Organometallics **1998,** *17,* 5275−5286

Palladium Coordination Compounds of $\sigma^3\lambda^5$-Phosphoranes: First Examples of Phosphonio−Methylene(imino)metallophosphorane $[(R_3P)(Me_3Si)C{=}P(ML_n){=}NSiMe_3]$ and Phosphonio−Methylene(oxo)phosphorane $[(R_3P)(Me_3Si)C{=}P({=}O)NSiMe_3]$ Ligands

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The oxidative addition reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$ forms the phosphavinyl phosphonium complex $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ **(IIIa)**, which results from PPh_3 migration from Pd to carbon in the η^1-phosphavinyl intermediate *trans*-$Cl(Ph_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIa)**. The reaction of Pd(dba)(dppe) with $Cl_2C{=}PN(SiMe_3)_2$ forms the η^1-phosphavinyl complex *cis*-$Cl(dppe)Pd[C(Cl){=}PN(SiMe_3)_2]$ **(VI)**, which does not undergo phosphine migration. Compound **IIIa** undergoes substitution of the chloride ligand by PPh_3 or MeCN in the presence of KPF_6 to generate $[(Ph_3P)_2Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ **(IV)** or $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ **(V)**, respectively; the structure of **V** was determined by X-ray diffraction studies. The reaction of $Pd(PEt_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$ forms the η^1-phosphavinyl complex *trans*-$Cl(Et_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIb)**, which does not undergo PEt_3 migration. When 2 equiv of $Pd(PEt_3)_4$ are reacted with $Cl_2C{=}PN(SiMe_3)_2$ the phosphonio−methylene(imino)metallophosphorane complex $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ **(VIIa-b)** forms as a 1:1 isomeric mixture. Compound **VIIa-b** reacts with MeI or NaI to generate $Pd(PEt_3)(I)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)I$ **(VIIIa-b)** and reacts with traces of water to generate $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ **(IX)**. The structure of **VIIIb** was partially determined, and the structure of **IX** was determined by X-ray diffraction studies. Compounds **VIIa-b**, **VIIIa-b**, and **IX** exhibit the first examples of coordinated methylene(imino, oxo)phosphorane ligands.

Introduction

Carbon−phosphorus multiply bonded ligands have received much attention recently because of the rich coordination chemistry that they afford. In particular, the C═P double bonds in several different types of ligands have been found to exhibit a preferential η^2-coordination mode in many transition metal complexes. Several examples of η^2-coordinated phosphaalkenes are known,[1−4] and there are examples of η^3-coordinated diphosphaallyl complexes,[5−8] in which two bonds having C═P double-bond character are coordinated; in addition, a few examples of η^2-coordinated diphosphaallenes have been reported.[9] There are also examples of cyclic phosphorus-substituted ligands including η^4-phosphacyclobutadienes, η^5-phosphacyclopentadienyls, and η^6-phosphabenzenes in which delocalized rings containing C═P double bonds are coordinated to transition metal complexes.[10] The propensity for η^2-coordination of C═P double bonds is especially evident in phosphallenes **(A)** which coordinate through the C═P double bond in preference to the C═C double bond.[11,12] In view of the many different coordination compounds with ligands containing C═P double bonds, it is interesting that there are none of methylene(oxo)phosphoranes $R_2C{=}P({=}O)R$ (**B**) or methylene(imino)phosphoranes $R_2C{=}P({=}NR)R$ (**C**). These compounds are included in a recent review[13] of three-coordinate pentavalent phosphorus compounds

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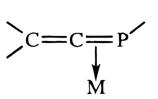
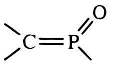


(A)



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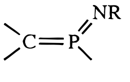
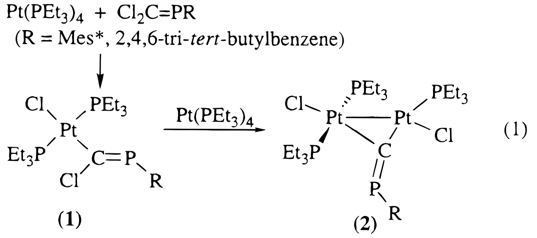


(C)

($\sigma^3\lambda^5$-phosphoranes) and constitute an area of recently increased study. In these methylene(oxo, imino)phosphoranes, the C=P double bond should allow for η^2-coordination to a transition metal, although such complexes have not been previously discussed.

We recently succeeded in preparing the first example of a coordinated isocyaphide (C≡PR) ligand by oxidative addition of the C−X bond in the phosphavinyl complex (**1**) (eq 1) to generate a diplatinum complex [(Cl)(Et$_3$P)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Cl)] (**2**) containing a semibridging C≡PR group.[14] A series of phosphavinyl compounds X(R′$_3$P)$_2$M[C(=PR)X] (M = Pt, Pd; X = Cl, Br; R′ = Ph, Et; R = 2,4,6-tri-*tert*-butylbenzene) analogous to **1** were prepared and in all cases exhibited a novel R-group migration from phosphorus to carbon to generate Mes*C≡P and M(PR′$_3$)$_2$X$_2$.[15] Romanenko and co-workers[16] reported the reaction of Pd(PPh$_3$)$_4$ with Cl$_2$C=P-Mes*, which resulted in the formation of Mes*C≡P and Pd(PPh$_3$)$_2$Cl$_2$ with no observable intermediates (eq 2).

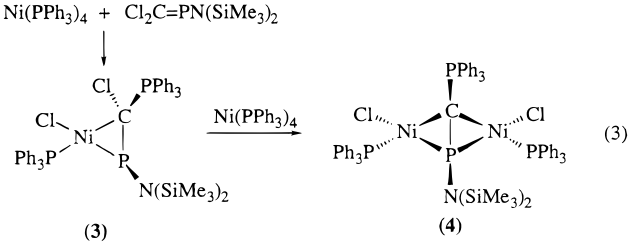


(1)

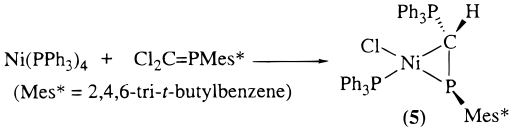
$$\mathrm{Pd(PPh_3)_4 + Cl_2C{=}PMes^*} \longrightarrow \mathrm{Mes^*\text{-}C{\equiv}P + Pd(PPh_3)_2Cl_2} \qquad (2)$$

(Mes* = 2,4,6-tri-*tert*-butylbenzene)

The Mes* group rearrangement in these reactions prompted us to attempt similar oxidative addition reactions between dihalophosphaalkenes containing nonaromatic R-groups and low-valent transition metals. In the course of these studies, we have prepared[17] (eq 3) and structurally characterized the first example of a complex **4**, containing a phosphavinylidene phosphorane (Ph$_3$P=C=PR) ligand, which forms from an intermediate phosphavinyl phosphonium complex **(3)**, which was not isolated. In a similar reaction[17] (eq 4) with Mes* as the R-group, we were able to isolate and structurally characterize the first example of a complex **5**, containing a phosphavinyl phosphonium ligand. In these reactions, the R-group migration from phosphorus to carbon was avoided and an interesting PPh$_3$ migration to the C=P carbon afforded the new ligands. The reactions in eqs 3 and 4 were postulated to involve η^1-phosphavinyl intermediates similar to that **(1)** in eq 1, which then rearranged to η^2-phosphavinyl complexes having carbene-like character, which facilitated the attack of PPh$_3$ on the C=P carbon atoms.[17]

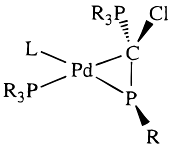


(3)

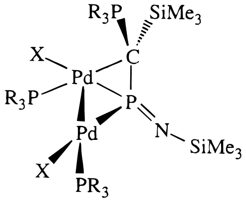


(4)

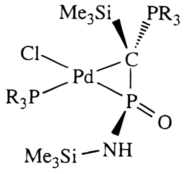
In our continuing studies of oxidative addition reactions of dihalophosphaalkenes with low-valent transition metal complexes, we explore in the present paper reactions of Cl$_2$C=PN(SiMe$_3$)$_2$ with Pd(0) complexes. During the course of these studies, we isolated a stable phosphavinyl phosphonium complex that is the palladium analogue of the unstable nickel complex **3** (eq 3) and explored ligand substitution reactions to generate a series of these complexes with η^2-(R$_3$P)(Cl)C=PR ligands acting as three-electron donors **(D)**. We have also isolated the first example of a complex with a phosphonio−methylene(imino)metallophosphorane ligand η^2-coordinated to one palladium center and η^1-coordinated to another in a dinuclear complex **(E)**. This new ligand results from a 1,3-SiMe$_3$ migration from nitrogen to carbon and was further functionalized by a hydrolysis reaction into the first example of a phosphonio−methylene(oxo)phosphorane ligand, which is η^2-coordinated to a palladium atom with the (R$_3$P)(Me$_3$Si)C=P(=O)-NSiMe$_3$ ligand acting as a three-electron donor **(F)**. The ligands in **E** and **F** represent the first examples of transition metal-coordinated methylene(imino)phosphoranes and methylene(oxo)phosphoranes, respectively. Although these ligands contain phosphonio substituents on the C=P carbon atoms, their η^2-coordination through the C=P double bond opens up the possibility of coordinating other members of this well-known class of $\sigma^3\lambda^5$-phosphoranes.



(D)



(E)



(F)

The preparations of complexes of types **D**, **E**, and **F** are discussed, along with substitution reactions, likely pathways of formation, and chemical reactivity. Structure and bonding in the complexes containing these new ligands are also examined.

Experimental Section

General Procedure. All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. Solvents were reagent grade and dried

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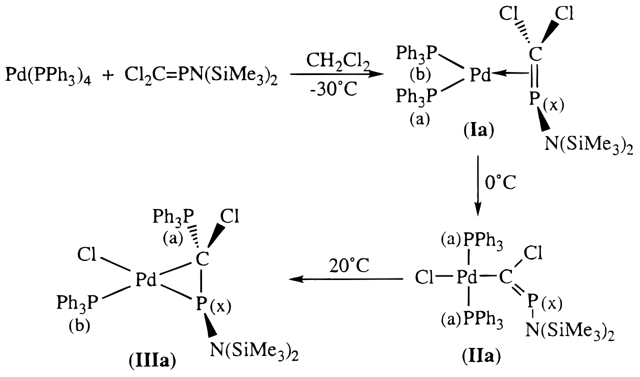
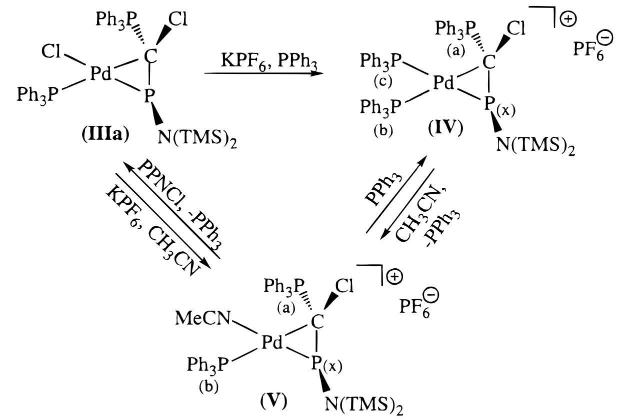
Scheme 1



Scheme 2



by refluxing over appropriate drying agents under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium benzophenone ketyl, while hexanes, toluene, and dichloromethane were distilled over CaH_2. Acetonitrile was distilled over anhydrous $MgSO_4$.

The ^1H NMR spectra of compounds were recorded on a Varian VXR 300 MHz spectrometer with TMS (δ 0.00 ppm) as the internal standard. The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a 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. FAB mass spectra were recorded on a Kratos MS 50 spectrometer using THF as solvent. The compounds Pd(dppe)(dba),[18] $Pd(PPh_3)_2(dba)$,[18] $Pd(PPh_3)_4$,[19] $Pd(PEt_3)_3$,[20] and $Cl_2C{=}PN(SiMe_3)_2$[21] were prepared by literature methods. Phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh_3, which was recrystallized from MeOH.

Preparation of $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ (IIIa) through Intermediates $(Ph_3P)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]$ (Ia) and *trans*-$Cl(Ph_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ (IIa). To a cooled (−50 °C) slurry of $Pd(PPh_3)_4$ (1.00 g, 0.865 mmol) in CH_2Cl_2 (20 mL) was added $Cl_2C{=}PN(SiMe_3)_2$ (0.261 g, 0.952 mmol). The initially light yellow solution was warmed slowly with stirring. A $^{31}P\{^1H\}$ NMR spectrum taken after the initial addition (−50 °C) showed **Ia** as the only intermediate. After the solution was allowed to warm slowly to 0 °C, the color turned dark red. A $^{31}P\{^1H\}$ NMR spectrum was taken (0 °C) and showed traces of **Ia** along with **IIa** as the main product. When the solution reached room temperature after about 1 h, **IIa** had converted almost completely to **IIIa**, along with formation of $Pd(PPh_3)_2Cl_2$ (characterized by comparison of its ^{31}P NMR spectrum with that of an authentic sample).[22] The solution was filtered and the solvent was removed under vacuum from the filtrate to yield a red oily solid. The residue was treated with 25 mL of THF, the red solution was filtered to remove $Pd(PPh_3)_2Cl_2$, and the filtrate was reduced to 2 mL. After adding 20 mL of hexanes and cooling to 0 °C, a light yellow precipitate formed, which was collected on a medium-porosity fritted glass filter, washed with 3 × 5 mL portions of hexanes, and dried under vacuum to give analytically pure **IIIa** (0.580 g, 74% based on Pd). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) (see Scheme 1 for atom labels) for **Ia**, −50 °C: $\delta(P(x))$ 41.8 (dd, $^2J_{P(x)P(b)} = 35.3$ Hz, $^2J_{P(x)P(a)} = 23.4$ Hz), $\delta(P(a))$ 25.8 (d, $^2J_{P(a)P(x)} = 23.4$ Hz), $\delta(P(b))$ 21.3 (d, $^2J_{P(b)P(x)} = 35.3$ Hz). For **IIa**, 0 °C: $\delta(P(x))$ 213.9 (t, $^3J_{P(x)P(a)} = 50.1$ Hz), $\delta(P(a))$ 22.3 (d, $^3J_{P(a)P(x)} = 50.1$ Hz). For **IIIa**, 25 °C: $\delta(P(x))$ 124.4 (d, $^2J_{P(x)P(a)} = 91.4$ Hz), $\delta(P(a))$ 25.8 (dd, $^2J_{P(a)P(x)} = 91.4$ Hz, $^3J_{P(a)P(b)} = 10.1$ Hz), $\delta(P(b))$ 21.3 (d, $^3J_{P(b)P(a)} = 10.1$ Hz). Electrospray MS (for **IIIa**): *m/e* 870 ($M^+ - Cl$), 608 ($M^+ - (Cl + PPh_3)$). Anal. Calcd for $C_{43}H_{48}Cl_2N_1P_3Pd_1Si_2$ (**IIIa**): C, 57.05; H, 5.34; N, 1.55. Found: C, 56.75; H, 5.46; N, 1.68.

Preparation of $[(Ph_3P)_2Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (IV). Method A. To a cooled (−50 °C), stirred slurry of $Pd(PPh_3)_4$ (1.00 g, 0.865 mmol) in CH_2Cl_2 (20 mL) was added $Cl_2C{=}PN(SiMe_3)_2$ (0.261 g, 0.952 mmol) and KPF_6 (0.319 g, 1.73 mmol). The initially light yellow solution turned red upon warming slowly to room temperature with stirring over a period of about 1 h. The solution was filtered, the filtrate was reduced to 5 mL, and 25 mL of hexanes was added to form a yellow precipitate, which was collected on a medium-porosity fritted glass filter and washed with 3 × 10 mL portions of Et_2O to yield 0.715 g of crude product. A ^{31}P NMR spectrum (in CH_2Cl_2) showed that this precipitate contained almost pure **IV**, with a small amount (≈5%) of $[Pd(PPh_3)_3Cl](PF_6)$ (characterized by comparison of its ^{31}P NMR spectrum with literature values).[23] Further attempts to purify compound **IV** resulted in decomposition with formation of $[Pd(PPh_3)_3Cl](PF_6)$ and unidentifiable products.

Method B. To a solution of $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ **(IIIa)** (0.100 g, 0.110 mmol) in CH_2Cl_2 (5 mL) was added PPh_3 (0.0318 g, 0.121 mmol) and KPF_6 (0.0223 g, 0.121 mmol). After stirring for 30 min the solution was filtered, the filtrate was reduced to 5 mL, and 25 mL of hexanes was added to form a yellow precipitate, which was collected on a medium-porosity fritted glass filter and washed with 3 × 10 mL portions of Et_2O. A ^{31}P NMR spectrum in CH_2Cl_2 showed that this precipitate contained **IV** with a small amount of $[Pd(PPh_3)_3Cl](PF_6)$ impurity, which could not be separated. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 0 °C) (see Scheme 2 for atom labels): $\delta(P(x))$ 118.2 (ddd, $^2J_{P(x)P(a)} = 123.6$ Hz, $^2J_{P(x)P(c)} = 32.5$ Hz, $^2J_{P(x)P(b)} = 5.1$ Hz), $\delta(P(a))$ 25.1 (ddd, $^2J_{P(a)P(x)} = 123.6$ Hz, $^3J_{P(a)P(b)} = 20.1$ Hz, $^3J_{P(a)P(c)} = 20.6$ Hz), $\delta(P(b))$ 17.4 (ddd, $^3J_{P(b)P(a)} = 20.1$ Hz, $^2J_{P(b)P(c)} = 11.9$ Hz, $^2J_{P(b)P(x)} = 5.1$ Hz), $\delta(P(c))$ 13.8 (ddd, $^2J_{P(c)P(x)} = 32.5$ Hz, $^3J_{P(c)P(a)} = 20.6$ Hz, $^2J_{P(c)P(b)} = 11.9$ Hz), $\delta(PF_6)$ −144 (sept., $^1J_{PF} = 709.1$ Hz). Electrospray MS: *m/e* 870 ($M^+ - PPh_3$), 608 ($M^+ - (Cl + PPh_3)$).

Preparation of $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (V). Method A. To a cooled (−30 °C), stirred slurry of $Pd(PPh_3)_4$ (1.00 g, 0.865 mmol) in MeCN (30 mL) was added $Cl_2C{=}PN(SiMe_3)_2$ (0.261 g, 0.952 mmol) and KPF_6 (0.319 g, 1.73 mmol). The initially light yellow solution turned red upon warming slowly to room temperature with stirring over a period of about 1 h. The solution was filtered, filtrate was reduced to 5 mL, and a mixture of 15 mL of hexanes and 15 mL of Et_2O was added with stirring. The resulting red

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precipitate was collected by filter cannula, redissolved in minimal MeCN, filtered, and cooled slowly to −30 °C. After approximately 3 days at −30 °C, compound **V** separated from the solution as clear crystals (0.445 g, 49%).

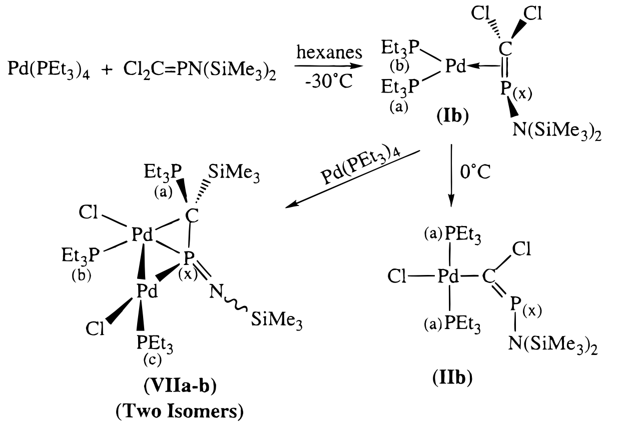
Method B. To a stirred solution of $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3)=PN(SiMe_3)_2]$ **(IIIa)** (0.500 g, 0.552 mmol) in MeCN (20 mL) at room temperature was added KPF_6 (0.112 g, 0.608 mmol). The solution was stirred for 15 min and filtered over Celite to remove KCl. The filtrate was reduced to 3 mL, and a mixture of 15 mL of hexanes and 15 mL of Et_2O was added with stirring. The resulting red precipitate was collected by filter cannula and redissolved in minimal MeCN; the solution was then filtered and cooled slowly to −30 °C. After approximately 3 days at −30 °C, compound **V** was separated from the solution as light yellow crystals (0.357 g, 61%). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.1−7.7 (30H, PPh_3), 1.66 (s, 3H, MeCN), 0.15 (s, 18H, $N(SiMe_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) (see Scheme 2 for atom labels): $\delta(P(x))$ 132.8 (d, $^2J_{P(x)P(a)} = 97.0$ Hz), $\delta(P(a))$ 28.0 (dd, $^2J_{P(a)P(x)} = 97.0$ Hz, $^3J_{P(a)P(b)} = 6.4$ Hz), $\delta(P(b))$ 21.1 (d, $^3J_{P(b)P(a)} = 6.4$ Hz), $\delta(PF_6)$ −144 (sept., $^1J_{PF} = 709.5$ Hz). Electrospray MS: *m/e* 870 ($M^+ - MeCN$), 608 ($M^+ - (MeCN + PPh_3)$). Anal. Calcd for $C_{45}H_{51}Cl_1F_6N_2P_4Pd_1Si_2$: C, 51.19; H, 4.87; N, 2.65. Found: C, 50.90; H, 4.85; N, 2.66.

Conversion of $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3)=PN(SiMe_3)_2)](PF_6)$ (V) to $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3)=PN(SiMe_3)_2]$ (IIIa). To a stirred solution of $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3)=PN(SiMe_3)_2)](PF_6)$ **(V)** (0.100 g, 0.0947 mmol) in CH_2Cl_2 (10 mL) at 25 °C was added $(Ph_3P)_2N^+Cl^-$ (PPNCl) (0.109 g, 0.189 mmol). After stirring for 5 min, a ^{31}P NMR spectrum showed quantitative conversion to $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3)=PN(SiMe_3)_2]$ **(IIIa)**.

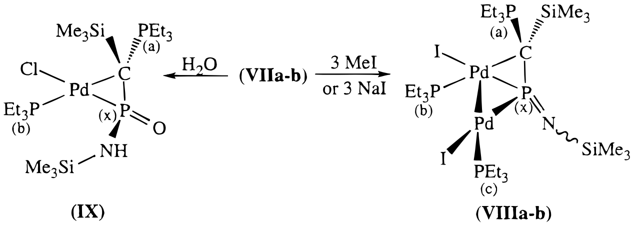
Preparation of *cis*-$Cl(dppe)Pd[C(Cl)=PN(SiMe_3)_2]$ (VI). To a solution of Pd(dppe)(dba) (1.00 g, 1.35 mmol) in CH_2Cl_2 (30 mL) was added $Cl_2C=PN(SiMe_3)_2$ (0.371 g, 1.35 mmol). The color turned from dark orange to light yellow immediately after the addition. After stirring for 5 min, the solution was filtered, and the solvent was removed from the filtrate under vacuum to yield a light yellow oily solid residue. The residue was stirred vigorously with 20 mL of Et_2O to produce a yellow precipitate, which was collected on a medium-porosity fritted glass filter. The precipitate was washed with 2 × 10 mL of Et_2O, followed by 3 × 5 mL of MeCN to give **VI** (0.745 g, 71%) that was pure by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) (see eq 5 for atom labels): $\delta(P(x))$ 230.1 (dd, $^3J_{P(x)P(b)} = 41.8$ Hz, $^3J_{P(x)P(a)} = 29.9$ Hz), $\delta(P(a))$ 55.8 (dd, $^3J_{P(a)P(x)} = 29.9$ Hz, $^2J_{P(a)P(b)} = 22.1$ Hz), $\delta(P(b))$ 41.9 (dd, $^3J_{P(b)P(x)} = 41.8$ Hz, $^2J_{P(b)P(a)} = 22.1$ Hz).

Preparation of *trans*-$Cl(Et_3P)_2Pd[C(Cl)=PN(SiMe_3)_2]$ (IIb) through Intermediate $(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2=PN(SiMe_3)_2]$ (Ib). To a stirred solution of $Pd(PEt_3)_3$ (1.35 g, 2.93 mmol) in hexanes (20 mL) at 0 °C was added dropwise $Cl_2C=PN(SiMe_3)_2$ (0.803 g, 2.93 mmol). The color changed from orange to almost colorless during the addition. A ^{31}P NMR spectrum taken after 5 min of stirring at 0 °C showed quantitative formation of $(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2=PN(SiMe_3)_2]$ **(Ib)**. The solution was allowed to warm slowly to room temperature and stirred for 1 h. A ^{31}P NMR spectrum showed that all of **Ib** had converted to *trans*-$Cl(Et_3P)_2Pd[C(Cl)=PN(SiMe_3)_2]$ **(IIb)**. The solution was reduced to 5 mL under vacuum, filtered, and cooled slowly to −78 °C to form colorless crystals of **IIb**. Compound **IIb** melts at ≈10 °C and could not be isolated in pure form, as it contains small amounts of $Pd(PEt_3)_2Cl_2$ (characterized by comparison of its ^{31}P NMR spectrum with an authentic sample). $^{31}P\{^1H\}$ NMR (hexanes) (see Scheme 3 for atom labels), for **Ib**, 0 °C: $\delta(P(x))$ 38.0 (dd, $^2J_{P(x)P(b)} = 38.5$ Hz, $^2J_{P(x)P(a)} = 24.8$ Hz), $\delta(P(a))$ 5.5 (dd, $^2J_{P(a)P(x)} = 24.8$ Hz, $^2J_{P(a)P(b)} = 5.5$ Hz), $\delta(P(b))$ 4.0 (dd, $^2J_{P(b)P(x)} = 38.5$ Hz, $^2J_{P(b)P(a)} = 5.5$ Hz). For **IIb**, 25 °C: $\delta(P(x))$ 223.8 (t, $^3J_{P(x)P(a)} = 33.4$ Hz), $\delta(P(a))$ 16.1 (d, $^3J_{P(a)P(x)} = 33.4$ Hz). $^{13}C\{^1H\}$ NMR (hexanes), for **IIb**, 25 °C: $\delta(C=PR)$ 191.0 (dt, $^1J_{CP(x)} = 135.1$ Hz, $^2J_{CP(a)} = 9.6$ Hz).

Scheme 3



Scheme 4



Synthesis of $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)Cl$ (VIIa-b) through Intermediate $(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2=PN(SiMe_3)_2]$ (Ib). To a stirred solution of $Pd(PEt_3)_3$ (1.58 g, 3.43 mmol) in hexanes (25 mL) at 0 °C was added dropwise $Cl_2C=PN(SiMe_3)_2$ (0.470 g, 1.71 mmol). The color remained orange during the addition. A ^{31}P NMR spectrum taken after 5 min of stirring at 0 °C showed a mixture of $(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2=PN(SiMe_3)_2]$ **(Ib)** and unreacted Pd(0). The solution was warmed quickly to room temperature and stirred for 15 min, during which time the color turned red. Stirring was then stopped, and the flask was allowed to sit at room temperature overnight to form crystals of $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)Cl$ **(VIIa-b)**. The filtrate was removed by cannula, and the crystals were washed with 3 × 5 mL of hexanes and dried under vacuum to give pure **VIIa-b** (0.824 g, 57%). $^{31}P\{^1H\}$ NMR (THF) (see Scheme 3 for atom labels), for **VIIa**: $\delta(P(x))$ 194.9 (dd, $^2J_{P(x)P(a)} = 18.0$ Hz, $^2J_{P(x)P(b)} = 8.3$ Hz), $\delta(P(a))$ 38.2 (dd, $^2J_{P(a)P(x)} = 18.0$ Hz, $^3J_{P(a)P(b)} = 5.5$ Hz), $\delta(P(b))$ 27.2 (ddd, $^3J_{P(b)P(c)} = 63.3$ Hz, $^2J_{P(b)P(x)} = 8.3$ Hz, $^3J_{P(b)P(a)} = 5.5$ Hz), $\delta(P(c))$ 16.2 (d, $^3J_{P(c)P(b)} = 63.3$ Hz). For **VIIb**: $\delta(P(x))$ 182.2 (ddd, $^2J_{P(x)P(a)} = 16.8$ Hz, $^2J_{P(x)P(b)} = 5.5$ Hz, $^2J_{P(x)P(c)} = 5.5$ Hz), $\delta(P(a))$ 31.3 (dd, $^2J_{P(a)P(x)} = 16.8$ Hz, $^3J_{P(a)P(b)} = 16.5$ Hz), $\delta(P(b))$ 26.0 (ddd, $^3J_{P(b)P(c)} = 55.0$ Hz, $^3J_{P(b)P(a)} = 16.5$ Hz, $^2J_{P(b)P(x)} = 5.5$ Hz), $\delta(P(c))$ 14.0 (dd, $^3J_{P(c)P(b)} = 55.0$ Hz, $^2J_{P(c)P(x)} = 5.5$ Hz). Anal. Calcd for $C_{25}H_{63}Cl_2N_1P_4Pd_2Si_2$ (mixture of **VIIa** and **VIIb**): C, 35.68; H, 7.55; N, 1.66. Found: C, 35.20; H, 7.31; N, 1.49.

Synthesis of $Pd(PEt_3)(I)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)I$ (VIIIa-b). To a stirred solution of $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)Cl$ **(VIIa-b)** (0.200 g, 0.238 mmol) in THF (10 mL) was added MeI (0.101 g, 0.713 mmol). After stirring for 24 h at room temperature, the color had changed from orange to deep red. The solvent was removed under vacuum, and the red, oily residue was taken up in 35 mL of Et_2O. The solution was filtered quickly, and the filtrate was cooled slowly to −30 °C to form red crystals. A ^{31}P NMR spectrum showed the red crystals to be composed of approximately 90% **VIIIb** and 10% **VIIIa**. Yield: 0.0635 g, 24%. $^{31}P\{^1H\}$ NMR (THF) (see Scheme 4 for atom labels), for **VIIIa**: $\delta(P(x))$ 196.8 (d, $^2J_{P(x)P(a)} = 18.3$ Hz), $\delta(P(a))$ 37.2 (dd, $^2J_{P(a)P(x)} = 18.3$ Hz, $^3J_{P(a)P(b)} = 7.0$

Table 1. Crystal and Data Collection Parameters for $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (V) and $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (IX)

	V	IX
formula	$C_{51}H_{60}ClF_6N_5P_4PdSi_2$	$C_{42}H_{108}Cl_2N_2O_3P_6Pd_2Si_4$
space group	*C*2/*c*	*Fdd*2
a, Å	45.7520(3)	24.7392(4)
b, Å	12.1002(2)	46.7039(6)
c, Å	25.1991(4)	11.2593(1)
α, deg	90	90
β, deg	123.146(1)	90
γ, deg	90	90
V, Å^3	11680.4(3)	13009.2(3)
Z	8	8
d_{calc}, g/cm^3	1.341	1.298
crystal size, mm	0.45 × 0.36 × 0.09	0.22 × 0.19 × 0.09
μ, mm^{-1}	0.570	0.889
data collection instrument	Siemens SMART	Siemens SMART
radiation (monochromated in incident beam)	Mo Kα ($\gamma = 0.710\ 73$ Å)	Mo Kα ($\gamma = 0.710\ 73$ Å)
temp, K	173(2)	173(2)
scan method	area detector, ω-frames	area detector, ω-frames
data collection range, θ, deg	1.06-25.03	1.74-25.03
no. of data collected	28 232	16 542
no. of unique data total	10 122	5542
with $I \geq 2\sigma(I)$	7618	4860
no. of parameters refined	660	324
trans factors, max/min	1.000/0.811	1.000/0.840
R^a ($I > 2\sigma(I)$)	0.0529	0.0417
$R_w{}^b$ ($I > 2\sigma(I)$)	0.1043	0.0967
quality of fit indicators^c	1.063	1.087
largest peak, e/Å^{-3}	0.584	0.839

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Hz), δ(P(b)) 21.5 (dd, $^3J_{P(b)P(c)} = 71.1$ Hz, $^3J_{P(b)P(a)} = 7.0$ Hz), δ(P(c)) 17.4 (d, $^3J_{P(c)P(b)} = 71.1$ Hz). For **VIIIb**: δ(P(x)) 183.9 (d, $^2J_{P(x)P(a)} = 17.2$ Hz), δ(P(a)) 30.7 (dd, $^2J_{P(a)P(x)} = 17.2$ Hz, $^3J_{P(a)P(b)} = 15.1$ Hz), δ(P(b)) 19.8 (dd, $^3J_{P(b)P(c)} = 61.0$ Hz, $^3J_{P(b)P(a)} = 15.1$ Hz), δ(P(c)) 13.1 (d, $^3J_{P(c)P(b)} = 61.0$ Hz).

Preparation of $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (IX). To a stirred solution of $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ **(VIIa-b)** (0.100 g, 0.118 mmol) in THF (10 mL) was added deionized, degassed H_2O (4.28 μL, 0.238 mmol). After stirring for 5 min at room temperature, the color had changed from orange to dark orange. The solvent was reduced to 5 mL, and 25 mL of Et_2O was added with stirring. The solution was filtered, and the filtrate was cooled slowly to −78 °C to form yellow crystals. The crystals were isolated by removing the mother liquor with a cannula and washing with 3 × 5 mL of hexanes at 0 °C to yield **IX** (0.058 g, 82%). $^{31}P\{^1H\}$ NMR (THF) (see Scheme 4 for atom labels): δ(P(x)) 80.0 (d, $^2J_{P(x)P(b)} = 11.0$ Hz), δ(P(a)) 37.1 (d, $^2J_{P(a)P(b)} = 8.3$ Hz), δ(P(b)) 24.2 (dd, $^2J_{P(b)P(a)} = 8.3$ Hz, $^2J_{P(b)P(x)} = 11.0$ Hz). FABMS: *m*/*e* 598 ($M^+ - H$), 561 ($M^+ - (H + Cl)$), 338 ($M^+ - (H + Cl + Pd + PEt_3)$).

X-ray Crystallographic Analyses of $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (V) and $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (IX). Diffraction-quality crystals of **V** were obtained by recrystallization from acetonitrile at −30 °C; crystals of **IX** were obtained from Et_2O at −30 °C. Data collection and reduction information are given in Table 1. A colorless crystal of **V** and a yellow platelike crystal of **IX** were mounted on glass fibers for data collection. Initial sets of cell constants were calculated from reflections taken from three sets of 20 frames, oriented such that orthogonal wedges of reciprocal space were surveyed to produce orientation matrixes determined from 91 reflections in **V** and 114 in **IX**. Final cell constants were calculated from a set of 6961 strong reflections in **V** and 5673 in **IX** taken during the data collections. Hemisphere-type data collections were employed in both structure determinations in which randomly oriented regions of space were 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. The space group *C*2/*c* was unambiguously determined in **V**, and *Fdd*2 in **IX** by systematic absences and intensity statistics.[24] Successful direct methods solutions were calculated, which provided most non-hydrogen atoms from the E-maps. 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. The structure of **V** contained three acetonitrile solvent molecules, and the PF_6 anion was split between two sites with 0.50:0.50 site occupancy, with one of the sites showing disorder. A total of 102 restraints were used. The structure of **IX** contained one Et_2O solvent molecule which was disordered on a 2-fold axis. Several ethyl groups were also disordered, and 260 total restraints were used. Selected bond distances and bond angles for **V** and **IX** are given in Tables 2 and 3.

Results

Reactions of PPh_3 or dppe Complexes of Pd(0) with $Cl_2C{=}PN(SiMe_3)_2$. The reaction (Scheme 1) of $Pd(PPh_3)_4$ with 1.1 equiv of $Cl_2C{=}PN(SiMe_3)_2$ at −50 °C in CH_2Cl_2 results in the formation of the phosphavinyl phosphonium compound $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ **(IIIa)**. Variable-temperature (−50 to 25 °C) ^{31}P NMR monitoring of the reaction solution shows two intermediates (Scheme 1). At −50 °C, the only species present is the η^2-phosphaalkene complex $(PPh_3)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]$ **(Ia)** and free PPh_3. Upon warming to 0 °C, **Ia** undergoes oxidative addition of one of the C−Cl bonds to form the phosphavinyl compound *trans*-$Cl(Ph_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIa)**. After the solution reaches room temperature and is stirred for 3 h, compound **IIIa** is the only product, along with a small amount of $Pd(PPh_3)_2Cl_2$. When the reaction is carried out with only 2 equiv of PPh_3 using

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[24] *SHELXTL-Plus V5.0*; Siemens Industrial Automation Inc.: Madison, WI, 1994.

Table 2. Selected Bond Distances and Angles for $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)]$ (PF_6) (V)

Distances (Å)

Pd(1)−C(1)	2.161(4)	C(1)−P(1)	1.803(4)	C(1)−Cl(1)	1.793(4)
Pd(1)−P(1)	2.2688(11)	C(1)−P(2)	1.771(4)	N(2)−Si(1)	1.784(4)
Pd(1)−N(1)	2.168(4)	P(1)−N(2)	1.704(3)	N(2)−Si(2)	1.788(4)
Pd(1)−P(3)	2.3451(11)	N(1)−C(2)	1.127(6)		

Angles (deg)

P(1)−C(1)−P(2)	115.8(2)	C(1)−Pd(1)−P(1)	47.95(11)
P(1)−C(1)−Pd(1)	69.15(13)	C(1)−Pd(1)−P(3)	153.92(11)
P(2)−C(1)−Pd(1)	110.0(2)	P(1)−Pd(1)−P(3)	106.48(4)
P(1)−C(1)−Cl(1)	122.4(2)	C(1)−P(1)−Pd(1)	62.90(13)
P(2)−C(1)−Cl(1)	109.2(2)	N(2)−P(1)−Pd(1)	114.90(13)
C(1)−Pd(1)−N(1)	109.85(14)	P(1)−N(2)−Si(1)	107.7(2)
N(1)−Pd(1)−P(1)	157.80(10)	P(1)−N(2)−Si(2)	129.2(2)
N(1)−Pd(1)−P(3)	95.58(10)		

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

Table 3. Selected Bond Distances and Angles for $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (IX)

Distances (Å)

C(1)−P(1)	1.787(6)	Pd(1)−Cl(1)	2.459(2)	P(1)−O(1)	1.489(4)
C(1)−P(2)	1.744(5)	Pd(1)−P(3)	2.270(2)	C(1)−Si(2)	1.871(5)
Pd(1)−C(1)	2.228(5)	P(1)−N(1)	1.657(4)	N(1)−Si(1)	1.748(4)
Pd(1)−P(1)	2.1696(13)				

Angles (deg)

P(1)−Pd(1)−C(1)	47.92(14)	P(1)−C(1)−Si(2)	119.1(3)
C(1)−Pd(1)−P(3)	155.79(14)	P(2)−C(1)−Si(2)	120.7(3)
C(1)−Pd(1)−Cl(1)	108.07(14)	Pd(1)−C(1)−Si(2)	107.1(2)
P(1)−Pd(1)−P(3)	108.33(7)	O(1)−P(1)−Pd(1)	124.3(2)
P(1)−Pd(1)−Cl(1)	155.67(7)	O(1)−P(1)−N(1)	109.7(2)
P(3)−Pd(1)−Cl(1)	95.91(7)	N(1)−P(1)−C(1)	114.0(3)
P(2)−C(1)−P(1)	117.5(3)	O(1)−P(1)−C(1)	118.6(2)
P(2)−C(1)−Pd(1)	111.7(3)	P(1)−N(1)−Si(1)	128.2(3)
P(1)−C(1)−Pd(1)	64.3(2)	N(1)−P(1)−Pd(1)	116.6(2)

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

$Pd(dba)(PPh_3)_2$ and 1.1 equiv of $Cl_2C{=}PN(SiMe_3)_2$ in CH_2Cl_2, compound **IIIa** forms at the same temperature in the same amount of time. However, if less polar solvents (e.g., THF, hexanes, toluene) are used, **Ia** still forms but decomposes to unidentified products instead of isomerizing to **IIa** and **IIIa**.

Compounds **Ia**, **IIa**, and **IIIa** were characterized by their ^{31}P and $^{31}P\{^1H\}$ NMR spectra; compound **IIIa** was further characterized by elemental analysis and electrospray mass spectrometry. Compound **IIIa** is air stable in the solid state, but air sensitive in solution. The peaks corresponding to P(x) in the ^{31}P NMR for compounds **Ia**, **IIa**, and **IIIa** are conveniently assigned by proton-coupled ^{31}P NMR, in which the P(x) signal remains sharp, while the PPh_3 signals are broadened dramatically by the phenyl protons. The assignment of **Ia** as an η^2-coordinated phosphaalkene is consistent with the chemical shift for P(x) at δ 41.8, which is 210 ppm upfield from $Cl_2C{=}PN(SiMe_3)_2$.[21] This is similar to the upfield shift of 266 ppm found for the P(x) phosphorus atom in $(Ph_3P)_2Pt[\eta^2\text{-}Ph_2C{=}PMes]$ relative to free $Ph_2C{=}PMes$.[2] The peak for P(x) in **Ia** is split into a doublet of doublets ($^2J_{P(x)P(b)} = 35.3$ Hz, $^2J_{P(x)P(a)} = 23.4$ Hz) by the two inequivalent PPh_3 groups on Pd, which is also consistent with the proposed η^2-structure. In **IIa**, the chemical shift (δ 213.9) for P(x) is 172 ppm downfield from that in **Ia** in the region (200−350 ppm)[25] typical of uncoordinated C=P double-bond compounds and is now split into a triplet ($^3J_{P(x)P(a)} = 50.1$ Hz) by the two equivalent PPh_3 groups on Pd. This is consistent with the proposed *trans*-phosphavinyl structure of **IIa** and is quite similar to the ^{31}P NMR spectra (δ 223−243 ppm, $^3J_{PP} = 25{-}43$ Hz) of a series of *trans*-phosphavinyl compounds of the type $X(Et_3P)_2M[C(X){=}PMes^*]$ (X = Cl, Br; M = Pd, Pt; Mes* = tri-*tert*-butylphenyl).[15] In compound **IIIa**, where a PPh_3 group has migrated from palladium to the C=P carbon atom, the chemical shift of P(x) is δ 124.4 ppm, which is far upfield from P(x) in uncoordinated phosphavinyl phosphonium cations (e.g., in $[(Ph_3P)(H)C{=}PN(i\text{-}Pr)_2](BF_4)$, δ 303.5),[26] consistent with the η^2-coordinated structure in Scheme 1. The peak for P(x) in **IIIa** is split into a doublet with a large coupling constant ($^2J_{P(x)P(a)} = 91.4$ Hz) by the carbon-bound PPh_3 group. This is analogous to the large $^2J_{PP}$ coupling constants found in the uncoordinated phosphavinyl phosphonium cations (e.g., in $[(Ph_3P)(H)C{=}PNi\text{-}Pr_2]$ (BF_4), $^2J_{PP} = 124.6$ Hz).[26] Further evidence for the structure of **IIIa** is the similarity of its ^{31}P NMR spectrum (see Experimental Section) to that of the cationic MeCN analogue $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ **(V)**, which was characterized by X-ray diffraction.

The reaction (eq 5) of Pd(dppe)(dba) with 1 equiv of $Cl_2C{=}PN(SiMe_3)_2$ in CH_2Cl_2 at room temperature results in the formation of *cis*-Cl(dppe)Pd[C(Cl)=PN(SiMe$_3$)$_2$] **(VI)**. This compound contains a chelating phosphine and did not rearrange further to form a phosphavinyl phosphonium compound, as in the formation of **IIIa**. The ^{31}P NMR spectrum of **VI** exhibits a signal for P(x) at $\delta = 230.1$ ppm, which is split into a doublet of doublets ($^3J_{P(x)P(b)} = 41.8$ Hz, $^3J_{P(x)P(a)} = 29.9$ Hz) by the two inequivalent phosphorus atoms in the

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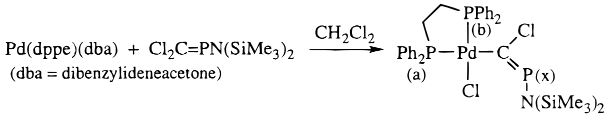

(5)

(VI)

chelating dppe ligand. The chemical shifts and coupling constants are quite similar to those in the previously characterized *cis*-$\mathrm{Cl(Ph_3P)_2Pt[C(Cl){=}PMes^*]}$ (P(x): δ 234.6 dd, $^3J_{\mathrm{P(x)P(b)}} = 45.4$ Hz, $^3J_{\mathrm{P(x)P(a)}} = 22.5$ Hz).[15]

Substitution Reactions of $\mathbf{Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]}$ (IIIa). The reaction (Scheme 2) of $\mathrm{Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]}$ **(IIIa)** with 1.1 equiv of $\mathrm{PPh_3}$ and 2 equiv of $\mathrm{KPF_6}$ in $\mathrm{CH_2Cl_2}$ at room temperature results in the substitution of the $\mathrm{Cl^-}$ ligand by $\mathrm{PPh_3}$ to form the cationic complex $\mathrm{[(Ph_3P)_2Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)}$ **(IV)** along with a small amount of $\mathrm{[Pd(PPh_3)_3Cl](PF_6)}$,[23] which could not be separated. Compound **IV** was also prepared by the addition of 1.1 equiv of $\mathrm{Cl_2C{=}PN(SiMe_3)_2}$ and 2 equiv of $\mathrm{KPF_6}$ to a cooled (−50 °C) solution of $\mathrm{Pd(PPh_3)_4}$ in $\mathrm{CH_2Cl_2}$. When compound **IV** is dissolved in MeCN at room temperature, one of the $\mathrm{PPh_3}$ ligands is substituted by MeCN to form $\mathrm{[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)}$ **(V)**. Compound **V** was also prepared by the addition of 1.1 equiv of $\mathrm{Cl_2C{=}PN(SiMe_3)_2}$ and 2 equiv of $\mathrm{KPF_6}$ to a cooled (−30 °C) solution of $\mathrm{Pd(PPh_3)_4}$ in MeCN, but is best prepared by substitution of the $\mathrm{Cl^-}$ ligand in $\mathrm{Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]}$ **(IIIa)** with MeCN, in the presence of $\mathrm{KPF_6}$. When compound **V** is isolated and dissolved in $\mathrm{CD_2Cl_2}$, its ^{1}H NMR spectrum shows a signal for the coordinated MeCN ligand. However, when **V** is dissolved in $\mathrm{CD_3CN}$, the signal for the coordinated MeCN group disappears, indicating that the coordinated MeCN ligand undergoes exchange with the $\mathrm{CD_3CN}$ solvent. When compound **V** is treated with PPNCl at room temperature, the MeCN ligand is immediately displaced by $\mathrm{Cl^-}$ to form compound **IIIa**. Compound **V** is air sensitive in solution, but only slightly air sensitive in the solid state. These substitution reactions are summarized in Scheme 2.

Compound **IV** was characterized by ^{31}P NMR spectroscopy and electrospray mass spectrometry, while compound **V** was characterized by ^{1}H NMR and ^{31}P spectroscopy, electrospray mass spectroscopy, elemental analysis, and X-ray diffraction studies. The peaks corresponding to P(x) in the ^{31}P NMR spectra of compounds **IV** and **V** are conveniently assigned from their proton-coupled ^{31}P NMR, in which the P(x) signals are sharp, but the $\mathrm{PPh_3}$ signals are broadened dramatically by the phenyl protons. The chemical shifts of P(x) in **IV** (δ 118.2) and **V** (δ 132.8) are similar to that for P(x) in **IIIa** (δ 124.4), which is consistent with an η^2-coordinated phosphavinyl phosphonium ligand in all of these complexes. As also found for **IIIa**, compounds **IV** and **V** both show characteristically large $^2J_{\mathrm{P(x)P(a)}}$ coupling constants (123.6 Hz in **IV** and 97.0 Hz in **V**) between the phosphonium substituent and the C=P phosphorus atom. In **IV**, the signal for P(x) is also split into a doublet of doublets by P(b) ($^2J_{\mathrm{P(x)P(b)}} = 5.1$ Hz) and P(c) ($^2J_{\mathrm{P(x)P(c)}} = 32.5$ Hz); the larger value for $^2J_{\mathrm{P(x)P(c)}}$ is consistent with $\mathrm{PPh_3}$ being situated trans to P(x).[27,28] The MeCN ligand in **V** exhibits a signal in the ^{1}H NMR spectrum at 1.66 ppm, which is 0.28 ppm upfield of free MeCN (δ 1.94) and similar to other N-coordinated MeCN ligands.[29]

Reactions of $\mathbf{Pd(PEt_3)_3}$ with $\mathbf{Cl_2C{=}PN(SiMe_3)_2}$. The reaction (Scheme 3) of $\mathrm{Pd(PEt_3)_3}$ with 1 equiv of $\mathrm{Cl_2C{=}PN(SiMe_3)_2}$ in hexanes at 0 °C results in the formation of the $\mathrm{PEt_3}$ analogue of **IIa**, *trans*-$\mathrm{Cl(Et_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]}$ **(IIb)**. Low-temperature (0 °C) ^{31}P NMR monitoring of the reaction shows the $\mathrm{PEt_3}$ analogue of **Ia**, $\mathrm{(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]}$ **(Ib)**, as the only observable intermediate in the reaction. When the solution reaches room temperature and is allowed to stir for 1 h, one of the C−Cl bonds in compound **Ib** undergoes oxidative addition to Pd to form **IIb** along with a small amount of $\mathrm{Pd(PEt_3)_2Cl_2}$.

When $\mathrm{Pd(PEt_3)_3}$ is reacted (Scheme 3) with 0.5 equiv of $\mathrm{Cl_2C{=}PN(SiMe_3)_2}$ in hexanes at 0 °C, ^{31}P NMR monitoring of the reaction solution again shows **Ib** as an intermediate along with free $\mathrm{Pd(PEt_3)_3}$. However, upon warming the solution to room temperature and stirring for 30 min, orange crystals of the 1:1 isomeric mixture of $\mathrm{Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl}$ **(VIIa-b)** begin to form. After sitting overnight, the crystals of **VIIa-b** are isolated and the remaining filtrate contains a small amount of dissolved **VIIa-b** along with **IIb**, which forms as a byproduct. To determine whether **IIb** is an intermediate that forms before **VIIa-b**, a sample of **IIb** was dissolved in hexanes and 1 equiv of $\mathrm{Pd(PEt_3)_3}$ was added; no reaction was evident after several hours of stirring at room temperature, which strongly suggests that **IIb** is not a precursor to **VIIa-b**.

Compounds **Ib** and **IIb** were characterized by ^{31}P NMR spectroscopy; the spectra of these compounds were quite similar to those of **Ia** and **IIa** (see Experimental Section), and assignments of the peaks were made in a similar manner (see results of **IIIa**). The 1:1 mixture of isomers **VIIa-b** was characterized by ^{31}P NMR spectroscopy and elemental analysis as well as by the similarity of the spectra of **VIIa-b** to those of **VIIIa-b** (see Experimental Section); the structure of **VIIIb** was determined by a partially successful X-ray diffraction study. The peaks corresponding to P(x) in the ^{31}P NMR of compounds **VIIa-b** are conveniently assigned by proton-coupled ^{31}P NMR spectroscopy, which shows that the P(x) signal remains sharp, while the $\mathrm{PEt_3}$ signals are broadened dramatically by the ethyl protons. A ^{31}P−^{31}P COSY experiment was undertaken which showed that the very complex ^{31}P NMR spectrum of **VIIa-b** results from the presence of two isomers as opposed to a large palladium cluster; it also allowed for the assignment of the P−P coupling constants. The exact nature of the different isomers in **VIIa-b** could not be determined but is likely due to E/Z isomers around the P=N double bond. E/Z isomers are known in iminophosphines (RN=PR)[30] and imino(methylene)-

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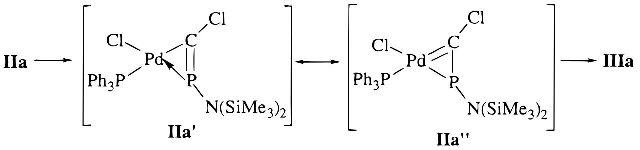
phosphoranes ($RN{=}P(R){=}CR_2$),[31] and the chemical shift difference in P(x) between **VIIa** (δ 194.9) and **VIIb** (δ 182.2) is similar to the difference found in the E/Z isomers around the P=N double bond in $Me_3SiN{=}P[N(SiMe_3)_2]{=}C(H)Me$ (δ 105.5, 98.1).[32] However, because of the complexity of the molecule, this assignment of the isomers must be regarded as tentative. The chemical shifts of P(x) in **VIIa** and **VIIb** may be compared with that in the uncoordinated imino(phosphoranylidenemethyl)phosphane compound $[(Me_2N)_3P](Me_3Si)C{=}P{=}N(SiMe_3)$ (δ 407.5 (C=P=N)),[33] which differs from the ligand in **VIIa-b** only by the $P(Me_2N)_3$ group on carbon instead of a PPh_3 group; the upfield shifts of P(x) in **VIIa-b** are indicative of η^2-coordination of the C=P double bond; such shifts are also known to occur upon η^2-coordination of phosphaalkenes.[1−4]

Reactions of $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ (VIIa-b). When the isomeric mixture of **VIIa-b** is reacted (Scheme 4) with 3 equiv of MeI in THF at room temperature for 24 h under anhydrous conditions, the color of the solution turns dark red and the only products are the iodide-substituted analogues (both isomers) of **VIIa-b**, $Pd(PEt_3)(I)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)I$ **(VIIIa-b).** Presumably, MeCl gas is liberated during this halide exchange reaction. A similar reaction using 3 equiv of NaI resulted in the formation of **VIIIa-b** in only 5 min, but the product was contaminated with $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ **(IX)**, which forms when **VIIa-b** is exposed to traces of water, even though the NaI was heated under vacuum for several hours to remove water. When the isomeric mixture of **VIIIa-b** is crystallized from Et_2O, isomer **VIIIb** crystallizes preferentially, although some of **VIIIa** is also present in the crystals. Compounds **VIIIa-b** were characterized by ^{31}P NMR spectroscopy, and the structure of compound **VIIIb** was partially determined by X-ray diffraction studies. Although the refinement of the structure of **VIIIb** is not suitable for publication (final *R* factor 9%), the connectivity of the molecule was unambiguously determined. The ^{31}P NMR spectrum of **VIIIa-b** is consistent with the structure obtained for **VIIIb**, and assignments were made as in the very similar compounds **VIIa-b** (see results of **VIIa-b**).

When a pure sample of **VIIa-b** is reacted (Scheme 4) with 2 equiv of degassed, deionized H_2O in THF at room temperature, the color darkens immediately and the ^{31}P NMR spectrum shows the formation of the phosphonio−methylene(oxo)phosphorane compound **IX** along with two singlets that are most likely due to palladium phosphine complexes. Although these byproducts were not identified, they were easily separated from **IX**. Compound **IX** was characterized by ^{31}P NMR spectroscopy, and FAB mass spectrometry, and the structure was determined by X-ray diffraction. The peak corresponding to P(x) at δ 80.0 in the ^{31}P NMR spectrum of **IX** is readily assigned by the proton-coupled ^{31}P NMR spectrum, in which the P(x) signal remains sharp, while the PEt_3 signals at δ 37.1 and 24.2 are broadened dramatically by coupling to the ethyl protons. In **IX**, the chemical shift of P(x) at δ 80.0 is upfield from the two known methylene(oxo)phosphoranes, $Mes^*P({=}O){=}CR(SiMe_3)$ (R = Ph, δ 153.7; R = $SiMe_3$, δ 161.1),[34] which are somewhat related to the ligand in **IX**, but without a phosphonio substituent on the C=P carbon. This upfield shift is consistent with the upfield shifts found in η^2-coordinated phosphaalkene compounds.[1−4] As in compounds **VIIa-b** and **VIIIa-b**, the coupling constants between the PEt_3 groups and the P(x) atom in **IX** are quite small ($^2J_{P(x)P(b)} = 11.0$ Hz, $^2J_{P(x)P(a)} = 0$ Hz), much smaller than the large coupling constant found in **IIIa** ($^2J_{P(x)P(a)} = 91.4$ Hz). This is most likely due to the pentavalent nature of the P(x) atom in **VIIa-b**, **VIIIa-b**, and **IX**, which allows for less phosphorus s-character in the bonding and results in smaller coupling constants.

Scheme 5



Discussion

$Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ (IIIa), $[(Ph_3P)_2Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (IV), and $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (V). In contrast to the reaction (eq 2) of $Pd(PPh_3)_4$ with $Cl_2C{=}PMes^*$ (Mes* = 2,4,6-tri-*tert*-butylphenyl)[16] which results in the migration of the Mes* group to carbon to form $Mes^*{-}C{\equiv}P$ and $Pd(PPh_3)_2Cl_2$ with no observed intermediates, the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$ results in the formation of the η^2-coordinated phosphavinyl phosphonium compound $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ **(IIIa)** via intermediates $(Ph_3P)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]$ **(Ia)** and *trans*-$Cl(Ph_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIa)**. This rearrangement is analogous to the reported reaction of an η^1-vinyl complex of palladium which rearranged upon heating to an η^2-vinyl phosphonium complex.[35] We previously obtained a nickel analogue **(3)** of **IIIa** in a reaction (eq 3) of $Ni(PPh_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$, but in that case the product was unstable and reacted further with another equivalent of $Ni(PPh_3)_4$ to generate the dinuclear phosphavinylidene phosphorane complex **(4)**.[17] However, compound **IIIa** is air stable and does not react with $Pd(PPh_3)_4$. The isomerization reaction of **IIa** to **IIIa** can be rationalized by proposing (Scheme 5) the rearrangement of the η^1-phosphavinyl **(IIa)** to an η^2-phosphavinyl (**IIa′** and **IIa″**) intermediate, which is attacked by PPh_3 to form the phosphavinyl phosphonium complex **IIIa**. The carbene−phosphido resonance structure **(IIa″)** is probably more favored than the alkyl−phosphine resonance form **(IIa′)** because the high-energy C=P double bond[36] is avoided; the electrophilic nature of the carbene-like carbon atom provides the driving force for nucleophilic attack by the PPh_3 group to form **IIIa**. This carbene-like resonance structure in the η^2-phosphavinyl ligand **(IIa″)** is precedented

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by the X-ray structure of a similar η^2-phosphavinyl complex of tungsten Cp(CO)$_2$W[η^2-C(Ph)=PPh{W(CO)$_5$}] which exhibited a W−C bond length (1.954(8) Å) that is typical of a W=C double bond.[37] A similar mechanism for this phosphine migration was proposed previously for the formation of the nickel analogue (**3**, eq 3) of **IIIa**.[17]

When Cl$_2$C=PN(SiMe$_3$)$_2$ is reacted with Pd(dba)(PPh$_3$)$_2$, the formation of **IIIa** occurs quantitatively under the same conditions in the same amount of time. In this case there is no excess PPh$_3$ present in the reaction, which suggests that the PPh$_3$ that attacks the C=P carbon atom in **IIa″** must have dissociated from palladium. Since dissociative mechanisms in square planar group 10 complexes are very rare, the most likely mechanism is an associative mechanism where the C=P phosphorus lone pair attacks above the square plane in **IIa** with loss of a PPh$_3$ ligand to generate **IIa′** and **IIa″**. When Pd(dba)(dppe) is used as the Pd(0) reagent, the reaction (eq 5) stops at the phosphavinyl compound *cis*-Cl(dppe)Pd[C(Cl)=PN(SiMe$_3$)$_2$] **(VI)**. Here, dissociation of one P-donor of the chelating phosphine ligand is more difficult, and an analogue of **IIIa** does not form. Compound **VI** does not react with PPh$_3$ and KPF$_6$ to generate an analogue of **IV** containing a dppe ligand in place of the two PPh$_3$ ligands on palladium, presumably because the chelating phosphine and chloride ligands in **VI** are not displaced easily enough to form an η^2-phosphavinyl intermediate.

The chloride ligand in compound **IIIa** is easily substituted (Scheme 2) by neutral ligands upon addition of KPF$_6$; stirring in MeCN results in formation of the cationic phosphavinyl phosphonium complex [(Ph$_3$P)(MeCN)Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)](PF$_6$) **(V)**, while addition of PPh$_3$ leads to [(Ph$_3$P)$_2$Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)](PF$_6$) **(IV)**. One of the palladium-coordinated PPh$_3$ ligands in **IV** is replaced by stirring in MeCN to generate **V**; the MeCN ligand in **V** is displaced by CD$_3$CN by stirring in CD$_3$CN, or by PPh$_3$ to generate **IV**, or by Cl$^-$ to generate **IIIa**. Thus, each of the compounds **IIIa**, **IV**, and **V** contains a labile ligand on palladium, which is evident in the electrospray mass spectra, which show the same highest molecular ion peak at *m/e* 870, corresponding to the fragment (Ph$_3$P)Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)]$^+$, generated by the loss of Cl$^-$, PPh$_3$, and MeCN from **IIIa**, **IV**, and **V**, respectively.

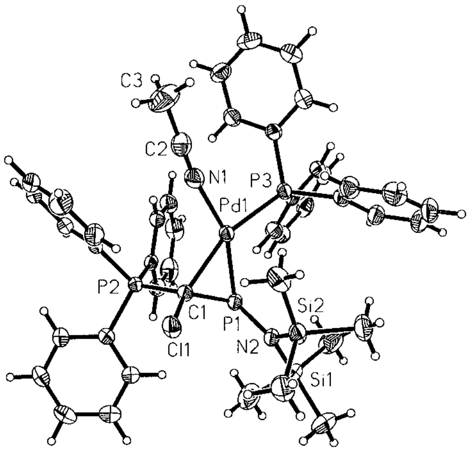
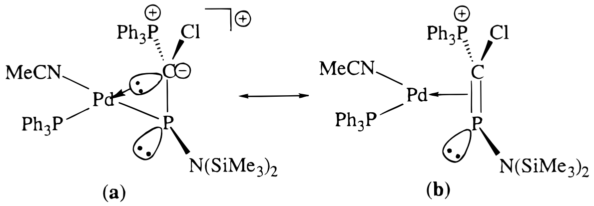


Figure 1. Thermal ellipsoid drawing of [(Ph$_3$P)(MeCN)Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)](PF$_6$) (**V**).

Scheme 6



(a) (b)

X-ray Crystal Structure of [(Ph$_3$P)(MeCN)Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)](PF$_6$) (V). A thermal ellipsoid drawing of **V** (Figure 1) shows that the palladium atom is in a planar environment as defined by the coordinating atoms of the PPh$_3$, MeCN, and [C(Cl)(PPh$_3$)=PR] ligands; the sum of angles around the palladium atom is 359.9°. The [C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] ligand is coordinated η^2 to palladium through the C(1) and P(1) atoms, with the Cl, PPh$_3$, and N(SiMe$_3$) groups bent back from planarity in the [C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] ligand; the sum of angles around C(1) involving P(1), P(3), and Cl(1) of 347.4° indicates that C(1) is roughly intermediate between sp^2 (360°) and sp^3 (328.5°) hybridization, which is similar to structural features of η^2-coordinated olefins and phosphaalkenes (for example, in Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$], the sum of angles around the C=P carbon is 343.5°).[4] The structure of **V** is similar to that of the nickel η^2-phosphavinyl phosphonium complex Cl(Ph$_3$P)Ni[η^2-C(H)(PPh$_3$)=PMes*] (**5**, eq 4).[17] The C(1)−P(1) distance in **V** (1.803(4) Å) is the same within error as that in the nickel complex Cl(Ph$_3$P)Ni[η^2-C(H)(PPh$_3$)=PMes*] **(5)** (1.796(5) Å);[17] both of these distances are much longer than the corresponding C=P distance in the free phosphavinyl phosphonium salt [(PPh$_3$)(H)C=PN(i-Pr)$_2$)](BF$_4$) (1.684(14) Å),[26] which is consistent with η^2-coordination of the phosphavinyl phosphonium ligand and is similar to the lengthening of C=P bonds that occurs upon η^2-coordination of phosphaalkenes.[1−4] The C(1)−P(2) distance in **V** (1.771(4) Å) is slightly longer than the C−PPh$_3$ distance in Cl(PPh$_3$)Ni[η^2-C(H)(PPh$_3$)=PMes*] **(5)** (1.742(5) Å); both of these distances are much longer than typical ylide C−P bond lengths, e.g., 1.661(8) Å in Ph$_3$P=CH$_2$,[38] but are shorter than the phosphonium-type C−PPh$_3$ distance in [(PPh$_3$)(H)C=PN(i-Pr)$_2$)](BF$_4$) (1.798(14) Å), indicating that there is more phosphonium (C−P$^+$) than ylidic (C$^-$−P$^+$) character in the C−PPh$_3$ bond in **V**. The Pd−P(1) distance in **V** (2.2688(11) Å) is significantly shorter than the Pd−P(3) distance (2.3451(11)). The bonding in **V** may be described as a mixture of two resonance structures (Scheme 6), analogous to those proposed for the bonding in Cl(Ph$_3$P)Ni[η^2-C(H)(PPh$_3$)=PMes*] **(5)**.[17] Resonance form **a** is an ylide−phosphido structure with a dative two-electron donation from C(1) and a phosphido-type covalent bond between P(1) and palladium, where the [C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] group donates three electrons to the 13-electron cationic metal fragment (Ph$_3$P)(MeCN)Pd$^+$. Resonance form **b** is an η^2-phosphavinyl phosphonium cation (1+) which donates two electrons

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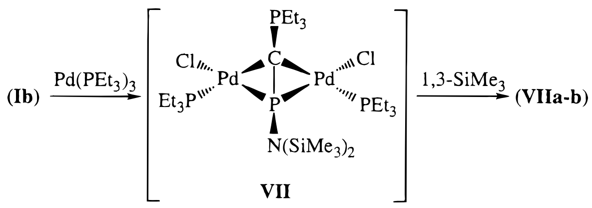
(37) Huy, N. H. T.; Fischer, J.; Mathey, F. *Organometallics* **1988**, *7*, 240.

(38) Bart, J. C. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 730.

Scheme 7

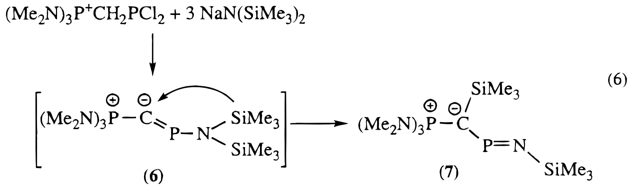


to a formally Pd(0) metal fragment. The somewhat long C(1)−P(2) distance argues for a contribution from form **b**, where the PPh_3 group on carbon has more phosphonium than ylide character.

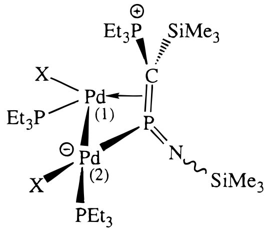
$Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ (VIIa-b) and $Pd(PEt_3)(I)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)I$ (VIIIa-b). The reaction of $Pd(PEt_3)_3$ with 1 equiv of $Cl_2C{=}PN(SiMe_3)_2$ (Scheme 3) in hexanes or CH_2Cl_2 resulted in the formation of *trans*-$Cl(Et_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIb)** through the intermediate $(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]$ **(Ib)**, as occurred in the reaction (Scheme 1) involving $Pd(PPh_3)_4$. However, **IIb** did not undergo PEt_3 migration from Pd to the C=P carbon, as in the PPh_3 case, to form a PEt_3 analogue of **IIIa**, even after stirring overnight followed by refluxing in hexanes for 4 h. A possible explanation is that the weaker coordinating ability of PPh_3 as compared with PEt_3 allows the dissociation of PPh_3, which results in the formation of **IIIa**; on the other hand, the PEt_3 ligands in **IIb** are so strongly bound that formation of the η^2-phosphavinyl intermediate analogous to **IIa′**, **IIa″** (Scheme 5) is unfavorable.

When the reaction of $Pd(PEt_3)_3$ is carried out with only 0.5 equiv of $Cl_2C{=}PN(SiMe_3)_2$ (Scheme 3) and warmed to room temperature, the reaction takes a different route, forming the dimeric complex $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ **(VIIa-b)**, in which a PEt_3 group and an $SiMe_3$ group have migrated to the C=P carbon atom. This reaction again goes through intermediate **Ib**, and a small amount of **IIb** forms as a byproduct. As mentioned in the Results, compound **IIb** is apparently not an intermediate in the formation of **VIIa-b**. Evidently, when 2 equiv of $Pd(PEt_3)_3$ are used in this reaction, **Ib** reacts with $Pd(PEt_3)_3$ to form **VIIa-b** before undergoing oxidative addition to form **IIb**. When the reaction of $Pd(PEt_3)_3$ with 0.5 equiv of $Cl_2C{=}PN(SiMe_3)_2$ is carried out and kept at −30 °C for one week as opposed to warming to room temperature above, the oxidative addition reaction prevails and compound **IIb** forms along with unreacted $Pd(PEt_3)_3$, with no formation of **VIIa-b**. Although **Ib** was the only observable intermediate in ^{31}P NMR spectra recorded during the formation of **VIIa-b**, a plausible intermediate to explain its formation (Scheme 7) is the dinuclear phosphavinylidene phosphorane complex $Pd_2Cl_2(PEt_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PEt_3){=}PN(SiMe_3)_2]$ **(VII)**.

Intermediate **VII** is analogous to the nickel complex $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**4**, eq 3) that was previously characterized by X-ray diffraction studies.[17] This intermediate must isomerize quickly to **VIIa-b** by undergoing a 1,3 $SiMe_3$ migration from nitrogen to carbon, a process that is well documented in the chemistry of phosphaalkenes[39] and amino methylene phosphoranes[40] and has also been proposed to occur (eq 6) in the formation of an imino(phosphoranylidenemethylene)phosphine **(7)** from a phosphavinylidene phosphorane intermediate **(6)**.[33] The proposed intermediate **(6)** is the same as the ligand in **VII**, but with a $P(Me_2N)_3$ group on carbon instead of PPh_3, while compound **7**, which was characterized by an X-ray diffraction study, is analogous to the ligand in **VIIa-b**, thus supporting **VII** as a reasonable intermediate that undergoes 1,3 $SiMe_3$ migration to form **VIIa-b**.



The isomeric mixture **VIIa-b** reacts (Scheme 4) with MeI or NaI to form the iodide-substituted isomeric mixture **VIIIa-b**. The structure of **VIIIb** was determined by X-ray diffraction studies, but the final refinement was unacceptable for publication. However, the connectivity was unambiguously determined and the bond lengths and angles were reasonable with respect to related structures. Because of the similarity of their ^{31}P NMR spectra, compounds **VIIa-b** and **VIIIa-b** are very likely isostructural. The $(Et_3P)(Me_3Si)C{=}P{=}NSiMe_3$ ligand in **VIIa-b** and **VIIIa-b** is best described as an η^2-coordinated phosphonio−methylene(imino)metallophosphorane ligand **(c)**, which is a zwitterionic structure with the positive charge on the phosphonium PEt_3 group and the minus charge on Pd(2). Both palladium atoms are then formally +1 with Pd(2) bonded covalently to the C=P phosphorus and Pd(1) bonded η^2 to the C=P double bond. If the phosphonium $(PEt_3)^+$ and $[(X)(PEt_3)Pd(2)]^-$ groups are mentally replaced with R-groups, this complex is then analogous to an η^2-coordinated methylene(imino)phosphorane. Compounds **VIIa-b** and **VIIIa-b** are the first to contain a phosphonio−methylene(imino)metallophosphorane ligand; they are also the first examples of complexes with an η^2-methylene(imino)phosphorane ligand, in general. An analogue, $[(Me_2N)_3P](Me_3Si)C{=}P{=}N(SiMe_3)$ (**7**, eq 6), of the free ligand $(Ph_3P)(Me_3Si)C{=}P{=}N(SiMe_3)$ in **VIIa-b** and **VIIIa-b**, except possessing a $P(NMe_2)_3$ group on the C=P carbon instead of PPh_3, is known,[33] but no attempts to coordinate it to a transition metal



(c)

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(39) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; pp 157−219.

(40) Boske, J.; Niecke, E.; Nieger, M.; Ocando, E.; Majoral, J. P.; Bertrand, G. *Inorg. Chem.* **1989**, *28*, 499.

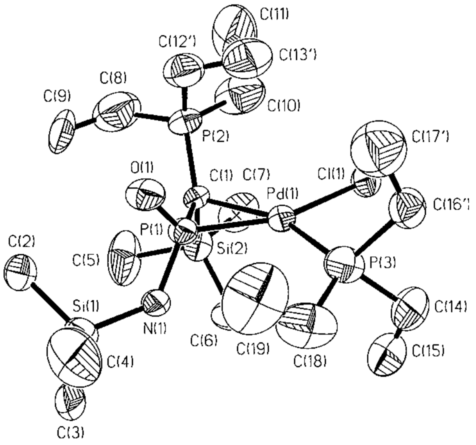
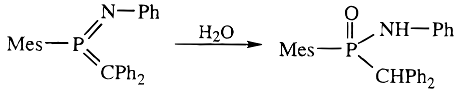


Figure 2. Thermal ellipsoid drawing of $Cl(Et_3P)Pd[\eta^2$-$C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (**IX**).

complex were reported. In light of the fact that the $(Ph_3P)(Me_3Si)C{=}P{=}N(SiMe_3)$ group has been coordinated for the first time in **VIIa-b** and **VIIIa-b**, it seems reasonable that the coordination chemistry of these types of ligands could be explored further, as the P═N bond and the lone pair electrons on nitrogen are also available for bonding. It is also reasonable to assume that the well-known class of methylene(imino)phosphoranes $(R_2C{=}P({=}NR)R)$[13] should show interesting coordination properties, especially with respect to coordination of the C═P double bond as in **VIIa-b** and **VIIIa-b**.

$Cl(Et_3P)Pd[\eta^2$-$C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (IX). The isomeric mixture of dimeric **VIIa-b** undergoes hydrolysis with even traces of water (Scheme 4) to form one isomer of the mononuclear compound $Cl(Et_3P)Pd[\eta^2$-$C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (**IX**). This is analogous to the known hydrolysis reaction (eq 7) of methylene(imino)phosphoranes $(R_2C{=}P({=}NR)R)$.[13] In

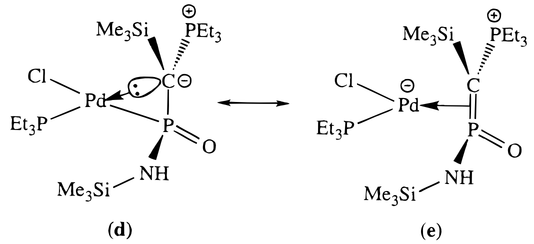


(7)

the formation of **IX**, the oxygen from the water adds to the phosphorus and a hydrogen adds to the nitrogen. The second hydrogen from the water presumably leaves with the Pd(PEt$_3$)Cl fragment, but the complex that forms was not isolated.

X-ray Crystal Structure of $Cl(Et_3P)Pd[\eta^2$-$C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (IX). The structure of **IX** exhibits an η^2-coordinated phosphonio−methylene(oxo)phosphorane $(Et_3P)(Me_3Si)C{=}P({=}O)NH(SiMe_3)$ ligand. The thermal ellipsoid drawing of **IX** (Figure 2) shows that the palladium atom is in a planar environment defined by the donor atoms of the PEt$_3$, Cl, and $(Et_3P)(Me_3Si)C{=}P({=}O)NH(SiMe_3)$ ligands; the sum of angles around the palladium atom is 360.2°. In contrast to the one structurally characterized methylene(oxo)phosphorane compound $[(SiMe_3)(Ph)C{=}P({=}O)Mes^*]$,[41] which has a trigonal planar geometry at phosphorus, the η^2-coordinated ligand in **IX** contains a pyramidalized C═P phosphorus atom (sum of angles around P(1) involving O(1), C(1), and N(1) is 342.3°). However, the sum of angles around C(1) involving P(1), P(2), and Si(2) is 357.3°, which suggests that C(1) is close to sp^2 hybridization. This contrasts with η^2-phosphaalkenes in which both the carbon and phosphorus are generally pyramidalized between sp^2 and sp^3 hybridization. The C(1)−P(1) distance in **IX** (1.787(6) Å) is much longer than the C═P distance in $[(Me_3Si)(Ph)C{=}P({=}O)Mes^*]$ (1.657(4) Å), which is indicative of η^2-coordination of the phosphonio−methylene(oxo)phosphorane ligand and is consistent with the lengthening of C═P bonds which occurs upon η^2-coordination of phosphaalkenes.[1−4] The P═O distance in **IX** (1.489(4) Å) is similar to that in $[(Me_3Si)(Ph)C{=}P({=}O)Mes^*]$ (1.458(3) Å). The C(1)−P(2) distance in **IX** (1.744(5) Å) is similar to the C−PPh$_3$ distance in $Cl(PPh_3)Ni[\eta^2$-$C(H)(PPh_3){=}PMes^*]$ (1.742(5) Å);[17] both of these distances are much longer than typical ylide C−P bond lengths, e.g., 1.661(8) Å in $Ph_3P{=}CH_2$,[38] but are shorter than the phosphonium C−PPh$_3$ distance in $[(PPh_3)(H)C{=}PN(i\text{-}Pr)_2)](BF_4)$ (1.798(14) Å),[26] suggesting that the C(1)−P(2) bond in **IX** has more phosphonium ($C{-}P^+$) than ylidic ($C^-{-}P^+$) character. The Pd−P(1) distance in **IX** (2.1696(13) Å) is significantly shorter than the Pd−P(3) distance (2.270(2) Å).

Scheme 8



The bonding in **IX** may be described as a mixture of two resonance structures as shown in Scheme 8. Resonance form **d** is an ylide−phosphido structure with a dative two-electron donation from C(1) and a phosphido-type covalent bond between P(1) and palladium, where the $(Et_3P)(Me_3Si)C{=}P({=}O)NH(SiMe_3)$ group acts as a three-electron donor to the 13-electron Pd(PEt$_3$)Cl fragment. Resonance form **e** is a zwitterionic structure, where the minus charge is located on palladium, with the η^2-phosphonio−methylene(oxo)phosphorane cation (1+) donating two electrons to a formally Pd(0) metal fragment. The somewhat long C(1)−P(2) distance argues for a contribution from form **e**, where the PPh$_3$ group on carbon has more phosphonium than ylide character. Although only two stable methylene(oxo)phosphoranes are known,[34,41] quite a few have been postulated as intermediates and characterized by trapping experiments.[13] Coordination of the phosphonio−methylene(oxo)phosphorane ligand in **IX** suggests that these compounds should have the ability to coordinate through the C═P bond in other transition metal complexes and may be a way of stabilizing these reactive compounds for further study.

Conclusion

In contrast to the reactions of $Pt(PR_3)_4$ or $Pd(PR_3)_4$ with $Cl_2C{=}PMes^*$ which result in the rearrangement of the aromatic Mes* group from phosphorus to carbon to generate $Mes^*{-}C{\equiv}P$ via phosphavinyl intermedi-

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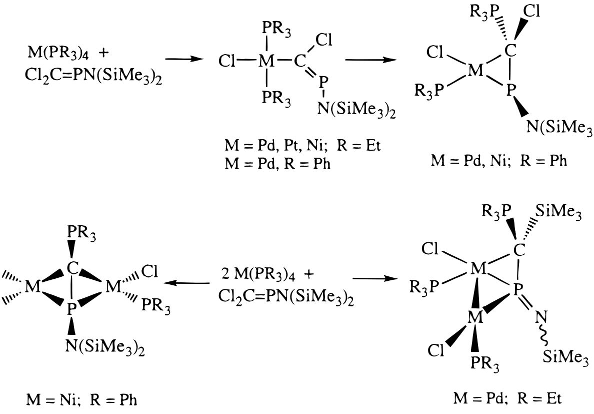
[41] Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 157.

ates,[15,16] the reactions of Pd(0) reagents with $Cl_2C{=}PN(SiMe_3)_2$ resulted in the formation of complexes containing new carbon−phosphorus multiply bonded ligands. The reaction (Scheme 1) of $Pd(PPh_3)_4$ with $Cl_2C{=}PN(SiMe_3)_2$ formed the phosphavinyl phosphonium complex $Cl(Ph_3P)Pd[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ **(IIIa)** via the η^2-phosphaalkene $(Ph_3P)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]$ **(Ia)** and the η^1-phosphavinyl *trans*-$Cl(Ph_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIa)**. The labile chloride ligand on palladium in **IIIa** was substituted (Scheme 2) by PPh_3 or MeCN in the presence of KPF_6 to generate $[(Ph_3P)_2Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ **(IV)** or $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ **(V)**, respectively. The structure of **V** was determined by X-ray diffraction studies, which confirmed the η^2-coordination of the $C(Cl)(PPh_3){=}PN(SiMe_3)_2$ ligand. When $Pd(PEt_3)_3$, instead of $Pd(PPh_3)_4$, was reacted (Scheme 3) with $Cl_2C{=}PN(SiMe_3)_2$, the phosphavinyl complex *trans*-$Cl(Et_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIb)** formed but did not rearrange to form a phosphavinyl phosphonium complex analogous to **IIIa**. However, when 2 equiv of $Pd(PEt_3)_3$ were reacted (Scheme 3) with $Cl_2C{=}PN(SiMe_3)_2$, the novel, dimeric phosphonio−methylene(imino)metallophosphorane complex $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ **(VIIa-b)** formed as a mixture of two isomers; its formation involved migration of a $SiMe_3$ group from nitrogen to carbon and a PEt_3 group from palladium to the C=P carbon. The chloride ligands in **VIIa-b** were substituted by iodide using MeI or NaI to generate $Pd(PEt_3)(I)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)I$ **(VIIIa-b)**; the structure of **VIIIb** was partially determined by X-ray diffraction studies. Compound **VIIa-b** also undergoes hydrolysis with traces of water to form the phosphonio−methylene(oxo)phosphorane complex $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ **(IX)**, the structure of which was determined by X-ray diffraction studies. The ligands in **VIIa-b**, **VIIIa-b**, and **IX** represent the first examples of coordinated methylene(imino, oxo)phosphorane ligands.

The results for Pd(0) obtained herein may be compared with those from reactions of Ni(0) and Pt(0) reagents with $Cl_2C{=}PN(SiMe_3)_2$, which in some cases gave much different results (Scheme 9).[17] When $M(PEt_3)_4$ was reacted with $Cl_2C{=}PN(SiMe_3)_2$, phosphavinyl complexes were observed with M = Pd, Pt, and Ni, and there was no evidence for PEt_3 migration to carbon. However, when $M(PPh_3)_4$ was reacted with $Cl_2C{=}PN(SiMe_3)_2$, only in the case of M = Pd was a phosphavinyl complex observed (Scheme 1), which underwent PPh_3 rearrangement upon warming to form a phosphavinyl phosphonium complex. In the case of M = Ni, a phosphavinyl intermediate was postulated, but only the phosphavinyl phosphonium complex (**3**, eq 3) was observed. Compound **3** was not isolated, but reacted with another equivalent of $Ni(PPh_3)_4$ to generate the novel dinuclear phosphavinylidene phosphorane complex (**4**, eq 3). In all of the reactions with $Cl_2C{=}PN(SiMe_3)_2$, there is no R-group rearrangement from phosphorus to carbon as in the reactions with $Cl_2C{=}PMes^*$.[15,16] Evidently, the presence of PPh_3 ligands favors the formation of the phosphavinyl phosphonium complexes, while PEt_3 tends to stabilize the phosphavinyl complexes.

Scheme 9



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Supporting Information Available: A fully labeled structural drawing of **V**, tables of non-hydrogen atomic coordinates and equivalent 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 **V** and **IX** (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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