1,3,2-Diazaphosphinines: New, Versatile Precursors of 1,2-Azaphosphinines and Polyfunctional Phosphinines

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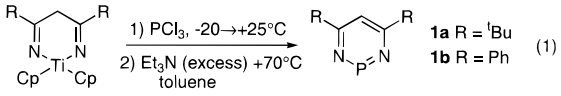
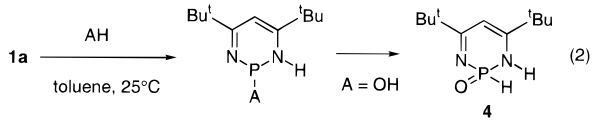
Whereas all of the possible azaphosphinines are known to date,[1−3] our knowledge of diazaphosphinines is presently limited to a couple of examples.[4] We wish to describe here a very simple access to 1,3,2-diazaphosphinines and their use to prepare 1,2-azaphosphinines and polyfunctional phosphinines. Recently, Doxsee et al. have described the synthesis of 1,3,2-diazatitanacyclohexa-3,6-dienes by reaction of nitriles with $Cp_2Ti{=}CH_2$ or Cp_2TiMe_2.[5−9] The reaction of such compounds with PCl_3 and triethylamine directly affords 1,3,2-diazaphosphinines (eq 1).



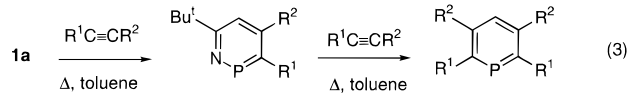
(1)

These very reactive heterocycles have been characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopies and mass spectrometry.[10] They readily react at room temperature with protic reagents to give the corresponding 1,2-dihydro-1,3,2-diazaphosphinines[11] (eq 2).



(2)

More interestingly, their reaction with alkynes affords 1,2-azaphosphinines[12] with extrusion of one molecule of nitrile. This [4 + 2] cycloaddition−cycloreversion process mimics the conversion of 1,3-azaphosphinines into phosphinines.[2,13,14] Upon further heating at higher temperature with a second equivalent of alkyne, these 1,2-azaphosphinines can, in turn, be converted into phosphinines. In such a way, we have prepared several polyfunctional phosphinines,[15] as shown in the following equation (eq 3).



(3)

5 R^1 = H, R^2 = Ph
6 $R^1 = R^2$ = Et

7 R^1 = H, R^2 = 2-py
8 $R^1 = R^2 = SiMe_3$
9 $R^1 = SiMe_3$, R^2 = Ph
10 $R^1 = SiMe_3$, R^2 = H
11 $R^1 = PPh_2$, R^2 = Ph
12 R^1 = Ph, R^2 = -C≡C-Ph

This new synthetic pathway to azaphosphinines and phosphinines offers several distinct advantages: (a) its simplicity, all of the syntheses can be carried out in one pot; (b) its yields, the [4 + 2] cycloadditions take place under relatively mild conditions (compare with 1,3-azaphosphinines[2,13,14]) and this means high yields; (c) its versatility, two different alkynes can be used and the reaction tolerates several functional groups such as CO_2Et, 2-py (pyridine), $SiMe_3$, PPh_2, and $CH(OEt)_2$; (d) its regioselectivity, in almost all cases, essentially one regioisomer is obtained. On the basis of simple electronegativity arguments, it is clear that both 1,3,2-diaza- and 1,2-azaphosphinines are highly polarized molecules with substantial positive charge at P and negative charge at C_5. This favors a good regioselectivity.

(1) 1,4-Azaphosphinines: Märkl, G.; Matthes, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1019.
(2) 1,3-Azaphosphinines: Märkl, G.; Dorfmeister, G. *Tetrahedron Lett.* **1987**, *28*, 1093.
(3) 1,2-Azaphosphinines: Bourdieu, C.; Foucaud, A. *Tetrahedron Lett.* **1987**, *28*, 4673.
(4) A 1,2,4-diazaphosphinine has been mentioned in a review: Memmesheimer, H.; Regitz, M. *Rev. Heteroat. Chem.* **1994**, *10*, 61. 2,4,6-Triaryl-1,3,5-diazaphosphinines have been synthesized: Märkl, G.; Dörges, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 106. The λ^5-derivatives are better known: Granier, M.; Baceiredo, A.; Nieger, M.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1123.
(5) Doxsee, K. M.; Farahi, J. B. *J. Am. Chem. Soc.* **1988**, *110*, 7239.
(6) Doxsee, K. M.; Farahi, J. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1452.
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(8) Doxsee, K. M.; Juliette, J. J. J.; Mouser, J. K. M.; Zientara, K. *Organometallics* **1993**, *12*, 4682.
(9) Petasis, N. A.; Fu, D.-K. *Organometallics* **1993**, *12*, 3776.
(10) Typical procedure: A solution of Cp_2TiMe_2 (1.9 g, 9×10^{-3} mol) and pivalonitrile (1.52 g, 18×10^{-3} mol) in toluene (50 mL) was stirred at 65−68 °C for 4−5 d under nitrogen in a Schlenk tube. After the solution was cooled to −20 °C, degassed PCl_3 (1.25 g, 9×10^{-3} mol) was added to the solution via a syringe. After the solution was to room temperature and NEt_3 (15−20 equiv) was added, the mixture was further heated for 2−3 h at 70 °C. After the reaction mixture was cooled, the resulting suspension was filtered on a glass frit and the solvent evaporated under vacuum. Crude **1a** was thus obtained in 45% yield as an orange oil, very sensitive to air and moisture. For **1a**: NMR (C_6D_6) ^{31}P δ 267.5; ^1H δ 7.22 (d, 1H, $^4J_{(HP)}$ = 4.4 Hz, C_5H); ^{13}C δ 29.5 (s, Me), 39.9 (d, $^3J_{(CP)}$ = 4.5 Hz, *C*Me$_3$), 111.3 (d, $^3J_{(CP)}$ = 44.1 Hz, C_5H), 182.1 (d, $^2J_{(C\text{-}P)}$ = 18.1 Hz, C_4 and C_6). For **1b**: ^{31}P NMR (toluene) δ 269.2.
(11) For **2**: 80% yield; ^{31}P δ 81.9 (C_6D_6). For **3**: 85% yield; ^{31}P δ 90.3 ($CDCl_3$). For **4**: 90% yield; ^{31}P δ −1.7, $^1J_{(PH)}$ = 642.3 Hz ($CDCl_3$).
(12) Typical procedure: A solution of diazaphosphinine **1a** (0.5 g, 2.4 × 10^{-3} mol) and 3-hexyne (0.975 g, 11.9 × 10^{-3} mol) in toluene (8 mL) was stirred at 70 °C for 10 h in a closed Schlenk tube filled with nitrogen. After the solution was cooled, the evaporation of toluene and unreacted hexyne left 0.3 g (ca. 60%) of crude **6** as an orange oil. For **5**: 60% yield; NMR (C_6D_6) ^{31}P δ 273.1, ^1H δ 1.38 (s, 9H, ^{t}Bu), 6.98−7.45 (m, 6H, Ph + HC_5), 8.64 (d, $^1J_{(HP)}$ = 31.1 Hz, 1H, HC_3); ^{13}C δ 30.0 (s, Me), 40.4 (d, $^3J_{(CP)}$ = 7.7 Hz, Me$_3$*C*), 117.4 (d, $^3J_{(CP)}$ = 31.9 Hz, C_5), 152.8 (d, $^2J_{(CP)}$ = 10.6 Hz, C_4), 153.5 (d, $^1J_{(CP)}$ = 74.9 Hz, C_3), 177.0 (d, $^2J_{(CP)}$ = 29.0 Hz, C_6); MS (Cl, NH_3) *m*/*z* 230 (M^+ + 1, 100). The crude 1,2-azaphosphinine **5** contains ca. 10% of its 2-phenyl isomer **5′** (^{13}P δ 261.1). For **6**: NMR (C_6D_6) ^{31}P δ 270.5; ^1H δ 0.97 (t, 3H, Me), 1.14 (t, 3H, Me), 1.42 (s, 9H, ^{t}Bu), 2.37 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 7.05 (s, 1H, HC_5); ^{13}C: δ: 15.6 (s, Me), 18.0 (d, $^3J_{(C\text{-}P)}$ = 12.6 Hz, Me), 24.8 (d, $^2J_{(C\text{-}P)}$ = 27.3 Hz, CH_2), 27.6 (s, CH_2), 31.0 (s, *Me*$_3$C), 40.6 (d, $^3J_{(C\text{-}P)}$ = 8.7 Hz, Me$_3$*C*), 119.2 (d, $^3J_{(C\text{-}P)}$ = 29.8 Hz, C_5), 155.1 (d, $^2J_{(C\text{-}P)}$ = 6.1 Hz, C_4), 174.8 (d, $^1J_{(C\text{-}P)}$ = 77.0 Hz, C_3), 175.4 (d, $^2J_{(C\text{-}P)}$ = 27.2 Hz, C_6); MS (Cl, NH_3) *m*/*z* 210 (M^+ + 1, 100).
(13) Märkl, G.; Dörges, C.; Riedl, T.; Klärner, F.-G.; Lodwig, C. *Tetrahedron Lett.* **1990**, *31*, 4589.
(14) Märkl, G.; Dorsch, S. *Tetrahedron Lett.* **1995**, *36*, 3839.
(15) For **7**: 2-ethynylpyridine was heated with **1a** in toluene at 100 °C for 15 h; 85% yield; NMR (C_6D_6) ^{31}P δ 202.5; ^1H δ 9.57 (dd, $^2J_{(HP)}$ = 37.3 Hz, $^4J_{(HH)}$ = 1.4 Hz, H_2, H_6). Compound **7** contains 5% of the 2,5-isomer (δ 201.3). For **8**: Bis(trimethylsilyl)acetylene was heated with **1a** in toluene at 80 °C for 15 h. The 1,2-azaphosphinine thus formed (^{31}P δ 305.5) was further heated in toluene with more alkyne at 120 °C for 20 h (overall yield 85%, ^{31}P δ 266.5). For **9**: (1) PhC≡CSiMe$_3$, 70 °C, 10 h, toluene; 1,2-azaphosphinine (^{31}P δ 303.6); (2) PhC≡CSiMe$_3$, 90 °C, 10 h, toluene; 80% yield; NMR (C_6D_6) ^{31}P δ 269.4; ^1H δ 0.26 (d, $^4J_{(HP)}$ = 1.6 Hz, SiMe$_3$); ^{13}C δ 3.0 (d, $^3J_{(CP)}$ = 9.5 Hz, SiMe$_3$). In **8**, only the α- but not the β-silyl groups are coupled with P. For **10**: (1) HC≡CSiMe$_3$, 70 °C, 3 h, toluene; 1,2-azaphosphinine (^{31}P δ 300.0); (2) HC≡CSiMe$_3$, 75 °C, 5 h, toluene; 85% yield; NMR (C_6D_6) ^{31}P δ 254.6; ^1H δ 0.36 (d, $^4J_{(HP)}$ = 0.8 Hz, SiMe$_3$), 7.22 (dt, $^4J_{(HP)}$ = 2.1 Hz, $^3J_{(HH)}$ = 8.0 Hz, H_4), 7.92 (dd, $^3J_{(HP)}$ = 9.4 Hz, H_3, H_5); ^{13}C δ 0.7 (d, $^3J_{(CP)}$ = 6.1 Hz, SiMe$_3$). For **11**: (1) PhC≡CPPh$_2$, 70 °C, 12 h, toluene; 1,2-azaphosphinine (^{31}P δ 289.5 and −19.0, $^2J_{(PP)}$ = 10.0 Hz); (2) PhC≡CPPh$_2$, 120 °C, 20 h, toluene; 80% yield; NMR ($CDCl_3$) ^{31}P δ 254.7 and −10.7, $^2J_{(PP)}$ = 22.0 Hz; ^{13}C δ 153.0 (dd, $^2J_{(CP)}$ = 10.7 and 26.4 Hz, C_3, C_5), 166.7 (dd, $^1J_{(CP)}$ = 26.0 and 88.7 Hz, C_2, C_6). For **12**: (1) PhC≡CC≡CPh, 70 °C, 8 h, toluene; 1,2-azaphosphinine (^{31}P δ 262.9); (2) PhC≡CC≡CPh, 100 °C, 8 h, toluene; 80% yield; NMR ($CDCl_3$) ^{31}P δ 198.1; ^{13}C δ 89.3 (d, $^3J_{(CP)}$ = 4.6 Hz, sp C), 95.0 (s, sp C), 141.9 (d, $^2J_{(CP)}$ = 23.4 Hz, C *ipso*).

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Except in the case of diynes, it appears that the most shielded sp carbon of the alkyne is connected to phosphorus in the final phosphinine.

In addition to allowing us to study in depth the almost unknown chemistry of 1,2-azaphosphinines and to prepare either mono-, bi-, tri-, or tetrafunctional phosphinines, this synthetic scheme underlines several interesting applications in coordination chemistry and might be generalized to other heteroatoms.

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Supporting Information Available: Experimental data for **1a**, **1b**, and **3**−**12** (3 pages). See any current masthead page for ordering and Internet access instructions.

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