

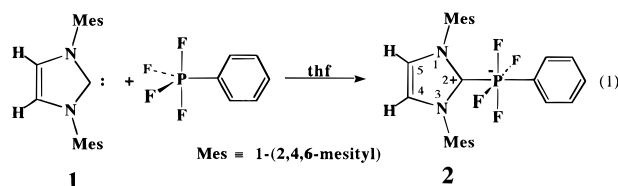
A Carbene–Phosphorus(V) Adduct

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Received November 27, 1996

The isolation of stable crystalline carbenes^{4,5} has led to a renaissance in the chemistry of these interesting compounds. A number of new and interesting adducts of these carbenes have been recently reported.⁶ These carbenes represent carbon compounds in oxidation state II and as such are good reducing agents. In a reflection of this reducing potential most of the imidazol-2-ylidene adducts that have been isolated so far are derived from oxidatively stable or low oxidation state element centers (*e.g.*, P(I), S(0), I(I), Ni(0), *etc.*). We now report the synthesis and structure of the first carbene complex of a phosphorus(V) center (**2**). Perphosphoranide (**2**) is formed in quantitative yield by the direct reaction of the stable imidazol-2-ylidene **1**⁵ with phenyltetrafluorophosphorane in thf (tetrahydrofuran) solution (eq 1).⁷



Compound **2** is a stable colorless solid, melting at 148–149 °C. The ³¹P NMR spectrum shows a quintet at δ –141.06 with ¹J_{PF} = 860.70 Hz. This ³¹P shift is 91 ppm upfield of C₆H₅PF₄ (δ –50.0 CD₂Cl₂) consistent with the 6-coordinate perphosphoranide center. A smaller average one-bond P–F spin-coupling is observed for **2** compared with that for C₆H₅PF₄ (¹J_{PF}

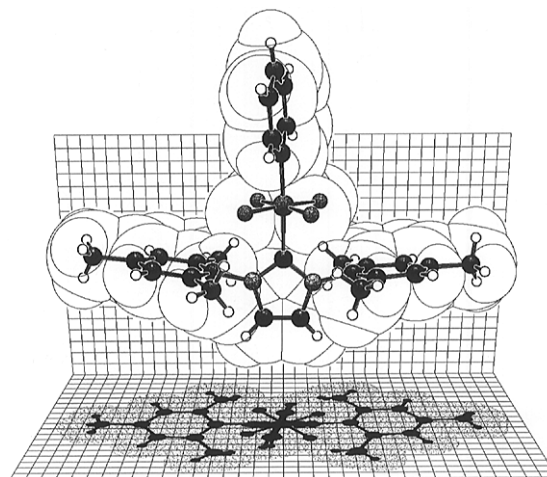


Figure 1. KANVAS⁹ drawing of the X-ray structure of **2**.

= 962.76 Hz) which suggests a decrease in the s-orbital character of the P–F bonds (on average) for **2**. The ¹⁹F resonance in **2** occurs as a doublet at δ –42.55 (¹J_{PF} = 861.04 Hz). The ¹³C NMR signal for C₂ of **2** (δ 164.7) appears 55 ppm upfield from the free carbene (δ 219.7) as a doublet of quintets (¹J_{CP} = 305.79 Hz and ²J_{CF} = 71.92 Hz). The *ipso*-carbon of the phenyl is the only other carbon that is directly attached to phosphorus and shows a ¹³C chemical shift of δ 149.8 with couplings to ³¹P (¹J_{CP} = 292.36 Hz) and ¹⁹F (²J_{CF} = 41.99 Hz). The two-bond ¹⁹F spin-coupling observed at C₂ is almost twice that observed to the phenyl *ipso*-carbon but the one-bond phosphorus couplings are similar for these two carbons that are directly attached to phosphorus. For comparison, the value of ¹J_{PC} in C₆H₅PF₄ is 265.14 Hz. The ¹H NMR spectrum of **2** (thf-*d*₈) shows a doublet for the H_{4,5} imidazole ring protons at δ 7.26 (⁴J_{HP} = 2.31 Hz). This signal is shifted downfield from the corresponding resonance in **1** (δ 7.02).⁵ In the ¹⁵N NMR of **2**, a doublet of quintets is observed at δ –191.2 (²J_{NP} = 7.94 Hz and ²J_{CF} = 1.42 Hz) upfield of the resonance in **1** (δ –178.9).

Crystals of **2** suitable for X-ray crystallographic studies were obtained from a CH₂Cl₂/toluene solution (1:4) at 23 °C.⁸ The X-ray crystal structure of **2** is illustrated by the KANVAS⁹ drawing in Figure 1. Selected bond lengths and angles are given in Table 1. Two crystallographically unique molecules of **2** are found in the X-ray structure but these molecules are essentially identical. In subsequent discussion the structural data from the second molecule appear in square brackets.

The structure of **2** shows the expected octahedral geometry at the phosphorus center. The C₂–P bond distance [191.0 [191.0] pm] is surprisingly long considering the large ¹³C–³¹P spin-coupling observed in the NMR spectrum. The C–P bond to the *ipso*-carbon of the phenyl substituent [184.2 [184.3] pm]

(7) In a drybox, a 50 mL flask was charged with 400 mg (1.31 mmol) of 1,3-dimesitylimidazol-2-ylidene and 25 mL of thf. To this solution was added 290 mg (1.31 mmol) phenyltetrafluorophosphorane. The reaction mixture was stirred for 5 min. The solvent and volatiles were removed *in vacuo* to give the crude product **2** as a pale yellow solid (640 mg, 100% yield). The crude product was recrystallized from dichloromethane/toluene (1:4) to give the pure product as colorless crystals: (mp 148–149 °C); ¹H NMR (thf-*d*₈) δ 2.12 (s, 12 H, *o*-CH₃), 2.27 (s, 6 H, *p*-CH₃), 6.90 (m, 3 H, Ph-H_{3,4,5}), 6.93 (s, 4 H, Mes-H_{3,5}), 7.26 (d, 2 H, ⁴J_{HP} = 2.31 Hz, Im-H_{4,5}), 7.24–7.33 (dm, 2 H, Ph-H_{2,6}); ¹⁹F{¹H} NMR (thf-*d*₈) δ –42.55 (d, ¹J_{FP} = 861.04 Hz); ¹³C{¹H} NMR (thf-*d*₈) δ 17.95 (quint, ⁶J_{CF} = 1.86 Hz, *o*-CH₃), 21.14 (s, *p*-CH₃), 123.78 (d, ³J_{CP} = 8.54 Hz, Im C_{4,5}), 126.65 (d, ³J_{CP} = 20.18 Hz, Ph C_{3,5}), 126.96 (d, ⁴J_{CP} = 3.70 Hz, Ph C₄), 129.24 (s, Mes C_{3,5}), 131.53 (dq, ²J_{CP} = 10.99 Hz, ³J_{CF} = 3.66 Hz, Ph C_{2,6}), 135.90 (s, Mes C_{2,6}), 137.23 (s, Mes C₁), 139.32 (s, Mes C₄), 149.84 (dq, ¹J_{CP} = 292.36 Hz, ²J_{CF} = 41.99 Hz, Ph C₁), 164.73 (dq, ¹J_{CP} = 305.79 Hz, ²J_{CF} = 71.92 Hz, Im C₂); ³¹P{¹H} NMR (thf-*d*₈) δ –141.06 (quint, ¹J_{PF} = 860.40 Hz); ¹⁵N{¹H} NMR (thf-*d*₈) δ –191.28 (dq, ²J_{NP} = 9.6 Hz, ³J_{NF} = 1.3 Hz). Anal. (C₂₇H₂₉F₄N₂P) C, H, N, P, F.

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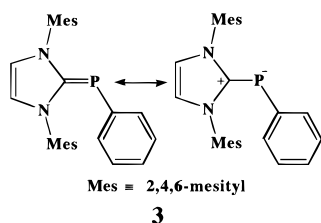
Table 1. Selected Bond Lengths (pm) and Angles (deg) in **2** and Related Structures^a

property	1·HCl ^b	1 ^c	2	3
<i>r</i> (C ₂ –P)			191.0(4) [191.0(4)]	176.3(6)
<i>r</i> (P–C _{Phenyl})			184.2(4) [184.3(4)]	183.9(5)
<i>r</i> (C ₂ –N ₁₍₃₎)	133.2(5), 131.9(5)	136.5(4), 137.1(4)	135.1(4), 135.5(4) [135.5(4), 135.1(4)]	136.9(7), 137.8(7)
<i>r</i> (C ₄ –C ₅)	135.3(6)	133.1(5)	131.7(6) [130.8(5)]	131.8(9)
<i>r</i> (N ₁₍₃₎ –C ₅₍₄₎)	138.5(5), 138.2(5)	138.1(4), 137.8(4)	137.5(5), 138.8(5) [138.3(4), 137.9(5)]	139.3(8), 139.1(8)
<i>r</i> (N ₁₍₃₎ –C _{Mes})	145.6(5), 144.5(5)	144.1(4), 144.2(4)	145.1(4), 144.6(4) [145.0(4), 145.7(4)]	144.0(7), 144.7(7)
θ (C ₂ –P–C _{Phenyl})			177.2(2) [178.4(3)]	99.9(3)
θ (N ₁ –C ₂ –N ₃)	108.7(4)	101.4(2)	105.0(3) [105.1(3)]	104.0(5)
θ (N ₁₍₃₎ –C ₂ –P)			128.9(3), 126.1(3) [127.0(3), 127.8(3)]	123.2(5), 132.8(5)
θ (C ₅₍₄₎ –N ₁₍₃₎ –C ₂)	109.0(4), 108.7(4)	112.8(3), 112.8(3)	110.1(4), 109.9(3) [109.5(3), 110.0(3)]	110.4(5), 110.2(5)
θ (N ₁₍₃₎ –C ₅₍₄₎ –C ₄₍₅₎)	106.1(4), 107.5(4)	106.5(3), 106.5(3)	108.0(4), 107.0(4) [107.8(4), 107.6(4)]	107.7(7), 107.7(7)
θ (C ₂ –N ₁₍₃₎ –C _{Mes})	125.8(4), 127.1(4)	121.8(2), 122.6(2)	130.0(3), 131.2(3) [130.9(3), 130.9(3)]	125.2(5), 127.0(5)

^a The numbering scheme for all compounds is as indicated for **2**. ^b See ref 60. ^c See ref 5.

resembles a normal P–C single bond. The C₂–P–C_{phenyl} angle is 177.2° [178.4°]. The four fluorines form a good plane with no fluorine deviating more than 0.5 [0.2] pm. The phosphorus center is only 6.1 [6.3] pm out of the plane of the four fluorines and is displaced toward the phenyl substituent. The imidazole ring is planar to within 0.1 [0.5] pm. Both nitrogens are also essentially planar with N₁ being 3.5 [0.4] pm out of the plane of its three attached atoms and N₃ being 0.1 [6.3] pm out of the plane of its three attached atoms. The N–C–N angle at the former carbene center (105.0° [105.1°]) is intermediate between those in the free carbene **1** (101.4°) and 1,3-dimesitylimidazolium chloride (1·HCl, 108.7°).⁶⁰

Another phosphorus adduct of the carbene **1** has been recently reported.^{6p} This adduct is the phenylphosphinidene·carbene adduct **3**. Compounds **3** and **2** differ by the oxidation state at phosphorus such that **2** is the formal addition product of 2 mol of fluorine to **3**. The two structures make an interesting comparison possible.



The ³¹P resonance in **2** (δ –141.1) is at substantially higher field than the value in **3** (δ –23.0), as expected for the change from a 2-coordinate to a 6-coordinate phosphorus center. The ¹³C chemical shifts at the former carbene centers are similar (**2**, δ 164.7; **3**, δ 170.0) but there is a difference in the one-bond spin-couplings. The C₂–P spin-coupling in **3** is only 102.8 Hz compared to the value of 305.9 Hz in **2**. To the extent that s-orbital character at the phosphorus center of **3** is used to stabilize the lone pair(s) of electrons at phosphorus, the remaining P–C bonds would have a relatively large p-orbital component from phosphorus. The higher one-bond C₂–P spin-coupling in **2** relative to **3** may indicate an increase in the phosphorus s-orbital component of this bond through an approximate sp-hybridization at phosphorus. In this arrangement, the two carbon substituents are bonded to phosphorus by the sp-orbitals and the four fluorines are bonded by two orthogonal sets of 3-center, 4-electron bonds at phosphorus utilizing the two remaining phosphorus p-orbitals. This arrangement is consistent with both the C–P and F–P spin-couplings.

The ¹⁵N NMR resonance in **3** occurs at δ –219.7, about 28.5 Hz upfield of the resonance in **2**, but shows a similar (7.3 Hz) coupling to phosphorus. The imidazole ring protons in **2** are about 0.5 ppm further downfield than in **3** (δ 6.69). This Δδ would be indicative of more imidazolium ion character in **2** relative to **3**. The *ortho*-methyls of the mesityl substituents in

2 resonate at δ 2.12 and those in **3** are similar with a chemical shift of δ 2.16. The *para*-methyls are slightly more differentiated between **2** and **3** with values of δ 2.27 and 2.17, respectively.

The structures of **2** and **3** differ quite substantially in the vicinity of the phosphorus centers. Whereas **2** possesses an essentially linear C–P–C arrangement at an octahedrally coordinated phosphorus, the C–P–C angle in **3** is an acute 99.9°. The C₂–P bond in **2** (191.0 pm) is substantially longer than observed in **3** (176.3 pm). This increase in bond distance to phosphorus is consistent with the increased coordination number at phosphorus in **2** relative to **3** but it is somewhat at odds with the corresponding ¹³C–³¹P spin-coupling which is approximately three times larger in **2** than **3**. The P–C bonds to the phenyl substituents in **2** and **3** are approximately the same lengths, but this one-bond ¹³C–³¹P spin-coupling is about seven times larger in **2** than **3** (42.3 Hz). This spin-coupling would again favor the sp-hybridization description for **2**. The geometries in the imidazole rings of **2** and **3** are similar but this ring in **2** is more planar than in **3**. The nitrogens (especially N₃, syn to the phenyl substituent) tend to be more pyramidal in **3** than **2**. The C–N bond distances also tend to be slightly shorter in **2** than **3**.

As a whole this structural and NMR data suggest that the imidazole moiety in **2** possesses more imidazolium-like character while the imidazole ring in **3** retains some of its carbene character. The depiction of the valence bond structure of **2** as zwitterionic (eq 1) is consistent with this trend. Further work is in progress in our laboratories on other adducts of these nucleophilic carbenes with high oxidation state element centers.

Acknowledgment. The authors are indebted to Fredric Davidson for his work on the NMR spectroscopy of **2** and to Dr. Jens R. Goerlich for his assistance with the analyses of **2**. A.J.A. gratefully acknowledges the support of the Alexander von Humboldt Stiftung through a Senior Research Prize that made this work possible.

Supporting Information Available: A complete description of the X-ray crystallographic structure determination on **2** including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and an ORTEP drawing (14 pages). See any current masthead page for ordering and Internet access instructions.

JA964094H

(8) Crystal data for **2** at –70 °C with Mo Kα radiation (Enraf-Nonius CAD4 diffractometer): *a* = 1502.2(2), *b* = 2129.0(4), and *c* = 1728.0(4) pm, β = 113.21(2)°, monoclinic, *P*2₁/*n*, *Z* = 8, μ(Mo) = 1.49 cm^{–1}, *V* = 488.52, *V* = 5079.2 Å³, *D*_c = 1.278. The final *R* factors were *R* = 0.043 and *R*_w = 0.036. Error of fit = 1.22, max Δ/σ = 1.36, largest residual density = 0.23 e/Å³. Further details of the crystal structure are available in the Supporting Information.

(9) 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.