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Regiospecific reaction of phosphaimines with a zirconocene–benzyne complex. Synthesis and reactivity of novel azaphosphazirconaindans

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Summary — Azaphosphazirconaindan systems $(RCp)_2\overline{ZrN(R^1)P(NR^2R^3)(o\text{-}C}_6H_4)$ **4a** (R = H) and **5a,b** (R = *t*-Bu) are easily synthesized in a regiospecific way via a zirconocene–benzyne intermediate by means of thermolysis of $Cp_2ZrMePh$ **1** or $(t\text{-}BuCp)_2ZrPh_2$ **2** in the presence of phosphaimines $R^1N{=}P\text{-}NR^2R^3$ (**3a**: $R^1 = R^2 = R^3 = SiMe_3$; **3b**: $R^1 = R^2 = t\text{-}Bu$, $R^3 = SiMe_3$). After selective reaction of elemental sulfur on the phosphorus atom, Zr–N and Zr–C bond cleavage occurs on treatment with methanol, affording phosphine sulfides $PhP(S)(NHR^1)(NHR^2)$ **8a,b**. In these two reactions, complexes $(t\text{-}BuCp)_2\overline{ZrN(R^1)P(S)(NHR^2)(o\text{-}C}_6H_4)$ **7a,b** resulting from a selective cleavage of one $N\text{-}SiMe_3$ bond linked by the phosphorus atom can be isolated. With selenium powder, similar behavior leads to complexes $(t\text{-}BuCp)_2\overline{ZrN(R^1)P(Se)(NHR^2)(o\text{-}C}_6H_4)$ **10a,b**.

zirconocene–benzyne complex / phosphaimine / azaphosphazirconaindan / phosphine sulfide

Résumé — **Réaction régiospécifique de phosphaimines avec un complexe benzyne-zirconocène. Synthèse et réactivité de nouveaux azaphosphazirconaindanes.** *Les azaphosphazirconaindanes* $(RCp)_2\overline{ZrN(R^1)P(NR^2R^3)(o\text{-}C}_6H_4)$ **4a** *(R = H) et* **5a,b** *(R = t-Bu) sont régiospécifiquement préparés par simple chauffage de* $Cp_2ZrMePh$ **1** *ou* $(t\text{-}BuCp)_2ZrPh_2$ **2** *en présence de phosphaimines* $R^1N{=}P\text{-}NR^2R^3$ *(***3a***:* $R^1 = R^2 = R^3 = SiMe_3$*;* **3b***:* $R^1 = R^2 = t\text{-}Bu$, $R^3 = SiMe_3$*) via un intermédiaire benzyne-zirconocène. Après réaction sélective de soufre élémentaire sur l'atome de phosphore, les liaisons Zr–N et Zr–C sont coupées par traitement avec le méthanol conduisant aux sulfures de phosphine* $PhP(S)(NHR^1)(NHR^2)$ **8a,b***. Dans ces deux réactions, les complexes* $(t\text{-}BuCp)_2\overline{ZrN(R^1)P(S)(NHR^2)(o\text{-}C}_6H_4)$ **7a,b** *résultant de la coupure d'une liaison* $N\text{-}SiMe_3$ *liée à l'atome de phosphore ont pu être isolés. Avec la poudre de sélénium, le même comportement conduit aux complexes* $(t\text{-}BuCp)_2\overline{ZrN(R^1)P(Se)(NHR^2)(o\text{-}C}_6H_4)$ **10a,b***.*

complexe benzyne-zirconocène / phosphaimine / azaphosphazirconaindane / sulfure de phosphine

Regioselective generation and coupling reactions of zirconocene-stabilized benzyne complexes are well documented and offer a route to useful organic and inorganic products via subsequent conversion of the resulting metallacycles. For example, inter- and intramolecular insertion reactions of such benzyne complexes provide, after cleavage of the zirconacycle with electrophiles, a route to a variety of heterocycles [1]. Although numerous trapping reactions of transient zirconocene–benzyne species with unsaturated molecules (alkenes, alkynes, aldehydes, ketones, nitriles, etc) have been reported, to the best of our knowledge there are only two examples of insertion of an inorganic fragment containing a heteroatom [2]. The long-standing interest of some of us in phosphorus nitrogen species [3] prompted us to investigate the reactivity of phosphaimines R–P=N–R′ with zirconocene complexes. Herein, we report the formation of new azaphosphazirconacycles and some preliminary results concerning their reactivity.

Results and discussion

Thermolysis of methylphenylzirconocene **1** in benzene solution at 80 °C in the presence of one equivalent

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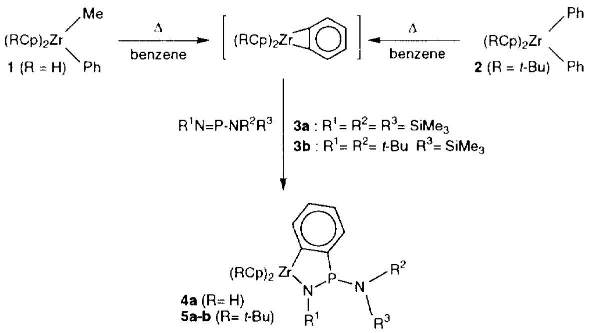
of phosphaimine $Me_3Si-N=P-N(SiMe_3)_2$ **3a** leads to a bright violet solution. Removal of the solvent in vacuo allows the isolation of the unique complex **4a** as an air- and moisture-sensitive powder in a quantitative yield. Recrystallization from hot hexane affords pink crystals of pure **4a** in 38% yield. Mass spectrometry and ^1H and ^{31}P NMR data are consistent with the suggested structure (scheme 1), an azaphosphazirconaindan derivative resulting from the coupling of phosphaimine with the in-situ-generated zirconocene–benzyne complex. The insertion of an N=P moiety into the Zr–C bond of the transient zirconocene–benzyne species is regiospecific with the nitrogen atom bonded to the zirconium. This result has been displayed previously in the hydro- and carbozirconation of **3a,b** [4] and was expected considering the strong polarization of the nitrogen–phosphorus double bond ($N^{\delta-}=P^{\delta+}$) towards the electrophilic zirconium(IV). The mass spectrum of **4a** exhibits a parent peak $(M+1)^+$ at m/e 575. The ^1H NMR spectrum for the trimethylsilyl groups consists of two doublets and one singlet at 0.53 (2.4 Hz), 0.15 (0.8 Hz) and 0.32 ppm while the signals for the diastereotopic Cp protons appear as two singlets at 5.92 and 6.04 ppm indicating that the azaphosphaindan cycle is not planar. No proton–phosphorus coupling constant is detected like in the diphosphino metallacycle $Cp_2ZrP(2,4,6\text{-}(OMe)_3C_6H_2)P(N(SiMe_3)_2)N(SiMe_3)$ [6.41 (d, $^3J_{HP}$ = 1.5 Hz), 6.02 (s)] [5] or in the three-membered phosphorus zirconacycle $Cp_2(Cl)ZrN(SiMe_3)P(H)(N(SiMe_3)_2)$ [5.85 (d, $^3J_{HP}$ = 2.7 Hz), 6.00 (d, $^3J_{HP}$ = 1.9 Hz)] [6]. Furthermore, **4a** exhibits a broad single ^{31}P NMR resonance at 101.2 ppm.

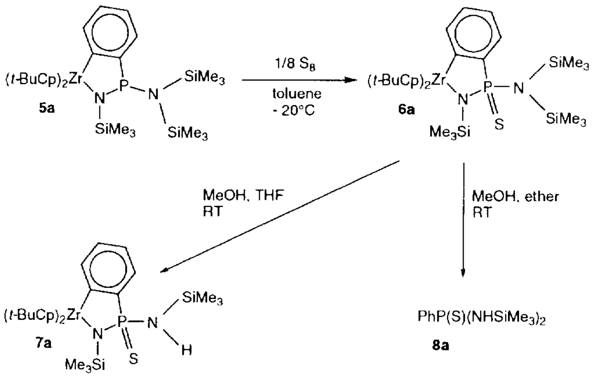


Scheme 1

The same reactions performed with bis(*tert*-butylcyclopentadienyl)diphenyl zirconium **2** and phosphaimines **3a** or **3b** lead to the fully characterized more stable *t*-BuCp-substituted azaphosphazirconacycles **5a,b** (scheme 1). These compounds present similar spectroscopic data to **4a**. ^{31}P chemical shifts for **5a** and **5b** are found at 101.8 and 92.3 ppm respectively. The ^1H NMR spectrum displays eight pseudo quadruplets in the range 5.5–7.1 ppm and two singlets around 1 ppm with no phosphorus–hydrogen coupling constants for the two inequivalent *t*-BuCp ligands.

Attempts to obtain crystals of **5a** or **5b** suitable for X-ray analysis have so far failed. Nevertheless, preliminary investigations concerning the reactivity of **5a** and **5b** corroborate the structure of these new azaphosphazirconacycles.

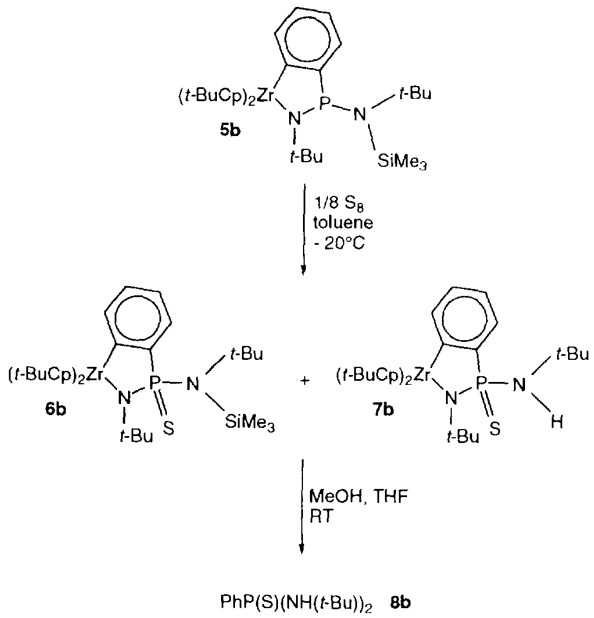
Elemental sulfur reacts rapidly and cleanly with azaphosphazirconaindan **5a** in toluene to provide a yellow solution. After removal of the solvent, the ^{31}P NMR spectrum of the crude powder reveals the presence of a major signal at 56.5 ppm besides that of a minor peak at 48.6 ppm. Reaction carried out at low temperature (−20 °C) allows the isolation of the major product, which is characterized as the corresponding sulfide complex $(t\text{-}BuCp)_2ZrN(SiMe_3)P(S)(N(SiMe_3)_2)(o\text{-}C_6H_4)$ **6a** by usual analytical and spectroscopic methods (scheme 2). The ^{31}P chemical shift (56.5 ppm) is in the expected range, ≈ 45 ppm upfield from that of **5a** (δ ^{31}P 101.8 ppm), indicating clearly the formation of a P=S bond [7]. Another evidence for the sulfurization on phosphorus is the dramatic increase of the $^1J_{CP}$ coupling constant (**5a**: $^1J_{CP}$ = 6.1 Hz, **6a**: $^1J_{CP}$ = 136.4 Hz) in the $^{13}C\{^1H\}$ NMR spectrum for the *ipso* carbon of the $o\text{-}C_6H_4$ group linked to phosphorus. The minor compound was identified as **7a** and will be discussed later.



Scheme 2

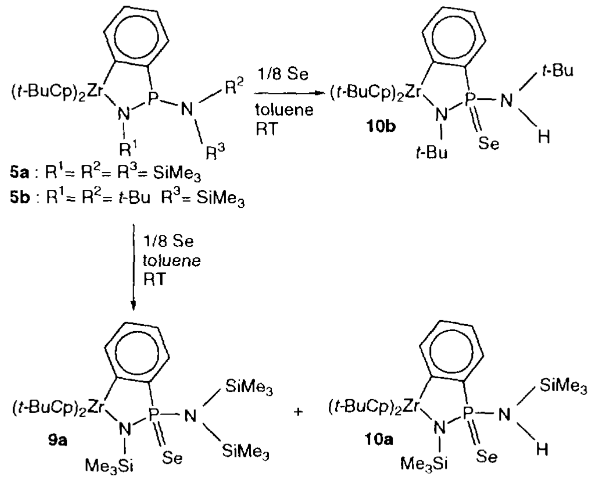
Sulfurization of the azaphosphazirconacycle **5b** affords, even at low temperature, two sulfide complexes **6b** and **7b**, the latter being isolated in pure form by crystallization (scheme 3). Analytical and spectroscopic data for **7b** are consistent with a $(t\text{-}BuCp)_2ZrN(t\text{-}Bu)P(S)(NH(t\text{-}Bu))(o\text{-}C_6H_4)$ formula. Indeed the ^{31}P NMR resonance (54.1 ppm) clearly indicates formation of the phosphorus–sulfur double bond. No resonance corresponding to the trimethylsilyl group could be detected in ^1H and $^{13}C\{^1H\}$ NMR. In addition, the ^1H NMR spectrum exhibits a broad doublet at 2.17 ppm ($^2J_{HP}$ = 2.2 Hz) which can be assigned to the NH group. Desilylation of **6b** due to traces of moisture can be reasonably postulated to explain the formation of **7b**.

Such a selective nitrogen–silicon bond cleavage is observed when **6a** is reacted with excess methanol for 5 min; at room temperature, compound **7a** (δ ^{31}P 48.6 ppm) is isolated in 63% yield (scheme 2). ^1H and $^{13}C\{^1H\}$ NMR spectra show that one of the three singlets due to the $SiMe_3$ groups disappears and is replaced by a broad doublet ($^2J_{HP}$ = 7.1 Hz) at 2.17 ppm due to an NH group. However, treatment of **6a** with excess methanol for 2 h at room temperature provides the phosphine sulfide PhP(S)(NH(SiMe$_3$))$_2$ **8a** (δ ^{31}P 57.8 ppm; literature: δ ^{31}P 57.9 ppm [8]) (scheme 2). Its formation is of particular interest since **8a** results from cleavage of nitrogen–silicon, zirconium–nitrogen and zirconium–carbon bonds and proves the structure of azaphosphazirconaindans **4–7**. The known phosphine sulfide PhP(S)(NH(*t*-Bu))$_2$ **8b** [9] is also isolated upon methanolysis of a mixture of **6b** and **7b** (scheme 3).



Scheme 3

The behavior of azaphosphazirconaindans **5a** and **5b** towards powdered selenium is quite similar to previous results of sulfurization. The reaction of **5a** with Se in toluene at room temperature leads to a mixture of selenide complexes **9a** and **10a** (scheme 4). Only (*t*-BuCp)$_2$ZrN(SiMe$_3$)P(Se)(NH(SiMe$_3$))(*o*-C$_6$H$_4$) **10a** can be isolated in pure form. The same reaction carried out with **5b** provides exclusively the similar selenide complex **10b** (scheme 4).



Scheme 4

Full characterization of **10a,b** shows that their main spectroscopic difference concerns the ^{31}P NMR spectrum. The resonances are found at 36.8 (**10a**) and 42.7 ppm (**10b**) and consist of a broad singlet (100%) and a doublet (7%) with a large P–^{77}Se coupling constant (689 Hz).

Investigations concerning the behavior of these new azaphosphazirconaindans towards various electrophilic reagents are underway.

Experimental section

Materials and methods

All reactions were routinely carried out under a dry and oxygen-free argon atmosphere, using standard Schlenk and high-vacuum-line techniques. Solvents were carefully dried and distilled from a sodium or potassium benzophenone ketyl complex prior to use.

^{1}H (200.132 MHz), ^{31}P (81.026 MHz) and ^{13}C{^{1}H} (50.323 MHz) NMR spectra were recorded on a Bruker AC-200 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to SiMe$_4$ as external reference. Downfield ^{31}P NMR chemical shifts are expressed with a positive sign, in parts per million, relative to external 85% H$_3$PO$_4$. Melting points were measured with a Kofler beam without any correction.

Cp$_2$ZrMePh **1** [10], (*t*-BuCp)$_2$ZrPh$_2$ **2** [11], Me$_3$SiN=PN(SiMe$_3$)$_2$ **3a** [12] and *t*-Bu-N=P-N(*t*-Bu)(SiMe$_3$) **3b** [13] were synthesized according to the literature.

Synthesis of complexes **4a**, **5a,b**, **6a,b**, **7a,b**, **9a** *and* **10a,b**

- *Cp$_2$ZrN(SiMe$_3$)P(N(SiMe$_3$)$_2$)(o-C$_6$H$_4$)* **4a**

A solution of Cp$_2$ZrMePh **1** (0.488 g, 1.609 mmol) and Me$_3$SiN=PN(SiMe$_3$)$_2$ **3a** (0.448 g, 1.611 mmol) in 25 mL benzene was refluxed for 8 h. After removal of the solvent in vacuo the pink violet solid obtained was recrystallized from hot hexane (60 °C, 8 mL) to yield 0.352 g (38%) of azaphosphazirconacycle **4a** as pink crystals.

^{31}P NMR (C$_6$D$_6$) δ 101.2 (broad s).

^{1}H NMR (C$_6$D$_6$) δ 7.51–6.74 (m, 4H, *o*-C$_6$H$_4$), 6.04, 5.92 (s, 5H, Cp), 0.53 (d, 9H, $^4J_{HP}$ = 2.4 Hz, SiMe$_3$), 0.32 (s, 9H, SiMe$_3$), 0.15 (d, 9H, $^4J_{HP}$ = 0.8 Hz, SiMe$_3$).

- *(t-BuCp)$_2$ZrN(SiMe$_3$)P(N(SiMe$_3$)$_2$)(o-C$_6$H$_4$)* **5a**

A solution of (*t*-BuCp)$_2$ZrPh$_2$ **2** (1.475 g, 3.030 mmol) and Me$_3$SiN=PN(SiMe$_3$)$_2$ **3a** (0.843 g, 3.030 mmol) in 50 mL of benzene was refluxed for 8 h. After removal of the solvent in vacuo, the purple oil obtained was washed with cold pentane (−30 °C, 3 mL) to afford 1.770 g (87%) of azaphosphazirconacycle **5a** as a purple powder.

^{31}P NMR (C$_6$D$_6$) δ 101.8 (broad s).

^{1}H NMR (C$_6$D$_6$) δ 7.47-6.95 (m, 4H, *o*-C$_6$H$_4$), 7.14, 7.04, 6.57, 6.49, 6.20, 5.90, 5.83 and 5.75 (pseudo q, 1H, *t*-BuCp), 1.18 and 0.83 (s, 9H, *t*-BuCp), 0.56 (d, 9H, $^4J_{HP}$ = 2.4 Hz, SiMe$_3$), 0.30 (s, 9H, SiMe$_3$), 0.28 (d, 9H, $^4J_{HP}$ = 1 Hz, SiMe$_3$).

^{13}C{^{1}H} NMR (CDCl$_3$) δ 187.09 (d, $^2J_{CP}$ = 21.3 Hz, C*ipso*-Zr), 164.46 (d, $^1J_{CP}$ = 6.1 Hz, C*ipso*-P), 145.75 and 144.88 (s, C quaternary *t*-BuCp), 129.61 (d,

J_{CP} = 27.5 Hz, *o*-C_6H_4), 109.72 (d, J_{CP} = 12.2 Hz, *o*-C_6H_4), 139.27, 125.73, 124.80, 119.45, 118.99, 115.27, 109.95, 108.30, 107.07 and 105.47 (s, *o*-C_6H_4 and *t*-BuCp), 34.51 and 33.97 (s, C quaternary *t*-BuCp), 32.02 and 30.86 (s, *t*-BuCp), 6.17 (s, $SiMe_3$), 5.62 (d, $^3J_{CP}$ = 23.2 Hz, $SiMe_3$), 4.04 (d, $^3J_{CP}$ = 7.6 Hz, $SiMe_3$).

- $(t\text{-}BuCp)_2\overline{ZrN(t\text{-}Bu)P(N(t\text{-}Bu)(SiMe_3))(o\text{-}C}_6H_4)$ **5b**

A solution of $(t\text{-BuCp})_2ZrPh_2$ **2** (0.653 g, 1.340 mmol) and *t*-BuN=PN(*t*-Bu)($SiMe_3$) **3b** (0.330 g, 1.341 mmol) in 20 mL of benzene was refluxed for 9 h. After removal of the solvent in vacuo, the red oil obtained was washed with cold pentane (−30 °C, 3 mL) to afford a red powder (0.711 g, 81%) which was recrystallized from hot pentane to yield 0.381 g (43%) of the azaphosphazirconacycle **5b** as red crystals.

^{31}P NMR (C_6D_6) δ 92.3 (broad s).

^{1}H NMR (C_6D_6) δ 7.71–6.94 (m, 4H, *o*-C_6H_4), 6.57, 6.09, 6.03, 5.95, 5.89, 5.80, 5.74 and 5.56 (pseudo q, 1H, *t*-BuCp), 1.44 and 1.20 (s, 9H, *t*-BuCp), 1.32 (d, 9H, $^4J_{HP}$ = 0.5 Hz, *t*-Bu), 0.98 (d, 9H, $^4J_{HP}$ = 0.7 Hz, *t*-Bu), 0.61 (d, 9H, $^4J_{HP}$ = 3.4 Hz, $SiMe_3$).

^{13}C{^{1}H} NMR ($CDCl_3$) δ 196.12 (d, $^2J_{CP}$ = 17.3 Hz, C*ipso*-Zr), 149.25 (d, $^1J_{CP}$ = 4.6 Hz, C*ipso*-P), 144.87 and 141.35 (s, C quaternary *t*-BuCp), 139.36 (s, *o*-C_6H_4), 132.61 (d, J_{CP} = 37.8 Hz, *o*-C_6H_4), 123.52 (d, J_{CP} = 8.2 Hz, *o*-C_6H_4), 124.26, 113.83, 113.53, 113.38, 111.82, 111.17, 109.48 and 101.27 (s, *o*-C_6H_4 and *t*-BuCp); 58.56 to 58.05 (2d overlapped, C quaternary *t*-Bu), 33.68 (s, C quaternary *t*-BuCp), 33.49 (s, *t*-BuCp), 32.81 (s, C quaternary *t*-BuCp), 31.60 (s, *t*-BuCp), 31.17–30.66 (2d overlapped, *t*-Bu), 7.44 (d, $^3J_{CP}$ = 19.7 Hz, $SiMe_3$).

- $(t\text{-}BuCp)_2\overline{ZrN(SiMe_3)P(S)(N(SiMe_3)_2)(o\text{-}C}_6H_4)$ **6a**

To a solution of complex **5a** (0.113 g, 0.164 mmol) in 4 mL toluene cooled at −20 °C was added powdered sulfur (8 mg, 0.249 mmol). The mixture was stirred at −20 °C for 15 min and the purple solution turned rapidly to yellow. Solvent was removed in vacuo leading to a yellow powder which was extracted with ether (6 mL). After filtration of the resulting yellow solution and evaporation of the solvent, the crude complex was recrystallized from an ether/pentane (4:1) mixture to yield 0.043 g (37%) of **6a** as yellow crystals.

^{31}P NMR ($CDCl_3$) δ 56.5 (broad s).

^{1}H NMR (C_6D_6) δ 7.49–7.44 (m, 1H, *o*-C_6H_4), 7.43 (pseudo q, 1H, *t*-BuCp), 7.06–6.99 (m, 3H, *o*-C_6H_4), 6.96, 6.82, 6.60, 6.47, 6.26, 6.13 and 5.82 (pseudo q, 1H, *t*-BuCp), 1.43 and 0.94 (s, 9H, *t*-BuCp), 0.64 (s, 9H, $SiMe_3$), 0.28 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR ($CDCl_3$) δ 185.41 (d, $^2J_{CP}$ = 31.5 Hz, C*ipso*–Zr), 158.63 (d, $^1J_{CP}$ = 136.4 Hz, C*ipso*–P), 146.36 and 145.06 (s, C quaternary *t*-BuCp), 138.94 (d, J_{CP} = 23.3 Hz, *o*-C_6H_4), 129.12 (d, J_{CP} = 18 Hz, *o*-C_6H_4), 126.17 (d, J_{CP} = 14.3 Hz, *o*-C_6H_4), 127.61, 122.32, 120.51, 118.99, 115.52, 110.06, 109.01 and 108.90 (s, *o*-C_6H_4 and *t*-BuCp); 35.01 and 34.05 (s, C quaternary *t*-BuCp), 32.27 and 31.55 (s, *t*-BuCp), 9.71, 6.36 and 5.90 (s, $SiMe_3$).

- $(t\text{-}BuCp)_2\overline{ZrN(SiMe_3)P(S)(NH(SiMe_3))(o\text{-}C}_6H_4)$ **7a**

To a solution of complex **6a** (30 mg, 0.0436 mmol) in 3 mL THF were added two drops of methanol. The mixture was stirred for 5 min at room temperature. Volatiles were removed in vacuo. Recrystallization from an ether/pentane (2:1) mixture gave 20 mg (63%) of **7a** as pale yellow crystals.

^{31}P NMR (C_6D_6) δ 48.6 (broad s).

^{1}H NMR (C_6D_6) δ 8.12–8.01 (m, 1H, *o*-C_6H_4), 7.15–6.99 (m, 2H, *o*-C_6H_4), 6.88–6.92 (m, 2H, *t*-BuCp and *o*-C_6H_4), 6.63, 6.18, 6.12, 6.01 and 5.87 (pseudo q, 1H, *t*-BuCp), 5.70 (m, 2H, *t*-BuCp), 2.17 (broad d, 1H, $^2J_{HP}$ = 7.1 Hz, NH), 0.96 and 0.95 (s, 9H, *t*-BuCp), 0.55 (s, 9H, $SiMe_3$), 0.39 (s, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR ($CDCl_3$) δ 183.38 (d, $^2J_{CP}$ = 30.5 Hz, C*ipso*–Zr), 156.03 (d, $^1J_{CP}$ = 134.1 Hz, C*ipso*–P), 145.96 and 142.50 (s, C quaternary *t*-BuCp), 139.11 (d, J_{CP} = 23.1 Hz, *o*-C_6H_4), 129.27 (d, J_{CP} = 18.5 Hz, *o*-C_6H_4), 126.74 (d, J_{CP} = 2.8 Hz, *o*-C_6H_4), 126.39 (d, J_{CP} = 14.8 Hz, *o*-C_6H_4), 118.32, 114.79, 114.76, 114.46, 111.49, 111.12, 110.68 and 106.69 (s, *t*-BuCp); 33.55 (s, 2 C quaternary *t*-BuCp), 31.34 and 31.03 (s, *t*-BuCp), 4.58 (d, $^3J_{CP}$ = 3.7 Hz, $SiMe_3$), 2.69 (d, $^3J_{CP}$ = 2.8 Hz, $SiMe_3$).

- $(t\text{-}BuCp)_2\overline{ZrN(t\text{-}Bu)P(S)(N(t\text{-}Bu)(SiMe_3))(o\text{-}C}_6H_4)$ **6b** *and*

  $(t\text{-}BuCp)_2\overline{ZrN(t\text{-}Bu)P(S)(NH(t\text{-}Bu))(o\text{-}C}_6H_4)$ **7b**

To a solution of complex **5b** (0.257 g, 0.312 mmol) in 10 mL of toluene cooled at −20 °C was added powdered sulfur (13 mg, 0.406 mmol). The mixture was stirred at −20 °C for 15 min. The red solution turned to yellow. After removal of the solvent in vacuo, the resulting orange oil was extracted with ether (8 mL), filtered and concentrated to 4 mL. After one night at −20 °C, 0.048 g (21.6%) of pure **7b** as yellow crystals was isolated.

6b: ^{31}P NMR (C_6D_6) δ 61.1 (broad s).

^{1}H NMR (C_6D_6) δ 8.13–8.01 (m, 1H, *o*-C_6H_4), 7.18–6.18 (m, 4H, *o*-C_6H_4 and *t*-BuCp), 6.54, 6.44 and 6.31 (pseudo q, 1H, *t*-BuCp), 6.00 (m, 3H, *t*-BuCp), 5.87 (pseudo q, 1H, *t*-BuCp), 1.41 and 1.40 (s, 9H, *t*-BuCp), 1.13 and 1.07 (s, 9H, *t*-Bu), 0.98 (s, 9H, $SiMe_3$).

7b: ^{31}P NMR (C_6D_6) δ 54.1 (broad s).

^{1}H NMR (C_6D_6) δ 8.70 (m, 1H, *o*-C_6H_4), 7.10–6.90 (m, 3H, *o*-C_6H_4), 6.29–6.24 (m, 2H, *t*-BuCp), 6.07 and 6.00 (pseudo q, 1H, *t*-BuCp), 5.94–5.87 (m, 2H, *o*-C_6H_4), 5.77 (pseudo q, 1H, *t*-BuCp), 5.63 (pseudo q, 1H, *t*-BuCp), 2.17 (broad d, 1H, $^1J_{HP}$ = 2.2 Hz, NH), 1.49 (s, 18H, *t*-BuCp), 1.08 and 0.98 (s, 9H, *t*-Bu).

^{13}C{^{1}H} NMR ($CDCl_3$) δ 184.05 (d, $^2J_{CP}$ = 29.6 Hz, C*ipso*–Zr), 149.80 (d, $^1J_{CP}$ = 140.5 Hz, C*ipso*–P), 145.13 and 142.23 (s, C quaternary *t*-BuCp), 139.19 (d, J_{CP} = 21.3 Hz, *o*-C_6H_4), 130.51 (d, J_{CP} = 21.3 Hz, *o*-C_6H_4), 126.55 (d, J_{CP} = 3.7 Hz, *o*-C_6H_4), 125.06 (d, J_{CP} = 14.8 Hz, *o*-C_6H_4), 114.22, 114.17, 113.08, 112.57, 111.89, 111.03 and 107.26 (s, *t*-BuCp), 59.54 (d, $^2J_{CP}$ = 4.6 Hz, C quaternary *t*-Bu), 53.00 (d, $^2J_{CP}$ = 3.7 Hz, C quaternary *t*-Bu), 33.83 and 33.64 (s, C quaternary *t*-BuCp), 32.21–31.91 (2d overlapped, *t*-Bu), 31.56 and 31.16 (s, *t*-BuCp).

- $(t\text{-}BuCp)_2\overline{ZrN(SiMe_3)P(Se)(N(SiMe_3)_2)(o\text{-}C}_6H_4)$ **9a** *and*

  $(t\text{-}BuCp)_2\overline{ZrN(SiMe_3)P(Se)(NH(SiMe_3))(o\text{-}C}_6H_4)$ **10a**

To a solution of complex **5a** (0.250 g, 0.363 mmol) in 8 mL toluene was added powdered selenium (31 mg, 0.400 mmol). After 1 h, the mixture turned to orange. After removal of the solvent in vacuo, the resulting powder was extracted with ether (2 x 10 mL) and filtered over celite to remove excess selenium. The solvent was concentrated. After 2 days at −20 °C, 180 mg (71%) of pure **10a** was obtained.

9a: ^{31}P NMR ($CDCl_3$) δ 39.6 (broad s/100%, d/7%, $^1J_{PSe}$ = 671 Hz).

^1H NMR ($CDCl_3$) δ 7.57 (pseudo q, 1H, *t*-BuCp), 7.48–7.38 (m, 1H, *o*-C_6H_4), 7.05–6.93 (m, 4H, *o*-C_6H_4 and *t*-BuCp), 6.74, 6.57, 6.43, 6.29, 6.08 and 5.77 (pseudo q, 1H, *t*-BuCp), 1.39 and 0.91 (s, 9H, *t*-BuCp), 0.67, 0.25 and 0.07 (s, 9H, $SiMe_3$).

10a: ^{31}P NMR ($CDCl_3$) δ 36.8 (broad s/100%, d/7%, $^1J_{PSe}$ = 689 Hz).

^1H NMR ($CDCl_3$) δ 7.67–7.55 (m, 1H, *o*-C_6H_4), 7.14 (pseudo q, 1H, *t*-BuCp), 7.08–7.00 (m, 1H, *o*-C_6H_4), 6.95 (m, 2H, *o*-C_6H_4), 6.63, 6.45, 6.36 and 6.30 (pseudo q, 1H, *t*-BuCp), 6.22 (m, 2H, *t*-BuCp), 5.94 (pseudo q, 1H, *t*-BuCp), 2.19 (d, 1H, $^2J_{HP}$ = 9.5 Hz, NH), 1.12 and 0.97 (s, 9H, *t*-BuCp), 0.38 and 0.30 (s, 9H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 183.14 (d, $^2J_{CP}$ = 31.7 Hz, C*ipso*-Zr), 156.80 (d, $^1J_{CP}$ = 123.1 Hz, C*ipso*-P), 146.61 and 142.83 (s, C quaternary *t*-BuCp), 139.34 (d, J_{CP} = 23.0 Hz, *o*-C_6H_4), 129.85 (d, J_{CP} = 19.9 Hz, *o*-C_6H_4), 127.11 (d, J_{CP} = 3.1 Hz, *o*-C_6H_4), 126.76 (d, J_{CP} = 4.6 Hz, *o*-C_6H_4), 119.18, 115.25, 115.10, 114.75 (s, *t*-BuCp), 111.70 (s, 2C, *t*-BuCp), 111.26 and 107.01 (s, *t*-BuCp), 33.89 (s, 2 C quaternary *t*-BuCp), 31.67 and 31.40 (s, *t*-BuCp), 4.92 (d, $^3J_{CP}$ = 3.8 Hz, $SiMe_3$), 3.18 (s, $SiMe_3$).

- $(t\text{-}BuCp)_2\overline{ZrN(t\text{-}Bu)P(Se)(NH(t\text{-}Bu))(o\text{-}C}_6H_4)$ **10b**

To a solution of complex **5b** (186 mg, 0.285 mmol) in 5 mL ether was added powdered selenium (30 mg, 0.380 mmol). The mixture was stirred at room temperature for 1 h. The solution was filtered over celite to remove excess selenium and the solvent was concentrated. After one night in the refrigerator (−20 °C), 0.110 g (53%) pure **10b** was obtained.

^{31}P NMR ($CDCl_3$) δ 42.7 (broad s/100%, d/7%, $^1J_{PSe}$ = 689 Hz).

^1H NMR ($CDCl_3$) δ 8.08–8.03 (m, 1H, *o*-C_6H_4), 7.13–6.92 (m, 3H, *o*-C_6H_4), 6.49, 6.46, 6.36 and 6.33 (pseudo q, 1H, *t*-BuCp), 6.19–6.16 (m, 2H, *t*-BuCp), 6.13 and 6.00 (pseudo q, 1H, *t*-BuCp), 2.32 (broad d, 1H, NH), 1.46 and 1.28 (s, 9H, *t*-BuCp), 1.22 and 0.97 (s, 9H, *t*-Bu).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 184.15 (d, $^2J_{CP}$ = 29.8 Hz, C*ipso*-Zr), 149.14 (d, $^1J_{CP}$ = 130.0 Hz, C*ipso*-P), 144.34 and 142.65 (s, C quaternary *t*-BuCp), 139.20 (d, J_{CP} = 20.6 Hz, *o*-C_6H_4), 131.49 (d, J_{CP} = 22.9 Hz, *o*-C_6H_4), 127.19 (d, J_{CP} = 3.8 Hz, *o*-C_6H_4), 125.39 (d, J_{CP} = 15.3 Hz, *o*-C_6H_4), 115.21, 113.82, 113.22, 112.83, 112.75, 112.24, 111.71 and 111.17 (s, *t*-BuCp), 59.99 (d, $^2J_{CP}$ = 3.8 Hz, C quaternary *t*-Bu), 54.02 (d, $^2J_{CP}$ = 5.3 Hz, C quaternary *t*-Bu), 34.09 and 34.02 (s, C quaternary *t*-BuCp), 32.49 (d, $^3J_{CP}$ = 8.4 Hz, *t*-Bu), 32.34 (d, $^3J_{CP}$ = 3.0 Hz, *t*-Bu), 31.99 and 31.65 (s, *t*-BuCp).

Satisfactory elemental analysis (Service central d'analyses du CNRS) and mass fragmentation using DC1/CH_4 method on a Nermag R10-10H were obtained for all complexes.

Synthesis of phosphine sulfides **8a,b**

- *Bis[(trimethylsilyl)amino]phenylphosphine sulfide* **8a**

To a solution of complex **6a** (0.203 g, 0.282 mmol) in 8 mL ether was added an excess of methanol (0.1 mL, 2.473 mL). The mixture was stirred for 2 h at room temperature. Volatiles were removed in vacuo. The residue was extracted with 7 mL pentane and the crude product was purified by flash chromatography on silica gel (ethyl acetate/pentane, 8:2) to afford 50 mg (56%) of the pure product **8a** as colorless crystals.

Mp: 91 °C.

^{31}P NMR ($CDCl_3$) δ 57.8 (broad s).

^1H NMR ($CDCl_3$) δ 7.97–7.85 (m, 1H, Ph), 7.50–7.39 (m, 4H, Ph), 2.37 (broad d, 2H, $^2J_{HP}$ = 5.5 Hz, NH), 0.21 (s, 18H, $SiMe_3$).

- *Bis(*tert*-butylamino)phenylphosphine sulfide* **8b**

A THF solution of a mixture (0.100 g) of **6b**, **7b** and methanol (0.1 mL) was stirred at room temperature overnight, the red solution slowly turned yellow. Volatiles were removed in vacuo, the yellow oil obtained was extracted with 4 mL ether and twice with 4 mL pentane and the resulting solution was filtered twice, yielding 28 mg (53% based on the complex **5b**) of pure **8b**.

Mp 106 °C.

^{31}P NMR ($CDCl_3$) δ 54.1 (broad s).

^1H NMR ($CDCl_3$) δ 8.08–7.96 (m, 2H, Ph), 7.45–7.41 (m, 3H, Ph), 2.34 (broad d, 2H, $^2J_{HP}$ = 5.1 Hz, NH), 1.32 (s, 18H, *t*-Bu).

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