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Bonding of Phosphinidene or Arsenidene Fragments to a Fluorenylidene. Interrelationships between Phosphaalkenes or Arsaalkenes and Donor−Acceptor Complexes

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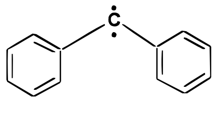
The fluorenylidene-substituted phosphaalkene Mes*P═Fl* (**13**) and arsaalkene Mes*As═Fl* (**14**) (Mes* = 2,4,6-*t*-$Bu_3C_6H_2$, Fl* = 2,7-di-*tert*-butylfluorenylidene) have been prepared by treatment of Fl*(H)Li with Mes*ECl_2 (E = P, As) followed by dehydrochlorination with DABCO (1,4-diazabicyclo[2.2.2]octane). In the synthesis of **13** it was possible to isolate the intermediate, Mes*(Cl)P−(H)Fl* (**11**). Attempts to prepare the stibaalkene, Mes*Sb═Fl* (**15**), resulted in an unstable product. Compounds **11**, **13**, and **14** were characterized by X-ray crystallography: **11**, triclinic, $P\bar{1}$, $a = 11.548(2)$ Å, $b = 12.189(3)$ Å, $c = 14.223(3)$ Å, $\alpha = 114.13(1)°$, $\beta = 92.79(1)°$, $\gamma = 107.14(1)°$, $V = 1712.8(2)$ Å^3, Z = 2, wR2 = 0.1344, R1 = 0.0560; **13**, monoclinic, $P2_1/n$, $a = 24.597(7)$ Å, $b = 11.185(2)$ Å, $c = 26.914(7)$ Å, $\beta = 112.16(2)°$, $V = 6857(3)$ Å^3, $Z = 8$, wR2 = 0.1477, R1 = 0.0794; **14**·Et_2O, monoclinic, $P2_1/n$, $a = 15.577(4)$ Å, $b = 15.274(4)$ Å, $c = 17.255(5)$ Å, $\beta = 108.17(2)°$, $V = 3901(2)$ Å^3, $Z = 4$, wR2 = 0.1275, R1 = 0.0578. The P═C (1.686(5) Å) and As═C (1.807(3) Å) bond distances in **13** and **14** are consistent with double-bonding descriptions; moreover, there is a zero angle of twist between the E−C(Mes*) moieties and the plane of the Fl* ligand in both molecules.

Introduction

Carbenes such as **1** persist as triplets,[1] while certain cyclic systems with α-heteroatoms, most notably the imidazol-2-ylidenes (**2**),[2] can be isolated as ground-state singlets. Since the difference between Fischer- and Schrock-type transition metal carbene complexes depends *inter alia* on whether the carbene moiety bonds as a singlet (**3**) or triplet (**4**), respectively,[3]



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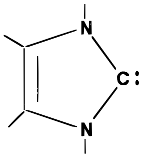


2

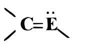
$R_2C\rightarrow ML_n$

3

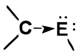
$R_2C{=}ML_n$

4

a similar bonding dichotomy can be anticipated in the context of main group chemistry. In the specific case of the interaction between carbenes and phosphinidenes or arsenidenes, two canonical forms, **5** and **6**, can be written to highlight the different

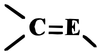


5



6

bonding possibilities. Structure **5** represents the classical picture of the bonding in a phosphaalkene or arsaalkene and stems from the interaction of triplet carbene and pnictinidene fragments.[4] For these molecules, a carbon−phosphorus or carbon−arsenic bond order of two is observed,



the skeleton is planar, and there is evidence for only one lone pair of electrons on the E center.[5] In contrast, when a singlet carbene is employed, the bond order of the resulting donor−acceptor complex is close to unity as shown in **6**.[6,7] Moreover, the pnictinidene moiety is twisted with respect to the carbene plane, and the Lewis base behavior is consistent with the presence of two lone pairs on the group 15 center.[8] A further distinguishing feature of structure types **5** and **6** is the observation by NMR of free rotation around the C → E bond in the latter. Of course, structures **5** and **6** represent extremes of behavior and a continuum of intermediate bonding descriptions can be envisioned. Such intermediate cases can be recognized, for example, on the basis of solution phase ^{31}P NMR chemical shifts.[5,9] Thus, phosphaalkenes with exclusive hydrocarbyl substitution (i.e. type **5** species) exhibit deshielded ^{31}P chemical shifts in the range δ 230−420 due to the anisotropy of the P═C bond, while carbene−phosphinidene donor−acceptor complexes, **6**, display very shielded ^{31}P chemical shifts (δ -20 to

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(1) See: Tomioka, H.; Hattori, M.; Hirai, K.; Murata, S. *J. Am. Chem. Soc.* **1996**, *118*, 8723. Tomioka, H; Okada, H.; Watanabe, T.; Banno, K.; Komatsu, K.; Hirai, K. *J. Am. Chem. Soc.* **1997**, *119*, 1582 and references therein.

(2) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. Arduengo, A. J., III; Rasika Dias, H. V.; Davidson, R. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(3) See for example: Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1575.

(4) The phosphinidene, P(mesityl), has been isolated and shown to possess a triplet ground state on the basis of ESR evidence (Li, X.; Weissman, S. I.; Lin, T.-S.; Gaspar, P. P.; Cowley, A. H.; Smirnov, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 7899). Also, the triplet−singlet energy gap of PH has been measured in flowing afterglow experiments (Zittel, P. F.; Lineberger, W. C. *J. Chem. Phys.* **1976**, *65*, 126).

(5) For a review of phosphaalkenes, see for example: Appel, R.; Knoll, F. *Advances in Inorganic Chemistry*; Sykes, A. G., Ed.; Academic Press: New York, 1989; Vol. 33, p 259.

(6) Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C. *Chem. Lett.* **1997**, 143.

(7) Arduengo, A. J., III; Calabrese, J. C.; Cowley, A. H.; Rasika Dias, H. V.; Goerlich, J. R.; Marshall, W. J.; Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151.

(8) Arduengo, A. J., III; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Pyati, R. *Chem. Commun.* **1997**, 981.

(9) Cowley, A. H.; Norman, N. C.; Chapter 17 In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; Chapter 17.

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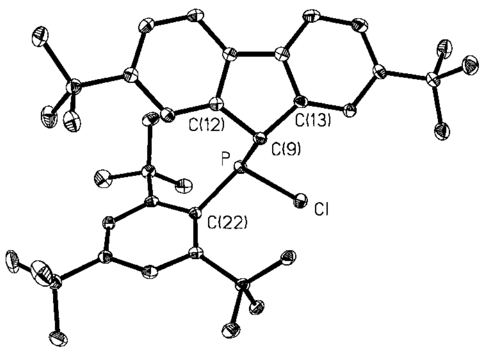
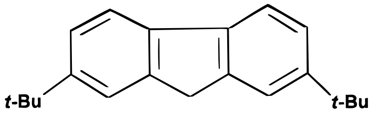


Figure 1. View of the molecular structure of **11** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

−50).[6,7] Representative examples of intermediate bonding situations include (Me$_2$N)$_2$CPPh (δ 28.6)[10] and (Me$_2$N)(H)CPPh (δ 69.5).[10]

In the present paper, we explore the ability of the fluorenylidene (Fl) ligand to bond to pnictinidene fragments. It was anticipated that, since fluorenylidene exists as a triplet ground state,[11] species with C=E double bonds would be formed. To the best of our knowledge, there are only three examples of fluorenylidene-substituted phosphaalkenes in the literature, namely (2,6-Me$_2$Ph)P=Fl (**7**),[12] PhP=Fl (**8**),[13] and Mes*N(H)P=Fl (**9**, Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$).[14] However, only the amidophosphorus derivative has been structurally characterized.[14] There are no examples of fluorenylidene-substituted arsaalkenes. The specific objectives of the present work were 3-fold: (i) to prepare and structurally characterize a fluorenylidene-substituted phosphaalkene uncomplicated by the presence of conjugating ligands, (ii) to prepare and structurally characterize the first example of a fluorenylidene-substituted arsaalkene, and (iii) to attempt the preparation of a fluorenylidene-substituted stibaalkene. In approaching these objectives, we opted to employ a variant of the fluorenylidene ligand (Fl*H$_2$, **10**) with a view to increasing product solubilities through the use of flanking *t*-Bu groups. A further advantage of the presence of these substituents was simplification of NMR spectral interpretation.



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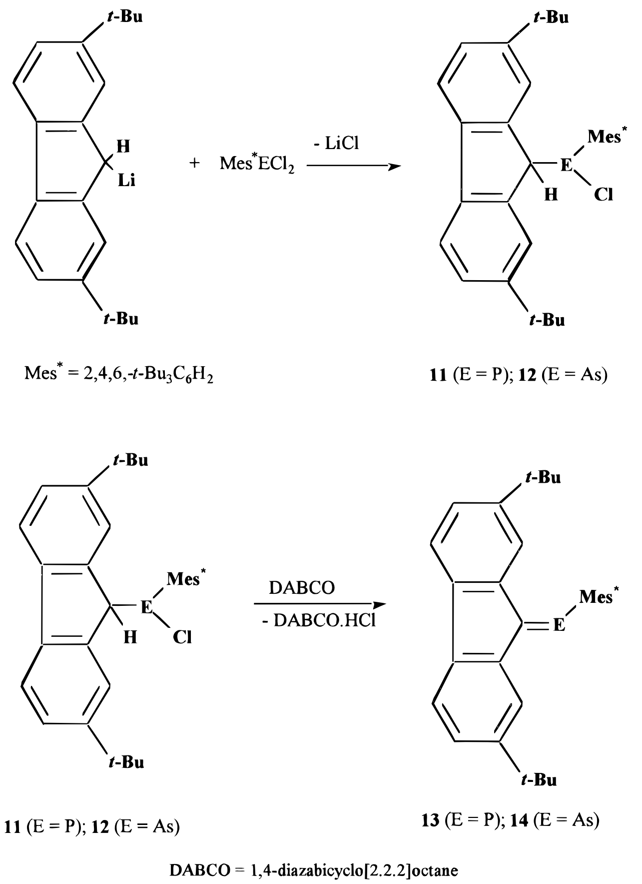
Results and Discussion

Synthesis and Characterization. The Fl*-substituted phosphaalkene, Mes*P=Fl* (**13**), and arsaalkene, Mes*As=Fl* (**14**), were prepared by means of the two-step process summarized in Scheme 1. In the case of **13**, the metathetical and dehydrochlorination steps proceed in yields of 92 and 74%, respectively. Moreover, it was possible to isolate the intermediate hydrochloride, Mes*(Cl)P−(H)Fl* (**11**), as a crystalline solid. The synthetic procedure for the arsaalkene **14** was somewhat different in that the Mes*AsCl$_2$ was prepared *in situ*;[15] moreover, no attempt was made to isolate the presumed intermediate **12**. The overall yield of **14** was 33%. In an effort to prepare the stibaalkene, Mes*Sb=Fl* (**15**), Mes*SbCl$_2$ was prepared *in situ* at −78 °C and treated with Fl*(H)Li using an procedure identical to that described for the synthesis of **14**. However, due to thermal instability, it was only possible to obtain mass spectroscopic evidence for the existence of **15** (calcd for $C_{36}H_{53}Sb$, *m/e* 642.318 551; found, *m/e* 642.318 000).

Scheme 1



Compounds **11**, **13**, and **14** were characterized by elemental analysis, NMR, and high-resolution mass spectroscopy. The ^{31}P NMR chemical shift for **13** (δ 250) is similar to those for **7** (δ 242.5),[12] **8** (δ 225.11),[13] and **9** (δ 256)[14] and in the region anticipated for the presence of a P=C bond (i.e. structure **5**).[5,9] This suggestion was corroborated by the ^{1}H and ^{13}C{^{1}H} spectral observations that the two benzene rings of the fluorenylidene ligand are nonequivalent. Comparable nonequivalencies were observed for the arsenic analogue **14**; hence, for both **13** and **14** rotation around the C=E bond is slow on the NMR time scale.

X-ray Crystal Structures. Compound **11** crystallizes in the monoclinic space group $P\bar{1}$ with two molecules per unit cell. The phosphorus atom adopts a pyramidal geometry (Figure 1) with an average bond angle of 105.9(1)° (Table 1). The C(9)−P bond distance of 1.880(1) Å corresponds to a bond order of unity and is slightly longer than the P−C(Mes*) distance (1.852(3) Å); the geometry at C(9) is approximately tetrahedral.

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[10] Markovskii, L. N.; Romanenko, V. D.; Pidvarko, T. I. *Zh. Obshch. Khim.* **1982**, *52*, 1925.

[11] For a review, see for example: Hartzler, H. D. In *Carbenes*; John Wiley and Sons: New York, 1975; Vol. 2, Chapter 2.

[12] van der Knaap, T. A.; Bickelhaupt, F. *Chem. Ber.* **1984**, *117*, 915.

[13] Märkl, G.; Raab, K. M. *Tetrahedron Lett.* **1989**, *30*, 1077.

[14] Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460.

[15] It is necessary to carry out this synthesis at −78 °C.[16] Higher reaction temperatures promote the formation of a cyclic monochloroarsine.[17]

[16] Weber, L.; Bungardt, D.; Sonnenberg, U.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1537. Weber, L.; Bungardt, D.; Boese, R. *Z. Anorg. Allg. Chem.* **1988**, *578*, 205.

[17] Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **11**, **13**, and **14**

compd **11**		compd **13**		compd **14**	
P−C(22)	1.852(3)	P(1)−C(22)	1.849(4)	As−C(22)	1.794(11)
P−C(9)	1.880(3)	P(1)−C(9)	1.686(5)	As−C(9)	1.948(12)
P−Cl	2.0982(2)	C(9)−C(12)	1.473(6)	C(1)−C(10)	1.483(4)
C(9)−C(12)	1.528(4)	C(9)−C(13)	1.489(6)	C(1)−C(13)	1.473(4)
C(9)−C(13)	1.522(4)	P(2)−C(122)	1.852(4)		
		P(2)−C(109)	1.677(5)		
		C(109)−C(112)	1.475(6)		
		C(109)−C(113)	1.496(6)		
C(22)−P−C(9)	105.32(3)	C(22)−P−C(9)	107.3(2)	C(22)−As−C(9)	105.0(4)
C(22)−P−Cl	108.19(1)	C(12)−C(9)−P	135.8(3)	C(10)−C(1)−As	118.9(2)
C(9)−P−Cl	104.53(1)	C(13)−C(9)−P	119.1(3)	C(13)−C(1)−As	135.9(2)
C(12)−C(9)−P	104.1(2)	C(112)−C(109)−P	136.3(3)		
C(13)−C(9)−P	107.3(2)	C(113)−C(109)−P	119.4(3)		

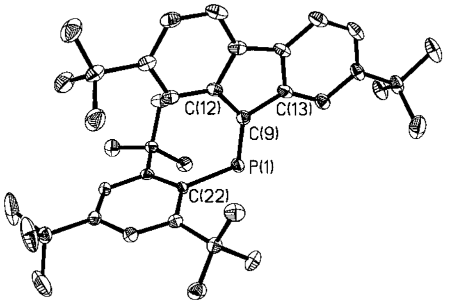

Figure 2. View of the molecular structure of **13** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

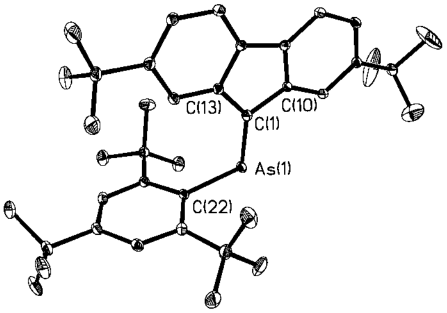

Figure 3. View of the molecular structure of **14** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Compound **13** crystallizes in the monoclinic space group $P2_1/n$ with eight molecules per unit cell (Figure 2). There are two independent molecules in the asymmetric unit. The P−C(Mes*) bond distance (average 1.850(4) Å) is virtually identical to that in **11**. However, the P−C(fluorenylidene) bond distance (average 1.681(5) Å) is ~0.2 Å shorter than that in **11** and commensurate with a bond order of two (Table 1); the geometry at C(9) is trigonal planar. The implication of the adoption of a fully-fledged phosphaalkene structure (**5**) receives additional support from the observation that the torsion angle, ϕ, between the five-membered ring of the Fl* ligand and the C(9)−P(1)−C(22) plane is 0° within experimental error. As pointed out earlier, nonzero angles of ϕ are characteristic of donor−acceptor character (i.e. structure **6**). The fact that the P−C(fluorenylidene) bond distance in **9** (1.707(9) Å) is slightly longer than in **13** is presumably a consequence of conjugation between the amido substituent and the phosphorus atom.

Interestingly, the analogous arsenic compound, **14**, is not isomorphous with **13** and crystallizes in the monoclinic space group $P2_1/n$ with four molecules of **14** and four molecules of diethyl ether per unit cell. However, the general features of the individual molecules of **13** and **14** are very similar (Figure 3). The As−C(Mes*) bond distance of 1.983(3) Å is appropriate for an arsenic−carbon single bond.[18] A search of the Cambridge Structure Database[19] reveals that there are no examples of structurally characterized arsaalkenes bearing solely hydrocarbyl substituents. The As−C(fluorenylidene) bond distance of 1.807(3) Å in **14** is shorter than the corresponding arsenic−carbon distances in the closest available comparisons, namely (t-Bu)(Me_3SiO)C═AsFe(CO)$_2$(η-C_5H_5) (**16**, 1.821(2) Å)[20] and (Et_2N)(F)C═AsCF$_3$ (**17**, 1.867(9) Å).[21] Note, however, that in **16** and **17** the carbene carbon is substituted with groups capable of conjugation; hence, for both molecules the carbon−arsenic bonding picture might be intermediate between **5** and **6**. Such an idea gains support from the observation that the bond angle at arsenic in **17** (94.3(4)°) is more acute than that in **14** (105.51(2)°). The fact that the latter angle is ~2° smaller that that in the analogous phosphaalkene **13** is consistent with normal periodic group trends. Together with the observation of a zero angle of twist between the As−C(Mes*) moiety and the fluorenylidene ligand (i.e. $\phi = 0$), the foregoing metrical parameters indicate that **14** is a *bona fide* example of an arsaalkene, **5** (E = As).

Conclusions

The 2,7-di-*tert*-butylfluorenylidene (Fl*)-substituted phosphaalkene, Mes*P═Fl* (**13**, Mes* = 2,4,6-t-Bu$_3$C$_6$H$_2$), and arsaalkene, Mes*As═Fl* (**14**), have been prepared by a metathetical/dehydrochlorination procedure. Compound **14** represents the first example of a fluorenylidene-substituted arsaalkene. X-ray structural assays reveal that **13** and **14** feature element−carbon double bonds; hence, both compounds can be viewed as originating from the interaction of triplet carbene and pnictinidene fragments. Although mass spectrometric evidence was obtained for the existence of the fluorenylidene-substituted stibaalkene, Mes*Sb═Fl* (**15**), this compound is too unstable to isolate.

Experimental Section

General Procedures. All reactions were carried out under a dry, oxygen-free argon atmosphere utilizing standard Schlenk manifold techniques or an HE-493 Vacuum Atmospheres drybox. All solvents were dried and distilled under nitrogen immediately prior to use. The starting materials, Mes*Br,[22] Mes*PCl$_2$,[22] Mes*AsCl$_2$,[16] and 2,7-di-*tert*-butylfluorene (Fl*H$_2$)[23] were prepared according to the literature

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(18) *Interatomic Distances Supplement Special Publication No. 18*; The Chemical Society: London, 1965.

(19) Cambridge Structure Database (Version 5.11, April 1996).

(20) Weber, L.; Meine, G.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 469. Weber, L.; Meine, G.; Boese, R.; Bungardt, D. *Z. Anorg. Allg. Chem.* **1987**, *549*, 73.

(21) Albers, T.; Grobe, J.; Le Van, D.; Krebs, B.; Lage, M. *Z. Naturforsch.* **1995**, *B50*, 94.

procedures; other reagents were obtained from commercial suppliers and used without further purification. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Physical Measurements. NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.16 MHz; ^{13}C, 75.48 MHz; ^{31}P, 121.50 MHz), and chemical shifts are referenced to the solvent and are reported relative to $Si(CH_3)_4$ ($\delta = 0.00$) for ^{13}C and ^{1}H. ^{31}P NMR spectra are referenced to 85% H_3PO_4 (external). Partial assignment of ^{13}C NMR was facilitated using an attached proton test (ATP). Low-resolution mass spectra were obtained with a Finnigan MAT TSQ-70 triple stage quadrupole mass spectrometer operating in the chemical ionization mode with CH_4 as the ionizing gas. High-resolution mass spectra were obtained using a VG Analytical ZAB2-E mass spectrometer operating in the chemical ionization mode with isobutane as the ionizing gas. Melting points were obtained in capillaries sealed under argon and are uncorrected.

Synthesis of Compound 11. Fl*H_2 (0.50 g, 1.8 mmol) in THF (10 mL) was treated with *n*-BuLi (1.2 mL, 1.6 M, 1.9 mmol) at −78 °C. The solution turned orange immediately and was added to Mes*PCl_2 (0.63 g, 1.8 mmol) in THF (10 mL). The solution turned clear and colorless, and the reaction mixture was stirred at −78 °C for 1 h before being allowed to warm to room temperature. The solvent was removed *in vacuo*, and the product was separated from LiCl by extraction into Et_2O (10 mL). Concentration of the filtrate afforded a crop of pale yellow crystals characterized as Mes*P(Cl)Fl*H (0.98 g, 1.6 mmol, 92% yield). Mp: 80 °C (dec). ^{1}H NMR (C_6D_6): 8.38−6.06 (m, 6H, fluorenyl), 7.42 (s, 2H, Mes*), 5.72 (d, $^2J_{PH} = 11$ Hz, 1H); 1.41 (s, 9H); 1.37 (s, 9H); 1.34 (s, 18H); 1.08 (s, 9H). ^{31}P{^{1}H} NMR (THF): 77 (s) . HRMS (CI$^+$): calcd for $C_{39}H_{54}ClP$, *m/e* 589.3729; found, *m/e* 589.3717. Anal. Calcd for $C_{36}H_{54}ClP$: C, 79.49; H, 9.24; Cl, 6.02. Found: C, 79.64; H, 9.32; Cl, 5.89.

Synthesis of Compound 13. Compound **11** (0.35 g, 0.60 mmol) and DABCO (0.07 g, 0.60 mmol) were allowed to react in diethyl ether solution for 24 h. The resulting precipitate was removed by filtration, and the filtrate was concentrated and stored at −20 °C, giving a crop of yellow, air-stable crystals of composition Mes*P═Fl* (0.24 g, 0.44 mmol, 74% yield). Mp: 154−7 °C (dec). ^{1}H NMR (C_6D_6): 8.70−6.56 (m, 6H, fluorenyl), 7.42 (s, 2H, Mes*), 1.49 (s, 18H), 1.40 (s, 9H), 1.30 (s, 9H), 1.07 (s, 9H). ^{13}C NMR (C_6D_6): 170.8 (d, $^1J_{PC} = 41.9$ Hz, P═*C*); 154.9 (d; $J_{PC} = 2$ Hz, q); 151.1 (s, q); 150.4 (d, $J_{PC} = 3$ Hz, q); 149.3 (d, $J_{PC} = 4$ Hz, q); 144.2 (s, q), 143.9 (s, q) 139.9 (d, $J_{PC} = 18$ Hz, q); 138.0 (d, $J_{PC} = 10$ Hz, q); 135.1 (d, $J_{PC} = 59$ Hz, q); 126.4 (d, $J_{PC} = 7$ Hz, CH); 125.4 (s, CH); 125.4 (s, CH); 123.4 (s, CH); 119.7 (s, CH); 118.8 (d, $J_{PC} = 3$ Hz, CH); 117.5 (d, $J_{PC} = 25$ Hz, CH); 35.5 (s, q); 35.2 (s, q); 35.1 (s, q); 34.9 (s, q); 32.9 (s, CH_3); 32.8 (s, CH_3); 31.9 (s, CH_3); 31.7 (s, CH_3). ^{31}P NMR (THF): 250 (impurity at 248). HRMS: calcd for $C_{39}H_{53}P$, *m/e* 552.3885; found, *m/e* = 552.3872. Anal. Calcd for $C_{36}H_{53}P$: C, 84.73; H, 9.66. Found: C, 84.48; H, 9.86.

Synthesis of Compound 14. Mes*$AsCl_2$ was prepared *in situ* at −78 °C by treatment of *n*-BuLi (5.0 mL, 1.6 M, 8 mmol) with Mes*Br (2.6 g, 8 mmol) in THF (30 mL) solution followed by the addition of $AsCl_3$ (1.45 g, 8 mmol). After 1 h at this temperature, Li[Fl*H] (prepared from 1.1 g of Fl*H_2 and 2.5 mL of *n*-BuLi (2.5 mL, 1.6 M, 4 mmol) in 20 mL of THF at −78 °C) was added and the reaction mixture was stirred for 2 h at −78 °C. The solvent was removed (−30 to −50 °C), and a solution of DABCO (0.45 g, 4 mmol) in diethyl ether (50 mL) was added at −78 °C. The mixture was warmed to room temperature overnight and subsequently filtered to remove all insoluble materials. Concentration of the filtrate, followed by cooling overnight to −20 °C, gave a crystalline material of composition Mes*As═Fl* (0.78 g, 1.32 mmol, 33% based on lithium fluorenide). Mp: 135−41 °C (dec). HRMS: calcd for $C_{39}H_{53}As$, *m/e* 596.3363; found, *m/e* 596.3351. ^{1}H NMR (C_6D_6): 8.70−6.80 (m, 6H, fluorenyl), 7.73 (s, 2H, Mes*), 1.47 (s, 18H), 1.42 (s, 9H), 1.26 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (C_6D_6): 185.5 (s, As═*C*), 155.4 (q), 150.6 (q), 149.8 (q), 149.3 (q), 145.0 (q), 142.5 (q), 138.7 (q), 137.0 (q), 134.9 (q), 126.1 (CH), 125.1 (CH), 123.9 (CH), 123.5 (CH), 119.7 (CH), 118.7 (CH), 118.7 (CH), 117.3 (CH), 40.1 (q), 39.3 (q), 39.1 (q), 38.6 (q), 34.6 (CH_3), 32.9 (CH_3), 31.8 (CH_3), 31.7 (CH_3).

Table 2. Crystal Data and Details of Intensity, Measurement, and Structure Refinement for **11**, **13**, and **14**

	11	**13**	**14**
formula	$C_{36}H_{53}ClP$	$C_{36}H_{53}P$	$C_{36}H_{53}AsO$
fw	589.24	552.78	670.85
temp (°C)	−100	−100	−100
λ	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	11.548(2)	24.597(7)	15.577(4)
b (Å)	12.189(3)	11.185(2)	15.274(4)
c (Å)	14.223(3)	26.914(7)	17.255(5)
α (deg)	114.13(1)	90	90
β (deg)	92.79(1)	112.16(2)	108.17(2)
γ (deg)	107.14(1)	90	90
V (Å^3)	1712.8(6)	6857(3)	3901(2)
Z	2	8	4
d(calc) (g/cm^3)	1.143	1.071	1.142
abs coeff (cm^{-1})	1.83	1.04	9.01
cryst size (mm)	0.26 × 0.35 × 0.44	0.26 × 0.40 × 0.42	0.38 × 0.38 × 0.35
θ range (deg)	2.19−25.01	2.03−25.02	2.04−28.00
tot. no. of rflns	6029	12375	9747
no. of obsd rflns	5741	12063	9416
no. of ref params	381	761	427
GOF on F^2	1.093	1.017	1.022
wR2/R1^a [$I > 2\sigma(I)$]	0.0560/0.1344	0.0794/0.1477	0.0538/0.1275

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(0,F_o^2)/3 + 2F_c^2/3]$.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **11**, **13,** and **14** are presented in Table 2. Crystals of **11**, **13**, and **14** were grown from diethyl ether solutions at −20 °C and mounted on glass fibers. Data sets for **11**, **13**, and **14** were collected on a Siemens P4 diffractometer at −100 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Accurate unit cell parameters were determined by recentering 25 optimal high-angle reflections. Four standard reflections were measured every 96 reflections during data collection, and no decreases in intensities were noted. Corrections were applied for Lorentz−polarization and absorption effects (SHELXA for **11**, face-indexing for **13**). The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using the Siemens SHELXL PLUS 5.0 (PC) software package.[24] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. Hydrogen atoms were included at calculated positions (C−H 0.96 Å) and were refined using a riding model and a general isotropic thermal parameter.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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