In summary, the use of the t-Bu$_3$CO$^-$ group permits the stabilization of low-coordinate transition-metal complexes which display novel geometries and can contain close Li···CH$_3$ interactions. The steric bulk of the ligand prevents the formation of multiply bridged manganese chains which result when less sterically demanding groups such as t-Bu$_2$CHO$^-$ or mesityl are used. The tri-*tert*-butylmethoxide ligand can be incorporated into transition-metal complexes by exchange with metal amides or by treating the lithium alkoxide with metal halides. These two methods permit the formation of different species even when a similar solvent system is employed.

We are currently investigating the properties of the t-Bu$_3$CO$^-$ ligand with later first-row transition metals and will present our results in a future article.[14]

Acknowledgment. We are grateful to the Research Corporation and the National Science Foundation for financial support and to Professor Håkon Hope of the University of California, Davis, and to Professor Jan Hvoslef of the University of Oslo, Norway, for their helpful discussions. B.D.M. thanks the University of California, Davis, for a graduate research award.

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Supplementary Material Available: Complete tables of bond distances, angles, structure factors, and calculated hydrogen positional and thermal parameters for **4** and **5** (50 pages). Ordering information is given on any current masthead page.

Synthesis and Structures of Free and Coordinated Phosphaalkenes

**A. H. Cowley,*† R. A. Jones,*† J. G. Lasch,† N. C. Norman,† C. A. Stewart,†
A. L. Stuart,† J. L. Atwood,*‡ W. E. Hunter,‡ and H.-M. Zhang‡**

*Contribution from the Departments of Chemistry, University of Texas at Austin,
Austin, Texas 78712, and University of Alabama, University, Alabama 35486.*
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Abstract: Treatment of (Me$_3$P)$_2$NiCl$_2$ with [(Me$_3$Si)$_2$CH]$_2$PNa affords the η^2-phosphaalkene complex (Me$_3$P)$_2$Ni[(Me$_3$Si)$_2$CPC(H)(SiMe$_3$)$_2$] (**1**). The structure of **1** has been determined by single-crystal X-ray diffraction. Compound **1** crystallizes in the space group $P2_1/c$ with $Z = 4$ and $a = 8.742$ (6) Å, $b = 19.225$ (6) Å, $c = 20.111$ (8) Å, and $\beta = 99.21$ (9)°. The geometry at nickel is close to square planar, and the phosphaalkene is η^2-bonded. The free phosphaalkenes (Me$_3$Si)$_2$C=PR (R = (Me$_3$Si)$_2$CH) (**2**), 2,4,6-(t-Bu)$_3$C$_6$H$_2$ (**4**), and (Me$_3$Si)$_3$C (**5**) have been prepared by treatment of (Me$_3$Si)$_2$C=PCl (**3**) with the appropriate organolithium reagent. Compounds **3** and **5** are liquids at ambient temperature. However, **4** is a crystalline solid and has been investigated by single-crystal X-ray diffraction. Compound **4** crystallizes in the space group $P\bar{1}$ with $Z = 2$ and $a = 9.118$ (5) Å, $b = 11.860$ (8) Å, $c = 14.403$ (6) Å, $\alpha = 69.41$ (4)°, $\beta = 79.61$ (4)°, and $\gamma = 83.63$ (5)°. The molecule adopts a planar conformation about the P=C bond, and the C=P—C bond angle is 110.7 (2)°. The phosphorus–carbon bond lengths and ^{31}P NMR spectra of free and coordinated phosphaalkenes are discussed.

Compounds containing P=C double bonds, phosphaalkenes, have been known for many years. The first such compounds to be isolated contained resonance-stabilized double bonds.[1] However, following the pioneering work of Becker,[2] an increasingly large number of isolable, acyclic compounds featuring localized P=C double bonds have been discovered.[3] In contrast, the chemistry of phosphaalkenes coordinated to transition-metal species is less well developed. Interest in such complexes stems from a potential for two types of bonding mode, namely, η^1 through the phosphorus lone pair or η^2 through the P=C π bond. Prior to the commencment of this work, there were no definitive examples of η^2-complexation of phosphaalkenes. However, following our initial disclosure of the synthesis of the η^2-bonded complex (Me$_3$P)$_2$Ni[(Me$_3$Si)$_2$CPC(H)(SiMe$_3$)$_2$] (**1**),[4] two other examples of this type of complex have been reported, namely, (triphos)Pt(P(mesityl)=CPh$_2$)[5] and (bpy)Ni(P(xylyl)=CPh$_2$).[6] Examples of η^1 complexation are somewhat more plentiful, this mode of phosphaalkene coordination now having been recognized for Ni(0),[6] Cr(0),[7,8] W(0),[7] Rh(I),[7] and Pt(II).[7] The compound (Ph$_3$P)$_2$Pt(P(mesityl)=CPh$_2$) is particularly intriguing because of the subtle equilibrium between the η^1 and η^2 bonding modes.[9] The implied closeness in energy of these bonding modes is consistent with MO calculations on the model phosphaalkene HP=CH$_2$, which indicate that the MO's corresponding to the phosphorus lone pair and the P=C π bond are closely spaced.[10]

In the present paper, we report details of the synthesis and structure of the η^2-phosphaalkene complex **1**. We also report the synthesis of the uncoordinated phosphaalkenes (Me$_3$Si)$_2$C=PR [R = (Me$_3$Si)$_2$CH (**2**)], 2,4,6-(t-Bu)$_3$C$_6$H$_2$ (**4**), and (Me$_3$Si)$_3$C (**5**). We have determined the structure of **4** by single-crystal X-ray diffraction. Although fragmentary information is available in the literature, e.g., the P=C bond lengths of phosphaalkenes,[3,6,11] to

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† University of Texas at Austin.
‡ University of Alabama.

(1) (a) Allmann, R. *Angew. Chem.* **1965**, *77*, 134; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 150. (b) Markl, G. *Angew. Chem.* **1966**, *78*, 907; *Angew. Chem, Int. Ed. Engl.* **1966**, *5*, 846. (c) Ashe, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 3293.

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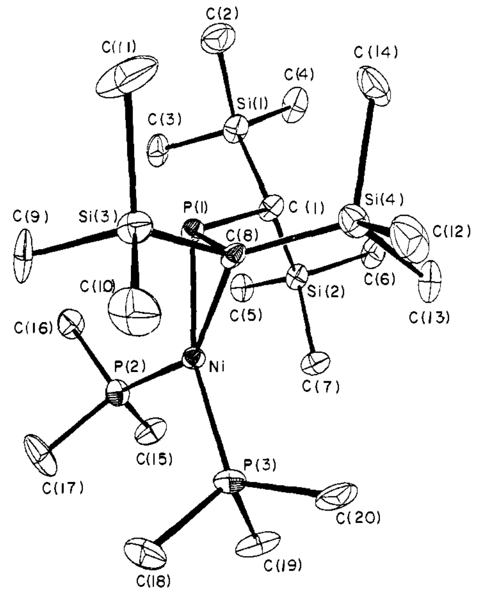

Figure 1. ORTEP view of $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**) showing the atom numbering scheme.

Table I. Intensity Data Collection and Crystal Data for **1** and **4**

	1	**4**
formula	$C_{20}H_{55}NiP_3Si_4$	$C_{25}H_{47}PSi_2$
fw	559.62	434.79
crystal class	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	8.742 (6)	9.118 (5)
b, Å	19.225 (6)	11.860 (8)
c, Å	20.111 (8)	14.403 (6)
α, deg		69.41 (4)
β, deg	99.21 (9)	79.61 (4)
γ, deg		83.63 (5)
U, Å^3	3336 (5)	1432 (1)
Z	4	2
ρ(calcd), g cm^{-3}	1.11	1.005
crystal size, mm	0.35 × 0.35 × 0.10	0.5 × 0.5 × 0.3
μ(Mo Kα), cm^{-1}	8.73	1.8
radiation	graphite-monochromated Mo radiation, $\lambda = 0.71069$ Å	graphite-monochromated Mo radiation, $\lambda = 0.71069$ Å
reflcts measd	3523	4701
reflcts obsd	1492	3135
data omission factor	$I > 2.0\sigma(I)$	$I > 3.0\sigma(I)$
2θ range, deg	$2.0 \leqslant 2\theta \leqslant 40.0$	$2.0 \leqslant 2\theta \leqslant 50.0$
no. of parameters varied	244	370
R^{25}	0.031	0.061
R_w	0.030	0.060

Table II. Bond Lengths (Å) for $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**)[a]

atoms	distance	atoms	distance
Ni–P(1)	2.239 (2)	Ni–P(2)	2.195 (3)
Ni–P(3)	2.202 (3)	Ni–Si(3)	3.077 (3)
Ni–C(8)	2.020 (8)	P(1)–C(1)	1.912 (8)
P(1)–C(8)	1.773 (8)	P(2)–C(15)	1.83 (1)
P(2)–C(16)	1.83 (1)	P(2)–C(17)	1.83 (1)
P(3)–C(18)	1.830 (9)	P(3)–C(19)	1.82 (1)
P(3)–C(20)	1.82 (1)	Si(1)–C(1)	1.895 (8)
Si(1)–C(2)	1.87 (1)	Si(1)–C(3)	1.87 (1)
Si(1)–C(4)	1.882 (9)	Si(2)–C(1)	1.873 (9)
Si(2)–C(5)	1.87 (1)	Si(2)–C(6)	1.89 (1)
Si(2)–C(7)	1.873 (9)	Si(3)–C(8)	1.894 (8)
Si(3)–C(9)	1.90 (1)	Si(3)–C(10)	1.889 (9)
Si(3)–C(11)	1.85 (1)	Si(4)–C(8)	1.879 (8)
Si(4)–C(12)	1.877 (9)	Si(4)–C(13)	1.87 (1)
Si(4)–C(14)	1.89 (1)		

[a] Estimated standard deviations in parentheses.

Table III. Bond Angles (deg) for $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**)

atoms	angle	atoms	angle
P(1)–Ni–P(2)	99.9 (1)	P(1)–Ni–P(3)	157.9 (1)
P(2)–Ni–P(3)	102.1 (1)	P(1)–Ni–Si(3)	64.95 (8)
P(2)–Ni–Si(3)	122.8 (1)	P(3)–Ni–Si(3)	102.29 (9)
P(1)–Ni–C(8)	48.9 (2)	P(2)–Ni–C(8)	144.9 (2)
P(3)–Ni–C(8)	109.9 (2)	Si(3)–Ni–C(8)	36.8 (2)
Ni–P(1)–C(1)	114.1 (3)	Ni–P(1)–C(8)	59.1 (3)
C(1)–P(1)–C(8)	110.3 (4)	Ni–P(2)–C(15)	121.2 (4)
Ni–P(2)–C(16)	116.7 (3)	C(15)–P(2)–C(16)	100.4 (5)
Ni–P(2)–C(17)	115.7 (4)	C(15)–P(2)–C(17)	101.1 (5)
C(16)–P(2)–C(17)	97.9 (5)	Ni–P(3)–C(18)	118.4 (4)
Ni–P(3)–C(19)	114.4 (3)	C(18)–P(3)–C(19)	100.6 (5)
Ni–P(3)–C(20)	120.4 (3)	C(18)–P(3)–C(20)	99.3 (5)
C(19)–P(3)–C(20)	100.3 (5)	C(1)–Si(1)–C(2)	111.2 (4)
C(1)–Si(1)–C(3)	113.3 (4)	C(2)–Si(1)–C(3)	106.5 (5)
C(1)–Si(1)–C(4)	112.8 (4)	C(2)–Si(1)–C(4)	105.7 (5)
C(3)–Si(1)–C(4)	106.9 (5)	C(1)–Si(2)–C(5)	111.9 (4)
C(1)–Si(2)–C(6)	110.3 (5)	C(5)–Si(2)–C(6)	107.7 (5)
C(1)–Si(2)–C(7)	113.6 (4)	C(5)–Si(2)–C(7)	107.8 (5)
C(6)–Si(2)–C(7)	105.1 (5)	Ni–Si(3)–C(8)	39.6 (2)
Ni–Si(3)–C(9)	80.5 (3)	C(8)–Si(3)–C(9)	111.6 (4)
Ni–Si(3)–C(10)	103.7 (3)	C(8)–Si(3)–C(10)	115.5 (4)
C(9)–Si(3)–C(10)	106.0 (5)	Ni–Si(3)–C(11)	147.4 (3)
C(8)–Si(3)–C(11)	112.2 (4)	C(9)–Si(3)–C(11)	105.6 (5)
C(10)–Si(3)–C(11)	105.2 (5)	C(8)–Si(4)–C(12)	114.1 (4)
C(8)–Si(4)–C(13)	115.4 (4)	C(12)–Si(4)–C(13)	104.5 (4)
C(8)–Si(4)–C(14)	112.0 (4)	C(12)–Si(4)–C(14)	103.5 (4)
C(13)–Si(4)–C(14)	106.2 (4)	P(1)–C(1)–Si(1)	103.1 (4)
P(1)–C(1)–Si(2)	119.6 (5)	Si(1)–C(1)–Si(2)	116.3 (4)
Ni–C(8)–P(1)	72.0 (3)	Ni–C(8)–Si(3)	103.6 (4)
P(1)–C(8)–Si(3)	106.6 (4)	Ni–C(8)–Si(4)	130.0 (4)
P(1)–C(8)–Si(4)	123.1 (4)	Si(3)–C(8)–Si(4)	113.8 (4)

the best of our knowledge, this represents the first complete structural information for this type of compound.

Results and Discussion

Initial studies on the bulky phosphide anion $[(Me_3Si)_2CH]_2P^-$ centered on its reaction with $(Me_3P)_2NiCl_2$ as a possible source of dinuclear nickel complexes featuring bulky phosphido bridging ligands.[12] Treatment of a hexane solution of $(Me_3P)_2NiCl_2$ with a 2:1 molar ratio of $([(Me_3Si)_2CH]_2P)Na$[13] in Et_2O afforded an initially cobalt-blue solution. ^{31}P NMR spectroscopy of this solution revealed many signals, one of which was assigned to $[(Me_3Si)_2CH]_2PH$.[15] However, on standing for 2 days at −20 °C, a color change from blue to dark brown occurred with concomitant deposition of red-brown crystals. Recrystallization afforded pure $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**), an η^2-phosphaalkene complex characterized by means of standard spectroscopic methods and X-ray crystallography.

The X-ray structure determination revealed that **1** exists as isolated molecules with no short intermolecular contacts. The geometry about the central nickel atom (Figure 1) is best described as square planar with mean deviations (Å) from planarity being Ni (−0.08), P(1) (−0.17), P(2) (0.12), P(3) (−0.07), and C(8) (0.21). This geometry is analogous to that of P_2M(olefin) complexes where M = Ni or Pt.[16] The P—C bond length, P(1)—C(8)

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(11) Kroto, H. W.; Nixon, J. F; Ohno, K.; Simmons, N. P. C. *J. Chem. Soc., Chem. Commun.* **1980**, 709.

(12) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Rogers, R. D. *Organometallics* **1982**, *1*, 1721.

(13) This solution can be made by treatment of a mixture of the phosphinyl radical ($[(Me_3Si)_2CH]_2P$) and the corresponding dimer with an equimolar quantity of Na in *n*-hexane at 65 °C for 14 h.[14] However, it is more readily prepared by treatment of $[(Me_3Si)_2CH]_2PCl$ with Li powder in Et_2O at 25 °C for 24 h: Power, P. P., personal communication.

(14) Cowley, A. H.; Ebsworth, E. A. V.; Kemp, R. A.; Rankin, D. W. H.; Stewart, C. A. *Organometallics* **1982**, *1*, 1720.

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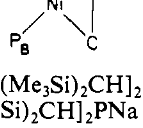
(16) See, for example: (a) Cheng, P.-T.; Cook, C. D.; Chung Hoe Koo; Kyburg, S. C.; Shiomi, M. T. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1904. (b) Dreissig, W.; Dietrich, H. *Ibid.* **1968**, *B24*, 108. (c) Crüger, C.; Yi-Hung Tsay, *J. Organomet. Chem.* **1972**, *34*, 387.

Table IV. Atomic Coordinates for $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U* (eqv)
Ni	0.7536 (1)	0.10846 (6)	0.17738 (5)	0.037
P(1)	0.6823 (3)	0.0554 (1)	0.2667 (1)	0.039
P(2)	0.5913 (3)	0.1964 (1)	0.1664 (1)	0.053
P(3)	0.8853 (3)	0.1266 (1)	0.0944 (1)	0.049
Si(1)	0.6851 (3)	0.0512 (2)	0.4150 (1)	0.062
Si(2)	0.9061 (3)	0.1643 (1)	0.3623 (1)	0.053
Si(3)	0.6480 (3)	−0.0434 (1)	0.1537 (1)	0.050
Si(4)	0.9781 (3)	−0.0355 (1)	0.2444 (1)	0.051
C(1)	0.810 (1)	0.0770 (5)	0.3504 (4)	0.049
C(2)	0.633 (1)	−0.0429 (6)	0.4078 (5)	0.091
C(3)	0.499 (1)	0.1003 (6)	0.4065 (5)	0.085
C(4)	0.786 (1)	0.0638 (6)	0.5042 (5)	0.096
C(5)	0.769 (1)	0.2333 (5)	0.3808 (5)	0.079
C(6)	1.072 (1)	0.1616 (6)	0.4350 (5)	0.088
C(7)	0.994 (1)	0.1936 (5)	0.2882 (4)	0.066
C(8)	0.7911 (9)	0.0107 (4)	0.2129 (4)	0.037
C(9)	0.454 (1)	0.0020 (6)	0.1320 (5)	0.081
C(10)	0.710 (1)	−0.0663 (5)	0.0705 (4)	0.078
C(11)	0.606 (1)	−0.1277 (6)	0.1914 (5)	0.101
C(12)	1.050 (1)	−0.0917 (5)	0.1797 (5)	0.066
C(13)	1.146 (1)	0.0222 (5)	0.2769 (4)	0.069
C(14)	0.958 (1)	−0.0982 (5)	0.3149 (4)	0.076
C(15)	0.658 (1)	0.2851 (5)	0.1870 (5)	0.085
C(16)	0.429 (1)	0.1911 (5)	0.2131 (5)	0.080
C(17)	0.480 (1)	0.2087 (6)	0.0825 (5)	0.103
C(18)	0.785 (1)	0.1167 (6)	0.0078 (4)	0.090
C(19)	0.961 (1)	0.2142 (5)	0.0910 (5)	0.098
C(20)	1.059 (1)	0.0761 (6)	0.0886 (5)	0.089

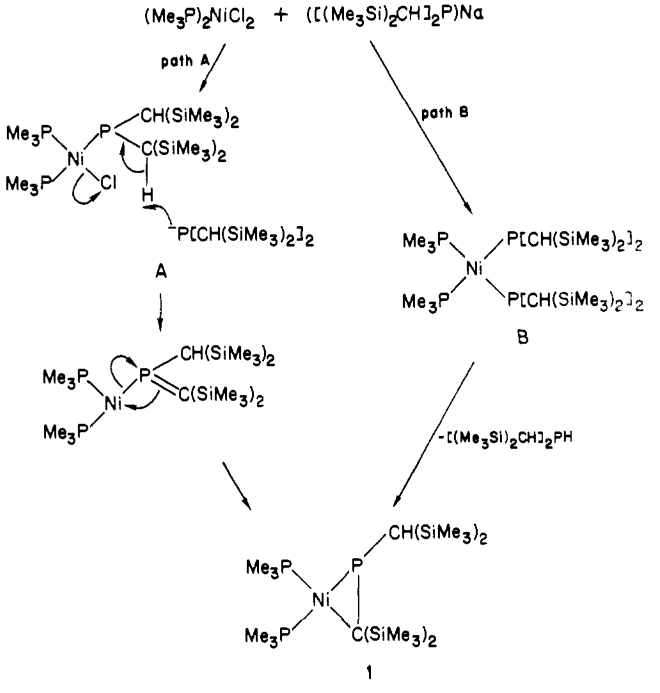
= 1.773 (8) Å, is approximately midway between that of a P—C single bond (1.85 Å)[17] and the P═C bond length of ~1.67 Å reported for uncoordinated phosphaalkenes (vide infra). This increase in bond length on coordination is analogous to that found in C═C[18] and P═P[19] complexes. Interestingly, the P—C bond length in the η^2-complex (bpy)Ni(P(xylyl)═CPh$_2$) is 1.832 (6) Å and thus close to that of a single bond. The sum of bond angles at C(8), excluding those to Ni, is 343.5°, indicating that the hybridization is between sp^2 and sp^3 which also has parallels in coordinated olefin complexes.[18] Unexpectedly, the corresponding sum of carbon bond angles in (bpy)Ni(P(xylyl)═CPh$_2$) is much larger (353.8°) than in **1**. The geometries of the Me_3P ligands and Me_3Si groups are normal and deserve no special comment. Pertinent crystallographic data are summarized in Table I, and listings of bond lengths, bond angles, and positional parameters appear in Tables II–IV.

Examination of the solution $^{31}P\{^1H\}$ NMR spectrum of **1** at room temperature reveals an ABX spin system which is consistent with the view that the solid-state structure persists in solution. Computer simulation by routine methods afforded the following parameters: $\delta(P_A)$ −18.2, $\delta(P_B)$ −19.7, $\delta(P_X)$ +23.4, and $^2J_{P_BP_X} = 28.6$ Hz, $^2J_{P_AP_B} = 27.0$ Hz, and $^2J_{P_AP_X} = 45.8$ Hz. The P_A and P_B assignments are predicated on the assumption that $^2J_{PP_x}$(trans) > $^2J_{PP_x}$(cis).

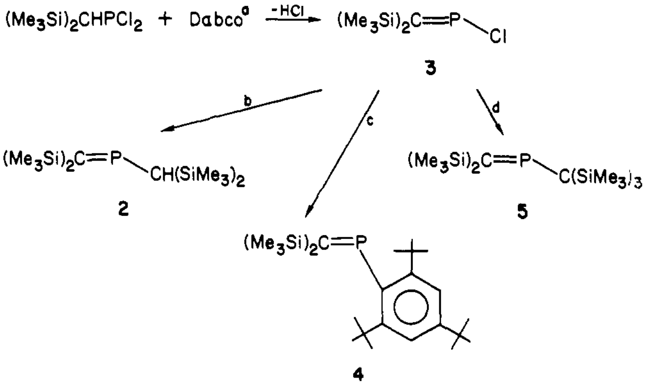


The isolation of **1** and $[(Me_3Si)_2CH]_2PH$ from the reaction of $(Me_3P)_2NiCl_2$ with $[(Me_3Si)_2CH]_2PNa$ was unexpected, and its mechanism of formation remains, at present, obscure. The initial presence of a blue solution which disappears to produce **1** is indicative of an intermediate. Two possible mechanisms are suggested in Scheme I. If the reaction proceeds via path A, only one chloride is displaced by the phosphide anion, the second phosphide removing an α proton from the coordinated phosphide—CH(SiMe$_3$)$_2$ group thus forming $[(Me_3Si)_2CH]_2PH$. The formation of a P═C double bond followed by loss of Cl$^-$ and η^2-complexation of the phosphaalkene would give **1**. Alternatively, a diphosphido nickel complex, **B**, may be formed by direct replacement of both chloride ligands by phosphide. Intramolecular elimination of $[(Me_3Si)_2CH]_2PH$ would then lead to **1** as indicated in path B. Studies are in progress in an attempt to clarify the mechanism.

Scheme I



Scheme II[a]



[a] (a) 1,4-diazabicyclo[2.2.2]octane. (b) $(Me_3Si)_2CHLi$. (c) 2,4,6-(t-Bu)$_3C_6H_2Li$. (d) $(Me_3Si)_3CLi$.

The phosphaalkene $(Me_3Si)_2C{=}PCH(SiMe_3)_2$ (**2**), which occurs coordinated to nickel in **1**, can be made independently as outlined in Scheme II.[14] Treatment of the chlorophosphine $(Me_3Si)_2CHPCl_2$ with the base Dabco (1,4-diazabicyclo[2.2.2]octane) affords, via HCl elimination, the chlorophosphaalkene **3**, $(Me_3Si)_2C{=}PCl$.[20] Treatment of **3** with $(Me_3Si)_2CHLi$ then affords **2**.[21] Treatment of **3** with 2,4,6-(t-Bu)$_3C_6H_2Li$ or $(Me_3Si)_3CLi$ affords **4** and **5**, respectively, in a similar manner. It was intended to carry out an X-ray study on **2** in order to compare the structures of both the free and the coordinated lig-

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(17) For example, the P–C bond length in Me_2PH is 1.848 Å: Nelson, R. *J. Chem. Phys.* **1963**, *39*, 2382.

(18) For a review of η^2-alkene complexes of nickel, see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel. Organonickel Complexes"; Academic Press: New York, 1974; Vol. 1, Chapter 5, p 244.

(19) For a review on the structures of free and η^2 coordinated diphosphenes, see: Cowley, A. H. *Polyhedron* **1984**, *3*, 389. Relevant ^{1}H and ^{13}C NMR data for **2**, **4**, and **5** are presented in Table IX.

(20) This compound was first described by: Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159.

(21) Phosphaalkene **2** is also produced as a side product from the reaction of $[(Me_3Si)_2CH]_2PCl$ with sodium in n-hexane at 60 °C.[14]

Table V. Bond Distances (Å) for $(Me_3Si)_2C{=}P(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**4**)

atom 1	atom 2	distance	atom 1	atom 2	distance
P1	C1	1.847 (4)	C4	C41	1.527 (6)
P1	C7	1.665 (4)	C5	C6	1.387 (6)
Si1	C7	1.891 (4)	C5	H5	0.86 (4)
Si1	C11	1.856 (8)	C6	C51	1.554 (6)
Si1	C12	1.838 (7)	C31	C32	1.509 (7)
Si1	C13	1.847 (7)	C31	C33	1.525 (7)
Si2	C7	1.887 (4)	C31	C34	1.531 (8)
Si2	C21	1.858 (7)	C41	C42	1.604 (10)
Si2	C22	1.870 (6)	C41	C43	1.583 (12)
Si2	C23	1.840 (6)	C41	C44	1.558 (11)
C1	C2	1.418 (6)	C51	C52	1.512 (8)
C1	C6	1.421 (6)	C51	C53	1.525 (8)
C2	C3	1.382 (6)	C51	C54	1.518 (8)
C2	C31	1.570 (6)			
C3	C4	1.378 (6)	C41	C42A	1.58 (3)
C3	H3	0.93 (4)	C41	C43A	1.57 (3)
C4	C5	1.378 (7)	C41	C44A	1.68 (3)

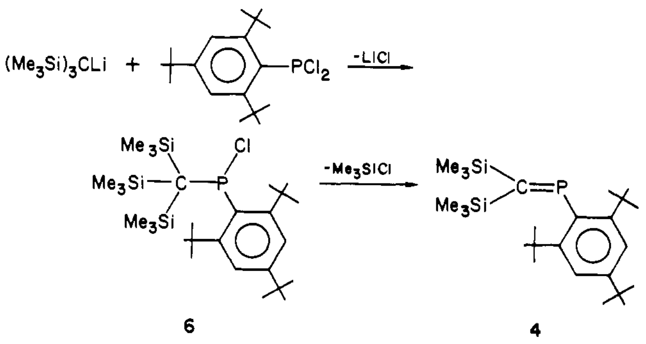
ands, but unfortunately **2** is a liquid at room temperature. However, the phosphaalkene **4** is a solid, and we were able to grow crystals suitable for X-ray diffraction experiments.

A view of the phosphaalkene **2** is shown in Figure 2 along with the atom numbering scheme. Compilations of bond lengths, angles, and atomic positional parameters are given in Tables V–VII, and pertinent crystallographic data are summarized in Table I. The molecule adopts a planar conformation about the P=C bond containing the atoms C(1), P(1), C(7), Si(1), and Si(2) (mean deviation = 0.06 Å). The P=C bond length, P(1)—C(7) = 1.665 (4) Å, compares with those reported for other phosphaalkenes,[3] a list of which is given in Table VIII. The angle at P(1), C(1)–P(1)–C(7) = 110.7 (2)°, is almost halfway between that expected for sp^2 (120°) and sp (90°) hybridization at phosphorus. This trend toward sp hybridization, i.e., a smaller angle, parallels that found in disphosphene and diarsene complexes and has been discussed elsewhere.[19,22] The angles at C(2) show a marked cis/trans asymmetry. Thus the angle to Si(2), P-(1)–C(7)–Si(2) = 133.1 (3)°, is much larger than the angle to Si(1), P(1)–C(7)–Si(1) = 107.7 (2)°. This difference is almost certainly due to steric effects, the large angle to Si(2) being caused by the *cis*-2,4,6-$(t\text{-}Bu)_3C_6H_2$ group. Also with regard to steric effects, we note that the conformation of the 2,4,6-$(t\text{-}Bu)_3C_6H_2$ and $SiMe_3$ groups are such as to minimize intramolecular contacts. Thus the C_6 ring of the aryl moiety lies perpendicular to the plane defined by the P=C double bond (dihedral angle 90.2°) with the Me_3Si methyl carbon C(23), both over the C_6 ring and midway between the *o*-(*t*-Bu) groups.

The ^{31}P NMR data for **2**, **4**, and **5**, and other phosphaalkenes are summarized in Table VIII. For the phosphaalkenes with nonconjugating substituents, ^{31}P chemical shifts are ~400 ppm. Similarly, the ^{31}P chemical shifts of compounds with P=P, P=As, and P=Sb bonds fall in the range 500–670 ppm.[19,22] The deshielding effect in these double-bonded compounds is due to the importance of the paramagnetic shielding term which is caused by the existence of low-lying excited states. Note that when **2** is coordinated to a metal, as in **1**, a marked upfield shift occurs (δ(P) +23.4). This effect is consistent with π donation from nickel to the π^* orbital of the phosphaalkene with concomitant rehybridization at phosphorus toward sp^3 and reduction of the P–C bond order. In contrast, no marked upfield shift is observed in η^1 coordinated phosphaalkenes since only the phosphorus lone pair and not the P=C π bond is involved in bonding to the metal.[6-8]

Phosphaalkene **4** is also produced as the major product in a reaction that was originally dsigned to produce an unsymmetrical diphosphene.[23] Thus while the reaction of $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$ produced $[(Me_3Si)_3CP]_2$, a similar reaction involving equimolar quantities of $(Me_3Si)_3CPCl_2$ and 2,4,6-$(t\text{-}Bu)_3C_6H_2PCl_2$ and $(Me_3Si)_3CLi$ produced **4** together with small amounts of the two symmetrical diphosphenes. It is proposed that **4** is produced via an intermediate, **6**, which loses Me_3SiCl as suggested in Scheme III. It is interesting that reaction of $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$ does not result in detectable amounts of **5**.[23]

Scheme III



Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents used were freshly distilled over CaH_2 or Na/benzophenone immediately prior to use. Microanalytical data were obtained from the Canadian Microanalytical Service Ltd., Vancouver, British Columbia.

Spectroscopic Measurements. ^1H NMR spectra were recorded on Varian EM390 and Nicolet NT200 instruments operating at 90.0 and 200.0 MHz, respectively. ^{13}C spectra were recorded on a Varian FT80A instrument operating at 20.0 MHz. ^{31}P spectra were recorded on Varian FT80A and Nicolet NT200 instruments operating at 32.384 and 80.988 MHz, respectively. ^1H and ^{13}C spectra were referenced to internal Me_4Si (0.0 ppm) and ^{31}P spectra to external 85% H_3PO_4 (0.0 ppm), positive values to high frequency in all cases. Medium- and high-resolution mass spectra were measured on Du Pont-Consolidated Model 21-491 and 21-100 instruments, respectively. Perfluorokerosene was used as the calibrant for HRMS. IR spectra were measured on a Perkin-Elmer 1330 spectrophotometer.

Starting Materials. The chloro compounds $[(Me_3Si)_2CH]_2PCl$[24] and $(Me_3Si)_2C{=}PCl$[20] (**3**) were prepared according to literature methods. The phosphide salt $[(Me_3Si)_2CH]_2PLi$ was prepared by treatment of $[(Me_3Si)_2CH]_2PCl$ with Li powder in Et_2O,[14] and $(Me_3P)_2NiCl_2$ was prepared by the literature method.[12] The preparations of the lithium reagents, RLi (R = $(Me_3Si)_2CH$),[25] 2,4,6-$(t\text{-}Bu)_3C_6H_2$,[26] and $(Me_3Si)_3C$[27] have also been described in the literature. All other materials were procured commercially and used without subsequent purification.

Preparation of $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)]$ (1). A solution of 0.314 g (1.1 mmol) of $(Me_3P)_2NiCl_2$ in 50 mL of *n*-hexane was placed in a 100-mL Schlenk flask and cooled to −78 °C. The stirred reaction mixture turned dark blue upon slow addition of 16.5 mL of a 0.14 M Et_2O solution of $[(Me_3Si)_2CH]_2PNa$. Stirring was continued for 1 h, following which the volatiles were removed at −50 °C. The resulting blue oil was extracted with three 20-mL portions of *n*-hexane. After filtration and concentration the solution was stored at −20 °C for ~2 weeks during which time a 26% yield of red-brown crystals of **1** (mp 169 °C) were formed. Compound **1** was characterized by X-ray crystallography and ^{31}P NMR spectroscopy as described in the text.

Preparation of $(Me_3Si)_2C{=}PC(H)(SiMe_3)_2$ (2). A stirred solution of 3.65 g (16.2 mmol) of **3** in 50 mL of *n*-hexane was cooled to −50 °C and treated slowly with 10.7 mL of a 1.51 M Et_2O solution of $(Me_3Si)_2CHLi$. Stirring of the reaction mixture was continued for 2 h after the addition, during which time it gradually warmed up to room

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[26] Yoshifuji, M.; Shima, I.; Inamoto, N. *Tetrahedron Lett.* **1979**, 3963.

[27] Cook, M. A.; Eaborn, C.; Jukes, A. E.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 529.

Table VI. Bond Angles (deg) for $(MeSi)_2C{=}P(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**4**)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C1	P1	C7	110.7 (2)	C1	C2	C31	124.5 (4)	C2	C31	C32	111.1 (4)
C7	Si1	C11	109.1 (3)	C3	C2	C31	117.3 (4)	C2	C31	C33	110.8 (4)
C7	Si1	C12	115.1 (3)	C2	C3	C4	123.6 (5)	C2	C31	C34	110.2 (4)
C7	Si1	C13	111.8 (3)	C2	C3	H3	119 (3)	C32	C31	C33	111.1 (5)
C11	Si1	C12	107.5 (4)	C4	C3	H3	118 (3)	C32	C31	C34	107.6 (5)
C11	Si1	C13	107.4 (4)	C3	C4	C5	116.6 (4)	C33	C31	C34	105.8 (5)
C12	Si1	C13	105.6 (4)	C3	C4	C41	122.2 (5)	C4	C41	C42	113.7 (5)
C7	Si2	C21	108.7 (3)	C5	C4	C41	121.2 (4)	C4	C41	C43	108.5 (5)
C7	Si2	C22	108.4 (3)	C4	C5	C6	123.7 (4)	C4	C41	C44	110.7 (5)
C7	Si2	C23	116.7 (2)	C4	C5	H5	121 (3)	C42	C41	C43	106.9 (6)
C21	Si2	C22	109.2 (3)	C6	C5	H5	115 (3)	C42	C41	C44	107.0 (6)
C21	Si2	C23	107.9 (3)	C1	C6	C5	117.8 (4)	C43	C41	C44	109.9 (7)
C22	Si2	C23	105.8 (3)	C1	C6	C51	124.2 (4)	C6	C51	C52	112.2 (4)
P1	C1	C2	120.2 (3)	C5	C6	C51	118.0 (4)	C6	C51	C53	111.1 (5)
P1	C1	C6	121.0 (3)	P1	C7	Si1	107.7 (2)	C6	C51	C54	109.1 (4)
C2	C1	C6	118.8 (4)	P1	C7	Si2	133.1 (3)	C52	C51	C53	107.3 (5)
C1	C2	C3	118.2 (4)	Si1	C7	Si2	119.2 (2)	C52	C51	C54	110.6 (5)
								C53	C51	C54	106.4 (5)

Table VII. Atomic Positional Parameters (Fractional Coordinates) for $(Me_3Si)_2C{=}P(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**4**)

atom	x	y	z	B, Å^2
P1	0.3823 (1)	0.1575 (1)	0.33602 (8)	3.96 (3)
Si1	0.3188 (2)	0.2863 (1)	0.47538 (9)	4.63 (3)
Si2	0.1474 (2)	0.3895 (1)	0.2797 (1)	4.38 (3)
C1	0.3715 (4)	0.1515 (3)	0.2110 (3)	3.44 (9)
C2	0.4715 (4)	0.2160 (3)	0.1260 (3)	3.32 (9)
C3	0.4436 (5)	0.2263 (4)	0.0320 (4)	3.9 (1)
C4	0.3282 (5)	0.1725 (4)	0.0166 (3)	4.1 (1)
C5	0.2450 (5)	0.0977 (4)	0.1009 (3)	4.4 (1)
C6	0.2646 (5)	0.0818 (4)	0.1981 (3)	3.9 (1)
C7	0.2798 (5)	0.2745 (4)	0.3546 (3)	3.6 (1)
C11	0.4974 (8)	0.3604 (6)	0.4507 (4)	8.9 (2)
C12	0.1752 (8)	0.3716 (6)	0.5341 (4)	8.5 (2)
C13	0.3377 (6)	0.1367 (5)	0.5722 (4)	6.0 (1)
C21	0.2009 (7)	0.5423 (5)	0.2642 (4)	6.3 (2)
C22	−0.0453 (6)	0.3648 (5)	0.3515 (4)	6.7 (2)
C23	0.1359 (6)	0.3859 (4)	0.1546 (1)	5.5 (1)
C31	0.6147 (5)	0.2747 (4)	0.1309 (3)	4.1 (1)
C32	0.5754 (6)	0.3934 (4)	0.1478 (4)	5.8 (1)
C33	0.7005 (5)	0.1888 (5)	0.2117 (4)	6.1 (1)
C34	0.7219 (6)	0.2990 (5)	0.0320 (4)	6.3 (2)
C41	0.2958 (5)	0.1910 (4)	−0.0884 (3)	4.9 (1)
C42[a]	0.4079 (9)	0.2778 (7)	−0.1769 (6)	10.6 (2)
C43[a]	0.134 (1)	0.2517 (8)	−0.0983 (7)	10.4 (3)
C44[a]	0.306 (1)	0.0685 (7)	−0.1068 (6)	10.6 (2)
C51	0.1720 (5)	−0.0138 (4)	0.2858 (4)	4.8 (1)
C52	0.0543 (6)	0.0431 (5)	0.3461 (4)	6.3 (2)
C53	0.0921 (7)	−0.0903 (5)	0.2466 (5)	7.8 (2)
C54	0.2767 (7)	−0.0995 (5)	0.3526 (5)	7.3 (2)
C42A[a]	0.435 (3)	0.140 (2)	−0.147 (2)	13.3 (7)
C43A[a]	0.243 (3)	0.326 (2)	−0.137 (2)	14.6 (7)
C44A[a]	0.150 (3)	0.112 (2)	−0.082 (2)	18.8 (8)

[a] Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

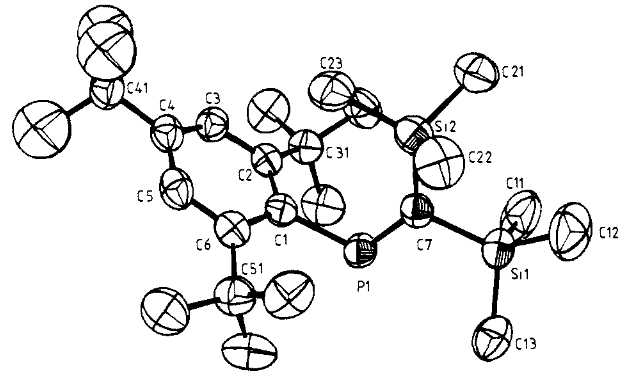


Figure 2. ORTEP view of $(Me_3Si)_2CP(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**4**) showing atom numbering scheme.

temperature. After filtration and removal of the volatiles, the resulting oil was purified by vacuum distillation using a short path column (bp 79 °C at 5 × 10^{-3} torr). The 4.25 g of **2** that was isolated represented a 75% yield. Anal. Calcd for $C_{14}H_{37}PSi_4$: C, 48.4; H, 10.7. Found: C, 48.7; H, 10.8. HRMS for **2**: calcd 348.1710; found 348.1717.

Preparation of $(Me_3Si)_2C{=}P(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (4). A stirred solution of 3.33 g (14.8 mmol) of **3** in 30 mL of *n*-hexane was cooled to −40 °C and was treated with a solution of 14.5 mmol of $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2Li$ in 30 mL of THF. All solvent and volatiles were stripped from the reaction mixture after allowing it to warm to room temperature. The resulting solid residue was then extracted with two 20-mL portions of *n*-hexane. After filtration, crystals of **4** (mp 96 °C) formed in 78% yield from concentrated *n*-hexane solutions maintained at −20 °C. Anal. Calcd for $C_{25}H_{47}PSi_2$: C, 69.0; H, 10.9. Found: C, 68.8; H, 11.0. HRMS for **4**: calcd 434.2954; found 434.2961.

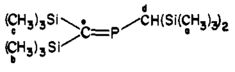
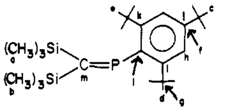
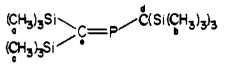
Preparation of $(Me_3Si)_2C{=}PC(SiMe_3)_3$ (5). A stirred solution of 2.084 g (9.3 mmol) of **3** in 50 mL of Et_2O was cooled to −40 °C and treated with 25.0 mL of a 0.37 M solution of $(Me_3Si)_3CLi$ in THF. The resulting dark-brown reaction mixture was stirred for an additional 2 h and allowed to warm to room temperature. After all volatiles were stripped off, the dark oily residue was redissolved in *n*-hexane and filtered. After removal of the *n*-hexane the resulting dark oil was purified by vacuum distillation using a short path column (bp 116 °C (5 × 10^{-3} torr)); yield 30%. The clear oil **5** decomposed on standing at room temperature; hence it was characterized by NMR (see text)[19] and

Table VIII. Phosphorus–Carbon Bond Length and ^{31}P NMR Chemical Shift Data for Phosphoaalkenes

compd	P=C bond length, Å	^{31}P chemical shift, ppm	ref
$(Me_3Si)_2C{=}PCl$ (**3**)		343	20
$(Me_3Si)_2C{=}PCH(SiMe_3)_2$ (**2**)		404	this work
$(Me_3Si)_2C{=}P(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**4**)	1.665 (4)	393	this work
$(Me_3Si)_2C{=}PC(SiMe_3)_3$ (**5**)		422	this work
$((t\text{-}Bu)_2P)P{=}C(Ph)(SiMe_3)$	1.68	331	3
$PhP{=}C[N(OClC_6H_4)][P(Ph)(SiMe_3)]$	1.702	140	3
$[PhP{=}C(N(Ph)(SiMe_3))(PhP{-})]_2$	1.686 (9)	258	3
$MesP{=}CPh_2$	1.692 (3)	233[a]	6

[a] For this datum, see: Klebach, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4886.

Table IX. ^1H and ^{13}C NMR Data for Phosphaalkenes **2**, **4**, and **5**

compd	$^{13}C\{^1H\}$, ppm	^1H, ppm
 **2**	2.3 (d, C_a, $^3J_{PC} = 5.3$ Hz) 3.6 (d, C_b, $^3J_{PC} = 15.3$ Hz) 4.6 (d, C_c, $^3J_{PC} = 3.3$ Hz) 41.0 (d, C_d, $^1J_{PC} = 87.3$ Hz) 190.6 (d, C_e, $^1J_{PC} = 89.7$ Hz)	0.20 (s, H_a) 0.25 (d, H_b, $^4J_{PH} = 2.8$ Hz) 0.30 (s, H_c) 2.80 (d, H_d, $^2J_{PH} = 3.0$ Hz)
 **4**	1.2 (d, C_a, $^3J_{PC} = 3.2$ Hz) 3.4 (d, C_b, $^3J_{PC} = 14.7$ Hz) 31.8 (s, C_c) 34.0 (s, C_d) 34.4 (s, C_e) 35.5 (s, C_f) 38.8 (s, C_g) 122.4 (s, C_h) 144.0 (d, C_i, $^1J_{PC} = 85.8$ Hz) 150.9 (s, C_j) 153.3 (s, C_k) 153.5 (s, C_l) 187.8 (d, C_m. $^1J_{PC} = 89.7$ Hz)	−0.40 (s, H_a) 0.20 (d, H_b, $^4J_{PH} = 1.5$ Hz) 1.25 (s, H_c) 1.45 (s, H_d) 7.40 (s, H_h)
 **5**	5.1 (d, C_a, $^3J_{PC} = 2.8$ Hz) 5.9 (d, C_b, $^3J_{PC} = 7.5$ Hz) 6.1 (d, C_c, $^3J_{PC} = 2.8$ Hz) 42.0 (d, C_d, $^1J_{PC} = 125.1$ Hz) 193.2 (d, C_e, $^1J_{PC} = 121.3$ Hz)	0.2–0.3 (multiplet)

HRMS. Calcd for $C_{17}H_{45}PSi_5$: 420.2105. Found: 420.2117.

X-ray Analysis of $(Me_3P)_2Ni[(Me_3Si)_2CPCH(SiMe_3)_2]$ (1). Crystals of **1** suitable for X-ray diffraction were grown from *n*-hexane at −20 °C. A single crystal was sealed under nitrogen in a Lindemann capillary prior to mounting on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters were determined from a least-squares fit of the angular settings of 15 reflections, $10° < 2\theta < 20°$, and subsequently refined using accurately centered data with $2\theta > 38°$. The lattice parameters indicated a monoclinic cell, for which systematic absences uniquely determined the space group as $P2_1/c$. From a total of 3523 unique measured reflections, collected using ω–2θ scans, 1492 were considered observed ($I > 2.0\sigma(I)$). After correction for Lorentz and polarization but not for absorption, the structure was solved by direct methods (MULTAN)[28] which revealed the positions of the Ni and P atoms. Subsequent refinement (full matrix-least squares) using the SHELX 76[29] system revealed the positions of all non-hydrogen atoms. Refinement using anisotropic thermal parameters and unit weights converged smoothly to give final residuals $R = 0.031$ and $R_W = 0.030$. No chemically significant peaks were present in the final difference map. Hydrogen atoms were neither located nor refined. Tables of bond lengths, angles, and atomic positional parameters are given in the text (Tables II–IV), and pertinent crystallographic data are collected in Table I. Thermal parameters and tables of observed and calculated structure factors are available as supplementary material (Tables 1 and 2).

X-ray Analysis of $(Me_3Si)_2CP(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (4). Crystals of **4** suitable for X-ray diffraction were grown from *n*-hexane at −20 °C. Lattice parameter determination and data collection procedures were as described for **1** and indicated a triclinic cell. The space group $P\bar{1}$ was chosen and confirmed on the basis of successful refinement. Data collection parameters are collected in Table I (see text).

The structure was solved by using a Patterson map which revealed the phosphorus atom position. Subsequent refinement[30] using difference Fourier maps and full-matrix least squares revealed the positions of all non-hydrogen atoms which, excepting those of the *t*-Bu group C(42)–C(44), were refined by using anisotropic thermal parameter. The aforementioned *t*-Bu group showed a distinct twofold rotational disorder of the methyl group positions. Atoms C(42), C(43), and C(44) comprised one *t*-Bu position with reasonable bond lengths and angles while C(42A), C(43A), and C(44A) comprised the other. Both sets of atoms refined successfully with isotropic temperature factors and an occupancy ratio of ~2:1. No disorder in the other *t*-Bu groups or the $SiMe_3$ group was detected. All hydrogen atoms except for those about the disordered *t*-Bu group were located and refined positionally but with a fixed isotropic temperature factor. A final difference map revealed no chemically significant peaks, and refinement converged smoothly to give final residuals $R = 0.061$ and $R_W = 0.060$. Listings of bond lengths, angles, and atomic positional parameters are given in Tables V–VII (see text).

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Registry No. 1, 85650-29-9; **2**, 83436-93-5; **3**, 79454-85-6; **4**, 84751-28-0; **5**, 92284-88-3; $(Me_3P)_2NiCl_2$, 19232-05-4; $[(Me_3Si)_2CH]_2PNa$, 85709-83-7; $(Me_3Si)_2CHLi$, 41823-71-6; $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2Li$, 35383-91-6; $(Me_3Si)_3CLi$, 28830-22-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

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(28) Main, P. MULTAN 82; University of York, York, England, 1982.

(29) Sheldrick, G. M. SHELX 76; University of Cambridge, Cambridge, England, 1976.

(30) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_W = [\sum w(|F_o| - |F_c|)^2|\sum w|F_o|^2]^{1/2}$.

(31) **Note Added in Proof:** Since submission of the present manuscript, two developments have come to our attention. Bickelhaupt et al. have published the crystal structure of $(2,4,6\text{-}Me_3C_6H_2)P{=}CPh_2$ (Van der Knaap, Th. A.; Klebach, Th. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* **1984**, *40*, 765) and Appel et al. (Appel, R., private communication) have determined the crystal structure of $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)P{=}C(Ph)(SiMe_3)$. For the latter compound the P=C bond length is 1.68 Å and the C—P=C bond angle is 107°. We thank Professor Appel for providing this information.