2*H*-1,2-Azaphosphindoles – Synthesis and Characterization

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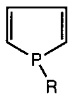
The first 1,2-azaphosphindoles **14a,b**, **15a,b** were obtained in a straightforward manner upon heating diphenylzirconocene in the presence of a cyanophosphane, which afforded azazirconacyclopentenes **11a,b** which can be reacted with various dichlorophosphanes. The use of the tetrachlorodiphosphane $Cl_2P(CH_2)_2PCl_2$ instead of a dichlorophosphane allowed the preparation of the bis(1,2-azaphosphindoles) **19**, **19′**. The monosulfur adduct of the azaphosphindole **14a**, i.e. **16a**, was characterized by X-ray structure analysis. Alkylation of **14a** or **16a** with methyltrifluoromethane sulfonate occurred selectively on the intracyclic phosphorus atom or on the sulfur atom, giving the salts **20** or **21**, respectively.

Introduction

Chemistry of 1*H*-phospholes **1** and of the corresponding fused-ring systems phosphindoles **2** (phosphorus analogs of indoles) and dibenzophospholes **3** has attracted considerable attention in the past two decades and is now well-documented.[1] The chemical behavior of these phosphorus heterocycles appeared to be quite different from that of the common heterocyclopentadiene systems such as furan, pyrrole and thiophene, and was the source of a rich and versatile chemistry.[1]

In marked contrast, synthesis and properties of analogous systems containing both phosphorus and one additional heteroatom are quite undeveloped and only a very few examples of 1*H*-1,2-azaphospholes **4**,[2a] 1*H*-1,3-λ^3-azaphospholes of type **5** or 1,3-λ^3-thiaphospholes of type **6** were reported.[2b,2c] Moreover, in all these derivatives the phosphorus atom is dicoordinated and not tricoordinated as in compounds **1–3**. Indeed, only recently was reported the formation of unique 2*H*-1,2-azaphosphole tungsten complexes **8** by the thermal decomposition of 2*H*-azaphosphirene **7** in toluene at 75 °C in the presence of DMAD[3] (Scheme 1). However, such a method suffers from two main drawbacks: 2*H*-azaphosphirenes are not easy to prepare, and yields of isolated complexes **8** are poor (5–12%).



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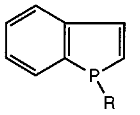

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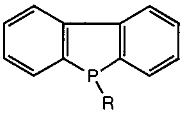

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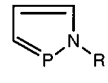

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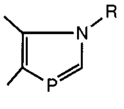

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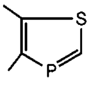

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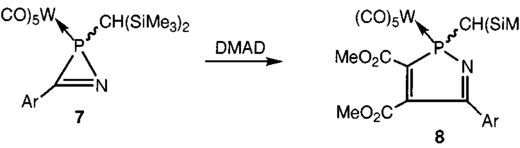
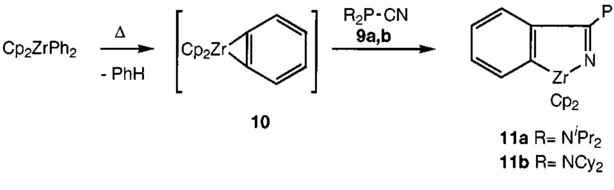


Scheme 1. Synthesis of 2*H*-1,2-azaphosphole tungsten complexes **8**

To our knowledge the preparation of free 1,2-azaphospholes and 1,2-azaphosphindoles has not yet been reported. We now present the facile synthesis of a number of azaphosphindoles, the X-ray characterization of an azaphosphindole, as well as preliminary studies concerning their reactivity.

Results and Discussion

Thermolysis of diphenylzirconocene in the presence of a wide variety of nitriles has previously been shown to generate azazirconacyclopentenes as dimers in the solid state in good to excellent yields.[4] A similar reaction was undertaken with the bisamino-cyanophosphanes **9a,b**[5] and diphenylzirconocene (Scheme 2). The transient zirconocene–benzyne complex **10** was trapped by **9a,b** to give the new azazirconacyclopentenes **11a,b** in 95% and 93% yield respectively. The reaction can be monitored by ^{31}P NMR spectroscopy, which shows the disappearance of the signal of the starting phosphane (**9a:** δ = 29.5, **9b:** δ = 33.7), which is replaced by a new signal at δ = 45.5 (**11a**) or δ = 55.8 (**11b**). Mass spectrometry (FAB) is in agreement with the expected compounds **11a** and **11b**.



Scheme 2. Synthesis of azazirconacyclopentenes **11a, b**

Infrared spectroscopy ($\tilde{\nu}_{C=N}$ = 1581–1583 cm^{-1}), and ^{13}C NMR [**11a:** $\delta_{C=N}$ = 191.3 (d, $^{1}J_{CP}$ = 19.0 Hz); **11b:** $\delta_{C=N}$ = 191.2 (d, $^{1}J_{CP}$ = 19.5 Hz)] corroborated the presence of an imino group. All the other NMR data are in agreement with the proposed azazirconacyclopentene structure.

Treatment of **11a** or **11b** with phenyldichlorophosphane **12** or *tert*-butyldichlorophosphane **13** at room temperature

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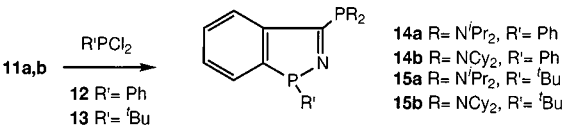
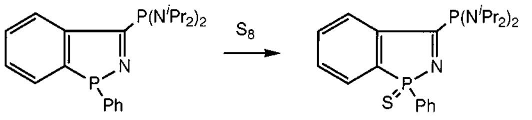
led to elimination of Cp_2ZrCl_2 to form the unprecedented 1,2-azaphosphindoles **14a,b** or **15a,b** as yellow solids obtained in 69–86% yield after workup (Scheme 3). The ^{31}P NMR spectrum exhibited, as expected, two doublets for compounds **14a**, **14b**, and **15b** {**14a:** $\delta = 41.1$ [P(N*i*Pr$_2$)$_2$], 77.0 (PPh), $J_{PP} = 6.7$ Hz; **14b:** $\delta = 44.1$ [P(NCy$_2$)$_2$], 76.5 (PPh), $J_{PP} = 13.7$ Hz; **15b:** $\delta = 44.9$ [P(N*i*Pr$_2$)$_2$], 99.0 (P*t*Bu), $J_{PP} = 6.5$ Hz}; only two singlets were detected for **15a** at $\delta = 43.8$ [P(N*i*Pr$_2$)$_2$] and at $\delta = 100.2$ (P*t*Bu). Both 1,2-azaphosphindoles were further characterized by ^1H and ^{13}C NMR, IR, mass spectrometry and elemental analyses. Addition of sulfur to **14a** afforded selectively the monosulfide **16a** {$\delta = 39.8$ (PN*i*Pr$_2$)$_2$ and 81.9 [P(S)Ph], $J_{PP} = 6.5$ Hz} (Scheme 4). Confirmation of the identity of **16a** and as a consequence of **14a** and the other 1,2-azaphosphindoles was achieved by a single-crystal X-ray study. The representation of the structure of **16a** is shown in Figure 1 , and the most representative bond lengths and angles are summarized.



Scheme 3. Synthesis of 1,2-azaphosphindoles **14a,b, 15a,b**



14a **16a**

Scheme 4. Synthesis of the monosulfide adduct **16a**

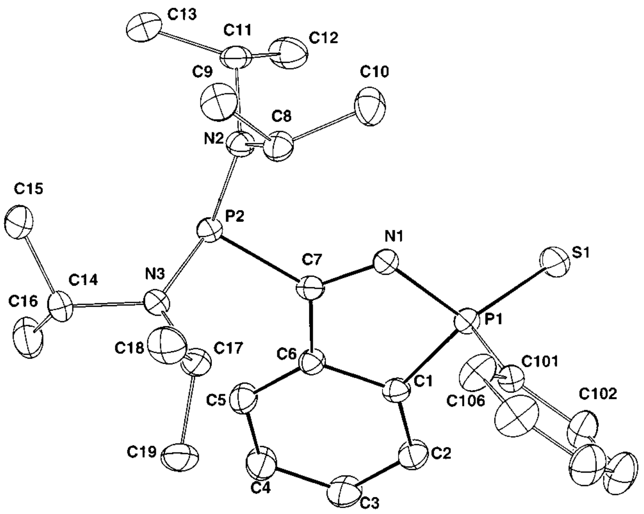
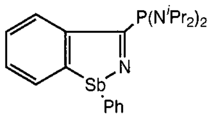


Figure 1. Molecular structure of **16a** with crystallographic numbering scheme; selected bond lengths (Å) and bond angles (°): P(1)–N(1) 1.702 (3), P(1)–C(1) 1.791 (4), C(7)–N(1) 1.300 (4), C(6)–C(7) 1.498 (5), C(6)–C(1) 1.393 (5), P(2)–N(3) 1.674 (3), N(1)–P(1)–C(1) 94.94 (15), C(7)–N(1)–P(1) 110.0 (2)

It appears therefore that such a one-pot reaction involving diphenylzirconocene, a cyanophosphane then by a dichlorophosphane, constitutes a very efficient method for the preparation of the first 3-phosphanyl-1,2-azaphosphindoles. A similar exchange reaction involving **11a** and phenyldichlorostilbene led to the formation of the corresponding 1,2-azastilbindole **17** obtained in 72% yield after workup. The ^{31}P chemical shift of **17** ($\delta = 83.8$) as well as the $^1J_{CP}$ coupling constant of the imino carbon atom ($J_{CP} = 0$ Hz) differ notably from the values detected for the azaphosphindoles described above. However, such a variation of chemical shift and very small $^1J_{CP}$ values were already observed in different systems incorporating a bis(diisopropylamino)-phosphanyl group. Mass spectrometry (*m*/*z*: 532 [M + H]$^+$) and the other NMR data corroborate the proposed structure.

Such a methodology can be applied to the preparation of derivatives incorporating more than one 1,2-azaphosphindole unit. As an example, treatment of a solution of the complex **11a** in toluene with the phosphane $Cl_2P(CH_2)_2PCl_2$ **18** at 0 °C for 15 min afforded the expected bis 1,2-azaphosphindole in 91% yield as two diastereoisomers **19** and **19'** in a 2:1 ratio (Scheme 5). The formation of these two diastereoisomers can be detected mainly by ^{31}P NMR spectroscopy, where two singlets were observed for the P(N*i*Pr$_2$)$_2$ group at $\delta = 41.4$ and 42.6.



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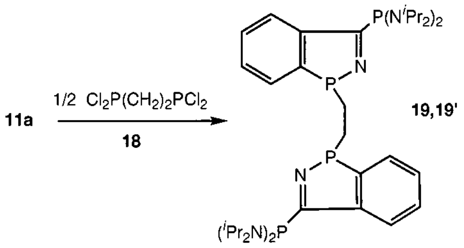
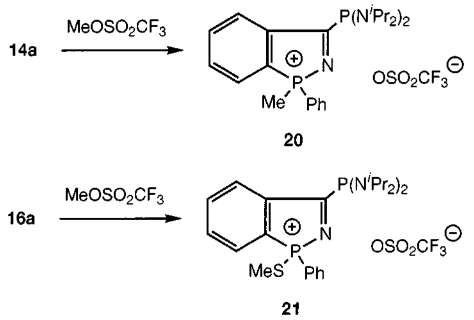


Scheme 5. Synthesis of bis(1,2-azaphosphindoles)

A preliminary study of the reactivity of these new phosphorus heterocycles was undertaken. Alkylation of **14a** by means of methyltrifluoromethane sulfonate selectively occurred on the intracyclic phosphorus atom leading to **20**. The signal of this phosphorus atom was deshielded ($\Delta\delta = 8.2$) while the signal of the P(N*i*Pr$_2$)$_2$ unit was shielded ($\Delta\delta = 6.9$). ^1H and ^{13}C NMR spectroscopy clearly indicated that the methyl group was linked to the P(Ph) group [^1H NMR: $\delta_{CH3} = 2.69$ (d, $J_{HP} = 14.6$ Hz); ^{13}C NMR: $\delta_{CH3} = 8.7$ (dd, $J_{CP} = 61.0$ Hz, $J_{CP} = 4.0$ Hz]. Alkylation of the sulfur adduct **16a** with methyltrifluoromethane sulfonate also took place selectively on sulfur, giving **21**

(Scheme 6). Alkylation did not occur on nitrogen or on the bis(diisopropylamino)phosphanyl group.



Scheme 6

Conclusion

In conclusion a simple and efficient way for the preparation of a new type of phosphorus heterocycles, namely 1,2-azaphosphindole, can be proposed through the thermolysis of benzynezirconocene in the presence of a cyanophosphane, followed by an exchange reaction involving the resulting azazirconacyclopentene and various dichlorophosphanes, or a tetrachlorodiphosphane. Taking into account the fascinating versatile chemistry of classical phospholes, azaphosphindoles should be reagents of choice to develop new applications of phosphorus heterocycles in different areas such as coordination and heterocyclic chemistry, and catalysis, to name a few. Such studies are under active investigation.

Experimental Section

General Remarks: All manipulations were conducted under a dry argon atmosphere using standard Schlenk techniques. All reagents were purchased from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under argon before use. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AC-200, AM-250 or MSL 400 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1} H, ^{13}C) or H_3PO_4 (^{31}P). IR spectra were recorded on a Perkin–Elmer FT 1725x spectrometer. Mass spectrum analyses and elemental analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS.

General Procedure for the Synthesis of Compounds 11a,b: To a solution of Cp_2ZrPh_2 (0.410 g, 1.09 mmol) in toluene (5 mL) was added at room temperature the corresponding cyanophosphane $(R_2N)_2PC{\equiv}N$ [R = iPr (**9a**), Cy (**9b**)] (1.09 mmol). The mixture was heated at reflux for 45 min, and then evaporated to dryness. The resulting solid residue was washed with pentane (3 mL) to give compounds **11a**,**b** as red solids.

Compound 11a: 95% yield. – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1581 cm^{-1}. – ^{31}P{^{1}H} NMR (C_6D_6): δ = 45.5 (s). – ^{1}H NMR (C_6D_6): δ = 1.29 (d, J_{HH} = 2.2 Hz, 12 H, CH_3), 1.32 (d, J_{HH} = 2.4 Hz, 12 H, CH_3), 3.56 (m, 4 H, NCH), 5.94 (s, 10 H, CH_{Cp}), 6.95–7.12 (m, 3 H, CH_{arom}), 7.91 (m, 1 H, CH_{arom}). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.7 (d, J_{CP} = 5.6 Hz, CH_3), 25.2 (d, J_{CP} = 6.5 Hz, CH_3), 48.9 (d, J_{CP} = 9.3 Hz, NCH), 111.6 (s, CH_{Cp}), 124.4, 126.5, 126.8 and 138.7 (s, CH_{arom}), 166.2 (d, J_{CP} = 51.7 Hz, ZrC*C*), 191.3 (d, J_{CP} = 19.0 Hz, C=N), 192.0 (d, J_{CP} = 7.7 Hz, ZrC). – MS (FAB.); *m/z*: 554 [M + H]$^+$, 453 [M – *i*Pr_2N]$^+$ – $C_{29}H_{42}N_3PZr$ (554.86): calcd. C 62.77, H 7.63, N 7.57; found C 62.68, H 7.59, N 7.65.

Compound 11b: 93% yield. – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1583 cm^{-1}. – ^{31}P{^{1}H} NMR (C_6D_6): δ = 55.8 (s). – ^{1}H NMR (C_6D_6): δ = 1.07–2.17 (m, 40 H, CH_2), 3.07 (m, 4 H, NCH), 6.02 (s, 10 H, CH_{Cp}), 7.00–7.33 (m, 3 H, CH_{arom}), 7.96 (d, J_{HH} = 7.1 Hz, 1 H, CH_{arom}). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 26.7, 27.5 and 27.8 (s, CH_2), 35.7 (br s, CH_2), 58.4 (d, J_{CP} = 9.2 Hz, NCH), 59.2 (br s, NCH), 59.8 (d, J_{CP} = 9.1 Hz, NCH), 111.6 (s, CH_{Cp}), 124.2, 126.7 and 138.5 (s, CH_{arom}), 126.9 (d, J_{CP} = 8.6 Hz, CH_{arom}), 166.3 (d, J_{CP} = 50.8 Hz, ZrC*C*), 191.2 (d, J_{CP} = 19.5 Hz, C=N), 191.9 (d, J_{CP} = 7.8 Hz, ZrC). – MS (FAB.); *m/z*: 714 [M + H]$^+$. – $C_{41}H_{58}N_3PZr$ (715.13): calcd. C 68.86, H 8.17, N 5.87; found C 68.75, H 8.09, N 5.96.

General Procedure for the Synthesis of Compounds 14a,b: To a solution of the corresponding complex **11a**,**b** (0.364 mmol) in toluene (5 mL) was added at room temperature $PhPCl_2$ (**12**) (0.049 mL, 0.364 mmol). The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give compounds **14a**,**b** as yellow solids.

Compound 14a: 86% yield. – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1571 cm^{-1} . – ^{31}P{^{1}H} NMR (C_6D_6): δ = 41.1 [d, J_{PP} = 6.7 Hz, P(N*i*$Pr_2)_2$], 77.0 (d, J_{PP} = 6.7 Hz, PPh). – ^{1}H NMR (C_6D_6): δ = 1.15 (d, J_{HH} = 6.4 Hz, 6 H, CH_3), 1.22 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 1.28 (d, J_{HH} = 6.7 Hz, 6 H, CH_3), 3.63 (m, 4 H, NCH), 6.97–7.58 (m, 8 H, CH_{arom}), 8.45 (m, 1 H, CH_{arom}). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.6 (d, J_{CP} = 5.3 Hz, CH_3), 24.9 (d, J_{CP} = 6.8 Hz, CH_3), 48.6 (d, J_{CP} = 11.4 Hz, NCH), 49.1 (d, J_{CP} = 10.7 Hz, NCH), 126.2 (d, J_{CP} = 12.6 Hz, CH_{arom}), 127.8 and 128.3 (s, CH_{arom}), 128.6 (d, J_{CP} = 3.8 Hz, CH_{arom}), 129.1 (d, J_{CP} = 7.2 Hz, *o*-PPh), 130.2 (s, *p*-PPh), 132.7 (d, J_{CP} = 20.8 Hz, *m*-PPh), 135.6 (dd, J_{CP} = 18.7 Hz, J_{CP} = 4.5 Hz, *i*-PPh), 145.9 (dd, J_{CP} = 41.4 Hz, J_{CP} = 22.0 Hz, *C*CPPh), 154.0 (dd, J_{CP} = 17.0 Hz, J_{CP} = 3.8 Hz, CPPh), 187.5 (pt, J_{CP} = 15.5 Hz, J_{CP} = 15.5 Hz, C=N). – MS (DCI/NH_3); *m/z*: 442 [M + H]$^+$. – $C_{25}H_{37}N_3P_2$ (441.53): calcd. C 68.00, H 8.44, N 9.51; found C 67.91, H 8.58, N 9.70.

Compound 14b: 75% yield. – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1601 cm^{-1}. – ^{31}P{^{1}H} NMR (C_6D_6): δ = 44.1 [d, J_{PP} = 13.7 Hz, P(N$Cy_2)_2$], 76.5 (d, J_{PP} = 13.7 Hz, PPh). – ^{1}H NMR (C_6D_6): δ = 0.97–2.06 (m, 40 H, CH_2), 3.21 (m, 4 H, NCH), 6.99–7.82 (m, 8 H, CH_{arom}), 8.50 (d, J_{HH} = 8.0 Hz, 1 H, CH_{arom}). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 26.7 (d, J_{CP} = 4.3 Hz, CH_2), 27.2 (d, J_{CP} = 5.5 Hz, CH_2), 27.6 (d, J_{CP} = 2.7 Hz, CH_2), 35.6 (d, J_{CP} = 4.7 Hz, CH_2), 58.6 (d, J_{CP} = 7.8 Hz, NCH), 126.4 (d, J_{CP} = 10.3 Hz, CH_{arom}), 127.9 and 128.3 (s, CH_{arom}), 128.6 (d, J_{CP} = 2.8 Hz, CH_{arom}), 129.1 (d, J_{CP} = 6.5 Hz, *o*-PPh), 129.7 (s, *p*-PPh), 132.0 (d, J_{CP} = 18.1 Hz, *m*-PPh), 136.5 (dd, J_{CP} = 18.9 Hz, J_{CP} = 5.1 Hz, *i*-PPh), 145.8 (dd, J_{CP} = 40.7 Hz, J_{CP} = 22.2 Hz, *C*CPPh), 153.6 (dd, J_{CP} = 18.4 Hz, J_{CP} = 3.4 Hz, CPPh), 187.9 (dd, J_{CP} = 18.3 Hz, J_{CP} = 13.9 Hz, C=N). – $C_{37}H_{53}N_3P_2$ (601.79): calcd. C 73.84, H 8.87, N 6.98; found C 73.70, H 8.67, N 7.15.

General Procedure for the Synthesis of Compounds 15a,b: To a solution of the corresponding complex **11a**,**b** (0.673 mmol) in toluene (8 mL) was added at room temperature *t*BuPCl_2 (**13**) (0.107 g, 0.673 mmol). The mixture was stirred at room temperature for 8 h and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give compounds **15a,b** as yellow solids.

Compound 15a: 72% yield. – IR (KBr): 1571 cm^{-1} $\tilde{\nu}$(C=N). – ^{31}P{^{1}H} NMR (C_6D_6): δ = 43.8 [s, P(N*i*Pr$_2$)$_2$], 100.2 (s, P*t*Bu). – ^{1}H NMR (C_6D_6): δ = 1.09 (d, J_{HP} = 22.9 Hz, 9 H, CCH$_3$), 1.18 (d, J_{HH} = 6.6 Hz, 6 H, CHC*H*$_3$), 1.20 (d, J_{HH} = 8.3 Hz, 6 H, CHC*H*$_3$), 1.32 (d, J_{HH} = 4.4 Hz, 6 H, CHC*H*$_3$), 1.35 (d, J_{HH} = 4.3 Hz, 6 H, CHC*H*$_3$), 3.30–3.73 (m, 4 H, NCH), 6.99–7.24 (m, 2 H, CH$_{arom}$), 7.63 (d, J_{HH} = 7.4 Hz, 1 H, CH$_{arom}$), 8.44 (d, J_{HH} = 7.7 Hz, 1 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.7 (d, J_{CP} = 6.5 Hz, CH*C*H$_3$), 25.0 (d, J_{CP} = 6.4 Hz, CH*C*H$_3$), 27.4 (d, J_{CP} = 12.6 Hz, C*C*H$_3$), 35.2 (dd, J_{CP} = 16.7 Hz, J_{CP} = 3.9 Hz, *C*CH$_3$), 48.7 (d, J_{CP} = 10.9 Hz, NCH), 126.2 (d, J_{CP} = 8.0 Hz, CH$_{arom}$), 127.7 (d, J_{CP} = 4.9 Hz, CH$_{arom}$), 127.9 and 128.2 (s, CH$_{arom}$), 146.4 (dd, J_{CP} = 41.8 Hz, J_{CP} = 19.2 Hz, *C*CP*t*Bu), 152.0 (dd, J_{CP} = 24.1 Hz, J_{CP} = 4.2 Hz, CP*t*Bu), 186.2 (pt, J_{CP} = 14.9 Hz, J_{CP} = 14.9 Hz, C=N). – $C_{23}H_{41}N_3P_2$ (421.54): calcd. C 65.53, H 9.80, N 9.96; found: C 65.60, H 9.77, N 10.10. – MS (DCI/NH$_3$); *m/z*: 422 [M + H]$^+$.

Compound 15b: 69% yield. – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1566 cm^{-1}. – ^{31}P{^{1}H} NMR (C_6D_6): δ = 44.9 [d, J_{PP} = 6.5 Hz, P(NCy$_2$)$_2$], 99.0 (d, J_{PP} = 6.5 Hz, P*t*Bu). – ^{1}H NMR (C_6D_6): δ = 0.88–1.93 (m, 49 H, CH$_2$ and CH$_3$), 3.30 (m, 4 H, NCH), 7.09–7.14 (m, 4 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 25.0 (s, CH$_3$), 26.3, 26.7 and 27.5 (s, CH$_2$), 27.7 (d, J_{CP} = 6.0 Hz, CH$_2$), 34.7 (d, J_{CP} = 8.9 Hz, *C*CH$_3$), 35.6 (br s, CH$_2$), 57.7 (d, J_{CP} = 10.6 Hz, NCH), 58.6 (d, J_{CP} = 8.5 Hz, NCH), 59.8 (d, J_{CP} = 9.7 Hz, NCH), 126.2 (d, J_{CP} = 14.4 Hz, CH$_{arom}$), 127.6 (d, J_{CP} = 4.3 Hz, CH$_{arom}$), 127.8 and 129.8 (s, CH$_{arom}$), 146.6 (dd, J_{CP} = 41.7 Hz, J_{CP} = 20.1 Hz, *C*CP*t*Bu), 151.8 (dd, J_{CP} = 26.1 Hz, J_{CP} = 4.8 Hz, CP*t*Bu), 185.9 (pt, J_{CP} = 17.1 Hz,J_{CP} = 17.1 Hz, C=N). – $C_{34}H_{57}N_3P_2$ (569.79): calcd. C 71.67, H 10.08, N 7.37; found C 71.40, H 9.91, N 7.62.

Synthesis of Compound 16a: To a solution of compound **14a** (0.150 g, 0.339 mmol) in toluene (5 mL) was added at room temperature S_8 (0.128 g, 0.5 mmol). The mixture was stirred at room temperature for 2 h and then evaporated to dryness. The resulting solid residue was dissolved in THF (3 mL) and transferred to a silica gel chromatography column. Elution with pentane gave a yellow band from which compound **16a** was isolated after removal of the solvent (78% yield). – M.p. 121–122 °C (decomp.). – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1511 cm^{-1}. – ^{31}P{^{1}H} NMR (C_6D_6): δ = 39.8 [d, J_{PP} = 6.5 Hz, P(N*i*Pr$_2$)$_2$], 81.9 [d, J_{PP} = 6.5 Hz, P(S)Ph]. – ^{1}H NMR (C_6D_6): δ = 1.12 (d, J_{HH} = 6.6 Hz, 18 H, CH$_3$), 1.18 (d, J_{HH} = 6.6 Hz, 6 H, CH$_3$), 3.54 (m, 4 H, NCH), 6.95–7.17 (m, 5 H, CH$_{arom}$), 7.48 (m, 1 H, CH$_{arom}$), 7.88 (m, 2 H, CH$_{arom}$), 8.15 (d, J_{HH} = 7.6 Hz, 1 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.5 (d, J_{CP} = 5.9 Hz, CH$_3$), 24.7 (d, J_{CP} = 7.5 Hz, CH$_3$), 25.0 (d, J_{CP} = 7.0 Hz, CH$_3$), 48.9 (d, J_{CP} = 11.2 Hz, NCH), 49.6 (d, J_{CP} = 10.3 Hz, NCH), 126.0 (pt, J_{CP} = 12.4 Hz, J_{CP} = 12.4 Hz, CH$_{arom}$), 128.8 (d, J_{CP} = 11.9 Hz, CH$_{arom}$), 128.9 [d, J_{CP} = 12.7 Hz, *o*-P(S)Ph], 131.5 [d, J_{CP} = 11.6 Hz, *m*-P(S)Ph], 131.8 (d, J_{CP} = 9.8 Hz, CH$_{arom}$), 132.2 [s, *p*-P(S)Ph], 132.6 (d, J_{CP} = 2.0 Hz, CH$_{arom}$), 142.3 [dd, J_{CP} = 82.0 Hz, J_{CP} = 2.6 Hz, CP(S)Ph], 144.3 [dd, J_{CP} = 43.9 Hz, J_{CP} = 37.3 Hz, *C*CP(S)Ph], 192.8 (pt, J_{CP} = 21.7 Hz, J_{CP} = 21.7 Hz, C=N). *i*-P(S)Ph not observed. – $C_{25}H_{37}N_3P_2S$ (473.59): calcd. C 63.40, H 7.87, N 8.87; found C 63.23, H 7.92, N 8.99.

Synthesis of Compound 17: To a solution of complex **11a** (0.345 g, 0.623 mmol) in toluene (5 mL) was added at room temperature PhSbCl$_2$ (0.168 g, 0.623 mmol). The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was washed with pentane (3 × 20 mL) and diethyl ether (3 × 5 mL) to give compound **17** as a yellow solid (72% yield). – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1591 cm^{-1}. – ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 83.8 (s). – ^{1}H NMR (CD_2Cl_2): δ = 1.08 (d, J_{HH} = 5.9 Hz, 6 H, CH$_3$), 1.19 (d, J_{HH} = 6.9 Hz, 6 H, CH$_3$), 1.37 (d, J_{HH} = 6.9 Hz, 6 H, CH$_3$), 1.47 (d, J_{HH} = 6.9 Hz, 6 H, CH$_3$), 3.94 (m, 2 H, NCH), 4.25 (m, 2 H, NCH), 7.12–8.05 (m, 9 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 24.7 (br s, CH$_3$), 25.2 (br s, CH$_3$), 50.9 (d, J_{CP} = 6.3 Hz, NCH), 51.2 (d, J_{CP} = 6.5 Hz, NCH), 123.8, 127.4, 128.3, 128.6, 129.8, 136.3 and 141.7 (s, CH$_{arom}$), 134.0 (s, *i*-Ph), 144.7 (d, J_{CP} = 26.1 Hz, *C*CSbPh), 146.9 (d, J_{CP} = 10.3 Hz, *C*SbPh), 194.6 (s, C=N). – MS (DCI/CH$_4$); *m/z*: 532 [M + H]$^+$. – $C_{25}H_{37}N_3PSb$ (532.30): calcd. C 56.42, H 7.00, N 7.89; found C 56.30, H 7.11, N 7.95.

Synthesis of Compounds 19, 19’: To a solution of complex **11a** (0.417 g, 0.753 mmol) in toluene (8 mL) was added at 0 °C $Cl_2PCH_2CH_2PCl_2$ (**18**) (0.056 mL, 0.376 mmol). The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatiles were removed from the solution to give a yellow solid containing an inseparable mixture of two diastereoisomers **19** and **19’** in a ratio of *ca.* 2:1 (91% yield). – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1566 cm^{-1}. – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 41.4 [s, P(N*i*Pr$_2$)$_2$ major isomer], 42.6 [s, P(N*i*Pr$_2$)$_2$ minor isomer], 81.5 (s, PCH$_2$). – ^{1}H NMR (CDCl$_3$): δ = 1.00–1.66 (m, 52 H, CH$_3$ and CH$_2$), 3.52 (m, 8 H, NCH), 7.25–7.65 (m, 6 H, CH$_{arom}$), 8.20 (m, 2 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 23.0 (dd, J_{CP} = 28.5 Hz, J_{CP} = 3.9 Hz, CH$_2$), 23.9 (br s, CH$_3$), 24.1 (d, J_{CP} = 7.1 Hz, CH$_3$), 24.3 (d, J_{CP} = 7.2 Hz, CH$_3$), 47.9 (d, J_{CP} = 10.8 Hz, NCH), 48.3 (d, J_{CP} = 8.5 Hz, NCH), 48.4 (d, J_{CP} = 8.0 Hz, NCH), 125.5 (d, J_{CP} = 10.3 Hz, CH$_{arom}$), 126.5 (dd, J_{CP} = 14.9 Hz, J_{CP} = 10.7 Hz, CH$_{arom}$), 127.2 and 127.4 (s, CH$_{arom}$), 145.4 (dd, J_{CP} = 41.4 Hz, J_{CP} = 31.6 Hz, *C*CPCH$_2$), 151.7 (m, *C*PCH$_2$), 187.0 (pt, J_{CP} = 19.7 Hz, J_{CP} = 19.7 Hz, C=N). – $C_{40}H_{68}N_6P_4$ (756.91): calcd. C 63.47, H 9.05, N 11.10; found C 63.22, H 9.13, N 11.30.

Synthesis of Compound 20: To a solution of compound **14a** (0.115 g, 0.260 mmol) in dichloromethane (5 mL) was added at 0 °C CF$_3$SO$_3$Me (0.029 mL, 0.260 mmol). The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was washed with pentane (3 × 15 mL) and dried in vacuo to give compound **20** as a red solid (81% yield). – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1631 cm^{-1}. – ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 49.2 [d, J_{PP} = 2.7 Hz, P(N*i*Pr$_2$)$_2$], 70.1 [d, J_{PP} = 2.7 Hz, P(Me)Ph]. – ^{1}H NMR (CD_2Cl_2): δ = 1.14–1.32 (m, 24 H, CH$_3$), 2.69 (d, J_{HP} = 14.6 Hz, 3 H, PCH$_3$), 3.60 (m, 4 H, NCH), 7.66–8.59 (m, 9 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 8.7 (dd, J_{CP} = 61.0 Hz, J_{CP} = 4.0 Hz, PCH$_3$), 23.9 (br s, CH$_3$), 49.5 (d, J_{CP} = 11.1 Hz, NCH), 49.6 (d, J_{CP} = 13.1 Hz, NCH), 117.8 [dd, J_{CP} = 93.3 Hz, J_{CP} = 5.0 Hz, *C*P(Me)Ph], 127.6 (pt, J_{CP} = 12.6 Hz, J_{CP} = 12.6 Hz, CH$_{arom}$), 130.3 (d, J_{CP} = 12.9 Hz, CH$_{arom}$), 131.8 [d, J_{CP} = 11.0 Hz, *o*-P(Me)Ph or CH$_{arom}$], 131.9 [d, J_{CP} = 8.9 Hz, *o*-P(Me)Ph or CH$_{arom}$], 133.5 [d, J_{CP} = 9.3 Hz, *m*-P(Me)Ph], 135.5 and 135.8 [s, CH$_{arom}$ and *p*-P(Me)Ph], 146.8 [dd, J_{CP} = 42.3 Hz, J_{CP} = 32.2 Hz, *C*CP(Me)Ph], 208.5 (dd, J_{CP} = 29.6 Hz, J_{CP} = 18.2 Hz, C=N). *i*-P(Me)Ph not observed. – $C_{27}H_{40}N_3O_3F_3P_2S$ (605.64): calcd. C 53.54, H 6.65, N 6.93; found C 53.42, H 6.59, N 7.10.

Synthesis of Compound 21: To a solution of compound **16a** (0.100 g, 0.211 mmol) in dichloromethane (5 mL) was added at room temperature CF$_3$SO$_3$Me (0.023 mL, 0.211 mmol). The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was washed with pentane (2 × 15 mL) and dried in vacuo to give compound **21** as a red solid (93% yield). – IR (KBr): $\tilde{\nu}_{(C=N)}$ = 1521 cm^{-1}. – ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 55.6 [s, P(N*i*Pr$_2$)$_2$], 82.9 [s, P(SMe)Ph]. – ^{1}H NMR (CD_2Cl_2): δ = 1.28 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 1.34 (d, J_{HH} = 6.5 Hz, 12 H, CH_3), 2.21 (d, J_{HP} = 15.9 Hz, 3 H, SCH_3), 3.61 (m, 4 H, NCH), 7.44–8.50 (m, 9 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 18.4 (s, SCH_3), 23.6 (br s, CH_3), 47.9 (br s, NCH), 50.1 (br s, NCH), 117.2 [dd, J_{CP} = 96.3 Hz, J_{CP} = 4.0 Hz, *C*P(SMe)Ph], 128.3 (dd, J_{CP} = 14.6 Hz, J_{CP} = 9.6 Hz, CH$_{arom}$), 130.9 [d, J_{CP} = 14.1 Hz, *o*-P(SMe)Ph or CH$_{arom}$], 131.2 [d, J_{CP} = 9.9 Hz, *o*-P(SMe)Ph or CH$_{arom}$], 132.1 (d, J_{CP} = 10.5 Hz, CH$_{arom}$), 134.5 [d, J_{CP} = 10.1 Hz, *m*-P(SMe)Ph], 136.6 and 137.0 [s, CH$_{arom}$ and *p*-P(SMe)Ph], 146.8 [dd, J_{CP} = 48.6 Hz, J_{CP} = 30.7 Hz, *C*CP(SMe)Ph], 210.2 (dd, J_{CP} = 28.5 Hz, J_{CP} = 23.4 Hz, C=N). *i*-P(SMe)Ph not observed. – $C_{27}H_{40}N_3O_3F_3S_2P_2$ (637.70): calcd. C 50.85, H 6.32, N 6.58; found C 50.91, H 6.40, N 6.71

X-ray Crystallographic Study of 16a: $C_{25}H_{37}N_3P_2S$. M=473.58; tetragonal, space group *P*, 42/*n*; *a* = 15.743(2) Å, *b* = 15.746(2) Å, *c* = 21.684(3) Å; *V* = 5375.4(12) Å^3; D_{calcd} = 1.170 g cm^{-3}; graphite-monochromated Mo-$K_($ radiation (λ = 0.71073 Å); μ = 0.256 mm^{-1}; *T* = 293(2) K. – Data collection was performed at room temperature on a STOE Imaging Plate Diffraction System (I.P.D.S) and corrected for Lorentz and polarisation effects: 3868 unique data in the range 2.05°< θ <23.26°, final unit cell parameters were obtained by a least-squares refinement on a set of 5000 reflections equally distributed in reciprocal space; crystal decay was monitored by measuring two hundred reflections per image. Any fluctuations in the intensity were observed over the course on the data collection. – Structure was solved by Direct Methods using (SIR92),[6] and refined by least-squares procedures on a F^2 with the aid of (SHELXL-97).[7] Final $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.0441$ for 3868 $F_o > 4\sigma F_o$ and 0.1002 for all data, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2} = 0.0988$, 0.1238 for all data, G.O.F = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^2 = 0.853$ for 289 parameters and with a Scheme of ponderation following: Weight = $1/[\sigma^2(F_o^2) + (0.0696P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Residual electron density extrema are: 0.444 and –0.273e Å^{-3}. Drawing of molecules were performed using the program ZORTEP[8] with a 50% probability displacement ellipsoids for non-hydrogen atoms. – Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary information number CCDC-132612. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

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