ 15.9, and P(c) at δ 17.2 ppm were assigned on the basis of similar signals in the ^{31}P NMR spectrum of **II**, while the peak corresponding to P(d) at δ 5.2 ppm was assigned to the PEt_3 group in the $Pt(PEt_3)(Cl)_2$ fragment that is coordinated to the C≡P phosphorus atom. The peak for P(x) in **II** is split into a doublet of doublet of triplets, while the same peak in **III** is now split into a doublet of doublet of doublet of triplets; the extra splitting is from the PEt_3 ligand on the $Pt(PEt_3)(Cl)_2$ fragment ($^2J_{P(x)P(d)} = 472.3$ Hz). This is a very large two-bond P–P coupling constant that is indicative of a *trans*-orientation between P(d) and P(x), similar to the *trans*-$^2J_{PP} = 557$ found in the bridging phosphaalkyne complex $Mo_2(CO)_4(Cp)_2\{t\text{-}BuCP[Pt(PEt_3)(Cl)_2]\}$[18] and to the values of *trans*-$^2J_{PP} = 462-483$ Hz measured in a series of *trans*-$[PtCl_2(PR_3)(PR'_3)]$ complexes.[19] The coordination of the $Pt(PEt_3)(Cl)_2$ fragment to compound **II** also imparts a large change on the two-bond coupling constant between P(x) and the *trans*-like PEt_3 ligand P(b); the value of $^2J_{P(x)P(b)} = 13.7$ Hz in **II** increases to $^2J_{P(x)P(b)} = 148.0$ Hz in **III**. This effect has also been seen in η^2-phosphaalkyne complexes; in the complex $[Pt(dppe)(\eta^2\text{-}t\text{-}BuC{\equiv}P)]$, the coupling constant between the C≡P phosphorus and the *trans*-P atom is 28.1 Hz, but when a $Cr(CO)_5$ fragment is coordinated to the C≡P phosphorus atom, this value increases to 177.5 Hz.[17] In fact, all of the couplings between P(x) and the other phosphorus signals are increased upon coordination of the $Pt(PEt_3)(Cl)_2$ group (see Table 1). Evidently, the cyaphide phosphorus atom undergoes a change in hybridization upon coordination to the metal fragment, which gives the phosphorus more s-orbital character in its bond with the metal.

Complex **IV** exhibits four distinct signals in its ^{31}P NMR spectrum; the peaks corresponding to P(a) at δ 3.1, P(b) at δ 16.6, and P(c) at δ 13.9 ppm were assigned based on similar signals in the ^{31}P NMR spectrum of **II** and **III**, while the peak at δ 41.4 ppm was assigned to P(x) based on a sharp proton-coupled ^{31}P NMR signal and the doublet of doublet of triplets splitting pattern. The chemical shift of 41.4 ppm is 66 ppm upfield from that of P(x) in compound **II** and is similar to the upfield shift of 42 ppm that was measured upon coordination of a $W(CO)_5$ fragment to the C≡P phosphorus atom in the η^2-phosphaalkyne complex $[Pt(dppe)(\eta^2\text{-}t\text{-}BuC{\equiv}P)]$.[17] The coordination of the $W(CO)_5$ group to complex **II** results in increased $^{31}P-^{31}P$ coupling constants (see Table 1) similar to those for **III**. The two-bond coupling constant between P(x) and the *trans*-like PEt_3 ligand P(b) is again very large, $^2J_{P(x)P(b)} = 152.9$ Hz, and similar to that ($^2J_{P(x)P(b)} = 148.0$ Hz) in **III**. Only one set of platinum satellites ($^2J_{P(x)Pt(1)} = 507$ Hz) could be distinguished for P(x) in compound **IV** because of the complexity of this signal; this coupling constant is larger than that (255 Hz) in **II**, but still smaller than that (676 Hz) in **Ib**. Although no tungsten satellites could be found for P(x), the signal for P(b) exhibited an unusually large three-bond coupling to tungsten ($^3J_{WP(b)} = 150.8$ Hz), most likely because of the enhanced coupling between P(x) and P(b).

X-ray Crystal Structure of $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ (IV). A thermal ellipsoid drawing of **IV** (Figure 2) shows that the complex contains a $W(CO)_5$ fragment attached to the C≡P phosphorus atom and has many structural features in common with the X-ray-determined structure of complex **II**.[9] Both of the platinum atoms in **IV** are in planar environments; the sum of angles around Pt(1) as defined by C(1), P(2), P(3), and Cl(1) is 360.1°, while the sum of angles around Pt(2) as defined by C(1), P(1), P(4), and P(5) is 360.4°. The C(1)–P(1) distance (1.663(9) Å) in

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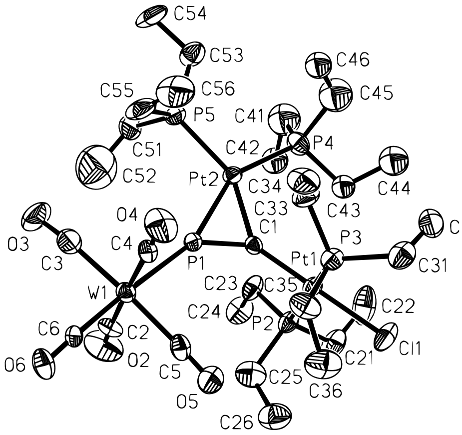
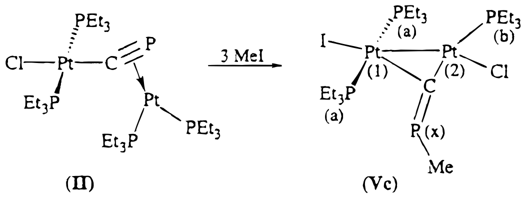


Figure 2. Thermal ellipsoid drawing of $Cl(Et_3P)_2Pt[\mu$-η^1,η^1,η^2-C≡P{W(CO)$_5$}]Pt(PEt$_3$)$_2$ (**IV**).

IV is the same within error as that (1.666(6) Å) in **II**, indicating that coordination of the W(CO)$_5$ unit has not dramatically changed the character of the cyaphide C−P bond. This distance is similar to a C−P double-bond distance (e.g., 1.67 Å in Ph(H)C=PMes*)[20] and to the C−P distance (1.67(2) Å) in the η^2-phosphaalkyne complex [Pt(PPh$_3$)$_2$(η^2-t-BuC≡P)][21] and is consistent with back-bonding from Pt(2) into the π* orbital of the C≡P bond, affording some metallaphosphacyclopropene character in this three-atom unit in **IV**. The Pt(1)−C(1)−P(1) angle (145.2(6)°) is similar to that in **II** (144.0(3)°), and the W(1)−P(1)−C(1) angle (136.1(3)°) is also bent, indicating that P(1) is close to sp^2 hybridization. This is also evident from the sum of the angles (355.3°) around P(1) involving W(1), Pt(2), and C(1), which indicates that P(1) is nearly planar. The W(1)−P(1) distance (2.531(3) Å) is very similar to the W−P bond length (2.539(3) Å) in the bridging phosphaalkyne complex Mo$_2$(CO)$_4$(Cp)$_2${t-BuCP[W(CO)$_5$]}[22] and is slightly longer than typical W−P distances in structurally characterized W(CO)$_4$(PR$_3$)$_2$ complexes (e.g., 2.502 Å in *cis*-W(CO)$_4$(PMe$_3$)$_2$).[23] The Pt(2)−C(1) distance (2.104(9) Å) in **IV** is the same within experimental error as the corresponding distance (2.083(5) Å) in **II**, and the Pt(1)−C(1) distances (1.952(9) Å in **IV** and 1.950(6) Å in **II**) are also the same within error. However, the Pt(2)−P(1) distance (2.292(3) Å) in **IV** is shorter than the corresponding distance (2.337(2) Å) in **II**.

Alkylation Reactions of Cl(Et$_3$P)$_2$Pt(μ-η^1,η^2-C≡P)Pt(PEt$_3$)$_2$ (II). The reaction (eq 7) of 3 equiv of MeI with Cl(Et$_3$P)$_2$Pt(μ-η^1,η^2-C≡P)Pt(PEt$_3$)$_2$ (**II**) in THF for 12 h at 25 °C results in the formation of the methyl isocyaphide complex (Cl)(Et$_3$P)Pt(μ-C=PMe)Pt(PEt$_3$)$_2$(I) (**Vc**) with concomitant formation of the phosphonium salt (MePEt$_3$)$^+$ I$^-$. This reaction entails the conversion of a cyaphide (C≡P)$^-$ ligand to an isocyaphide (C≡PMe) ligand and substitution of a coordinated PEt$_3$ ligand (lost as (MePEt$_3$)$^+$ I$^-$) with an iodide ligand; thus, the MeI acts both as a methylating agent and as a phosphine scavenger. Although complex **Vc** is stable in THF solution at room temperature for several weeks, suitable crystals could not be obtained for an X-ray diffraction study as the compound only forms an oil. However, the complex is likely isostructural with the previously obtained semibridging isocyaphide complex (Cl)(Et$_3$P)Pt(μ-C=PMes*)Pt(PEt$_3$)$_2$(Cl) **(2)**[9] on the basis of its ^{31}P NMR spectrum (Table 2) and the ^{13}C−^{31}P coupling constants obtained from the use of ^{13}C-labeled MeI in this reaction. Thus, the η^1,η^2-cyaphide ligand in **II** is converted to a semibridging isocyaphide ligand in **Vc** with the formation of a Pt−Pt bond. This reaction has some precedent in related isocyanide chemistry, as the conversion of coordinated cyanide (C≡N)$^-$ ligands to isocyanide (C≡NR) ligands with various alkylating agents is a well-known synthetic route to isocyanide complexes, although these reactions have been carried out only on terminal cyanide complexes.[24] This new synthetic route to an isocyaphide complex is much different than the reaction (eq 1) of the phosphavinyl complex *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PMes*] **(1)** with Pt(PEt$_3$)$_4$ to generate the semibridging isocyaphide complex (Cl)(Et$_3$P)Pt(μ-C=PMes*)Pt(PEt$_3$)$_2$(Cl) **(2)**[9] or the reactions (eq 2) of [Cp$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-CSMe)]$^+$ with RP(H)(SiMe$_3$) and DBU to generate the bridging isocyaphide complexes [Cp$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-C=PR)] **(3)**;[7] both of these syntheses were limited by the use of bulky aryl R-groups on the C≡PR phosphorus atom. In contrast, the reaction of **II** with MeI allows for the formation of an isocyaphide with a sterically small methyl group and could conceivably be a more general route to diplatinum isocyaphide complexes. To test this, the reaction in eq 7 was attempted with several different alkyl and aryl halides (e.g., benzyl bromide, isopropyl iodide, allyl bromide, *o*-iodo toluene, and 2,4,6-tri-*tert*-butylbenzyl bromide) under the same reaction conditions and stoichiometry as in the MeI reaction. The reactions of both benzyl bromide (BnBr) and isopropyl iodide (i-PrI) with **II** afforded similar isocyaphide products, (Cl)(Et$_3$P)Pt(μ-C=PBn)Pt(PEt$_3$)$_2$(Br) **(VI)** and (Cl)(Et$_3$P)Pt(μ-C=P*i*-Pr)Pt(PEt$_3$)$_2$(I) **(VII)**, respectively, as evidenced by ^{31}P NMR spectroscopy (see Table 2). However, the benzyl derivative could not be separated from impurities that were present, and the i-Pr derivative was unstable and decomposed before the reaction was complete. The reaction of allyl bromide with **II** formed completely different products that could not be isolated, while the aryl halides did not react with compound **II**, even after stirring for several days at room temperature.



(II) (Vc) (7)

Complex **Vc** was characterized by electrospray mass spectrometry and ^{31}P, ^{31}P{^{1}H}, and ^{13}C{^{1}H) NMR spectroscopy. The ^{31}P NMR spectrum of complex **Vc** shows chemical shifts and coupling constants (Table 2) very similar to those measured in the semibridging isocyaphide complex (Cl)(Et$_3$P)Pt(μ-C=PMes*)Pt(PEt$_3$)$_2$(Cl) **(2)**[9] and is thus proposed to have the same structure.

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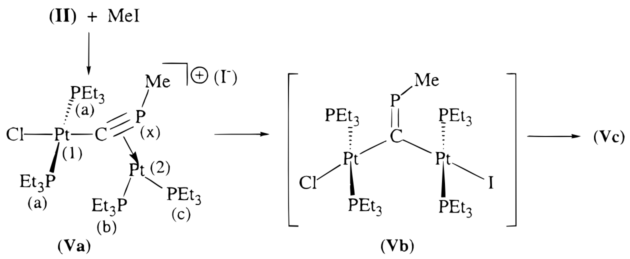
Table 2. Comparison of ^{31}P NMR Data for $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMes^*)Pt(PEt_3)_2(Cl)$ (2), $(Cl)(Ph_3P)Pt(\mu\text{-}CO)Pt(PPh_3)_2(Cl)$ (4), and Complexes $Cl(Et_3P)Pt(\mu\text{-}C{\equiv}PR)Pt(PEt_3)_2(X)$ (Vc, R = Me, X = I; VI, R = Bn, X = Br; VII, R = i-Pr, X = I)[a]

cmpd	δ P(x) (ppm)	δ P(b) (ppm)	δ P(a) (ppm)	$^{3}J_{(x)-(b)}$ (Hz)	$^{3}J_{(x)-(a)}$ (Hz)	$^{2}J_{Pt2-(x)}$ (Hz)	$^{2}J_{Pt1-(x)}$ (Hz)	$^{1}J_{Pt2-(b)}$ (Hz)	$^{2}J_{Pt1-(b)}$ (Hz)	$^{1}J_{Pt1-(a)}$ (Hz)	$^{2}J_{Pt2-(a)}$ (Hz)
2	151.3	22.8	19.6	35	23	321	110	4814	512	2428	67
4		30.2	21.74					5440	804	2680	59
Vc	155.4	21.5	8.7	15.3	12.1	565	232	5174	463	2339	43.5
VI	172.1	22.8	13.3	13.8	11.7	593	228	5223	497	2332	47.0
VII	200.3	25.9	12.9	15.2	12.1	538	232	5257	473	2367	46.4

[a] See eq 7 for atom labels.

The ^{31}P NMR spectrum of **Vc** exhibits three different signals. The peak at δ 155.4 ppm, assigned to P(x), is split into a doublet of triplets with two different ^{195}Pt satellites, indicative of the unsymmetrical, semibridging bonding mode of the C≡PMe ligand. The doublet ($^{2}J_{P(x)P(b)} = 15.3$ Hz) arises from coupling to the single PEt_3 ligand (P(b)) on Pt(2), while the triplet ($^{3}J_{P(x)P(a)} = 12.1$ Hz) results from coupling to the two equiv PEt_3 ligands (P(a)) on Pt(1). The larger coupling constant to platinum ($^{2}J_{Pt(2)P(x)} = 564.7$ Hz) is assigned to coupling with the four-coordinate platinum Pt(2), while the smaller Pt−P coupling constant ($^{2}J_{Pt(1)P(x)} = 231.9$ Hz) is assigned to coupling with the five-coordinate platinum atom Pt(1); these assignments are made on the basis of the assignments in compound **2** and by the larger J_{PtP} coupling constants that are typically found in platinum complexes with lower coordination numbers.[25] From these J_{PP} coupling constants, the signal at δ 8.7 ppm is assigned to P(a), while the signal at δ 21.52 is assigned to P(b). Because the signal for P(a) is farther upfield than the analogous peak in **2**, while the peaks for P(b) in **Vc** and **2** have quite similar chemical shifts, it is assumed that the iodide ligand in **Vc** is on the platinum (Pt(1)) that contains two PEt_3 groups (P(a)). One aspect of the ^{31}P NMR spectrum of **Vc** that supports its structural assignment as being similar to that of **2** is the large difference in the one-bond J_{PtP} coupling constants in the signals for P(a) and P(b); for P(a) in **Vc**, the value of $^{1}J_{Pt(1)P(a)} = 2338.9$ Hz is similar to those found in *trans*-$Pt(PEt_3)_2X_2$ complexes;[25] while for P(b), the value of $^{1}J_{Pt(2)P(b)} = 5173.7$ Hz is very large and more similar to those found in three-coordinate Pt(0) complexes.[25] This difference in the J_{PtP} coupling constants is greater in **Vc** than in compound **2** and has been discussed previously in the analogous semibridging carbonyl complex $(Cl)(Ph_3P)Pt(\mu\text{-}CO)Pt(PPh_3)_2(Cl)$ **(4)**, which is very similar in structure to **Vc** and **2**, but with PPh_3 instead of PEt_3 ligands and a semibridging CO ligand in place of the C≡PR ligands.[26,27] Complex **4** exhibits a value of $^{1}J_{PtP} = 2680$ Hz for the two equiv PPh_3 groups (P(a)) on the five-coordinate platinum and a value of $^{1}J_{PtP} = 5440$ Hz for the PPh_3 group (P(b)) on the four-coordinate platinum (see Table 2 for further comparisons). This difference was rationalized by suggesting some degree of mixed valence character between the two platinum atoms.[26] To further verify that the methyl group is attached to the phosphorus atom in complex **Vc**, the reaction (eq 7) was carried out using ^{13}C-labeled MeI. The ^{31}P NMR spectrum of labeled **Vc** exhibited an extra doublet in the signal for P(x) from coupling to the labeled methyl group with $^{1}J_{P(x)C} = 48.9$ Hz. This value is similar to the value of $^{1}J_{PC} = 51.1$ Hz found in the phosphonium salt $(MePEt_3)^+ I^-$ product of this reaction. Interestingly, the signal for P(b) also exhibited a small coupling ($^{4}J_{P(x)C} = 10.6$ Hz) to the methyl group. The ^{13}C NMR signal for the methyl group at δ 10.5 was split into a doublet of doublets by P(x) and P(b). This peak also exhibited a small Pt−C coupling constant of $^{3}J_{PtC} = 51.2$ Hz, which is most likely a coupling with Pt(2), which is bonded more strongly to the C≡PR group. The ^{31}P NMR spectra of complexes **VI** and **VII** (Table 2) are quite similar to those of **Vc**, and these compounds are proposed to be of similar structure. These spectroscopic results, along with comparisons with those of compounds **2** and **4**, strongly suggest that complexes **Vc, VI**, and **VII** contain semibridging isocyaphide ligands.

Scheme 1



Mechanistic Studies of the Formation of $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)$ (Vc). A likely pathway (Scheme 1) for the formation of complex **Vc** from complex **II** is the initial methylation of the C≡P phosphorus atom to generate a cationic η^1,η^2-isocyaphide intermediate **(Va)**. The iodide anion then attacks at Pt(2) to generate the bridging isocyaphide intermediate **Vb**, which loses a PEt_3 group and forms a metal−metal bond to generate the product **Vc**. An intermediate similar to **Vb** was postulated in the reaction (eq 1) of the phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$ **(1)** with $Pt(PEt_3)_4$ to generate the semibridging isocyaphide complex $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMes^*)Pt(PEt_3)_2(Cl)$ **(2)**.[9] In an attempt to verify this pathway by isolation of the cationic η^1,η^2-isocyaphide intermediate **(Va)**, complex **II** was reacted with 1 equiv of MeI in the presence of 2 equiv of $NaBPh_4$ in THF at room temperature. The color of the solution turned to a very deep ruby red color after 1 h, and a ^{31}P NMR spectrum (see below) showed a new complex that matches the structure drawn for **Va** where the iodide anion has been replaced with (BPh_4^-). This complex was then isolated in reasonably pure form by filtering the solution and adding hexanes to form an oil of mainly

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Va. When a 10-fold excess of NaI was added to a solution of **Va** in THF, the color changed from deep red to light orange in 10 min, and a ^{31}P NMR spectrum showed that this complex was completely converted to the semibridging isocyaphide complex **Vc**, which strongly suggests that **Va** is an intermediate that forms before **Vc** in the reaction of MeI with complex **II**. In a separate experiment, complex **II** was reacted with MeO_3SCF_3 in THF; the color turned to deep red within a few minutes, and a ^{31}P NMR spectrum of the solution again showed complex **Va** where a triflate anion is substituted for the iodide anion. Reaction of this solution with a 10-fold excess of NaI afforded complex **Vc**, providing further evidence for the pathway outlined in Scheme 1. Although there was no evidence in the ^{31}P NMR spectra for other intermediates, **Vb** is a likely intermediate that explains the rearrangement of the η^1,η^2-isocyaphide ligand in **Va** to the semibridging isocyaphide ligand in **Vc**. In contrast to **Vc**, which contains a Pt−Pt bond, the ^{31}P NMR spectrum (see below) of **Va** suggests that there is no Pt−Pt bond in this cationic isocyaphide complex. Clearly, compound **Va** does not contain a semibridging isocyaphide similar to that in **Vc**, and it is not clear why substitution of a PEt_3 group in **Va** by an iodide anion causes this rearrangement to take place. Complex **Va** is the first to exhibit an η^1,η^2-bridging isocyaphide ligand.

Although complex **Va** could not be isolated in pure form, the ^{31}P NMR spectrum is characteristic of an η^1,η^2-bridging isocyaphide structure and shows features (Table 1) very similar to those in the spectra of the η^1,η^1,η^2-bridging trimetallic cyaphide complexes with a $Pt(Cl)_2(PEt_3)$ fragment **(III)** and a $W(CO)_5$ fragment **(IV)** on the cyaphide phosphorus atom. The signal at δ 34.7 ppm in **Va**, assigned to P(x), is shifted 120 ppm upfield from the corresponding P(x) peak in **Vc**; this shift is most consistent with an η^1,η^2-bridged species. The chemical shift is quite similar to that (δ 41.4 ppm) in the tungsten-coordinated cyaphide complex **IV**, which differs only in that it is neutral and contains a $W(CO)_5$ group in place of the Me group on **Va**. Also supporting the proposed structure is the fact that the splitting patterns and coupling constants in **Va**, **III**, and **IV** are all quite similar (Table 1). The coupling constants between P(x) and the PEt_3 groups again are larger than those in the η^1,η^2-cyaphide complex **(II)**, with the most dramatic effect again being a large coupling ($^2J_{P(x)P(b)}$ = 148.9 Hz) between P(x) and P(b). This is very similar to the $^2J_{P(x)P(b)}$ values found in **III** ($^2J_{P(x)P(b)}$ = 148.0 Hz) and **IV** ($^2J_{P(x)P(b)}$ = 152.9 Hz). The ^{195}Pt−^{31}P coupling constants found in **Va** are also similar to those found in **III** and **IV** (Table 1) and provide further evidence for the proposed structure. Since there is no ^{195}Pt−^{31}P coupling of P(a) with Pt(2) or between P(b) and P(c) with Pt(1), the existence of a Pt−Pt bond in **Va** is doubtful; in **Vc** and **2**, which contain Pt−Pt bonds, these couplings to the platinum atom of the adjacent metal fragment were significant (43−512 Hz). To further verify that the methyl group is attached to the cyaphide phosphorus atom, complex **Va** was prepared by reacting complex **II** with ^{13}C-labeled MeI in the presence of $NaBPh_4$. The ^{31}P NMR spectrum of this labeled complex exhibited additional doublets [P(x) ($^1J_{P(x)C}$ = 71.5 Hz), P(b) ($^3J_{P(b)C}$ = 8.4 Hz) and P(c) ($^3J_{P(c)C}$ = 12.6 Hz)] as a result of coupling to the labeled methyl group. The ^{13}C NMR spectrum also displayed a peak for the methyl group at δ 8.7 ppm that was split into a doublet of doublet of doublets by these three phosphorus atoms. These results are entirely consistent with the proposed structure of **Va** and indicate that the attachment of a $W(CO)_5$, $Pt(Cl)_2(PEt_3)$, or Me^+ group to the cyaphide phosphorus atom in complex **II** gives products with very similar ^{31}P NMR spectra and structures.

Summary

The new structurally characterized, phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ **(Ib)** reacts (eq 5) with $Pt(PEt_3)_2Cl_2$ and Na/benzophenone ketyl to form the known η^1,η^2-bridged cyaphide complex $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** but this route is much simpler and gives higher yields than previously reported (eq 3).[9] Lewis acid adducts at the electron pair on the phosphorus of the cyaphide $(C{\equiv}P)^-$ ligand in complex **II** are obtained by reaction with 0.5 equiv of $[Pt(Cl)_2(PEt_3)]_2$ or with 1 equiv of $W(CO)_5(THF)$ to generate (eq 6) the first examples of trinuclear metal cyaphide complexes $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{Pt(PEt_3)(Cl)_2\}]Pt(PEt_3)_2$ **(III)** and $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ **(IV)**, respectively. The phosphorus of the cyaphide $(C{\equiv}P)^-$ ligand in complex **II** is also alkylated (eq 7) by MeI to give the semibridging methyl isocyaphide ($C{\equiv}PMe$) complex $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)$ **(Vc)**. This transformation (Scheme 1) was demonstrated to involve a cationic η^1,η^2-bridging isocyaphide intermediate $[(Cl)(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}PMe)Pt(PEt_3)_2](I)$ **(Va)**, which was isolated as the triflate salt when complex **II** was reacted with MeO_3SCF_3. The $\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}PMe$ ligand in compound **Va** represents a new bonding mode for isocyaphide ligands, and the methylation reaction of compound **II** to form **Vc** provides a new method of forming semibridging isocyaphide complexes. Compound **Vc** is also the first example of a complex to contain an isocyaphide ligand with a nonbulky alkyl group, demonstrating that steric protection of the reactive C≡P bond by bulky R-groups is not necessary for the stabilization of transition metal-coordinated isocyaphide ligands.

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 nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium benzophenone ketyl, while hexanes and dichloromethane (CH_2Cl_2) were distilled over CaH_2.

The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using 85% H_3PO_4 (δ 0.00 ppm) as the external standard. The $^{13}C\{^1H\}$ and ^{13}C NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer using $CDCl_3$ as the internal standard. Electrospray mass spectra were recorded on a Finnigan TSQ 700 spectrometer using CH_2Cl_2 as solvent. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. The compounds $Pt(PEt_3)_4$,[28] $Cl_2C{=}PN(SiMe_3)_2$,[29] $[Pt(Cl)_2(PEt_3)]_2$,[30] $Pt(PR_3)_2Cl_2$,[31] and Na/benzophenone ketyl were prepared by

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literature methods. Phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh_3, which was recrystallized from MeOH. Methyl iodide (MeI) and methyl triflate (MeO_3SCF_3) were purchased from Aldrich and used without further purification. $W(CO)_5$(THF) was prepared by photolysis of $W(CO)_6$ in THF for 6 h at 20 °C.[32]

Preparation of *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (Ib) through Intermediate *cis*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (Ia). To a cooled (−50 °C) solution of $Pt(PEt_3)_4$ (1.50 g, 2.25 mmol) in hexanes (20 mL) was added $Cl_2C{=}PN(SiMe_3)_2$ (0.616 g, 2.25 mmol). A $^{31}P\{^1H\}$ NMR spectrum taken 10 min after the addition (−50 °C) showed complete conversion to **Ia**. After the solution had warmed to 0 °C over the course of 30 min, a $^{31}P\{^1H\}$ NMR spectrum showed that compound **Ia** had completely isomerized to **Ib**. The almost colorless solution was warmed to room temperature over the course of 10 min, and the solvent was removed under vacuum. The residue was treated with 20 mL of hexanes and filtered, and the filtrate was concentrated to 10 mL. A white precipitate formed, which was found to be $Pt(PEt_3)_2Cl_2$ by comparison of its ^{31}P NMR spectrum with that of an authentic sample. The precipitate was filtered off, and the filtrate was concentrated to 5 mL under vacuum. The light orange/brown solution was cooled slowly to −78 °C for 3 days, after which time large, light yellow crystals had formed. The crystals were isolated by cannulating off the mother liquor, washing with 2 × 5 mL portions of hexanes at −78 °C, and drying under vacuum to give air-stable **Ib** (1.24 g, 78%). $^{31}P\{^1H\}$ NMR (hexanes) (see eq 4 for atom labels) for **Ia**, −50 °C: δ(P(x)) 225.1 (dd, $^3J_{P(x)P(b)} = 33.0$ Hz, $^3J_{P(x)P(a)} = 8.3$ Hz, $^2J_{PtP(x)} = 410.0$ Hz), δ(P(b)) 10.1 (dd, $^3J_{P(b)P(x)} = 33.0$ Hz, $^2J_{P(b)P(a)} = 16.2$ Hz, $^1J_{PtP(b)} = 1908$ Hz), δ(P(a)) 5.6 (dd, $^2J_{P(a)P(b)} = 16.2$ Hz, $^3J_{P(a)P(x)} = 8.3$ Hz, $^1J_{PtP(a)} = 3874$ Hz). For **Ib**, 25 °C: δ(P(x)) 222.3 (t, $^3J_{P(x)P(a)} = 20.0$ Hz, $^2J_{PtP(x)} = 676.0$ Hz), δ(P(a)) 14.1 (d, $^3J_{P(a)P(x)} = 20.0$ Hz, $^1J_{PtP(a)} = 2680$ Hz). Electrospray MS (for **Ib**): *m*/*e* 705 (M^+). Anal. Calcd for $C_{19}H_{48}Cl_2N_1P_3Pt_1Si_2$ **(Ib)**: C, 32.34; H, 6.86; N, 1.98. Found: C, 31.25; H, 6.62; N, 1.87. Although the carbon analyses were consistently low for repeated analyses of **Ib**, the composition of the compound is strongly supported by the NMR and mass spectra, as well as the X-ray diffraction study.

Preparation of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (II). To a dry mixture of *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ **(Ib)** (1.00 g, 1.42 mmol) and $Pt(PEt_3)_2Cl_2$ (0.747 g, 1.49 mmol) at room temperature was added dropwise with stirring 20.8 mL of a solution of 0.204 M Na/benzophenone ketyl in THF (4.25 mmol) (the molarity of the Na/benzophenone solution was determined by quenching a measured amount with water and titrating with standardized HCl solution). The addition was done at a rate that was determined by the color change; as the color turned blue, addition was halted until the color changed back to orange. The total time of the addition was ca. 45 min, after which time the color of the solution was dark red with a large amount of NaCl precipitate. The solution was filtered through Celite, and the solvent was removed from the filtrate under vacuum. Extended drying under vacuum, especially with heating, was found to cause decomposition. The dark red residue was treated with hexanes (30 mL), the mixture was filtered through Celite, and the filtrate was reduced in volume to 10 mL. A ^{31}P NMR spectrum of this solution showed **II**; benzophenone was present as the only impurity. The solution was cooled slowly to −78 °C and kept at this temperature for 1 week, after which time dark red crystals of **II** had formed. The crystals were isolated by cannulating off the mother liquor, washing with 2 × 5 mL portions of hexanes at −78 °C, and drying under vacuum to give **II** (1.05 g, 79%). Compound **II** was characterized by comparison of its ^{31}P NMR spectrum with that of an authentic sample. $^{31}P\{^1H\}$ NMR (THF) (see eq 5 for atom labels): δ(P(x)) 107.0 (ddt, $^2J_{P(x)P(b)} = 13.7$ Hz, $^2J_{P(x)P(c)} = 10.7$ Hz, $^3J_{P(x)P(a)} = 10.7$ Hz, $^2J_{Pt(1)P(x)} = 255$ Hz, $^1J_{Pt(2)P(x)} = 58$ Hz), δ(P(c)) 18.6 (dd, $^2J_{P(c)P(b)} = 35.1$ Hz, $^2J_{P(c)P(x)} = 10.7$ Hz, $^1J_{Pt(2)P(c)} = 3619$ Hz, $^3J_{Pt(1)P(c)} = 137$ Hz), δ(P(b)) 15.0 (ddt, $^2J_{P(b)P(c)} = 35.1$ Hz, $^2J_{P(b)P(x)} = 13.7$ Hz, $^4J_{P(b)P(a)} = 4.5$ Hz, $^1J_{Pt(2)P(b)} = 3155$ Hz), δ(P(a)) 4.9 (dd, $^3J_{P(a)P(x)} = 10.7$ Hz, $^2J_{P(a)P(b)} = 4.5$ Hz, $^1J_{Pt(1)P(a)} = 2936$ Hz).

Preparation of $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{Pt(PEt_3)(Cl)_2\}]Pt(PEt_3)_2$ (III). To a dry mixture of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** (0.100 g, 0.106 mmol) and $[Pt(Cl)_2(PEt_3)]_2$ (0.0408 g, 0.0531 mmol) at room temperature was added 10 mL of THF with stirring. The color turned from dark orange to light orange immediately. A ^{31}P NMR spectrum taken after 5 min of stirring showed quantitative formation of **III**, with a small amount of $Pt(PEt_3)_2Cl_2$ present (characterized by comparison of its ^{31}P NMR spectrum with that of an authentic sample). The volume of the solvent was reduced to 2 mL, and 5 mL of hexanes was added to precipitate the $Pt(PEt_3)_2Cl_2$ impurity. The solution was filtered, and a ^{31}P NMR spectrum of the filtrate showed very pure **III**. Compound **III** is stable in hexanes for several days at −30 °C, but decomposes at room temperature in about 1 day. Compound **III** could not be purified for elemental analysis, as it decomposed to unidentified products under vacuum, and was characterized by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (THF) (see eq 6 for atom labels): δ(P(x)) 111.2 (dddt, $^2J_{P(x)P(d)} = 472.3$ Hz, $^2J_{P(x)P(b)} = 148.0$ Hz, $^2J_{P(x)P(c)} = 42.5$ Hz, $^3J_{P(x)P(a)} = 21.4$ Hz), δ(P(c)) 17.2 (ddd, $^2J_{P(c)P(x)} = 42.5$ Hz, $^4J_{P(c)P(d)} = 22.0$ Hz, $^2J_{P(c)P(b)} = 8.7$ Hz, $^1J_{Pt(2)P(c)} = 2926$ Hz), δ(P(b)) 15.9 (ddd, $^2J_{P(b)P(x)} = 148.0$ Hz, $^4J_{P(b)P(d)} = 56.0$ Hz, $^2J_{P(b)P(c)} = 8.7$ Hz, $^1J_{Pt(2)P(b)} = 3601$ Hz), δ(P(d)) 5.21 (ddd, $^2J_{P(d)P(x)} = 472.3$ Hz, $^4J_{P(d)P(b)} = 56.0$ Hz, $^4J_{P(d)P(c)} = 22.0$ Hz, $^1J_{Pt(3)P(d)} = 3020$ Hz), δ(P(a)) 5.0 (d, $^3J_{P(a)P(x)} = 21.4$ Hz, $^1J_{Pt(1)P(a)} = 2829$ Hz). (The $^{195}Pt{-}^{31}P$ coupling constants in the P(x) signal were not possible to determine because of the complexity of the splittings.)

Preparation of $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ (IV). To a solution of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** (0.500 g, 0.531 mmol) in THF (10 mL) at room temperature was added $W(CO)_5$(THF) (0.531 mmol) in THF (20 mL) with stirring. The color of the solution turned from dark orange to dark red after 1 h of stirring. The solvent volume was reduced to ca. 3 mL under vacuum, and 15 mL of hexanes was added. The flask was cooled to −30 °C for 1 h with formation of an oily solid impurity. The solution was filtered, and the filtrate was reduced in volume to 5 mL and then cooled slowly to −78 °C for 3 days, after which time light orange crystals of **IV** had formed. The crystals were isolated by cannulating off the mother liquor, washing them with 2 × 5 mL portions of hexanes at −78 °C, and drying under vacuum at −50 °C to give **IV** (0.375 g, 56%) that was pure by ^{31}P NMR spectroscopy. Further drying under vacuum at room temperature resulted in partial decomposition to an oily solid, which prevented proper elemental analysis. $^{31}P\{^1H\}$ NMR (THF) (see eq 6 for atom labels): δ(P(x)) 41.4 (ddt, $^2J_{P(x)P(b)} = 152.9$ Hz, $^2J_{P(x)P(c)} = 38.7$ Hz, $^3J_{P(x)P(a)} = 18.9$ Hz, $^1J_{Pt(1)P(x)} = 507$ Hz), δ(P(c)) 13.9 (dd, $^2J_{P(c)P(x)} = 38.7$ Hz, $^2J_{P(c)P(b)} = 9.1$ Hz, $^1J_{Pt(2)P(c)} = 2917$ Hz), δ(P(b)) 16.6 (dd, $^2J_{P(b)P(x)} = 152.9$ Hz, $^2J_{P(b)P(c)} = 9.1$ Hz, $^3J_{WP(b)} = 150.8$ Hz, $^1J_{Pt(2)P(b)} = 3568$ Hz), δ(P(a)) 3.1 (d, $^3J_{P(a)P(x)} = 18.9$ Hz, $^1J_{Pt(1)P(a)} = 2818$ Hz).

Preparation of $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)]$ (Vc). To a stirred solution of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** (0.500 g, 0.531 mmol) in THF (10 mL) at room temperature was added MeI (0.226 g, 1.59 mmol) all at once. After stirring for 12 h at 25 °C, the color had changed from dark orange to light orange and a precipitate of $[MePEt_3]I^-$ had formed (characterized by comparison of its ^{31}P NMR with an authentic sample). The solution was filtered, the solvent was removed from the filtrate under vacuum, and the residue

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Table 3. Crystal and Data Collection Parameters for *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2$ (Ib) and $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ (IV)

	Ib	IV
formula	$C_{19}H_{48}Cl_2NP_3Si_2Pt$	$C_{30}H_{60}ClO_5P_5Pt_2W$
space group	*Pbca*	$P2_1/n$
a, Å	11.802(2)	11.0994(2)
b, Å	15.060(3)	33.5717(2)
c, Å	35.060(3)	12.4301(1)
α, deg	90	90
β, deg	90	111.659(1)
γ, deg	90	90
V, Å^3	6231.7(16)	4304.76(9)
Z	8	4
d_{calc}, g/cm^3	1.504	1.952
crystal size, mm	0.377 × 0.377 × 0.125	0.4 × 0.12 × 0.12
μ, mm^{-1}	12.244	9.429
data collection instrument	Siemens P4RA	Siemens SMART
radiation (monochromated in incident beam)	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 73 Å)
temp, K	213(2)	173(2)
scan method	$2\theta-\theta$	Area Detector, ω-frames
data collection range	4.0−115.0; θ, deg	1.21−25.07; 2θ, deg
no. of data collected	7857	21 054
no. of unique data total with $I \geq 2\sigma(I)$	3207	5738
no. of params refined	278	390
trans factors; max/min	0.2836/0.0379	1.000/0.433
R^a $(I > 2\sigma(I))$	0.0368	0.0476
$R_w{}^a$ $(I > 2\sigma(I))$	0.0442	0.0942
quality of fit indicator^c	1.33	1.023
largest peak, e/Å^3	1.57	1.462

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

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was treated with 25 mL of hexanes. After reducing the solvent under vacuum to 5 mL, the solution was filtered and cooled slowly to −78 °C for 2 days to form an oil of **Vc** that was pure by ^{31}P NMR spectroscopic studies (yield 0.386 g, 75%). A similar preparation was carried out using ^{13}C-labeled MeI in order to obtain $^{13}C-^{31}P$ coupling constants. $^{31}P\{^1H\}$ NMR (THF) (see eq 7 for atom labels): δ(P(x)) 155.4 (dt, $^3J_{P(x)P(b)}$ = 15.3 Hz, $^3J_{P(x)P(a)}$ = 12.1 Hz, $^2J_{Pt(2)P(x)}$ = 564.7 Hz, $^2J_{Pt(1)P(x)}$ = 231.9 Hz), δ(P(b)) 21.5 (d, $^3J_{P(b)P(x)}$ = 15.3 Hz, $^1J_{Pt(2)P(b)}$ = 5173.7 Hz, $^2J_{Pt(1)P(b)}$ = 463.4 Hz), δ(P(a)) 8.7 (d, $^3J_{P(a)P(x)}$ = 12.1 Hz, $^1J_{Pt(1)P(a)}$ = 2338.9 Hz, $^2J_{Pt(2)P(a)}$ = 43.5 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ(CH_3P) 10.5 (dd, $^1J_{CP(x)}$ = 48.9 Hz, $^4J_{CP(b)}$ = 10.6 Hz, $^3J_{CPt(2)}$ = 51.2 Hz). Electrospray MS (for **Vc**): *m*/*e* 963 ($M^+ - H$).

Formation of $[Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}PMe)Pt(PEt_3)_2]^+$ (Va). Method A. To a stirred solution of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** (0.350 g, 0.372 mmol) in THF (15 mL) at room temperature was added MeO_3SCF_3 (0.0610 g, 0.372 mmol) all at once. After stirring for 5 min, the color of the solution changed from dark orange to dark, ruby red. The volume of the solution was reduced to 2 mL, and 15 mL hexanes was added to form a dark red oil that separated from solution. The remaining light red solution was removed from the oil with a cannula, and the oil was washed with 3 × 8 mL portions of hexanes to afford the triflate salt of **Va** (crude yield 0.279 g, 68%). A ^{31}P NMR spectrum showed that this oil contained a small amount of impurities, which were more prevalent after 1 day. Complete decomposition was evident after 1 week at room temperature. (The ^{31}P NMR spectrum was the same as that for the BPh_4^- salt below.)

Method B. To a stirred solution of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** (0.200 g, 0.212 mmol) and $NaBPh_4$ (0.145 g, 0.425 mmol) in THF (10 mL) at room temperature was added MeI (0.302 g, 0.212 mmol) all at once. The color of the solution turned from dark orange to very dark red after 3 h of stirring. The solution was treated with 10 mL of hexanes, and a large amount of oily precipitate formed. The solution was filtered, and the solvent in the filtrate was removed under vacuum. The residue was dissolved in 2 mL of THF, and 15 mL of hexanes was added to form a dark red oil that separated from the solution. The oil was isolated by cannulating off the solution and washing with 3 × 8 mL portions of hexanes followed by 3 × 5 mL portions of Et_2O to afford the BPh_4^- salt of **Va** (crude yield 0.103 g, 38%). A similar preparation was carried out using ^{13}C-labeled MeI in order to obtain $^{13}C-^{31}P$ coupling constants. $^{31}P\{^1H\}$ NMR (THF) (see Scheme 1 for atom labels): δ(P(x)) 34.7 (ddt, $^2J_{P(x)P(b)}$ = 148.9 Hz, $^2J_{P(x)P(c)}$ = 23.8 Hz, $^3J_{P(x)P(a)}$ = 20.6 Hz), δ(P(c)) 20.1 (dd, $^2J_{P(c)P(x)}$ = 23.8 Hz, $^2J_{P(c)P(b)}$ = 10.2 Hz, $^1J_{Pt(2)P(c)}$ = 2441 Hz), δ(P(b)) 18.7 (ddt, $^2J_{P(b)P(x)}$ = 148.9 Hz, $^2J_{P(b)P(c)}$ = 10.2 Hz, $^4J_{P(b)P(a)}$ = 5.7 Hz, $^1J_{Pt(2)P(b)}$ = 3640 Hz), δ(P(a)) 8.1 (dd, $^3J_{P(a)P(x)}$ = 20.6 Hz, $^4J_{P(a)P(b)}$ = 5.7 Hz, $^1J_{Pt(1)P(a)}$ = 2661 Hz). (The $^{195}Pt-^{31}P$ coupling constants in the P(x) signal were not possible to determine because of the complexity of the splittings). $^{13}C\{^1H\}$ NMR (THF): δ(CH_3P) 8.7 (ddd, $^1J_{CP(x)}$ = 71.5 Hz, $^3J_{CP(c)}$ = 12.6 Hz, $^3J_{CP(b)}$ = 8.4 Hz).

Conversion of $[Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}PMe)Pt(PEt_3)_2]^+$ (Va) to $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)]$ (Vc). To a stirred solution of **Va** (0.100 g, 0.0784 mmol) in THF (20 mL) at room temperature, prepared as in method B above, was added NaI (0.118 g, 0.784 mmol) as a solid. After stirring for 10 min, the color had changed from dark red to light orange. The solvent was removed under vacuum, and the residue was taken up in 20 mL of hexanes. The solution was filtered over Celite, and the filtrate was shown to contain mainly **Vc** by a ^{31}P NMR spectrum, but it could not be isolated pure, as it contained impurities that likely resulted from decomposition of **Va** before or during the reaction.

X-ray Crystallographic Study of *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (Ib). Diffraction-quality crystals of **Ib** were obtained by recrystallization from hexanes at −78 °C. Data collection and reduction information are given in Table 3. A light orange crystal of **Ib** was mounted on a glass fiber for data collection. Cell constants were determined from reflections found in a rotation photograph. High-angle cell constants were determined from a subset of intense reflections in the range 35.0−50.0° 2θ. The data were corrected for Lorentz and polarization effects. A correction based on nonlinear decay in the three standard reflections was applied to the data. An absorption correction based on measured crystal faces was applied. The space group *Pbca* was unambiguously determined by systematic absences and intensity statistics.[33] A successful direct methods solution was calcu-

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Table 4. Selected Bond Distances (Å) and Angles (deg) for *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PN(SiMe$_3$)$_2$] (Ib)

Distances

Pt−C(1)	1.990(7)	Pt−Cl(2)	2.373(2)	P(1)−N(1)	1.741(6)
Pt−P(2)	2.314(2)	C(1)−P(1)	1.690(7)	N(1)−Si(1)	1.744(6)
Pt−P(3)	2.313(2)	Cl(1)−C(1)	1.778(7)	N(1)−Si(2)	1.762(6)

Bond Angles

Cl(2)−Pt−P(2)	144.4(4)	Cl(2)−Pt−P(3)	162.4(2)
Cl(2)−Pt−C(1)	48.8(2)	P(2)−Pt−P(3)	104.2(2)
P(2)−Pt−C(1)	158.1(2)	P(3)−Pt−C(1)	152.57(9)
C(1)−P(1)−C(2)	101.5(2)	Pt−C(1)−Cl(1)	93.41(8)
Pt−C(1)−P(1)	147.54(10)	Cl(1)−C(1)−P(1)	113.85(9)
C(1)−P(1)−N(1)	110.7(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

lated which provided all non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined as riding atoms with C−H distances of 0.96 Å. The hydrogen atoms in methylene groups were refined with individual isotropic displacement parameters, while methyl hydrogen atoms were refined as groups. Selected bond distances and bond angles are given in Table 4.

X-ray Crystallographic Study of Cl(Et$_3$P)$_2$Pt[μ-η^1,η^1,η^2-C≡P{W(CO)$_5$}]Pt(PEt$_3$)$_2$ (IV). Diffraction-quality crystals were obtained by slow evaporation of an Et$_2$O solution of **IV**. Data collection and reduction information are given in Table 3. An orange crystal of **IV** was mounted on a glass fiber for data collection. An initial set of cell constants was calculated from reflections taken from three sets of 20 frames. Final cell constants were calculated from a set of 5625 strong reflections taken during the data collection. The space group $P2_1/n$ was unambiguously determined by systematic absences and intensity statistics.[33] A hemisphere-type data collection was employed in which a randomly oriented region of space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω, providing a high degree of redundancy. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms. One triethylphosphine group (P4) was disordered in a 0.50:0.50 ratio and required the use of 426 restraints. The P4 group is duplicated (P4′) in order to make a separate group, both of which have the same parameters. These groups were refined isotropically with additional restraints, and the other triethylphosphine groups in the molecule were used to group the two partially occupied groups in SHELTXTL SAME restraints.[33] Selected bond distances and bond angles are given in Table 5.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Cl(Et$_3$P)$_2$Pt[μ-η^1,η^1,η^2-C≡P{W(CO)$_5$}]Pt(PEt$_3$)$_2$ (IV)

Distances

Pt(1)−C(1)	1.952(9)	Pt(2)−P(1)	2.292(3)	W(1)−C(2)	2.042(13)
Pt(1)−P(3)	2.324(3)	Pt(2)−P(4)	2.270(3)	W(1)−C(3)	2.048(14)
Pt(1)−P(2)	1.977(5)	Pt(2)−P(5)	2.285(3)	W(1)−C(4)	2.014(12)
Pt(1)−Cl(1)	2.393(3)	C(1)−P(1)	1.663(9)	W(1)−C(5)	2.032(13)
Pt(2)−C(1)	2.104(9)	P(1)−W(1)	2.531(3)	W(1)−C(6)	1.978(11)

Bond Angles

C(1)−Pt(1)−Cl(1)	179.1(3)	Cl(1)−Pt(1)−P(2)	90.12(10)
C(1)−Pt(1)−P(3)	90.8(3)	P(2)−Pt(1)−P(3)	169.82(11)
Cl(1)−Pt(1)−P(3)	89.37(10)	C(1)−Pt(2)−P(4)	105.6(3)
C(1)−Pt(2)−P(1)	44.2(3)	P(1)−Pt(2)−P(4)	149.29(11)
C(1)−Pt(2)−P(5)	149.0(3)	P(4)−Pt(2)−P(5)	105.17(11)
P(1)−Pt(2)−P(5)	105.43(10)	Pt(1)−C(1)−Pt(2)	140.8(5)
Pt(1)−C(1)−P(1)	145.2(6)	Pt(2)−C(1)−P(1)	73.9(4)
Pt(2)−P(1)−C(1)	61.9(3)	W(1)−P(1)−C(1)	136.1(3)
C(1)−Pt(1)−P(2)	89.8(3)	W(1)−P(1)−Pt(2)	157.31(13)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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Supporting Information Available: Tables of non-hydrogen atomic coordinates and equiv isotropic parameters, anisotropic displacement parameters, complete bond distances and angles, hydrogen coordinates and isotropic diplacement parameters, torsion angles, and unit cell and packing diagrams for **Ib** and **IV** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(33) *SHELXTL-Plus V5.0*; Siemens Industrial Automation Inc., Madison, WI, 1994.