1997

Synthesis, characterization and reactions of complexes containing new ligands with carbon-phosphorus multiple bonds

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Synthesis, characterization and reactions of complexes containing new ligands with carbon-phosphorus multiple bonds

by

Wayde Vincent Konze

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Inorganic Chemistry
Major Professor: Robert J. Angelici

Iowa State University
Ames, Iowa
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To my family, who have given me love, life and the
comfort of a milestone from which I may always know
how far I have come and how far there is yet to go:
Rebecca Ann, Nicolette Amber and
Joseph Allen Konze

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ABBREVIATIONS

Mes*, 2,4,6-tri-*tert*-butylbenzene

Mes, 2,4,6-tri-methylbenzene

xyl, 2,6-dimethylbenzene

COD, 1,5-cyclooctadiene

Cp, η^5-C_5H_5 ligand

Cp*, η^5-C_5Me_5 ligand

Me, -CH_3 group

Et, -CH_2CH_3

i-Pr, -$CH(CH_3)_2$

t-Bu, -$C(CH_3)_3$

Ph, -C_6H_5 group

Cy, -C_6H_{11} group

Bn, -CH_2Ph

dppm, $Ph_2PCH_2PPh_2$

dppe, $Ph_2PCH_2CH_2PPh_2$

dba, dibenzylideneacetone

GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains three papers in the format required for journal publication, describing the research I performed at Iowa State University. Preceding these papers is a literature review of π-complexation of carbon-phosphorus double and triple bonds. In the literature review as well as the papers, the literature citations, schemes, tables and figures pertain only to the chapters in which they appear. After the final paper is a general summary.

Literature Review

Introduction

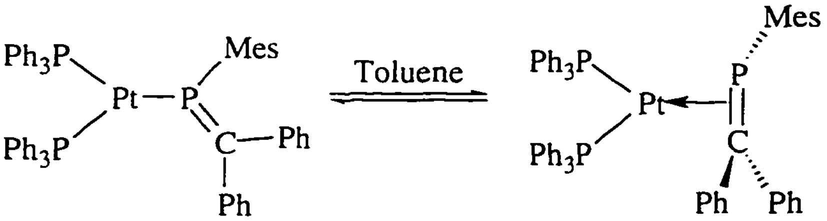
The field of carbon-phosphorus multiply bonded compounds has seen remarkable growth in a relatively short period of time. These compounds violate the outdated "double bond rule" which stated that 4th and 5th row main group elements should not be capable of forming multiple bonds. This reluctance to take part in multiple bond formation is a manifestation of the inert s-pair effect in higher main group elements;[1] the s-orbitals are contracted due to the greater nuclear charge and this spatial inequity between the s and p-orbitals makes the formation of hybrid orbitals less favored, even though the energy differences between the s and p-orbitals in 4th and 5th row main group elements are comparable to those in second row elements. Although C=P π-bonds are calculated to be 22.3 kcal/mol less stable than C=C π-bonds,[2] Becker was able to isolate the first example of a stable phosphaalkene compound[3] in 1976 by incorporating bulky R-groups on the carbon and phosphorus atoms in order to kinetically stabilize the reactive C=P double bond. Since this discovery, many examples of stable phosphaalkene and other interesting C=P containing compounds have been reported and the coordination chemistry of these compounds has developed at a very rapid pace. Theoretical calculations and photoelectron studies on $MeP{=}CH_2$ have shown that the HOMO consists mainly of the C=P π-orbital and that the LUMO consists mainly of the relatively low lying C=P π^* orbital.[4-6] Consequently, compounds containing C-P multiple bonds have shown a rich olefin-like η^2-coordination chemistry. In fact, complexes containing C-P multiple bond analogs of almost all C-C multiple bond ligands are known, including phosphaalkenes, phosphaalkynes, phosphaallyls, phosphaallenes, phosphabutadienes, phosphacyclopropenes, phosphacyclobutadienes, phosphacyclopentadienyls and phosphaarenes.[7-9] All of these C-P multiple bond ligands exhibit the ability to coordinate to metals through the C-P π-system, and offer the additional coordination site of the phosphorus lone pair as well. The ^{31}P NMR spectroscopy of these ligands has proven useful for structure elucidation and bonding explanations and is a very important diagnostic tool. Although these π-bonded C-P multiple bond ligands are in many cases analogous to their carbon counterparts, they also exhibit important differences which have allowed them to become more than just phosphorus analogs of common ligands. Unlike commonly tetravalent carbon, phosphorus is able to form mono, di, tri, tetra, penta and hexavalent compounds, which has allowed for the coordination of several C-P multiple bond ligands that have no analogs in carbon chemistry.

This review covers structure and bonding aspects of π-complexes of carbon-phosphorus unsaturated ligands in the literature through the middle of 1997.

η^2-Phosphaalkene ($R_2C{=}PR$) Complexes

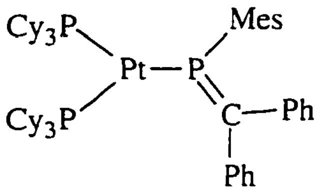
Both *ab initio* STO/3G calculations and[4-6] photoelectron spectroscopic results on phosphaalkenes indicate that the σ-phosphorus lone pair and the C=P π-orbitals are very close in energy, with the π-orbital as the HOMO in the parent compound $CH_2{=}PH$. These results suggest that phosphaalkenes should be capable of coordination either η^2 through the C=P double bond or η^1 through the phosphorus lone pair, both of which have been accomplished in practice; there are several examples of complexes containing η^1-P coordinated or η^2-C=P coordinated phosphaalkenes, as well as mixed, η^1, η^2-coordinated phosphaalkenes.[8,10] There are also a few examples of cluster-stabilized phosphaalkenes with the phosphaalkene bridging between several metals.[8,10] The majority of these complexes have been prepared by displacing weakly coordinating ligands on a transition metal complex with stable phosphaalkene ligands. Both steric and electronic factors determine whether the phosphaalkene ligands will coordinate η^1 or η^2 to a transition metal complex; electron-rich metal centers are better able to donate into the π^* orbital and thus favor η^2-coordination, while complexes containing bulky ancillary ligands tend to prefer η^1-coordination to avoid interaction with the often bulky R-groups on the C=P carbon atom.

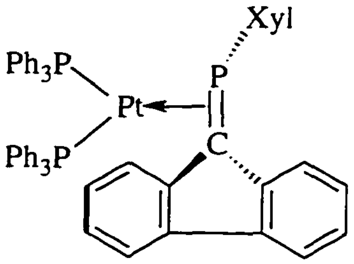
In the phosphaalkene complex $Pt(PPh_3)_2(P(Mes)=CPh_2)$,[11] both η^1 and η^2 forms of the phosphaalkene ligand were present and an equilibrium was established (eq 1) between these



(1)

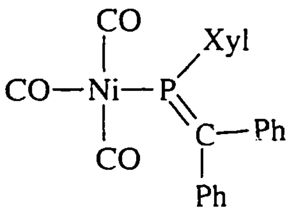
two forms. At low temperatures the η^2-coordinated complex was prevalent, while at higher temperatures and in the solid state the η^1-coordinated complex was more favored; the structure of the η^1 complex was determined by X-ray diffraction studies.[12] Both calculations and equilibrium studies found that the η^2-coordinated form was more stable (smaller enthalpy), but the difference was small (~4 kcal/mol).[11] When the PPh_3 ligands were replaced with PCy_3 (tricyclohexyl phosphine) groups, only the η^1-phosphaalkene complex was observed with no evidence of the η^2-form,[13] evidently because the greater steric bulk in the PCy_3 ligands favors the less crowded η^1-form. However, when $Pt(PPh_3)_2$ was coordinated to the phosphaalkene (9-fluorenylidene)C=P(xyl) (xyl = 2,6 dimethylphenyl), only the η^2-phosphaalkene complex

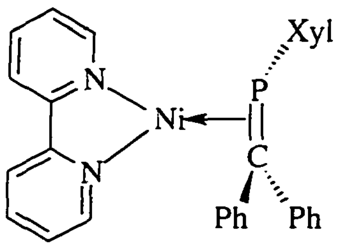




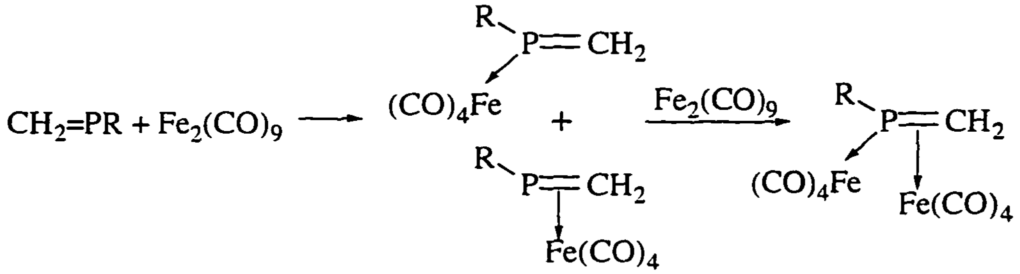
was present in both the solid state and in solution.[14] In this complex, the two aryl rings on the C=P carbon are forced into one plane, which allows the $Pt(PPh_3)_2$ fragment to coordinate the C=P double bond with little steric interaction.

As mentioned, electronic factors also play a role in determining the coordination mode of phosphaalkene ligands; $Ni(CO)_4$ reacted with $Ph_2C{=}P(xyl)$ to form the η^1-phosphaalkene complex $(CO)_3Ni[\eta^1\text{-}(xyl)P{=}CPh_2]$, while the same phosphaalkene coordinated in η^2-fashion to the 2,2'-bipyridyl-nickel fragment.[15] An explanation for this difference is that the CO





ligands in the former are strongly π-accepting, which reduces the ability of nickel to backbond into the π* orbital of an η^2-phosphaalkene ligand, but favors the η^1-coordination through the phosphorus lone pair in which more electron density is donated to the $Ni(CO)_3$ fragment. However, when the better σ-donor ligand 2,2'-bipyridyl is present on nickel, the η^2-form of the phosphaalkene becomes more stable. A similar effect was found in complexes of platinum, where the phosphaalkene $Ph_2C{=}P(xyl)$ coordinated η^1 to the Pt(COD) fragment, but η^2 to the Pt(triphos) fragment,[16] with the triphos ligand acting as a bidentate ligand instead of the usual tridentate form to accommodate the phosphaalkene ligand. Again, the more π-accepting COD ligand favors η^1-coordination, while the better σ-donating triphos ligand favors η^2-coordination. However, there are also examples of η^2-coordinated phosphaalkenes in which the ancillary ligands are all strongly π-accepting. For instance, $Ni(CO)_4$ reacted with two equivalents of $(SiMe_3)_2C{=}PCl$ to generate $(CO)Ni[\eta^2\text{-}C(SiMe_3)_2{=}PCl]_2$, in which two phosphaalkene ligands are coordinated η^2 to the Ni(CO) fragment.[10] Also, in the reactions of $Fe_2(CO)_9$ with either $H_2C{=}PMes^*$ or (H)(t-Bu)C=P(t-Bu), mixtures of the η^1-P and η^2-C=P complexes were afforded (eq 2).[17] Treatment in both cases (eq 2) with another equivalent of



(2)

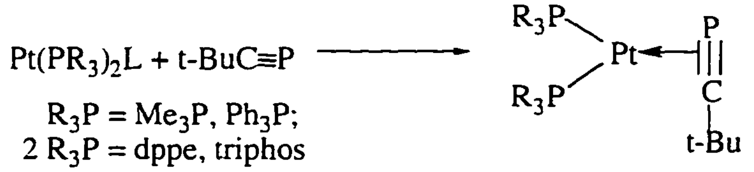
$Fe_2(CO)_9$ resulted in formation of the η^1, η^2-coordinated phosphaalkene complexes which were structurally characterized.[17]

The π-complexation of the C=P bond in phosphaalkenes is analogous to the η^2-coordination of olefins and has also been described[11] by the Dewar-Chatt-Duncanson model in which the π-orbital (HOMO) donates to the transition metal fragment with a synergistic back bonding from the metal fragment to the π*-orbital (LUMO). This causes a lengthening of the C-P bond distance that is on the order of the lengthening of the C-C bond distance in coordinated olefins; a comparison of C-P bond lengths in free phosphaalkenes (typically about 1.67 Å)[10] with the C-P bond lengths in the complexes $(Me_3P)_2Ni[\eta^2\text{-}C(SiMe_3)_2{=}PC(H)(SiMe_3)$[18] and $(Ph_3P)_2Pt[\eta^2$-C(9-fluorenylidene)=P(xyl)][14] (1.773(8) Å and 1.832(6) Å, respectively) shows that the phosphaalkene C=P bonds are lengthened to almost a typical C-P single bond length (1.82-1.87 Å).[19] Also, the ^{31}P NMR chemical shift of the C=P phosphorus atom in η^2-coordinated phosphaalkene complexes is far upfield from that in free phosphaalkenes, analogous to the upfield shifts found in the ^{13}C NMR of η^2-coordinated olefins. For instance, the ^{31}P chemical shift of the C=P phosphorus in $(Me_3P)_2Ni[\eta^2\text{-}C(SiMe_3)_2{=}PC(H)(SiMe_3)$ is δ 23.4 ppm, 380 ppm upfield from the free phosphaalkene $(Me_3Si)_2C{=}PC(H)(SiMe_3)$ at δ 404 ppm,[18] while an upfield shift of 266 ppm is found for the C=P phosphorus atom in $(Ph_3P)_2Pt[\eta^2\text{-}Ph_2C{=}PMes]$ relative to free $Ph_2C{=}PMes$.[11] Another distinguishing ^{31}P NMR feature of η^2-coordinated phosphaalkenes is the extremely small $^1J_{PM}$ coupling constants that are found when the coordinating metal contains an NMR active nucleus. An illustrative example is the difference between the η^1 and η^2 coordinated phosphaalkene complexes $(Ph_3P)_2Pt[\eta^1\text{-}P(Mes){=}CPh_2]$ and $(Ph_3P)_2Pt[\eta^2\text{-}Ph_2C{=}PMes]$; the η^1-phosphaalkene complex has $^1J_{PPt}$ = 4960 Hz, while the η^2-complex of the same phosphaalkene has $^1J_{PPt}$ = 500 Hz.[11] The former is a typical one bond P-Pt coupling constant in three-coordinate platinum phosphine complexes, while the latter is extremely small, indicating the small amount of s-character present in the Pt-P bond. This is a manifestation of the "inert s-pair" effect found in 3rd and 4th row main group elements in which the s-pair of electrons is reluctant to take part in hybridization, causing the C=P double bond to contain very little phosphorus s-character, while the phosphorus lone pair contains mainly s-character.

η^2-Phosphaalkyne (R-C≡P) Complexes

Photoelectron spectroscopic studies[20,21] on a series of phosphaalkynes has shown that the HOMO is of the π-type and the π-n separation is greater than in corresponding nitriles (R-C≡N), indicating that η^2-coordination of the C≡P bond should be preferred over η^1-coordination through the phosphorus lone-pair. This contrasts with the known propensity of nitriles to coordinate η^1 through the nitrogen lone pair. These calculations are consistent with the fact that only a few examples of η^1-P coordinated phosphaalkynes are known, while the vast majority of these complexes are either η^2-coordinated through the C≡P bond to a single metal fragment or bridged μ-η^2, η^2 between two metals.

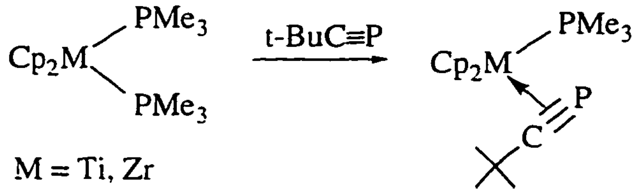
The first examples of mononuclear η^2-coordinated phosphaalkynes were prepared by reacting (eq 3) zerovalent platinum complexes with t-Bu-C≡P to form $(R_3P)_2Pt(\eta^2\text{-}t\text{-}BuC{\equiv}P)$



(3)

($R_3P = Me_3P, Ph_3P$; 2 R_3P = dppe, triphos).[7,16,22] The structure of $(Ph_3P)_2Pt(\eta^2\text{-t-BuC≡P})$ was determined by an X-ray diffraction study which showed that the C-P bond length (1.672(17) Å) was much longer than that (1.536(2) Å) in free t-BuC≡P.[22] The C-P distances in η^2-coordinated phosphaalkynes are similar to those found in typical phosphaalkenes, which is consistent with back-bonding into the π^* orbitals in R-C≡P by electron rich metal fragments. Similar increases in C-C bond lengths have been reported in η^2-coordinated alkyne complexes as well, indicating a similar type of bonding in these species. The ^{31}P NMR spectrum of $(Ph_3P)_2Pt(\eta^2\text{-t-BuC≡P})$ exhibits a signal at δ 82.1 ppm that is far downfield from that of t-BuC≡P at δ -69.2 ppm, consistent with the C=P double-bond-like character, and the value of $^1J_{PPt}$ = 62 Hz is the smallest one-bond Pt-P coupling constant yet recorded.[22] As in the η^2-phosphaalkene complexes, this small coupling constant is due to the low s-character on phosphorus in the C=P bond. More recently, the complex $(Ph_3P)_2Pt[\eta^2\text{-(i-Pr}_2\text{N)C≡P}]$ was prepared, which showed similar ^{31}P NMR properties to the t-BuC≡P complexes.[23]

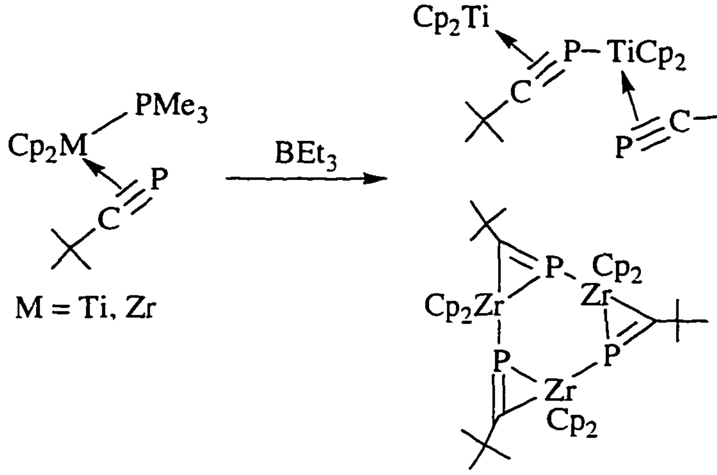
The reactions (eq 4) of $Cp_2M(PMe_3)_2$ (M = Ti, Zr) with t-BuC≡P resulted in the η^2-coordinated phosphaalkyne complexes $Cp_2M(PMe_3)[\eta^2\text{-t-BuC≡P}]$ (M = Ti, Zr) by



(4)

displacement of one PMe_3 ligand.[24] The structure of the titanium complex was determined by X-ray diffraction and revealed a C-P distance of 1.634 Å, which is lengthened from the free phosphaalkyne but not as much as in the platinum complex. The ^{31}P NMR of the titanium and zirconium complexes exhibited signals for the phosphaalkyne phosphorus atoms at δ 122.7

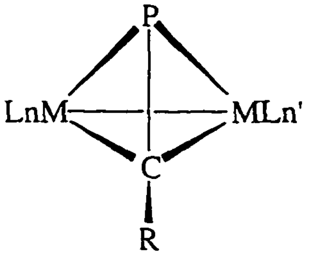
ppm and δ 196.9 ppm, respectively, which are even farther downfield than that of the platinum phosphaalkyne complex. The titanium and zirconium complexes also exhibited ^{13}C NMR chemical shifts for the C≡P carbon atoms at δ 298.6 ppm and δ 310.7 ppm, respectively, which are far downfield in the region of metal-carbene or metal-acyl complexes.[24] Interestingly, these compounds reacted (eq 5) with BEt_3 to remove the PMe_3 ligand and generate a titanium dimer



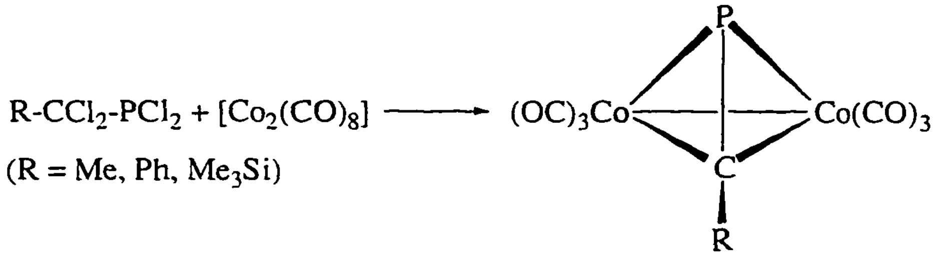
(5)

and a zirconium trimer in which the t-BuC≡P ligands were coordinated η^1,η^2 through both the C≡P triple bond and the phosphorus lone pair.[25]

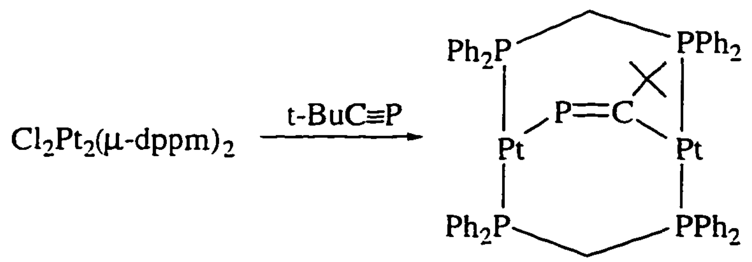
Several dinuclear phosphaalkyne complexes have been prepared in which the phosphaalkynes are bridged μ-perpendicular-η^2, η^2 to two metals forming complexes with



a tetrahedral M_2CP core where the R-C≡P ligand acts as a four-electron donor to the two metals. These compounds are similar to μ-η^2, η^2-bridged alkynes and have been prepared similarly by reacting R-C≡P with dimeric metal complexes containing metal-metal single, double or triple bonds.[7] The majority of these complexes contain the readily available phosphaalkyne t-BuC≡P; complexes thus obtained with R = t-Bu include $L_nM[\mu_2\text{-}\eta^2, \eta^2\text{-(t-Bu)C≡P}]ML_n'$; $L_nM = ML_n' = Co(CO)_3$;[22,26] $L_nM = ML_n'$ = NiCp;[27] $L_nM = ML_n' = Mo(Cp)(CO)_2$;[19,26] $L_nM = (CO)_3Co$, ML_n' = NiCp;[27] $L_nM = Cp(CO)_2Mo$, $ML_n' = W(Cp)(CO)_2$.[28] With the dicobalt metal system, the complexes $(CO)_3Co[\mu_2\text{-}\eta^2, \eta^2\text{-RC≡P}]Co(CO)_3$ with R = $N(i\text{-}Pr)_2$,[23] Me, Ph and $SiMe_3$ have also been prepared, although the complexes with R = Me, Ph and $SiMe_3$ were not formed by reacting R-C≡P with the dimeric metal complex, but rather were formed by the dechlorination of $R\text{-}CCl_2\text{-}PCl_2$ with $Co_2(CO)_8$.[29,30] The crystal structure of $(Cp)(CO)_2Mo[\mu_2\text{-}\eta^2,\eta^2\text{-(t-Bu)C≡P}]Mo(Cp)(CO)_2$



exhibited a phosphaalkyne C-P bond length (1.719 Å) that was quite a bit longer than those in mononuclear η^2-bonded phosphaalkyne complexes, but not quite as long as a C-P single bond (1.82-1.87 Å).[19] There are also some recent examples of $\mu_2\text{-}\eta^2$, η^2-phosphaalkyne complexes containing bridging ancillary ligands, e.g., $Fe_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-}\eta^2, \eta^2\text{-t-BuC≡P})$[31, 32] and $Co_2(CO)_4(\mu\text{-}\eta^2, \eta^2\text{-t-BuC≡P})(\mu\text{-}Ph_2PNHPPh_2\text{-P,P'})$[32]; the structure of both of these complexes were determined by X-ray diffraction studies and showed similar C-P bond lengths to those in other $\mu_2\text{-}\eta^2$, η^2-phosphaalkyne complexes. There is also an example of a dinuclear, μ-perpendicular-η^2, η^2-bridging phosphaalkyne complex $Cl_2Pt(\mu\text{-dppm})_2(\mu\text{-t-BuC≡P})$ which was formed by reacting (eq 6) the Pt-Pt bonded dimer $Cl_2Pt_2(\mu\text{-dppm})_2$ with t-BuC≡P.[33] In


(6)

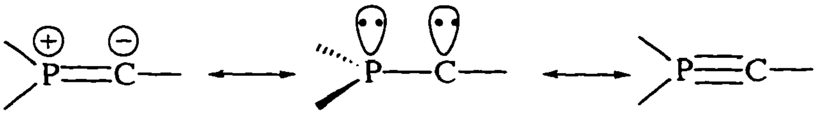
this complex, the phosphaalkyne donates one electron to each Pt center and is perhaps best viewed as a C,P-dimetallaphosphaalkene.[34]

Recently, mononuclear η^2-complexes of phosphaalkynes acting as four-electron donors have been described.[35,36] Although none have been structurally characterized because of the tendency to react further to form 1,3-diphosphacyclobutadiene complexes, these compounds represent a new class of phosphaalkyne complexes which are related to η^2-(4e) alkyne and nitrile complexes. In the complex $[WF(C_6H_4CH_2NMeCH_2CH_2NMe_2)(CO)(\eta^2\text{-t-BuC}{\equiv}P)]$,[36] the ^{31}P NMR chemical shift of the phosphaalkyne phosphorus atom (δ 452.4 ppm) is far downfield, even more so than in μ-η^2, η^2-phosphaalkynes, and the ^{13}C NMR spectrum showed a similar downfield signal for the phosphaalkyne carbon at δ 315.2 ppm. The large $^1J_{CP}$ value of 117.7 Hz is much larger than that in the free phosphaalkyne ($^1J_{CP}$ = 38.5 Hz) which is also indicative of the η^2-(4e) coordination mode.[36] These complexes underwent interesting coupling reactions[35,36] with phosphaalkynes and CO, which do not occur in the related η^2-(4e) nitrile complexes whose chemistry is dominated by ready dissociation of the nitrile ligand.

A great deal of work has been recently devoted to the functionalization of coordinated phosphaalkyne ligands by dimerization into η^4-diphosphacyclobutadiene complexes and by trimerization into η^6-triphosphaarene complexes. Also, phosphaalkynes have been functionalized into η^5-coordinated phosphacyclopentadienyl complexes having various numbers of phosphorus substituents. The chemistry of these ligands is quite well-developed, but is outside the scope of this review. However, several reviews[7-9] have been written on these fascinating new C=P multiply bonded ligands.

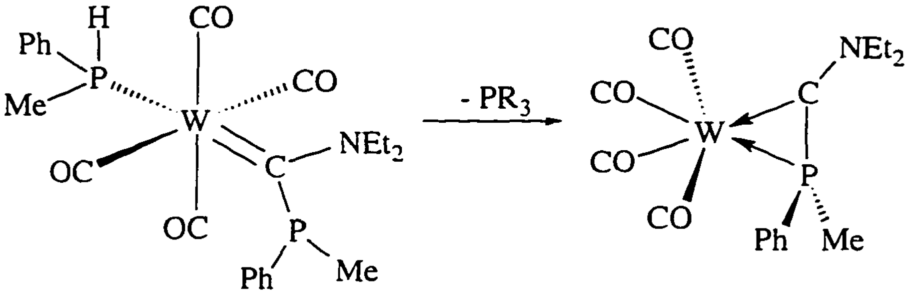
η^2-λ^5-Phosphaalkyne ($RC{\equiv}PR_2$) Complexes

In contrast to λ^3-phosphaalkynes (R-$C{\equiv}P$) which possess a triple bond, λ^5-phosphaalkynes must be regarded as a mixture of three resonance structures including a



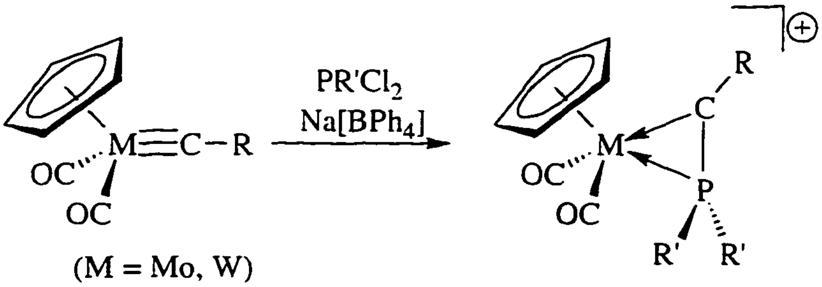
(A) **(B)** **(C)**

phosphorus-vinyl ylide (**A**), a phosphino-carbene (**B**) and a λ^5-phosphaalkyne (**C**). From ab initio calculations on the parent compound $HCPH_2$, the carbon-phosphorus overlap population is larger than in the isomeric phosphaalkene H_2CPH, and the calculated bond length was rather short (1.61 Å), indicating a strong contribution from resonance form **C**.[37] A series of these free λ^5-phosphaalkynes was prepared, but no X-ray structures were reported.[38] Although direct complexation of a free λ^5-phosphaalkyne has not yet been accomplished, a few examples of complexes containing η^2-λ^5-phosphaalkynes were prepared by other methods. When the tungsten carbene complex $(CO)_4[(Me)(H)(Ph)P]W(=C(NEt_2)(PMePh)$ was heated (eq 7), the phosphine ligand was removed with concomitant rearrangement of the carbene ligand from



(7)

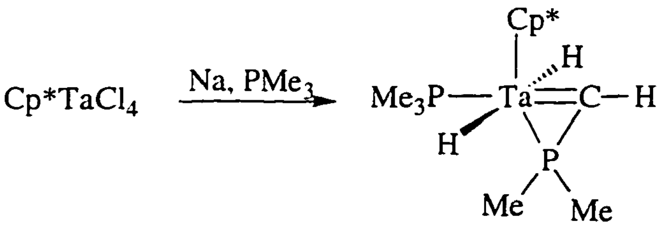
η^1-C to η^2-C,P forming $(CO)_4W[\eta^2\text{-}C(NEt_2){\equiv}P(Me)(Ph)]$. The structure of this compound was determined by X-ray diffraction studies to exhibit an η^2-λ^5-phosphaalkyne ligand acting as a four-electron donor.[39] Recently, a series of these complexes were prepared in a different manner (eq 8) by treating molybdenum and tungsten carbyne complexes of the type



(8)

$Cp(CO)_2M{\equiv}CR'$ with PR_2Cl and $NaBPh_4$ to form $[CpM(CO)_2\{\eta^2\text{-}C(R'){\equiv}P(R_2)\}](BPh_4)$ (M = Mo, W), or with PMe_3 followed by PR_2Cl and $NaBPh_4$ to generate $[CpM(CO)(PMe_3)\{\eta^2\text{-}C(R'){\equiv}P(R_2)\}](BPh_4)$ (M = W).[40-42] Although no crystal structures were determined in this system, spectroscopic properties were consistent with the presence of η^2-λ^5-phosphaalkyne ligands in the metal complexes.

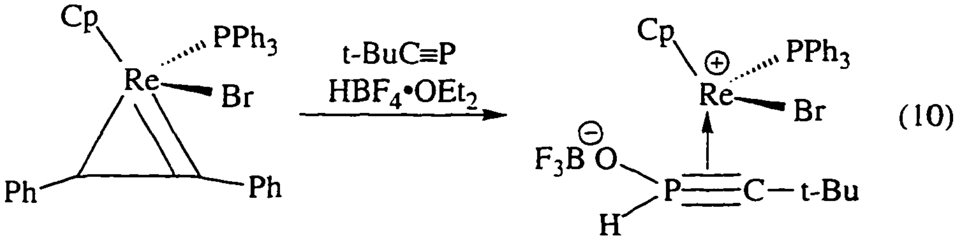
A different method of preparing η^2-λ^5-phosphaalkyne complexes involved the double intramolecular C-H bond activation of a coordinated PMe_3 ligand in early transition metal complexes to generate (η^2-(H)C≡PMe_2) ligands. When Cp^*TaCl_4 was reacted (eq 9) with metallic sodium in neat PMe_3, the complex $Cp^*(Me_3P)(H)_2Ta[\eta^2\text{-}(H)C{\equiv}PMe_2]$ formed in good

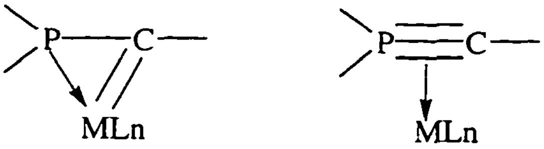


(9)

yield, where the two hydride ligands originated from a PMe_3 ligand to form the η^2-λ^5-phosphaalkyne complex.[43] Interestingly, if this complex was reacted with CO or H_2, the hydride ligands migrated back to the HC≡PMe_2 ligand to form $Cp^*Ta(PMe_3)_2(CO)_2$ or $Cp^*Ta(PMe_3)_2(H)_4$, respectively. However, when treated with MeX (X = Cl, Br) or $CHCl_3$, the HC≡PMe_2 ligand remained intact. Similar to eq 9, if $TaCl_5$ was treated with sodium in neat PMe_3, the complex $(Me_3P)_4(Cl)Ta[\eta^2\text{-}(H)C{\equiv}PMe_2]$ resulted which was further reacted with butadiene to generate the complex $(Me_3P)_2(Cl)Ta(\eta^4\text{-}C_4H_6)[\eta^2\text{-}(H)C{\equiv}PMe_2]$, the structure of which was determined by X-ray diffraction studies.[44]

A more recent example of an η^2-λ^5-phosphaalkyne complex involved the functionalization of a coordinated λ^3-phosphaalkyne complex. When the η^2-vinyl complex Cp(Ph$_3$P)(Br)Re[=C(Ph)CH(Ph)] was reacted (eq 10) with t-BuC≡P and HBF$_4$•OEt$_2$, the vinyl ligand was protonated and removed as *trans*-stilbene, and the complex Cp(Ph$_3$P)(Br)Re[η^2-(t-Bu)C≡P(H)(O$^-$•BF$_3$] formed; the structure of this complex was determined by X-ray diffraction studies to contain an η^2-λ^5-phosphaalkyne with a short C-P bond (1.699(7) Å).[45] This complex formed presumably by protonation of an η^2-λ^3-phosphaalkyne intermediate followed by oxygen transfer and conversion of BF$_4^-$ to BF$_3$, although detailed mechanistic information was not obtained. In all of the η^2-λ^5-phosphaalkyne complexes that were characterized by X-ray analysis, the metal-carbon distances were within the range for metal-carbon double bonds, indicating a strong contribution from a phosphino-carbene resonance form (**D**). However, the C-P distances (1.683-1.807 Å) are considerably shorter than that expected for a C-P single bond (1.82-1.87 Å), indicating a substantial contribution from an η^2-λ^5-phosphaalkyne resonance form (**E**). The NMR properties of these complexes are also characteristic, exhibiting downfield ^{13}C NMR chemical shifts for the C≡P carbon (δ 170-287 ppm) and upfield ^{31}P NMR chemical shifts for the C≡P phosphorus (δ -62 to -153 ppm). Also, a few examples of cluster-stabilized η^2-λ^5-phosphaalkyne osmium complexes have been prepared.[46]

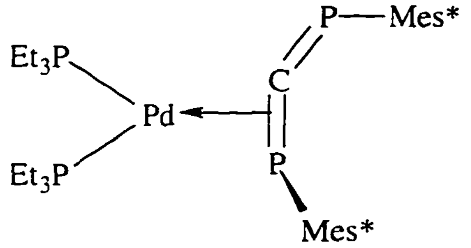




(D) **(E)**

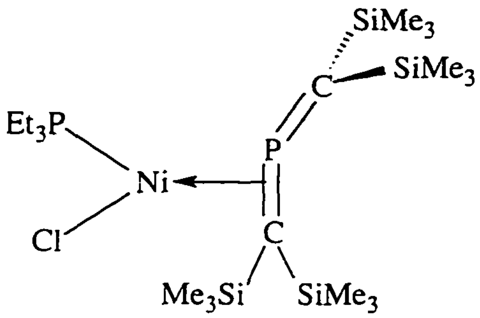
η^2-Phosphaallene ($R_2C{=}C{=}PR$) and Diphosphaallene ($RP{=}C{=}PR$) Complexes

Only a few examples of mono- and diphosphaallene metal complexes are known. *Ab initio* calculations on $HP{=}C{=}PH$ have shown that the two sets of σ-phosphorus lone pair (n) orbitals and the $C{=}P$ π-orbitals are similar in energy and act as the quasi-degenerate HOMOs; similar calculations on $HP{=}C{=}CH_2$ showed that the $C{=}P$ π-orbital is the HOMO.[47,48] In accord with these findings, the complexes $(PR_3)_2M(\eta^2\text{-Mes*P=C=PMes*})$ (M = Ni, R = Ph; M = Pd, R = Ph, Et; M = Pt, R = Ph) have been prepared, in which one of the $C{=}P$ bonds is η^2-coordinated to the transition metal.[8,49,50] The structure of $(PEt_3)_2Pd(\eta^2\text{-Mes*P=C=PMes*})$ was determined by X-ray diffraction and showed that the η^2-ligated $C{=}P$ bond length (1.73(3) Å) is slightly longer than that in the non-coordinated $C{=}P$ bond (1.67(3) Å).[50] Interestingly, in the η^2-monophosphaallene Pt(0) complexes $(PR_3)_2Pt(\eta^2\text{-Mes*P=C=CPh}_2)$, the metal coordinates through the $C{=}P$ bond rather than the $C{=}C$ bond, indicating the propensity of $C{=}P$ bonds to participate in π-bonding to transition metals.[50] When metal carbonyl fragments (e.g., $W(CO)_5$ and $Ni(CO)_3$) were coordinated to mono- and di-phosphaallenes, η^1-ligation through the phosphorus lone pair took place.[51] This is analogous to the situation in phosphaalkenes in which π-accepting ancillary ligands favor η^1-P over η^2-$C{=}P$ coordination. There are also a few examples of cluster-stabilized phosphaallene complexes.[52]



More recently, the first examples of η^2-coordinated 2-phosphaallene complexes $(PR_3)(Cl)M(\eta^2\text{-C(SiMe}_3)_2\text{=P=C(SiMe}_3)_2)$ (M = Pt, Ni) were reported from the reactions of

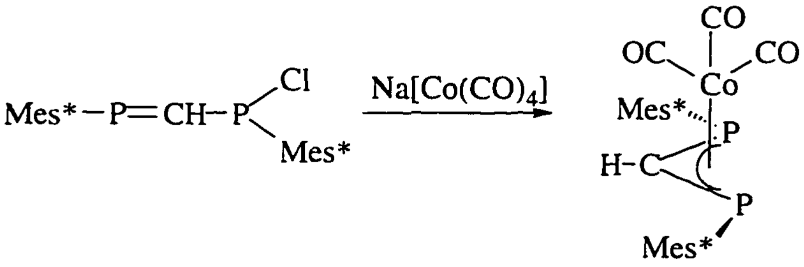
$M(PR_3)_2(COD)$ with $(SiMe_3)_2C{=}P(Cl){=}C(SiMe_3)_2$.[53] The structure of the nickel compound with $PR_3 = PEt_3$ was determined from X-ray diffraction studies and showed that the $(SiMe_3)_2C{=}P{=}C(SiMe_3)_2$ ligand was coordinated through one of the C=P bonds, acting as a



three-electron donor to the $Ni(PEt_3)Cl$ fragment. The η^2-coordinated C=P bond length (1.732(7) Å) was longer than that in the non-coordinated C=P bond (1.663(8) Å), consistent with the lengthening of η^2-coordinated C=P bonds in other phosphaallene systems.

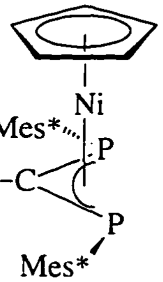
η^3-1-Phosphaallyl ($RP\text{-}CR{=}CR_2$) and 1,3-Diphosphaallyl ($RP\text{-}CR{=}PR$) Complexes

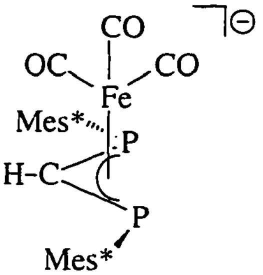
Similar to allyl compounds which contain a delocalized π-system and tend to coordinate η^3 to transition metal fragments, phosphaallyl and diphosphaallyl compounds (where PR groups are substituted for CR_2 groups in an allyl) have also been found to contain delocalized π-systems and can coordinate in an η^3-fashion. There is only one known example of an η^3-coordinated monophosphaallyl complex, $Cp(CO)Fe[\eta^1,\eta^3\text{-}CH_2CHPPh]W(CO)_5$, which was additionally η^1-coordinated through the phosphorus lone pair to a $W(CO)_5$ fragment.[54,55] NMR studies of this complex showed that the $W\text{-}P\text{-}CH{=}CH_2$ moiety is planar, and the P-C=C unit is η^3-coordinated to the Cp(CO)Fe fragment. In contrast, there are several known examples of η^3-coordinated 1,3-diphosphaallyl complexes. These complexes were first prepared by reacting (eq 11) $Na[Co(CO)_4]$ with the chlorophosphino-substituted 1,3-diphosphapropene compound Mes*P=CH-P(Cl)(Mes*) to form $(CO)_3Co[\eta^3$-



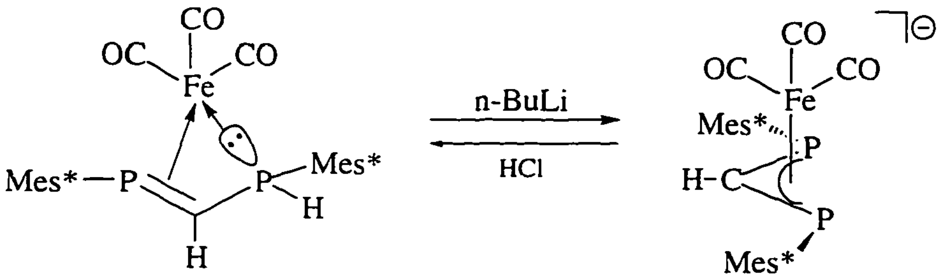
(11)

diphosphaallyl].[56] The X-ray-determined structure showed a planar arrangement of the PCP-skeleton and the C(1) atoms of the aryl moieties: the three atoms of the PCP triad are coordinated to cobalt.[56] The C-P bond lengths were both very similar and intermediate between single and double C-P bonds, further supporting the delocalized bonding. Similarly, K[CpNi(CO)] and Na$_2$[Fe(CO)$_4$] were reacted with Mes*P=CH-P(Cl)(Mes*) to form CpNi[η^3-diphosphaallyl][57] and [(CO)$_3$Fe(η^3-diphosphaallyl)]$^-$,[58] respectively. The



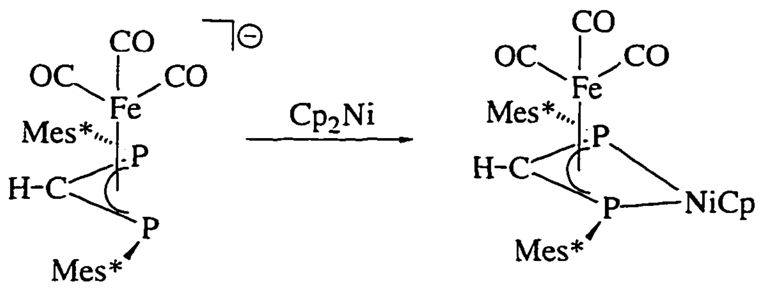


diphosphaallyl complex of iron was also formed by reacting the diphosphaallyl anion [Mes*P=CH-P(Mes*)]Li with Fe(CO)$_5$ or by reacting (eq 12) the η^1,η^2-diphosphapropene complex (CO)$_3$Fe[η^1,η^2-P(Mes*)=CH-PHMes*] with n-BuLi.[58] This η^1,η^2-



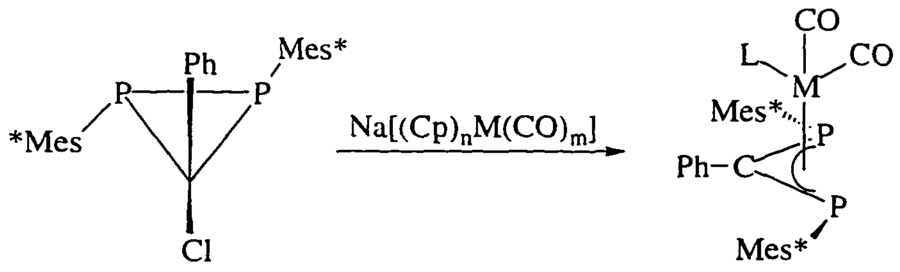
(12)

diphosphapropene complex was then regenerated (eq 12) by protonating the η^3-diphosphaallyl complex with HCl. When the η^3-diphosphaallyl complex of iron was reacted with nickelocene (eq 13), a new type of complex was obtained which, in addition to the η^3-coordination of the Fe(CO)$_3$ group, contained a NiCp fragment coordinated to both of the lone pairs of the diphosphaallyl ligand.[59] The X-ray determined structure showed a planar diphosphaallyl fragment that is still η^3-coordinated to iron, and the Ni-P distances were very similar to those in related nickel phosphine complexes.



(13)

More recently, a series of η^3-diphosphaallyl complexes have been prepared (eq 14) by reacting anionic metal complexes with diphosphirane compounds.[60] Some of these reactions also produced intermediate η^1-P bound diphosphaallyl complexes, which were characterized by NMR spectroscopy. All of the X-ray structures of these diphosphaallyl complexes exhibit planar PCP units that have very similar C-P bond lengths that are intermediate between single and double bond lenths, indicative of the delocalization in these complexes.

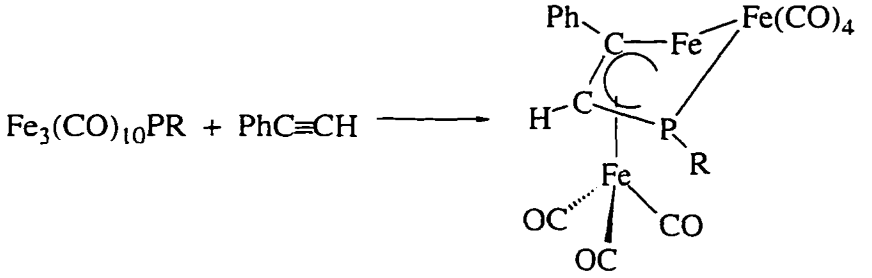


(14)

M=Mo, L=Cp
M=W, L=Cp
M=Co, L=CO

η^4-Phosphabutadiene (RP=C(R)-C(R)=CR$_2$) and Diphosphabutadiene (RP=C(R)-C(R)=PR) Complexes

By analogy with the many η^4-butadiene complexes that are known to involve delocalized π-bonds within the planar C_4 skeleton of the ligand, a variety of phosphorus-substituted analogs have been investigated as ligands. A few examples of η^4-coordinated tungsten 1-phosphabutadienes are known of the type $(CO)_4W(\eta^4\text{-}RP{=}C(R)\text{-}C(R){=}CR_2)$; although no structures have been reported, NMR evidence suggests planar, delocalized PCCC frameworks in these complexes.[61] There is also an example of an η^4-coordinated 1-phospha-4-metallabutadiene complex that was formed (eq 15) by insertion of an alkyne into one of the Fe-P bonds of the phosphinidene complex $[Fe_3(CO)_{10}PR]$ (R = *p*-$MeOC_6H_4$).[62] The structure of this complex exhibited a nearly planar FeCCP moiety that is η^4-coordinated to an $Fe(CO)_3$ fragment. There have been two recent examples of η^4-coordinated 2-phosphabutadiene complexes, both of which contain a $W(CO)_5$ fragment coordinated to the phosphabutadiene phosphorus lone pair and were characterized by X-ray diffraction studies. When the η^1-2-phosphabutadiene tungsten complex $(CO)_5W[\eta^1\text{-}(SiMe_3)_2C{=}P\text{-}C(OEt){=}C(H)Ph]$ was reacted (eq 16) with $Fe_2(CO)_9$, an η^1, η^4-2-phosphabutadiene complex resulted, in which the CPCC



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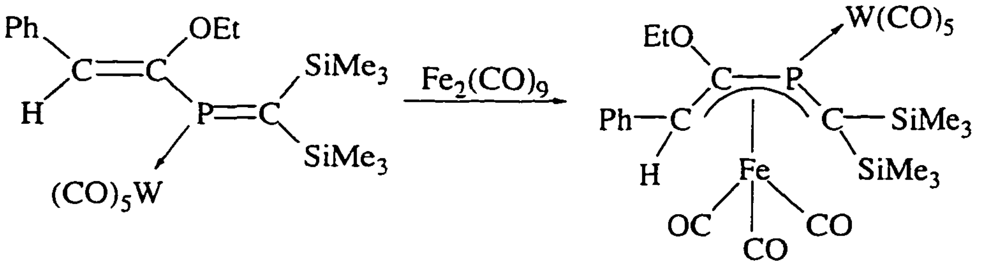
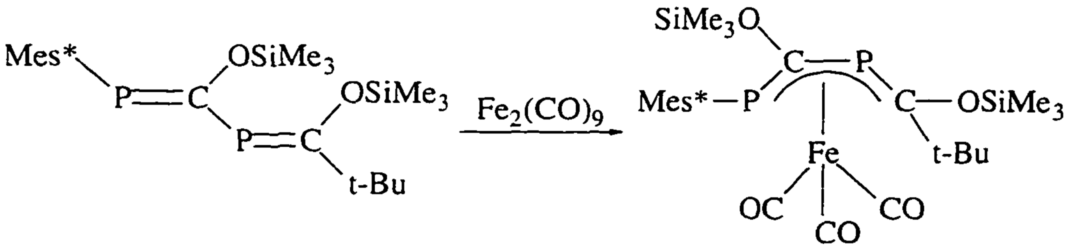
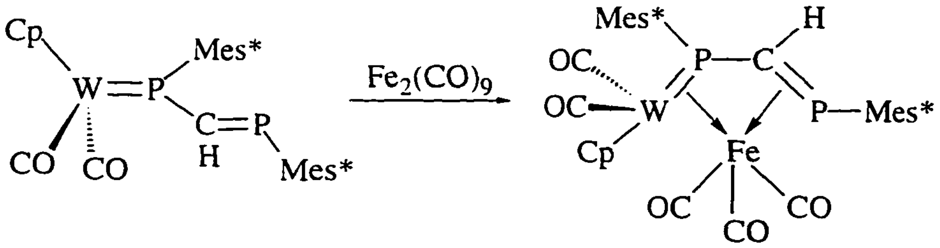

(16)

moiety is almost planar and only partially delocalized with C-P distances of 1.754(8) Å and 1.814(8) Å, indicating partial C=P-C=C character in the phosphabutadiene ligand.[63] In contrast, full delocalization occurs in the η^1, η^4-2-phosphabutadiene complex [(CO)$_3$Fe{η^4-CHMe$_2$(H)C=P-C(H)=C(H)Ph[W(CO)$_5$]}], where the C-P distances of 1.753(4) Å and 1.743(4) Å are the same within error, and the CPCC skeleton is planar.[64]

There are a few examples of η^4-coordinated 1,3-diphosphabutadiene complexes, which tend to exhibit planar PCPC skeletons as in monophosphabutadiene complexes. These have been prepared by reacting 1,3-diphosphabutadienes with transition-metal carbonyl complexes. In the reaction (eq 17) of Mes*P=C(OSiMe$_3$)-P=C(OSiMe$_3$)t-Bu with Fe$_2$(CO)$_9$, the η^4-


(17)

coordinated 1,3-diphosphabutadiene complex [(CO)$_3$Fe{η^4-Mes*P=C(OSiMe$_3$)-P=C(OSiMe$_3$)t-Bu}] formed, but a reaction with the same 1,3-diphosphabutadiene and Ni(CO)$_4$ resulted in formation of the η^1-P coordinated complex.[65] The ^{31}P NMR spectra of these complexes showed peaks at δ -14.5 and -62.5 ppm in the former and at δ 179.8 and 138.3 ppm in the latter; the upfield shift of the signals in the η^4-complex is typical of the large upfield shifts seen in side-on bound C=P compounds. There is also a report of an interesting η^4-coordinated 1,3-diphospha-4-metallabutadiene complex that was prepared (eq 18) by



(18)

reacting a tungsten phosphinidene complex with $Fe_2(CO)_9$.[66] The structure of this complex, determined by X-ray diffraction studies, exhibits a nearly planar arrangement of the W-P-C-P framework and the two P-C bonds were the same within error, supporting the view that this is a delocalized heterobutadiene complex.

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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

A paper submitted to *Organometallics*

Wayde V. Konze, Victor G. Young, Jr.[†], and Robert J. Angelici*

Abstract

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 4-coordinate, planar nickel atoms in a butterfly arrangement with a Ni-Ni distance that is too long for 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 $RP{=}C{=}PR$ which 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 which 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.

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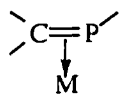
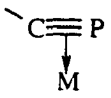
Introduction

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**).


(A)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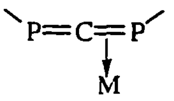
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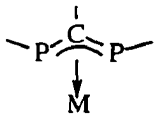
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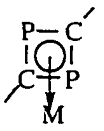
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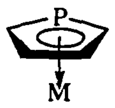
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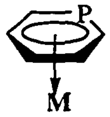
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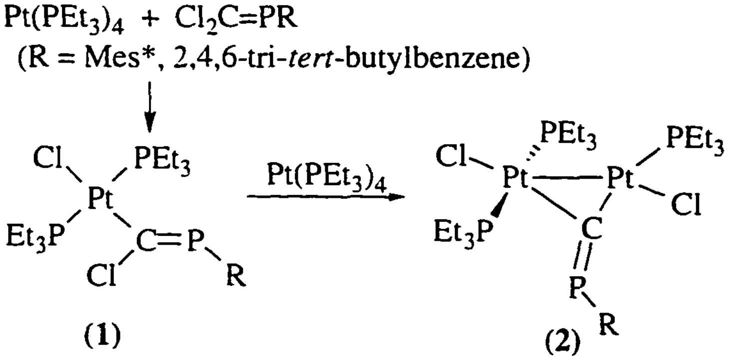
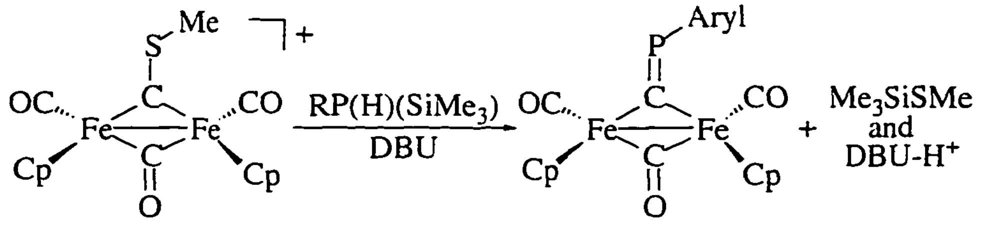
The coordination chemistry of phosphaalkenes (**A**) and phosphaalkynes (**B**) has been reviewed,[1] as has the coordination chemistry of the cyclic phosphorus-substituted compounds of types **E-G**.[2] However, the coordination chemistry of diphosphaallenes (**C**) and diphosphaallyls (**D**) is much less developed.[3] Phosphorus ylides ($R'_2C{=}PR_3$), which are the tetracoordinate (σ^4) phosphorus analogs 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 analogs of diphosphaallenes, i.e. ($R_3P{=}C{=}PR_3$)[5] and diphosphaallyls, i.e. $[(R_3P)HC{=}PR_3]^+$,[6] as well as mixed σ^2, σ^4-diphosphaallyls $[(R_3P)HC{=}PR']^+$.[7-10] However, there are no examples 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=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 semi-bridging :C=PR group.[12] More recently, Weber and coworkers reported the synthesis (eq 2) of a diiron complex containing a symmetrically-bridged :C=PR ligand (**3**) by a different route.[13]



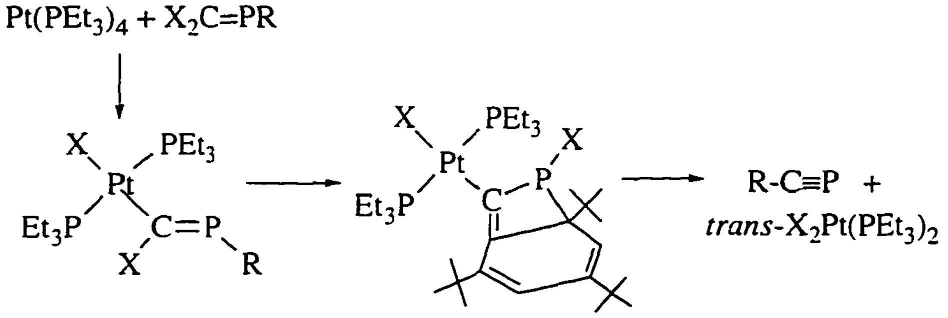
(1)



(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=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]

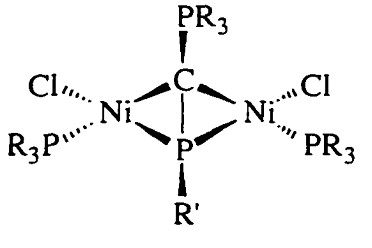


(4)

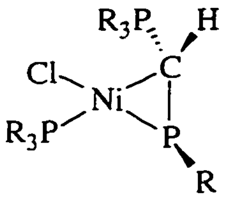
(3)

X=Cl, Br
R=2,4,6-tri-*tert*-butylphenyl

In order to probe the generality of eq 1 for the synthesis of other complexes containing :C=PR ligands, we explore in the present paper reactions of $Cl_2C=PR$ with Ni(0) complexes. We chose $Cl_2C=PR$ reactants with non-aromatic 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, which 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 ligands can also be called isocyaphides ($C{\equiv}PR$) and are phosphorus analogs 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 $:C{=}PR$ ligand in **H** illustrates that phosphorus analogs of isocyanides offer unique differences in bonding with respect to their well-studied isoelectronic analogs. We have also isolated the first example of a coordinated σ^2, σ^4-diphosphaallyl, or phosphavinyl phosphonium ligand, which 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 appropriate drying agents 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 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. Phosphine ligands were purchased from Strem and used without further purification, with the exception of PPh_3, which was recrystallized from MeOH.

Preparation of $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (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 one hour, **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 and washed with 3x5 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 warming to room temperature with stirring over the course of an hour, the reaction mixture was worked up as above.

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 warming to room temperature with stirring over the course of an hour, the reaction mixture 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.

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 reaching room temperature in about 1 h, a $^{31}P\{^1H\}$ NMR showed **Ib** as the main product. Compound **Ib** decomposed into non-isolable products after one 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 warming 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 non-isolable products after one day in solution and was characterized by $^{31}P\{^1H\}$ NMR spectroscopy as discussed in the

Results. $^{31}P\{^{1}H\}$ NMR (THF, -40°C) (see Scheme 2 for atom labels): δ(P(x)) 39.5 (dt, $^{2}J_{P(x)P(a)}$ = 54.3 Hz, $^{2}J_{P(x)P(b)}$ = 49.9 Hz), δ(P(a)) 20.3 (dt, $^{2}J_{P(a)P(x)}$ = 54.3 Hz, $^{3}J_{P(a)P(b)}$ = 5.5 Hz), δ(P(b)) 10.9 (dd, $^{2}J_{P(b)P(x)}$ = 49.9 Hz, $^{3}J_{P(b)P(a)}$ = 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 warming 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 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 x10 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 warming slowly to room temperature with stirring, the reaction mixture was worked up as above.

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 warming slowly to room temperature with stirring, the reaction mixture was worked up as above to yield 0.121 g of **Va** (34% based on $Cl_2C{=}PMes^*$). $^{31}P\{^{1}H\}$ NMR (toluene) (see eq 4 for atom labels): δ(P(a)) 25.5 (d, $^{2}J_{P(a)P(x)}$ = 33.1 Hz), δ(P(x)) 21.6 (dd, $^{2}J_{P(x)P(a)}$ = 33.1 Hz, $^{2}J_{P(x)P(b)}$ =82.5 Hz), δ(P(b)) 17.8 (d, $^{2}J_{P(b)P(x)}$ = 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$_2$C=PMes* (0.375 g, 0.909 mmol) in toluene (10 mL). After warming 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), filtered, and crystals of **Vb** (0.295 g, 35% based on Br$_2$C=PMes*) were obtained by cooling the filtrate slowly to -78°C. ^{31}P{^{1}H} 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$_2$C=PMes* (0.150 g, 0.364 mmol) in toluene (10 mL). After warming 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{^{1}H} NMR spectroscopy as discussed in the Results. ^{31}P{^{1}H} 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$_3$P)Ni[η^2-^{13}C(H)(PPh$_3$)=P(Mes*)] by using the procedure in Method A above. ^{31}P{^{1}H} 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{^{1}H} 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 $Br(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3)=P(Mes^*)]$ (Vb) to $Br(Et_3P)Ni[\eta^2\text{-}C(H)(PPh_3)=P(Mes^*)]$ (VI). To a THF solution of compound **Vb** (0.050 g, 0.0545 mmol) in an NMR tube was added one equivalent 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 section. 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).

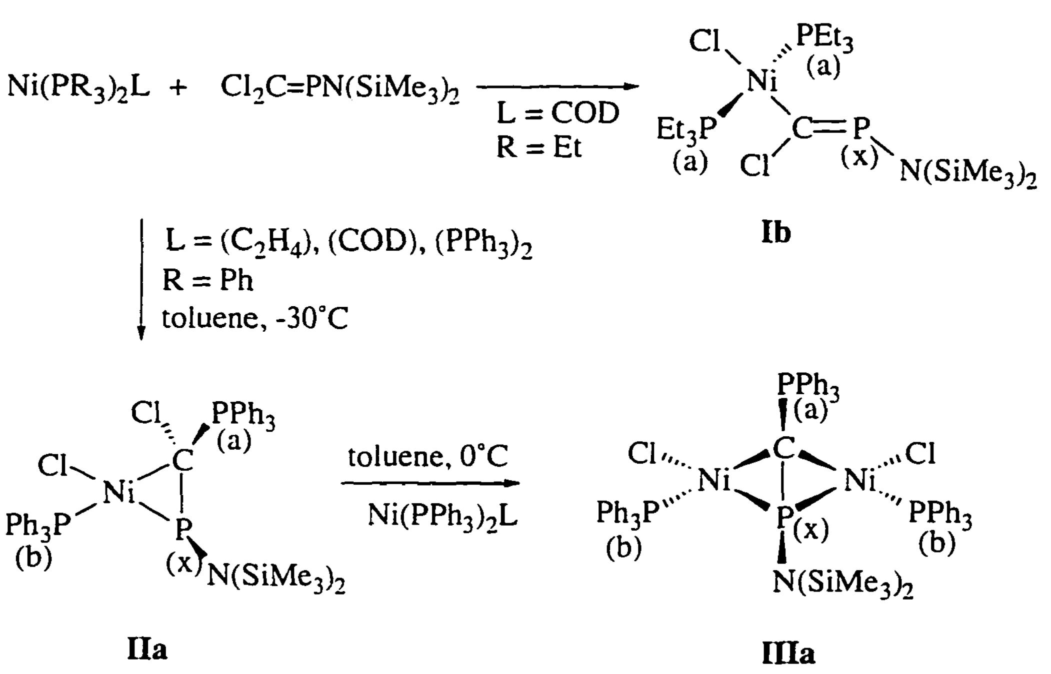
X-ray Crystallographic Study of $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C(PPh_3)=PN(SiMe_3)_2]$ (IIIa) Diffraction-quality crystals of **IIIa** were obtained by recrystallization from toluene at -78°C. Data collection and reduction information are given in Table 1. A dark green crystal 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 twin law could be applied. However, eight reflections which had $F_o^2 >> F_c^2$ 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 one-half equivalent 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 $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**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.

Scheme 1



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** 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., $^2J_{P\text{-}P} = 124.6$ Hz in $[(Ph_3P)(H)C{=}PN(i\text{-}Pr)_2]^+$, which also contains an $R_3P\text{-}C{=}PR$ 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 $^2J_{P\text{-}P}$ 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 $^2J_{P\text{-}P} = 28.6$ 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.

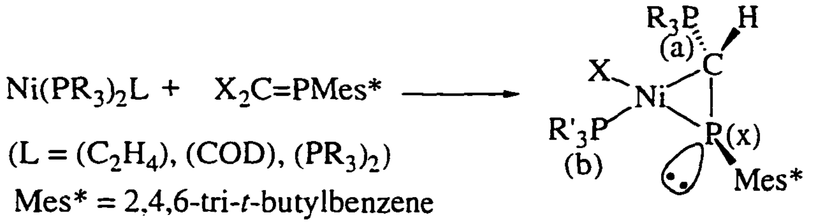
The ^{31}P NMR spectrum of **IIa** is similar to that of the analogous compound **Va** (eq 4). The peak at δ 103.7 ppm is assigned to the C=PR phosphorus P(x), since a proton-coupled ^{31}P NMR spectrum showed this peak as a sharp doublet of doublets, while the peaks at δ 22.4 and 19.0 ppm were broadened 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 analogs of **IIa** or **IIIa**, even when two equivalents 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 analog $Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$, 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 one-half equivalent 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 $(Ph_3P)_3ClNi{\bullet}(Me_2C{=}O)$, 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 product. When only one equivalent 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 one half equivalent of Br$_2$C=PMes* gave an analogous product (**Vc**), which was characterized by its ^{31}P NMR spectrum.



$$\mathrm{Ni(PR_3)_2L} + \mathrm{X_2C{=}PMes^*} \longrightarrow \qquad (4)$$

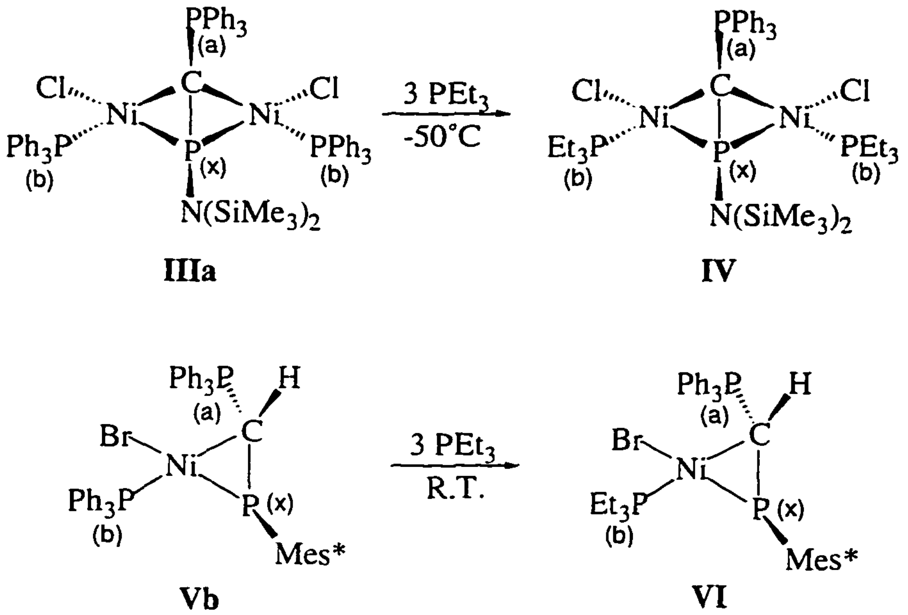
(L = (C$_2$H$_4$), (COD), (PR$_3$)$_2$)
Mes* = 2,4,6-tri-*t*-butylbenzene

Va (X=Cl, R=R'=Ph)
Vb (X=Br, R=R'=Ph)
Vc (X=Br, R=R'=Cy)

Compounds **Va**-**Vc** were characterized by ^{31}P{^{1}H} 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$_2$C=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$_3$)$_2$[η^2-(Me$_3$Si)$_2$C=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 ^{1}H NMR spectrum, and the presence of this proton was deduced indirectly from the ^{1}H-coupled ^{13}C NMR spectrum of ^{13}C-labeled **Va**, [Cl(Ph$_3$P)Ni[η^2-^{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 ${}^1J_{CH3P}$ = 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., ${}^1J_{CH2P}$ = 100.7 Hz in $Ph_3P{=}CH_2$) and η^1 C-coordinated (e.g., ${}^1J_{CH2P}$ = 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 two equivalents 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 one day and

Scheme 2



could not be isolated. Substitution of the carbon-bound PPh_3 group was not observed, even when three equivalents 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'-bi-borabicyclo[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.

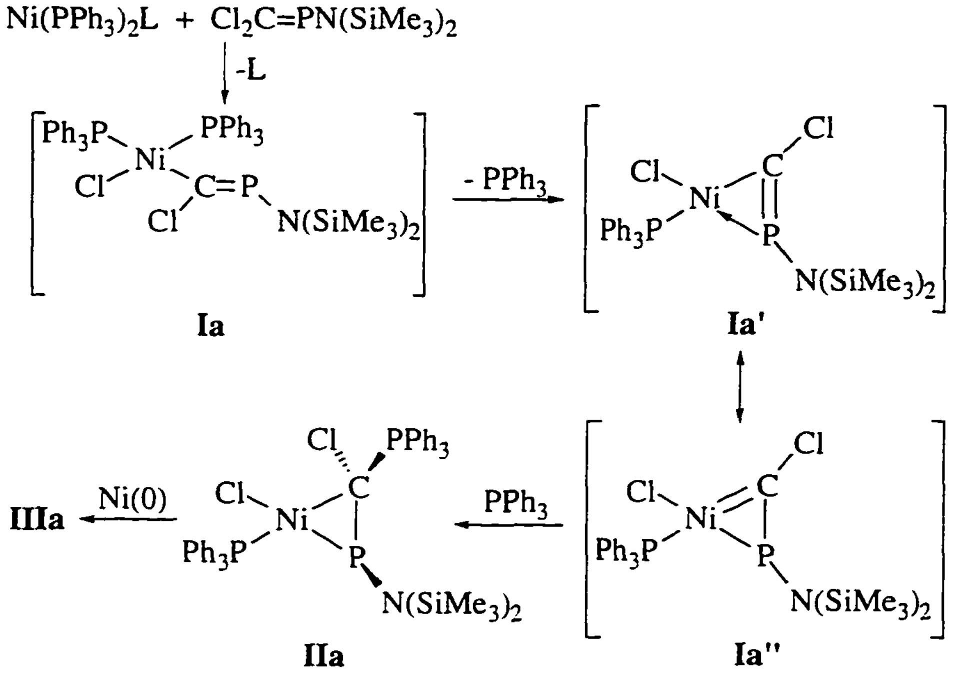
Evidently, the carbon-bound PPh_3 group in **IIIa** is much more difficult to substitute or remove than the nickel-bound PPh_3 ligands, which precludes the formation of a phosphavinylidene complex from **IIIa**.

Compound **Vb** reacts with one equivalent 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.

Discussion

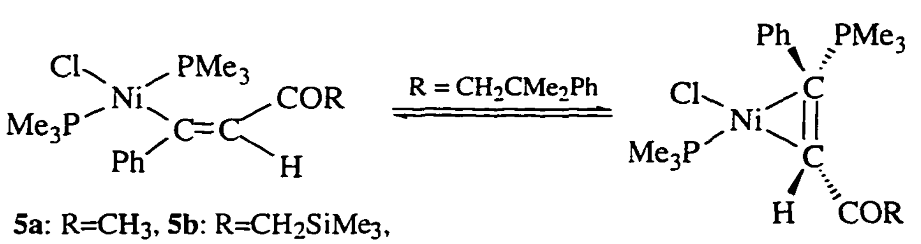
$Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (IIIa). Compound **IIIa** contains the first example of a phosphavinylidene phosphorane ($R_3P{=}C{=}PR$) ligand, or phosphine donor stabilized phosphavinylidene, which acts as a six-electron donor to the two nickel atoms 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 phosphavinylidenes (:C=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 analogs 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 a phosphavinylidene 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

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°C to -30°C; at -30°C, compound **IIa** begins to form. However, when triethylphosphine is used in this reaction, the phosphavinyl compound $Cl(Et_3P)_2Ni[C(Cl)=PN(SiMe_3)_2]$ (**Ib**) forms and was characterized by ^{31}P NMR spectroscopy as discussed in the Results section, which indirectly supports **Ia** as an intermediate. It is not clear why compound **Ib** does not go on to form triethylphosphine analogs 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 section.

The step involving rearrangement of **Ia** to **IIa** is similar to the intramolecular 1,2 shift of PMe_3 in an η^1-vinyl nickel complex (eq 5) to form an η^2-vinyl phosphonium compound.[42]

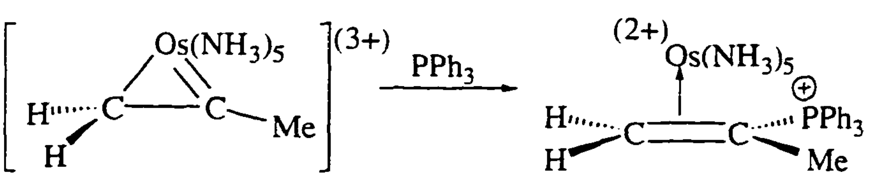


(5)

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

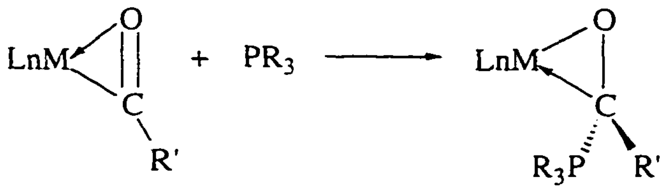
6d

In the structurally characterized η^1-vinyl 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 analogs 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



(6)

also a few examples of phosphine attack on related η^2-acyl ligands[51-53] (eq 7). A plausible



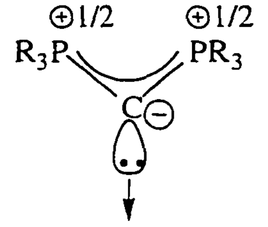
(7)

explanation 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 $Cp(CO)_2W[\eta^2$-$C(Ph)=PPh\{W(CO)_5\}]$ 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 one equivalent 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 section), 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**.

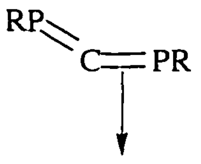
$Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3){=}P(Mes^*)]$ Va. The reactions of Ni(0) complexes with $Cl_2C{=}PN(SiMe_3)_2$ (Scheme 1) and $Cl_2C{=}PMes^*$ (eq 4) occur under the same mild conditions but give quite different products. In an effort to understand why different R groups in the phosphaalkenes ($Cl_2C{=}PR$) 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) compounds $Ni(PPh_3)_3Cl$, 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 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 two equivalents 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 dry box 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 d) 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 non-deuterated 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.

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). Thermal ellipsoid drawings (Figures 1 and 2) of complex **IIIa** show 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 as found in $Cl_2C{=}PN(SiMe_3)_2$ (1.685(2) Å)[60] than to that (1.773(8) Å) of the side-on π-bound phosphaalkene in $Ni(PMe_3)_2[\eta^2\text{-}(Me_3Si)_2CHP{=}C(SiMe_3)_2]$.[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 $Ph_3P{=}CH_2$,[61] and C-coordinated ylide C-P bond lengths, e.g. 1.745(8) Å in $(CO)_3Ni[(H)(Me)C{=}PCy_3]$.[62] The C(1)-P(2) distance indicates more ylidic ($C^-\text{-}P^+$) than phosphonium ($C\text{-}P^+$) 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 $[(Ph_3P)(H)C{=}PN(i\text{-}Pr_2)](BF_4)$.[7] The Ni(1)-P(1) and Ni(2)-P(1) distances (2.133(2) Å 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) Å and 2.195(2) Å, respectively) and are also shorter than the Ni-P (phosphaalkene) distance (2.239(2) Å) found in $Ni(PMe_3)_2[\eta^2\text{-}(Me_3Si)_2CHP{=}C(SiMe_3)_2]$.[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]

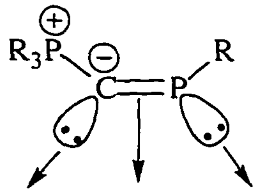
The structure of **IIIa** (Fig. 1) suggests that the novel phosphavinylidene-phosphorane ligand ($R_3P{=}C{=}PR$) is a six-electron donor, providing two electrons from the ylide carbon, two from the C=P double bond and two from the lone pair on phosphorus as shown in **L**. As mentioned, this ligand 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 $R_3P{=}C{=}PR$ in **L** ligand is drawn as the ylide rather than ylene form, which is a more appropriate representation as *ab initio* calculations have shown that the short C-PR_3 bond lengths found in ylides are more due to strong electrostatic attraction between the anionic carbon and the cationic phosphorus R_2C^{-}-PR_3^{+} than to a true ylene form $R_2C{=}PR_3$ with a C=P double bond.[63,64] A more appropriate comparison of the bridging phosphavinylidene-phosphorane ligand **L** is with diimino (**M**), iminophosphine (**N**), diphosphene (**O**) and disulfur (**P**) ligands.[65] 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 $\mu_2{:}\eta^2,\eta^2$-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**.[65-67] The tetrahedrane dimers **7**-**10** are closely related to **IIIa**, although they contain



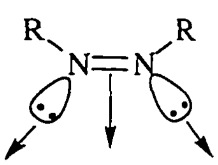
(J)



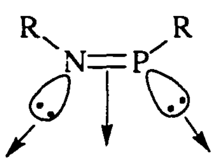
(K)



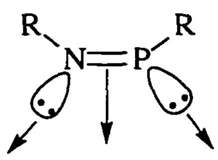
(L)



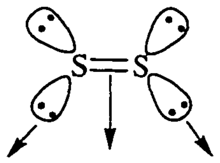
(M)



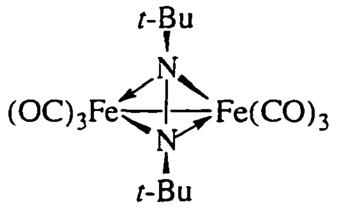
(N)



(O)



(P)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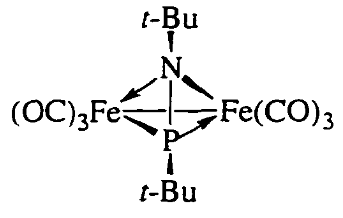
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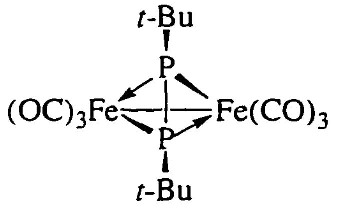
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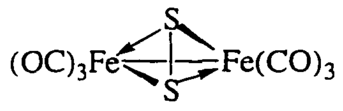
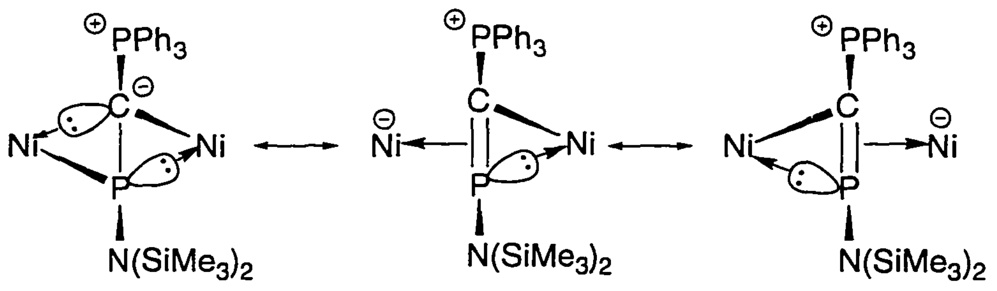

(10)

metal-metal bonds to give an eighteen electron count, while in **IIIa** the two nickel atoms have a total of sixteen valence electrons each and no metal-metal bond is needed. 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_3P=C=PR group acting as a six-electron donor overall. This is quite similar to the bonding in the related dimers **7-10**.[65-67] The short Ni(1)-P(1) and Ni(2)-P(1) bond lengths support a contribution from this phosphido-type of resonance form, and the short C(1)-P(2) bond length is explained by the electrostatic attraction

Scheme 4

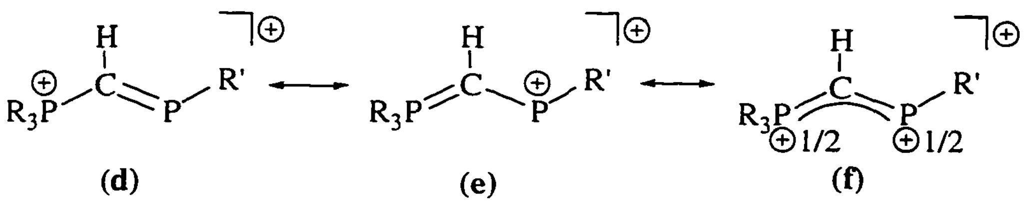

(a) (b) (c)

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 minus 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_3P=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), while the neutral nickel atom is formally Ni(II). Here the R_3P=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_3P)Ni[η^2-C(H)(PPh_3)=P(Mes*)] (Va). The structural drawing (Figure 3) 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_3P)(H)C=PN(i-Pr_2)](BF_4),[7] which is a cationic analog 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_3P)(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_3Si)$_2$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 $Ph_3P{=}CH_2$,[61] but shorter than the corresponding Ph_3P-C bond (1.798(14) Å) in $[(PPh_3)(H)C{=}PN(i\text{-}Pr_2)](BF_4)$. The Ni-C(1) distance in **Va** (1.977(5) Å) is the same within error as the Ni-C distances (1.97(1) and 1.95(2) Å) in the related η^2-vinyl phosphonium compound $(Me_3P)_2ClNi[\eta^2\text{-}PhC{=}CH(COCH_2CMe_2Ph)]$ (**6d**, eq 5).[42] The Ni-P(1) distance in **Va** (2.1793(13) Å) is the same within error as the Ni-P(3) distance (2.1783(14) Å) which suggests the lack of participation of a Ni-P(1) phosphido-like resonance structure as observed in **IIIa**.

Compound **Va** is the first example of a complex containing a coordinated phosphavinyl phosphonium ligand. A few examples of uncoordinated phosphavinyl phosphonium salts $[(R_3P)RC{=}PR]^+$ [7-10] have been reported in the literature and the structure of $[(PPh_3)(H)C{=}PN(i\text{-}Pr_2)](BF_4)$ 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

Scheme 5

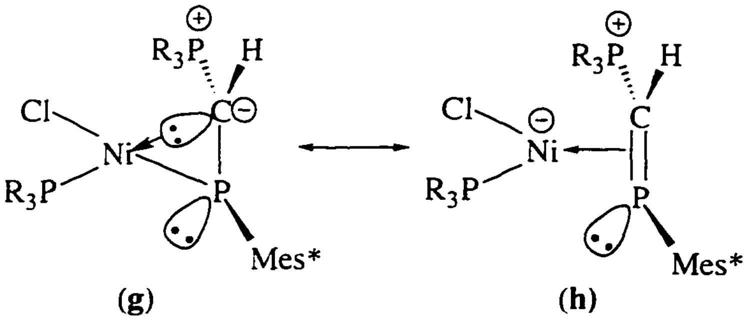


behavior in the $(Ph_3P)(H)C{=}PMes^*$ ligand which is bound η^2 through the C(1)-P(1) bond in **Va** as opposed to η^3 through the P(2)-C(1)-P(1) allyl-like unit as in compounds of the type $(R_3P)(X)Ni[\eta^3\text{-allyl}]$. There are a few examples of η^3-coordinated σ^2, σ^2-diphosphaallyl ligands,[68-71] but the $(Ph_3P)(H)C{=}PMes^*$ 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 $(Ph_3P)(H)C{=}PMes^*$ 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 $(Ph_3P)(H)C{=}PMes^*$ ligand donates three electrons to the thirteen-electron nickel fragment, which is formally Ni(II). Resonance form **h** can be viewed as an η^2-phosphavinyl phosphonium cation (1+) coordinated to a formally Ni(0) metal fragment. This is a zwitterionic structure with the minus charge located on nickel and the C=P double bond acting as a two-electron donor. The somewhat short C(1)-P(2) distance found in **Va** suggests a contribution from form g in Scheme 6. However, the Ni-P(1) distance is typical of Ni-phosphine bonds, and is not indicative of a phosphido structure, suggesting more of a contribution from resonance form **h**. Unlike structure **IIIa**, the C=P phosphorus lone pair is unavailable for bonding 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]

Scheme 6



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.[72,73] 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 $Cp(CO)_2FeP{=}PMes^*$ (**12**)[74], 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**),[75] 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**)[76] 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, Fig. 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-*t*-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 analog (**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 American Chemical Society, for support of this research through grant 27360-AC3.

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Table 1. Crystal and Data Collection Parameters for $Ni_2Cl_2(PPh_3)_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(PPh_3)\text{=}PN(SiMe_3)_2]$ (**IIIa**) and $Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3)\text{=}P(Mes^*)]$ (**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
crystal size, mm	0.25 x 0.12 x 0.03	0.4 x 0.34 x 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	2θ-θ	Area Detector, ω-frames
data collection range, *θ*, deg	2.34-56.82	1.75-24.11
no. of data collected	9814	10481
no. of unique data total	9227	7384

Table 1. (continued)

	IIIa	Va
with I$\geq$ 2σ (I)	9207	5879
no. of parameters refined	840	613
trans factors; max; min	0.78/0.55	0.818/0.649
R^a (I>2σ (I))	0.0699	0.0622
$R_w{}^b$ (I>2σ (I))	0.1753	0.1378
quality of fit indicator[c]	1.052	1.090
largest peak, e/Å^{-3}	0.642	0.610

---

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

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

Distances (Å)

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 (deg)

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$_3$P)Ni[η^2-C(H)(PPh$_3$)=P(Mes*)] (**Va**).

Distances (Å)

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 (deg)

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.

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
$Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3)=P(Mes^*)]$ **(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) Ref. 12.

d) Ref. 12.

e) This work.

f) Ref. 75.

g) Ref. 73.

h) Ref. 74.

Figure Captions

Figure 1. Thermal ellipsoid drawing of $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C(PPh_3)=PN(SiMe_3)_2]$ (**IIIa**)

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

Figure 3. Thermal ellipsoid drawing of $Cl(PPh_3)Ni[\eta^2\text{-}C(H)(PPh_3)=P(Mes^*)]$ (**Va**)

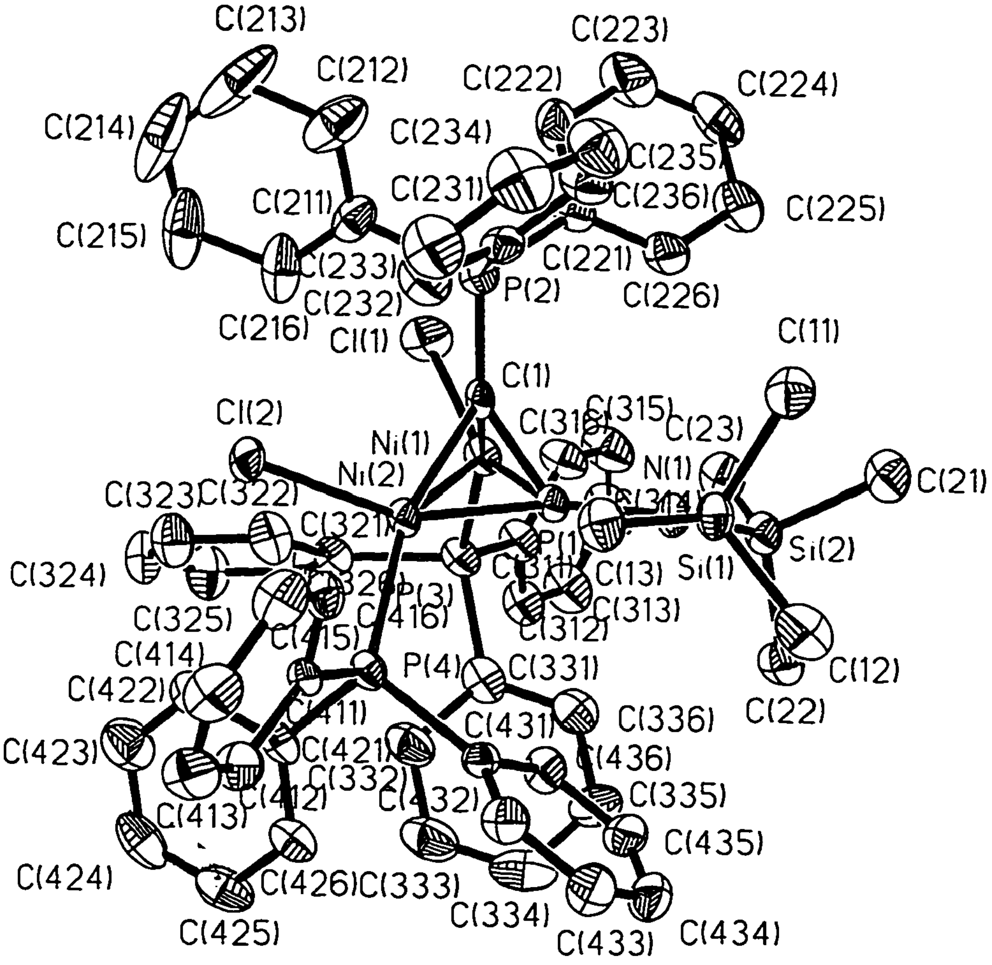
C(213)
C(223)
C(212)
C(222)
C(224)
C(214)
C(234)
C(235)
C(231)
C(236)
C(211)
C(225)
C(215)
C(233)
C(221)
C(232)
P(2)
C(226)
C(216)
Cl(1)
C(11)
C(1)
Cl(2)
C(316)
C(315)
Ni(1)
C(23)
N(1)
C(21)
Ni(2)
C(323)
C(322)
C(314)
C(321)
P(1)
Si(2)
C(311)
C(13)
Si(1)
C(324)
C(326)
P(3)
C(416)
C(313)
C(325)
C(415)
C(312)
C(414)
P(4)
C(331)
C(12)
C(422)
C(411)
C(336)
C(22)
C(423)
C(421)
C(431)
C(436)
C(332)
C(335)
C(412)
C(432)
C(413)
C(435)
C(424)
C(426)
C(333)
C(334)
C(433)
C(434)
C(425)

Figure 1.

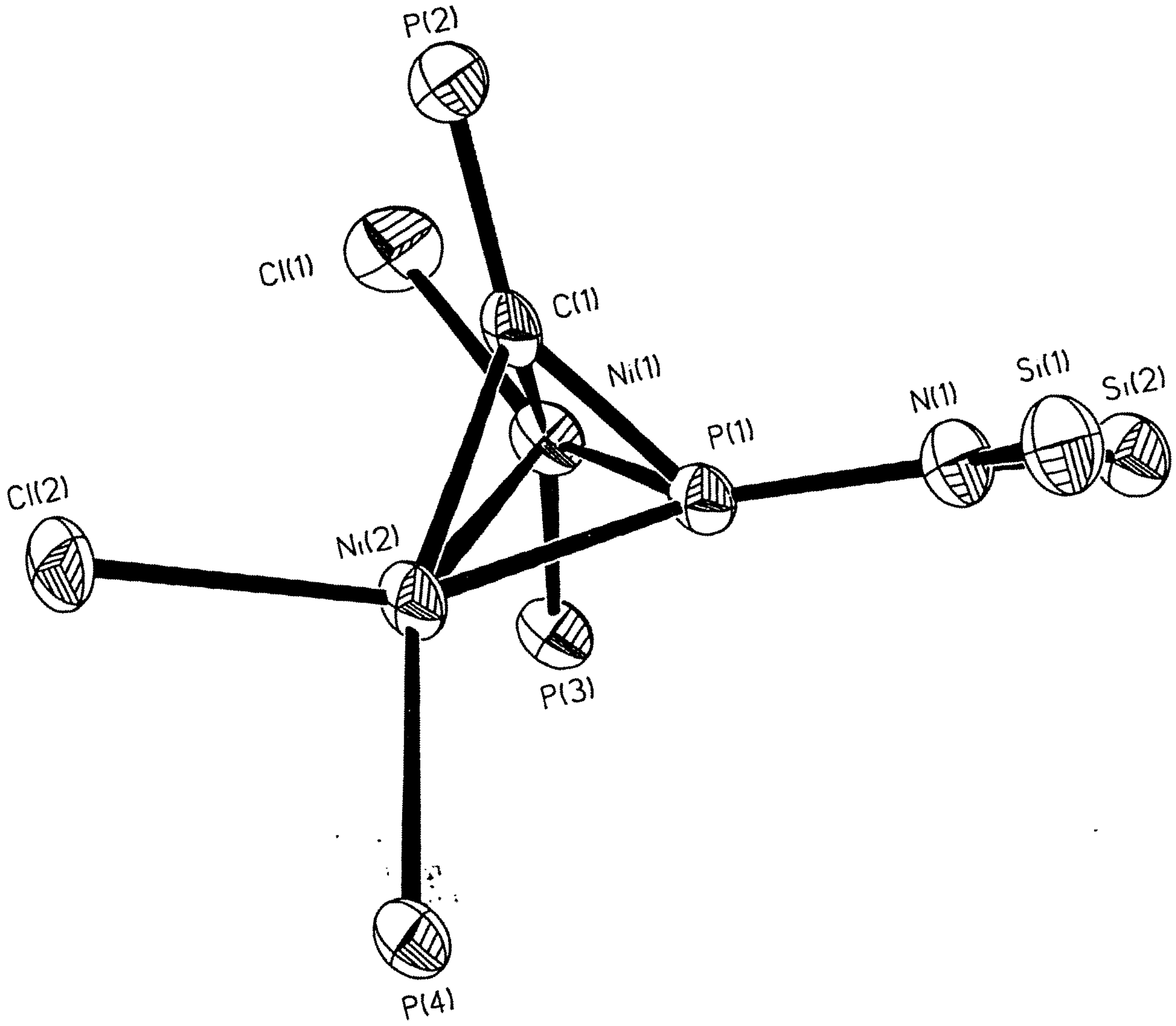

Figure 2.

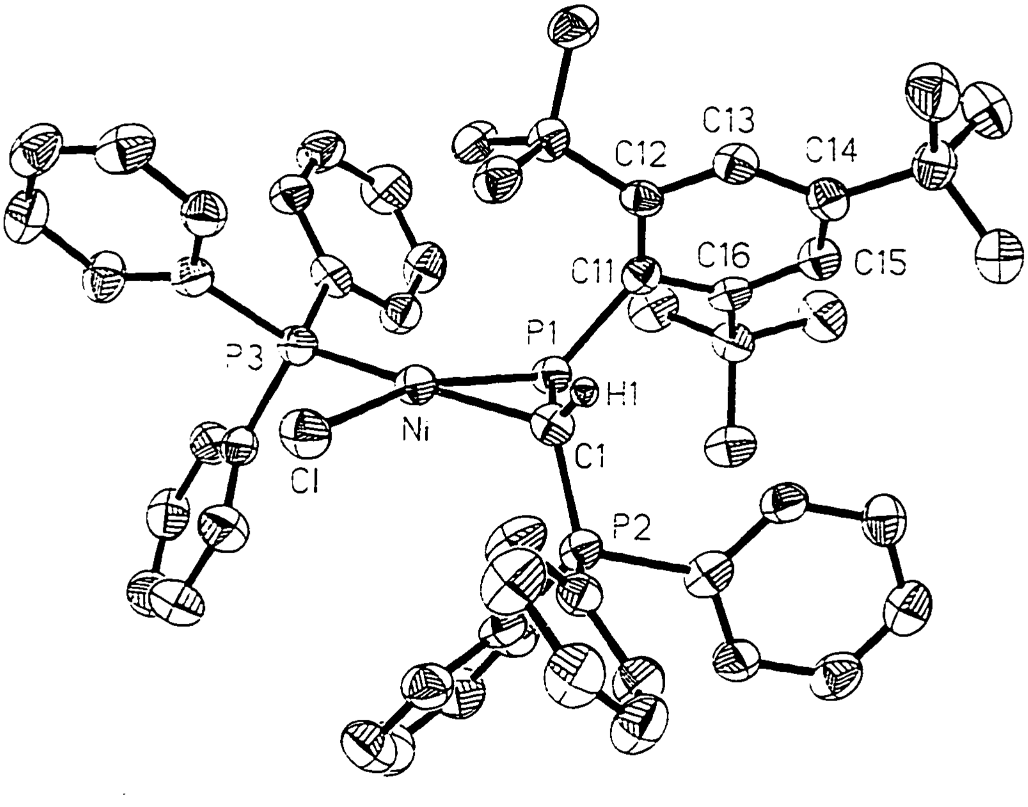

Figure 3.

PALLADIUM COORDINATION COMPOUNDS OF $\sigma^3\lambda^5$-PHOSPHORANES: FIRST EXAMPLES OF PHOSPHONIOMETHYLENE(IMINO)METALLOPHOSPHORANE $[(R_3P)(Me_3Si)C{=}P(ML_n){=}NSiMe_3]$ AND PHOSPHONIOMETHYLENE(OXO)PHOSPHORANE $[(R_3P)(Me_3Si)C{=}P({=}O)NSiMe_3]$ LIGANDS

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Abstract

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 two equivalents of $Pd(PEt_3)_4$ are reacted with $Cl_2C{=}PN(SiMe_3)_2$ the phosphoniomethylene(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.

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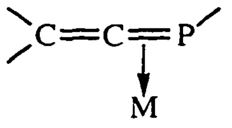
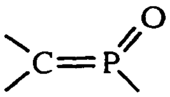
Introduction

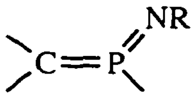
Carbon-phosphorus multiply-bonded ligands have received much attention recently because of the rich coordination chemistry that they afford. In particular, the C=P double bonds in several different types of ligands have been found to exhibit a preferential η^2-coordination mode in many transition metal 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



(A)



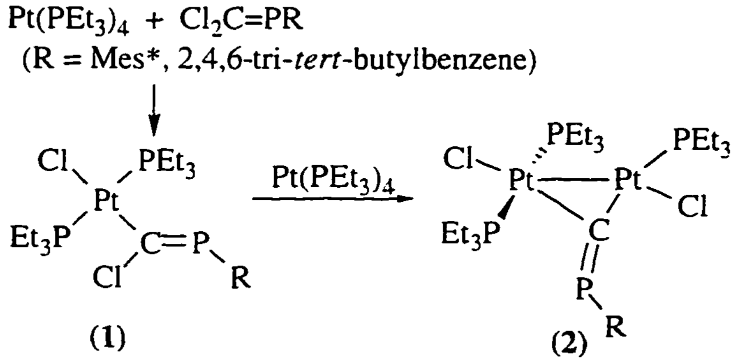
(B)



(C)

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 ($\sigma^3\lambda^5$-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.

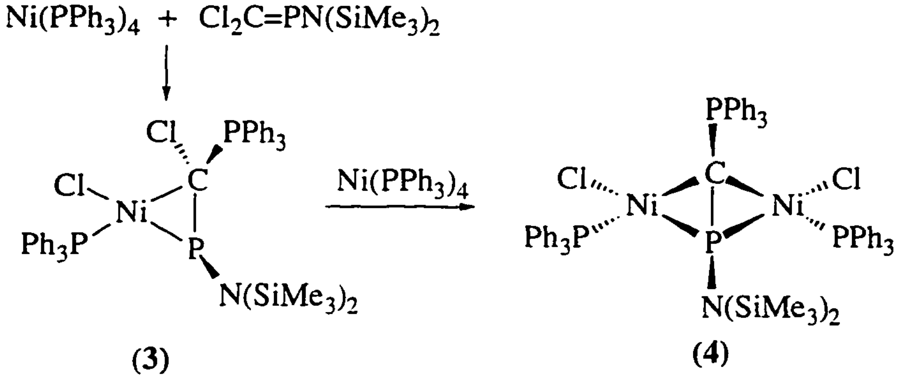
We recently succeeded in preparing the first example of a coordinated isocyaphide (:C=PR) ligand by oxidative addition of the C-X bond in the phosphavinyl complex (**1**) (eq 1) to generate a diplatinum complex $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(Cl)]$ (**2**) containing a semi-bridging :C=PR group.[14] A series of phosphavinyl compounds $X(R'_3P)_2M[C({=}PR)X]$ (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 $M(PR'_3)_2X_2$.[15] Romanenko and coworkers[16] reported the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PMes^*$ which resulted in the formation of Mes*C≡P and $Pd(PPh_3)_2Cl_2$ with no observable intermediates (eq 2). The Mes* group rearrangement in these reactions prompted us to attempt similar oxidative addition reactions between dihalophosphaalkenes containing non-aromatic R-groups and low-valent transition metals. In the course of these



(1)

$$Pd(PPh_3)_4 + Cl_2C{=}PMes^* \longrightarrow Mes^*\text{-}C{\equiv}P + Pd(PPh_3)_2Cl_2 \quad (2)$$
(Mes* = 2,4,6-tri-*tert*-butylbenzene)

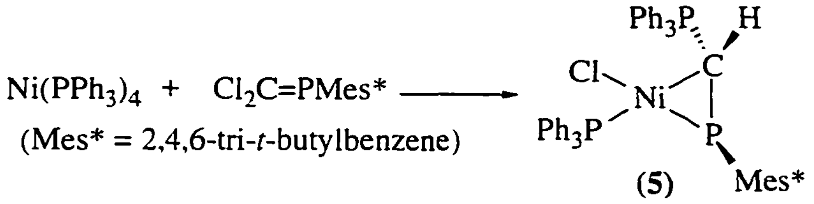
studies, we have prepared[17] (eq 3) and structurally characterized the first example of a complex (**4**) containing a phosphavinylidene phosphorane ($Ph_3P=C=PR$) ligand, which forms from an intermediate phosphavinyl phosphonium complex (**3**) which was not isolated. In a similar reaction[17] (eq 4) with Mes* as the R-group, we were able to isolate and structurally



(**3**) (**4**)

(3)

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

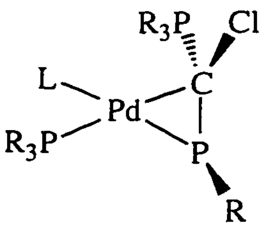


(**5**)

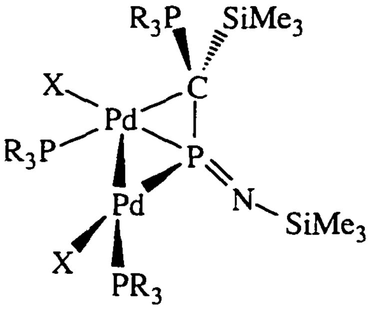
(4)

an interesting PPh_3 migration to the C=P carbon afforded the new ligands. The reactions in eq 3-4 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]

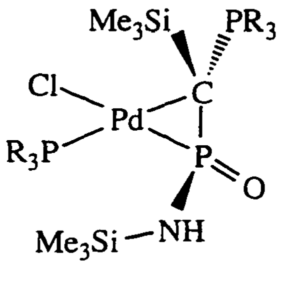
In our continuing studies of oxidative addition reactions of dihalophosphaalkenes with low valent transition metal complexes, we explore in the present paper reactions of $Cl_2C=PN(SiMe_3)_2$ with Pd(0) complexes. During the course of these studies, we isolated a stable phosphavinyl phosphonium complex that is the palladium analog of the unstable nickel complex (**3**) (eq 3) and explored ligand substitution reactions to generate a series of these complexes with η^2-$(R_3P)(Cl)C=PR$ 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- 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 $(R_3P)(Me_3Si)C{=}P({=}O)NSiMe_3$ 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



(D)



(E)



(F)

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.

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 by refluxing over appropriate drying agents under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et$_2$O) 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 3x5 mL portions of hexanes and dried under vacuum to give analytically pure **IIIa** (0.580 g, 74% based on Pd). $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2) (see Scheme 1 for atom labels) for **Ia**, -50°C: δ(P(x)) 41.8 (dd, $^{2}J_{P(x)P(b)}$ = 35.3 Hz, $^{2}J_{P(x)P(a)}$ = 23.4 Hz), δ(P(a)) 25.8 (d, $^{2}J_{P(a)P(x)}$ = 23.4 Hz), δ(P(b)) 21.3 (d, $^{2}J_{P(b)P(x)}$ = 35.3 Hz). For **IIa**, 0°C: δ(P(x)) 213.9 (t, $^{3}J_{P(x)P(a)}$ = 50.1 Hz), δ(P(a)) 22.3 (d, $^{3}J_{P(a)P(x)}$ = 50.1 Hz). For **IIIa**, 25°C: δ(P(x)) 124.4 (d, $^{2}J_{P(x)P(a)}$ = 91.4 Hz), δ(P(a)) 25.8 (dd, $^{2}J_{P(a)P(x)}$ = 91.4 Hz, $^{3}J_{P(a)P(b)}$ = 10.1 Hz), δ(P(b)) 21.3 (d, $^{3}J_{P(b)P(a)}$ = 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 [$(Ph_3P)_2Pd(\eta^2$-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 3x10 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 $Cl(Ph_3P)Pd[\eta^2$-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 3x10 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. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 0°C) (see Scheme 2 for atom labels): δ(P(x)) 118.2 (ddd, $^{2}J_{P(x)P(a)}$ = 123.6 Hz, $^{2}J_{P(x)P(c)}$ = 32.5 Hz, $^{2}J_{P(x)P(b)}$ = 5.1 Hz), δ(P(a)) 25.1 (ddd, $^{2}J_{P(a)P(x)}$ = 123.6 Hz, $^{3}J_{P(a)P(b)}$ = 20.1 Hz, $^{3}J_{P(a)P(c)}$ = 20.6 Hz), δ(P(b)) 17.4 (ddd, $^{3}J_{P(b)P(a)}$ = 20.1 Hz, $^{2}J_{P(b)P(c)}$ = 11.9 Hz, $^{2}J_{P(b)P(x)}$ = 5.1 Hz), δ(P(c)) 13.8 (ddd, $^{2}J_{P(c)P(x)}$ = 32.5 Hz, $^{3}J_{P(c)P(a)}$ = 20.6 Hz, $^{2}J_{P(c)P(b)}$ = 11.9 Hz), δ(PF_6) -144 (sept., $^{1}J_{PF}$ = 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, the filtrate was reduced to 5 mL and a mixture of 15 mL hexanes and 15 mL Et_2O was added with stirring. The resulting red 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 hexanes and 15 mL 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%). ^{1}H NMR (CD_2Cl_2, 25°C): δ 7.1-7.7 (30H, PPh_3), 1.66 (s, 3H, MeCN), 0.15 (s, 18H, $N(SiMe_3)_2$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25°C) (see Scheme 2 for atom labels): δ(P(x)) 132.8 (d, $^{2}J_{P(x)P(a)}$ = 97.0 Hz), δ(P(a)) 28.0 (dd, $^{2}J_{P(a)P(x)}$ = 97.0 Hz, $^{3}J_{P(a)P(b)}$ = 6.4 Hz), δ(P(b))

21.1 (d, $^3J_{P(b)P(a)} = 6.4$ Hz), δ(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(η^2-C(Cl)(PPh_3)=PN($SiMe_3$)$_2$)] (PF_6) (V) to Cl(Ph_3P)Pd[η^2-C(Cl)(PPh_3)=PN($SiMe_3$)$_2$] (IIIa). To a stirred solution of [(Ph_3P)(MeCN)Pd(η^2-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[η^2-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 Et_2O to produce a yellow precipitate which was collected on a medium porosity fritted glass filter. The precipitate was washed with 2x10 mL Et_2O, followed by 3x5 mL MeCN to give pure VI (0.745 g, 71%). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25°C) (see eq 5 for atom labels): δ(P(x)) 230.1 (dd, $^3J_{P(x)P(b)} = 41.8$ Hz, $^3J_{P(x)P(a)} = 29.9$ Hz), δ(P(a)) 55.8 (dd, $^3J_{P(a)P(x)} = 29.9$ Hz, $^2J_{P(a)P(b)} = 22.1$ Hz), δ(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)$_2$Pd[C(Cl)=PN($SiMe_3$)$_2$] (IIb) through Intermediate (Et_3P)$_2$Pd[η^2-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)$_2$Pd[η^2-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).

$^{31}P\{^{1}H\}$ NMR (hexanes) (see Scheme 3 for atom labels); for **Ib**, 0°C: δ(P(x)) 38.0 (dd, $^{2}J_{P(x)P(b)}$ = 38.5 Hz, $^{2}J_{P(x)P(a)}$ = 24.8 Hz), δ(P(a)) 5.5 (dd, $^{2}J_{P(a)P(x)}$ = 24.8 Hz, $^{2}J_{P(a)P(b)}$ = 5.5 Hz), δ(P(b)) 4.0 (dd, $^{2}J_{P(b)P(x)}$ = 38.5 Hz, $^{2}J_{P(b)P(a)}$ = 5.5 Hz). For **IIb**, 25°C: δ(P(x)) 223.8 (t, $^{3}J_{P(x)P(a)}$ = 33.4 Hz), δ(P(a)) 16.1 (d, $^{3}J_{P(a)P(x)}$ = 33.4 Hz). $^{13}C\{^{1}H\}$ NMR (hexanes); for **IIb**, 25°C: δ(C=PR) 191.0 (dt, $^{1}J_{CP(x)}$ = 135.1 Hz, $^{2}J_{CP(a)}$ = 9.6 Hz).

Synthesis 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) 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 $Pd(PEt_3)(Cl)[\mu\text{-}\eta^{1}\text{:}\eta^{2}\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)Cl$ (**VIIa-b**). The filtrate was removed by cannula and the crystals were washed with 3x5 mL hexanes and dried under vacuum to give pure **VIIa-b** (0.824 g, 57%). $^{31}P\{^{1}H\}$ NMR (THF) (see Scheme 3 for atom labels); for **VIIa**: δ(P(x)) 194.9 (dd, $^{2}J_{P(x)P(a)}$ = 18.0 Hz, $^{2}J_{P(x)P(b)}$ = 8.3 Hz), δ(P(a)) 38.2 (dd, $^{2}J_{P(a)P(x)}$ = 18.0 Hz, $^{3}J_{P(a)P(b)}$ = 5.5 Hz), δ(P(b)) 27.2 (ddd, $^{3}J_{P(b)P(c)}$ = 63.3 Hz, $^{2}J_{P(b)P(x)}$ = 8.3 Hz, $^{3}J_{P(b)P(a)}$ = 5.5 Hz), δ(P(c)) 16.2 (d, $^{3}J_{P(c)P(b)}$ = 63.3 Hz). For **VIIb**: δ(P(x)) 182.2 (ddd, $^{2}J_{P(x)P(a)}$ = 16.8 Hz, $^{2}J_{P(x)P(b)}$ = 5.5 Hz, $^{2}J_{P(x)P(c)}$ = 5.5 Hz), δ(P(a)) 31.3 (dd, $^{2}J_{P(a)P(x)}$ = 16.8 Hz, $^{3}J_{P(a)P(b)}$ = 16.5 Hz), δ(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), δ(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)[μ-η^1:η^2-C(SiMe$_3$)(PEt$_3$)=P=N(SiMe$_3$)]Pd(PEt$_3$)I (VIIIa-b). To a stirred solution of Pd(PEt$_3$)(Cl)[μ-η^1:η^2-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 hours 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 Et$_2$O. 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{^{1}H} NMR (THF) (see Scheme 4 for atom labels) (for **VIIIa**): δ(P(x)) 196.8 (d, $^2J_{P(x)P(a)}$ = 18.3 Hz), δ(P(a)) 37.2 (dd, $^2J_{P(a)P(x)}$ = 18.3 Hz, $^3J_{P(a)P(b)}$ = 7.0 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$_3$P)Pd[η^2-C(SiMe$_3$)(PEt$_3$)=P(=O)NH(SiMe$_3$)] (IX). To a stirred solution of Pd(PEt$_3$)(Cl)[μ-η^1:η^2-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$_2$O (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$_2$O 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 3x5 mL hexanes at 0°C to yield pure **IX** (0.058 g, 82%). ^{31}P{^{1}H} 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))

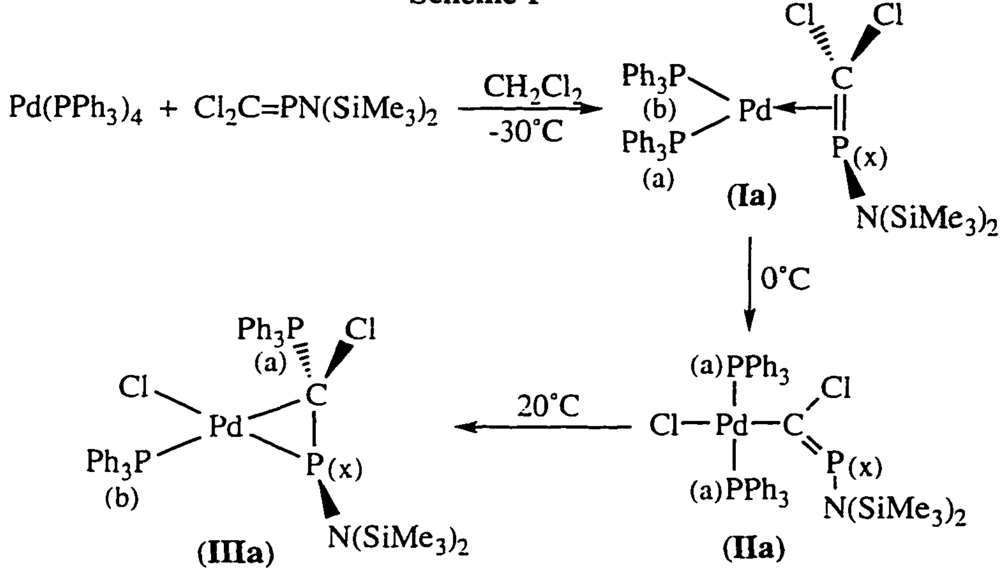
24.2 (dd, ${}^2J_{P(b)P(a)}$ = 8.3 Hz, ${}^2J_{P(b)P(x)}$ = 11.0 Hz). FABMS: *m/e* 598 (M^+-H), 561 (M^+-(H+Cl)), 338 (M^+-(H+Cl+Pd+PEt$_3$)).

X-ray Crystallographic Analyses of [$(Ph_3P)(MeCN)Pd(\eta^2$-$C(Cl)(PPh_3)$=$PN(SiMe_3)_2)$] (PF_6) (V) and Cl(Et_3P)Pd[η^2-$C(SiMe_3)(PEt_3)$=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 plate-like 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 matrices 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 C2/c was unambiguously determined in **V**, and Fdd2 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. 102 restraints were used altogether. The structure of **IX** contained one Et_2O solvent molecule which was disordered on a two-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 equivalent 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°C to 25°C) ^{31}P NMR monitoring

Scheme 1



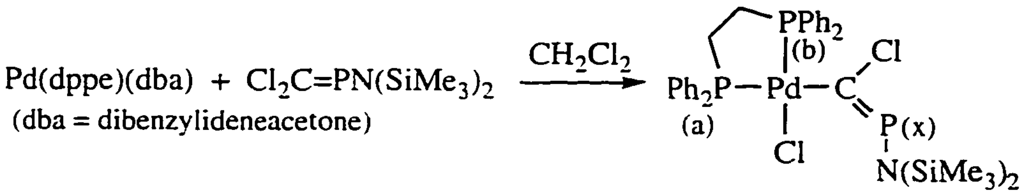
of the reaction solution shows two intermediates (Scheme 1). At -50°C, the only species present is the η^2-phosphaalkene complex $(PPh_3)_2Pd[\eta^2\text{-}C(Cl_2)=PN(SiMe_3)_2]$ **(Ia)** and free PPh_3. Upon warming to 0°C, **Ia** undergoes oxidative addition of one of the C-Cl bonds to form the phosphavinyl compound *trans*-$Cl(Ph_3P)_2Pd[C(Cl)=PN(SiMe_3)_2]$ **(IIa)**. After the solution reaches room temperature and is stirred for 3 hours, 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 two equivalents of PPh_3 using $Pd(dba)(PPh_3)_2$ and 1.1 equivalent 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{^{1}H} NMR spectra; compound **IIIa** was further characterized by elemental analysis and electrospray mass spectroscopy. 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, $^3J_{PP} = 25\text{-}43$ 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 $[(Ph_3P)(H)C{=}PNiPr_2]$ (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) to that of the cationic MeCN analog [(Ph$_3$P)(MeCN)Pd(η^2-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 one equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ in CH$_2$Cl$_2$ at room temperature results in the formation of *cis*-Cl(dppe)Pd[C(Cl)=PN(SiMe$_3$)$_2$]



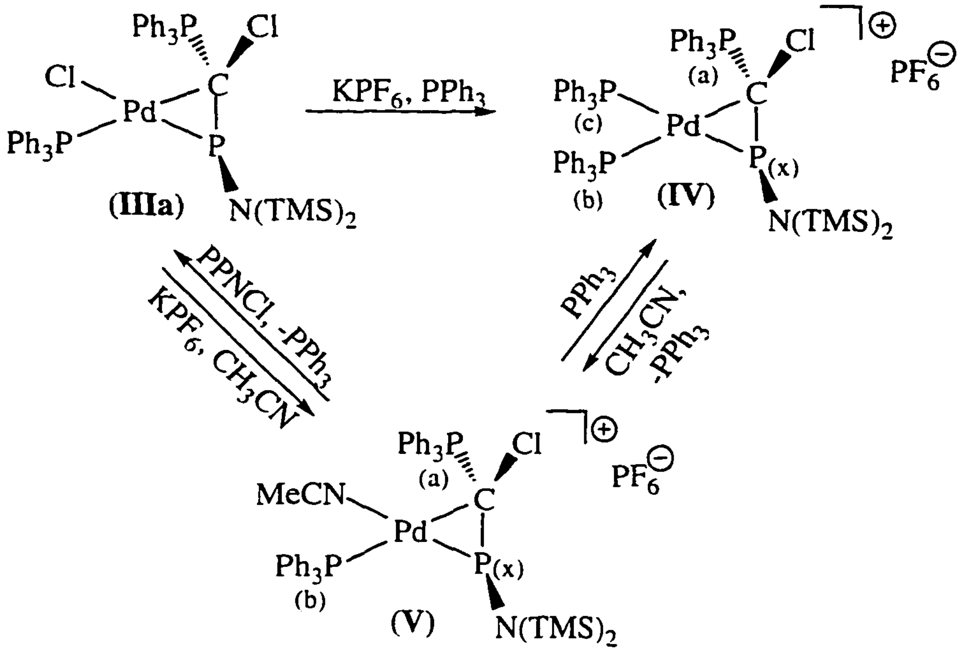
(VI)

(5)

(**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 ($^3J_{\mathrm{P(x)P(b)}} = 41.8$ Hz, $^3J_{\mathrm{P(x)P(a)}} = 29.9$ Hz) by the two inequivalent phosphorus atoms in the chelating dppe ligand. The chemical shifts and coupling constants are quite similar to those in the previously characterized *cis*- Cl(Ph$_3$P)$_2$Pt[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 Cl(Ph$_3$P)Pd[η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (IIIa). The reaction (Scheme 2) of Cl(Ph$_3$P)Pd[η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (**IIIa**) with 1.1 equivalent of PPh$_3$ and 2 equivalents of KPF$_6$ in CH$_2$Cl$_2$ at room temperature results in the

Scheme 2



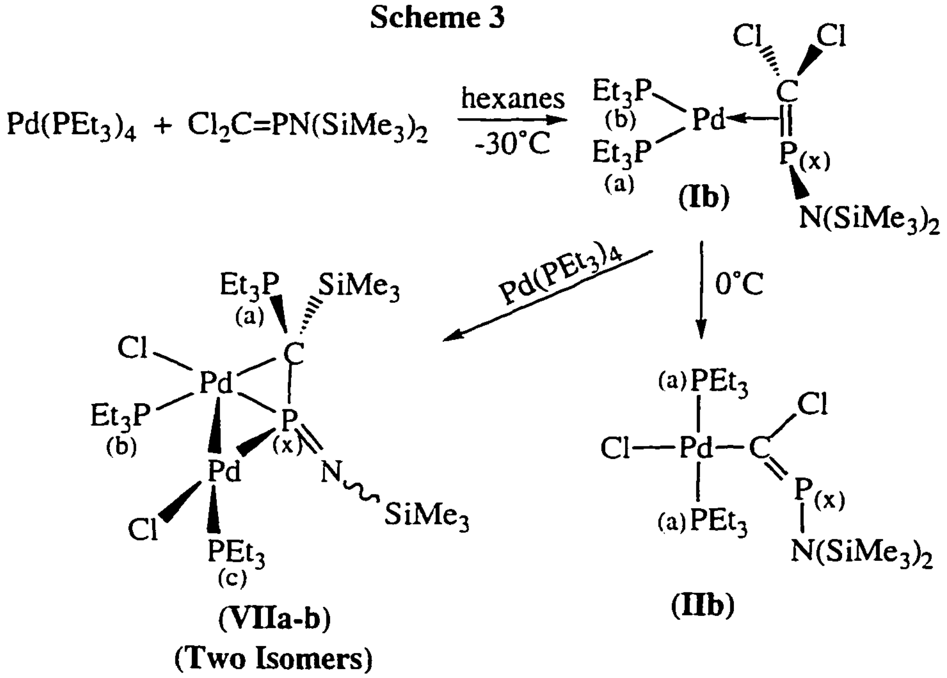
substitution of the Cl$^-$ ligand by PPh$_3$ to form the cationic complex [(Ph$_3$P)$_2$Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (**IV**) along with a small amount of [Pd(PPh$_3$)$_3$Cl] (PF$_6$)[23] which could not be separated. Compound **IV** was also prepared by the addition of 1.1 equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ and 2 equivalents of KPF$_6$ to a cooled (-50°C) solution of Pd(PPh$_3$)$_4$ in CH$_2$Cl$_2$. When compound **IV** is dissolved in MeCN at room temperature, one of the PPh$_3$ ligands is substituted by MeCN to form [(Ph$_3$P)(MeCN)Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (**V**). Compound **V** was also prepared by the addition of 1.1 equivalent of Cl$_2$C=PN(SiMe$_3$)$_2$ and 2 equivalents of KPF$_6$ to a cooled (-30°C) solution of Pd(PPh$_3$)$_4$ in MeCN, but is best prepared by substitution of the Cl$^-$ ligand in Cl(Ph$_3$P)Pd[η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$] (**IIIa**) with MeCN, in the presence of KPF$_6$. When compound **V** is isolated and dissolved in CD$_2$Cl$_2$, its ^{1}H NMR spectrum shows a signal for the coordinated MeCN ligand. However, when **V** is dissolved in CD$_3$CN, the signal for the coordinated MeCN group disappears, indicating that the coordinated MeCN ligand undergoes exchange with the CD$_3$CN solvent. When compound **V** is treated with PPNCl at room temperature, the MeCN ligand is immediately displaced by 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 spectroscopy, 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 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 $^2J_{P(x)P(a)}$ 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) ($^2J_{P(x)P(b)}$ = 5.1 Hz) and P(c) ($^2J_{P(x)P(c)}$ = 32.5 Hz); the larger value for $^2J_{P(x)P(c)}$ is consistent with 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 $Pd(PEt_3)_3$ with $Cl_2C{=}PN(SiMe_3)_2$. The reaction (Scheme 3) of $Pd(PEt_3)_3$ with one equivalent of $Cl_2C{=}PN(SiMe_3)_2$ in hexanes at 0°C results in the formation of the PEt_3 analog of **IIa**, *trans*-$Cl(Et_3P)_2Pd[C(Cl){=}PN(SiMe_3)_2]$ **(IIb)**. Low temperature (0°C) ^{31}P NMR monitoring of the reaction shows the PEt_3 analog of **Ia**, $(Et_3P)_2Pd[\eta^2\text{-}C(Cl)_2{=}PN(SiMe_3)_2]$ **(Ib)** as the only observable intermediate in the reaction. When the solution reaches room temperature and is allowed to stir for 1 hour, one of the C-Cl bonds in compound **Ib** undergoes oxidative addition to Pd to form **IIb** along with a small amount of $Pd(PEt_3)_2Cl_2$.

Scheme 3

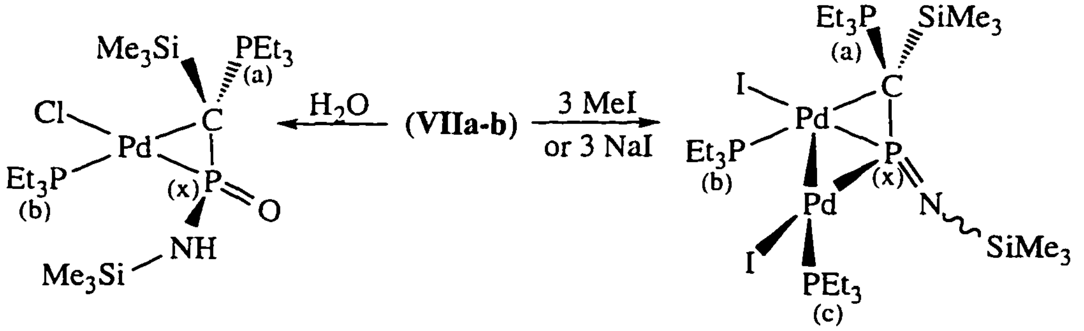


When $Pd(PEt_3)_3$ is reacted (Scheme 3) with one-half equivalent of $Cl_2C{=}PN(SiMe_3)_2$ in hexanes at 0°C, ^{31}P NMR monitoring of the reaction solution again shows **Ib** as an intermediate along with free $Pd(PEt_3)_3$. However, upon warming the solution to room temperature and stirring for 30 min, orange crystals of the 1:1 isomeric mixture of $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3){=}P{=}N(SiMe_3)]Pd(PEt_3)Cl$ (**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 by-product. In order to determine whether **IIb** is an intermediate that forms before **VIIa-b**, a sample of **IIb** was dissolved in hexanes and one equivalent of $Pd(PEt_3)_3$ 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) 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); the structure of **VIIIb** was determined by a partially succesful 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 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)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 three equivalents of MeI in THF at room temperature for 24 hours under anhydrous conditions, the color of the solution turns dark red and the only

Scheme 4



(IX) **(VIIIa-b)**

products are the iodide-substituted analogs (both isomers) of **VIIa-b**, Pd(PEt$_3$)(I)[μ-η^1:η^2-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 three equivalents of NaI resulted in the formation of **VIIIa-b** in only 5 minutes, but the product was contaminated with Cl(Et$_3$P)Pd[η^2-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$_2$O, 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**).

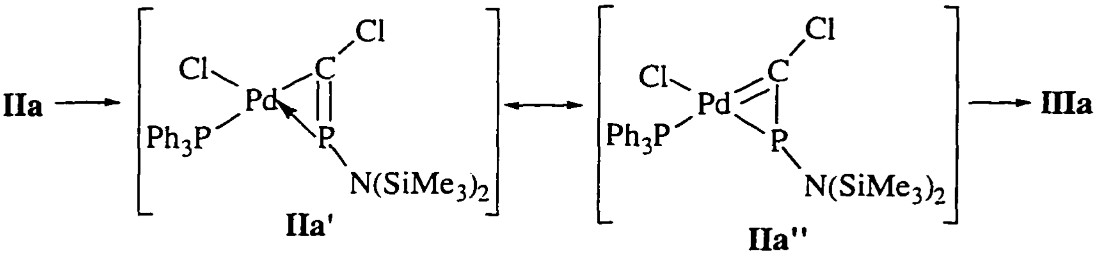
When a pure sample of **VIIa-b** is reacted (Scheme 4) with two equivalents of degassed, deionized H$_2$O in THF at room temperature, the color darkens immediately and the ^{31}P NMR spectrum shows the formation of the phosphonio-methylene(oxo)phosphorane compound **IX** along with two singlets that are most likely due to palladium phosphine complexes. Although these by-products were not identified, they were easily separated from

IX. Compound **IX** was characterized by ^{31}P NMR spectroscopy, FAB mass spectroscopy 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.

Discussion

$Cl(Ph_3P)Pd[\eta^2$-$C(Cl)(PPh_3)=PN(SiMe_3)_2]$ (IIIa), $[(Ph_3P)_2Pd(\eta^2$-$C(Cl)(PPh_3)=PN(SiMe_3)_2)]$ (PF_6) (IV) and $[(Ph_3P)(MeCN)Pd(\eta^2$-$C(Cl)(PPh_3)=PN(SiMe_3)_2)]$ (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≡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 $Cl(Ph_3P)Pd[\eta^2$-$C(Cl)(PPh_3)=PN(SiMe_3)_2]$ (**IIIa**) via intermediates $(Ph_3P)_2Pd[\eta^2$-$C(Cl)_2=PN(SiMe_3)_2]$ (**Ia**) and *trans*-$Cl(Ph_3P)_2Pd[C(Cl)=PN(SiMe_3)_2]$ (**IIa**). This 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 analog (**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**.

Scheme 5



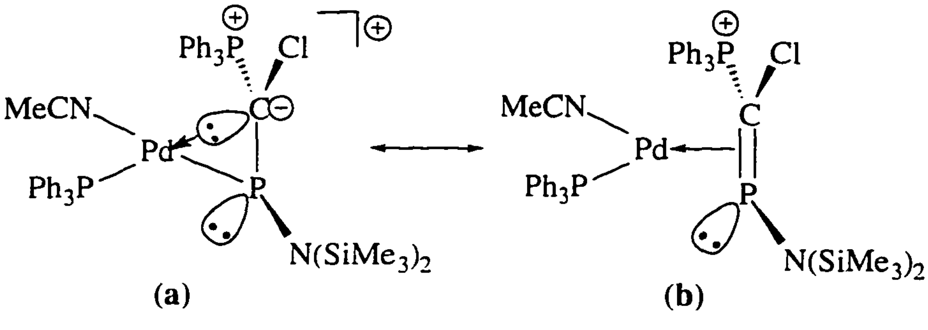
The carbene-phosphido resonance structure (**IIa"**) is probably more favored than the alkyl-phosphine resonance form (**IIa'**) because the high energy C=P double bond[36] is avoided; the electrophilic nature of the carbene-like carbon atom provides the driving force for nucleophilic attack by the PPh_3 group to form **IIIa**. This carbene-like resonance structure in the η^2-phosphavinyl ligand (**IIa"**) is precedented 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.[37] A similar mechanism for this phosphine migration was proposed previously for the formation of the nickel analog (**3**, eq 3) of **IIIa**.[17]

When $Cl_2C=PN(SiMe_3)_2$ 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 analog of **IIIa** does not form. Compound **VI** does not react with PPh_3 and KPF_6 to generate an analog 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_3P)(MeCN)Pd(η^2-C(Cl)(PPh_3)=PN$(SiMe_3)_2$)] (PF_6) (**V**), while addition of PPh_3 leads to [$(Ph_3P)_2$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_3CN by stirring in CD_3CN, or by PPh_3 to generate **IV**, or by Cl^- to generate **IIIa**. Thus, each of the compounds **IIIa**, **IV** and **V** contain 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_3P)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.

X-ray Crystal Structure of [(Ph_3P)(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 (e.g., in $Ni(PMe_3)_2[\eta^2-(Me_3Si)_2CHP=C(SiMe_3)_2]$, 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 $Cl(Ph_3P)Ni[\eta^2-C(H)(PPh_3)=PMes^*]$ (**5**, eq 4).[17] The C(1)-P(1) distance in **V** (1.802(4) Å) is the same within error as that in the nickel complex $Cl(Ph_3P)Ni[\eta^2-C(H)(PPh_3)=PMes^*]$ (**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 $[(PPh_3)(H)C=PN(i\text{-}Pr)_2)](BF_4)$ (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 which 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 $Cl(PPh_3)Ni[\eta^2-C(H)(PPh_3)=PMes^*]$ (**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 $Ph_3P=CH_2$,[38] but are shorter than the phosphonium-type C-PPh$_3$ distance in $[(PPh_3)(H)C=PN(i\text{-}Pr)_2)](BF_4)$ (1.798(14) Å), indicating that there is more phosphonium ($C\text{-}P^+$) than ylidic ($C^-\text{-}P^+$) 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 (2.3449(11)). The bonding in **V** may be described as a mixture of two resonance structures (Scheme 6), analogous to those

Scheme 6



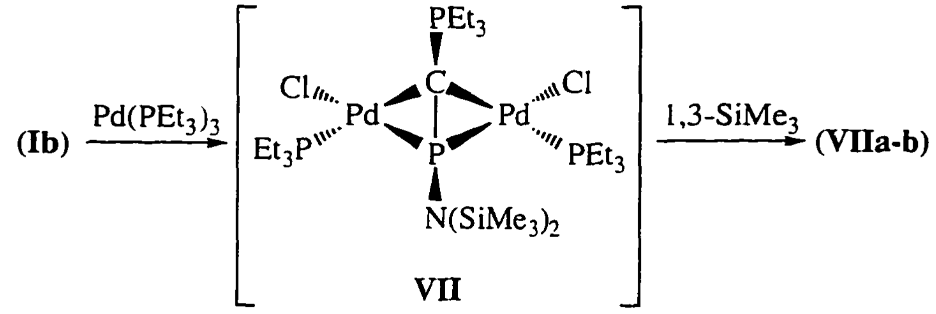
proposed for the bonding in $Cl(Ph_3P)Ni[\eta^2\text{-}C(H)(PPh_3)=PMes^*]$ **(5)**.[17] Resonance form **a** is an ylide-phosphido structure with a dative two electron donation from C(1) and a phosphido-type covalent bond between P(1) and palladium, where the $[C(Cl)(PPh_3)=PN(SiMe_3)_2]$ group donates three electrons to the thirteen electron cationic metal fragment $(Ph_3P)(MeCN)Pd^+$. Resonance form **b** is an η^2-phosphavinyl phosphonium cation (1+) which donates two electrons 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, while the short Pd-P(1) distance argues for a contribution from form **a** with some Pd-P phosphido-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 one equivalent 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 analog 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.

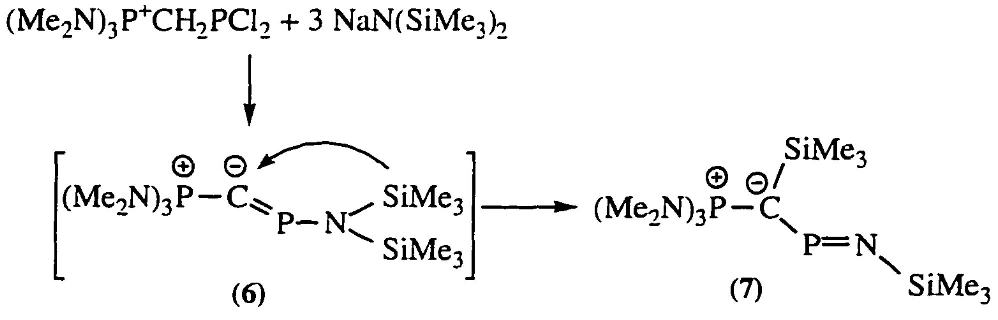
When the reaction of $Pd(PEt_3)_3$ is carried out with only one-half equivalent of $Cl_2C=PN(SiMe_3)_2$ (Scheme 3) and warmed to room temperature, the reaction takes a different route forming the dimeric complex $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)Cl$ **(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 by-product. As mentioned in the Results, compound **IIb** is apparently not an intermediate in the formation of **VIIa-b**. Evidently, when two equivalents 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 one-half equivalent 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**

Scheme 7



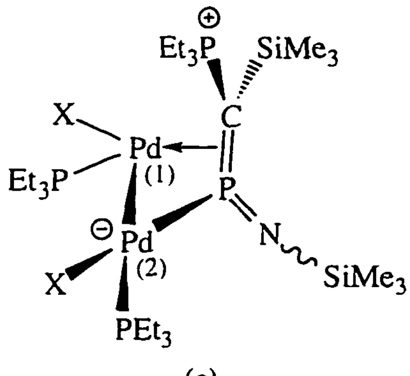
is analogous to the nickel complex $Ni_2Cl_2(PPh_3)_2[\mu_2\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2]$ (**4**, eq 3) that was previously characterized by X-ray diffraction studies.[17] This intermediate must isomerize quickly to **VIIa-b** by undergoing a 1,3 $SiMe_3$ migration from nitrogen 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



(6)

$P(Me_2N)_3$ group on carbon instead of PPh_3; and 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

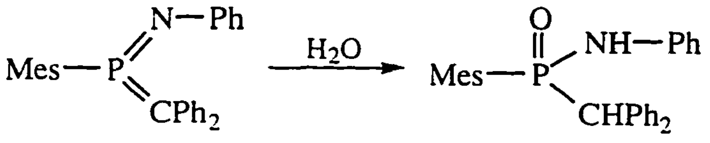


(c)

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 analog, $[(Me_2N)_3P](Me_3Si)C{=}P{=}N(SiMe_3)$ (**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 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**.

$Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (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 $Cl(Et_3P)Pd[\eta^2\text{-}C(SiMe_3)(PEt_3){=}P({=}O)NH(SiMe_3)]$ (**IX**). This is analogous to the known hydrolysis reaction (eq 7) of methylene(imino)phosphoranes $(R_2C{=}P({=}NR)R)$.[13] In the formation of **IX**, the oxygen from



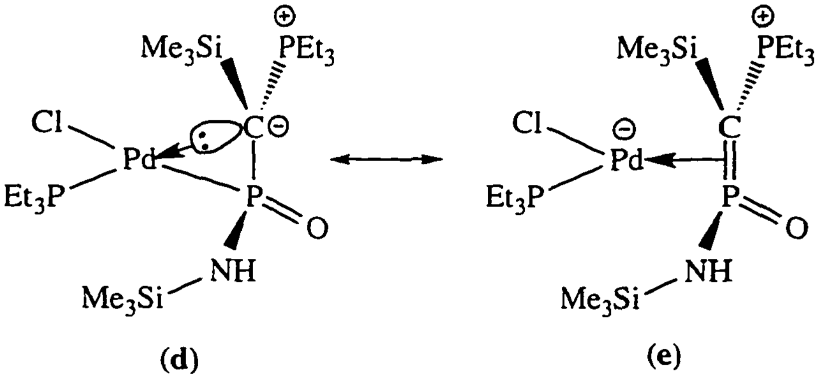
(7)

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$_3$P)Pd[η^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$_3$P)(Me$_3$Si)C=P(=O)NH(SiMe$_3$) ligand. The ORTEP 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$_3$P)(Me$_3$Si)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 pyramidalized to roughly 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$_3$Si)(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$_3$Si)(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[η^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$_3$P=CH$_2$,[38] but are shorter than the phosphonium C-PPh$_3$ distance in [(PPh$_3$)(H)C=PN(*i*-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).

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-

Scheme 8



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 thirteen 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, while the short Pd-P(1) distance argues for a contribution from form **d** with some Pd-P phosphido-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.

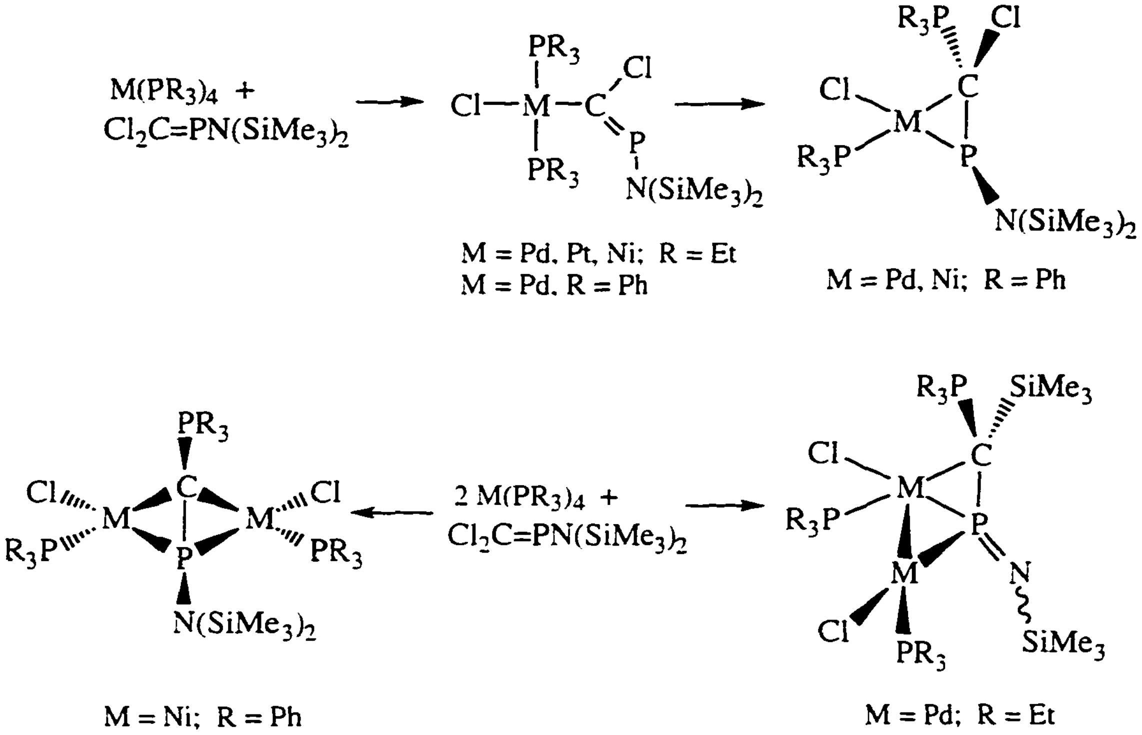
Conclusion

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≡P via phosphavinyl intermediates,[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 two equivalents of $Pd(PEt_3)_3$ were reacted (Scheme 3) with $Cl_2C=PN(SiMe_3)_2$, the novel, dimeric phosphonio-methylene(imino)metallophosphorane complex $Pd(PEt_3)(Cl)[\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)Cl$ (**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 $Pd(PEt_3)(I)[\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(SiMe_3)(PEt_3)=P=N(SiMe_3)]Pd(PEt_3)I$ (**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

Scheme 9



M = Pd, Pt, Ni; R = Et
M = Pd, R = Ph

M = Pd, Ni; R = Ph

M = Ni; R = Ph

M = Pd; R = Et

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.

Acknowledgment

We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research through grant 27360-AC3.

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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	$C_{51}H_{57}ClF_6N_5P_4PdSi_2$	$C_{42}H_{108}Cl_2N_2O_3P_6Pd_2Si_4$
space group	C2/c	Fdd2
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	1.337	1.298
crystal size, mm	0.45 x 0.36 x 0.09	0.22 x 0.19 x 0.09
μ, mm^{-1}	0.570	0.889
data collection instrument	Siemens SMART	Siemens SMART
radiation (monochromated in incident beam)	Mo Kα (λ=0.71073 Å)	Mo Kα (λ=0.71073 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

Table 1. (Continued)

	V	IX
no. of data collected	28232	16542
no. of unique data total	10125	5544
with I≥ 2σ (I)	10122	5542
no. of parameters refined	660	324
trans factors; max; min	1.000/0.811	1.000/0.840
R^a (I>2σ (I))	0.0534	0.0417
$R_w{}^b$ (I>2σ (I))	0.1074	0.0967
quality of fit indicator[c]	1.073	1.087
largest peak, e/Å^{-3}	0.582	0.839

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for [(Ph$_3$P)(MeCN)Pd(η^2-C(Cl)(PPh$_3$)=PN(SiMe$_3$)$_2$)] (PF$_6$) (V).

Distances (Å)

Pd(1)-C(1)	2.162(4)	C(1)-P(1)	1.802(4)	C(1)-Cl(1)	1.792(4)
Pd(1)-P(1)	2.2688(11)	C(1)-P(2)	1.771(4)	N(2)-Si(1)	1.785(4)
Pd(1)-N(1)	2.166(4)	P(1)-N(2)	1.704(3)	N(2)-Si(2)	1.788(4)
Pd(1)-P(3)	2.3449(11)	N(1)-C(2)	1.131(6)		

Bond Angles (deg)

P(1)-C(1)-P(2)	115.8(2)	C(1)-Pd(1)-P(1)	47.93(11)
P(1)-C(1)-Pd(1)	69.13(13)	C(1)-Pd(1)-P(3)	153.91(11)
P(2)-C(1)-Pd(1)	109.9(2)	P(1)-Pd(1)-P(3)	106.49(4)
P(1)-C(1)-Cl(1)	122.4(2)	C(1)-P(1)-Pd(1)	62.94(13)
P(2)-C(1)-Cl(1)	109.2(2)	N(2)-P(1)-Pd(1)	114.87(14)
C(1)-Pd(1)-N(1)	109.86(14)	P(1)-N(2)-Si(1)	107.7(2)
N(1)-Pd(1)-P(1)	157.79(10)	P(1)-N(2)-Si(2)	129.3(2)
N(1)-Pd(1)-P(3)	95.57(10)		

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for Cl(Et$_3$P)Pd[η^2-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)				

Bond Angles (deg)

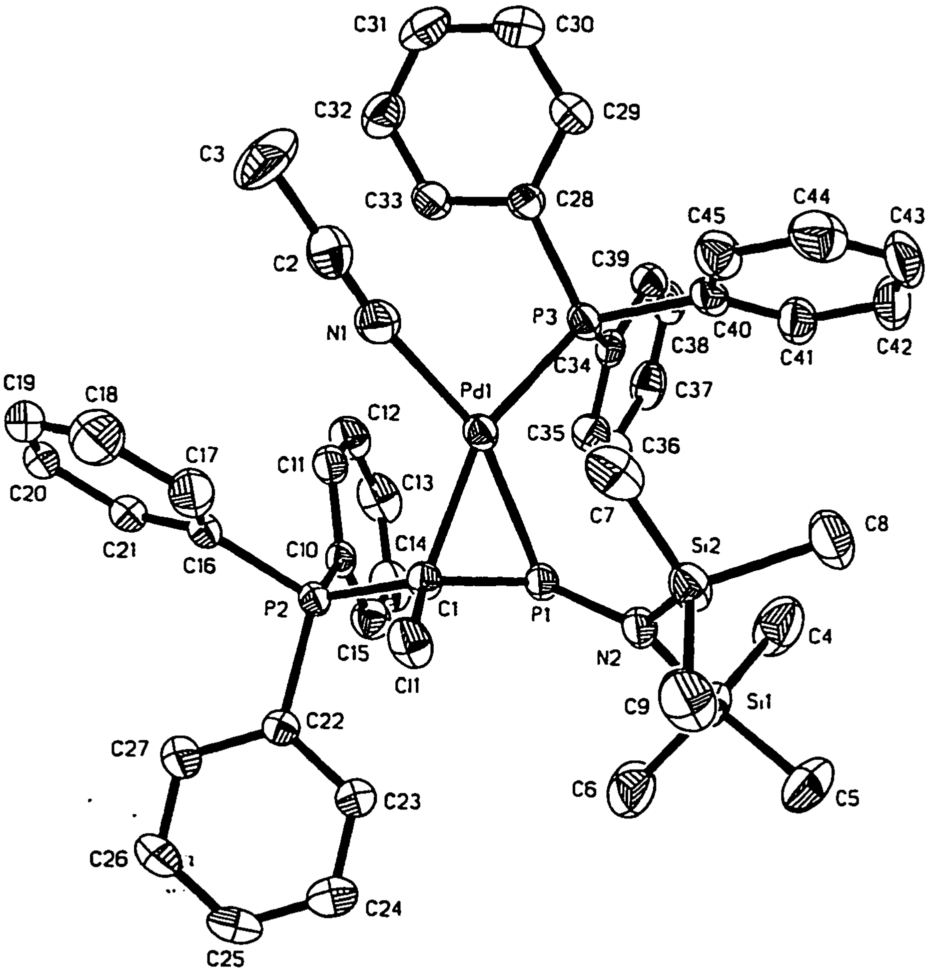
P(1)-Pd(1)-C(1)	47.92(14)	P(1)-C(1)-Si(2)	119.1(3)
C(1)-Pd(1)-P(3)	155.79(14)	P(2)-C(1)-Si(2)	120.7(3)
C(1)-Pd(1)-Cl(1)	108.07(14)	Pd(1)-C(1)-Si(2)	107.1(2)
P(1)-Pd(1)-P(3)	108.33(7)	O(1)-P(1)-Pd(1)	124.3(2)
P(1)-Pd(1)-Cl(1)	155.67(7)	O(1)-P(1)-N(1)	109.7(2)
P(3)-Pd(1)-Cl(1)	95.91(7)	N(1)-P(1)-C(1)	114.0(3)
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.

Figure Captions

Figure 1. Thermal ellipsoid drawing of $[(Ph_3P)(MeCN)Pd(\eta^2\text{-}C(Cl)(PPh_3){=}PN(SiMe_3)_2)](PF_6)$ (**V**).

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


C31
C30
C32
C29
C3
C33
C28
C45
C44
C43
C2
C39
P3
C40
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C41
C42
C34
C19
C18
C37
Pd1
C12
C35
C36
C17
C11
C13
C20
C7
C8
C21
C16
C10
C14
Si2
P2
C1
P1
C15
N2
C4
Cl1
C9
Si1
C22
C27
C6
C5
C23
C26
C24
C25

Figure 1.

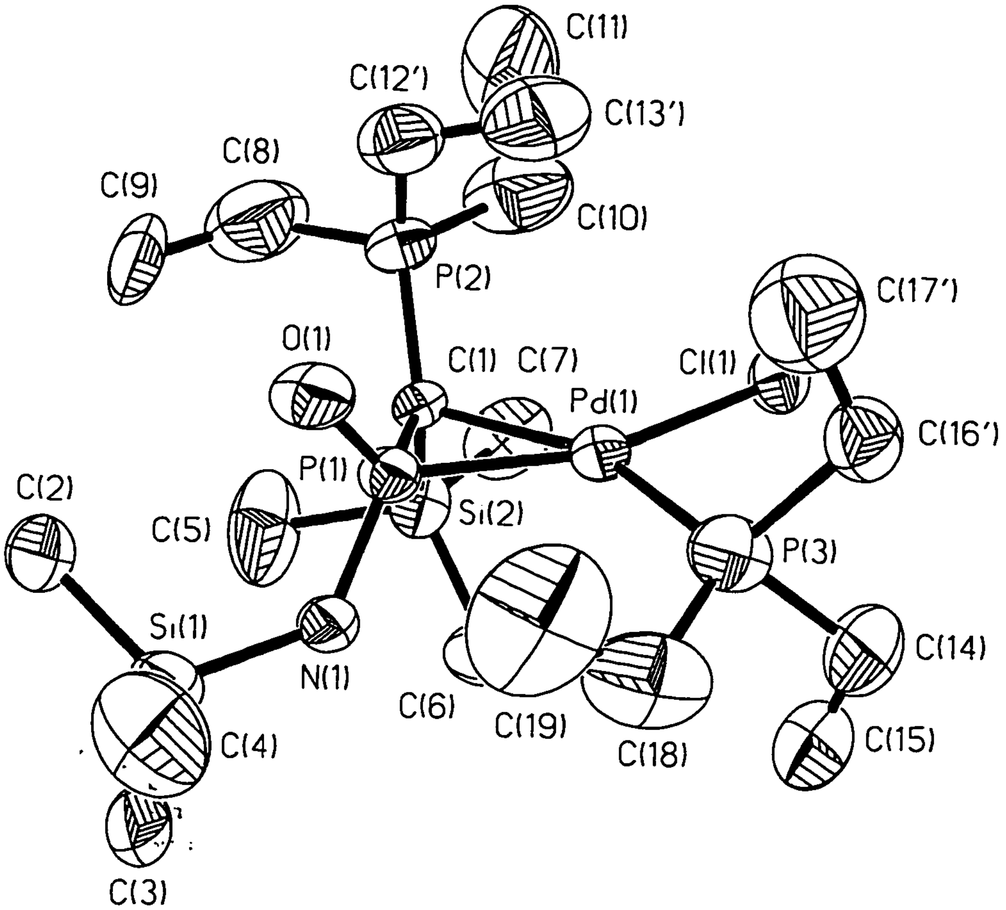
C(11)
C(12')
C(13')
C(8)
C(9)
C(10)
P(2)
C(17')
O(1)
C(1)
C(7)
Cl(1)
Pd(1)
C(16')
P(1)
C(2)
C(5)
Si(2)
P(3)
Si(1)
N(1)
C(14)
C(6)
C(19)
C(4)
C(18)
C(15)
C(3)

Figure 2.

FUNCTIONALIZATION OF η^1, η^2-BRIDGING CYAPHIDE ($C{\equiv}P^-$) LIGANDS: TRINUCLEAR η^1, η^1, η^2-BRIDGING CYAPHIDE AND DINUCLEAR BRIDGING ISOCYAPHIDE ($C{\equiv}PR$) COMPLEXES OF PLATINUM

A paper to be submitted to *Organometallics*

Wayde V. Konze, Victor G. Young, Jr.[+], and Robert J. Angelici*

Abstract

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

C≡PMe)Pt(PEt$_3$)$_2$](OTf) (**Va**), which is likely coordinated in an η^1, η^2-bridging mode. Compound **Va** reacts with NaI to form **Vc**, which suggests that **Va** forms as an intermediate before **Vc** in the reaction of **II** with MeI.

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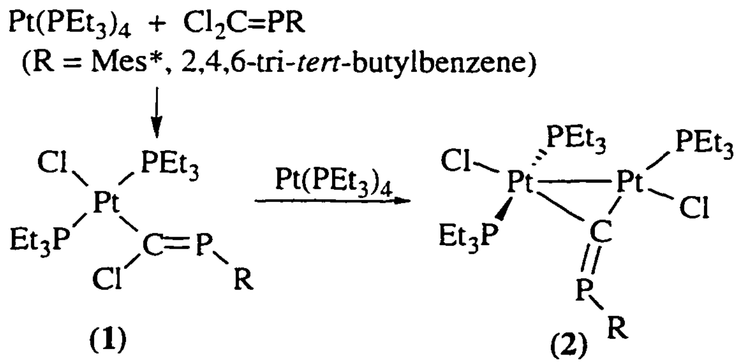
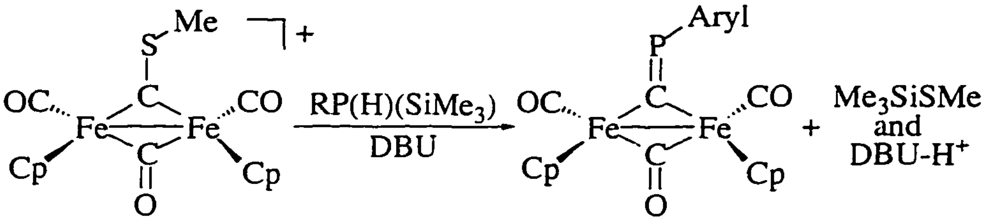
Introduction

Studies involving phosphorus analogs of common organic ligands have evolved at a very rapid pace recently, and coordination compounds of C-P analogs of almost all C-C multiple bond ligands are now known, including phosphaalkenes, phosphaalkynes, phosphaallyls, phosphaallenes, phosphabutadienes, phosphacyclopropenes, phosphacyclobutadienes, phosphacyclopentadienyls and phosphaarenes.[1-6] However, phosphorus analogs of the well studied cyanide (C≡N$^-$) and isocyanide (C≡NR) ligands have been limited.[7-9] These phosphorus compounds have been calculated to be high energy species; the heat of formation in C≡P$^-$ (cyaphide anion) is calculated to be ca. 40 kcal/mol less exothermic than that of C≡N$^-$,[10] and C≡PH (isocyaphide) is calculated to be 85 kcal/mol less stable than its isomer H-C≡P (phosphaalkyne).[11] Nevertheless, we recently succeeded in preparing the first example of a coordinated isocyaphide ligand by oxidative addition of the C-Cl bond in the phosphavinyl complex (**1**) (eq 1) to generate a diplatinum complex [(Cl)(Et$_3$P)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Cl)] (**2**),



(1)

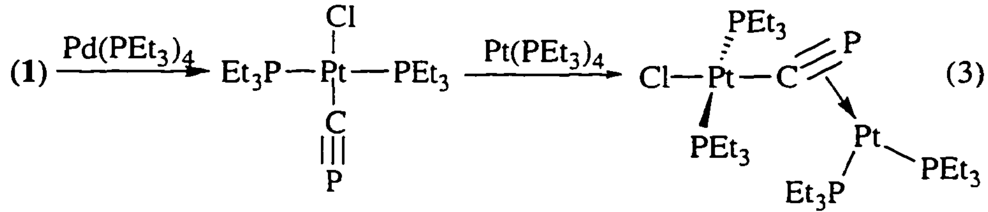
in which the isocyaphide ligand exhibits a semi-bridging coordination mode.[9] However, this preparation was limited by the few examples of dichlorophosphaalkenes available and by the bulky R-groups that are incorporated in these reagents. More recently, Weber and coworkers reported the synthesis (eq 2) of some diiron complexes containing symmetrically-bridged isocyaphide ligands (**3**) by a different route.[7] In these reactions, the isocyaphide products



(3)

(2)

were only prepared with bulky R-groups on phosphorus. We also obtained the first example of a cyaphide complex $(Et_3P)_2ClPt(C{\equiv}P)$ (**4**) from a reaction (eq 3) of the phosphavinyl

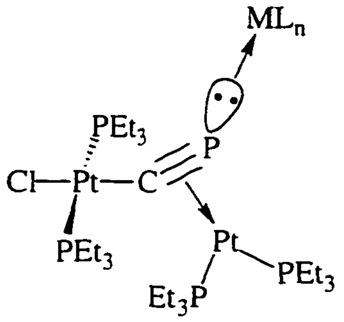


(4) (II)

(3)

complex (**1**) with $Pd(PEt_3)_4$, in which the Mes* group was transferred from phosphorus to palladium forming $(Et_3P)_2(Cl)Pd(Mes^*)$ as a side product.[9] Compound **4** could only be characterized by NMR, but reacted (eq 3) with $Pt(PEt_3)_4$ to generate the η^1, η^2-cyaphide dimer $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (**II**), which was characterized by X-ray diffraction studies.

We describe in the present paper a high yield preparation of complex **II** utilizing a one-step reaction from the phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PN(SiMe_3)_2]$ **(Ib)**, which has much different reactivity than the analogous phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PMes^*]$ **(1)**.[12] We also investigate further functionalization of the cyaphide ligand in complex **II** by virtue of the accessible lone pair of electrons on the C≡P phosphorus atom. During the course of these studies, we have isolated the first examples of trinuclear metal-cyaphide compounds (**A**) that were formed by

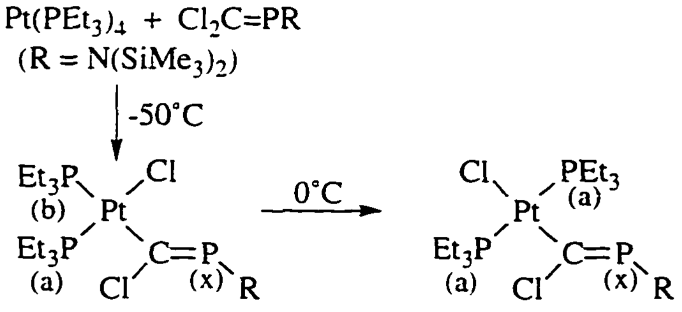


(A)

coordinating the C≡P phosphorus atom in **II** to other transition metal fragments. We have also found that the cyaphide ligand in **II** can be easily converted to an alkyl isocyaphide ligand by using various alkylating agents, constituting the first examples of cyaphide-isocyaphide conversions and demonstrating that isocyaphide ligands with less bulky alkyl R-groups can be stabilized on transition metals.

Results and Discussion

Synthesis of *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PN(SiMe_3)_2]$ (Ib). The reaction (eq 4) of $Pt(PEt_3)_4$ with $Cl_2C=PN(SiMe_3)_2$ in THF or hexanes at -50°C immediately and quantitatively forms the η^1-phosphavinyl complex *cis*-$Cl(Et_3P)_2Pt[C(Cl)=PN(SiMe_3)_2]$ **(Ia)** by oxidative



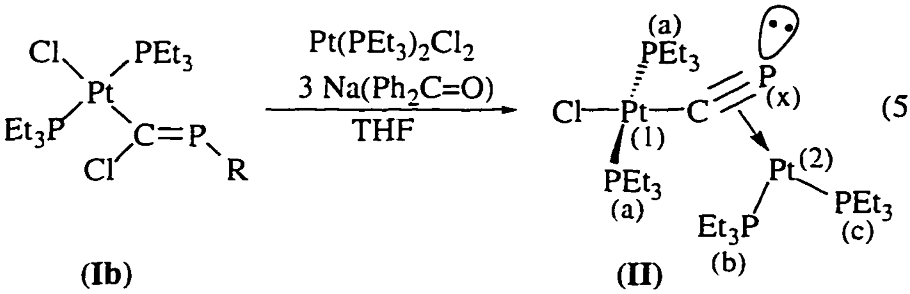
(Ia) (Ib) (4)

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

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

X-ray Crystal Structure of *trans*-$\mathrm{Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]}$ (Ib). A thermal ellipsoid drawing of **Ib** (Figure 1) shows that the complex is isostructural with the previously characterized compound *trans*-$\mathrm{Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]}$ **(1)**. The platinum atom is in a square-planar environment as defined by the two $\mathrm{PEt_3}$, Cl, and [C(Cl)=PR] ligands; the sum of angles around the platinum atom is 360.0°. The C(1)-P(1) distance of 1.690(7) Å is marginally longer than that (1.678(5) Å) in compound **1** and is the same within error as the C=P distance (1.685(2) Å) in the free phosphaalkene $\mathrm{Cl_2C{=}PN(SiMe_3)_2}$.[13] The Pt-C(1) distance in **Ib** (1.990(7) Å) is slightly shorter than the corresponding distance (2.013 (4) Å) in **1**.[12] The nitrogen atom in **Ib** is in a trigonal planar environment, and the P(1)-N(1)-Si(1)-Si(2) plane is almost orthogonal (96.4°) to the plane defined by Pt, Cl(1), C(1), P(1) and N(1). This orthogonality rules out any conjugative effects from the nitrogen lone pair; in a series of X-ray determined structures of phosphaalkenes containing $\mathrm{NR_2}$ groups on phosphorus, orthogonal $\mathrm{NR_2}$ groups were found to show no conjugative effects with the C=P double bond.[14] If the [C(Cl)=PR] ligands in **1** and **Ib** were significantly different, the bond lengths between platinum and the *trans* ligands (Cl(2)) would be affected by this difference. However, the Pt-Cl(2) length in **Ib** (2.373(2) Å) is the same within error as that (2.377(2) Å) in **1**. Thus, a comparison of the structures of **1** and **Ib** indicate that the $N(SiMe_3)_2$ and Mes* groups show similar structural effects in phosphavinyl complexes of the type *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PR]$.

Preparation of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (II). The reaction (eq 5) of 1.05 equivalents of *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PN(SiMe_3)_2]$ **(Ib)** and 1 equivalent of



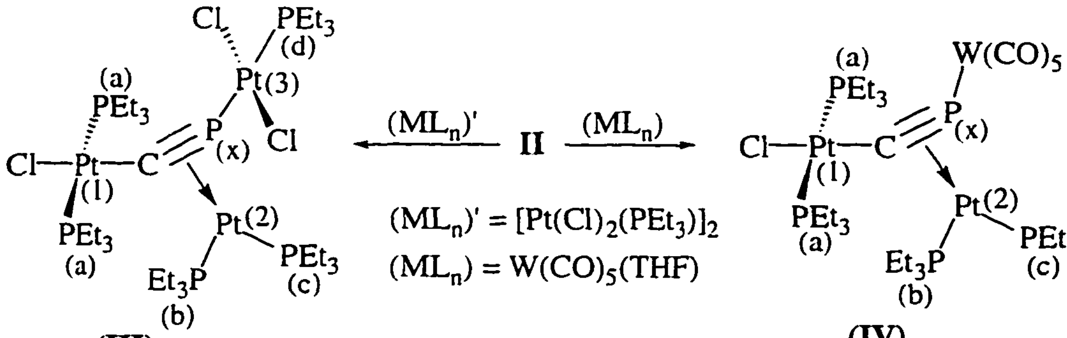
(5)

(Ib) **(II)**

$Pt(PEt_3)_2Cl_2$ with 3 equivalents of a dropwise added 0.2 M solution of sodium benzophenone ketyl in THF forms the bridging cyaphide dimer $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** in good yield. This preparation is much simpler than the original (eq 3) which involved the reaction of *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PMes^*]$ (**1**) with $Pd(PEt_3)_4$ to first generate a mixture of $(Et_3P)_2ClPt(C{\equiv}P)$ (**4**) and $(Et_3P)_2(Cl)Pd(Mes^*)$; complex **4** was then purified by crystallizing out $(Et_3P)_2(Cl)Pd(Mes^*)$ and finally reacted further with $Pt(PEt_3)_4$ to generate the product **II**.[9] In this new preparation, the intermediate isolation of complex **4** is avoided, and highly reactive Pd(0) and Pt(0) reagents are not necessary. Further, this reaction can be done on a several gram scale and gives excellent yields of complex **II** in pure, crystalline form.

In order to gain an understanding of how this interesting reaction proceeds, several different stoichiometries of different reagents were investigated, as was the order of addition. The use of 3 equivalents of the Na/benzophenone ketyl reducing agent was found to be ideal as more equivalents cause decomposition while fewer causes an incomplete reaction, which suggests that the two chlorides from $Pt(PEt_3)_2Cl_2$ and one chloride from **Ib** are removed as NaCl. The $N(SiMe_3)_2$ R-group is possibly removed as $(SiMe_3)_2N\text{-}N(SiMe_3)_2$, although this was not investigated. Interestingly, the reaction of *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PMes^*]$ (**1**) with $Pt(PEt_3)_2Cl_2$ and 3 equivalents of sodium benzophenone ketyl also results in the formation of **II**, but it also gives impurities that could not be separated. In order to investigate the role of the reducing agent, a reaction was attempted between **Ib** and Na/benzophenone ketyl without any $Pt(PEt_3)_2Cl_2$ present; no reaction was apparent after six hours. Also, if $Pt(PEt_3)_2Cl_2$ is reduced with Na/benzophenone ketyl followed by addition of **Ib**, a ^{31}P NMR spectrum shows that **Ib** is unreacted in solution. Evidently, both **Ib** and $Pt(PEt_3)_2Cl_2$ must be present during the addition of the reducing agent for this reaction to occur. The reduction reaction of $Pt(PEt_3)_2Cl_2$ in the presence of ethylene is known to produce $Pt(PEt_3)_2(C_2H_4)$, and it has been reported that if a suitable ligand is not present in solution the $Pt(PEt_3)_2$ fragment that is generated oligomerizes to Pt(0) clusters.[15] It is possible that the $Pt(PEt_3)_2$ fragment that is generated in eq 5 coordinates to the C=P double bond of **Ib** and activates the carbon-bound Cl toward reduction by a third equivalent of Na/benzophenone ketyl, while in the absence of **Ib** the $Pt(PEt_3)_2$ oliomerizes and does not react with **Ib**. Similar reactions to that in eq 5 were attempted between **Ib** and $Pt(PPh_3)_2Cl_2$, $Pt(Pi\text{-}Pr_3)_2Cl_2$, $Pt(PCy_3)_2Cl_2$, and $Pt(depe)Cl_2$; in all cases, compound **Ib** remained unreacted in solution indicating that this reaction is not general for other phosphines.

Preparation of Trinuclear Metal-Cyaphide Complexes. The cyaphide ligand that is coordinated to two platinum centers in complex **II** contains a lone pair of electrons on the C≡P phosphorus atom that is a potential site for further coordination. Accordingly, the reactions (eq 6) of either one-half equivalent of $[Pt(Cl)_2(PEt_3)]_2$ or one equivalent of



(III) **(IV)** (6)

W(CO)$_5$(THF) with **II** in THF at room temperature afford the first examples of trinuclear metal-cyaphide complexes Cl(Et$_3$P)$_2$Pt[μ-η^1, η^1, η^2-C≡P{Pt(PEt$_3$)(Cl)$_2$}]Pt(PEt$_3$)$_2$ (**III**) and Cl(Et$_3$P)$_2$Pt[μ-η^1, η^1, η^2-C≡P{W(CO)$_5$}]Pt(PEt$_3$)$_2$ (**IV**), respectively. Complex **III** forms immediately after the addition of [Pt(Cl)$_2$(PEt$_3$)]$_2$ to **II** and a ^{31}P NMR spectrum of the reaction mixture showed practically quantitative conversion to **III** with a small amount of Pt(PEt$_3$)$_2$Cl$_2$ formed as a by-product; complex **III** could not be isolated in pure form as it decomposes under vacuum to unidentified materials, presumably through loss of PEt$_3$. In the reaction of W(CO)$_5$(THF) with **II**, the formation of complex **IV** is complete after 1 h and a small amount of W(CO)$_5$(PEt$_3$) forms as a by-product that was easily separated. These reactions are similar to those of the η^2-coordinated phosphaalkyne complexes (R$_3$P)$_2$Pt(η^2-R-C≡P); in these, η^2-coordination of the phosphaalkyne to the platinum fragment enhances the coordinating ability of the lone pair of electrons on phosphorus.[3,16]

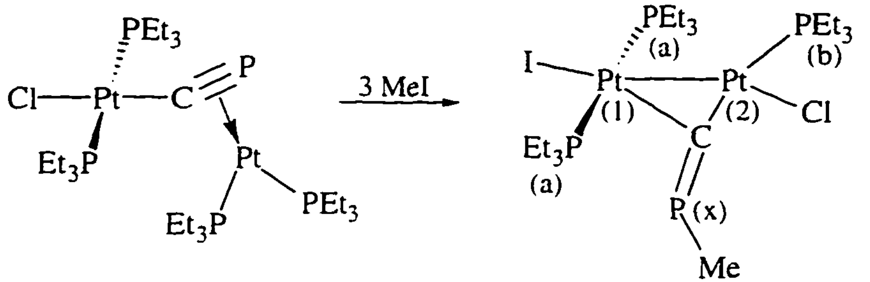
Compounds **III** and **IV** were characterized by ^{31}P and ^{31}P{^{1}H} NMR spectroscopy and the structure of complex **IV** was determined by X-ray diffraction studies. The ^{31}P NMR data for these compounds are compared in Table 4 along with the starting cyaphide complex (**II**) and the methyl isocyaphide complex (**Va**) which is a cationic complex of similar structure (see below). In all of these complexes, the peaks corresponding to P(x) are conveniently assigned by proton-coupled ^{31}P NMR spectroscopy, in which the P(x) signals remain sharp, while the PEt$_3$ signals are broadened by coupling to the ethyl protons. Complex **III** exhibits 5 distinct signals in its ^{31}P NMR spectrum; peaks corresponding to P(x) at δ 111.2, P(a) at δ 5.0, P(b) at δ 15.9 and P(c) at δ 17.2 ppm were assigned based on similar signals in the ^{31}P NMR spectrum of **II**, while the peak corresponding to P(d) at δ 5.2 ppm was assigned to the PEt_3 group in the $Pt(PEt_3)(Cl)_2$ fragment that is coordinated to the C≡P phosphorus atom. The peak for P(x) in **II** is split into a doublet of doublet of triplets, while the same peak in **III** is now split into a doublet of doublet of doublet of triplets; the extra splitting is from the PEt_3 ligand on the $Pt(PEt_3)(Cl)_2$ fragment ($^2J_{P(x)P(d)} = 472.3$ Hz). This is a very large two-bond P-P coupling constant that is indicative of a *trans*-orientation between P(d) and P(x), similar to the *trans*-$^2J_{PP}$ = 557 found in the bridging phosphaalkyne complex $Mo_2(CO)_4(Cp)_2${t-BuCP[$Pt(PEt_3)(Cl)_2$]}[17] and to the values of *trans*-$^2J_{PP}$ = 462-483 Hz measured in a series of *trans*-[$PtCl_2(PR_3)(PR'_3)$] complexes.[18] The coordination of the $Pt(PEt_3)(Cl)_2$ fragment to compound **II** also imparts a large change on the two-bond coupling constant between P(x) and the *trans*-like PEt_3 ligand P(b); the value of $^2J_{P(x)P(b)} = 13.7$ Hz in **II** increases to $^2J_{P(x)P(b)} = 148.0$ Hz in **III**. This effect has also been seen in η^2-phosphaalkyne complexes; in the complex [Pt(dppe)(η^2-t-BuC≡P)], the coupling constant between the C≡P phosphorus and the *trans*-P atom is 28.1 Hz, but when a $Cr(CO)_5$ fragment is coordinated to the C≡P phosphorus atom, this value increases to 177.5 Hz.[16] In fact, all of the couplings between P(x) and the other phosphorus signals are increased upon coordination of the $Pt(PEt_3)(Cl)_2$ group (see Table 4). Evidently, the cyaphide phosphorus atom undergoes a change in hybridization upon coordination to the metal fragment, acquiring more phosphorus s-electron character in the C≡P bond.

Complex **IV** exhibits 4 distinct signals in its ^{31}P NMR spectrum; the peaks corresponding to P(a) at δ 3.1, P(b) at δ 16.6 and P(c) at δ 13.9 ppm were assigned based on similar signals in the ^{31}P NMR spectrum of **II** and **III**, while the peak at δ 41.4 ppm was assigned to P(x) based on a sharp proton-coupled ^{31}P NMR signal and the doublet of doublet of triplets splitting pattern. The chemical shift of 41.4 ppm is 66 ppm upfield from that of P(x) in compound **II** and is similar to the upfield shift of 42 ppm that was measured upon coordination of a $W(CO)_5$ fragment to the C≡P phosphorus atom in the η^2-phosphaalkyne complex [Pt(dppe)(η^2-t-BuC≡P)].[16] The coordination of the $W(CO)_5$ group to complex **II** results in increased ^{31}P-^{31}P coupling constants (see Table 4) similar to those for **III**. The two-bond coupling constant between P(x) and the *trans*-like PEt_3 ligand P(b) is again very large $^2J_{P(x)P(b)} = 152.9$ Hz, and similar to that ($^2J_{P(x)P(b)} = 148.0$ Hz) in **III**. Only one set of platinum satellites ($^2J_{P(x)Pt(1)} = 507$ Hz) could be distinguished for P(x) in compound **IV** because of the complexity of this signal; this coupling constant is larger than that (255 Hz) in **II**, but still a bit smaller than that (676 Hz) in **Ib**. Although no tungsten satellites could be found for P(x), the signal for P(b) exhibited an unusually large three bond coupling to tungsten ($^3J_{WP(b)} = 150.77$ Hz), most likely because of the enhanced coupling between P(x) and P(b).

X-Ray Crystal Structure of $Cl(Et_3P)_2Pt[\mu$-η^1, η^1, η^2-C≡P{$W(CO)_5$}]$Pt(PEt_3)_2$ (IV). A thermal ellipsoid drawing of **IV** (Figure 2) shows that the complex contains a $W(CO)_5$ fragment attached to the C≡P phosphorus atom and has many structural features in common with the X-ray-determined structure of complex **II**.[9] Both of the platinum atoms in **IV** are in planar environments; the sum of angles around Pt(1) as defined by C(1), P(2), P(3) and Cl(1) is 360.1°, while the sum of angles around Pt(2) as defined by C(1), P(1), P(4) and P(5) is 360.4°. The C(1)-P(1) distance (1.663(9) Å) in **IV** is the same within error as that (1.666(6) Å) in **II** indicating that coordination of the $W(CO)_5$ unit has not dramatically changed the character of the cyaphide C-P bond. This distance is similar to a C-P double-bond distance (e.g., 1.67 Å in Ph(H)C=PMes*)[19] and to the C-P distance (1.67(2) Å) in the η^2-phosphaalkyne complex [$Pt(PPh_3)_2$(η^2-t-BuC≡P)],[20] and is consistent with backbonding from Pt(2) into the π^* orbital of the C≡P bond affording some metallacyclophosphapropene character in this 3-atom unit in **IV**. The Pt(1)-C(1)-P(1) angle (145.2(6)°) is bent from linearity similar to that in **II** (144.0(3)°) and the W(1)-P(1)-C(1) angle (136.1(3)°) is bent even further, also consistent with metallacyclophosphapropene character in this complex. The W(1)-P(1) distance (2.531(3) Å) is very similar to the W-P bond length

(2.539(3) Å) in the bridging phosphaalkyne complex $Mo_2(CO)_4(Cp)_2\{t\text{-}BuCP[W(CO)_5]\}$[21] and is slightly longer than typical W-P distances in structurally characterized $W(CO)_4(PR_3)_2$ complexes (e.g., 2.502 Å in *cis*-$W(CO)_4(PMe_3)_2$).[22] The Pt(2)-C(1) distance (2.104(9) Å) in **IV** is slightly longer than the corresponding distance (2.083(5) Å) in **II**, while the Pt(1)-C(1) distances (1.952(9) Å in **IV** and 1.950(6) Å in **II**) are the same within error. However, the Pt(2)-P(1) distance (2.292(3) Å) in **IV** is shorter than the corresponding distance (2.337(2) Å) in **II**. This is consistent with more s-electron character on phosphorus in the C≡P bond.

Alkylation Reactions of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (II). The reaction (eq 7) of three equivalents of MeI with $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (**II**) in THF for 12 h at 25°C results in the formation of the methyl isocyaphide complex



(7)

(II) **(Vc)**

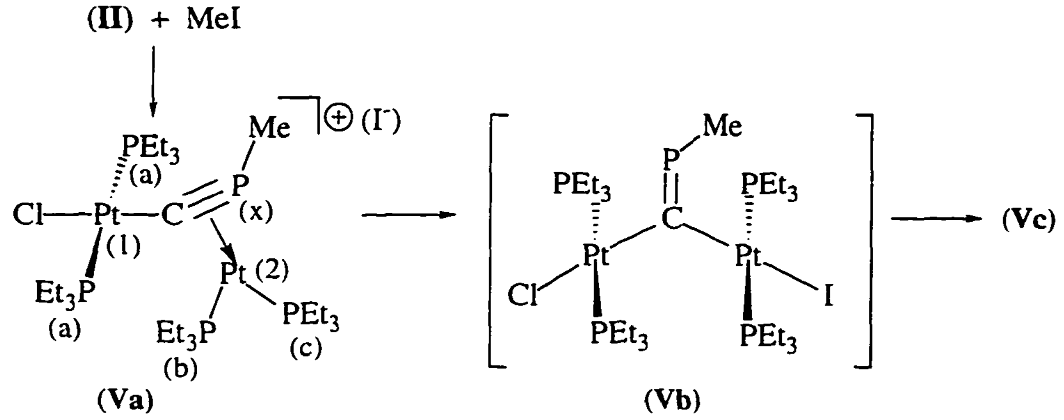
$(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)$ (**Vc**) with concomitant formation of the phosphonium salt $(MePEt_3)^+ I^-$. This reaction entails the conversion of a cyaphide ($C{\equiv}P^-$) ligand to an isocyaphide (C≡PMe) ligand and substitution of a coordinated PEt_3 ligand (lost as $(MePEt_3)^+ I^-$) with an iodide ligand; thus, the MeI acts both as a methylating agent and as a phosphine scavenger in this reaction. Although complex **Vc** is stable in THF solution at room temperature for several weeks, suitable crystals could not be obtained for an X-ray diffraction study as the compound only forms an oil. However, the complex is likely isostructural with the previously obtained semi-bridging isocyaphide complex $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMes^*)Pt(PEt_3)_2(Cl)$ (**2**)[9] based upon its ^{31}P NMR spectrum (Table 5) and the $^{13}C\text{-}^{31}P$ coupling constants obtained from the use of ^{13}C-labeled MeI in this reaction. Thus, the η^1, η^2-cyaphide ligand in **II** is converted to a semibridging isocyaphide ligand in **Vc** with the formation of a Pt-Pt bond. This reaction has some precedent in related isocyanide chemistry as the conversion of coordinated cyanide (C≡N$^-$) ligands to isocyanide (C≡NR) ligands with various alkylating agents is a well known synthetic route to isocyanide complexes, although these reactions have only been carried out on terminal cyanide complexes.[23] This new synthetic route to an isocyaphide complex is much different than the reaction (eq 1) of the phosphavinyl complex *trans*-Cl$(Et_3P)_2$Pt[C(Cl)=PMes*] **(1)** with $Pt(PEt_3)_4$ to generate the semi-bridging isocyaphide complex (Cl)(Et_3P)Pt(μ-C=PMes*)Pt$(PEt_3)_2$(Cl) **(2)**[9] or the reactions (eq 2) of $[Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CSMe)]^+$ with RP(H)$(SiMe_3)$ and DBU to generate the bridging isocyaphide complexes $[Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}PR)]$ **(3)**;[7] both of these syntheses were limited by the use of bulky aryl R-groups on the CPR phosphorus atom. In contrast, the reaction of **II** with MeI allows for the formation of an isocyaphide with a sterically small methyl group and could conceivably be a more general route to diplatinum isocyaphide complexes. In order to test this, the reaction in eq 7 was attempted with several different alkyl and aryl halides (e.g., benzyl bromide, *i*-propyl iodide, allyl bromide, *o*-iodo toluene and 2,4,6-tri-*tert*-butylbenzyl bromide) under the same reaction conditions and stoichiometry as in the MeI reaction. The reactions of both benzyl bromide (BnBr) and *i*-propyl iodide (*i*-PrI) with **II** afforded similar isocyaphide products (Cl)(Et_3P)Pt(μ-C=PBn)Pt$(PEt_3)_2$(Br) **(VI)** and (Cl)(Et_3P)Pt(μ-C=P*i*-Pr)Pt$(PEt_3)_2$(I) **(VII)**, respectively, as evidenced by ^{31}P NMR spectroscopy (see Table 5). However, the benzyl derivative could not be separated from impurities that were present, and the *i*-Pr derivative was unstable and decomposed before the reaction was complete. The reaction of allyl bromide with **II** formed completely different products that could not be isolated, while the aryl halides did not react with compound **II**, even after stirring for several days at room temperature. However, the results with BnBr and *i*-PrI are encouraging and suggest that other alkyl halides may be successful in this reaction.

Complex **Vc** was characterized by ^{31}P, ^{31}P{^{1}H} and ^{13}C{^{1}H) NMR spectroscopy. The ^{31}P NMR spectrum of complex **Vc** shows very similar chemical shifts and coupling constants (Table 5) to those measured in the semi-bridging isocyaphide complex (Cl)(Et$_3$P)Pt(μ-C=PMes*)Pt(PEt$_3$)$_2$(Cl) (**2**)[9] and is thus proposed to exhibit the same structure. The ^{31}P NMR spectrum of **Vc** exhibits three different signals. The peak at δ 155.4 ppm, assigned to P(x), is split into a doublet of triplets with two different ^{195}Pt satellites, indicative of the unsymmetrical, semibridging bonding mode of the C=PMe ligand. The doublet ($^2J_{P(x)P(b)}$ = 15.3 Hz) arises from coupling to the single PEt$_3$ ligand (P(b)) on Pt(2), while the triplet ($^3J_{P(x)P(a)}$ = 12.1 Hz) results from coupling to the two equivalent PEt$_3$ ligands (P(a)) on Pt(1). The larger coupling constant to platinum ($^2J_{Pt(2)P(x)}$ = 564.7 Hz) is assigned to coupling with the 4-coordinate platinum Pt(2), while the smaller Pt-P coupling constant ($^2J_{Pt(1)P(x)}$ = 231.9 Hz) is assigned to coupling with the 5-coordinate platinum atom Pt(1); these assignments are made based upon the assignments in compound **2** and by the larger J_{PtP} coupling constants that are typically found in platinum complexes with lower coordination numbers.[24] From these J_{PP} coupling constants, the signal at δ 8.7 ppm is assigned to P(a), while the signal at δ 21.52 is assigned to P(b). Because the signal for P(a) is farther upfield than the analogous peak in **2**, while the peaks for P(b) have quite similar chemical shifts, it is assumed that the iodide ligand is on the platinum that contains the two P(a) PEt$_3$ groups (Pt(1)). One of the unique aspects of the ^{31}P NMR spectra of **Vc**, which gives precedent to it being isostructural with **2**, is the large differences in the one-bond J_{PtP} coupling constants in the signals corresponding to P(a) and P(b); for P(a) in **Vc**, the value of $^1J_{Pt(1)P(a)}$ = 2338.9 Hz is similar to those found in *trans*-Pt(PEt$_3$)$_2$X$_2$ complexes,[24] while for P(b), the value of $^1J_{Pt(2)P(b)}$ = 5173.7 Hz is very large and more similar to those found in three-coordinate Pt(0) complexes.[24] This difference in the J_{PtP} coupling constants is greater in **Vc** than in compound **2** and has been discussed previously in the analogous semibridging carbonyl complex (Cl)(Ph$_3$P)Pt(μ-CO)Pt(PPh$_3$)$_2$(Cl) (**4**) which is very similar in structure to **Vc** and **2**, but with PPh$_3$ instead of PEt$_3$ ligands and a semibridging

CO ligand in place of the CPR ligands.[25,26] Complex **4** exhibits a value of $^1J_{PtP}$ = 2680 Hz for the two equivalent 5-coordinate platinum PPh_3 groups (P(a)) and a value of $^1J_{PtP}$ = 5440 Hz in the 4-coordinate platinum PPh_3 group (P(b)) (see Table 5 for further comparisons). This difference was rationalized by suggesting some degree of mixed valence character between the two platinum atoms.[25] To further verify that the methyl group is attached to the phosphorus atom in complex **Vc**, the reaction was carried out using ^{13}C-labeled MeI. The ^{31}P NMR spectrum of labeled **Vc** exhibited an extra doublet in the signal for P(x) from coupling to the labeled methyl group with $^1J_{P(x)C}$ = 48.9 Hz. This value is similar to the value of $^1J_{PC}$ = 51.1 Hz found in the phosphonium salt $(MePEt_3)^+ I^-$ product of this reaction. Interestingly, the signal for P(b) also exhibited a small coupling ($^4J_{P(x)C}$ = 10.6 Hz) to the methyl group. The ^{13}C NMR signal for the methyl group occurred at δ 10.5 and was split into a doublet of doublets by P(x) and P(b). This peak also exhibited a small Pt-C coupling constant of $^3J_{PtC}$ = 51.2 Hz, which is most likely a coupling with Pt(2) which is bonded more strongly to the CPR group. The ^{31}P NMR spectra of complexes **VI** and **VII** (Table 5) are quite similar to those of **Vc**, and these compounds are proposed to be of similar structure. These spectroscopic results, along with comparisons with those of compounds **2** and **4**, strongly suggest that complexes **Vc, VI** and **VII** contain semibridging isocyaphide ligands.

Mechanistic Studies of the Formation of $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2(I)$ (Vc). A likely pathway (Scheme 1) for the formation of complex **Vc** from complex **II** is the initial methylation of the C≡P phosphorus atom to generate a cationic η^1, η^2-isocyaphide intermediate (**Va**). The iodide anion can then attack at Pt(2) to generate the

Scheme 1



bridging isocyaphide intermediate **Vb**, which loses a PEt_3 group and forms a metal-metal bond to generate the product **Vc**. An intermediate similar to **Vb** was postulated in the reaction (eq 1) of the phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PMes^*]$ (**1**) with $Pt(PEt_3)_4$ to generate the semi-bridging isocyaphide complex $(Cl)(Et_3P)Pt(\mu\text{-}C=PMes^*)Pt(PEt_3)_2(Cl)$ (**2**).[9] In an attempt to verify this pathway by isolation of the cationic η^1, η^2-isocyaphide intermediate (**Va**), complex **II** was reacted with one equivalent of MeI in the presence of two equivalents of $NaBPh_4$ in THF at room temperature. The color of the solution turned to a very deep ruby red color after 1h, and a ^{31}P NMR spectrum (see below) showed a new complex that matches the structure drawn for **Va** where the iodide anion has been replaced with (BPh_4^-). This complex was then isolated in reasonably pure form by filtering the solution and adding hexanes to form an oil of mainly **Va**. When a ten-fold excess of NaI was then added to a solution of **Va** in THF, the color changed from deep red to light orange in 10 min, and a ^{31}P NMR spectrum showed that this complex was completely converted to the semibridging isocyaphide complex **Vc**, which strongly suggests that **Va** is an intermediate that forms before **Vc** in the reaction of MeI with complex **II**. In a separate experiment, complex **II** was reacted with MeOTf in THF; the color turned to deep red in a matter of minutes and a ^{31}P NMR spectrum of the solution again showed complex **Va** where a triflate anion is substituted for the iodide anion. Reaction of this solution with a ten-fold excess of NaI afforded complex **Vc**, providing further evidence for the pathway outlined in Scheme 1. Although there was no evidence in the ^{31}P NMR spectra for other intermediates, **Vb** is a likely intermediate that explains the rearrangement of the η^1, η^2-isocyaphide ligand in **Va** to the semibridging isocyaphide ligand in **Vc**. In contrast to **Vc**, which contains a Pt-Pt bond, the ^{31}P NMR spectrum (see below) of **Va** suggests that there is no Pt-Pt bond in this cationic isocyaphide complex. Clearly, compound **Va** does not contain a semibridging isocyaphide similar to **Vc**, and it is not clear why substitution of a PEt_3 group in **Va** by an iodide anion causes this rearrangement to take place. Complex **Va** contains the first example of an η^1, η^2-bridging isocyaphide ligand.

Although complex **Va** could not be isolated in pure form, the ^{31}P NMR spectrum is characteristic of an η^1, η^2-bridging isocyaphide structure and shows features (Table 4) very similar to those in the spectra of the η^1, η^1, η^2-bridging trimetallic cyaphide complexes with a $Pt(Cl)_2(PEt_3)$ fragment **(III)** and a $W(CO)_5$ fragment **(IV)** on the cyaphide phosphorus atom. The signal at δ 34.7 ppm in **Va**, assigned to P(x), is shifted 120 ppm upfield from the corresponding P(x) peak in **Vc**; this shift is most consistent with an η^1, η^2-bridged species. Interestingly, the chemical shift is quite similar to that (δ 41.4 ppm) in the tungsten-coordinated cyaphide complex **IV**, which differs only in that it is neutral and contains a $W(CO)_5$ group in place of the Me group on **Va**. Also supporting the proposed structure is the fact that the splitting patterns and coupling constants in **Va**, **III** and **IV** are all quite similar (Table 4). The coupling constants between P(x) and the PEt_3 groups again are larger than those in the η^1, η^2-cyaphide complex **(II)**, with the most dramatic effect again being a large coupling ($^2J_{P(x)P(b)}$ = 148.9 Hz) between P(x) and P(b). This is very similar to the $^2J_{P(x)P(b)}$ values found in **III** ($^2J_{P(x)P(b)}$ = 148.0 Hz) and **IV** ($^2J_{P(x)P(b)}$ = 152.9 Hz). The ^{195}Pt-^{31}P coupling constants found in **Va** are also similar to those found in **III** and **IV** (Table 4) and provide further evidence for the proposed structure. Since there is no ^{195}Pt-^{31}P coupling of P(a) with Pt(2) or between P(b) and P(c) with Pt(1), the existence of a Pt-Pt bond in **Va** is doubtful; in **Vc** and **2** which contain Pt-Pt bonds, these couplings to the platinum atom of the adjacent metal fragment were somewhat large (43-512 Hz). To further verify that the methyl group is attached to the cyaphide phosphorus atom, complex **Va** was prepared by reacting complex **II** with labeled MeI in the presence of $NaBPh_4$. The ^{31}P NMR spectrum of this labeled complex exhibited additional doublets [P(x) ($^1J_{P(x)C}$ = 71.5 Hz), P(b) ($^3J_{P(b)C}$ = 8.4 Hz) and P(c) ($^3J_{P(c)C}$ = 12.6 Hz)] as a result of coupling to the labeled methyl group. The ^{13}C NMR spectrum also displayed a peak for the methyl group at δ 8.7 ppm that was split into a doublet of doublets of doublets by these three phosphorus atoms. These results are entirely consistent with the proposed structure of **Va** and indicate that the attachment of a $W(CO)_5$, $Pt(Cl)_2(PEt_3)$ or Me^+ group to the cyaphide phosphorus atom in complex **II** gives products with very similar ^{31}P NMR spectra and structures.

Summary

Comparison of the reactivity of the new phosphavinyl complex *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (**Ib**) with the previously obtained complex *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PMes^*]$ (**1**)[12] has shown that the substitution of the Mes* group with a $N(SiMe_3)_2$ group does not result in large changes in the NMR properties or structural features of these two complexes; the structure of (**Ib**) was determined by X-ray diffraction studies to be quite similar to that of **1** with no evidence for conjugation from the nitrogen lone pair of electrons into the C=P double bond. However, compound **Ib** showed much different reactivity than that of **1** and reacted with $Pt(PEt_3)_2Cl_2$ and Na/benzophenone ketyl to afford a new synthetic route to the previously obtained η^1, η^2-bridged cyphide dimer $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (**II**). This reaction provided a much simpler and more efficient preparation of complex **II** and allowed us to further study the reactivity of this useful complex. Thus, complex **II** was reacted with one-half equivalent of $[Pt(Cl)_2(PEt_3)]_2$ or with one equivalent of $W(CO)_5(THF)$ to generate the first examples of trinuclear metal cyaphide complexes $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C{\equiv}P\{Pt(PEt_3)(Cl)_2\}]Pt(PEt_3)_2$ (**III**) and $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}$

$C\equiv P\{W(CO)_5\}]Pt(PEt_3)_2$ (**IV**), respectively, in which the lone pair of electrons on the cyaphide ($C\equiv P$) phosphorus atom has been utilized to coordinate to a third metal fragment. The structure of the tungsten adduct (**IV**) was determined by X-ray diffraction studies and showed that the cyaphide ligand has some metallacyclophosphapropene character as both the $Pt(PEt_3)_2Cl$ and the $W(CO)_5$ fragments are bent back from the axis of the $C\equiv P$ bond. Complex **II** also reacted with alkylating agents to generate semibridging isocyaphide complexes of the type $(Cl)(Et_3P)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(X)$; when R = Me (**Vc**), it was found that a cationic η^1, η^2-bridging isocyaphide complex $[(Cl)(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C\equiv PMe)Pt(PEt_3)_2](I)$ (**Va**) formed first in this reaction and was isolated as the triflate salt by reacting complex **II** with MeOTf. This complex was converted into the semibridging isocyaphide complex (**Vc**), by reacting it with excess NaI. These alkylation reactions represent the first examples of conversion of a cyaphide ($C\equiv P^-$) ligand into an isocyaphide ($C\equiv PR$) ligand and demonstrate that isocyaphide complexes with non-bulky alkyl groups can be stabilized on transition metals. The ^{31}P NMR spectrum of the triflate salt of complex **Vc** strongly suggests that this is the first example of a complex containing an η^1, η^2-bridged isocyaphide ligand and demonstrates a further coordination mode of these new ligands.

Experimental Section

General Procedure. All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium benzophenone ketyl, while hexanes and dichloromethane (CH_2Cl_2) were distilled over CaH_2.

The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a Bruker AC 200-MHz spectrometer using 85% H_3PO_4 (δ 0.00 ppm) as the external standard. The $^{13}C\{^1H\}$ and ^{13}C NMR spectra were recorded on a Bruker DRX 400-MHz spectrometer using $CDCl_3$ as the internal standard. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. The compounds $Pt(PEt_3)_4$,[27] $Cl_2C{=}PN(SiMe_3)_2$,[28] $[Pt(Cl)_2(PEt_3)]_2$,[29] $Pt(PR_3)_2Cl_2$ [30] and Na/benzophenone ketyl 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. Methyl iodide (MeI) and methyl triflate (MeOTf) were purchased from Aldrich and used without further purification. $W(CO)_5(THF)$ was prepared by photolysis of $W(CO)_6$ in THF for 6 h at 20°C.

Preparation of *trans*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (Ib) through Intermediate *cis*-$Cl(Et_3P)_2Pt[C(Cl){=}PN(SiMe_3)_2]$ (Ia). To a cooled (-50°C) solution of $Pt(PEt_3)_4$ (1.50 g, 2.25 mmol) in hexanes (20 mL) was added $Cl_2C{=}PN(SiMe_3)_2$ (0.616 g, 2.25 mmol). A ${}^{31}P\{{}^1H\}$ NMR spectrum taken 10 min after the addition (-50°C) showed complete conversion to **Ia**. After the solution had warmed to 0°C over the course of 30 min, a ${}^{31}P\{{}^1H\}$ NMR spectrum showed that compound **Ia** had completely isomerized to **Ib**. The almost colorless solution was warmed to room temperature over the course of 10 min and the solvent was removed under vacuum. The residue was treated with 20 mL of hexanes, filtered, and the filtrate was concentrated to 10 mL. A white precipitate formed, which was found to be $Pt(PEt_3)_2Cl_2$ by comparison of its ${}^{31}P$ NMR spectrum with that of an authentic sample. The precipitate was filtered off and the filtrate was concentrated to 5 mL under vacuum. The light orange/brown solution was cooled slowly to -78°C for 3 d after which time large, light yellow crystals had formed. The crystals were isolated by cannulating off the mother liquor, washing with 2x5 mL portions of hexanes at -78°C, and drying under vacuum to give **Ib** (1.24 g, 78%). ${}^{31}P\{{}^1H\}$ NMR (hexanes) (see eq 4 for atom labels) for **Ia**, -50°C: $\delta(P(x))$ 225.1 (dd, ${}^3J_{P(x)P(b)} = 33.0$ Hz, ${}^3J_{P(x)P(a)} = 8.3$ Hz, ${}^2J_{PtP(x)} = 410.0$ Hz), $\delta(P(b))$ 10.1 (dd, ${}^3J_{P(b)P(x)} = 33.0$ Hz, ${}^2J_{P(b)P(a)} = 16.2$ Hz, ${}^1J_{PtP(b)} = 1908$ Hz), $\delta(P(a))$ 5.6 (dd, ${}^2J_{P(a)P(b)} = 16.2$ Hz, ${}^3J_{P(a)P(x)} = 8.3$ Hz, ${}^1J_{PtP(a)} = 3874$ Hz). For **Ib**, 25°C: $\delta(P(x))$ 222.3 (t, ${}^3J_{P(x)P(a)} = 20.0$ Hz, ${}^2J_{PtP(x)} = 676.0$ Hz), δ(P(a)) 14.1 (d, $^3J_{P(a)P(x)}$ = 20.0 Hz, $^1J_{PtP(a)}$ = 2680 Hz). Anal. Calcd for $C_{19}H_{48}Cl_2N_1P_3Pt_1Si_2$ **(Ib)**: C, 32.34; H, 6.86; N, 1.98. Found: C, 31.25; H, 6.62; N, 1.87.

Preparation of $Cl(Et_3P)_2Pt(\mu$-η^1, η^2-C≡P)$Pt(PEt_3)_2$ (II). To a dry mixture of *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PN(SiMe_3)_2]$ **(Ib)** (1.00 g, 1.42 mmol) and $Pt(PEt_3)_2Cl_2$ (0.747 g, 1.49 mmol) at room temperature was added dropwise with stirring 20.8 mL of a solution of 0.204 M Na/benzophenone ketyl in THF (4.25 mmol) (the molarity of the Na/benzophenone solution was determined by quenching a measured amount with water, and titrating with standardized HCl solution). The addition was done at a rate that was determined by the color change; as the color turned blue, addition was halted until the color changed back to orange. The total time of the addition was ca 45 min, after which time the color of the solution was dark red with a large amount of NaCl precipitate. The solution was filtered through Celite and the solvent was removed from the filtrate under vacuum. Extended drying under vacuum, especially with heating, was found to cause decomposition. The dark red residue was treated with hexanes (30 mL), filtered through Celite and the filtrate was reduced in volume to 10 mL. A ^{31}P NMR spectrum of this solution showed pure **II**, however benzophenone was present as the only impurity. The solution was cooled slowly to -78°C and kept at this temperature for 1 week, after which time dark red crystals of **II** had formed. The crystals were isolated by cannulating off the mother liquor, washing with 2x5 mL portions of hexanes at -78°C, and drying under vacuum to give **II** (1.05 g, 79%). Compound **II** was characterized by comparison of its ^{31}P NMR spectrum with that of an authentic sample. $^{31}P\{^1H\}$ NMR (THF) (see eqn 5 for atom labels): δ(P(x)) 107.0 (ddt, $^2J_{P(x)P(b)}$ = 13.7 Hz, $^2J_{P(x)P(c)}$ = 10.7 Hz, $^3J_{P(x)P(a)}$ = 10.7 Hz, $^2J_{Pt(1)P(x)}$ = 255 Hz, $^1J_{Pt(2)P(x)}$ = 58 Hz), δ(P(c)) 18.6 (dd, $^2J_{P(c)P(b)}$ = 35.1 Hz, $^2J_{P(c)P(x)}$ = 10.7 Hz, $^1J_{Pt(2)P(c)}$ = 3619 Hz, $^3J_{Pt(1)P(c)}$ = 137 Hz), δ(P(b)) 15.0 (ddt, $^2J_{P(b)P(c)}$ = 35.1 Hz, $^2J_{P(b)P(x)}$ = 13.7 Hz, $^4J_{P(b)P(a)}$ = 4.5 Hz, $^1J_{Pt(2)P(b)}$ = 3155 Hz), δ(P(a)) 4.9 (dd, $^3J_{P(a)P(x)}$ = 10.7 Hz, $^2J_{P(a)P(b)}$ = 4.5 Hz, $^1J_{Pt(1)P(a)}$ = 2936 Hz).

Preparation of $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C{\equiv}P\{Pt(PEt_3)(Cl)_2\}]Pt(PEt_3)_2$ (III). To a dry mixture of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (**II**) (0.100 g, 0.106 mmol) and $[Pt(Cl)_2(PEt_3)]_2$ (0.0408 g, 0.0531 mmol) at room temperature was added 10 mL of THF with stirring. The color turned from dark orange to light orange immediately. A ^{31}P NMR spectrum taken after 5 min of stirring showed quantitative formation of **III**, with a small amount of $Pt(PEt_3)_2Cl_2$ present (characterized by comparison of its ^{31}P NMR spectrum with that of an authentic sample). The volume of the solvent was reduced to 2 mL, and 5 mL of hexanes was added to precipitate the $Pt(PEt_3)_2Cl_2$ impurity. The solution was filtered, and a ^{31}P NMR spectrum of the filtrate showed very pure **III**. Compound **III** is stable in hexanes for several days at -30°C, but decomposes at room temperature in about 1 d. Compound **III** could not be purified for elemental analysis as it decomposed to unidentified products under vacuum and was characterized by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (THF) (see eq 6 for atom labels): $\delta(P(x))$ 107.0 (dddt, $^2J_{P(x)P(d)} = 472.3$ Hz, $^2J_{P(x)P(b)} = 148.0$ Hz, $^2J_{P(x)P(c)} = 42.5$ Hz, $^3J_{P(x)P(a)} = 21.4$ Hz), $\delta(P(c))$ 17.2 (ddd, $^2J_{P(c)P(x)} = 42.5$ Hz, $^4J_{P(c)P(d)} = 22.0$ Hz, $^2J_{P(c)P(b)} = 8.7$ Hz, $^1J_{Pt(2)P(c)} = 2926$ Hz), $\delta(P(b))$ 15.9 (ddd, $^2J_{P(b)P(x)} = 148.0$ Hz, $^4J_{P(b)P(d)} = 56.0$ Hz, $^2J_{P(b)P(c)} = 8.7$ Hz, $^1J_{Pt(2)P(b)} = 3601$ Hz), $\delta(P(d))$ 5.21 (ddd, $^2J_{P(d)P(x)} = 472.3$ Hz, $^4J_{P(d)P(b)} = 56.0$ Hz, $^4J_{P(d)P(c)} = 22.0$ Hz, $^1J_{Pt(3)P(d)} = 3020$ Hz), $\delta(P(a))$ 5.0 (d, $^3J_{P(a)P(x)} = 21.4$ Hz, $^1J_{Pt(1)P(a)} = 2829$ Hz) (The $^{195}Pt\text{-}^{31}P$ coupling constants in the P(x) signal were not possible to determine because of the complexity of the splittings).

Preparation of $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ (IV). To a solution of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ (**II**) (0.500 g, 0.531 mmol) in THF (10 mL) at room temperature was added $W(CO)_5(THF)$ (0.531 mmol) in THF (20 mL) with stirring. The color of the solution turned from dark orange to dark red after 1 h of stirring. The solvent volume was reduced to ca 3 mL under vacuum, and 15 mL of hexanes was added. The flask was cooled to -30°C for 1 h with formation of an oily-solid impurity. The solution was filtered, the filtrate was reduced in volume to 5 mL and then cooled slowly to -78°C for 3 d after which time light orange crystals of **IV** had formed. The crystals were isolated by cannulating off the mother liquor, washing them with 2x5 mL portions of hexanes at -78°C, and drying under vacuum to give **IV** (0.375 g, 56%). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (THF) (see eq 6 for atom labels): δ(P(x)) 41.4 (ddt, $^{2}J_{\mathrm{P(x)P(b)}} = 152.9$ Hz, $^{2}J_{\mathrm{P(x)P(c)}} = 38.7$ Hz, $^{3}J_{\mathrm{P(x)P(a)}} = 18.9$ Hz, $^{1}J_{\mathrm{Pt(1)P(x)}} = 507$ Hz), δ(P(c)) 13.9 (dd, $^{2}J_{\mathrm{P(c)P(x)}} = 38.7$ Hz, $^{2}J_{\mathrm{P(c)P(b)}} = 9.1$ Hz, $^{1}J_{\mathrm{Pt(2)P(c)}} = 2917$ Hz), δ(P(b)) 16.6 (dd, $^{2}J_{\mathrm{P(b)P(x)}} = 152.9$ Hz, $^{2}J_{\mathrm{P(b)P(c)}} = 9.1$ Hz, $^{1}J_{\mathrm{Pt(2)P(b)}} = 3568$ Hz), δ(P(a)) 3.1 (d, $^{3}J_{\mathrm{P(a)P(x)}} = 18.9$ Hz, $^{1}J_{\mathrm{Pt(1)P(a)}} = 2818$ Hz).

Preparation of $[(\mathrm{Cl})(\mathrm{Et_3P})\mathrm{Pt}(\mu\text{-C=PMe})\mathrm{Pt}(\mathrm{PEt_3})_2(\mathrm{I})]$ (Vc). To a stirred solution of $\mathrm{Cl}(\mathrm{Et_3P})_2\mathrm{Pt}(\mu\text{-}\eta^1, \eta^2\text{-C}{\equiv}\mathrm{P})\mathrm{Pt}(\mathrm{PEt_3})_2$ (**II**) (0.500 g, 0.531 mmol) in THF (10 mL) at room temperature was added MeI (0.226 g, 1.59 mmol) all at once. After stirring for 12 h at 25°C, the color had changed from dark orange to light orange and a precipitate of $[\mathrm{MePEt_3}]\mathrm{I}^-$ had formed (characterized by comparison of its ^{31}P NMR with an authentic sample). The solution was filtered, the solvent was removed from the filtrate under vacuum, and the residue was treated with 25 mL of hexanes. After reducing the solvent under vacuum to 5 mL, the solution was filtered and cooled slowly to -78°C for 2 d to form an oil of **Vc** that was pure by ^{31}P NMR spectroscopic studies (Yield 0.386 g, 75%). A similar preparation was carried out using ^{13}C-labeled MeI in order to obtain $^{13}\mathrm{C}\text{-}^{31}\mathrm{P}$ coupling constants. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (THF) (see eq 7 for atom labels): δ(P(x)) 155.4 (dt, $^{3}J_{\mathrm{P(x)P(b)}} = 15.3$ Hz, $^{3}J_{\mathrm{P(x)P(a)}} = 12.1$ Hz, $^{2}J_{\mathrm{Pt(2)P(x)}} = 564.7$ Hz, $^{2}J_{\mathrm{Pt(1)P(x)}} = 231.9$ Hz), δ(P(b)) 21.5 (d, $^{3}J_{\mathrm{P(b)P(x)}} = 15.3$ Hz, $^{1}J_{\mathrm{Pt(2)P(b)}} = 5173.7$ Hz, $^{2}J_{\mathrm{Pt(1)P(b)}} = 463.4$ Hz), δ(P(a)) 8.7 (d, $^{3}J_{\mathrm{P(a)P(x)}} = 12.1$ Hz, $^{1}J_{\mathrm{Pt(1)P(a)}} = 2338.9$ Hz, $^{2}J_{\mathrm{Pt(2)P(a)}} = 43.5$ Hz). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): $\delta(\mathrm{CH_3P})$ 10.5 (dd, $^{1}J_{\mathrm{CP(x)}} = 48.9$ Hz, $^{4}J_{\mathrm{CP(b)}} = 10.6$ Hz, $^{3}J_{\mathrm{CPt(2)}} = 51.2$ Hz).

Formation of $[\mathrm{Cl}(\mathrm{Et_3P})_2\mathrm{Pt}(\mu\text{-}\eta^1, \eta^2\text{-C}{\equiv}\mathrm{PMe})\mathrm{Pt}(\mathrm{PEt_3})_2]^+$ (Va). Method A. To a stirred solution of $\mathrm{Cl}(\mathrm{Et_3P})_2\mathrm{Pt}(\mu\text{-}\eta^1, \eta^2\text{-C}{\equiv}\mathrm{P})\mathrm{Pt}(\mathrm{PEt_3})_2$ (**II**) (0.350 g, 0.372 mmol) in THF (15 mL) at room temperature was added MeOTf (0.0610 g, 0.372 mmol) all at once. After stirring for 5 min, the color of the solution changed from dark orange to dark, ruby red.

The volume of the solution was reduced to 2 mL and 15 mL hexanes was added to form a dark red oil that separated from solution. The remaining light red solution was removed from the oil with a cannula, and the oil was washed with 3x8 mL portions of hexanes to afford the triflate anion of **Va** (crude yield 0.279 g, 68%). A ^{31}P NMR spectrum showed that this oil contained a small amount of impurities which were more prevalent after 1 d. Complete decomposition was evident after 1 week at room temperature. (The ^{31}P NMR spectrum was the same as that for the BPh_4^- salt below).

Method B. To a stirred solution of $Cl(Et_3P)_2Pt(\mu\text{-}\eta^1, \eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2$ **(II)** (0.200 g, 0.212 mmol) and $NaBPh_4$ (0.145 g, 0.425 mmol) in THF (10 mL) at room temperature was added MeI (0.302 g, 0.212 mmol) all at once. The color of the solution turned from dark orange to very dark red after 3 h of stirring. The solution was treated with 10 mL of hexanes, and a large amount of oily precipitate formed. The solution was filtered, and the solvent in the filtrate was removed under vacuum. The residue was dissolved in 2 mL of THF, and 15 mL of hexanes was added to form a dark red oil that separated from the solution. The oil was isolated by cannulating off the solution, washing with 3x8 mL portions of hexanes followed by 3x5 mL portions of Et_2O to afford the BPh_4^- salt of **Va** (crude yield 0.103 g, 38%). A similar preparation was carried out using ^{13}C-labeled MeI in order to obtain ^{13}C-^{31}P coupling constants. $^{31}P\{^1H\}$ NMR (THF) (see Scheme 1 for atom labels): δ(P(x)) 34.7 (ddt, $^2J_{P(x)P(b)}$ = 148.9 Hz, $^2J_{P(x)P(c)}$ = 23.8 Hz, $^3J_{P(x)P(a)}$ = 20.6 Hz), δ(P(c)) 20.1 (dd, $^2J_{P(c)P(x)}$ = 23.8 Hz, $^2J_{P(c)P(b)}$ = 10.2 Hz, $^1J_{Pt(2)P(c)}$ = 2441 Hz), δ(P(b)) 18.7 (ddt, $^2J_{P(b)P(x)}$ = 148.9 Hz, $^2J_{P(b)P(c)}$ = 10.2 Hz, $^4J_{P(b)P(a)}$ = 5.7 Hz, $^1J_{Pt(2)P(b)}$ = 3640 Hz), δ(P(a)) 8.1 (dd, $^3J_{P(a)P(x)}$ = 20.6 Hz, $^4J_{P(a)P(b)}$ = 5.7 Hz, $^1J_{Pt(1)P(a)}$ = 2661 Hz). (The ^{195}Pt-^{31}P coupling constants in the P(x) signal were not possible to determine because of the complexity of the splittings). $^{13}C\{^1H\}$ NMR (THF): δ(CH_3P) 8.7 (ddd, $^1J_{CP(x)}$ = 71.5 Hz, $^3J_{CP(c)}$ = 12.6 Hz, $^3J_{CP(b)}$ = 8.4 Hz).

Conversion of [Cl(Et$_3$P)$_2$Pt(μ-η^1, η^2-C≡PMe)Pt(PEt$_3$)$_2$]$^+$ (Va) to [(Cl)(Et$_3$P)Pt(μ-C=PMe)Pt(PEt$_3$)$_2$(I)] (Vc). To a stirred solution of **Va** (0.100 g, 0.0784 mmol) in THF (20 mL) at room temperature, prepared as in Method B above, was added NaI (0.118 g, 0.784 mmol) as a solid. After stirring for 10 min, the color had changed from dark red to light orange. The solvent was removed under vacuum, and the residue was taken up in 20 mL of hexanes. The solution was filtered over Celite, and the filtrate was shown to contain mainly **Vc** by a ^{31}P NMR spectrum, but could not be isolated pure as it contained impurities that likely resulted from decomposition of **Va** before or during the reaction.

X-ray Crystallographic Study of *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PN(SiMe$_3$)$_2$] (Ib). Diffraction-quality crystals of **Ib** were obtained by recrystallization from hexanes at -78°C. Data collection and reduction information are given in Table 1. A light orange crystal of **Ib** was mounted on a glass fiber for data collection. Cell constants were determined from reflections found in a rotation photograph. High-angle cell constants were determined from a subset of intense reflections in the range of 35.0 to 50.0° 2θ. The data were corrected for Lorentz and polarization effects. A correction based on nonlinear decay in the three standard reflections was applied to the data. An absorption correction based on measured crystal faces was applied. The space group Pbca was unambiguously determined by systematic absences and intensity statistics.[31] A successful direct methods solution was calculated which provided all non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined as riding-atoms with C-H distances of 0.96 Å. The hydrogen atoms in methylene groups were refined with individual isotropic displacement parameters while methyl hydrogen atoms were refined as groups. Selected bond distances and bond angles are given in Table 2.

X-ray Crystallographic Study of Cl(Et$_3$P)$_2$Pt[μ-η^1, η^1, η^2-C≡P{W(CO)$_5$}]Pt(PEt$_3$)$_2$ (IV). Diffraction-quality crystals were obtained by slow evaporation of an Et_2O solution of **IV**. Data collection and reduction information are given in Table 1. An orange crystal of **IV** was mounted on a glass fiber for data collection. An initial set of cell constants was calculated from reflections taken from three sets of 20 frames. Final cell constants were calculated from a set of 5625 strong reflections taken during the data collection. The space group $P2_1/n$ was unambiguously determined by systematic absences and intensity statistics.[31] A hemisphere-type data collection was employed in which a randomly oriented region of space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω, providing a high degree of redundancy. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms. One triethylphosphine group (P4) was disordered in a 0.50:0.50 ratio, and required the use of 426 restraints. The P4 group is duplicated (P4') in order to make a separate group, both of which have the same parameters. These groups were refined isotropically with additional restraints and the other triethylphosphine groups in the molecule were used to group the two partially occupied groups in SHELTXTL SAME restraints.[31] Selected bond distances and bond angles are given in Table 3.

Acknowledgment

We thank the donors of The Petroleum Research Fund (grant 27360-AC3), administered by the American Chemical Society, and the National Science Foundation (grant CHE-9414242) for support of this research.

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

	Ib	**IV**
formula	$C_{19}H_{48}Cl_2NP_3Si_2Pt$	$C_{30}H_{60}ClO_5P_5Pt_2W$
space group	Pbca	$P2_1/n$
a, Å	11.802(2)	11.0994(2)
b, Å	15.060(3)	33.5717(2)
c, Å	35.060(3)	12.4301(1)
α, deg	90	90
β, deg	90	111.659(1)
γ, deg	90	90
V, $Å^3$	6231.7(16)	4304.76(9)
Z	8	4
d_{calc}, g/cm^3	1.504	1.952
crystal size, mm	0.377 x 0.377 x 0.125	0.4 x 0.12 x 0.12
μ, mm^{-1}	12.244	9.429
data collection instrument	Siemens P4RA	Siemens SMART
radiation (monochromated in incident beam)	Cu Kα (λ=1.54178 Å)	Mo Kα (λ=0.71073 Å)
temp, K	213(2)	173(2)
scan method	2θ-θ	Area Detector, ω-frames
data collection range,	4.0-115.0; θ, deg	1.21-25.07; 2θ, deg
no. of data collected	7857	21054
no. of unique data total	4171	7544

Table 1. (continued)

	Ib	**IV**
with I$\geq$ 2σ (I)	3207	5738
no. of parameters refined	278	390
trans factors; max; min	0.2836/0.0379	1.000/0.433
R^a (I>2σ (I))	0.0368	0.0476
$R_w{}^b$ (I>2σ (I))	0.0442	0.0942
quality of fit indicator^c	1.33	1.023
largest peak, e/Å^{-3}	1.57	1.462

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for *trans*-Cl(Et$_3$P)$_2$Pt[C(Cl)=PN(SiMe$_3$)$_2$] (**Ib**)

Distances (Å)

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

Bond Angles (deg)

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

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C{\equiv}P\{W(CO)_5\}]Pt(PEt_3)_2$ (**IV**).

Distances (Å)

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

Bond Angles (deg)

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

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

Table 4. Comparison of ^{31}P NMR data (THF) for $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C{\equiv}P]Pt(PEt_3)_2$ (**II**) with those of the complexes $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C{\equiv}P\{ML_n\}]Pt(PEt_3)_2$, where ML_n = $Pt(Cl)_2(PEt_3)$ (**III**), $W(CO)_5$ (**IV**), Me^+ (**Va**).[a]

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

a) See eqns 5, 6 and Scheme 1 for atom labels.

Table 5. Comparison of ^{31}P NMR data for (Cl)(Et$_3$P)Pt(μ-C=PMes*)Pt(PEt$_3$)$_2$(Cl) (**2**), (Cl)(Ph$_3$P)Pt(μ-CO)Pt(PPh$_3$)$_2$(Cl) (**4**), and complexes (Cl)(Et$_3$P)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(X) (**Vc**: R = Me, X = I; **VI**: R = Bn, X = Br; **VII**: R = i-Pr, X = I)[a]

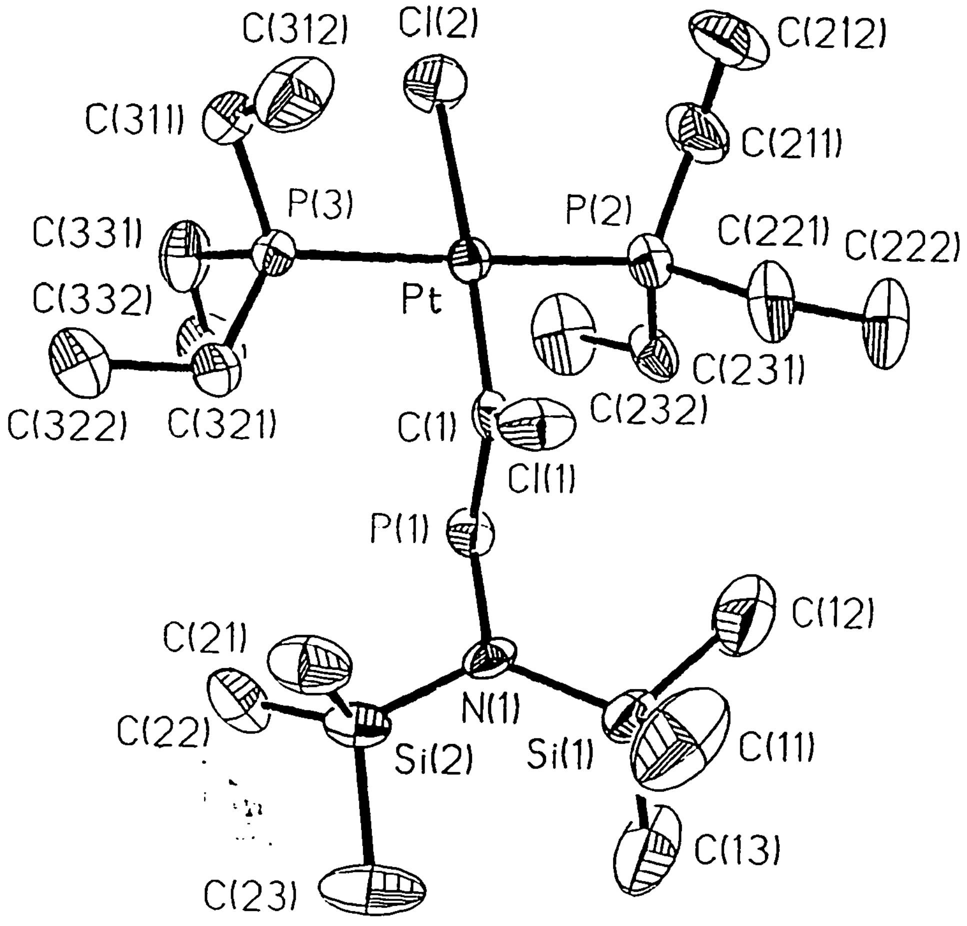
Cmpd	δ P(x) ppm	δ P(b) ppm	δ P(a) ppm	$^3J_{(x)-(b)}$ Hz	$^3J_{(x)-(a)}$ Hz	$^2J_{Pt2-(x)}$ Hz	$^2J_{Pt1-(x)}$ Hz	$^1J_{Pt2-(b)}$ Hz	$^2J_{Pt1-(b)}$ Hz	$^1J_{Pt1-(a)}$ Hz	$^2J_{Pt2-(a)}$ Hz
2	151.3	22.8	19.6	35	23	321	110	4814	512	2428	67
4	-	30.2	21.74	-	-	-	-	5440	804	2680	59
Vc	155.4	21.5	8.7	15.3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

a) See eqn 7 for atom labels.

Figure Captions

Figure 1. Thermal ellipsoid drawing of *trans*-$Cl(Et_3P)_2Pt[C(Cl)=PN(SiMe_3)_2]$ **(Ib).**

Figure 2. Thermal ellipsoid drawing of $Cl(Et_3P)_2Pt[\mu\text{-}\eta^1, \eta^1, \eta^2\text{-}C\equiv P\{W(CO)_5\}]Pt(PEt_3)_2$ **(IV).**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Cl(2)
C(212)
C(311)
C(211)
P(3)
P(2)
C(331)
C(221)
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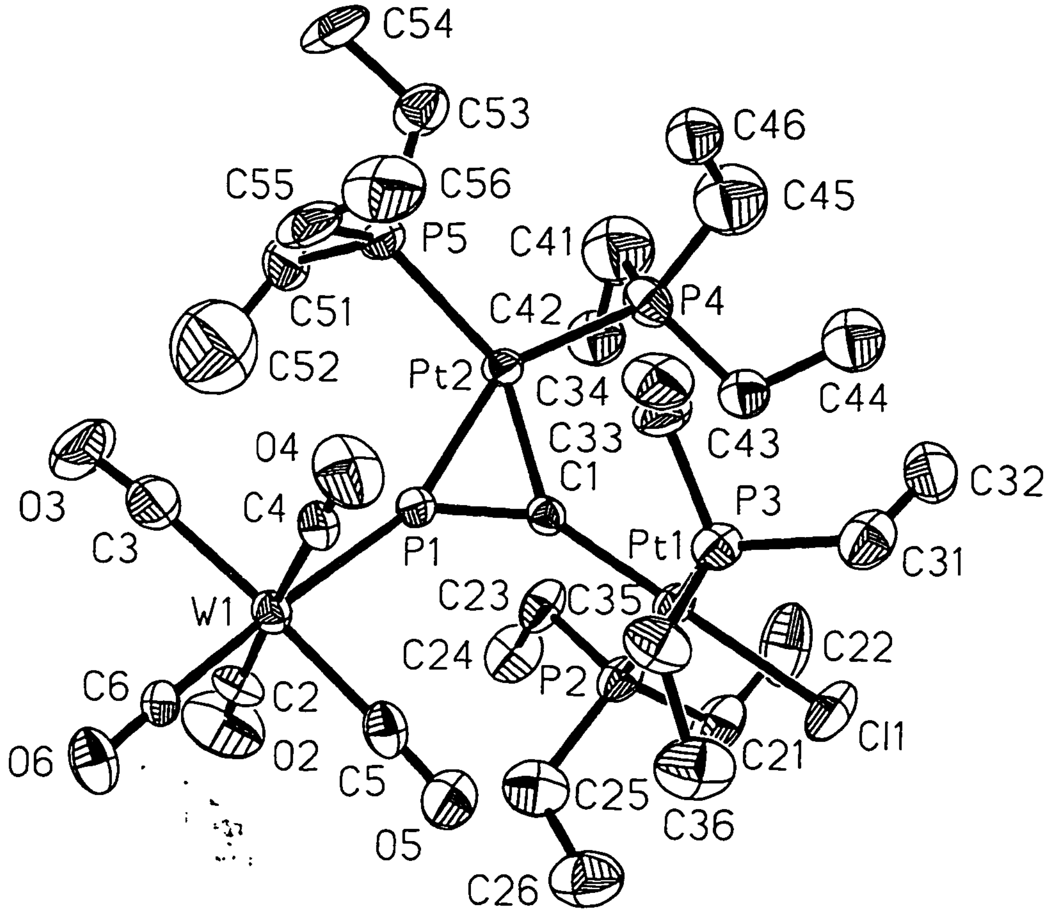
Pt
C(332)
C(231)
C(322)
C(321)
C(1)
C(232)
Cl(1)
P(1)
C(21)
C(12)
C(22)
N(1)
Si(2)
Si(1)
C(11)
C(13)
C(23)

Figure 1.


C54
C53
C46
C55
C56
C45
P5
C41
C42
P4
C51
C52
Pt2
C34
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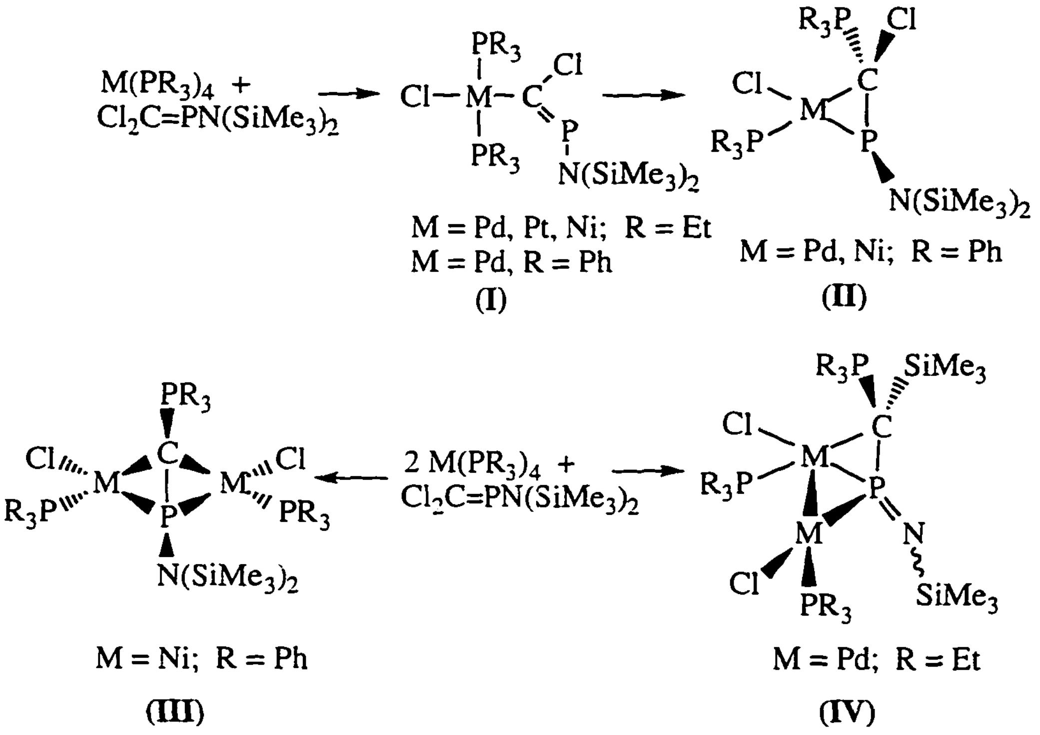
C33
C43
O4
O3
C4
C1
C32
P3
C3
P1
Pt1
C31
C23
C35
W1
C22
C24
C6
C2
P2
C21
Cl1
O6
O2
C5
C25
C36
O5
C26

Figure 2.

GENERAL SUMMARY

The oxidative addition reactions of zerovalent Ni, Pd and Pt phosphine complexes with dihalophosphaalkene compounds resulted in the formation of several complexes containing new carbon-phosphorus multiply bonded ligands. When $M(PEt_3)_4$ was reacted with $Cl_2C{=}PN(SiMe_3)_2$, phosphavinyl complexes (I) were observed with M = Pd, Pt and Ni. 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 (I) observed, which underwent PPh_3 rearrangement upon warming to form a phosphavinyl phosphonium complex (II). In the case of M = Ni, a phosphavinyl intermediate (I) was postulated, but only the phosphavinyl phosphonium complex (II) was observed; this nickel complex was not isolated, but reacted with another equivalent of $Ni(PPh_3)_4$ to generate the first example of a phosphavinylidene phosphorane complex (III). When $Ni(PPh_3)_4$ was reacted with $Cl_2C{=}PMes^*$, again a phosphavinyl phosphonium complex (II) formed, but having a proton in place of the chloride on the C-P



M = Pd, Pt, Ni; R = Et
M = Pd, R = Ph
(I)

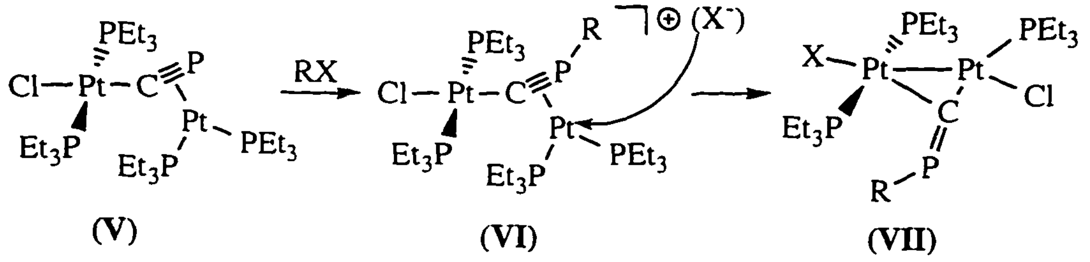
M = Pd, Ni; R = Ph
(II)

M = Ni; R = Ph
(III)

M = Pd; R = Et
(IV)

carbon; this was the first reported example of a complex containing a phosphavinyl phosphonium ligand. Evidently, the presence of PPh_3 ligands favors the formation of the phosphavinyl phosphonium complexes, while PEt_3 tends to stabilize the phosphavinyl complexes. When two equivalents of $Pd(PEt_3)_4$ were reacted with $Cl_2C{=}PN(SiMe_3)_2$, the first example of a phosphonio-methylene(imino)metallophosphorane (IV) formed. This complex underwent hydrolysis to form the first example of a phosphonio-methylene(oxo)phosphorane complex. Several of these compounds exhibited interesting substitution reactions and the structures that were obtained provided insights into the bonding properties of these new carbon-phosphorus unsaturated ligands.

A new high-yield synthesis of the η^1, η^2-bridging cyaphide ($C{\equiv}P^-$) dimer (V) was developed. This complex reacted with various alkyl halides to afford semi-bridging isocyaphide (C≡PR) complexes (VII). In the case of R = Me, an intermediate η^1, η^2-bridging isocyaphide complex (VI) was isolated during this reaction; this is the first example of an isocyaphide ligand coordinated in this type of bridging mode. These reactions demonstrated that isocyaphide complexes with non-bulky alkyl groups can be stabilized on transition metals and may provide for further functionalization of these interesting ligands.



The η^1, η^2-bridging cyaphide ($C{\equiv}P^-$) complex (V) was found to contain a further ligation site by virtue of its lone pair of electrons on the C≡P phosphorus atom; thus, the first examples of trinuclear metal-cyaphide complexes were obtained by coordination of this phosphorus atom to a $W(CO)_5$ fragment and a $Pt(Cl)_2(PEt_3)$ fragment.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Robert Angelici, for his support and guidance throughout my graduate studies; he has been a true mentor in both chemistry and in "real" life. His knowledge of chemistry is unsurpassed, and I will always fondly remember our discussions on many subjects and the tangential directions that they usually took, often leading to many more ideas than I could possibly carry out. I would also like to thank Dr. Gordie Miller, Dr. John Corbett, Dr. Robert Jacobson and Dr. Richard Seagrave for serving on my graduate committee. A special thanks to Dr. Louis H. Pignolet at the University of Minnesota, to whom I owe my entire beginning in chemistry and who I consider a very dear friend. I would also like to thank Dr. Victor G. Young, Jr. for working his magic on my often difficult crystals and for always finding the time for me; he is a truly gifted crystallographer and a great person, and I hope to work with him in the future.

I am also grateful to all of the people I have had the opportunity to work with in the Angelici group. I would like to thank Dr. John R. Sowa, Jr. for convincing me in the first place to come to Iowa State. I am grateful to Dr. Mary K. Rottink, Dr. Dongmei Wang, Dr. John Benson, Dr. Mitchell Robertson, Dr. Mike Sanger, and especially Dr. Carter White for all of the support and guidance in the early days of my studies. A special thanks to Dr. Hyoung Jun with whom I shared many wonderful discussions about research and about life in general, and with whom I shared plenty of good beer. A very special thanks to Dr. Chip Nataro, who always was able to find the time to talk about research and whom I consider a good friend. The rest of the Angelici group that I have been exposed to (James Rudd, Allyn Ontko, Mike 'Muffin' Reynolds, Jennifer Harnisch, Laurie Cardoza, Max Ovchinnikov, Ann Perera, Oltea Siclovan, Dr. Kuo-chen Shih, Dr. Hanrong Gao and Dr. Jiabi Chen) have all been wonderful to work with, and I hope to see them in the future.

I would also like to thank my parents, James and Annemarie Foley, who have always allowed me to explore my wild and crazy ideas, and were not afraid to sign for chemicals for me in my early days of chemistry; luckily they did not know that my beginning in chemistry revolved around the development of small explosive devices. They have always been supportive of the many different directions that I have taken, even when it involved a career as a musician in an alternative music group.

Most importantly, my deepest thanks go to my wonderful wife, Rebecca Ann; she has been supportive of me throughout my education and put her own career on hold to allow me to finish my graduate studies and to provide a nice home for our children. She has stood by me in good times and in very bad, and I hope she continues to do so. Her sense of humor and ability to always accept what time I can give her as golden has allowed me to finish this project. Last, but certainly not least, I want to thank my children, Joseph Allen and Nicolette Amber, who are the most beautiful creations that I have been a part of, and their running to greet me at the door when I came home brightened every day (or night!).