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Nucleophilic Reactivity of the Multiply Bonded Carbon Center in Group 4−Pincer Bis(iminophosphorano)methanediide Complexes

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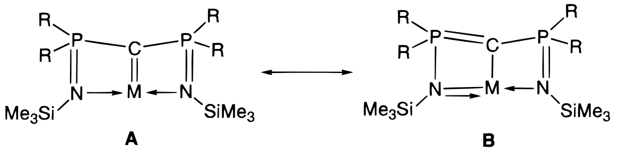
Summary: The bis(iminophosphorano)methanediide (carbene) complexes $[MCl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2N,N'\}]$ *(M = Hf (**1**), Zr (**2**)) form Lewis acid−base adducts with THF, nitriles, and isonitriles and undergo 1,2-addition reactions with amines, alcohols, and alkyl iodides and [2 + 2]-cycloaddition reactions with heteroallenes. The halide complexes can be alkylated with lithium alkyl reagents without attack at the carbene center. All these reactions are consistent with high-valent metal alkylidene character.*

The reactivity of a M═C(carbene) functionality is determined by several factors, such as the substituents on the carbon center, the ligation at the metal, and the oxidation state of the metal. Broadly, species with a M═C functionality can be subdivided into those in which the carbon has nucleophilic character (Schrock alkylidenes), when alkyl or hydrogen substituents are present on the carbene center, or where it is electrophilic, which is the general case when the carbon carries a heteroatom (O, S, N, etc.) substituent.[1] Many transition-metal complexes in these categories have been studied because of their relevance to organic syntheses.[2] Most contain CO or Cp substituents. Group 4 carbene complexes are rather rare,[3] being limited to a few titanium[4] and zirconium[5] alkylidenes and the zirconium Fischer carbene.[6] Heteroatom-substituted carbene complexes of group 4 metals have received only minor attention.[3] We recently reported a system of 12-valence-electron bis(iminophosphorano)methanediide complexes of the group 4 metals,[7,8] which contain a metal multiply bound to the carbon and which may be regarded as a carbene. In addition there are no CO or Cp substituents on the metal. The M═C unit is supported by two chelating iminophosphorane substituents to form a “pincer” type system with conjugation (Scheme 1) represented as the two limiting structures: a carbene (**A**) or the ylide−amide (**B**).

Scheme 1



The short metal−carbon bond in these new complexes, revealed by the structural characterization, and a semiempirical calculation support the metal carbene formulation.[7,8] Here we report reactions of representative Zr and Hf complexes **1** and **2** with selected electrophiles and nucleophiles which suggest alkylidene character. We observe both 1,2-addition and [2 + 2]-cycloaddition processes, with C−C bond formation (Scheme 2). The reactivity pattern of these carbene complexes implies that the carbon center is nucleophilic, and thus, the complexes are similar to high-oxidation-state metal alkylidenes.[9] The nucleophilicity may arise because the phosphorus substituents introduce behavior similar to phosphorus ylides.[10]

The halide substituents of **1** or **2** are readily replaced by alkyl groups using simple nucleophilic substitution

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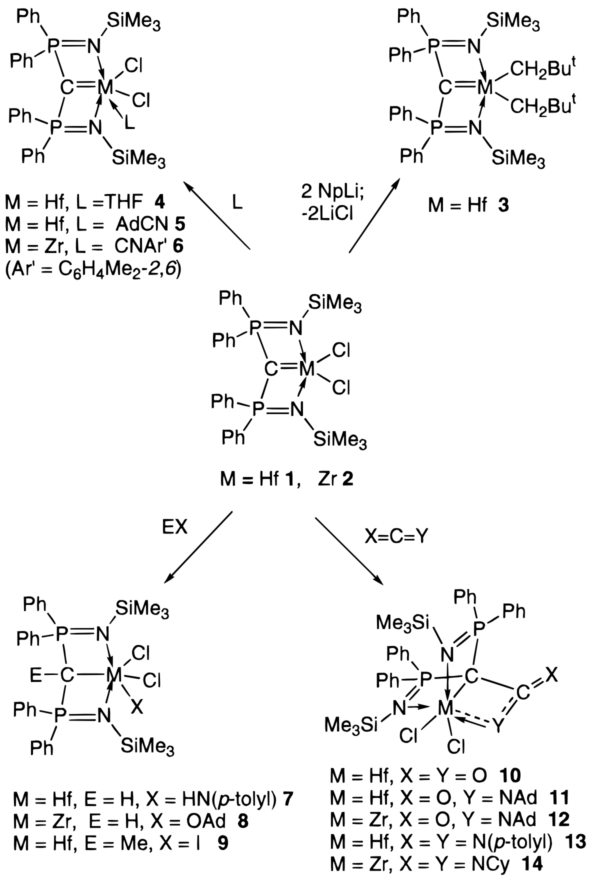
Scheme 2



reactions. Thus, reaction of **1** with *neo*-PeLi (*neo*-Pe = neopentyl) gave $[Hf(\textit{neo}\text{-}Pe)_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**3**).[11] It is notable that the carbon center in the complex is not attacked under these conditions, as is also the case for alkylidene complexes.[12] In Fischer type carbene complexes, the carbene center is attacked by alkyllithium to form an anionic carbon species.[13,14] Similar dialkylbis(iminophosphorano)methanediide complexes were prepared earlier using a direct route from the tetraalkylmetal precursors and the bis(iminophosphorano)methane ligand.[8]

The bis(iminophosphorano)methandiide complexes **1** and **2** readily form Lewis-base adducts $[M(L)Cl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (M = Hf, L = THF, **4**; M = Hf, L = AdCN, **5**[11a,15] (Ad = adamantyl); M = Zr, L = $CN(C_6H_4Me_2\text{-}2,6)$, **6**) with a coordinating solvent, e.g. nitriles or isonitrile) at room temperature. These adducts are 14-valence-electron complexes. Although M=C complexes generally yield insertion products with isonitriles or nitriles,[12,14,16] the formation of adducts in the present case is unique and may be due to the strong electrophilic character of the metal center aided by its coordinative unsaturation. No reaction was observed with carbon monoxide or hydrogen at atmospheric pressure.

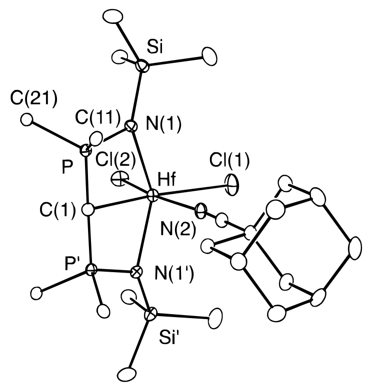


Figure 1. ORTEP[26] view of $[Hf(AdCN)Cl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**5**) showing the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Hf−C(1) = 2.211(6), Hf−N(1) = 2.184(3), Hf−N(2) = 2.308(5), P−N(1) = 1.628(4), P−C(1) = 1.652(1), P−C(11) = 1.820(4), Hf−Cl(1) = 2.456(2), Hf−Cl(2) = 2.419(2); P−C(1)−P′ = 170.6(4), Hf−C(1)−P = 92.3(2), N(1)−Hf−N(1′) = 142.1(2), N(1)−P−C(1) = 102.4(3).

The crystal structures of **4** and **5**[17] show that the tridentate pincer-type chelate frame, present in the starting complexes, is preserved in the adducts. A view of $[Hf(AdCN)Cl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**5**) is shown in Figure 1. The structure contains a mirror plane of symmetry, which passes through the plane defined by the Hf, C(1), Cl(1), Cl(2), and N(2) atoms. The P−C−P (170.6(4)°) unit is nearly linear, and the C(1) atom deviates by 0.12 Å from the least-squares plane containing P, N(1), Hf, N(1′), and P′. The Hf−C bond distance (2.211(6) Å) is slightly longer than that observed for an analogous cyclohexyl-substituted complex, $[HfCl_2\{C(Cy_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (2.162(6) Å),[18] containing no additional donor ligand group.

The methanediide complexes **1** and **2** react smoothly with compounds containing acidic protons such as aromatic amines, phenols, and aliphatic alcohols to yield the C_α-protonated product $[MCl_2(X)\{EC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3 C,N,N'\}]$ as a result of 1,2-addition of the substrate across the $M{=}C_\alpha$ bond. Representative products **7** (M = Hf)[11a,19] and **8** (M = Zr), isolated from the reactions

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(11) (a) All synthetic work described herein was carried out in an inert-atmosphere box under argon using carefully dried and degassed solvents. Typically, solid reactant was added to a stirred toluene solution of **1** or **2** at room temperature. (b) Complex **3**, $[HfNp_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$, was obtained when solid neopentyllithium was added to a stirred toluene solution of **1** at room temperature. The product was recrystallized (2 days) at −15 °C from hexane. Yield: 0.12 g, 56%. Anal. Calcd for $C_{41}H_{60}HfN_2P_2Si_2$: C, 56.12; H, 6.89; N, 3.19. Found: C, 55.72; H, 6.80; N, 3.12. Important NMR parameters: $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K) δ 71.6 (t, $^1J_{PC}$ = 160 Hz, carbene C of PCP); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K) δ 10.3 (s). Full details are given in the Supporting Information.

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(15) Complex **5**, $[Hf(AdCN)Cl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$, was obtained from the reaction of solid adamantyl cyanide with a stirred toluene solution of **1** at room temperature. The product was obtained by crystallization (3 days) from the reaction solution at room temperature. Yield: 0.18 g, 81%. Anal. Calcd for $C_{42}H_{53}Cl_2HfN_3P_2Si_2$: C, 52.15; H, 5.52; N, 4.34. Found: C, 52.23; H, 5.12; N, 4.25. Important NMR parameters: $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K) δ 83.4 (t, $^1J_{PC}$ = 153 Hz, carbene C of PCP); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K) δ 11.4 (s). Full details are given in the Supporting Information.

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(17) Crystal data for $[Hf(AdCN)Cl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**5**): monoclinic, $P2_1/m$ (No. 11), a = 10.4367(11) Å, b = 20.164(2) Å, c = 10.5730(9) Å, β = 100.243(6)°, V = 2189.6(4) Å^3, Z = 2. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R_1 = 0.0339 and wR_2 = 0.0834 for 3970 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ and all data, respectively.

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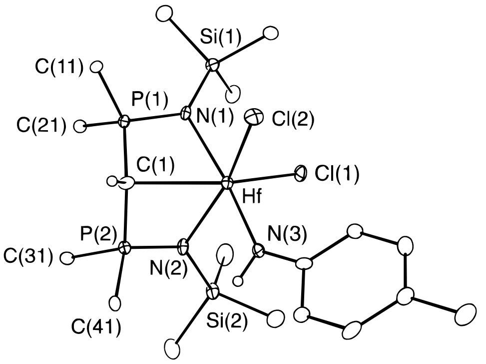

Figure 2. ORTEP[26] view of the central parts of $[HfCl_2(HN(p\text{-tolyl}))\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**7**) showing the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Hf−C(1) = 2.437(6), Hf−N(1) = 2.258(5), Hf−N(2) = 2.239(5), Hf−N(3) = 2.079(5), P(1)−N(1) = 1.614(5), P(2)−N(2) = 1.616(5), P(1)−C(1) = 1.761(6), P(2)−C(1) = 1.759(6), Hf−Cl(1) = 2.412(2), Hf−Cl(2) = 2.421(2); P(1)−C(1)−P(2) = 122.0(3), Hf−C(1)−P(1) = 88.1(3), Hf−C(1)−P(2) = 88.2(2), N(1)−Hf−N(2) = 95.5(2), N(1)−P(1)−C(1) = 104.2(3), N(2)−P(2)−C(1) = 100.9(3).

of *p*-toluidine and adamantanol addition reactions, respectively, are shown in Scheme 2. A similar addition reaction was observed with methyl iodide, wherein $[HfCl_2(I)\{MeC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**9**) was isolated in a low yield from a mixture of reaction products. These results show that an electrophilic (E) moiety adds specificially to the carbene center, thus further supporting the assignment of a nucleophilic character to the carbene center.[12] The metal−carbon bond order is clearly reduced in the products (vide infra), again substantiating the attribution of a multiply bonded nature in the parent complexes.

The complex $[HfCl_2(HN(p\text{-tolyl}))\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**7**)[20] is illustrated in Figure 2. There is no crystallographic symmetry present in this molecule. The hafnium center is a highly distorted octahedron, which presumably arises because of the constrained *fac* coordination geometry of the tricoordinated ligand. The structure contains two nearly planar four-membered (Hf, C(1), P(1), N(1) and Hf, C(1), P(2), N(2)) rings with a common Hf−C edge in an open-book conformation. The Hf−C(1) bond distance (2.437(6) Å) is elongated in comparison to similar group 4 carbene complexes reported earlier,[7,8,18] as it is now a formal single bond. This distance is slightly longer than the Hf−C bond distances in other hafnium hydrocarbyl complexes (mean primary alkyl ($Hf{-}CH_2(R)$)) distances are 2.300 Å[21] and secondary alkyl ($Hf{-}CH(R_2)$)) distances are 2.387 Å).[22] The reason may be the delocalization of electrons in the two four-membered rings which is evident from the comparison of P−N and endocyclic P−C bond distances relative to the bis(iminophosphorano)methane ligand.[23] The Hf−N amide (Hf−N(3) = 2.079(5) Å) distance is shorter than the other two phosphinimine nitrogen (mean 2.249(5) Å) distances.

Heteroallenes (CO_2, RNCO, and RN=C=NR) react readily with the methanediide complexes **1** and **2** to form [2 + 2]-cycloaddition products (Scheme 2). The CO_2 reaction with **1** gave, immediately on contact, a white, insoluble product (**10**) which showed IR bands indicative of a carbonate. Reasonable C, H, N analyses were obtained which were consistent with the tentative adduct structure **10**, illustrated in Scheme 2. Hydrolysis of **10** with MeOH-d_4 (99%), monitored by electrospray mass spectrometry, indicated a stepwise process, yielding first the corresponding protonated carboxylic acid $HC(CO_2H)(Ph_2P{=}NSiMe_3)_2$ (*m/z* 603.2 [MH^+]), which was then slowly converted (ca. 1 h) to $HC(CO_2H)(Ph_2P{=}NSiMe_3)(Ph_2P{=}NH)$ (*m/z* 531.2 [MH^+]) by the cleavage of one N−Si bond of $NSiMe_3$ groups. Finally, after a few hours, complete cleavage of the other trimethylsilyl group yielded $HC(CO_2H)(Ph_2P{=}NH)_2$ (*m/z* 459.1 [MH^+]). This evidence indicates that a C−C bond has been formed in the product via a cycloaddition reaction without affecting the rest of the ligand structure. We formulate the product **10** in Scheme 2 as a monomer to illustrate the parallels with the cycloaddition reactions described below, but the insolubility suggests that this product may be an oligomeric or polymeric species which, however, retains the characteristic feature of all of the cycloaddition products in general.

Soluble, directly characterizable, products were obtained when heteroallenes such as isocyanate or carbodiimide reacted with **1** or **2**. These new cycloaddition products (**11**−**14**)[11a,24] were obtained in high yields. The structure of $[ZrCl_2\{(C(NCy)NCy)C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa^2 N',N''\}]$ (**14**),[25] illustrated in Figure 3, shows several interesting features; the coordination sphere of the metal is defined by a propeller-shaped, dianionic tetradentate ligand bonded to zirconium in addition to the two chloride ligands. The three nitrogen ligand atoms adopt a tripodal arrangement and lie at the corners of an almost regular triangle. The Zr−C(1) distance (2.467 (4) Å) is slightly longer in comparison with the corresponding single-bond distances in secondary alkyl coordinated zirconium complexes, as noticed in complex **7**. The new C−C bond distance (C(1)−C(2) = 1.546(5) Å) is comparable to that of a typical single bond, but the C−N (C(2)−N(3) = 1.384(5) Å) bond length is slightly shorter than that expected for a single bond, which implies some partial π-interaction between these C, N, and Zr centers.

Thus, these bis(iminophosphorano)methandiide complexes react in a manner consistent with a nucleophilic central carbon and therefore resemble organometallic

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(19) Complex **7**, $HfCl_2(HN(p\text{-tolyl}))\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$, resulted from the addition of solid toluidine to a stirred toluene solution (10 mL) of **1** at room temperature. The product was recrystallized (3 days) from THF at −15 °C. Yield: 0.11 g, 71%. Anal. Calcd for $C_{38}H_{47}Cl_2HfN_3P_2Si_2$: C, 49.97; H, 5.19; N, 4.60. Found: C, 49.76; H, 5.32; N, 4.50. Important NMR observations: the normal-temperature NMR spectrum was broad, but sharp signals were observed at −40 °C which were assignable to two geometrical isomers of **7**. IR (Nujol mull): 3330 w (ν_{NH}). ^1H NMR (400.1 MHz, C_6D_6, 313 K): δ 6.46 (b. s, NH-tolyl), 2.36 (b. s CH of PCP), $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 313 K): δ 22.2 (b. s). Full details are given in the Supporting Information.

(20) Crystal Data for $[HfCl_2(HN(p\text{-tolyl}))\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (**7**): orthorhombic, $Pna2_1$ (No. 33), $a = 22.716(2)$ Å, $b = 14.2639(9)$ Å, $c = 12.4956(8)$ Å, $V = 4048.7(5)$ Å^3, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0354$ and $wR_2 = 0.0774$ for 7715 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ and all data, respectively.

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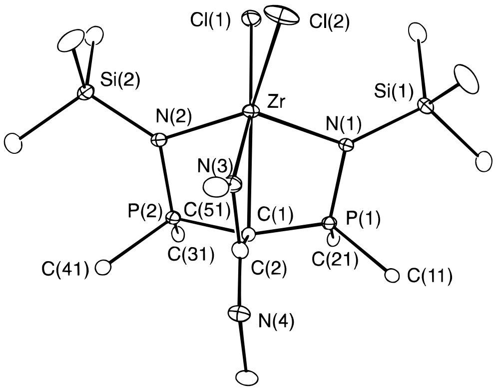

Figure 3. ORTEP[26] view of the central parts of $[ZrCl_2\{(C(NCy)NCy)C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa^2 N',N''\}]$ (**14**) showing the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Zr−C(1) = 2.467(4), Zr−N(1) = 2.162(4), Zr−N(2) = 2.195(4), Zr−N(3) = 2.173(3), P(1)−N(1) = 1.633(3), P(2)−N(2) = 1.618(3), P(1)−C(1) = 1.743(5), P(2)−C(1) = 1.762(4), P(1)−C(11) = 1.819(4), C(1)−C(2) = 1.546(5), C(2)−N(3) = 1.384(5), C(2)−N(4) = 1.285(5), Zr−Cl(1) = 2.507(1), Zr−Cl(2) = 2.442(1); P(1)−C(1)−P(2) = 130.3(2), Zr−C(1)−P(1) = 86.4(2), Zr−C(1)−P(2) = 86.4(2), N(1)−Zr−N(2) = 120.0(1), N(1)−P(1)−C(1) = 103.7(2), N(2)−P(2)−C(1) = 104.1(2), C(1)−C(2)−N(3) = 108.1(3).

alkylidene complexes. Also, the preservation of a M−C bond after 1,2-addition and [2 +2]-cycloaddition reactions confirms the property of multiple metal−carbon bond character assigned to the primary complexes. The facility of C−C bond formation processes, even in the presence of oxygen centers, in these complexes which contain highly oxophilic metal centers suggests useful applications to synthesis.

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Supporting Information Available: Text giving detailed synthetic and characterization data and tables giving X-ray crystal structure details for **4**, **7**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Complex **14**, $[ZrCl_2\{(C(NCy)NCy)C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa^2 N',N''\}]$, was obtained from the reaction of solid dicyclohexylcarbodiimide with a stirred solution of **2** in toluene at room temperature. The product was recrystallized (2 days) at from a layered THF/toluene solution at −15 °C. Yield: 0.27 g, 0.24 mmol, 86%. Anal. Calcd for $C_{51}H_{68}Cl_2N_4P_2Si_2Zr$: C, 60.21; H, 6.74; N, 5.51. Found: C, 59.95; H, 7.07; N, 5.66. Important NMR parameters: $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K) δ 148.7 (br t, $^2J_{PC} = 4$ Hz, quaternary C of CNCy), 15.5 (t, $^1J_{PC} = 96.0$ Hz, quaternary C of PCP); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K) δ 21.0 (s). Full details are given in the Supporting Information.

(25) Crystal Data for $[ZrCl_2\{(C(NCy)NCy)C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa^2 N',N''\}]$ (**14**): triclinic, $P2_1/n$ (No. 14), $a = 11.5636(8)$ Å, $b = 18.4194(12)$ Å, $c = 28.0498(19)$ Å, $\beta = 94.0569(13)°$, $V = 5959.5(7)$ Å^3, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0585$ and $wR_2 = 0.1657$ for 11 320 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ and all data, respectively.

(26) Johnson, C. K. ORTEP, Report ORNL No. 5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976. In all representations all of the hydrogen atoms and all of the phenyl carbon (except the *ipso*) atoms on phosphorus have been removed for clarity. Also in **14** only the *ipso* cyclohexyl carbon on N is shown. All illustrated atoms are represented by Gaussian ellipsoids at the 20% probability level.