A Carbene•Phosphinidene Adduct: "Phosphaalkene"[1]

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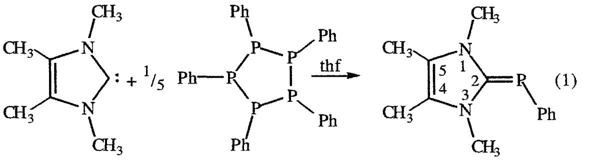
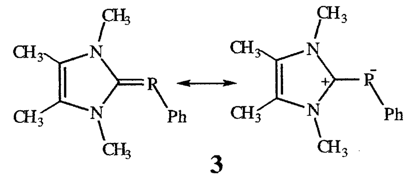
(Received October 15, 1996)

The synthesis, characterization and X-ray crystallographic structure determination are described for a "phosphaalkene" formally derived from 1,3,4,5-tetramethylimidazol-2-ylidene and phenylphosphinidene. This carbene•phosphinidene adduct has a central P-C bond length of 179.4 pm and a dihedral twist of 46° which indicates a very weak C-P pπ-pπ interaction. The valence angle at phosphorus is 102.3°.

Our original interests in stable nucleophilic carbenes arose from the synthesis of imidazol-2-thiones which are formed by the reaction of these carbenes with cyclooctasulfur.[2-6] We wondered if this type of reaction could be extended to the pnictogen family (group 15 elements) and possibly provide a synthesis of phosphaalkenes.



1 **2** **3**



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We have discovered that carbene **1**[7] reacts with pentaphenylcyclopentaphosphane (**2**) to form the carbene•phosphinidene adduct **3** (eq. 1).[8] Adduct **3** is a light yellow solid that melts without decomposition at 181-185 °C. The $^{31}P\{^1H\}$ NMR spectrum of **3** in thf-d_8 exhibits a single resonance at δ -53.5 upfield of 85% phosphoric acid. This resonance is high field for a 2-coordinate phosphorus center but it is consistent with the high electron density present at phosphorus in a strongly polarized phosphaalkene. The ^{13}C chemical shift for the former carbene center in **3** is δ 169 (44.7 ppm upfield of the resonance in **1**). Interestingly, this ^{13}C chemical shift is remarkably similar to the imidazol-2-thiones which typically have a resonance for C_2 that is about δ 161.9.[2] The C_2 center in **3** is also spin-coupled to the phosphorus center ($^1J_{C\text{-}P}$ = 97.95 Hz). The *ipso*-carbon of the phenyl substituent on phosphorus (δ 150.6) shows the only other 1-bond phosphorus spin-coupling in **3** but with a value of 49.72 Hz it is substantially smaller than the coupling to the former carbene center. The resonance for $C_{4(5)}$ of the imidazole ring of **3** (δ 123.8) is very similar to the value in the starting carbene, **1**, but shows a small (3.44 Hz) 4-bond coupling to phosphorus. In the ^1H NMR spectrum of **3** the signals for the imidazole ring methyls shift about 0.1 ppm relative to their positions in the carbene but in opposite directions. The resonance at δ 2.13 (CCH_3) is downfield of that for the carbene and the resonance at δ 3.37 (NCH_3) is upfield of its position in the carbene. The observation of only single NCH_3 and CCH_3 signals indicates that there is rapid rotation on the NMR timescale about the C_2-P bond. The ^{15}N NMR spectrum of **3** reveals an upfield shifted resonance for the nitrogen center (δ -219.7) relative to carbene **1** (δ -198.5) and shows a 2.1 Hz 2-bond coupling to the phosphorus.

A crystal of **3** was grown from tetrahydrofuran (thf) solution by cooling to -25 °C. The X-ray crystal structure of **3**[9] is depicted by the KANVAS[10] drawing in Figure 1. Representative bond lengths and angles are presented in Table 1 along with values for related structures.

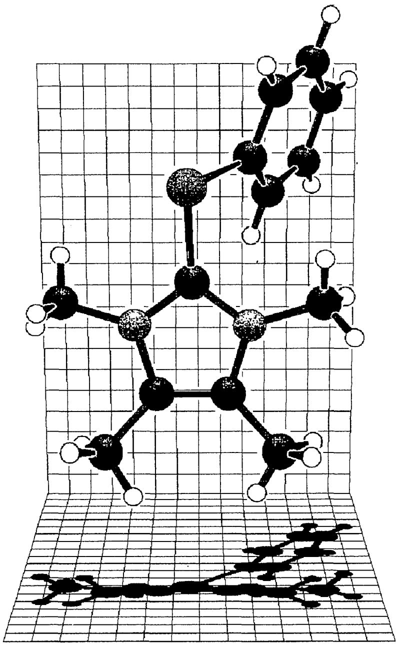


Figure 1. KANVAS[10] drawing of the structure of adduct **3**.

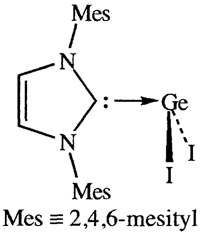
Table 1. Selected bond lengths (pm) and angles (deg.) in **3** and related structures[a]

Property	**1•HCl**[b]	**1**[c]	**3**
r(C2-X)	91.6	-	179.4 (3)
r(C2-N1(3))	132.6, 132.4	136.3	136.5 (4), 136.1 (4)
r(C4-C5)	135.8	135.2	134.4 (4)
r(N1(3)-C5(4))	139.0, 139.3	139.4	139.2 (4), 139.3 (3)
r(N1(3)-CH3)	146.5, 146.2	145.4	145.6 (4), 146.4 (4)
r(C4(5)-CH3)	148.7, 148.3	149.0	148.0 (4), 146.6 (4)
θ(N1-C2-N3)	108.7	101.5	104.7 (2)
θ(N1(3)-C2-X)	126, 125	-	124.7 (2), 130.2 (2)
θ(C5(4)-N1(3)-C2)	109.1, 108.9	113.5	110.5 (2), 110.7 (2)
θ(N1(3)-C5(4)-C4(5))	106.5, 106.7	105.8	107.1 (2), 106.9 (2)
θ(C2-N1(3)-CH3)	124.7, 124.5	122.9	124.9 (3), 124.8 (3)
θ(N1(3)-C5(4)-CH3)	121.9, 121.7	122.8	122.2 (3), 122.0 (3)

[a] The numbering scheme for all compounds is as indicated for **3**.
[b] See Reference 12. [c] See Reference 7.

The C-P-C angle in adduct **3** is 102.3°. This angle is smaller than would be expected for an ideally sp^2 hybridized phosphorus center but it is in the range of angles found for simple (not strongly polarized) phosphaalkenes.[11] The P-C_2 bond to the imidazole ring is 179.4 pm and is only slightly shorter than the P-C bond to the phenyl substituent (181.7 pm). This P-C_2 bond length is long for typical phosphaalkenes[11] indicating that the C=P double bond is not well developed and that this bond is strongly polarized as suggested by the NMR data. Another geometric indication of the polarization of the C_2=P bond is the 46° twist between the plane of the imidazole ring and the P-$C_{(phenyl)}$ bond. This twist is very evident in the shadow of the KANVAS drawing in Figure 1. The geometric data in Table 1 reveal a geometry for the imidazole ring in **3** that is intermediate between the carbene **1**[7] and 1,3,4,5-tetramethylimidazolium chloride (**1•HCl**).[12]

Although it is intermediate, the imidazole ring structure in **3** is remarkable close to that of the carbene **1**. The largest change in the geometry of the imidazole ring is the N_1-C_2-N_3 angle (104.7°) which is not as relaxed as the angle of 108.9° that is observed for the imidazolium ion. A very similar "intermediate" type of imidazole geometry was observed for the carbene-GeI_2 adduct **4**[13] and similarly suggests that the structure of **3** can be considered to be a carbene coordinated to a phosphinidene center with incomplete transition to a phosphaalkene type of bonding arrangement. This 'carbene-solvated-phosphinidene' structure is illustrated by structure **5**. The bonding in structure **5** explains both the retention of carbene-like structure in the imidazole ring of **3** and the absence of strong π-bonding character in the C_2-P bond.



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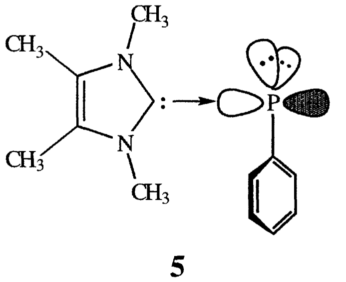

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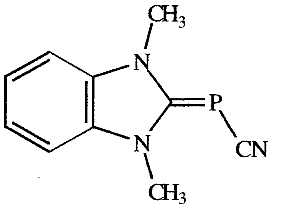
Two other related phosphaalkenes with strongly electron releasing groups on carbon, **6**[14] and **7**[15], were previously synthesized by indirect routes. Although no X-ray structure was reported for **7**, the available NMR data and the structure reported for **6** suggest these molecules have similar bonding arrangements to that observed in **3**.



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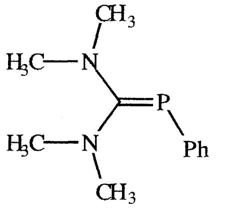

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The authors are indebted to F. Davidson for his work on the NMR spectroscopy of **3**. The excellent technical assistance of H. A. Craig and W. Marshall made the experimental work possible.

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† DuPont Visiting Research Scientist 1990-2.
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8 1,3,4,5-Tetramethylimidazol-2-ylidene (**1**) (1.00 g, 8.05 mmol) was dissolved thf (30 mL) and pentaphenylcyclopentaphosphane (**2**) (0.87 g, 8.05 mmol) was added as a single portion at room temperature. The solution immediately became deep red. After 10 minutes a yellow precipitate formed. The mixture was stirred for an additional 2 h, filtered and the precipitate was rinsed once with diethyl ether to obtain pure **3**, 1.47 g, 79% yield, mp 181-185 °C. Adduct **3** can be recrystallized from hot thf. ^1H NMR (C_6D_6): δ 1.25 (s, 6 H, CH_3), 3.02 (s, 6 H, NCH_3), 6.94 (m, 1 H, *p*-Ph), 7.14 (m, 2 H, *m*-Ph), 7.62 (m, 2 H, *o*-Ph); ^1H NMR (thf-d_8): δ 2.13 (s, 6H, CH_3), 3.37 (s, 6H, NCH_3), 6.66 (m, 1H, *p*-Ph), 6.86(m, 2H, *m*-Ph), 7.02 (m, 2H, *o*-Ph); $^{13}C\{^1H\}$ NMR (thf-d_8): δ 8.92 (s, CCH_3), 33.85 (d, $^3J_{C\text{-}P}$ = 10.34 Hz, NCH_3), 121.58 (s, *para*-C), 123.80 (d, $^3J_{C\text{-}P}$ = 3.44 Hz, $NCCH_3$), 127.68 (d, $^3J_{C\text{-}P}$ = 5.42 Hz, *meta*-C), 132.22 (d, $^2J_{C\text{-}P}$ = 19.20 Hz, *ortho*-C), 150.57 (d, $^1J_{C\text{-}P}$ = 49.72 Hz, *ipso*-C), 169.08 (d, $^1J_{C\text{-}P}$ = 97.95 Hz, NCN); $^{31}P\{^1H\}$ NMR (thf-d_8): δ -53.5; $^{15}N\{^1H\}$ NMR (thf-d_8): δ -219.7 (d, $^2J_{N\text{-}P}$ = 2.1 Hz); Anal. Calcd for $C_{13}H_{17}N_2P$: C, 67.23; H, 7.38; N, 12.06%. Found: C, 67.24; H, 7.32; N, 11.99%.
9 Crystal data for **3** at -70 °C with Mo Kα radiation: a = 1556.5 (3), b = 687.3 (2), c = 1258.0 (3) pm, β = 112.20 (3)°, monoclinic, $P2_1/c$, Z = 4, μ(Mo) = 1.90 cm^{-1}, 1367 unique reflections with I > 3σ(I). Dc = 1.238 g/cc. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F including anomalous terms for phosphorus. Phosphorus, carbon and nitrogen were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters. The data to parameter ratio was 6.42. The largest residual electron density in the final difference Fourier map was 0.25 e/$Å^3$ near the *ipso*-carbon of the phenyl ring. The error of fit was 1.51 and the maximum shift in the last least-squares cycle was 0.01. The final R factors were R = 0.038 and R_w = 0.042. Further details of the crystal structure have been deposited with the Cambridge Crystallographic Data Centre.
10 This drawing was made with the *KANVAS* computer graphics program. This program is based on the program *SCHAKAL* of E. Keller (Kristallographisches Institut der Universität Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.
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