Organometallics **2002,** *21,* 4919−4926

Unusual Approaches to Organophosphorus Compounds: The Surprising Reactivity of Bis(methylene)phosphoranes and Related Phosphoranylidene Carbenoids

Thomas Baumgartner,[†] Petra Moors, Martin Nieger, Heike Hupfer, and Edgar Niecke*

Anorganisch-Chemisches Institut der Universität, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

Received April 22, 2002

The reactivity of the isomeric LiX-phosphoranylidene carbenoids *E*-, *Z*-[P]═C(X)Li ([P] = Mes*P═CTms$_2$; X = Cl, Br) as well as the synthesis and reactivity of the corresponding *E*-[P]═C(F)Li carbenoid was examined. The carbenoids exhibit a pronounced carbanion character, and differences in their reactivity mainly stem from the configuration of the carbenoid centers and/or the nature of the halogen substituent. Reaction of the dibromo-substituted bis(methylene)phosphorane, [P]═CBr$_2$, with an excess of *n*-BuLi proceeded through a dilithio intermediate ([P]═CLi$_2$), which was trapped with MeI and H$_2$O. *Endo*-methylated bis(methylene)phosphoranes ([P]═C(Me)X) exhibit a surprising acidity that, depending on the substitution pattern, induces rearrangement and/or elimination reactions. Rearrangement reactions accompanied by the loss of LiX afford a phosphirene that was used as a ligand in a nickel complex. Fluoro-substituted bis(methylene)phosphoranes ([P]═C(F)R) show weak interactions with an adjacent γ-silyl group, leading to configurationally stable *Z*-systems and exhibit carbenoid character in the case of the α-silyl-substituted bis(methylene)phosphorane.

Introduction

Carbenoids exhibit a versatile reactivity due to their unique substitution pattern. The presence of a metal atom and an electronegative substituent (i.e., an alkali metal and a halogen) at the same carbon atom gives access to reactions with nucleophiles as well as electrophiles.[1−8] Their "chameleon-like" ambident character, as specified by the canonical structures **A**−**C** (Scheme 1), has therefore been widely used in organic chemistry. The synthetic scope reaches from umpolung reactions with carbonyls to cyclizations and intramolecular rearrangement reactions. The latter are accompanied by the loss of both the metal and the electronegative element and involve carbene intermediates.[9] The same applies for alkylidene carbenoids, where the carbenoid center is part of a C−C double bond.[10]

However, the presence of two leaving groups of opposite polarity at one carbon atom not only leads to enhanced reactivity but also facilitates fragmentation reactions; carbenoids are generally stable only at low temperatures.[10,11] Not surprisingly, the first crystal structure analysis of a LiCl-carbenoid, (4-ClC$_6$H$_4$)$_2$C═CClLi, was achieved only recently by Boche et al.[12] In the context of our work on P−C π-systems we have reported on the isolation and structural characterization of phosphorus analogue alkylidene carbenoids **I**[13] and **II**[14−16] (Scheme 2). Interestingly, the phosphoranylidene carbenoids **II** (E = CTms$_2$, NMes*) exhibit remarkable stability even at elevated temperatures (< −10 °C) due to the incorporation of the carbenoidic carbon atom into a heteroallylic π-system. The pronounced kinetic stability of such systems allowed us to perform extensive

---

* Corresponding author. Fax: 011-49 228-73 5327. E-mail: e.niecke@uni-bonn.de.

[†] Current address: Institut für Anorganische Chemie, Johannes Gutenberg-Universität, Duesbergweg 10-14, 55099 Mainz, Germany.

(1) Stang, P. J. *Methods Org. Chem. (Houben Weyl),* 4th ed.; 1989; Vol. E. 19b, pp 85−135.

(2) Köbrich, G.; Trapp, H. *Z. Naturforsch.* **1963**, *18b*, 1125−1128.

(3) Köbrich, G.; Büttner, *J. Organomet. Chem.* **1964**, *18*, 117−119.

(4) Köbrich, G.; Merkle, H. R.; Trapp, H. *Tetrahedron Lett.* **1965**, 969−972.

(5) Köbrich, G.; Trapp, H. *Chem. Ber.* **1966**, *99*, 670−680.

(6) Köbrich, G.; Goyert, W. *Tetrahedron* **1967**, *22*, 2621.

(7) Köbrich, G.; Heinemann. H.; Zünndorf, W. *Tetrahedron* **1967**, *23*, 565−570.

(8) Köbrich, G. *Angew. Chem.* **1967**, *79*, 15−27; *Angew. Chem., Int. Ed.* **1967**, *6*, 41−53.

(9) Stang, P. J. *Chem. Rev.* **1978**, *78*, 345−363.

(10) Braun, M. *Angew. Chem.* **1998**, *110*, 444−465; *Angew. Chem., Int. Ed.* **1998**, *37*, 430−451.

(11) (a) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046−2053. (b) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308−337.

(12) Boche, G.; Marsch, M.; Müller, A.; Harms, K. *Angew. Chem.* **1993**, *105*, 1081−1082; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1032−1033.

(13) Niecke, E.; Nieger, M.; Schmidt, O.; Gudat, D.; Schoeller, W. W. *J. Am. Chem. Soc.* **1999**, *121*, 519−522.

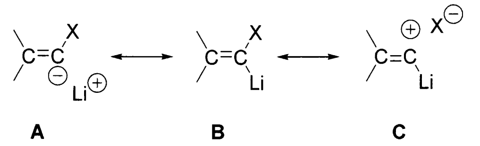
(14) Niecke, E.; Becker, P.; Nieger, M.; Stalke, D.; Schoeller, W. W. *Angew. Chem.* **1995**, *107*, 2012−2015; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1849−1852.

(15) Schilbach, W.; von der Gönna, V.; Gudat, D.; Nieger, M.; Niecke, E. *Angew. Chem.* **1994**, *106*, 1037−1038; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 982−983.

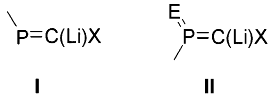
(16) Baumgartner, T.; Gudat, D.; Nieger, M.; Niecke, E.; Schiffer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 5953−5960.

10.1021/om020319n CCC: $22.00

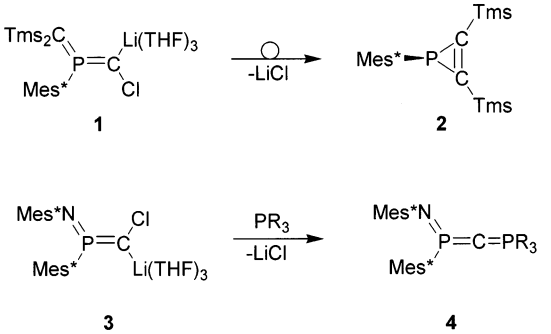
Scheme 1



Scheme 2



Scheme 3



investigations on their structure and dynamic behavior in solution.[16]

As anticipated from these studies as well as earlier experimental results, LiCl-phosphoranylidene carbenoids have to be considered as contact ion pairs of carbanions and solvated lithium cations, with carbanion rather than carbenoid character.[14,16] Therefore, reactions of these compounds were observed almost exclusively with electrophiles. Only two examples are known in which the phosphoranylidene carbenoids showed "carbenoid" reactivity: the formation of the phosphirene **2** from the *E*-configured LiCl-carbenoid **1**[14] and the reaction of the (imino)phosphoranylidene carbenoid **3** with phosphanes[17] (Scheme 3). We now report herein on the reactions of LiX-phosphoranylidene carbenoids and the related bis(methylene)phosphoranes that give access to novel organophosphorus compounds by unusual routes.

Results and Discussion

I. Reactions Involving LiBr-Phosphoranylidene Carbenoids. Our earlier observations on the reactivity of LiCl-phosphoranylidene carbenoids confirmed the carbanion character of such systems. We therefore imagined a change of the halogen substituent might shift the character more toward a carbenoid. Our efforts first concentrated on the corresponding *Z*-configured LiBr-carbenoid **6** (Scheme 4).[16] Due to the lower energy of the C−Br bond compared to the C−Cl bond, we anticipated reactions could occur at the C−Br bond as well.[18,19]

The LiBr-phosphoranylidene carbenoid **6** was accessible by treatment of the dibromo species **5** with 1 equiv of *n*-BuLi at −78 °C.[16] In typical carbanion fashion, **6** reacted with water to afford the protonated species **7a**. Bis(methylene)phosphorane **7a** was then observed to isomerize into the energetically more favored **7b** at ca. −10 °C. However, reactions of the carbenoid **6** with nucleophiles were not observed. The behavior was limited to a carbanion-type reactivity analogous to the observations on the corresponding chloro derivative.[14]

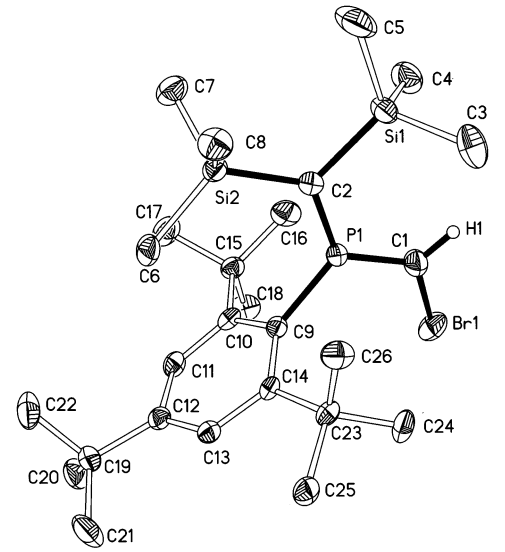


Figure 1. ORTEP view (50% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **7b** in the crystal. Selected bond lengths [Å] and angles [deg]: P1−C1: 1.659(3), P1−C2: 1.660(3), P1−C9: 1.797(3), C1−Br1: 1.877(3); C1−P1−C2: 124.5(1), C1−P1−C9: 114.9(1), C2−P1−C9: 120.6(1), P1−C1−Br1: 123.9(2), P1−C2−Si1: 113.9(2).

Figure 1 shows the molecular structure of **7b**. As in all known bis(methylene)phosphoranes,[20] the phosphorus atom adopts a trigonal planar geometry with the aryl substituent perpendicular to the PC_2 heteroallyl unit. The hydrogen atom occupies the *Z*-position (*endo)* as expected, in agreement with the isomerization process.[14] The C−Br bond length was observed to be 1.877(3) Å. The angle at the phosphorus center (C1−P1−C2 124.5(1)°) and the lengths of the bonds to the sp^2-hybridized carbon atoms (P1−C1 1.659(3) Å; P1−C2 1.660(3) Å) are similar to those of the related chloro-substituted compound.[14]

The reaction of the dibromo compound **5** with 2 equiv of *n*-BuLi was somewhat surprising. Quenching the reaction mixture with water or methyl iodide afforded the disubstituted products **9**[21] and **10**, respectively (Scheme 4). Compound **10** showed a ^{31}P NMR shift of $\delta = 129.0$ with a septet splitting due to the six methyl protons (^3J(P,H) = 25.4 Hz). The ^{13}C NMR data for the two methylene carbon atoms as well as the ^{1}H NMR data for the two methyl groups further supported a bis(methylene)phosphorane structure.[14,20,21]

The reaction conditions suggested a dilithiated intermediate in the synthesis of **9** and **10**, comparable to a 1,1-dilithioallene **11**. Theoretical calculations on dilithi-

---

(17) Schiffer, T. J.; Nieger, M.; Schoeller, W. W.; Shevchenko, I.; Niecke, E. Manuscript in preparation.

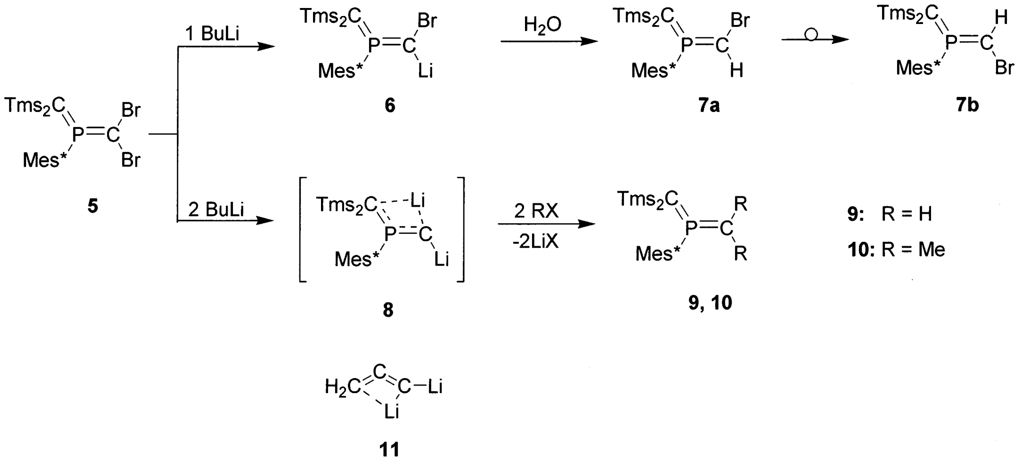
(18) Bürgi, H. B.; Dunitz, J. D. *Structure Correlation*; VCH: Weinheim, 1994; Vol. 2.

(19) Saspe, A. M.; Schleyer, P. v. R. In *Lithium Chemistry−A Theoretical and Experimental Overview*; John Wiley & Sons Inc.: New York, 1995.

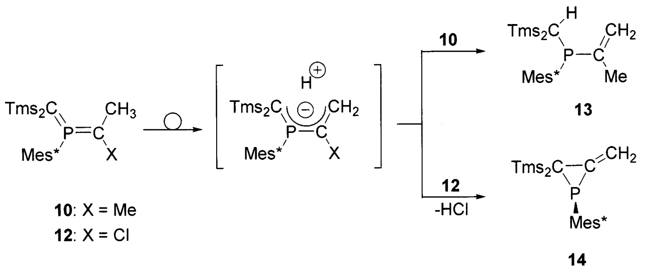
(20) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: New York, 1990; pp 157−219.

(21) Baumgartner, T.; Schinkels, B.; Gudat, D.; Nieger, M.; Niecke, E. *J. Am. Chem. Soc.* **1997**, *119*, 12410−12411.

Scheme 4



Scheme 5



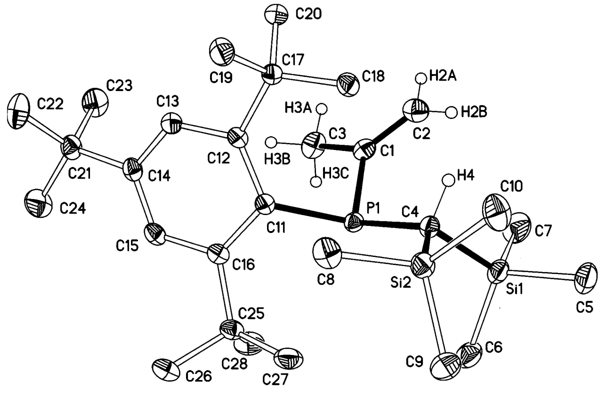


Figure 2. ORTEP view (50% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **13** in the crystal. Selected bond lengths [Å] and angles [deg]: P1−C1: 1.835(1), P1−C4: 1.867(1), P1−C11: 1.881(1), C1−C2: 1.328(2), C1−C3: 1.515(2); C1−P1−C4: 107.56(6), C1−P1−C11: 98.29(5), C4−P1−C11: 119.65(5), P1−C1−C2: 126.1(1), P1−C1−C3: 112.62(9), C2−C1−C3: 120.7(1), P1−C4−Si1: 105.66(6), P1−C4−Si2: 121.47(7), Si1−C4−Si2: 111.78(6).

ated hydrocarbons yield a bent allylic system for the 1,1-dilithioallene as stable intermediate, with one of the lithium atoms bridging the two terminal carbon atoms.[22] In the case of the phosphoranylidene system **8**, this kind of intermediate should be significantly stabilized due to the geometry of the central phosphorus atom that requires a bent system.[23] It should be mentioned in this context that the existence of dilithioalkenes is discussed controversially in the literature. The generation of geminally dimethylated alkenes from 1,1-dibromoalkenes is considered to proceed through a so-called "quasi dianion complex" (QUADAC) intermediate, but well-defined dilithioalkenes have also been reported.[24] However, recent investigations on Grignard reagents indicate that a QUADAC-type structure is an intermediate during the formation of the metalated organic species,[25] suggesting that both QUADAC *and* well-defined dilithioalkene play a role in the synthesis of dimethylated alkenes.

Surprisingly, the dimethylated bis(methylene)phosphorane **10** was not stable and rearranged within days, even at −25 °C, to form the vinyl-substituted $\sigma^3\lambda^3$-phosphane **13**. The high-field-shifted ^{31}P NMR resonance at $\delta = -20.7$ and the ^{13}C NMR data ($\delta = 133.2$; P*C*(Me)=CH$_2$, $\delta = 118.4$; PC(Me)=*C*H$_2$) indicated the generation of a vinyl functionality connected to a $\sigma^3\lambda^3$-phosphorus atom.[26] Furthermore, the rehybridization sp^2 → sp^3 of the silylated carbon atom is evident in a high-field-shifted ^{13}C NMR resonance ($\Delta\delta = 29.0$). This behavior was surprising since comparable bis(methylene)phosphoranes generally exhibit strong kinetic stabilization and rearrangement reactions can be observed only at elevated temperatures (~90−100 °C).[27]

The molecular structure of **13** (Figure 2) supports the rearrangement of **10** → **13** by the pyramidalization of the phosphorus as well as the silyl-substituted carbon atom C4 (sum of the angles: P1 = 325.50(5)°; C4 = 338.91(7)°). All three P−C bond lengths are in the range of single bonds (P1−C1 = 1.835(1) Å, P1−C4 = 1.867(1) Å, P1−C11 = 1.881(1) Å), whereas the C1−C2 bond length of 1.328(2) Å correlates to a double bond.[28] It is interesting to note that the *endo*-methylated bis(methylene)phosphorane **12**, accessible by treatment of the *E*-configurated LiCl-carbenoid **1** with methyl iodide, showed a behavior similar to **10** (Scheme 5). Compound

---

[22] (a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 2848−2856. (b) Maercker, A.; Theis, M. *Topics in Current Chemistry*; Springer: Berlin, 1987; Vol. 138, pp 1−57.

[23] Schoeller, W. W. Personal communication.

[24] (a) Maercker, A. *Methods Org. Chem. (Houben Weyl)*, 4th ed.; 1989; Vol. E. 19d, pp 448−566. (b) Marek, I. *Chem. Rev.* **2000**, *100*, 2887−2900.

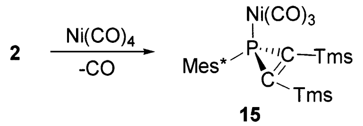
[25] Schulze, V.; Brönstrup, M.; Böhm, V. P. W.; Schwerdtfeger, P.; Schimeczek, M.; Hoffmann, R. W. *Angew. Chem.* **1998**, *110*, 869−871; *Angew. Chem., Int. Ed.* **1998**, *37*, 824−826.

[26] Mathey, F. *Chem. Rev.* **1990**, *90*, 997−1025.

[27] Becker, P. Ph.D. Thesis, University of Bonn, 1995.

[28] *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, pp 680ff.

Scheme 6



12 rearranged, accompanied by the loss of HCl, into the cyclic phosphirane **14** with an *exo*-cyclic methylene functionality after several days at room temperature. The ^{31}P NMR shift of $\delta = -16.8$ (^3J(P,H) = 4.7 Hz) as well as the ^{13}C NMR data for the *exo*- and *endo*-cyclic carbon atoms ($\delta = 119.3$; PC=CH$_2$, $\delta = 91.0$; PC=CH$_2$, $\delta = 43.8$; PCSi$_2$) also supported a phosphirane system.[26]

These observations suggested a strongly increased acidity of the *endo*-methyl group in bis(methylene)phosphoranes. The reason for this unusual behavior is currently unknown, but the formation of a delocalized anionic intermediate seemed to be involved in the rearrangement reactions. The pronounced leaving group character of chloride in contrast to a methyl substituent could explain the slight differences in the reaction pathways of **10** and **12**.

In a related reaction, the *E*-configurated LiCl-carbenoid **1** eliminated LiCl upon warming to room temperature (Scheme 3). The formation of the phosphirene **2** is explained by an ionic mechanism with chloride elimination as a final step.[14] A similar behavior was observed when **7b** was reacted with LDA. The *E*-configurated LiBr-carbenoid was assumed to be the intermediate in analogy with the LiCl system.[29] However, the structure of the phosphirene **2**, accessible from the *E*-configurated LiBr-carbenoid, could not ultimately be determined from the experimental results.

We therefore reacted **2** with Ni(CO)$_4$ at room temperature to obtain a crystalline complex in quantitative yield. The nickel complex **15** showed a low-field-shifted ^{31}P NMR resonance at $\delta = -158.6$ (cf.: **2** $\delta = -183.9$[14]) and correspondingly low-field-shifted ^{13}C NMR resonances for the ring carbon atoms.[26] We were able to perform a single-crystal X-ray analysis for **15** (Figure 3). The molecular structure of the tetrahedral complex **15** shows that one of the carbonyl ligands of the Ni(CO)$_4$ has been replaced by **2**. The Ni−P bond length of 2.276(1) Å is comparable to typical values of Ph$_3$P−Ni complexes (2.225 ± 0.079 Å).[28] The phosphirene unit exhibits the characteristic small angle at the phosphorus atom (42.8(1)°) and a C−C distance in the range of a double bond (C1−C2 = 1.327(3) Å).[26] The exohedral P1−C9 bond (1.873(2) Å) is significantly longer than the endohedral P−C bonds (1.821(2) Å for P1−C1 and 1.819(2) Å for P1−C2), which can be explained by the increased steric bulk at the phosphorus substituents. The bulkiness of the system is further apparent in the arrangement of the silyl groups, which are distorted out of the ring plane (torsion angle: 27.7(5)°).

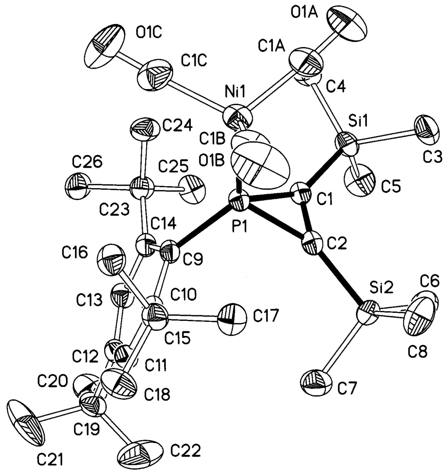


Figure 3. ORTEP view (40% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **15** in the crystal. Selected bond lengths [Å] and angles [deg]: P1−C1: 1.821(2), P1−C2: 1.819(2), P1−C9: 1.873(2), C1−C2: 1.327(3), Ni1−P1: 2.276(1); C1−P1−C2: 42.8(1), P1−C1−C2: 68.5(1), P1−C2−C1: 68.7(1), C1−P1−Ni1: 116.3(1), C2−P1−Ni1: 125.9(1), C9−P1−Ni1: 129.5(1), P1−C1−Si1: 148.4(1), P1−C2−Si2: 149.9(1).

II. Reactions Involving a LiF-Phosphoranylidene Carbenoid. Since the carbenoid character of the isomeric *E*-/*Z*-LiBr carbenoids was similar to their LiCl congeners, we concentrated our efforts on the synthesis of a corresponding Li−F system. It should be mentioned in this context that the isolation of Li−F carbenoids has long been considered impossible due to the high tendency to form LiF.[30] Although theoretical calculations supported this assumption, lithium-fluoro carbenoids have been reported in solution at −110 to −80 °C.[31,32] However, the direct proof of their existence was limited to a ^{19}F NMR study.[33] Attempts to isolate them in pure form have failed to date, apparently owing to their very low stability. Our work on the phosphoranylidene carbenoids, on the other hand, has shown that the phosphorus analogues show a significantly greater stability than their organic counterparts. The bis(ylene)phosphorane system was therefore expected be particularly suited to achieve the isolation of a LiF-carbenoid.

The first stable LiF-carbenoid **17** was accessible by treatment of the mixed halogenated bis(methylene)phosphorane **16** with *n*-butyllithium at −78 °C in THF.[16] Metalation occurred selectively at the C−Cl bond, affording the *Z*-configured carbenoid **17**. The existence of the lithium fluoro carbenoid in solution was determined by multinuclear NMR studies at −100 °C with a ^{6}Li-doped sample.[16] Surprisingly, **17** did not decompose through loss of lithium fluoride upon warming to room temperature; Li/H exchange with the solvent (THF) afforded the *Z*-configured H-F-substituted bis(methylene)phosphorane **18** instead. The ^{31}P chemical shift of $\delta = 104.4$ (^2J(P, H) = 59.2 Hz, ^2J(P, F) = 3.5 Hz), the ^{19}F NMR data ($\delta = -134.0$, ^2J(F, H) = 49.4 Hz, ^2J(F, P) = 3.3 Hz), and the ^{13}C NMR data of the two methylene carbon atoms supported a bis(methylene)phosphorane system for **18**.[14,20] Interestingly, no isomerization into the *E*-configurated species was observed, in contrast to the chloro and bromo derivatives. This finding can be explained by weak interactions between the fluoro substituent and the adjacent *endo*-

---

(29) The use of *n*-BuLi afforded the known phosphorus triylid Mes*P(=CTms$_2$)=CHLi(THF)$_3$ [see ref 21], which was trapped by addition of water to give **9**.

(30) Kerr, J. A. In *Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; 1995−96; pp 9-51−9-62.

(31) Burton, D. J.; Yang, Z.-Y.; Morken, P. A. *Tetrahedron* **1994**, *50*, 2993−3063.

(32) Normant, J.-F. *J. Organomet. Chem.* **1990**, *400*, 19−34.

(33) Pelter, A.; Kvicala, J.; Parry, D. E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2681−2682.

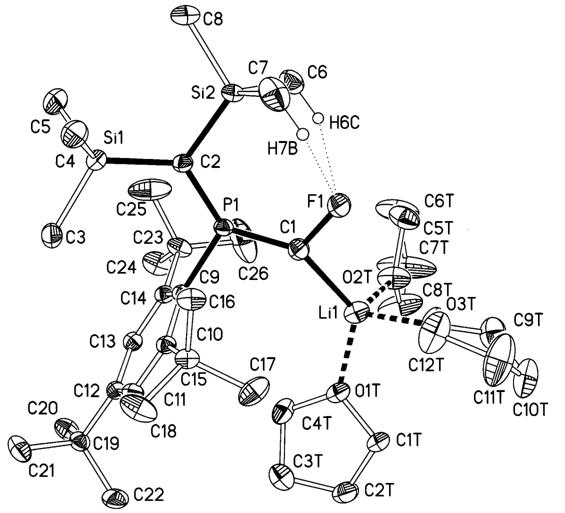


Figure 4. ORTEP view (40% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **17** in the crystal. Selected bond lengths [Å] and angles [deg]: P1−C1: 1.682(2), P1−C2: 1.700(2), P1−C9: 1.828(2), C1−Li1: 2.117(4), C1−F1: 1.438(2), Li1···F1: 2.871(6); C1−P1−C2: 134.4(1), C1−P1−C9: 105.8(1), C2−P1−C9: 119.3(1), P1−C1−Li1: 140.4(2), P1−C1−F1: 112.8(1), Li1−C1−F1: 106.1(2), P1−C2−Si2: 114.1(1).

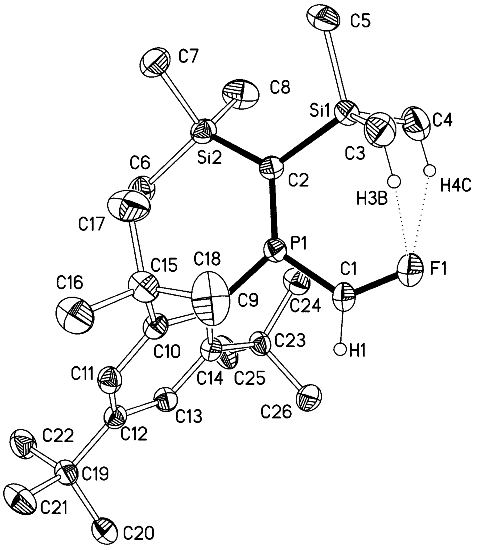
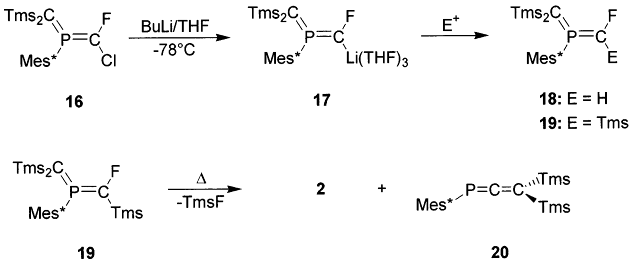


Figure 5. ORTEP view (50% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **18** in the crystal. Selected bond lengths [Å] and angles [deg]: P1−C1: 1.654(2), P1−C2: 1.655(2), P1−C9: 1.809(2), C1−F1: 1.381(2); C1−P1−C2: 128.2(1), C1−P1−C9: 104.3(1), C2−P1−C9: 127.0(1), P1−C1−F1: 122.7(2), P1−C2−Si1: 116.5(1).

Me_3Si group, observed in a through-space interaction by NMR (^6J(F,H) = 1.8 Hz; ^5J(F,C) = 5.0 Hz).[34] The fluoro-substituted compounds **17** and **18** were isolated in crystalline form at −50 and −30 °C, respectively. The single-crystal X-ray structural analyses revealed the effects on the bonding properties of the carbenoidic carbon atom and the central π-system by metalation (See Figures 4 and 5). In both compounds the phosphorus atom adopts a trigonal planar configuration (sum of the angles: 360°) with an orthogonal arrangement of the aromatic substituent.[20] In the structures of **17** and **18**, the fluorine atom exists in the *endo*-position with the anticipated weak interactions present between the fluoro substituent and the adjacent *endo*-silyl group (**17**: F1−Hb = 2.332 Å; F1−Hc = 2.462 Å; **18**: F1−Hb = 2.333 Å; F1−Hc = 2.480 Å). The structural changes **17** → **18** are evident in the decreased P1−C1−F1 angle of 112.8(1)° (cf. 122.7(2)° in **18**) and the lengthened C1−F1 bond of about 4% (Δ = 5.7 pm) in the carbenoid **17**. The small P1−C1−F1 angle in **17** reveals a higher p-character of the C−F bond and is accompanied by a widened P1−C1−Li1 angle of 140.4(2)°, indicating a higher s-character of the C−Li bond.[35] In addition, the Li1−C1−F1 angle of 106.1(2)° is consistent with an attractive interaction between lithium and fluorine, which has been previously proposed[8,11] and proven[12,14,16] for carbenoids in general. Due to attractive interactions, the Li1−F1 distance of 2.871(6) Å amounts to 86% of the sum of the van der Waals radii of Li and F.[28] The lithium atom is solvated by three oxygen atoms of THF and occupies the sterically more accessible *exo* position. The C1−Li1 bond length of 2.117(4) Å is similar to those of comparable phosphoranylidene carbenoids and ylids (2.09−2.13 Å).[14,16,21] Both P−C double bond lengths in **17** are widened (ΔP1−C1: 2.8 pm; ΔP1−C2: 4.5 pm) as well as the central C1−P1−C2 angle of 134.4(1)° (**18**: 128.2(1)°).

Scheme 7



Treatment of carbenoid **17** with chlorotrimethylsilane at −78 °C afforded the silyl-substituted bis(methylene)phosphorane **19** (Scheme 7). The *endo* configuration of the fluoro substituent is again supported by through-space interactions (^6J(F,H) = 2.8 Hz; ^5J(F,C) = 4.5 Hz), as observed for **17** and **18**.

It is interesting to note that **19** can be considered a Si−F-carbenoid itself. As expected, it showed carbenoid-type reactivity at elevated temperatures. Refluxing in toluene led to the loss of Me_3SiF and the formation of two products, **2**[14] and **20**,[36] in a 1:1 ratio. The generation of both products was assumed to proceed through a carbene intermediate (1,1-elimination of Me_3SiF). However, a 1,3-elimination of Me_3SiF with subsequent cyclization cannot be excluded as another possibility for the generation of **2**. The detailed mechanism for the formation of **2** and **20** cannot be determined from experiments performed to date.

Conclusion

Although phosphoranylidene carbenoids do not behave like their organic counterparts, they show some

---

[34] Compound **18** can be synthesized deliberately by reaction of **17** with methanol at −78 °C as well.

[35] Lambert, C.; Schleyer, P. v. R. *Methods Org. Chem. (Houben Weyl)*, 4th ed.; 1989; Vol. E. 19b, pp 15−19.

[36] Märkl, G.; Kreitmeier, P. *Angew. Chem.* **1988**, *100*, 1411−1412; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1360−1361.

interesting reactivity. They have to be considered as contact ion pairs with a pronounced carbanion character, as indicated by earlier studies. In this work we were able to show that variation of the halogen substituent does not shift the character toward a carbenoid. However, within the scope of our investigations we could demonstrate that the bis(ylene)phosphorane system is particularly suited to stabilize a LiF-carbenoid. Lithium and fluorine represent two opposite sides of the electronegativity spectrum, which has made previous attempts to isolate such a species unsuccessful due to the high tendency to form LiF.

Nevertheless, the substitution products arising from the carbanion reactivity show intriguing reactions and underline that trapping of the phosphoranylidene carbenoids does not terminate their use for further syntheses. The products themselves represent valuable starting points for the synthesis of unusual organophosphorus compounds that are not or hardly accessible by different routes. Interesting ring systems are accessible as well as functionalized systems of phosphorus(V) and phosphorus(III). A synthetically valuable dilithiated species is assumed to be the intermediate in the reaction of the dibromo bis(methylene)phosphorane with 2 equiv of a base. It allowed the synthesis of disubstituted bis(methylene)phosphoranes that again represent interesting synthons. A very intriguing feature is the increased acidity of methyl substituents at the *endo* position of bis(methylene)phosphoranes. These systems led to the generation of a vinyl-substituted phosphane and an *exo*-methylene-substituted phosphirane. The reason for this unusual behavior could not be explained by the experimental data and is currently verified by theoretical calculations.

Experimental Section

General Procedures. All manipulations were carried out under a dry argon atmosphere employing standard Schlenk techniques. Solvents were dried using standard procedures. *N*-BuLi (1.6 M in hexane), MeI, Ni(CO)$_4$, and Me$_3$SiCl were used as received. Compounds **1**,[14] **2**,[14] **5**,[16] **6**,[16] and **17**[16] were prepared by literature methods. ^{31}P{^{1}H} NMR spectra (121.5 MHz), ^{1}H NMR spectra (300.1 MHz), and ^{13}C{^{1}H} NMR spectra (75.5 MHz) were recorded on a Bruker AMX 300 instrument. ^{19}F NMR spectra were recorded on a DRX 500 spectrometer (470.6 MHz). Chemical shifts were referenced to external 85% H$_3$PO$_4$ (^{31}P), CFCl$_3$ (^{19}F), or TMS (^{13}C, ^{1}H). Electron ionization (70 and 24 eV) mass spectra were run on a VG 12-250. Melting points (in sealed capillaries) are uncorrected. Elemental analysis was performed at the Mikroanalytisches Labor der Universität Bonn.

Preparation of 7b. A 0.05 g (2.2 mmol) portion of water was added to a stirred solution of 2 mmol of the carbenoid **6**[16] in 5 mL of THF at −78 °C. After 5 min the solution was allowed to warm to room temperature. After removing the solvent under vacuum, the residue was taken up in pentane and filtered through Celite. **7b** was obtained from the concentrated solution at −25 °C as orange crystals. Yield: 1.02 g (97%). Mp: 89−91 °C. ^{31}P NMR (THF): δ 149.0 (d, ^{2}J(P,H) = 30.6 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.72 (d, ^{4}J(H,P) = 4.6 Hz, 2H, *m*-Ar), 4.67 (d, ^{2}J(H,P) = 30.2 Hz, 1H, P=C(*H*)Br), 1.88 (d, ^{5}J(H,P) = 0.7 Hz, 18H, *o*-*t*Bu), 1.31 (s, 9H, *p*-tBu), 0.47 (s, 9H, Si(CH$_3$)$_3$), 0.07 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 155.7 (d, ^{2}J(C,P) = 7.3 Hz, *o*-Ar), 154.4 (d, ^{4}J(C,P) = 3.1 Hz, *p*-Ar), 125.9 (d, ^{3}J(C,P) = 12.6 Hz, *m*-Ar), 119.8 (d, ^{1}J(C,P) = 86.6 Hz, *ipso*-Ar), 64.2 (d, ^{1}J(C,P) = 127.8 Hz, P=*C*HBr), 54.7 (d, ^{1}J(C,P) = 47.7 Hz, P=*C*Si$_2$), 40.6 (d, ^{3}J(C,P) = 2.7 Hz, *o*-*C*Me$_3$), 35.6 (d, ^{5}J(C,P) = 0.8 Hz, *p*-*C*Me$_3$), 34.5 (s, *o*-C*C*H$_3$), 32.2 (s, *p*-C*C*H$_3$), 4.0 (d, ^{3}J(C,P) = 4.6 Hz, Si*C*$_3$), 2.1 (d, ^{3}J(C,P) = 5.1 Hz, Si*C*$_3$). MS (70 eV): *m*/*z* (relative intensity) 526 (2) [M$^+$], 513 (7) [M$^+$ − Me], 447 (7) [M$^+$ − Br], 73 (50) [SiMe$_3$$^+$], 57 (100) [*t*Bu$^+$]. C$_{26}H_{48}$BrPSi$_2$ (526.22): found, 526.2215; calcd, 526.2207.

Preparation of 10. To a stirred solution of 0.61 g (1 mmol) of **5**[16] in 5 mL of THF was added 1.4 mL (2.2 mmol) of *n*-BuLi (1.6 M in hexane) at −78 °C. After 5 min at that temperature, 0.31 g (2 mmol) of methyl iodide was added, and the reaction stirred for a further 15 min before warming to room temperature. After removal of the solvent under vacuum, the residue was taken up in pentane and filtered through Celite. Evaporation of the solvent provided **10** as a yellow oil. Yield: 0.46 g (96%). ^{31}P NMR (THF): δ 129.0 (sept, ^{3}J(P,H) = 25.4 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.72 (d, ^{4}J(H,P) = 3.9 Hz, 2H, *m*-Ar), 2.11 (dd, ^{3}J(H,P) = 25.2 Hz, ^{4}J(H,H) = 0.8 Hz, 3H, P=C(CH$_3$)C*H*$_3$), 1.79 (d, ^{3}J(H,P) = 0.7 Hz, 18H, *o*-*t*Bu), 1.49 (dd, ^{3}J(H,P) = 25.6 Hz, ^{4}J(H,H) = 0.8 Hz, 3H, P=C(C*H*$_3$)CH$_3$), 1.39 (s, 9H, *p*-tBu), 0.58 (s, 9H, Si(CH$_3$)$_3$), 0.22 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 155.5 (d, ^{2}J(C,P) = 5.8 Hz, *o*-Ar), 153.4 (d, ^{4}J(C,P) = 3.1 Hz, *p*-Ar), 125.3 (d, ^{1}J(C,P) = 80.9 Hz, *ipso*-Ar), 125.1 (d, ^{3}J(C,P) = 11.8 Hz, *m*-Ar), 98.6 (d, ^{1}J(C,P) = 142.3 Hz, P=*C*Me$_2$), 41.3 (d, ^{1}J(C,P) = 50.0 Hz, P=*C*Si$_2$), 40.5 (d, ^{3}J(C,P) = 2.3 Hz, *o*-*C*Me$_3$), 35.5 (d, ^{5}J(C,P) = 1.1 Hz, *p*-*C*Me$_3$), 34.6 (s, *o*-C*C*H$_3$), 31.6 (s, *p*-C*C*H$_3$), 24.5 (d, ^{2}J(C,P) = 17.1 Hz, P=C(*C*H$_3$)CH$_3$), 24.3 (d, ^{2}J(C,P) = 15.5 Hz, P=C(CH$_3$)*C*H$_3$), 5.6 (d, ^{3}J(C,P) = 4.2 Hz, Si*C*$_3$), 5.3 (d, ^{3}J(C,P) = 3.4 Hz, Si*C*$_3$). MS (70 eV): *m*/*z* (relative intensity) 476 (14) [M$^+$], 461 (40) [M$^+$ − Me], 419 (95) [M$^+$ − *t*Bu], 73 (100) [SiMe$_3$$^+$], 57 (45) [*t*Bu$^+$]. C$_{28}H_{53}PSi_2$ (476.33): found, 476.3423; calcd, 476.3417.

Preparation of 13. Compound **13** was obtained from a concentrated solution of **10** in pentane over a period of 4 weeks at −25 °C as yellow crystals. Yield: 0.32 g (69%).

Spectroscopic Data for 13. ^{31}P NMR (THF): δ −20.7 (m br, ^{3}J(P,H) = 11.0 Hz, 10.8 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.67 (d, ^{4}J(H,P) = 2.1 Hz, 2H, *m*-Ar), 5.47 (ddq, ^{2}J(H,P) = 12.0 Hz, ^{2}J(H,H) = 1.5 Hz, ^{3}J(H,H) = 1.3 Hz, 1H, P=C(*H*)H), 5.16 (d br, ^{2}J(H,P) = 13.1 Hz, 1H, P=C(H)*H*), 1.90 (br, 18H, *o*-*t*Bu), 1.68 (br, 3H, P−C(C*H*$_3$)), 1.43 (dm, ^{2}J(H,P) = 13.8 Hz, 1H, P−C(Si$_2$)*H*), 1.38 (s, 9H, *p*-tBu), 0.44 (d, ^{4}J(H,P) = 0.7 Hz, 9H, Si(CH$_3$)$_3$), 0.34 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 150.9 (d, ^{4}J(C,P) = 2.3 Hz, *p*-Ar), 147.9 (d, ^{2}J(C,P) = 27.1 Hz, *o*-Ar), 133.2 (d, ^{1}J(C,P) = 56.1 Hz, P*C*(Me)=CH$_2$), 127.3 (br, *m*-Ar), 122.4 (br, *ipso*-Ar), 118.4 (d, ^{2}J(C,P) = 7.6 Hz, PC(Me)=*C*H$_2$), 40.7 (br, *o*-*C*Me$_3$), 35.2 (d, ^{5}J(C,P) = 0.9 Hz, *p*-*C*Me$_3$), 35.0 (br, *o*-C*C*H$_3$), 31.4 (s, *p*-C*C*H$_3$), 23.7 (d, ^{2}J(C,P) = 35.1 Hz, P−C(*C*H$_3$)=CH$_2$), 12.3 (d, ^{1}J(C,P) = 75.5 Hz, P*C*Si$_2$H), 5.0 (d, ^{3}J(C,P) = 1.1 Hz, Si*C*$_3$), 5.3 (d, ^{3}J(C,P) = 6.5 Hz, Si*C*$_3$). MS (70 eV): *m*/*z* (relative intensity) 476 (17) [M$^+$], 461 (15) [M$^+$ − Me], 419 (40) [M$^+$ − *t*Bu], 73 (100) [SiMe$_3$$^+$], 57 (55) [*t*Bu$^+$]. C$_{28}H_{53}PSi_2$ (476.33): found, 476.3426; calcd, 476.3424.

Preparation of 12. One millimole (0.16 g) of methyl iodide was added to a solution of 1 mmol of the carbenoid **1**[14] in 5 mL of THF at −78 °C. The solution was stirred for 5 min and then warmed to room temperature. The solvent was removed under vacuum, and the residue was taken up in pentane and filtered through Celite. After evaporation of the solvent **12** was obtained as a yellow oil in 63% yield (0.31 g). ^{31}P NMR (THF): δ 131.0 (q, ^{3}J(P,H) = 21.6 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.70 (d, ^{4}J(H,P) = 4.5 Hz, 2H, *m*-Ar), 2.41 (d, ^{3}J(H,P) = 21.4 Hz, P=C(Cl)C*H*$_3$), 1.80 (d, ^{3}J(H,P) = 0.7 Hz, 18H, *o*-*t*Bu), 1.30 (s, 9H, *p*-tBu), 0.50 (s, 9H, Si(CH$_3$)$_3$), 0.13 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 155.5 (d, ^{2}J(C,P) = 6.8 Hz, *o*-Ar), 154.4 (d, ^{4}J(C,P) = 3.5 Hz, *p*-Ar), 125.5 (d, ^{3}J(C,P) = 13.0 Hz, *m*-Ar), 123.1 (d, ^{1}J(C,P) = 90.4 Hz, *ipso*-Ar), 99.2 (d, ^{1}J(C,P) = 152.2 Hz, P=*C*(Cl)Me), 47.7 (d, ^{1}J(C,P) = 48.8 Hz, P=*C*Si$_2$), 40.5 (d, ^{3}J(C,P) = 2.6 Hz, *o*-*C*Me$_3$), 35.6 (d, ^{5}J(C,P) = 1.2 Hz, *p*-*C*Me$_3$), 34.5 (s, *o*-C*C*H$_3$), 31.4 (s, *p*-C*C*H$_3$), 26.6 (d, ^{2}J(C,P) = 11.8 Hz,

Table 1. Crystallographic Data and Summary of Data Collection and Refinement

	7b	**13**	**15**	**17**	**18**
formula	$C_{26}H_{48}BrPSi_2$	$C_{28}H_{53}PSi_2$	$C_{29}H_{47}NiO_3PSi_2$	$C_{38}H_{71}FLiO_3PSi_2$	$C_{26}H_{48}FPSi_2$
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$Pna2_1$ (No.33)	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)	$P2_1/c$ (No.14)
a, Å	17.3407(9)	9.8932(2)	9.906(1)	11.3067(1)	11.1716(4)
b, Å	9.1113(4)	11.3488(2)	17.878(1)	20.2126(3)	9.8730(2)
c, Å	18.1806(9)	26.7941(4)	19.704(2)	18.7715(3)	25.9970(10)
β, deg		97.267(1)	104.38(1)	97.719(1)	91.814(1)
V, Å^3	2872.5(2)	2984.17(9)	3380.2(6)	4251.12(10)	2865.96(16)
Z	4	4	4	4	4
ρ_{calc}, g cm^{-3}	1.220	1.06	1.158	1.077	1.082
μ	1.582	0.186	2.145	0.156	0.197
diffractometer	Nonius KappaCCD	Nonius KappaCCD	Enraf-Nonius MACH3	Nonius KappaCCD	Nonius KappaCCD
radiation	Mo Kα	Mo Kα	Cu Kα	Mo Kα	Mo Kα
λ, Å	0.71073	0.71073	1.54178	0.71073	0.71073
T, K	123(2)	123(2)	200(2)	123(2)	123(2)
max 2θ, deg	56.6	56.6	135.4	50.0	56.8
no. of data	22865	38199	6303	44288	29950
no. of unique data	6218	7254	5998	7226	5634
no. of unique data [$I > 2\sigma(I)$]	5375	6421	5459	5464	3921
no. of variables	272	290	326	415	274
no. of restraints	1	3	0	84	1
$R(F)^a$	0.033	0.037	0.045	0.045	0.042
wR2(F^2) for all data	0.077	0.107	0.127	0.133	0.124

[a] For $I > 2\sigma(I)$.

P═C(C)CH$_3$), 5.7 (d, ^3J(C,P) = 4.6 Hz, SiC_3), 4.9 (d, ^3J(C,P) = 4.5 Hz, SiC_3). MS (70 eV): m/z (relative intensity) 496 (10) [M$^+$], 481 (50) [M$^+$ − Me], 461 (95) [M$^+$ − Cl], 73 (100) [SiMe$_3^+$]. Due to the increased reactivity of **12**, no satisfactory high-resolution MS or elemental analysis could be obtained.

Preparation of 14. Compound **14** was formed in a concentrated solution of **12** in pentane over a period of 3 days at room temperature. After evaporation of the solvent under vacuum, **14** was obtained as a yellow oil. Yield: 0.31 g (97%).

Spectroscopic Data of 14. ^{31}P NMR (THF): δ −16.8 (d, ^3J(P,H) = 4.7 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.3 (d, ^2J(C,P) = 14.5 Hz, *o*-Ar), 156.7 (d, ^4J(C,P) = 2.7 Hz, *p*-Ar), 148.8 (d, ^1J(C,P) = 56.1 Hz, *ipso*-Ar), 125.0 (d, ^3J(C,P) = 7.6 Hz, *m*-Ar), 119.3 (d, ^2J(C,P) = 13.0 Hz, PC═CH$_2$), 91.0 (d, ^1J(C,P) = 37.7 Hz, PC═CH$_2$), 43.8 (d, ^1J(C,P) = 82.0 Hz, PCSi$_2$), 40.4 (d, ^3J(C,P) = 4.6 Hz, *o*-CMe$_3$), 38.7 (d, ^5J(C,P) = 1.6 Hz, *p*-CMe$_3$), 35.1 (s, *o*-CCH$_3$), 33.2 (s, *p*-CCH$_3$), 2.4 (s, SiC_3), 1.7 (s, SiC_3). MS (70 eV): m/z (relative intensity) 460 (15) [M$^+$], 445 (29) [M$^+$ − Me], 387 (73) [M$^+$ − SiMe$_3$], 73 (100) [SiMe$_3^+$]. $C_{27}H_{49}PSi_2$ (460.33): found, 460.3123; calcd, 460.3110.

Preparation of 15. A 0.38 g (2.2 mmol) sample of tetracarbonyl nickel was slowly added to a solution of 0.89 g (2 mmol) of the phosphirene **2**[14] in 5 mL of toluene at 0 °C. After 5 min the solution was warmed to room temperature and subsequently concentrated under vacuum. Complex **15** was obtained from the concentrated solution at −25 °C as light yellow crystals. Yield: 1.12 g (98%). Mp: 96−98 °C (dec). ^{31}P{^{1}H} NMR (toluene): δ −158.6. ^{1}H NMR (C_6D_6): δ 7.29 (d, ^4J(H,P) = 2.4 Hz, 2H, *m*-Ar), 1.85 (s, 18H, *o-t*Bu), 1.31 (s, 9H, *p*-tBu), 0.26 (s, 18H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 196.5 (s, CO), 167.2 (d, ^1J(C,P) = 45.0 Hz, PCSi), 155.3 (d, ^2J(C,P) = 4.2 Hz, *o*-Ar), 150.6 (s, *p*-Ar), 141.7 (d, ^1J(C,P) = 48.5 Hz, *ipso*-Ar), 122.6 (d, ^3J(C,P) = 4.2 Hz, *m*-Ar), 40.0 (s, *o*-CMe$_3$), 38.8 (s, *p*-CMe$_3$), 32.2 (s, *o*-CCH$_3$), 31.6 (s, *p*-CCH$_3$), 1.0 (s, SiC_3). IR (solid, KBr, cm^{-1}): 2063, 1990, 1953. Anal. Calcd for $C_{29}H_{47}O_3PNiSi_2$: C 59.08; H 8.04. Found: 58.69, H 7.69.

Preparation of 18. A 0.1 g (2.7 mmol) portion of methanol was added at −78 °C to a solution of 2 mmol of the LiF carbenoid **17**[16] in 5 mL of THF. After 5 min the solution was warmed to room temperature and the solvent removed under vacuum. The residue was taken up in pentane and subsequently filtered through Celite. **18** was obtained from the concentrated filtrate at −25 °C as yellow crystals. Yield: 0.85 g (91%). Mp: 121−122 °C. ^{31}P{^{1}H} NMR (THF): δ 104.4 (d, ^2J(P,F) = 3.5 Hz). ^{31}P NMR (THF): δ 104.4 (d br, ^2J(P,H) = 59.2 Hz). ^{19}F NMR: δ −134.0 (dd, ^2J(F,H) = 49.4 Hz, ^2J(F,P) = 3.3 Hz). ^{1}H NMR (C_6D_6): δ 7.53 (d, ^4J(H,P) = 4.7 Hz, 2H, *m*-Ar), 6.17 (dd, ^2J(H,F) = 49.9 Hz, ^2J(H,P) = 59.2 Hz, 1H, P═CHF), 1.70 (d, ^5J(H,P) = 0.5 Hz, 18H, *o-t*Bu), 1.30 (s, 9H, *p*-tBu), 0.25 (d, J(H,F) = 1.8 Hz, 9H, Si(CH$_3$)$_3$), −0.17 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 156.8 (dd, ^2J(C,P) = 7.2 Hz, ^4J(C,F) = 3.0 Hz, *o*-Ar), 154.4 (d, ^4J(C,P) = 3.0 Hz, *p*-Ar), 131.7 (dd, ^1J(C,F) = 273.7 Hz, ^1J(C,P) = 154.1 Hz, P═CHF), 124.8 (d, ^3J(C,P) = 12.2 Hz, *m*-Ar), 117.2 (dd, ^1J(C,P) = 89.7 Hz, ^3J(C,F) = 4.3 Hz, *ipso*-Ar), 40.7 (dd, ^1J(C,P) = 37.4 Hz, ^3J(C,F) = 3.4 Hz, P═CSi$_2$), 40.4 (d, ^3J(C,P) = 2.7 Hz, *o*-CMe$_3$), 38.6 (d, ^5J(C,P) = 1.0 Hz, *p*-CMe$_3$), 34.7 (s, *o*-CCH$_3$), 31.4 (s, *p*-CCH$_3$), 3.9 (d, ^3J(C,P) = 4.5 Hz, SiC_3), 3.4 (dd, J = 3.4 Hz, J = 5.0 Hz, SiC_3). MS (70 eV): m/z (relative intensity) 466 (8) [M$^+$], 451 (70) [M$^+$ − Me], 409 (40) [M$^+$ − *t*Bu], 73 (100) [SiMe$_3^+$], 57 (70) [*t*Bu$^+$]. $C_{26}H_{48}FPSi_2$ (466.30): found, 466.3018; calcd, 466.3016.

Preparation of 19. A 0.24 g (2.2 mmol) portion of chlorotrimethylsilane was added at −78 °C to a solution of 2 mmol of the LiF carbenoid **17**[16] in 5 mL of THF. After 5 min the solution was warmed to room temperature and the solvent removed under vacuum. The residue was taken up in pentane and subsequently filtered through Celite. After evaporation of the solvent, **19** was obtained as an orange oil. Yield: 1.03 g (96%). ^{31}P{^{1}H} NMR (THF): δ 133.4 (d, ^2J(P,F) = 39.4 Hz). ^{1}H NMR (C_6D_6): δ 7.51 (d, ^4J(H,P) = 4.3 Hz, 2H, *m*-Ar), 1.73 (d, ^5J(H,P) = 0.4 Hz, 18H, *o-t*Bu), 1.17 (s, 9H, *p*-tBu), 0.52 (d, J(H,F) = 2.8 Hz, 9H, Si(CH$_3$)$_3$), 0.11 (s, 9H, Si(CH$_3$)$_3$), −0.17 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 156.9 (dd, ^2J(C,P) = 7.0 Hz, ^4J(C,F) = 2.3 Hz, *o*-Ar), 154.6 (d, ^4J(C,P) = 3.2 Hz, *p*-Ar), 149.2 (dd, ^1J(C,F) = 201.4 Hz, ^1J(C,P) = 3.0 Hz, P═CSiF), 125.8 (d, ^3J(C,P) = 12.1 Hz, *m*-Ar), 119.8 (dd, ^1J(C,P) = 85.4 Hz, ^3J(C,F) = 3.6 Hz, *ipso*-Ar), 53.2 (dd, ^1J(C,P) = 36.1 Hz, ^3J(C,F) = 2.2 Hz, P═CSi$_2$), 40.9 (d, ^3J(C,P) = 2.5 Hz, *o*-CMe$_3$), 35.5 (d, ^5J(C,P) = 1.1 Hz, *p*-CMe$_3$), 35.1 (s, *o*-CCH$_3$), 31.3 (s, *p*-CCH$_3$), 4.7 (d, ^3J(C,P) = 4.4 Hz, SiC_3), 4.3 (dd, J = 7.0 Hz, J = 4.5 Hz, SiC_3), −1.3 (dd, J = 2.9 Hz, J = 2.1 Hz, SiC_3). MS (70 eV): m/z (relative intensity) 538 (10) [M$^+$], 523

(30) [$M^+ - Me$], 481 (25) [$M^+ - t$Bu], 73 (100) [$SiMe_3^+$], 57 (45) [$t$$Bu^+$]. $C_{29}H_{56}FPSi_2$ (538.34): found, 538.3415; calcd, 538.3419.

X-ray Crystallographic Studies of 7b, 13, 15, 17, and 18. The structures were solved by direct methods (SHELXS-97; G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473) and refined anisotropically on F^2 (SHELXL-97; G. M. Sheldrick, Universität Göttingen, 1997; and SHELXL-93 for **15** (G. M. Sheldrick, Universität Göttingen, 1993), respectively). H atoms were localized by electron density determination and refined using a riding model. In **15** an extinction correction was applied. Further details are given in Table 1.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Full tables of crystal data, final atomic coordinates, anisotropic thermal parameters, complete positional parameters, and bond distances and angles for **7b**, **13**, **15**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020319N