Nickel Complexes Containing New Carbon−Phosphorus Unsaturated Ligands: First Examples of Phosphavinylidene−Phosphorane [$R_3P{=}C{=}PR'$] and Phosphavinyl Phosphonium [$C(H)(PR_3){=}P(R')$]$^+$ Ligands

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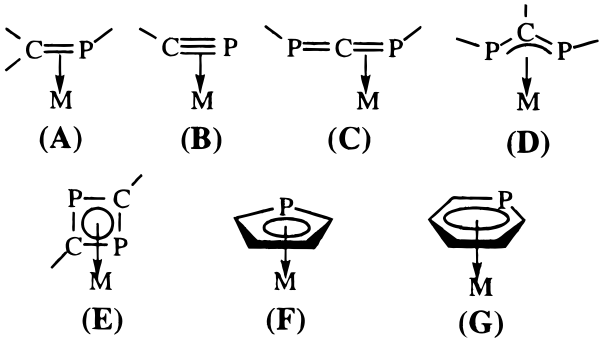
Received October 14, 1997

Oxidative-addition reactions of $Cl_2C{=}PN(SiMe_3)_2$ with 1:2 $Ni(COD)_2/PPh_3$, $Ni(PPh_3)_4$, or $(Ph_3P)_2Ni(C_2H_4)$ initially yields the phosphavinyl phosphonium complex $Cl(Ph_3P)Ni[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ (**IIa**). Addition of another equivalent of Ni(0) reagent to **IIa** results in the formation of the novel, dinuclear, phosphavinylidene−phosphorane complex $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**IIIa**); the structure of **IIIa** was established by X-ray diffraction and contains a $Ph_3P{=}C{=}PR'$ ligand bridged between two four-coordinate, planar nickel atoms in a butterfly arrangement with a Ni−Ni distance that is too long for a significant bonding interaction. The $Ph_3P{=}C{=}PR'$ ligand, which may be viewed as a phosphavinylidene (${=}C{=}PR$) ligand with a phosphine-donor substituent, acts as a six-electron donor to the two nickel atoms. This contrasts with the known diphosphaallene compounds of the types $R_3P{=}C{=}PR_3$ and $RP{=}C{=}PR$ that act as two-electron donor ligands. When the reaction of the Ni(0) reagent is performed with $Cl_2C{=}PMes^*$ (Mes* = 2,4,6-tri-*tert*-butylphenyl), the mononuclear phosphonio−phosphavinyl complex $Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (**Va**) forms. The structure of **Va** was established by X-ray diffraction and contains a $[C(H)(PR_3){=}P(R')]$ ligand that acts as a three-electron donor to the $Ni(PPh_3)Cl$ fragment. This structure also exhibits a puckered, boat-shaped supermesityl ring. Both **IIIa** and **Va** exhibit labile PPh_3 groups on nickel which are easily substituted with PEt_3, but the carbon-bound PPh_3 groups could not be substituted with PEt_3.

Introduction

Many recent advances have been made in the coordination chemistry of ligands containing carbon−phosphorus multiple bonds. There are numerous examples of phosphorus analogues of common unsaturated organic ligands which exhibit rich coordination chemistries due in part to the presence of the phosphorus lone electron pair. Examples of η^1- through η^6-coordinated phosphorus-substituted hydrocarbon ligands are known; representative examples include phosphaalkenes (**A**), phosphaalkynes (**B**), diphosphaallenes (**C**), diphosphaallyls (**D**), phosphacyclobutadienes (**E**), phosphacyclopentadienyls (**F**), and phosphabenzenes (**G**). The coordination chemistry of phosphaalkenes (**A**) and phosphaalkynes (**B**) has been reviewed,[1] as has the coordination chemistry of the cyclic phosphorus-substituted compounds of types **E**−**G**.[2] However, the coordination chemistry of diphosphaallenes (**C**) and diphosphaallyls (**D**) is much less developed.[3] Phosphorus ylides ($R'_2C{=}PR_3$), which are the tetracoordinate (σ^4) phosphorus analogues of phosphaalkenes, have been studied a great deal with respect to their utility in the Wittig reaction and have been studied to a lesser extent as ligands in transition-metal complexes.[4] Interestingly, the coordination chemistry of ylides, which is mainly limited to η^1-C-coordination,[4] is dramatically different than that of phosphaalkenes. There are also examples of σ^4-phosphorus analogues of diphosphaallenes, i.e., ($R_3P{=}C{=}PR_3$)[5] and diphosphaallyls ($[(R_3P)HC{=}PR_3]^+$),[6] as well as mixed σ^2,σ^4-diphosphaallyls $[(R_3P)HC{=}PR']^+$.[7−10] However, there are no examples



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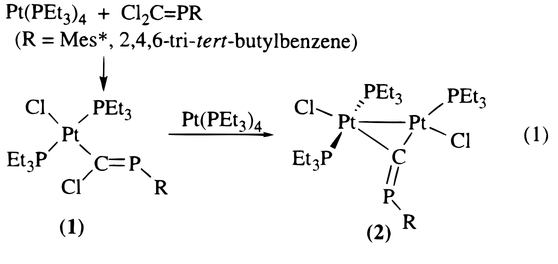
S0276-7333(97)00895-9 CCC: $15.00
Publication on Web 03/20/1998

of mixed σ^2,σ^4-diphosphaallenes ($R_3P{=}C{=}PR'$). Of these σ^4-diphosphaallene and diphosphaallyl compounds, only the σ^4,σ^4-diphosphaallenes ($R_3P{=}C{=}PR_3$) have been investigated as ligands,[11] exhibiting a preferential η^1-C-coordination as in the $R'_2C{=}PR_3$ compounds due to the strongly carbanionic character of the ylidic carbon.[4] The dramatic differences imparted by the σ^4-phosphorus should give these compounds interesting ligation properties that contrast with their σ^2-phosphorus counterparts, particularly in the case of the mixed σ^2,σ^4-diphosphaallyls $[(R_3P)HC{=}PR']^+$ and σ^2,σ^4-diphosphaallenes ($R_3P{=}C{=}PR'$) in which comparisons of bonding properties can be made directly between the σ^2 and σ^4 phosphorus atoms.

We recently succeeded in preparing the first example of a coordinated isocyaphide ($C{\equiv}PR$) ligand by oxidative addition of the C−X bond in the phosphavinyl complex (**1**; eq 1) to generate a diplatinum complex $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(Cl)]$ (**2**) containing a semibridging $C{\equiv}PR$ group.[12] More recently, Weber and co-workers reported the synthesis (eq 2) of a diiron complex containing a symmetrically bridged $C{\equiv}PR$ ligand (**3**) by a different route.[13]



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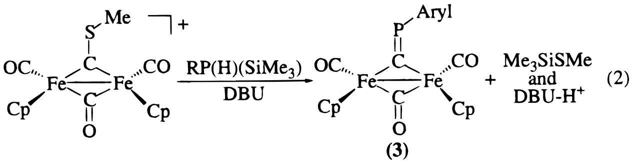
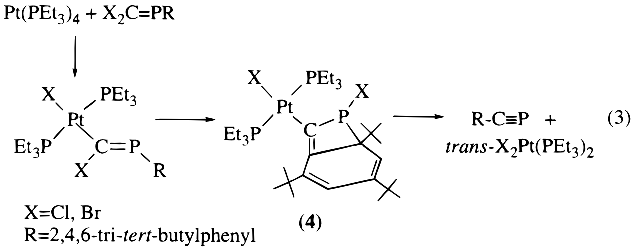


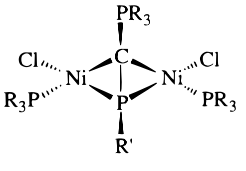
(3) (2)

We also reported an expanded study of the syntheses and reactions of the phosphavinyl compounds $X(R'_3P)_2M[C({=}PR)X]$ (M = Pt, Pd; X = Cl, Br; R′ = Ph, Et; R = 2,4,6-tri-*tert*-butylphenyl)[14] in order to assess the general usefulness of these starting materials for the preparation of complexes containing $C{\equiv}PR$ ligands according to eq 1. However, this approach was limited by the tendency of the R group to migrate from phosphorus to carbon, thereby forming the phosphaalkyne ($R{-}C{\equiv}P$, R = 2,4,6-tri-*tert*-butylphenyl). A detailed study of this migration in the case of R′ = Et showed that it proceeds through a novel bicyclic intermediate (**4**; eq 3).[14] Rearrangement of the 2,4,6-tri-*tert*-butylphenyl R group from phosphorus to carbon has also been reported in the conversion of $Li(Cl)C{=}PR$ to LiCl and $R{-}C{\equiv}P$[15−18] and in the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PR$ to give $Cl_2Pd(PPh_3)_2$ and $R{-}C{\equiv}P$.[19]

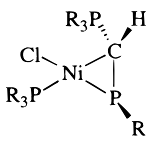


(4) (3)

To probe the generality of eq 1 for the synthesis of other complexes containing $C{\equiv}PR$ ligands, in the present paper we explore reactions of $Cl_2C{=}PR$ with Ni(0) complexes. We chose $Cl_2C{=}PR$ reactants with nonaromatic R groups in order to circumvent R-group rearrangement (eq 3). During the course of these studies, we isolated the first example of a mixed σ^2,σ^4-diphosphaallene or phosphavinylidene−phosphorane ligand that is bridged between two nickel atoms in a butterfly arrangement with the $R_3P{=}C{=}PR'$ ligand acting as a six-electron donor as in **H**. This ligand may be considered as a triphenylphosphine donor-stabilized phosphavinylidene ligand. Phosphavinylidene (${=}C{=}PR$) ligands can also be called isocyaphides ($C{\equiv}PR$) and are phosphorus analogues of isocyanides ($C{\equiv}NR$). Since there are no examples of donor-stabilized isocyanide $R_3P{=}C{=}NR$, carbonyl $R_3P{=}C{=}O$, or thiocarbonyl $R_3P{=}C{=}S$ ligands, the formation of the PPh_3-stabilized $C{\equiv}PR$ ligand in **H** illustrates that phosphorus analogues of isocyanides offer unique differences in bonding with respect to their well-studied isoelectronic analogues. We have also isolated the first example of a coordinated σ^2,σ^4-diphosphaallyl or phosphavinyl phosphonium ligand that is coordinated η^2 to a nickel atom with the $(R_3P)(H)C{=}PR'$ ligand acting as a three-electron donor as in **I**. The preparations of complexes of types **H** and **I** will be discussed, along with likely pathways of formation and chemical reactivity. Structure and bonding in these new ligands will also be discussed.



(H)



(I)

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 the appropriate drying agents

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under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium benzophenone ketyl, while hexanes and toluene were distilled over CaH_2. Acetone was distilled over anhydrous $MgSO_4$.

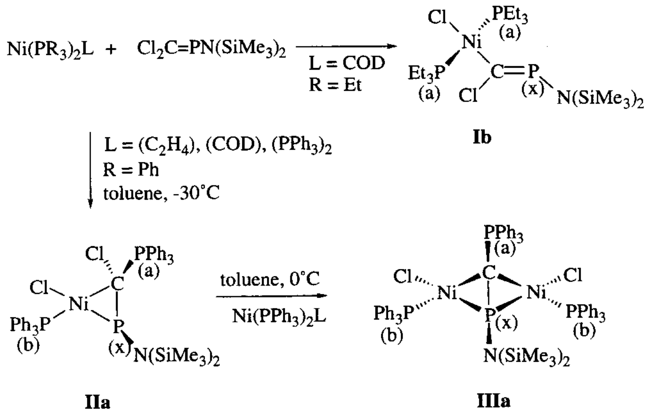
The ^1H NMR spectra of the compounds were recorded in C_6D_6 solvent unless otherwise specified using a Varian VXR 300-MHz spectrometer with TMS (δ 0.00 ppm) as the internal standard. The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a Bruker AC 200-MHz spectrometer using 85% H_3PO_4 (δ 0.00 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. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. The compounds $Ni(COD)_2$,[20] $(PPh_3)_2Ni(C_2H_4)$,[21] $Ni(PPh_3)_4$,[22] $Cl_2C{=}PN(SiMe_3)_2$,[23] $Cl_2C{=}PMes^*$,[24] and $Br_2C{=}PMes^*$[25] were prepared by literature methods. The phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh_3, which was recrystallized from MeOH.

Preparation of $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (IIIa) through Intermediate $Cl(Ph_3P)Ni[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ (IIa). Method A. To a cooled (−50 °C) slurry of $Ni(COD)_2$ (0.500 g, 1.82 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of PPh_3 (0.954 g, 3.64 mmol) and $Cl_2C{=}PN(SiMe_3)_2$ (0.249 g, 0.909 mmol) in toluene (10 mL). The dark red solution was allowed to warm slowly with stirring. A $^{31}P\{^1H\}$ NMR spectrum taken when the reaction had reached −20 °C after about 20 min showed **IIa** as an intermediate with no traces of **IIIa**. When the solution reached room temperature after about 1 h, **IIa** had converted almost completely to **IIIa**. The solution was filtered, and the solvent was removed under vacuum to yield a red-green oily solid. The residue was treated with 25 mL of Et_2O, and the flask was placed in a sonicating bath for 15 min to break up the solids. The dark green precipitate was collected on a medium porosity fritted glass filter, washed with 3 × 5 mL portions of Et_2O, and dried under vacuum. The solids were extracted with 25 mL of toluene, and after reducing the extract to one-fourth of its volume under vacuum, dark green crystals of **IIIa** (0.735 g, 69%) were obtained by slowly cooling the solution to −78 °C.

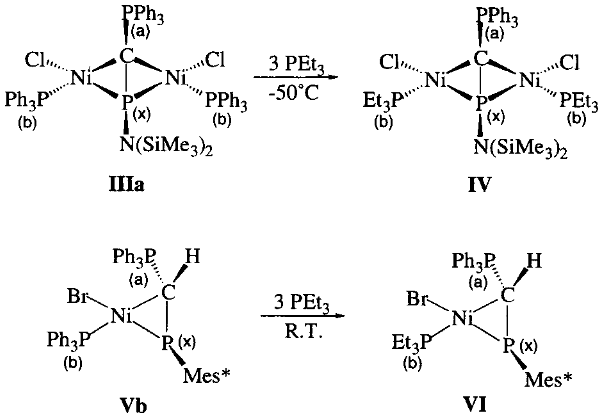
Method B. To a cooled (−50 °C) slurry of $Ni(PPh_3)_4$ (0.500 g, 0.451 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of $Cl_2C{=}PN(SiMe_3)_2$ (0.0619 g, 0.226 mmol) in toluene (5 mL). After the reaction mixture was warmed to room temperature with stirring over the course of 1 h, it was worked up as above, although the yield was about 10% less.

Method C. To a cooled (−50 °C) slurry of $(Ph_3P)_2Ni(C_2H_4)$ (0.500 g, 0.818 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of $Cl_2C{=}PN(SiMe_3)_2$ (0.112 g, 0.409 mmol) in toluene (5 mL). After the reaction mixture was warmed to room temperature with stirring over the course of 1 h, it was worked up as above to yield 0.369 g of **IIIa** (74%). $^{31}P\{^1H\}$ NMR (toluene, −50 °C) (see Scheme 1 for atom labels) for **IIa**: δ(P(x)) 103.7 (dd, $^2J_{P(x)P(b)}$ = 60.5 Hz, $^2J_{P(x)P(a)}$ = 24.7 Hz), δ(P(a)) 22.4 (d, $^2J_{P(a)P(x)}$ = 24.7 Hz), δ(P(b)) 19.0 (d, $^2J_{P(b)P(x)}$ = 60.5 Hz). For **IIIa**: δ(P(x)) 38.0 (dt, $^2J_{P(x)P(a)}$ = 57.8 Hz, $^2J_{P(x)P(b)}$ = 41.2 Hz), δ(P(a)) 22.3 (d, $^2J_{P(a)P(x)}$ = 57.8 Hz), δ(P(b)) 20.0 (d, $^2J_{P(b)P(x)}$ = 41.2 Hz). Anal. Calcd for $C_{61}H_{63}Cl_2N_1Ni_2P_4Si_2$ (**IIIa**): C, 62.17; H, 5.39; N, 1.19. Found: C, 62.08; H, 5.44; N, 1.25.

Scheme 1



Scheme 2



Reaction of $Ni(COD)_2$, PEt_3, and $Cl_2C{=}PN(SiMe_3)_2$; Characterization of $Cl(Et_3P)_2Ni[C(Cl){=}PN(SiMe_3)_2]$ (Ib). This reaction was carried out as in Method A above. The reagents used were $Ni(COD)_2$ (0.100 g, 0.364 mmol), PEt_3 (0.0859 g, 0.728 mmol), and $Cl_2C{=}PN(SiMe_3)_2$ (0.0498 g, 0.182 mmol) in toluene (10 mL). After the reaction mixture reached room temperature in about 1 h, a $^{31}P\{^1H\}$ NMR spectrum showed **Ib** as the main product. Compound **Ib** decomposed into nonisolable products after 1 day in solution and was characterized by $^{31}P\{^1H\}$ NMR spectroscopy as discussed in the Results. $^{31}P\{^1H\}$ NMR (toluene) (see Scheme 1 for atom labels): δ(P(x)) 221.7 (t, $^3J_{P(x)P(a)}$ = 27.5 Hz), δ(P(a)) 27.7 (d, $^3J_{P(a)P(x)}$ = 27.5 Hz).

Conversion of $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (IIIa) to $Ni_2Cl_2(PEt_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (IV). To a cooled (−78 °C) THF (5 mL) solution of **IIIa** (0.0500 g, 0.0424 mmol) was added PEt_3 (0.0151 g, 0.128 mmol). After the reaction mixture was warmed to −40 °C in 15 min with stirring, a $^{31}P\{^1H\}$ NMR spectrum showed that **IV** formed in essentially quantitative yield. Compound **IV** decomposed into nonisolable products after 1 day in solution and was characterized by $^{31}P\{^1H\}$ NMR spectroscopy as discussed in the Results. $^{31}P\{^1H\}$ NMR (THF, −40 °C) (see Scheme 2 for atom labels): δ(P(x)) 39.5 (dt, $^2J_{P(x)P(a)}$ = 54.3 Hz, $^2J_{P(x)P(b)}$ = 49.9 Hz), δ(P(a)) 20.3 (dt, $^2J_{P(a)P(x)}$ = 54.3 Hz, $^3J_{P(a)P(b)}$ = 5.5 Hz), δ(P(b)) 10.9 (dd, $^2J_{P(b)P(x)}$ = 49.9 Hz, $^3J_{P(b)P(a)}$ = 5.5 Hz).

Preparation of $Cl(PPh_3)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (Mes* = 2,4,6-Tri-*tert*-butylphenyl) (Va). Method A. To a cooled (−50 °C) slurry of $Ni(COD)_2$ (0.500 g, 1.82 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of PPh_3 (0.954 g, 3.64 mmol) and $Cl_2C{=}PMes^*$ (0.294 g, 0.909 mmol) in toluene (10 mL). After the reaction mixture was warmed slowly to room temperature with stirring, the dark red solution was filtered and the solvent was removed under vacuum. The deep red residue was dissolved in acetone (25 mL), and the

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acetone solution was reduced to one-fourth of its volume under vacuum and cooled to −78 °C to precipitate a mixture of dark red crystals of **Va** and yellow solids of $Ni(PPh_3)_3Cl$. The solids were isolated with a filter cannula and washed with 3 × 10 mL portions of acetone at 0 °C to remove the $Ni(PPh_3)_3Cl$ as a yellow solution. The remaining red solids were dissolved in a mixture of toluene (2 mL) and hexanes (6 mL) and cooled slowly to −78 °C to form red crystals of **Va**, which were isolated and dried under vacuum (0.387 g, 49% based on $Cl_2C{=}PMes^*$).

Method B. To a cooled (−50 °C) slurry of $Ni(PPh_3)_4$ (0.500 g, 0.451 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of $Cl_2C{=}PMes^*$ (0.0729 g, 0.226 mmol) in toluene (5 mL). After the reaction mixture was warmed slowly to room temperature with stirring, it was worked up as above, although the yield was much smaller.

Method C. To a cooled (−50 °C) slurry of $(Ph_3P)_2Ni(C_2H_4)$ (0.500 g, 0.818 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of $Cl_2C{=}PMes^*$ (0.132 g, 0.409 mmol) in toluene (5 mL). After the reaction mixture was warmed slowly to room temperature with stirring, it was worked up as above to yield 0.121 g of **Va** (34% based on $Cl_2C{=}PMes^*$). $^{31}P\{^1H\}$ NMR (toluene) (see eq 4 for atom labels): δ(P(a)) 25.5 (d, $^2J_{P(a)P(x)} = 33.1$ Hz), δ(P(x)) 21.6 (dd, $^2J_{P(x)P(a)} = 33.1$ Hz, $^2J_{P(x)P(b)} = 82.5$ Hz), δ(P(b)) 17.8 (d, $^2J_{P(b)P(x)} = 82.5$ Hz). Anal. Calcd for $C_{55}H_{60}Cl_1Ni_1P_3$ (**Va**): C, 72.74; H, 6.66. Found: C, 72.60; H, 6.42.

Preparation of Br(PPh$_3$)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (Vb). To a cooled (−50 °C) slurry of $Ni(COD)_2$ (0.500 g, 1.82 mmol) in toluene (10 mL) was added a cooled (−50 °C) solution of PPh_3 (0.954 g, 3.64 mmol) and $Br_2C{=}PMes^*$ (0.375 g, 0.909 mmol) in toluene (10 mL). After the reaction mixture was warmed slowly to room temperature with stirring, the dark red solution was filtered and the solvent was reduced to 5 mL under vacuum. The deep red solution was treated with hexanes (40 mL) and filtered, and crystals of **Vb** (0.295 g, 35% based on $Br_2C{=}PMes^*$) were obtained by cooling the filtrate slowly to −78 °C. $^{31}P\{^1H\}$ NMR (toluene) (see eq 4 for atom labels): δ(P(a)) 26.2 (d, $^2J_{P(a)P(x)} = 30.2$ Hz), δ(P(x)) 23.1 (dd, $^2J_{P(x)P(a)} = 30.2$ Hz, $^2J_{P(x)P(b)} = 85.2$ Hz), δ(P(b)) 19.2 (d, $^2J_{P(b)P(x)} = 85.2$ Hz).

Preparation of Br(Cy$_3$P)Ni[η^2-C(H)(PCy$_3$)=P(Mes*)] (Vc). This reaction was carried out as in the preparation of **Vb** above. The reagents used were $Ni(COD)_2$ (0.200 g, 0.727 mmol), tricyclohexylphosphine (PCy_3) (0.408 g, 1.45 mmol) and $Br_2C{=}PMes^*$ (0.150 g, 0.364 mmol) in toluene (10 mL). After the reaction mixture was warmed slowly to room temperature with stirring, the lilac-colored solution was filtered. Compound **Vc** could not be isolated pure as it decomposed during attempted crystallization and was characterized by $^{31}P\{^1H\}$ NMR spectroscopy as discussed in the Results. $^{31}P\{^1H\}$ NMR (toluene): δ(P(b)) 32.2 (d, $^2J_{P(b)P(x)} = 55.0$ Hz), δ(P(a)) 30.1 (d, $^2J_{P(a)P(x)} = 16.5$ Hz), δ(P(x)) 5.6 (dd, $^2J_{P(x)P(b)} = 55.0$ Hz, $^2J_{P(x)P(a)} = 16.5$ Hz).

^{13}C-Labeling Studies of Cl(Ph$_3$P)Ni[η^2-C(H)(PPh$_3$)=P-(Mes*)] (Va). The compound $Cl_2{}^{13}C{=}PMes^*$ was prepared by substituting labeled $^{13}CCl_4$ for CCl_4 in the literature preparation. This compound was then used to prepare $Cl(Ph_3P)Ni[\eta^2\text{-}^{13}C(H)(PPh_3){=}P(Mes^*)]$ by using the procedure in Method A above. $^{31}P\{^1H\}$ NMR (toluene) (see eq 4 for atom labels): δ(P(a)) 25.5 (dd, $^2J_{P(a)P(x)} = 33.1$ Hz, $^2J_{CP} = 30.7$ Hz), δ(P(x)) 21.6 (ddd, $^2J_{P(x)P(a)} = 33.1$ Hz, $^2J_{P(x)P(b)} = 82.5$ Hz, $^1J_{CP} = 93.5$ Hz), δ(P(b)) 17.8 (dd, $^2J_{P(b)P(x)} = 82.5$ Hz, $^1J_{CP} = 57.2$ Hz). $^{13}C\{^1H\}$ NMR (toluene): δ(C=P) 24.3 (ddd, $^1J_{CP(x)} = 93.5$ Hz, $^1J_{CP(b)} = 57.2$ Hz, $^2J_{CP(a)} = 30.7$ Hz). ^{13}C NMR (toluene): δ(C=P) 24.3 (dddd, $^1J_{CH} = 145.8$ Hz, $^1J_{CP(x)} = 93.5$ Hz, $^1J_{CP(b)} = 57.2$ Hz, $^2J_{CP(a)} = 30.71$ Hz).

Conversion of Br(Ph$_3$P)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (Vb) to Br(Et$_3$P)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (VI). To a THF solution of compound **Vb** (0.050 g, 0.0545 mmol) in an NMR tube was added 1 equiv of PEt_3 (8 μL) at room temperature. Compound **Vb** was converted immediately and completely to compound **VI**, which was characterized by $^{31}P\{^1H\}$ NMR spectroscopy as described in the Results. Addition of two more equivalents of PEt_3 (16 μL) did not cause further change. $^{31}P\{^1H\}$ NMR (THF) (see Scheme 2 for atom labels): δ(P(x)) 22.5 (dd, $^2J_{P(x)P(b)} = 30.2$ Hz, $^2J_{P(x)P(a)} = 90.5$ Hz), δ(P(a)) 18.5 (d, $^2J_{P(a)P(x)} = 90.5$ Hz), δ(P(b)) −5.5 (d, $^2J_{P(b)P(x)} = 30.2$ Hz).

Table 1. Crystal and Data Collection Parameters for Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ-η^2:η^2-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIa) and Cl(Ph$_3$P)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (Va)

	IIIa	Va
formula	$C_{75}H_{79}Cl_2NNi_2P_4Si_2$	$C_{58.50}H_{64}ClNiP_3$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.904(2)	10.7005(8)
b, Å	17.073(3)	12.968(1)
c, Å	18.936(3)	20.350(2)
α, deg	86.42(1)	74.537(1)
β, deg	86.60(2)	83.690(1)
γ, deg	79.24(2)	68.106(1)
V, Å^3	3452(1)	2525.1(4)
Z	2	2
d_{calc}, g/cm^3	1.311	1.255
cryst size, mm	0.25 × 0.12 × 0.03	0.4 × 0.34 × 0.02
μ, mm^{-1}	2.921	0.570
data collection instrument	Siemens P4RA	Siemens SMART
radiation (monochromated in incident beam)	Cu Kα (λ = 1.54178 Å)	Mo Kα (λ = 0.71073 Å)
temp, K	213(2)	173(2)
scan method	$2\theta-\theta$	area detector, ω-frames
data collection range, θ, deg	2.34−56.82	1.75−24.11
no. of data collected	9814	10 481
no. of total unique data	9227	7384
with $I \geq 2\sigma(I)$	9207	5879
no. of param refined	840	613
trans factors; max/min	0.78/0.55	0.818/0.649
R^a ($I > 2\sigma(I)$)	0.0699	0.0622
$R_w{}^b$ ($I > 2\sigma(I)$)	0.1753	0.1378
quality of fit indicator^c	1.052	1.090
largest peak, e/Å^{-3}	0.642	0.610

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

X-ray Crystallographic Study of Ni$_2$Cl$_2$(PPh$_3$)$_2$[μ_2-η^2:η^2-C(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIa). Diffraction-quality crystals of **IIIa** were obtained by recrystallization from toluene at −78 °C. Data collection and reduction information are given in Table 1. A dark green crystal of **IIIa** was mounted on a glass fiber for data collection. Cell constants were determined from a set of 25 reflections found by a random search routine. 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 a series of ψ-scans using the semiempirical method was applied. The space group $P\bar{1}$ was unambiguously determined by intensity statistics.[26] 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 toluene molecule is disordered over two partially occupied sites. The phenyl groups of the triphenylphosphines were used as a model to restrain C−C interatomic distances within both unique toluene solvent molecules. A secondary crystallite was unavoidably attached to the specimen used for data collection. An unsuccessful attempt was made to determine its orientation so a

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Ni_2Cl_2(PPh_3)_2[\mu\text{-}\eta^2\text{:}\eta^2C(PPh_3){=}PN(SiMe_3)_2]$ (IIIa)[a]

Distances

Ni(1)−Ni(2)	2.966(7)	Ni(2)−C(1)	2.036(7)	C(1)−P(2)	1.709(7)
Ni(1)−C(1)	1.983(7)	Ni(2)−P(1)	2.103(2)	P(1)−N(1)	1.684(6)
Ni(1)−P(1)	2.133(2)	Ni(2)−P(4)	2.195(2)	N(1)−Si(1)	1.773(6)
Ni(1)−P(3)	2.202(2)	Ni(2)−Cl(2)	2.205(2)	N(1)−Si(2)	1.795(6)
Ni(1)−Cl(1)	2.231(2)	C(1)−P(1)	1.707(7)		

Bond Angles

P(1)−C(1)−P(2)	144.4(4)	C(1)−Ni(2)−P(4)	162.4(2)
C(1)−Ni(1)−P(1)	48.8(2)	C(1)−Ni(2)−Cl(2)	104.2(2)
C(1)−Ni(1)−P(3)	158.1(2)	P(1)−Ni(2)−Cl(2)	152.57(9)
C(1)−Ni(1)−Cl(1)	101.5(2)	P(4)−Ni(2)−Cl(2)	93.41(8)
P(1)−Ni(1)−Cl(1)	147.54(10)	P(1)−Ni(2)−P(4)	113.85(9)
P(3)−Ni(1)−Cl(1)	94.01(9)	P(1)−N(1)−Si(1)	121.7(3)
P(1)−Ni(1)−P(3)	118.28(9)	P(1)−N(1)−Si(2)	119.3(3)
C(1)−Ni(2)−P(1)	48.7(2)		

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (Va)[a]

Distances

C(1)−P(1)	1.796(5)	Ni−Cl	2.2338(12)	C(13)−C(14)	1.389(6)
C(1)−P(2)	1.742(5)	P(1)−C(11)	1.892(4)	C(14)−C(15)	1.391(6)
Ni−C(1)	1.977(5)	C(1)−H(1)	0.86(4)	C(15)−C(16)	1.394(6)
Ni−P(1)	2.1793(13)	C(11)−C(12)	1.421(6)	C(16)−C(11)	1.432(6)
Ni−P(3)	2.1783(14)	C(12)−C(13)	1.393(6)		

Bond Angles

P(1)−C(1)−P(2)	118.5(3)	C(11)−C(12)−C(13)	118.5(4)
C(1)−Ni−P(1)	50.92(13)	C(12)−C(13)−C(14)	123.0(4)
C(1)−Ni−P(3)	157.11(13)	C(13)−C(14)−C(15)	116.4(4)
C(1)−Ni−Cl	105.68(13)	C(14)−C(15)−C(16)	123.1(4)
P(1)−Ni−P(3)	106.98(5)	C(15)−C(16)−C(11)	118.1(4)
P(1)−Ni−Cl	156.24(5)	C(16)−C(11)−C(12)	117.8(4)
P(3)−Ni−Cl	95.68(5)		

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

twin law could be applied. However, eight reflections which had $F_o^2 \gg F_c^2$ were removed from the least-squares refinement, reducing R1 by about 2%. Selected bond distances and bond angles are given in Table 2.

X-ray Crystallographic Study of $Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (Va). Diffraction-quality crystals of **Va** were obtained by recrystallization at −78 °C in acetone. Data collection and reduction information are given in Table 1. A dark red crystal of **Va** was mounted on a glass fiber for data collection. An initial set of cell constants was calculated from 50 reflections taken from three sets of 20 frames. Final cell constants were calculated from a set of 4943 strong reflections taken during the data collection. The space group $P\bar{1}$ was unambiguously determined by systematic absences and intensity statistics.[26] 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 0.87 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, except for the C═P hydrogen atom (H(1)), which was refined as an independent atom. PLATON/SQUEEZE was used to remove the effects of the disordered toluene solvent molecule on the data.[27] This solvent void was approximately 216.4 Å^3 or 8.6% of the total volume. A total of 41.1 electrons were located in the disordered void, and the refinement improved by 1.1% after applying the program. Selected bond distances and bond angles are given in Table 3.

Results

Reactions of Ni(0) Complexes with $Cl_2C{=}PN(SiMe_3)_2$. The reactions (Scheme 1) of 0.5 equiv of $Cl_2C{=}PN(SiMe_3)_2$ with 1:2 $Ni(COD)_2/PPh_3$, $Ni(PPh_3)_4$, or $(Ph_3P)_2Ni(C_2H_4)$ in toluene at −78 °C produce $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**IIIa**) in 69−74% yield. The reaction with $(Ph_3P)_2Ni(C_2H_4)$ (Method C) is preferred because it produces fewer impurities and gives slightly higher yields. Low-temperature (−30 °C) ^{31}P NMR monitoring shows complex **IIa** as the only observable intermediate in these reactions. A 1:1 stoichiometric reaction of $(Ph_3P)_2Ni(C_2H_4)$ with $Cl_2C{=}PN(SiMe_3)_2$ quantitatively forms **IIa** at −30 °C. However, complex **IIa** could not be isolated and decomposes to unidentified products in solution at room temperature. Formation of **IIIa** occurs upon addition of another equivalent of $(Ph_3P)_2Ni(C_2H_4)$ to the solution of **IIa** at 0 °C. In this reaction, the remaining C−Cl bond in **IIa** is oxidatively added to $(Ph_3P)_2Ni(C_2H_4)$, resulting in the formation of **IIIa**. Complex **IIIa** is oxygen-sensitive in the solid state and in solution but does not react with water; it is thermally sensitive and decomposes when heated above 30 °C.

Compounds **IIa** and **IIIa** were characterized by $^{31}P\{^1H\}$ NMR spectroscopy; the structure of **IIIa** was established by X-ray diffraction studies. The ^{31}P NMR spectrum of **IIIa** was collected at −50 °C, as signal broadening occurred at room temperature. Excess PPh_3 present in solution enhanced this broadening, and at room temperature the signal for free PPh_3 disappeared. This is most likely due to phosphine exchange, although detailed studies were not carried out. Compound **IIIa**

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(27) PLATON: Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

exhibits a ^{31}P NMR spectrum that is consistent with the structural data. A proton-coupled ^{31}P NMR spectrum shows the peak at δ 38.0 as a sharp doublet of triplets, which allows assignment of this peak to the C=PR phosphorus P(x), while the other two peaks are broadened due to coupling with phenyl protons and are assigned as PPh_3 groups. The characteristic doublet-of-triplets splitting pattern for P(x) allows for unambiguous assignments of the peaks; the doublet arises from splitting by the carbon-bound phosphine P(a) at δ 22.3 with $^2J = 57.8$ Hz, and the triplet is caused by the two equivalent nickel phosphines P(b) at δ 20.0 with $^2J = 41.2$ Hz. Although it is not possible to compare the ^{31}P NMR properties of **IIIa** with uncoordinated $R_3P{=}C{=}PR$ ligands since they are unknown, some comparisons with similar compounds can be made. The chemical shift of δ 38.0 for P(x) in **IIIa** is significantly upfield from that of the phosphaalkene $Cl_2C{=}PN(SiMe_3)_2$ (δ 251.7 ppm)[23] and the phosphavinyl phosphonium salt $[(Ph_3P)(H)C{=}PN(i\text{-}PR)_2]^+$ (δ 303.5 ppm for C=P).[7] This is consistent with similar dramatic upfield shifts which occur upon η^2-coordination of C=P double bonds; for example, $Ni(PMe_3)_2[\eta^2\text{-}(Me_3Si)_2C{=}PCH(SiMe_3)_2]$ (δ 23.4 ppm for C=P) is 380 ppm upfield from the free phosphaalkene $(Me_3Si)_2C{=}PCH(SiMe_3)_2$ (δ 404 ppm).[28] The coupling constant of $^2J = 57.8$ Hz between the C=P phosphorus P(x) and the carbon-bound phosphine P(a) in **IIIa** is smaller than values found for free phosphavinyl phosphonium salts, e.g., $^2J_{P-P} = 124.6$ Hz in $[(Ph_3P)(H)C{=}PN(i\text{-}PR)_2]^+$, which also contains an $R_3P{-}C{=}PR$ linkage.[7] However, in **IIIa**, the C=P phosphorus P(x) has sp^3-like character, which allows for less s-character in the bonding to carbon and would then result in a smaller coupling constant between P(x) and P(a). An even smaller $^2J_{P-P}$ value of 10.9 Hz was reported in the η^2-diphosphaallene complex $[(Ph_3P)_2Pt(\eta^2\text{-}RP{=}C{=}PR)]$[29] (R = tri-*tert*-butylbenzene) which contains an RP=C=PR unit with one of the C=P bonds coordinated. The coupling constant of $^2J = 41.2$ Hz in **IIIa** between the C=P phosphorus P(x) and the two equivalent nickel phosphines P(b) that are located cis to P(x) is slightly larger than the coupling constant of $^2J_{P-P} = 28.6$ Hz between P(x) and the PMe_3 group that is cis to it in $Ni(PMe_3)_2[\eta^2\text{-}(Me_3Si)_2C{=}PCH(SiMe_3)_2]$,[28] most likely because the P(x) lone pair is involved in bonding to the nickel atoms in **IIIa**, which allows for more s-character from phosphorus in the P(x)−Ni bonds.

The ^{31}P NMR spectrum of **IIa** is similar to that of the analogous compound **Va** (eq 4). The peak at δ 103.7 ppm is assigned to the C=PR phosphorus P(x), since a proton-coupled ^{31}P NMR spectrum showed this peak as a sharp doublet of doublets, while the peaks at δ 22.4 and 19.0 ppm were broadened by proton coupling, indicative of PPh_3 groups. The peak for P(x) in **IIa** is 82.1 ppm downfield from the corresponding peak for P(x) in **Va**. This may be partially due to the different R group on phosphorus or the proton on the carbon in **Va** instead of a chloride in **IIa**. However, a comparison of the ^{31}P NMR spectra of two phosphaalkenes with different substituents that correspond to the different C- and P-substituents in **IIa** and **Va**, $Cl_2C{=}PN(SiMe_3)_2$ (δ 251.7 ppm)[23] and (Cl)(H)C=PMes* (δ 245 ppm),[30] shows that changes in these particular substituents do not necessarily impart large changes on the ^{31}P NMR chemical shifts. A better explanation for the large differences in chemical shifts between **IIa** and **Va** is that the configuration around the C=P bond in **IIa** (*Z*) is different than that which was determined by X-ray diffraction for **Va** (*E*). It is well-documented that the *E* and *Z* configurations of phosphaalkenes can have a large effect on the ^{31}P chemical shift of the C=P phosphorus, although it is not possible to predict the relative shifts of the isomers.[31] An illustrative example is the phosphaalkene compound $[(Ph)(Me_3Si)N]C(Ph){=}P(Ph)$ in which the *E* isomer has a chemical shift of δ 225 ppm and the *Z* isomer is at δ 144 ppm.[32] Further evidence for the different configurations in **IIa** and **Va** is the appreciably smaller value of $^2J_{P(x)P(a)} = 60.5$ Hz in **IIa** than that ($^2J_{P(x)P(a)} = 82.5$ Hz) in **Va**. According to the cis rule in phosphaalkenes, substituents that are located cis to the phosphorus lone pair show larger couplings to the C=P phosphorus atom,[33] as is the case in the *E* configuration in **Va**. The value of $^2J_{P(x)P(a)}$ in **IIa** (60.5 Hz) is also quite similar to that in **IIIa** (57.8 Hz), in which the carbon-bound PPh_3 group and the $N(SiMe_3)_2$ group are arranged in a *Z* configuration as well.

In contrast to the reactions above with triphenylphosphine as the ligand, when a 1:2 $Ni(COD)_2/PEt_3$ mixture was reacted with $Cl_2C{=}PN(SiMe_3)_2$, complex **Ib** formed (Scheme 1). This compound did not react further to form the triethylphosphine analogues of **IIa** or **IIIa**, even when 2 equiv of the Ni(0) reagent were added. However, all attempts to isolate **Ib** resulted in decomposition to unidentified products. The ^{31}P NMR spectrum of compound **Ib**, δ 221.7 (t, $^3J_{PP} = 27.5$ Hz, C=P−R), 27.7 (d, $^3J_{PP} = 27.5$ Hz, Ni−PEt_3), is quite characteristic of a phosphavinyl structure (Scheme 1) and is very similar to that of a platinum analogue $Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$, δ 234.2 (t, $^3J_{PP} = 24.7$ Hz, C=P−R), 15.0 (d, $^3J_{PP} = 24.7$ Hz, Pt−PEt_3), that was characterized previously by X-ray diffraction studies.[14]

Reactions of Ni(0) Complexes with $X_2C{=}PMes^*$ (X=Cl, Br). The reactions (eq 4) of 0.5 equiv of $X_2C{=}PMes^*$ (X = Cl, Br) with 1:2 $Ni(COD)_2/PPh_3$, $Ni(PPh_3)_4$, or $(Ph_3P)_2Ni(C_2H_4)$ in toluene at −78 °C produce $X(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (**Va**, X = Cl; **Vb**, X = Br) in moderate yields, along with a roughly equimolar amount of $Ni(PPh_3)_3X$. This Ni(I) compound was characterized by X-ray diffraction studies as the acetone solvate $(Ph_3P)_3ClNi{\cdot}(Me_2C{=}O)$, but the structure of a toluene solvate of the same compound was reported previously.[34] The preparation of **Va** using $Ni(COD)_2$ and PPh_3 (Method A) is preferred because of the higher yield. The 2:1 metal complex to $X_2C{=}PMes^*$ stoichiometry is necessary to optimize the yield of

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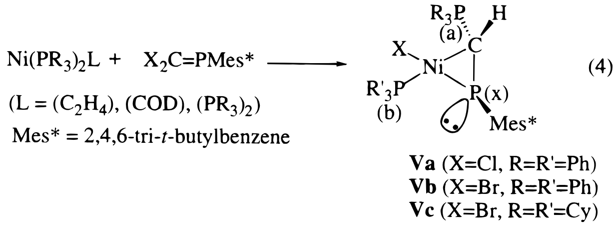

(4)

product. When only 1 equiv of metal complex is added, unreacted $X_2C{=}PMes^*$ remains in solution while all of the Ni(0) reagent is consumed. Compounds **Va** and **Vb** are moderately air-stable in the solid state but air-sensitive in solution. A similar reaction of 1:2 $Ni(COD)_2$/tricyclohexylphosphine (PCy_3) with 0.5 equiv of $Br_2C{=}PMes^*$ gave an analogous product (**Vc**), which was characterized by its ^{31}P NMR spectrum.

Compounds **Va**−**c** were characterized by $^{31}P\{^1H\}$ NMR spectroscopy; the structure of **Va** was established by X-ray diffraction studies. A preliminary X-ray-determined structure for **Vb** was also obtained and showed that it was isostructural with **Va**. However, due to disordered solvent molecules, the final refinement was unacceptable for publication. Compound **Va** exhibits a ^{31}P NMR spectrum that is consistent with the structural data. The signal at δ 21.6 is assigned to P(x) based on a proton-coupled ^{31}P spectrum which showed this peak as a sharp doublet of doublets, while the peaks at δ 25.5, assigned to P(a), and 17.8, assigned to P(b), were broadened due to phenyl proton couplings. The chemical shift of P(x) is significantly upfield from that in $Cl_2C{=}PMes^*$ (232.0 ppm)[24] and also significantly upfield from P(x) in the related complex **IIa** (103.7 ppm). The greater upfield shift of P(x) in **Va**, along with the larger $^2J_{P(x)P(a)}$ coupling constant of 82.5 relative to that in **IIa** ($^2J_{P(x)P(a)} = 60.5$), is indicative of the *E* configuration in **Va**, with the ylidic phosphine group being cis to the C=P phosphorus lone pair. The peak at δ 17.8 is assigned to P(b) and shows a cis $^2J_{P(b)P(x)} = 33.1$ Hz, which is similar to the cis $^2J_{P(b)P(x)} = 24.7$ Hz found in **IIa** and the cis $^2J_{P(b)P(x)} = 28.6$ Hz found in the η^2-phosphaalkene complex $Ni(PMe_3)_2[\eta^2\text{-}(Me_3Si)_2C{=}PCH(SiMe_3)_2]$.[28] The signal for the proton on the C=P carbon atom in **Va** is obscured by PPh_3 protons in the ^1H NMR spectrum, and the presence of this proton was deduced indirectly from the ^1H-coupled ^{13}C NMR spectrum of ^{13}C-labeled **Va**, $[Cl(Ph_3P)Ni[\eta^2\text{-}^{13}C(H)(PPh_3){=}P(Mes^*)]$. The measured $^1J_{CH}$ of 145.8 Hz is typical of one-bond sp^2 C−H coupling constants and is similar to $^1J_{CH} = 148.4$ Hz of the sp^2 carbon atom in $MeCH{=}C(Me)_2$.[35] The use of labeled **Va** also allowed for the elucidation of C−P coupling constants and unambiguous assignment of the signals in the ^{31}P NMR spectrum. The $^1J_{CP(x)}$ value of 93.5 Hz is similar to $^1J_{CP(x)} = 86.9$ Hz found in $(Me_3Si)_2C{=}PMes^*$[36] and to $^1J_{CP(x)} = 92.5$ Hz found in the phosphavinyl phosphonium salt $[(Ph_3P)(H)C{=}PN(i\text{-}PR)_2]^+$.[7] The $^1J_{CP(a)}$ value of 57.2 Hz is similar to that, $^1J_{CH_3P} = 52$ Hz, found in the phosphonium salt $(Ph_3P^+CH_3)I^-$ [35] and is roughly intermediate between C−P coupling constants[37] in free (e.g., $^1J_{CH_2P} = 100.7$ Hz in $Ph_3P{=}CH_2$) and η^1-C-coordinated (e.g., $^1J_{CH_2P} = 26.1$ Hz in $(CO)_3Ni(CH_2PPh_3)$) phosphorus ylides. Both $^1J_{CP(x)}$ and $^1J_{CP(a)}$ are larger than the two-bond C−P coupling constant $^2J_{CP(b)} = 30.7$ Hz between the Ni−PPh_3 phosphorus and the C=P carbon. The ^{31}P NMR spectra of **Vb** and **Vc** are very similar to that of **Va**; the peaks for P(x) at δ 26.19 for **Vb** and δ 5.64 for **Vc** are again split into doublets of doublets and do not show any signal broadening in the proton-coupled ^{31}P NMR spectra.

Phosphine Substitution Reactions of IIIa and Vb. Compound **IIIa** reacts with 2 equiv of triethylphosphine at −40 °C to generate $Ni_2Cl_2(PEt_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**IV**), in which the PPh_3 groups on nickel have been substituted by PEt_3 (Scheme 2). However, Compound **IV** decomposes in solution at −25 °C after 1 day and could not be isolated. Substitution of the carbon-bound PPh_3 group was not observed, even when 3 equiv of PEt_3 were added and the solution was warmed to room temperature. Compound **IV** was identified by the similarity of its ^{31}P NMR spectrum to that of **IIIa**. The chemical shifts for P(x) at δ 39.5 and P(a) at δ 20.3 are quite similar to those in **IIIa**, 38.0 and 22.3, respectively. However, the chemical shift for P(b) is now at δ 10.9, 9.1 ppm upfield from P(b) in **IIIa**, which indicates that the nickel-coordinated PPh_3 groups have been substituted by PEt_3. The coupling constants, $^2J_{P(a)P(x)} = 54.3$ Hz and $^2J_{P(b)P(x)} = 49.9$ Hz, in **IV** are similar to those in **IIIa**, $^2J_{P(a)P(x)} = 57.8$ Hz and $^2J_{P(b)P(x)} = 41.2$ Hz, indicating that the geometry of the molecule is the same.

Since compound **IIIa** can be viewed as a triphenylphosphine-donor-stabilized phosphavinylidene ($Ph_3P{=}C{=}PR$), an attempt was made to remove the carbon-bound phosphine-donor group to generate the parent phosphavinylidene complex. This was done by reacting **IIIa** with 9-BBN dimer (9, 9′-biborabicyclo[3.3.1]nonane), which is a known phosphine sponge reagent.[38] However, no phosphavinylidene compounds were isolated, as the reaction results in complete decomposition of the complex with no isolable products. Evidently, the carbon-bound PPh_3 group in **IIIa** is much more difficult to substitute or remove than the nickel-bound PPh_3 ligands, which precludes the formation of a phosphavinylidene complex from **IIIa**.

Compound **Vb** reacts with 1 equiv of triethylphosphine at room temperature to generate $Br(Et_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}PMes^*]$ **(VI)**, in which the PPh_3 group on nickel has been substituted by PEt_3 (Scheme 2). Substitution of the carbon-bound PPh_3 group did not occur, even when two more equivalents of PEt_3 were added at room temperature. The ^{31}P NMR spectrum of **VI** shows very similar splittings and chemical shifts to those of **Vb**. The chemical shifts for P(x) at δ 22.5 and P(a) at δ 18.5 are very similar to those in **Vb**, 23.1 and 19.2, respectively. However, the chemical shift for P(b) is now at δ −5.5, 31.7 ppm upfield from P(b) in **Vb**, which demonstrates that the nickel-coordinated PPh_3 group has been substituted by PEt_3. The coupling constants, $^2J_{P(a)P(x)} = 90.5$ Hz and $^2J_{P(b)P(x)} = 30.2$ Hz, are similar to those in **Vb**, $^2J_{P(a)P(x)} = 85.2$ Hz and $^2J_{P(b)P(x)} = 30.2$ Hz, indicating that the geometry of the molecule is the same.

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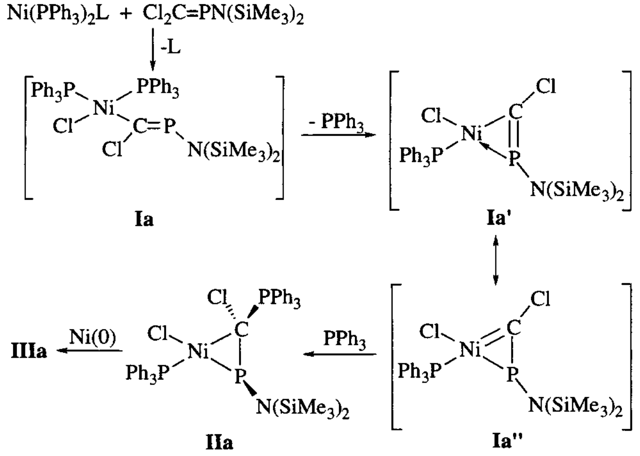
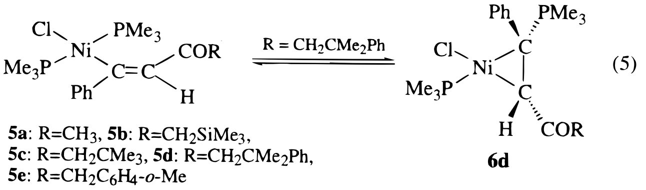
Scheme 3



Discussion

$Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (IIIa). Compound **IIIa** contains the first example of a phosphavinylidene phosphorane ($R_3P{=}C{=}PR$) ligand or phosphine-donor-stabilized phosphavinylidene that acts as a six-electron donor to the two nickel atoms in **IIIa**. Since there are no known examples of related isoelectronic $R_3P{=}C{=}O$, $R_3P{=}C{=}NR$, or $R_3P{=}C{=}S$ compounds in the chemistry of carbonyl, isocyanide, or thiocarbonyl ligands, the formation of the $R_3P{=}C{=}PR$ ligand in **IIIa** illustrates a new type of bonding capability in isocyaphides ($C{\equiv}PR$) that is not accessible with the more thoroughly studied, isoelectronic $C{\equiv}O$, $C{\equiv}NR$, and $C{\equiv}S$ ligands. There are some examples of free[39] and coordinated[40,41] vinylidene phosphoranes $R_3P{=}C{=}CR_2$, which are carbon analogues of $R_3P{=}C{=}PR$. However, these compounds are only known to coordinate η^1 through the ylidic carbon as two-electron-donor ligands. The phosphine-donor-stabilized phosphavinylidene ligand in **IIIa** is not formed simply by PPh_3 attack on an isocyaphide complex as compound **IIa** was observed as an intermediate in the reaction. A likely mechanism for the formation of compounds **IIa** and **IIIa** is outlined in Scheme 3. The first step in Scheme 3 involves the oxidative addition of a C−Cl bond from $Cl_2C{=}PN(SiMe_3)_2$ to the Ni(0) reagent. The product of this addition is the phosphavinyl intermediate **Ia**, which could not be observed in variable-temperature NMR experiments from −50 to −30 °C; at −30 °C, compound **IIa** begins to form. However, when triethylphosphine was used in this reaction, the phosphavinyl compound $Cl(Et_3P)_2Ni[C(Cl){=}PN(SiMe_3)_2]$ (**Ib**) formed and was characterized by ^{31}P NMR spectroscopy as discussed in the Results, which indirectly supports **Ia** as an intermediate. It is not clear why compound **Ib** does not go on to form triethylphosphine analogues of **IIa** and **IIIa**. Assuming **Ia** is an intermediate, it must rapidly isomerize to compound **IIa**, which was characterized by low-temperature ^{31}P NMR spectroscopy as discussed in the Results.



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5a: R=CH_3, **5b**: R=CH_2SiMe_3,
5c: R=CH_2CMe_3, **5d**: R=CH_2CMe_2Ph,
5e: R=$CH_2C_6H_4$-*o*-Me

6d

The step involving rearrangement of **Ia** to **IIa** is similar to the intramolecular 1,2-shift of PMe_3 in an η^1-vinylnickel complex (eq 5) to form an η^2-vinyl phosphonium compound.[42] In the structurally characterized η^1-vinylnickel complex $(Me_3P)_2ClNi[PhC{=}CH(COCH_2SiMe_3)]$ **(5b)**, the geometry around nickel is planar with a weak Ni−O interaction (Ni−O = 2.535(7) Å). It is interesting to note that the rearrangement to the η^2-vinyl phosphonium compound in eq 5 was not general, and only in the case of R = CH_2CMe_2Ph did the 1,2-PMe_3 shift occur to form $(Me_3P)_2ClNi[\eta^2\text{-}(Ph)(Me_3P)C{=}CH(COCH_2CMe_2Ph)]$ **(6d)**.[42] A similar reaction was found in a series of Mo and W η^1-vinyl compounds which react with PMe_3 to generate η^2-vinyl phosphonium compounds.[43] These η^2-vinyl phosphonium ligands may be considered as carbon analogues of the η^2-phosphavinyl phosphonium ligands in compounds **IIa** and **Va**. Although no mechanisms were postulated in these transformations, the reactions give precedent for the rearrangement of **Ia** to **IIa** and this isomerization can be rationalized by proposing (Scheme 3) the rearrangement of the η^1-phosphavinyl (**Ia**) to an η^2-phosphavinyl intermediate **(Ia′, Ia″)**, which is then attacked by PPh_3 at the carbon atom to generate **IIa**. Vinyl, acyl, and iminoacyl ligands are all known to exhibit both η^1- and η^2-coordination, and there are some examples of coordinated iminoacyl compounds[44] which undergo transformation from η^1- to η^2-coordination with concomitant loss of a phosphine ligand as in the rearrangement of **Ia** to **Ia′**, **Ia″** in Scheme 3. Structural, spectroscopic, and chemical studies of η^2-vinyl[45,46] and η^2-acyl ligands[47,48] suggest some influence of a carbene-like resonance form, similar to that (**Ia″**) proposed in Scheme 3. Since the attack of phosphines on carbene ligands is well-known,[49] the attack of PPh_3 on the carbene-like intermediate (**Ia″**) to generate **IIa** (Scheme 3) is reasonable. Further precedent for the postulated attack of PPh_3 on an η^2-phosphavinyl complex is a reaction (eq 6) involving PPh_3 attack on an η^2-vinyl intermediate.[50] There are also a few examples of phosphine attack on related η^2-acyl ligands[51−53] (eq 7). A plausible explana-

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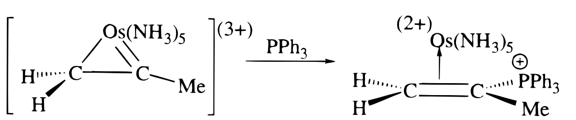

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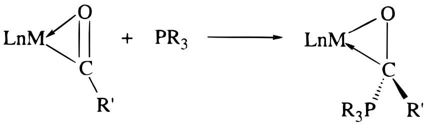

(7)

tion for the ease of nucleophilic attack by PPh_3 on the η^2-phosphavinyl ligand (**Ia′**, **Ia″**) in Scheme 3 is that the carbene−phosphido resonance structure (**Ia″**) is favored more than the alkyl−phosphine resonance form (**Ia′**) because of the known instability of C═P double bonds,[54] which gives more carbene-like character to this intermediate and favors PPh_3 attack. This carbene-like resonance structure in the η^2-phosphavinyl ligand (**Ia″**) is precedented by the X-ray structure of a similar η^2-phosphavinyl complex of tungsten $Cp(CO)_2W[\eta^2\text{-}C(Ph){=}PPh\{W(CO)_5\}]$ which contained a W−C bond length-(1.954(8) Å) that is typical of a W═C double bond.[55] When another equivalent of the Ni(0) reagent is added to compound **IIa** at 0 °C, compound **IIIa** is formed almost quantitatively. This reaction entails oxidative addition of the C−Cl bond in **IIa** to the Ni(0) reagent with subsequent loss of 1 equiv of PPh_3 and the formation of dinuclear **IIIa**. It should be noted that in the *Z* configuration which is postulated for **IIa** (see Results), the second equivalent of Ni(0) is sterically able to access the open side of the C═P bond to undergo oxidative addition and form the dinuclear complex **IIIa**. Thus, the reaction pathway outlined in Scheme 3 reasonably accounts for the formation of **IIa** and **IIIa**.

$Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (Va). The reactions of Ni(0) complexes with $Cl_2C{=}PN(SiMe_3)_2$ (Scheme 1) and $Cl_2C{=}PMes^*$ (eq 4) occur under the same mild conditions but give quite different products. In an effort to understand why different R groups in the phosphaalkenes ($Cl_2C{=}PR$) lead to different products, one might assume that both reactions proceed by a phosphavinyl phosphonium intermediate such as **IIa**. As discussed above, the reaction of this intermediate with Ni(0) reagents for R = $N(SiMe_3)_2$ leads to the dinuclear **IIIa** (Scheme 3) but when R is the more bulky supermesityl group, oxidative addition across the C−Cl bond in the phosphavinyl phosphonium intermediate does not occur. Instead, the Ni(0) reagent abstracts a Cl atom from this intermediate to generate the Ni(I) compound $Ni(PPh_3)_3Cl$, which was isolated from the reaction, and $Ni(PR_3)(X)[C(PR_3){=}PMes^*]$, which abstracts an H atom to form compound **Va**. The formation of Ni(I) species from the reaction of the Ni(II) phosphavinyl phosphonium intermediate with the Ni(0) reagent is somewhat similar to the known reaction of $Ni(PPh_3)_4$ with $Ni(PPh_3)_2Cl_2$ to generate 2 equiv of $Ni(PPh_3)_3Cl$.[56] Unfortunately, the reaction pathway could not be verified as no intermediates could be detected in variable-temperature (−50 °C to 20 °C) ^{31}P NMR studies. In an attempt to identify the source of the H atom in the $C(H)(PPh_3){=}PMes^*$ ligand, an experiment was carried out in a drybox in which $Ni(PPh_3)_4$ (0.0903 mmol) was dissolved in distilled C_6D_6 (3 mL, no H_2O present in ^1H NMR) in a flask (dried at 150 °C for 3 days) and reacted with $Cl_2{}^{13}C{=}PMes^*$ (0.0451 mmol). Compound **Va** formed, but the proton-coupled ^{13}C NMR spectrum showed the same multiplet (ddd) for the C═P carbon as observed when the reaction was performed in nondeuterated toluene; no broadening was detected due to deuterium incorporation. Thus, the H atom in the $C(H)(PPh_3){=}PMes^*$ ligand does not originate from the solvent. The phosphavinyl phosphonium ligands $C(H)(PR_3){=}PMes^*$ in **Va**−**c** are the first examples of this type of ligand.

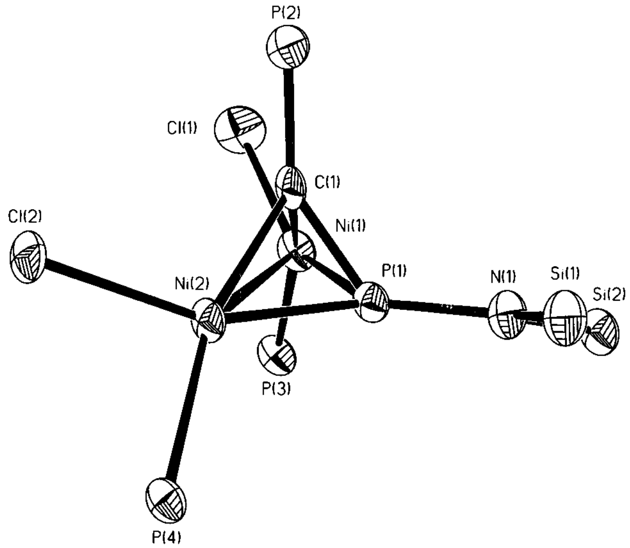

Figure 1. Thermal ellipsoid drawing of $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**IIIa**) with the phenyl and methyl groups removed for clarity.

Structure and Bonding in $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (IIIa). A thermal ellipsoid drawing with the phenyl rings removed for clarity (Figure 1) of complex **IIIa** shows that the nickel atoms are both in planar environments defined by the PPh_3, Cl, and $Ph_3P{=}C{=}PR$ ligands (sum of angles around nickel atoms are 360.2° for Ni(2) and 362.6° for Ni(1)). The dinuclear complex exhibits a butterfly geometry with a long Ni−Ni distance (2.966(7) Å) that is outside the range of a typical Ni−Ni single bond (2.4−2.7 Å).[57] This Ni−Ni distance in **IIIa** (Table 2) is longer than that in dinuclear nickel complexes in which a Ni−Ni bonding interaction has been excluded, e.g., d(Ni−Ni) = 2.908(3) Å in $[\{(Et_2PCH_2)_2Ni\}_2(\mu,\eta^2\text{-}P{\equiv}P)]$, which is a dinuclear complex with a similar butterfly geometry containing a bridging P≡P unit,[58] and d(Ni−Ni) = 2.874(2) Å in the A-frame complex $[Ni_2(\mu\text{-}C{=}CH_2)(dppm)_2Br_2]$.[59] The C(1)−P(1) distance in **IIIa** (1.707(7) Å) indicates some double bond character, as it is more similar to a typical C═P double bond found in $Cl_2C{=}PN(SiMe_3)_2$ (1.685(2) Å)[60] than to that (1.773(8) Å) of the

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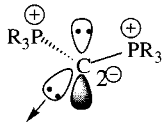
side-on π-bound phosphaalkene in Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$].[28] The C(1)−P(2) distance (1.709(7) Å) is very similar to the C(1)−P(1) distance and is intermediate between typical ylide C−P bond lengths, e.g., 1.661(8) Å in Ph$_3$P=CH$_2$,[61] and C-coordinated ylide C−P bond lengths, e.g., 1.745(8) Å in (CO)$_3$Ni[(H)(Me)C=PCy$_3$].[62] The C(1)−P(2) distance indicates more ylidic (C$^-$−P$^+$) than phosphonium (C−P$^+$) character in the bond, as it is significantly shorter than the C−PPh$_3$ distance (1.798(14) Å) found in the phosphavinyl phosphonium salt [(Ph$_3$P)(H)C=PN(i-PR$_2$)](BF$_4$).[7] The Ni(1)−P(1) and Ni(2)−P(1) distances (2.133(2) and 2.103(2) Å, respectively) are much shorter than the nickel−phosphine (Ni(1)−P(3) and Ni(2)−P(4)) distances (2.202(2) and 2.195(2) Å, respectively) and are also shorter than the Ni−P (phosphaalkene) distance (2.239(2) Å) found in Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$].[28] The nitrogen atom of the N(SiMe$_3$)$_2$ group is in a planar environment, which is generally preferred for this group in other structures.[60]

The structure of **IIIa** (Figure 1) suggests that the novel phosphavinylidene−phosphorane ligand (R$_3$P=C=PR) is a six-electron donor, providing two electrons from the ylide carbon, two from the C=P double bond, and two from the lone pair on phosphorus as shown in **L**.



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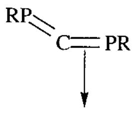

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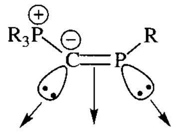

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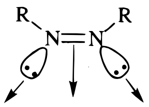

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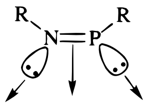

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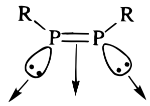

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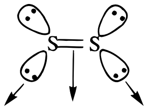
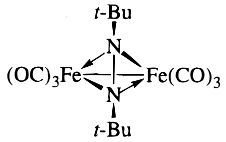
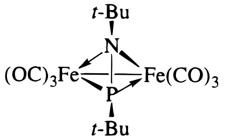


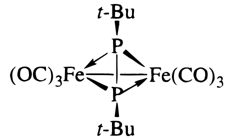
(P)



(7)



(8)



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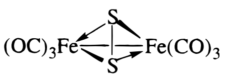

(10)

As mentioned, this ligand can also be considered the first example of a mixed σ^2,σ^4-diphosphaallene and has much different coordinating abilities than the known σ^4,σ^4-diphosphaallenes[11] **(J)** and σ^2,σ^2-diphosphaallenes[3] **(K)** which have only been coordinated as two-electron donor ligands through the ylidic carbon in **J** and through one of the C=P double bonds in **K**. The R$_3$P=C=PR ligand in **L** is also somewhat similar to a recently prepared PPh$_3$ adduct of a vinylidene phosphorane Ph$_3$P=C=P(Mes*)=NMes*, which contains a σ^3,λ^5 phosphorus atom instead of the σ^2,λ^3 phosphorus atom in **L**.[63] The R$_3$P=C=PR ligand is drawn as the ylide rather than ylene form in **L**, which is a more appropriate representation as ab initio calculations have shown that the short C−PR$_3$ bond lengths found in ylides are due more to a strong electrostatic attraction between the anionic carbon and the cationic phosphorus R$_2$C$^-$−PR$_3$$^+$ than to a true ylene form R$_2$C=PR$_3$ with a C=P double bond.[64,65] A more appropriate comparison of the bridging phosphavinylidene−phosphorane ligand **L** is with diimino (**M**), iminophosphine (**N**), diphosphene (**O**), and disulfur (**P**) ligands.[66] These ligands are isolobal with **L**, when **L** is drawn in the ylide form and have the capability of donating two electrons from each lone pair and two electrons from the double bond for a total of six electrons, as for **L**. These ligands are quite different than μ_2:η^2,η^2-alkynes which can only donate four electrons to two metal atoms in a dimer. All four of the ligand types **M**−**P** have been coordinated as six-electron donor ligands in the iron dimers **7**−**10**.[66−68] The tetrahedrane dimers **7**−**10** are closely related to **IIIa**, although they contain metal−metal bonds to give an 18-electron count, while in **IIIa**, the two nickel atoms have a total of 16-valence electrons each and no metal−metal bond is needed. The X-ray-determined structures for **7**, **8**, and **10** exhibit formally single-bond N−N, N−P, and S−S distances, while the P−P distance in **9** (2.059(3) Å) suggests that there is double-bond character in this bond. Although no explanation was given for this apparent anomaly, it is interesting that the C−P distance in **IIIa** is also consistent with double-bond character. The bonding in **IIIa** may be expressed by three resonance structures which are presented in Scheme 4. Resonance structure **a** may be viewed as a metalla−ylide−phosphido structure where the phosphorus atom is covalently bonded to one nickel atom and the phosphorus lone pair donates two electrons to the other nickel fragment; the carbon atom is also covalently bonded to one nickel atom and the ylide carbon lone pair donates two electrons to the other nickel fragment. Both of the nickel atoms are then Ni(II), with the R$_3$P=C=PR group acting as a six-electron donor overall. This is quite similar to the bonding in the related dimers **7**−**10**.[66−68] The short C(1)−P(2) bond length is explained by the electrostatic attraction between the adjacent charges on the cationic P(2) and anionic C(1) in this resonance form. Resonance structures **b** and **c** are formulated as zwitterionic structures where the negative charge is located on the nickel atom that is bound η^2 to the C=P double bond, while the other nickel atom coordinates to the R$_3$P=C=PR ligand as an η^2-phosphavinyl (three-electron-donor) ligand. In structures **b** and **c**, the anionic nickel atom is formally Ni(0)

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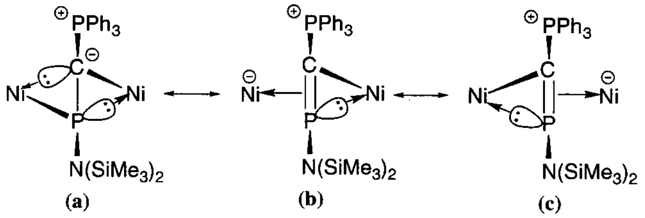
Scheme 4



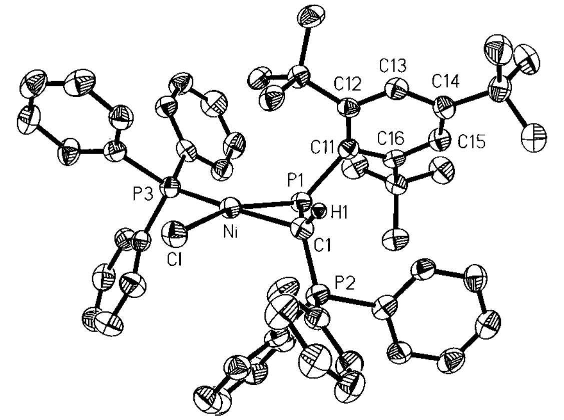
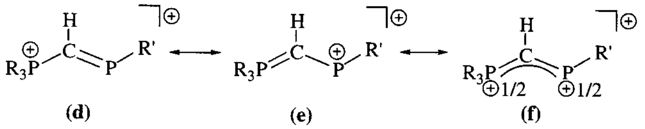


Figure 2. Thermal ellipsoid drawing of Cl(PPh$_3$)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (**Va**).

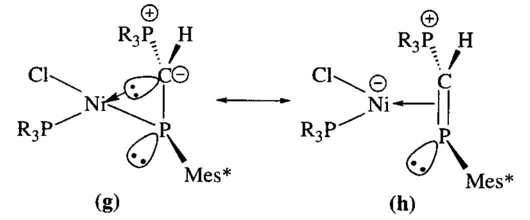
while the neutral nickel atom is formally Ni(II). Here the R$_3$P=C=PR group acts as a five-electron-donor ligand. The short C(1)−P(1) bond length suggests some contribution from these two resonance structures.

Structure and Bonding in Cl(Ph$_3$P)Ni[η^2-C(H)-(PPh$_3$)=P(Mes*)] (Va). The thermal ellipsoid drawing (Figure 2) of complex **Va** shows that the nickel atom is in a planar environment defined by the PPh$_3$, Cl, and [C(H)(PPh$_3$)=PR] ligands (sum of angles around the nickel atom is 359.3°). The carbon-bound PPh$_3$ and the Mes* groups are situated in a trans arrangement across the C(1)−P(1) bond. The H, PPh$_3$, and Mes* groups are bent back from planarity in the C(H)(PPh$_3$)=PMes* unit, indicating a pyramidalization at C(1) and P(1). This is seen in both the dihedral angle of C(11)−P(1)−C(1)−P(2) = −123.1(3)° and in the sum of angles around C(1) = 343.5°. This indicates that C(1) is roughly intermediate between sp^2 and sp^3 hybridization, which is similar to structural features of η^2-coordinated olefins and phosphaalkenes.[28] The C−P distances can be compared with those found in the phosphavinyl phosphonium salt [(Ph$_3$P)(H)C=PN(*i*-PR$_2$)](BF$_4$),[7] which is a cationic analogue of the C(H)(PPh$_3$)=PMes* ligand in **Va**, differing only in the R group on phosphorus. The C(1)−P(1) distance in **Va** (1.796(5) Å) is much longer than the analogous C=P distance found in [(Ph$_3$P)(H)C=PN(*i*-PR$_2$)](BF$_4$) (1.684(14) Å). This is consistent with the lengthening of C=P bonds which occurs upon η^2-coordination of phosphaalkenes, and in fact, the C(1)−P(1) distance in **Va** (1.796(5) Å) is quite similar to the C=P distance (1.773(8) Å) in the η^2-phosphaalkene complex Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$].[28] The C(1)−P(2) distance (1.742(5) Å), although shorter than the C(1)−P(1) distance, is longer than a typical ylide C−P bond length, e.g., 1.661(8) Å in Ph$_3$P=CH$_2$,[61] but shorter than the corresponding Ph$_3$P−C bond (1.798(14) Å) in [(PPh$_3$)(H)C=PN(*i*-PR$_2$)](BF$_4$). The Ni−C(1) distance in **Va** (1.977(5) Å) is the same within experimental error as the Ni−C distances (1.97(1) and 1.95(2) Å) in the related η^2-vinyl phosphonium compound (Me$_3$P)$_2$ClNi[η^2-Ph(Me$_3$P)C=CH(COCH$_2$CMe$_2$-Ph)] (**6d**, eq 5).[42]

Scheme 5



Scheme 6



Compound **Va** is the first example of a complex containing a coordinated phosphavinyl phosphonium ligand. A few examples of uncoordinated phosphavinyl phosphonium salts [(R$_3$P)RC=PR]$^{+}$ [7−10] have been reported in the literature, and the structure of [(PPh$_3$)(H)C=PN(*i*-PR$_2$)](BF$_4$) was determined by X-ray diffraction.[7] The NMR spectra of these compounds, along with the X-ray evidence, suggest that there is a contribution from both resonance forms **d** and **e** in Scheme 5, and these compounds have also been referred to as σ^2,σ^4-diphosphaallyl cations (resonance form **f**).[10] However, we find no evidence for allyl-like behavior in the (Ph$_3$P)(H)C=PMes* ligand which is bound η^2 through the C(1)−P(1) bond in **Va** as opposed to η^3 through the P(2)−C(1)−P(1) allyl-like unit as in compounds of the type (R$_3$P)(X)Ni[η^3-allyl]. There are a few examples of η^3-coordinated σ^2,σ^2-diphosphaallyl ligands,[69−72] but the (Ph$_3$P)(H)C=PMes* group in **Va** is best viewed as a phosphavinyl phosphonium ligand. Since it is generally accepted that the short bond lengths found in ylide C−P bonds are caused by an electrostatic interaction and not a genuine π bond and there are no structurally characterized examples of η^2-C=PR$_3$-coordinated ylide compounds, the η^3-coordination of the (Ph$_3$P)(H)C=PMes* ligand in **Va** is unlikely and further supports the lack of π-bonding in ylides.

The bonding in compound **Va** may be described as a mixture of two resonance structures as shown in Scheme 6. Resonance form **g** can be viewed as an ylide−phosphido structure with a dative two-electron donation from C(1) and a covalent, phosphido-type bond between P(1) and nickel. Here, the (Ph$_3$P)(H)C=PMes* ligand donates three electrons to the 13-electron nickel fragment, which is formally Ni(II). The somewhat short C(1)−P(2) distance found in **Va** suggests a contribution from form **g**, where the charges are located on adjacent atoms. Resonance form **h** can be viewed as an η^2-phosphavinyl phosphonium cation (1+) coordinated to

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Table 4. Deviations from Planarity in Supermesityl Rings

compound	C atom[a] deviation (Å)	P (or In) deviation[b] (Å)
$Pt(PEt_3)_2Cl[(Cl)C{=}PMes^*]$ (**1**)[c]	0.061	0.668
$(Et_3P)_2ClPt[\mu\text{-}(C{=}PMes^*)]Pt(PEt_3)Cl$ (**2**)[d]	0.052	0.499
$Cl(Ph_3PNi[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (**Va**)[e]	0.073	1.09
$In(Mes^*)_2Br$ (**11**)[f]	0.057	1.44
$Cp(CO)_2FeP{=}PMes^*$ (**12**)[g]	0.000	0.123
$Pt(PPh_3)_2[\eta^2\text{-}Cp(CO)_2FeP{=}PMes^*]$ (**13**)[h]	0.040	0.562

[a] Average deviation of ring C atoms from ring plane. [b] Deviation of P (or In) from average carbon ring plane. [c] Reference 12. [d] Reference 12. [e] This work. [f] Reference 75. [g] Reference 73. [h] Reference 74.

a formally Ni(0) metal fragment. This is a zwitterionic structure with the negative charge located on nickel and the C=P double bond acting as a two-electron donor. Unlike structure **IIIa**, the C=P phosphorus lone pair is unavailable for bonding to nickel in this structure, as it is pointing down and away from the metal center. The resonance structures in Scheme 6 are quite similar to those postulated for the related η^2-vinyl phosphonium compound $(Me_3P)_2ClNi[\eta^2\text{-}(Ph)(Me_3P)C{=}CH(COCH_2CMe_2Ph)]$ (**6d**, eq 5).[42]

The structure of **Va** exhibits an interesting feature in that it contains a somewhat distorted, boat-shaped supermesityl ring with the P(1) atom located 1.09 Å out of the plane of the carbon atoms in the arene ring. This is most likely a steric effect as compound **Va** is quite bulky and the supermesityl ring is forced to bend back away from the nickel-bound P(1) atom in order to alleviate steric strain with a concomitant puckering of the ring. Calculations have shown that in very bulky substituted phenyl rings in which the substituents are forced to bend out of the plane of the ring, a similar puckering of the aromatic ring occurs in order to maintain the greatest amount of delocalization in the ring, and such distortions were calculated to be favorable with much of the electron delocalization (aromaticity) of the ring remaining.[73,74] In other sterically encumbered supermesityl systems, a similar puckering of the ring is observed (Table 4). The cell coordinates and atomic positions for the compounds in Table 4 were obtained from the literature references and entered into CSC Chem 3D Plus (Version 3.1.1, Cambridge Scientific Computing) in order to ascertain the deviation from planarity in the rings. The first column of data represents the average deviation from planarity of the six carbon atoms making up the Mes* ring in the given compound, while the second data column gives the distance that the P or In atom is displaced out of the average plane defined by the six ring-carbon atoms of the supermesityl ring. As can be seen in Table 4, all of these compounds show similar distortions as those in **Va** to varying degrees and the most sterically crowded systems seem to show the greatest distortions. In the iron-coordinated diphosphene complex $Cp^*(CO)_2Fe\text{-}P{=}PMes^*$ (**12**),[75] in which there is no steric interference between the Mes* group and the rest of the complex, there is no deviation from planarity in the ring and the phosphorus atom is only 0.123 Å out of the plane of the ring. However, when the P=P bond is η^2-coordinated to the bulky $Pt(PPh_3)_2$ moiety in $Pt(PPh_3)_2[\eta^2\text{-}Cp^*(CO)_2FeP{=}PMes^*]$ (**13**),[76] the Mes* ring becomes puckered with an average deviation from planarity in the ring-C atoms of 0.040 Å and the phosphorus atom is situated 0.562 Å out of the average plane of the ring. The compound $In(Mes^*)_2Br$ (**11**)[77] exhibits a structure that is perhaps the most sterically bulky of all of the structures that were examined, containing two Mes* groups attached to the same atom. Correspondingly, this structure exhibits the greatest deviation of the heteroatom out of the average plane of the ring (1.44 Å), but its average deviation from planarity in the ring (0.057 Å) is similar to that of compounds **1** (0.061 Å), **2** (0.052 Å), and **Va** (0.073 Å). Thus, puckering of the ring and bending out of the plane of the P(1) atom in **Va** are most likely caused by steric congestion in the molecule, and this type of distortion is similar to that observed in other sterically bulky compounds containing Mes* rings.

Summary

Oxidative-addition reactions of $Ni(0){-}PPh_3$ reagents with $Cl_2C{=}PN(SiMe_3)_2$ results in formation of the first example of a phosphavinylidene phosphorane ligand ($Ph_3P{=}C{=}PR'$), which may also be viewed as a σ^2,σ^4-diphosphaallene, coordinated as a six-electron-donor ligand in the dinuclear nickel butterfly dimer $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**IIIa**) (Scheme 1, Figure 1). A phosphavinyl phosphonium intermediate $Cl(Ph_3P)Ni[\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2]$ (**IIa**) was identified in this reaction and most likely results from PPh_3 attack on an η^2-phosphavinyl intermediate that reacts like an electrophilic carbene (Scheme 3). The $Ph_3P{=}C{=}PR'$ ligand in **IIIa** is isolobal with diimine (RN=NR), iminophosphine (RN=PR), diphosphene (RP=PR), and disulfur (RS=SR) ligands, which also act as dibridging six-electron donors. A similar reaction using PEt_3 instead of PPh_3 resulted in formation of the η^1-phosphavinyl compound $Cl(Et_3P)_2Ni[C(Cl){=}PN(SiMe_3)_2]$ (**Ib**). In contrast, when the same $Ni(0){-}PPh_3$ reagents are reacted with $X_2C{=}PMes^*$ (X = Cl, Br; Mes* = 2,4,6-tri-*tert*-butylbenzene), the phosphavinyl phosphonium compounds $X(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ (**Va,b**) form along with $Ni(PPh_3)_3X$ (eq 4). A similar reaction using PCy_3 instead of PPh_3 formed an unstable PCy_3 analogue (**Vc**) of **Va**. The difference in reactivity between $Cl_2C{=}PN(SiMe_3)_2$ and $Cl_2C{=}PMes^*$ with Ni(0) reagents is likely due to the greater steric bulk of the Mes* group which prevents the formation of a dimer analogous to **IIIa**. Compound **Va** is the first example of a metal complex containing a phosphavinyl phosphonium ligand ($C(H)(PPh_3){=}PMes^*$), which may also be viewed as an η^2-coordinated σ^2,σ^4-diphosphaallyl ligand coordinated as a three-electron donor (Scheme 6). This compound also exhibits a somewhat distorted supermesityl ring, which is likely due to steric constraints in the molecule and has been observed in other bulky supermesityl-containing compounds.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the Ameri-

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can Chemical Society, for support of this research through Grant No. 27360-AC3.

Supporting Information Available: Fully labeled structural drawings, tables of non-hydrogen atomic coordinates and equivalent isotropic parameters, anisotropic displacement parameters, complete bond distances and angles, hydrogen coordinates and isotropic diplacement parameters, and torsion angles, and unit cell and packing diagrams for **IIIa** and **Va** (28 pages). Ordering information is given on any current masthead page.

OM970895X