Carbene−Pnictinidene Adducts

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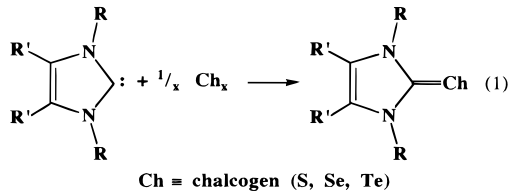
The syntheses, characterizations, and X-ray crystallographic structure determinations are described for adducts of stable nucleophilic carbenes with pnictinidenes. The adducts between 1,3-dimesitylimidazol-2-ylidene and phenylphosphinidene, phenylarsinidene, (trifluoromethyl)phosphinidene, and (pentafluorophenyl)arsinidene are reported. These carbene−pnictinidene adducts are formed by the direct reaction of a stable nucleophilic carbene with the corresponding pnictinidene cyclic oligomers. The synthesis and structure of the adduct between 1,3-dimesitylimidazolin-2-ylidene and phenylphosphinidene from the reaction of 1,3-dimesitylimidazolin-2-ylidene with phenylphosphorus dichloride are also reported. These carbene−pnictinidene adducts possess strongly polarized pnictinidene−carbene bonds. The C−Pn−C angles are all typically small at 97−102°, and there is only a 4% shortening of the nominal Pn═C double bond compared to the Pn−C single bond to the second substituent on the pnictogen. The ^{31}P NMR shifts of the phosphorus adducts suggest strongly shielded phosphorus centers in accord with the polarized structures.

Introduction

The reaction of imidazol-2-ylidenes with cyclooctasulfur to produce imidazole-2-thiones (eq 1) was the source of our

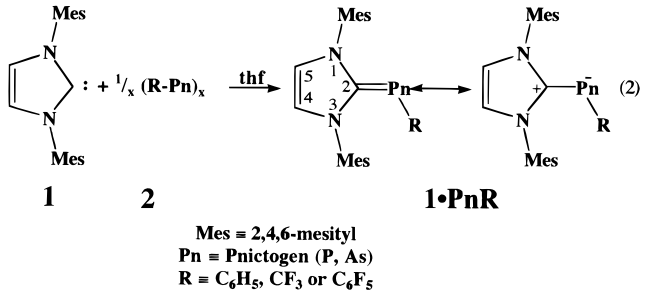


original interest in stable imidazol-2-ylidenes.[6−10] The imidazole-2-thiones obtained from these reactions have shown broad industrial applicability in catalysis.[7−10] It was demonstrated in our laboratory[6] as well as others[11,12] that the imidazol-2-ylidenes will also react with selenium and tellurium to produce selenones and tellurones.

By analogy with the chalcogens, it is possible that the cyclic oligomers of alkyl- or arylpnictinidenes will also react with these nucleophilic carbenes to directly produce carbene−pnictinidene adducts ("pnictaalkenes"). These carbene−pnictinidene adducts might also provide new alternatives to the imidazole-2-thiones as nucleophilic catalysts. We now report the results of our studies on these reactions.[13]

Results

The carbene 1,3-dimesitylimidazol-2-ylidene (**1**)[14] reacts with cyclic oligomers of pnictinidenes (**2**) to form the carbene−pnictinidene adducts (eq 2).



In the case of the reaction between the imidazol-2-ylidene (**1**) and pentaphenylcyclopentaphosphane (**2**, R= phenyl, Pn = phosphorus, $x = 5$), the product, **1·PPh**, is a dark yellow solid melting at 163−165 °C without decomposition. The ^{31}P{^{1}H} NMR spectrum of **1·PPh** in C_6D_6 exhibits a single resonance at δ −23.0 upfield of 85% phosphoric acid. This resonance is high field for a 2-coordinate phosphorus center but is consistent with the high electron density present at phosphorus in this strongly polarized "phosphaalkene". The ^{13}C chemical shift for the former carbene center in **1·PPh** is δ 170.0 (49.7 ppm upfield of the resonance for **1**). For comparison, the C_2 center in 1,3-dimesitylimidazole-2-thione resonates at δ 165.2.[15] The C_2 center in **1·PPh** is also spin-coupled to the phosphorus center ($^{1}J_{C-P}$ = 102.8 Hz). The other one-bond carbon−phosphorus spin-coupling in **1·PPh** is with the *ipso*-carbon of the phenyl

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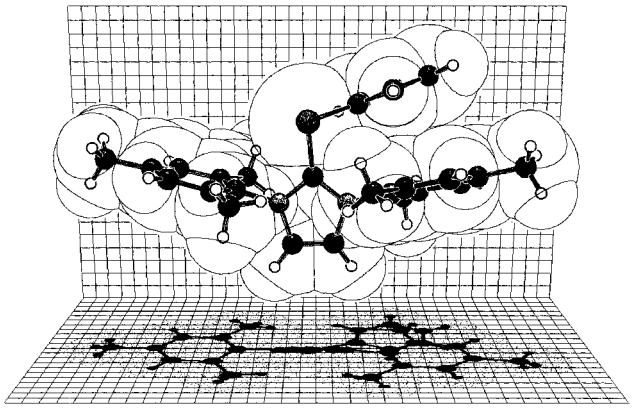

Figure 1. KANVAS[16] drawing of the X-ray structure of **1·PPh**.

substituent on phosphorus. This latter coupling, 42.3 Hz, is less than half the magnitude of the coupling to the former carbene center. The resonance for $C_{4(5)}$ of the imidazole ring of **1·PPh** (δ 119.8) is similar to the value for the starting carbene **1** (δ 121.3) but shows a small (3.8 Hz) four-bond coupling to phosphorus. In the ^{1}H NMR spectrum of **1·PPh** the signal for the imidazole ring hydrogens (δ 6.69) shifts by 0.35 ppm to higher field for **1·PPh** relative to the starting carbene. The signals for the *meta*-hydrogens on the mesityl rings of **1·PPh** are also in higher field positions (δ 6.70) relative to their positions in the spectrum of **1** (δ 6.94). The resonances for the *ortho*- and *para*-methyls of the mesityl rings in **1·PPh** are both shifted by about the same amount from their positions in the starting carbene spectrum although in opposite directions so that they are very close to one another. The signal for the *para*-methyls is shifted upfield of the carbene (δ 2.30 → 2.17), and the signal for the *ortho*-methyls in **1·PPh** is downfield of that for the carbene (δ 2.02 → 2.16). The mesityls appear equivalent to one another and are not differentiated from one face of the imidazole ring to the other, suggesting that there is rapid rotation on the NMR time-scale about the C_2-P bond. The ^{15}N NMR spectrum of **1·PPh** reveals an upfield-shifted resonance for the nitrogen center (δ −219.7) relative to carbene **1** (δ −178.9) and shows a 7.3 Hz two-bond coupling to the phosphorus.

Crystals of **1·PPh** suitable for X-ray diffraction structural determination were grown from toluene/hexane by cooling to −25 °C. The X-ray crystal structure of **1·PPh** is depicted by the KANVAS[16] drawing in Figure 1. Representative bond lengths and angles are presented in Table 1 along with values for related structures.

The C−P−C angle in **1·PPh** is 99.9°. An angle of 120° would be expected for an ideally sp^2-hybridized phosphorus center, but the small angle observed is in the range of angles found for simple (not strongly polarized) phosphaalkenes.[17−22] The $P-C_2$ bond to the imidazole ring is 176.3 pm. This phosphorus−imidazole bond is slightly shorter than the P−C bond to the phenyl substituent (183.9 pm). The $P-C_2$ bond length is long for typical phosphaalkenes[17−22] and suggests that double-bond character is not well developed between the C_2 and phosphorus centers. The lack of a strong $C_{p\pi}-P_{p\pi}$ interaction between phosphorus and the imidazole ring in **1·PPh** is also signaled by the 26.2° twist between the plane of the imidazole ring and the $P-C_{phenyl}$ bond. The shadow of the KANVAS drawing in Figure 1 clearly shows the phenyl substituent displaced to the right rear of the projection as a result of this twist. The imidazole ring in **1·PPh** is planar to within 0.8 pm, and the phosphorus atom is displaced 1.6 pm out of the imidazole plane. The phosphorus center is actually displaced more (7.4 pm) from the plane of the phenyl substituent (which is planar to within 0.3 pm) than from the imidazole plane. The nitrogens in **1·PPh** are both slightly pyramidal with N_3 9.4 pm out of the plane of its three attached atoms and N_1 2.5 pm out of the plane of its three attached atoms. The greater pyramidalization at N_3 can actually be seen in the shadow of the KANVAS drawing in Figure 1. This distortion at N_3 is probably influenced by steric interactions between the mesityl group at N_3 and the phenyl substituent on phosphorus.

For comparison against a maximally delocalized imidazole π-system, we have included the carbenium ion derived from **1** (1,3-dimesitylimidazolium chloride, **1·HCl**)[23] in Table 1. The geometry of the imidazole ring in **1·PPh** more closely resembles the carbene **1** than an imidazolium-like structure. The most obvious change in the geometry of the imidazole ring is the $N_1-C_2-N_3$ angle (104.0°), which is not fully relaxed to the angle of 108.7° that is observed for the imidazolium ion.

The reaction between nucleophilic carbenes and pnictinidene oligomers also occurs in the case of arsenic. Carbene **1** reacts with hexaphenylcyclohexaarsane (**2**, R = phenyl, Pn = arsenic, $x = 6$) to form the product **1·AsPh**. The arsinidene adduct **1·AsPh** is a yellow crystalline solid melting at 148−152 °C with decomposition. The ^{13}C chemical shift for the former carbene center in **1·AsPh** is δ 174.3 (C_6D_6), fairly similar to the value for **1·PPh** (δ 170.0, thf-d_8). The C_2 center in 1,3-dimesitylimidazole-2-selenone resonates at δ 159.5, which is about 14 ppm upfield of that of this arsenic analog (**1·AsPh**).[15] The resonance for $C_{4(5)}$ of the imidazole ring of **1·AsPh** (δ 120.7) is similar to the chemical shift observed for these carbons in **1·PPh** (δ 119.8). As with **1·PPh**, the signal for the imidazole ring hydrogens in **1·AsPh** (δ 6.08, C_6D_6) shifts to higher field ($\Delta\delta$ 0.4 ppm) relative to that of the starting carbene **1** (δ 6.48, C_6D_6). There is also no evidence for restricted rotation about the C_2-As bond in **1·AsPh** at room temperature, similar to the situation observed for **1·PPh**. Overall, the NMR spectral data for **1·AsPh** are quite similar to the data for **1·PPh**, which suggests that the structures and bonding schemes are also closely related.

Crystals of **1·AsPh** suitable for X-ray diffraction studies were grown from toluene by cooling to −15 °C. The X-ray crystal structure of **1·AsPh** is illustrated by the KANVAS[16] drawing in Figure 2. Representative bond lengths and angles are presented in Table 1 along with values for related structures.

The overall structure of **1·AsPh** is remarkably close to that of **1·PPh**, and the two X-ray structures are actually isomorphous. The C−As−C angle in **1·AsPh** is 97.3°. This angle is 2.6° smaller that the C−P−C angle in **1·PPh** but is consistent with

(16) 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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Table 1. Selected Bond Lengths (pm) and Angles (deg) in Carbene−Pnictinidene Adducts and Related Structures[a]

property	**1·HCl**[b]	**1**[c]	**1·PPh**	**1·AsPh**	**1·PCF$_3$**	**1·AsC$_6$F$_5$**	**3·PPh**
r(C$_2$−X)	94.4(30)		176.3(6)	189.9(3)	178.4(2)	190.2(7)	174.6(4)
r(X−subst)	241	183.9(5)	197.7(3)	184.5(2)	184.3(4)	197.6(7)	
r(C$_2$−N$_{1(3)}$)	133.2(5), 131.9(5)	136.5(4), 137.1(4)	136.9(7), 137.8(7)	137.3(3), 137.0(3)	137.0(2), 136.5(2)	136.1(8), 136.3(8)	135.2(5), 137.8(5)
r(C$_4$−C$_5$)	135.3(6)	133.1(5)	131.8(9)	133.8(4)	134.3(2)	134.4(10)	152.2(6)
r(N$_{1(3)}$−C$_{5(4)}$)	138.5(5), 138.2(5)	138.1(4), 137.8(4)	139.3(8), 139.1(8)	138.0(4), 139.5(4)	137.8(2), 139.0(2)	137.7(9), 139.3(9)	146.5(5), 146.9(5)
r(N$_{1(3)}$−C$_{Mes}$)	145.6(5), 144.5(5)	144.1(4), 144.2(4)	144.0(7), 144.7(7)	143.9(3), 144.6(3)	143.9(2), 144.6(2)	145.0(8), 145.7(8)	143.1(5), 143.2(5)
θ(C$_2$−X−subst)	170.7		99.9(3)	97.3(1)	101.66(8)	99.8(3)	100.5(2)
θ(N$_1$−C$_2$−N$_3$)	108.7(4)	101.4(2)	104.0(5)	104.2(2)	104.5(1)	104.6(6)	107.4(3)
θ(N$_{1(3)}$−C$_2$−X)	124(2), 127(2)		123.2(5), 132.8(5)	122.5(2), 133.3(2)	118.7(1), 136.7(1)	120.9(5), 134.1(5)	122.1(3), 130.5(3)
θ(C$_{5(4)}$−N$_{1(3)}$−C$_2$)	109.0(4), 108.7(4)	112.8(3), 112.8(3)	110.4(5), 110.2(5)	110.6(2), 110.5(2)	110.9(1), 110.1(1)	111.3(6), 110.0(5)	113.1(3), 111.2(3)
θ(N$_{1(3)}$−C$_{5(4)}$−C$_{4(5)}$)	106.1(4), 107.5(4)	106.5(3), 106.5(3)	107.7(7), 107.7(7)	107.8(3), 106.9(3)	107.0(2), 107.5(2)	106.7(6), 107.4(6)	101.9(3), 103.0(3)
θ(C$_2$−N$_{1(3)}$−C$_{Mes}$)	125.8(4), 127.1(4)	121.8(2), 122.6(2)	125.2(5), 127.0(5)	124.6(2), 127.6(2)	124.1(2), 128.6(2)	123.9(6), 126.1(6)	125.7(3), 127.0(3)

[a] The numbering scheme for all compounds is as indicated for **1·PPh**. [b] See ref 22. [c] See ref 14.

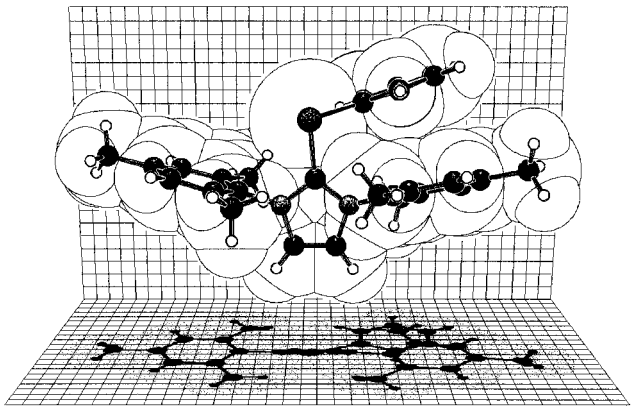


Figure 2. KANVAS[16] drawing of the X-ray structure of **1·AsPh**.

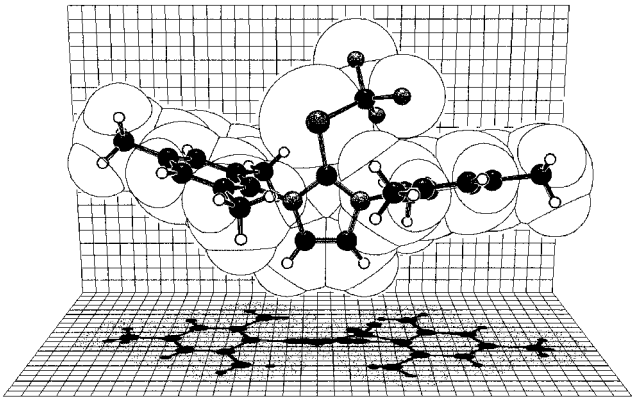


Figure 3. KANVAS[16] drawing of the X-ray structure of **1·PCF$_3$**.

the expected change as one moves to a heavier pnictogen. The C$_2$−As bond is 189.9 pm and is about 4% shorter than the As−C$_{phenyl}$ bond (197.7 pm), very similar to the situation in **1·PPh**. The 27.9° twist between the plane of the imidazole ring and the As-C$_{phenyl}$ bond indicates there is only a weak C$_{p\pi}$−As$_{p\pi}$ interaction between arsenic and the imidazole ring in **1·AsPh**. The imidazole ring in **1·AsPh** is planar to within 1.2 pm, and the arsenic center is displaced only 0.1 pm out of the imidazole best plane. As with **1·PPh**, the pnictogen center in **1·AsPh** is actually displaced more (1.0 pm) from the plane of the phenyl substituent (which is planar to within 0.8 pm) than from the imidazole plane. The nitrogens in **1·AsPh** are also slightly pyramidal (as for **1·PPh**) with N$_3$ 5.8 pm out of the plane of its three attached atoms and N$_1$ 3.7 pm out of the plane of its three attached atoms.

This reaction with cyclic pnictinidene oligomers is also successful with strongly electron-withdrawing groups on the pnictogen. The cyclic tetramer of (trifluoromethyl)phosphinidene (**2**, Pn = P, R = CF$_3$, x = 4) reacts smoothly with the imidazol-2-ylidene **1** to produce **1·PCF$_3$**. The carbene−(trifluoromethyl)phosphinidene adduct **1·PCF$_3$** is a yellow crystalline solid melting at 185−9 °C. The ^{31}P{^{1}H} NMR spectrum of **1·PCF$_3$** in C$_6$D$_6$ exhibits a single resonance at δ −23.6 upfield of 85% phosphoric acid. This resonance is strikingly similar to the phosphorus resonance of **1·PPh** (δ −23.0). The former carbene center in **1·PCF$_3$** exhibits a ^{13}C chemical shift of δ 168.1 (again similar to the value for **1·PPh**, δ 170.0). The phosphorus−carbon spin-coupling at C$_2$ ($^1J_{CP}$ = 100.5 Hz) is only 2.3 Hz smaller than that for **1·PPh**. The chemical shift of the ^{13}CF$_3$ center is δ 140.16 ($^1J_{CF}$ = 315.48 Hz, $^1J_{CP}$ = 90.49) . The positions of the remaining ^{13}C resonances for the 1,3-dimesitylimidazole group are all very similar to their positions in the spectrum of **1·PPh**. In the ^{1}H NMR spectrum of **1·PCF$_3$**, the positions of all of the proton chemical shifts are again very similar to their positions in the spectrum of **1·PPh**, with the largest differences being observed for the methyl substituents of the mesityl group. The signals of the *ortho*-methyls in **1·PCF$_3$** are about 0.2 ppm upfield of their positions in the spectrum of in **1·PPh**, and the signals of the *para*-methyls in **1·PCF$_3$** are about 0.1 ppm upfield of the corresponding resonances in the spectrum of **1·PPh**. Again, the equivalency of the mesityl substituents in **1·PCF$_3$** is consistent with a rapid rotation on the NMR time scale about the C$_2$−P bond.

Crystals of **1·PCF$_3$** were grown from a concentrated toluene solution at 23 °C. The X-ray crystal structure of **1·PCF$_3$** is presented in Figure 3. Representative bond lengths and angles are listed in Table 1 along with values for the related structures.

Although it is not isomorphous with those of the previous two pnictinidene−carbene adducts, the structure of **1·PCF$_3$** is quite similar. The C−P−C angle in **1·PCF$_3$** is 101.7°. This angle is somewhat larger than those observed in the previous two adducts and may reflect a greater steric influence of the trifluoromethyl group. The C$_2$−P bond is 178.4 pm, similar to its value in **1·PPh**. There is a 28.2° twist between the plane of the imidazole ring and the P−CF$_3$ bond, very similar to the values for the previous two structures. The imidazole ring in **1·PCF$_3$** is planar to within 0.5 pm, and the phosphorus center is displaced 7.7 pm out of the imidazole best plane. The nitrogens in **1·PCF$_3$** are again slightly pyramidal, with N$_3$ 5.0 pm out of the plane of its three attached atoms and N$_1$ 3.4 pm out of the plane of its three attached atoms.

The reaction at arsenic centers appears also to tolerate strongly σ-electron-withdrawing substituents on arsenic. The reaction of 1,3-dimesitylimidazol-2-ylidene (**1**) with tetrakis(pentafluorophenyl)cyclotetraarsane (**2**, Pn = As, R= C$_6$F$_5$, x = 4) proceeds smoothly to form the carbene−arsinidene adduct **1·AsC$_6$F$_5$** in 61% yield. The adduct **1·AsC$_6$F$_5$** is a yellow crystalline solid melting at 143−178 °C with decomposition. The ^{13}C{^{1}H} spectra of the carbene portions of **1·AsPh** and

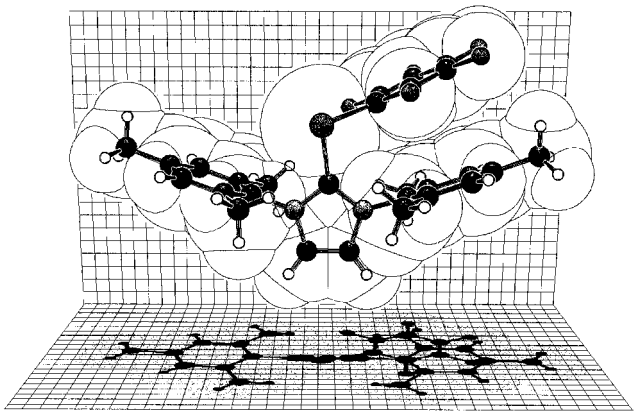


Figure 4. KANVAS[16] drawing of the X-ray structure of **1·AsC$_6$F$_5$**.

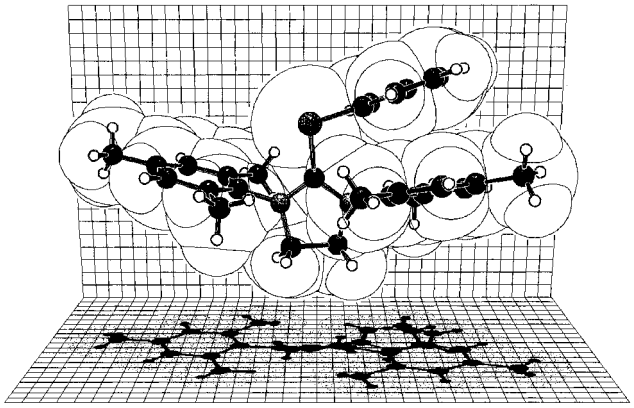
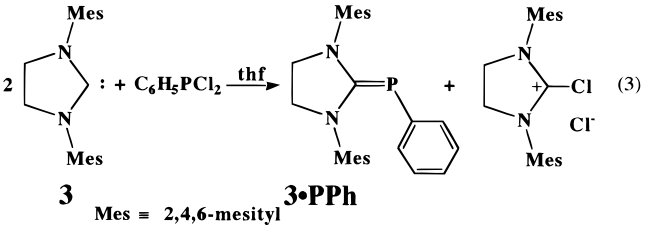


Figure 5. KANVAS[16] drawing of the X-ray structure of **3·PPh**.

1·AsC$_6$F$_5$ are strikingly similar in spite of the the great change in the electron demand of the substituent on arsenic. The position of the C_2 resonance of **1·AsPh** (δ 174.3) is only 2 ppm downfield of that of the same carbon in **1·AsC$_6$F$_5$** (δ 172.2). The ^{1}H NMR spectrum of the carbene fragment of **1·AsC$_6$F$_5$** is also little different from that of **1·AsPh**. Interestingly, the largest shift in the ^{1}H resonances occurs for $H_{4,5}$ of the imidazole ring and the position of this resonance for **1·AsC$_6$F$_5$** (δ 5.84) is actually upfield of that for **1·AsPh** (δ 6.08). One would have expected a shift for this proton resonance in the other direction if the pentafluorophenyl substituent had led to a more polarized C_2═As bond.

Crystals of **1·AsC$_6$F$_5$** suitable for an X-ray crystallographic structure determination were obtained from a concentrated hexane solution. The structure of **1·AsC$_6$F$_5$** is illustrated by the KANVAS[16] drawing in Figure 4 , and selected bond lengths and angles are included in Table 1. As had been suggested by the solution NMR data, the structures of **1·AsPh** and **1·AsC$_6$F$_5$** are very similar although they are not perfectly isomorphous.

The cyclic oligomers of pnictinidenes used in this study were prepared by reduction of higher oxidation state pnictogen compounds.[24−26] We have discovered that a separate reduction step is not necessary. It is possible to prepare carbene−phosphinidene adducts like those described above by direct reaction of a nucleophilic carbene with phenyldichlorophosphine. This reaction is illustrated in eq 3 for the saturated 1,3-dimesitylimidazolin-2-ylidene **3**.



The 2-chloro-1,3-dimesitylimidazolinium chloride byproduct is easily separated from the phosphinidene adduct **3·PPh** by filtration of a toluene/thf (4:1) solution. Evaporation of the solvent provides **3·PPh** as a yellow solid. The ^{31}P NMR (thf-d_8) spectrum of **3·PPh** shows a resonance at δ −12.0 (−10.4, C_6D_6). This phosphorus chemical shift is about 10 ppm downfield of the phosphorus resonance of **1·PPh**. The former carbene center in **3·PPh** resonates at δ 184.3 with a one-bond coupling to phosphorus of 86.7 Hz. This carbon shift is at 14 ppm lower field for **3·PPh** than for **1·PPh**, and the phosphorus−carbon spin coupling is 16 Hz smaller for **3·PPh** than for **1·PPh**. The *ipso*-carbon of the phenyl substituent on phosphorus in **3·PPh** has a chemical shift of δ 139.6 ($^1J_{CP}$ = 42.2 Hz), which is very similar to the value for **1·PPh** (δ 140.1, $^1J_{CP}$ = 42.3 Hz). The mesityl methyls (2, 4, and 6) show a single resonance in the ^{1}H NMR spectrum in thf-d_8 at δ 2.16. This methyl resonance is similar to those observed for **1·PPh**. The observation of similar shifts for the *ortho*-methyls in **1·PPh** and **3·PPh** is particularly noteworthy because these methyls are held in positions above and below the plane of the imidazol(in)e ring and can be expected to report on the anisotropy in the nitrogen heterocycle. Even though the saturation of the C_4-C_5 double bond in the imidazole is expected to lead to significant changes in the anisotropy of the imidazol(in)e ring in **3·PPh** relative to **1·PPh**, those changes are not observed. When C_6D_6 is used as a solvent, a comparable similarity is observed for the *ortho*-methyls (δ 2.29 for **3·PPh** and δ 2.23 for **3·PPh**). The singlets observed for the *ortho*-methyls in **3·PPh** again indicate a rapid rotation of the phenylphosphinidene group about the C_2-P bond in solution at room temperature, as has been observed for the other carbene−pnictinidene adducts.

Crystals of **3·PPh** for X-ray diffraction studies were grown by cooling a hexane solution to −25 °C. The X-ray crystal structure of **3·PPh** is shown in Figure 5. Representative bond lengths and angles are included in Table 1 along with values for the related structures.

The structure of **3·PPh** is again isomorphous with those of **1·PPh** and **1·AsPh**. As such, the structures of **3·PPh** and **1·PPh** are very similar except in the region of the C_4-C_5 bond. The C−P−C angle in **3·PPh** is 100.5°. The C_2-P bond is 174.6 pm and is again about 4% shorter than the $P-C_{phenyl}$ bond (184.3 pm). The 18.9° twist between the plane of the imidazole ring and the $P-C_{phenyl}$ bond is slightly smaller than those observed for the other three adducts. The imidazoline ring in **3·PPh** is not planar due to a twist about the C_4-C_5 single bond that places C_4 18.2 pm above and C_5 12.1 pm below the $N_1-C_2-N_3$ plane. The phosphorus center is 2.3 pm out of the plane of the $N_1-C_2-N_3$ group and 8.2 pm out of the plane of the phenyl substituent (which is planar to within 1.2 pm). The N_1 center in **3·PPh** is again slightly pyramidal (as in **1·PPh**) with this nitrogen 4.5 pm out of the plane of its three attached atoms. The N_3 nitrogen center (that is syn to the phenyl substituent on phosphorus) is moderately pyramidal and lies 13.8 pm out of the plane of its three attached atoms. The flexibility in the C_4-C_5 single bond probably contributes significantly to the ability of the nitrogens to pyramidalize.

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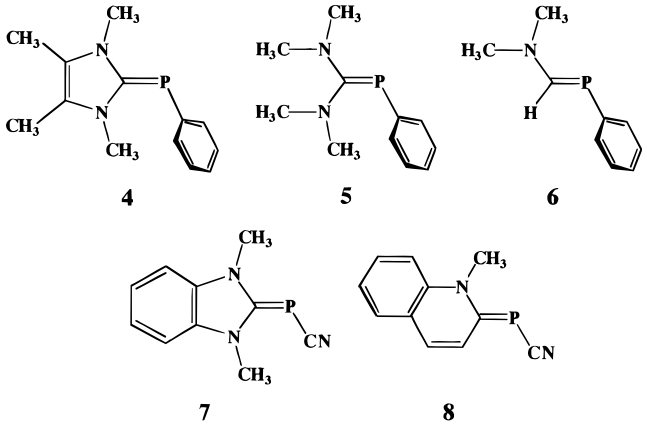
Discussion

The direct reaction of stable nucleophilic carbenes, imidazol-2-ylidenes, with cyclic oligomers of pnictinidenes is a convenient method for the preparation of carbene−pnictinidene adducts. This reaction appears to be analogous to the reaction between carbenes and chalcogens that leads to the formation of imidazole-2-chalcones (eq 1).[6−10] It has long been recognized that phosphines can be converted to phosphine sulfides by direct reactions between phosphines and cyclooctasulfur through a reaction that is somewhat analogous to that in eq 1. Similarly, it has been previously demonstrated that phosphines will react with certain cyclic phosphinidene oligomers to form phosphine−phosphinidene adducts (eq 4) through a reaction that is related to eq 2.[27,28] This analogy is most strongly evident for the synthesis of **1·PCF$_3$**.

$$R_3P + {}^1/_4\,(CF_3\text{-}P)_4 \longrightarrow R_3\overset{+}{P}\text{—}\overset{-}{P}(CF_3) \qquad (4)$$

The reaction of cyclic oligomers of phosphinidenes with imidazol-2-ylidenes produces "phosphaalkenes" that are strongly polarized. The ^{31}P NMR resonances for the two phosphinidene adducts derived from carbene **1**, **1·PPh** and **1·PCF$_3$**, are quite similar (δ −23.0 and −23.6, respectively). These shifts are at quite high field compared to those of typical (not strongly polarized) phosphaalkenes that normally show ^{31}P chemical shifts greater than δ 240.[17−22] The high-field positions of the phosphorus NMR signals of **1·PPh** and **1·PCF$_3$** (and **3·PPh**) are consistent with a high degree of shielding at the phosphorus center as a result of π-electron donation from the imidazole (and imidazoline) rings. The close similarity in chemical shifts between **1·PPh** and **1·PCF$_3$** may be coincidental but could also suggest that the phosphorus shift of these compounds is not strongly influenced by differences between the phenyl and trifluoromethyl substituents. We also note that the ^{13}C and ^{1}H NMR spectra of the carbene fragments in **1·AsPh** and **1·AsC$_6$F$_5$** are also very similar, further supporting the view that these compounds are not strongly influenced by the nature of the "single-bonded" substituent at the pnictogen center. On the other hand, when the phosphorus chemical shift of **1·PPh** is compared to that of **3·PPh** (which differ only by unsaturation in the imidazol(in)e ring) there is a noticeable difference. The **1·PPh** adduct shows a phosphorus chemical shift (δ −23.0) that is approximately 11 ppm upfield of the phosphorus resonance of **3·PPh** (δ −12.0). This difference is remarkable when one considers that changing the phenyl substituent to trifluoromethyl in **1·PPh** resulted in a $\Delta\delta$ of only 0.6 ppm. The phosphorus chemical shift difference between **1·PPh** and **3·PPh** is consistent with the imidazole ring being a more effective π-electron-releasing substituent than the saturated imidazoline ring. Indeed, we note that when the electron-releasing ability of the imidazole ring is further enhanced, the phosphorus chemical shift moves to even higher fields for similar carbene−phosphinidene adducts (*cf.* ^{31}P δ −53.5 for **4**).[13]

Compounds **4**,[13] **5**,[29] **6**,[29] **7**,[30] and **8**[30] represent other examples of strongly polarized "phosphaalkenes" that have been reported. The ^{31}P chemical shifts in the spectra of **5** and **6** would be expected to be downfield of those found for compounds derived from imidazoles or imidazolines if the trend with electron-releasing ability of the "ylidene" moiety continues. Furthermore, the shift for **6** would be expected to be downfield of that for **5**. Indeed, the ^{31}P chemical shifts reported for **5** and **6** are δ 28.6 and δ 69.5, respectively, consistent with these expectations.[29] The "phosphaalkenes" **7** and **8** appear to violate the trend between ^{31}P chemical shift and electron-releasing ability of the "ylidene" moiety. Both **7** and **8** show strongly shielded ^{31}P resonances (δ−133 and −38, respectively).[30] The upfield position of the ^{31}P resonance of **7** relative to that of **8** is consistent with the expectation of the benzimidazole group being more electron releasing than the quinoline group. However, the ^{31}P resonances of **7** and **8** are at higher field than observed for the imidazole series of compounds (**1·PPh** and **1·PCF$_3$**) although the imidazole group should be more electron releasing than either benzimidazole or quinoline. The seemingly anomalous positions of the ^{31}P chemical shifts of **7** and **8** relative to those of **1·PPh** and **1·PCF$_3$** may be the result of a strong shielding effect of the cyano group on phosphorus.



4 **5** **6** **7** **8**

The four adducts **1·PPh**, **1·AsPh**, **1·PCF$_3$**, and **1·AsC$_6$F$_5$** all show resonances for C_2 (the former carbene center) in the ^{13}C NMR spectra of about δ 170. The former carbene center in **3·PPh** resonates at a slightly lower field position, δ 184. The resonance for the corresponding carbon in **5** has been reported at even lower fields, δ 203. These trends in the ^{13}C NMR spectra seem to reflect those in the ^{31}P NMR spectra and are consistent with the expected electron-releasing ability of the "ylidene" moiety.

For all of the "pnictaalkene" structures reported here, the NMR data indicate that there is free rotation around the nominal Pn═C double bond in solution at room temperature. This also suggests a strongly polarized pπ−pπ interaction so that these "pnictaalkenes" possess considerable ylide character, as depicted by the last structure in eq 2. The solid state geometries of **1·PPh**, **1·AsPh**, **1·PCF$_3$**, **1·AsC$_6$F$_5$**, and **3·PPh** all show a twisting about the nominal Pn═C double bond that is consistent with this ylidic character. When compared to those of typical (not strongly polarized) phosphaalkenes,[17−22] the structures **1·PPh**, **1·PCF$_3$**, and **3·PPh** show slightly longer P═C "double" bonds. The few available C═As bond distances for acyclic arsaalkenes span the range 181.6−182.7 pm.[24,26,31,32] The nominal C═As double bond in **1·AsPh** (189.9 pm) is appreciably longer, as is the corresponding bond in **1·AsC$_6$F$_5$** (190.2 pm). We also note that the Pn═C "double" bonds in **1·PPh**, **1·AsPh**, **1·PCF$_3$**, and **3·PPh** are consistently only about 4% shorter than the Pn−C single bonds in these structures.

The importance of an ylidic structure in the polarized "pnictaalkenes" described here is not fully reflected by the extent

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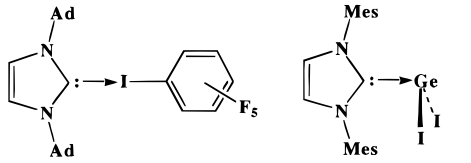
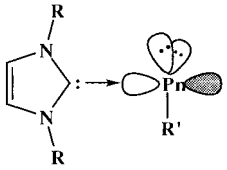
of the development of a delocalized imidazolium-like structure in the imidazole ring. Table 1 lists selected bond lengths and angles for **1·PPh**, **1·AsPh**, **1·PCF$_3$**, **1·AsC$_6$F$_5$**, and **3·PPh** and the reference structures for the carbene (**1**) and the imidazolium ion (**1·HCl**). Although the structures for **1·PPh**, **1·AsPh**, **1·PCF$_3$**, and **1·AsC$_6$F$_5$** clearly possess imidazole fragments with geometries between those of the carbene **1** and the maximally delocalized imidazolium **1·HCl**, the geometries more closely resemble that of the carbene. That is to say, some carbene structural character is preserved in these carbene−pnictinidene adducts. We previously observed this retention of carbene structural character in ylidic adducts formed between carbenes and other main group and transition metal centers. The adducts of nucleophilic carbenes with GeI_2 (**9**)[33] and iodopentafluorobenzene (**10**)[34] are two such examples.



9 **10**

The structure of **10** is derived from the coupling of a carbene center with a germylene center, but the transition to a planar germaalkene is incomplete and the final adduct retains some of the structural character of a earlier point on the non-least-motion coupling pathway.[33,35] In the same way, the structures of the polarized "pnictaalkenes" **1·PPh**, **1·AsPh**, **1·PCF$_3$**, **1·AsC$_6$F$_5$**, and **3·PPh** can be seen as arising from an intermediate structure along the non-least-motion pathway that couples singlet pnictinidenes and singlet carbenes to form pnictaalkenes. As with the "germaalkene" **10**, the transition to a fully developed pπ−pπ bonding system in **1·PPh**, **1·AsPh**, **1·PCF$_3$**, **1·AsC$_6$F$_5$**, and **3·PPh** is incomplete and the final structures retain considerable ylide character. The extreme representation of this bonding arrangement would be the carbene-solvated pnictinidene depicted by structure **11**.



11

Although it is doubtless extreme, the consideration of structure **11** provides insight into the long C$_2$═Pn distances, the small valence angles at the pnictogen centers, the ease of rotation about the C$_2$═Pn, bond and the retention of carbene-like structure in the ylidene moiety for these carbene−pnictinidene adducts.

Conclusions

The direct formation of "pnictaalkenes" proceeds smoothly from stable nucleophilic carbenes and pnictinidene cyclic oligomers for phosphorus and arsenic systems. A reduction reaction between 2 equiv of a nucleophilic carbene and phenyldichlorophosphine also leads to the formation of a "phosphaalkene". The strong electron-releasing characteristics of the imidazole ring render these "pnictaalkenes" strongly polarized. This strong polarization is evident in the multinuclear NMR data for these "pnictaalkenes". The ^{31}P NMR spectra of the phosphorus systems show a phosphorus chemical shift between δ −10 and −25 ppm upfield of 85% H_3PO_4. This shift range is at higher field than normally expected for the 2-coordinate phosphorus center of a phosphaalkene and suggests additional shielding by the accumulation of electron density donated from the imidazol(in)e ring. The chemical shifts of the phosphorus centers in **1·PPh** (δ −23.0) and **1·PCF$_3$** (δ −23.6) suggest that the chemical shift of the phosphorus center is not strongly dependent on the nature of the "singly-bonded" substituent at the phosphorus center. The shift of the phosphorus center in **3·PPh** (δ −12.0) indicates that the phosphorus chemical shift is sensitive to the ability of the nominally "double-bonded" substituent to release electrons to the phosphorus center. Thus the phosphorus centers in **1·PPh** and **1·PCF$_3$**, which bear the more strongly electron-releasing imidazole ring, are more strongly shielded than the phosphorus center in **3·PPh**, which bears the saturated imidazoline substituent.

The proton and carbon NMR spectra of these carbene−pnictinidene adducts indicate that at room temperature there is free rotation about the C$_2$−Pn bond. This free rotation is indicative of a weak π-bonding interaction between the imidazol(in)e C$_2$ center and the pnictogen center.

The arsenic-derived systems **1·AsPh** and **1·AsC$_6$F$_5$** are very similar both structurally and electronically to the corresponding phosphorus-derived system **1·PPh** although they are less stable and more difficult to handle.

The structures of **1·PPh**, **1·AsPh**, and **3·PPh** are particularly worthy of note because these three compounds have isomorphous crystal structures in spite of the variations in the pnictogen center and imidazol(in)e substituent. The solid state geometries of all these adducts (including **1·PCF$_3$** and **1·AsC$_6$F$_5$**) show small C−Pn−C angles (97−102°). The nominal Pn−C double bond to the C$_2$ imidazol(in)e center is twisted between 18 and 20° in these four adducts, suggesting that a pπ−pπ double bond between these centers is not well developed. Additionally, the C$_2$−Pn bond is only 4% shorter than Pn−C bond to the "single-bonded" substituent (CF_3 or C_6H_5), which further suggests a weak pπ−pπ interaction.

Experimental Section

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Solvents were dried (using standard procedures),[36] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. ^{1}H NMR spectra were recorded on a General Electric QE-300 spectrometer, and ^{13}C, ^{14}N, ^{15}N, and ^{31}P NMR spectra were recorded on a GE Omega 300WB spectrometer. NMR references are $(CH_3)_4Si$ (^{1}H, ^{13}C), $NH_4^+NO_3^-$ (^{14}N, ^{15}N), and 85% H_3PO_4 (^{31}P). Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Micro-Analyses Inc., Wilmington, DE or Oneida Research Services, Whitesboro, NY.

The preparations of the pnictinidene cyclic oligomers were accomplished by established literature procedures.[24−26]

Preparation of 1·PPh. 1,3-Dimesitylimidazol-2-ylidene (**1**) (400 mg, 1.31 mmol) and pentaphenylcyclopentaphosphane (142 mg, 1.31 mmol based on the monomer) were mixed, and 35 mL of thf was added at room temperature. The mixture was stirred under a nitrogen atmosphere, and the color slowly changed to yellow. The resulting mixture was warmed with a heat gun after 1 h and stirred for 4 h at 23

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°C, after which it was filtered over Celite and the filtrate was concentrated. Hexane was added to the concentrate, and the mixture was cooled at −25 °C. Dark yellow needles of **1·PPh** were obtained; first fraction 269 mg (second fraction 97 mg), 67% yield. **1·PPh** melts to an orange oil without decomposing at 163−165 °C. ^{1}H NMR (C_6D_6): δ 2.03 (s, 6 H, *p*-CH_3), 2.23 (s, 12 H, *o*-CH_3), 5.83 (s, 2 H, NCH), 6.57 (s, 4 H, Mes $H_{3,5}$), 6.70 (m, 3 H, Ph $H_{3,4,5}$), 7.45 (m, 2 H, Ph $H_{2,6}$). ^{1}H NMR (thf-d_8): δ 2.16 (s, 12 H, *o*-CH_3), 2.17 (s, 6 H, *p*-CH_3), 6.54−6.65 (m, 3 H, Ph $H_{3,4,5}$), 6.69 (s, 2H, NCH), 6.70 (s, 4 H, Mes $H_{3,5}$), 7.04 (m, 2 H, Ph $H_{2,6}$). ^{13}C{^{1}H} NMR (thf-d_8): δ 18.60 (d, J_{CP} = 3.0 Hz, o-CH_3), 21.03 (s, *p*-CH_3), 119.79 (d, $^3J_{CP}$ = 3.80 Hz, N*C*CN), 124.83 (d, $^4J_{CP}$ = 0.53 Hz, Ph C_4), 126.53 (d, $^3J_{CP}$ = 3.7 Hz, Ph $C_{3,5}$), 129.68 (s, Mes $C_{3,5}$), 134.99 (d, $^3J_{CP}$ = 0.45 Hz, Mes C_1), 136.36 (d, $^4J_{CP}$ = 2.0 Hz, Mes $C_{2,6}$), 137.52 (d, $^2J_{CP}$ = 14.5 Hz, Ph $C_{2,6}$), 138.82 (s, Mes C_4), 140.12 (d, $^1J_{CP}$ = 42.3 Hz, Ph C_1), 170.0 (d, $^1J_{CP}$ = 102.8 Hz, NCN). ^{31}P{^{1}H} NMR (thf-d_8): δ −23.0. ^{15}N{^{1}H} NMR (thf-d_8): δ −219.7 (d, $^2J_{NP}$ = 7.3 Hz). Anal. Calcd for $C_{27}H_{29}N_2P$: C, 78.61; H, 7.09; N, 6.79. Found: C, 78.14; H, 7.03; N, 6.67.

Preparation of 1·AsPh. 1,3-Dimesitylimidazol-2-ylidene (**1**) (4.00 g, 13.16 mmol) and hexaphenylcyclohexaarsane (2.90 g, 19.08 mmol based on the monomer, 45% excess) were mixed, and 200 mL of thf was added at 23 °C. The reaction mixture was first stirred for 2 h at 23 °C, then refluxed for 2.5 h, and finally stirred for an additional 12 h at 23 °C. The resulting suspension was filtered over Celite. The filtrate was evaporated to dryness and the solid residue recrystallized from 40 mL toluene by cooling to −15 °C. Yellow needles of **1·AsPh** were obtained (2.7 g, 45%) **1·AsPh** melts with decomposition at 148−152 °C. ^{1}H NMR (C_6D_6): δ 2.07 (s, 6 H, *p*-CH_3), 2.16 (s, 12 H, *o*-CH_3), 6.08 (s, 2 H, NCH), 6.50−6.65 (m, 3 H, Ph $H_{3,4,5}$), 6.54 (s, 4 H, Mes $H_{3,5}$), 7.51 (m, 2 H, Ph $H_{2,6}$). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.19 (s, *o*-CH_3), 20.96 (s, *p*-CH_3), 120.68 (s, N*C*CN), 124.38 (s, Ph C_4), 126.33 (s, Ph $C_{3,5}$), 129.05 (s, Ph $C_{2,6}$), 130.05 (s, Mes $C_{3,5}$), 134.19 (s, Mes C_1), 135.45 (s, Mes $C_{2,6}$), 137.29 (s, Mes C_4), 139.97 (s, Ph C_1), 174.29 (s, NCN). MS (CI/CH_4), *m/z* (relative intensity, %): 456.154 855 (100) (M^+, calcd for $C_{27}H_{29}N_2As$ 456.154 670), 304 (58) (**1**$^+$). Anal. Calcd for $C_{27}H_{29}N_2As$: C, 71.05; H, 6.40; N, 6.14. Found: C, 70.86; H, 6.40; N, 6.06.

Preparation of 1·PCF$_3$. 1,3-Dimesitylimidazol-2-ylidene (**1**) (0.24 g, 0.8 mmol) and tetrakis(trifluoromethyl)cyclotetraphosphane (0.08 g, 0.8 mmol based on the monomer) were mixed, and 50 mL of thf was added at 23 °C. The resulting yellow solution was stirred for 6 h at 23 °C. The solvent was removed in vacuo, and the solid residue was extracted with 50 mL of toluene. The resulting suspension was filtered over Celite. The bright yellow toluene solution was concentrated to 10 mL. The product, **1·PCF$_3$**, mp 185−189 °C (0.29 g, 0.72 mmol; 90% yield), crystallized from this toluene solution at 23 °C. ^{1}H NMR (C_6D_6): δ 1.94 (s, 6 H, *p*-CH_3), 2.03 (s, 12 H, *o*-CH_3), 5.87 (s, 2 H, NCH), 6.56 (s, 4 H, Mes $H_{3,5}$). ^{19}F{^{1}H} NMR (C_6D_6): δ −35.22 (d, $^2J_{FP}$ = 64.79 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 17.65 (s, *o*-CH_3), 20.74 (s, *p*-CH_3), 121.20 (s, N*C*CN), 129.44 (s, Mes $C_{3,5}$), 133.62 (s, Mes, C_1), 135.92 (Mes $C_{2,6}$), 139.39 (s, Mes C_4), 168.13 (dq, $^1J_{CP}$ = 100.5 Hz, $^3J_{CF}$ = 8.27 Hz, NCN) ($^{13}CF_3$ was not observed). ^{31}P{^{1}H} NMR (C_6D_6): δ −23,63 (q, $^1J_{PF}$ = 64.76 Hz). MS (CI/CH_4), *m/z* (relative intensity, %): 404.162 846 (35) (M^+, calcd for $C_{22}H_{24}N_2F_3P$ 404.162 922), 305.1139 (100). Anal. Calcd for $C_{22}H_{24}N_2F_3P$: C, 65.34; H, 5.98; N, 6.93. Found: C, 64.94; H, 6.07; N, 6.74.

Preparation of 1·AsC$_6$F$_5$. 1,3-Dimesitylimidazol-2-ylidene (**1**) (1.00 g, 3.29 mmol) and tetrakis(pentafluorophenyl)cyclotetraarsane (**2**, Pn = As, R= C_6F_5, x = 4) (0.79 g, 3.3 mmol based on the monomer) were mixed, and 150 mL of thf was added at 23 °C. The stirred solution immediately turned deep purple. The reaction mixture was stirred for 12 h at 23 °C. The solvent was evaporated, and the solid residue was extracted with 100 mL of warm hexane. The resulting suspension was filtered over Celite. The volume of the yellow solution was reduced to 40 mL in vacuo. Yellow crystals of **1·AsC$_6$F$_5$**, mp 143−178 °C, were obtained (1.1 g, 2.01 mmol; 61% yield) from the hexane solution at room temperature. ^{1}H NMR (C_6D_6): δ 2.04 (s, 6 H, *p*-CH_3), 2.14 (s, 12 H, *o*-CH_3), 5.84 (s, 2 H, NCH), 6.59 (s, 4 H, Mes $H_{3,5}$). ^{19}F{^{1}H} NMR (thf-d_8): δ −115.87 (m, 2 F, AsCCF), −160.41 (tm, 1 F, AsCCCCF), −164.66 (m, 2 F, AsCCCF). ^{13}C{^{1}H} NMR (thf-d_8): δ 18.41 (s, *o*-CH_3), 21.10 (s, *p*-CH_3), 109.86 (m, As*C*CF), 122.01 (s, N*C*CN), 129.86 (s, Mes $C_{3,5}$), 134.25 (s, Mes C_1), 136.56 (Mes $C_{2,6}$), 137.81 (dm, $^1J_{CF}$ = 272.7 Hz, AsC*C*CF), 139.96 (s, Mes C_4), 142.29 (dm, $^1J_{CF}$ = 240.5 Hz, AsCC*C*CF), 147.19 (dm, $^1J_{CF}$ = 242.2 Hz, AsC*C*F), 172.21 (s, NCN). MS (CI/CH_4), *m/z* (relative intensity, %): 546.108 404 (100) (M^+, calcd for $C_{27}H_{24}N_2AsF_5$ 546.107 561), 305.2169 (24). Anal. Calcd for $C_{27}H_{24}N_2AsF_5$: C, 59.33; H, 4.43; N, 5.13. Found: C, 59.30; H, 4.46; N, 5.04.

Preparation of 3·PPh. A solution of 45 mg (0.25 mmol) of phenyldichlorophosphine in 5 mL of toluene was added to a stirred solution of 153 mg (0.5 mmol) of 1,3-dimesitylimidazolin-2-ylidene (**3**) in 20 mL of thf at 23 °C under nitrogen. A colorless solid precipitated immediately. After 1 h, the precipitate was removed by filtration. The filtrate was evaporated to give a light yellow solid that was recrystallized from hexane to give **3·PPh** as yellow needles, mp 99−101 °C (72 mg, 69%). ^{1}H NMR (C_6D_6): δ 2.16 (s, 6 H, *p*-CH_3), 2.29 (s, 12 H, *o*-CH_3), 3.26 (s, 4 H, $C_{4,5}$-H), 6.82 (s, 4 H, *m*-CH), 6.65−7.35 (m, 5 H, C_6H_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −10.44 (s). ^{1}H NMR (thf-d_8): δ 2.16 (s, 18 H, *o*-CH_3 and *p*-CH_3), 3.72 (s, 4 H, $C_{4,5}$−H), 6.90 (s, 4 H, Mes *m*-CH), 6.52−7.01 (m, 5 H, Ph). ^{13}C{^{1}H} NMR (thf-d_8): δ 18.39 (s, *o*-CH_3), 20.90 (s, *p*-CH_3), 47.75 (d, $^3J_{PC}$ = 6.7 Hz, $C_{4,5}$), 125.41 (s, Ph C_4), 126.53 (d, $^3J_{PC}$ = 3.7 Hz, Ph $C_{3,5}$), 129.84 (s, Mes $C_{3,5}$), 135.26 (s, Mes C_1), 137.13 (d, $^2J_{PC}$ = 13.4 Hz, Ph $C_{2,6}$), 137.46 (s, Mes $C_{2,6}$), 138.67 (s, Mes C_4), 139.60 (d, $^1J_{PC}$ = 42.2 Hz, Ph C_1), 184.34 (d, $^1J_{PC}$ = 86.7 Hz, C_2). ^{31}P {^{1}H} NMR (thf-d_8): δ −12.01 (s). MS (70 eV), *m/z* (relative intensity, %): 414.2207 (70) (M^+, calcd for $C_{27}H_{31}N_2P$ 414.2225), 399.1956 (100) (M − CH_3, 399.1990), 337.1777 (40) (M^+ − C_6H_5, 337.1834), 305.2032 (10) (**3**$^+$ − H, 305.2018).

Crystal data for 1·PPh were obtained at −68 °C with Mo Kα radiation (Enraf-Nonius CAD4 diffractometer): a = 1698.1(5), b = 767.8(1), c = 1844.1(6) pm; β = 107.05(1)°; monoclinic, $P2_1/c$; Z = 4; μ(Mo) = 1.30 cm^{-1}; fw = 412.52; V = 2298.7 Å^3; D_c = 1.192 g cm^{-3}; 2.3° ≤ 2θ ≤ 50°; maximum hkl = 20,9,21; data octants +++, −++; ω scan method; scan width 1.20−2.50°; scan speed = 1.70−4.00°/min; typical half-height peak width = 0.15° ω; 2 standard reflections collected 41 times with a 2% fluctuation in intensity; 12% variation in azimuthal scan; no absorption correction; 1462 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F; scattering factors were from ref 37, including anomalous terms for phosphorus. Phosphorus, carbon, and nitrogen were refined with anisotropic thermal parameters. Hydrogens at positions 4 and 5 of the imidazole ring were refined with isotropic thermal parameters and all other hydrogens had their isotropic thermal parameters fixed on the basis of the carbon to which they were attached. The data/parameter ratio was 5.22. The final R factors were R = 0.059 and R_w = 0.047. Error of fit = 1.23; maximum Δ/σ = 0.05; largest residual density = 0.26 e/Å^3. Further details of the crystal structure are available in the Supporting Information.

Crystal data for 1·AsPh were obtained at −90 °C with Mo Kα radiation (Siemens P3 diffractometer): a = 1708.6(3), b = 769.4(2), c = 1857.4(5) pm; β = 107.49(2)°; monoclinic, $P2_1/c$; Z = 4; μ(Mo) = 14.75 cm^{-1}; fw = 456.44; V = 2328.9 Å^3; D_c = 1.302 g cm^{-3}; 2.26° ≤ θ ≤ 32.50°; maximum hkl = 25,11,28; data octants +++, −++, −+−, ++−; ω scan method; 4 standard reflections collected after every 96 reflections showed a 3.2% decrease in intensity; no absorption correction; 8433 independent reflections [R(int) = 0.0868]; 4235 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2; scattering factors were from ref 37, including anomalous terms for arsenic. Arsenic, carbon, and nitrogen were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters based on the carbon to which they were attached. The largest residual electron density in the final difference Fourier map was 0.40 e/Å^3. The data/parameter ratio was 8431/282. The final R factors were [$I > 2\sigma(I)$] R = 0.057 and R_w = 0.091. Error of fit = 0.987; maximum Δ/σ = 0.00. Further details of the crystal structure are available in the Supporting Information.

Crystal data for 1·PCF$_3$ were obtained at −115 °C with Mo Kα radiation (Siemens P3 diffractometer): a = 813.65(6), b = 762.65(4),

(37) *International Tables for X-ray Crystallography*; Reidel: Dordrecht, Holland, 1985; Vol. IV.

$c = 3425.1(3)$ pm; $\beta = 91.243(6)°$; monoclinic, $P2_1/n$; $Z = 4$; μ(Mo) = 1.64 cm^{-1}; fw = 404.40; $V = 2124.9$ Å^3; $D_c = 1.264$ g cm^{-3}; $2.38° \leq \theta \leq 32.50°$; maximum $hkl = 12,11,51$; data octants +++, −++, −+−, ++−; ω scan method; 4 standard reflections collected after every 96 reflections showed a 2.4% decrease in intensity; no absorption correction; 7582 independent reflections [R(int) = 0.0415]; 4542 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2; scattering factors were from ref 37, including anomalous terms for phosphorus. Phosphorus, fluorine, carbon, and nitrogen were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters based on the carbon to which they were attached. The largest residual electron density in the final difference Fourier map was 0.41 e/Å^3. The data/parameter ratio was 7576/263. The final R factors [$I > 2\sigma(I)$] were $R = 0.055$ and $R_w = 0.135$. Error of fit = 1.098; maximum $\Delta/\sigma = 0.01$. Further details of the crystal structure are available in the Supporting Information.

Crystal data for 1·AsC$_6$F$_5$ were obtained at −90 °C with Mo Kα radiation (Siemens P3 diffractometer): $a = 714.6(2)$, $b = 1230.6(2)$, $c = 1464.6(2)$ pm; $\alpha = 83.158(7)$, $\beta = 76.370(10)$, $\gamma = 84.310(10)°$; triclinic, $P\bar{1}$; $Z = 2$; μ(Mo) = 14.27 cm^{-1}; fw = 546.40; $V = 1239.4$ Å^3; $D_c = 1.464$ g/cm^{-3}; $2.09° \leq \theta \leq 27.50°$; maximum $hkl = 9,15,19$; data octants +++, +− −, +−+, ++−; ω scan method; 4 standard reflections collected after every 96 reflections showed a 2.4% decrease in intensity; no absorption correction; 5477 independent reflections [R(int) = 0.0599]. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2; scattering factors were from ref 37, including anomalous terms for arsenic. Arsenic, fluorine, carbon, and nitrogen were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters based on the carbon to which they were attached. The largest residual electron density in the final difference Fourier map was 1.415 e/Å^3. The data/parameter ratio was 5477/327. The final R factors [$I > 2\sigma(I)$] were $R = 0.0868$ and $R_w = 0.1834$. Error of fit = 1.1024; maximum $\Delta/\sigma = 0.01$. Further details of the crystal structure are available in the Supporting Information.

Crystal data for 3·PPh were obtained at −100 °C with Mo Kα radiation (Syntex R3 diffractometer): $a = 1704.4(5)$, $b = 762.6(2)$, $c = 1852.5(4)$ pm; $\beta = 107.76(2)°$; monoclinic, $P2_1/c$; $Z = 4$; μ(Mo) = 1.301 cm^{-1}; fw = 414.53; $V = 2293.1$ Å^3; $D_c = 1.201$ g cm^{-3}; $4.5° \leq 2\theta \leq 48°$; maximum $hkl = 19,8,21$; data octants +++, ++−; ω scan method; scan width 1.00°; scan speed = 2.00−8.40°/min; typical half-height peak width = 0.28° ω; 2 standard reflections were collected 43 times with a 2% fluctuation in intensity; no absorption correction; 1652 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F; scattering factors were from ref 37 including anomalous terms for phosphorus. Phosphorus, carbon, and nitrogen were refined with anisotropic thermal parameters. Because some of the methyl hydrogens gave unreasonable bond lengths (86−111 pm), all hydrogens were idealized close to their previously refined positions. The data/parameter ratio was 6.09. The final R factors were $R = 0.044$ and $R_w = 0.036$. Error of fit = 1.03; maximum $\Delta/\sigma = 0.02$; largest residual density = 0.25 e/Å^3. Further details of the crystal structure are available in the Supporting Information.

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Supporting Information Available: Listings of crystal data and X-ray experimental details, ORTEP diagrams, tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles for **1·PPh, 1·AsPh**, **1·PCF$_3$**, **1·AsC$_6$F$_5$**, and **3·PPh** (32 pages). Ordering information is given on any current masthead page.

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