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Communications

Zirconium-Assisted Functionalizations of an Unsaturated Phosphorus–Nitrogen–Sulfur Heterocycle

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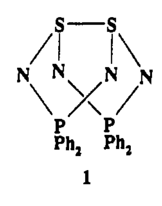
Organozirconium reagents are widely employed as catalysts in organic synthesis.[1] By contrast, zirconocene derivatives were first used to functionalize main group compounds only very recently.[2] Most of the preliminary work in this area, conducted by Majoral et al.,[2b,c,e–g] has involved the addition of Cp_2ZrHCl, Cp_2ZrH_2, or Cp_2ZrMe_2 across the P═N double bond in phosphaimines. More recently, Mathey et al. have shown that zirconocene itself will insert into the carbon–halogen bonds of 2-halophosphinines under very mild conditions.[2a] Moreover, the resulting zirconyl complexes react "cleanly" with selected electrophiles to give 2-deuterio-, 2-iodo-, or 2-cyanaphosphinines. We now wish to report the synthesis and structural characterization of the first zirconyl complex of the unsaturated $P_2N_4S_2$ ring (**1**), which exhibits a novel η^2-N,S bonding mode, and describe the use of this zirconathiaziridene for functionalizing the heterocyclic ring.

Reaction of the dilithio complex **2** (R = ^tBu) (produced by treatment of a THF solution of **1** with Bu^tLi)[3,4] with 2 equiv of Cp_2ZrCl_2 in THF at 0 °C furnished the complex $[Cp_2ZrCl(Ph_4P_2N_4S_2Bu^t)]$ (**3**) as highly air-sensitive colorless crystals in *ca.* 40% yield.



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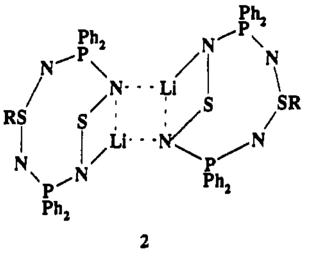

2

Complex **3** was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy[5] and by X-ray crystallography.[6] In contrast to the σ-S-bonded complexes $[MCl(PEt_3)_2(Ph_4P_2N_4S_2R)]$ (R = Me, M = Pd, Pt; R = Bu^t, M = Pt), which exhibit a single ^{31}P NMR resonance for the heterocyclic PPh_2 groups,[3] the ^{31}P NMR spectrum of **3** reveals inequivalent PPh_2 environments. Furthermore, two Cp resonances are observed in the ^1H NMR spectrum of **3**[5] indicating that the heterocyclic ring is attached asymmetrically to zirconium.

This conclusion was confirmed by an X-ray structural determination of **3**.[6] The molecular structure of **3**, depicted in Figure 1, shows that the $[Ph_4P_2N_4S_2Bu^t]^-$ ligand is coordinated to zirconium via adjacent sulfur and nitrogen atoms (i.e. η^2-N,S) with d(Zr–S) = 2.634(2) Å and d(Zr–N) = 2.206(5) Å. In view

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(1) See, for example: (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (c) Hessen, B.; Teuben, J. H. *Recl. Trav. Chim. Pays Bas* **1988**, *107*, 208. (d) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

(2) (a) La Flach, P.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1993**, 789. (b) Dufour, N.; Caminade, A.-M.; Basso-Bert, M.; Igau, A.; Majoral, J.-P. *Organometallics* **1992**, *11*, 1131. (c) Dufour, N.; Majoral, J.-P.; Caminade, A.-M.; Choukroun, R. *Organometallics* **1991**, *10*, 45. (d) Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergsträsser, U.; Hoffman, J.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207. (e) Igau, A.; Defour, N.; Mahieu, A.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 95. (f) Boutonnet, F.; Dufour, N.; Straw, T.; Igau, A.; Majoral, J.-P. *Organometallics* **1991**, *10*, 3939. (g) Majoral, J.-P.; Dufour, N.; Meyer, F.; Caminade, A.-M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1990**, 507.

(3) Chivers, T.; Edwards, M.; Hilts, R. W.; Meetsma, A.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1992**, 3053.

(4) Chivers, T.; Edwards, M.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1483. An X-ray structure determination of **2** (R = Ph) showed it to be a step-shaped dimer.

(5) NMR data for compounds **3**–**7** are as follows. $^{31}P\{^1H\}$ (recorded in THF at 23 °C, lock signal provided by a D_2O insert; δ (ppm) relative to 85% H_3PO_4): **3**, 45.3 (s), 36.3 (s); **4**, 14.1 (s); **5**, 26.6 (s); **6**, 39.7 (s); **7**, 33.3 (s, broad). Proton NMR (δ (ppm) relative to $SiMe_4$; all recorded at 23 °C): **3** (THF-d_8), 1.10 (s, 9H, C_4H_9), 5.46 (s, 5H, C_5H_5), 6.48 (s, 5H, C_5H_5), 7.08–8.23 (m, 20H, C_6H_5); **4** (benzene-d_6), 1.18 (s, 9H, $C(CH_3)_3$, 6.95–8.15 (m, 20H, C_6H_5); **5** ($CDCl_3$), 1.24 (s, 9H, $C(CH_3)_3$), 2.84 (s, 3H, CH_3), 7.30–7.95 (m, 20H, C_6H_5); **6** (CD_2Cl_2), 1.19 (s, 9H, $C(CH_3)_3$), 7.15–7.95 (m, 20H, C_6H_5), 10.32 (d, 2H, NH, ^2J(PH) = 21 Hz); 7 (toluene-d_8), 1.11 (bs, 9H, $C(CH_3)_3$), 7.05–8.10 (m, 20H, C_6H_5). $^{13}C\{^1H\}$ NMR (δ (ppm) relative to $SiMe_4$; all recorded at 23 °C): **3** (THF-d_8), 22.91 (s, $C(CH_3)_3$), 57.76 (t, $C(CH_3)_3$, ^3J(PC) = 15 Hz), 111.99 (s, C_5H_5), 114.92 (s, C_5H_5), 127.7–134.0 (m, C_6H_5); **5** ($CDCl_3$), 22.80 (s, $C(CH_3)_3$), 56.28 (t, $C(CH_3)_3$, ^3J(PC) = 15 Hz), 45.34 (t, CH_3, ^3J(PC) = 21 Hz), 127.6–131.9 (m, C_6H_5); **6** (CD_2Cl_2), 21.36 (s, $C(CH_3)_3$), 58.11 (t, $C(CH_3)_3$, ^3J(PC) = 15 Hz), 127.6–133.3 (m, C_6H_5). Mass spectra (m/e): **5**, 562 (M^+, 0.3%), 547 ($M^+ - CH_3$, 10%), 505 ($M^+ - C_4H_9$, 100%), 490 ($M^+ - CH_3 - C_4H_9$, 31%); **6**, 585 (M^+, 4%), 549 ($M^+ - Cl$, 100%), 491 ($M^+ - 2H - C_4H_9 - Cl$, 38%). Satisfactory C, H, and N analyses were obtained for **3**, **5**, and **6**. Compounds **4** and **7** were characterized only by NMR spectra.

(6) Crystals of **3** were grown from a 1:1 THF–Et_2O mixture at 0 °C. Crystallographic data for **3** at −73 °C: $C_{40}H_{42}N_4ClP_2S_2ZrO_{0.5}$, $P\bar{1}$, a = 12.439(4) Å, b = 18.220(5) Å, c = 10.370(2) Å, α = 100.40(2)°, β = 106.65(2)°, γ = 72.53(2)°, V = 2136(1) $Å^3$, Z = 2, D_{calcd} = 1.305 g cm^{-3}, $\mu(M_o\ K\alpha)$ = 0.525 mm^{-1}, 7957 measured reflections, 4223 of which were observed. The structure was solved by the heavy-atom method. Refinement converged at R (R_w) = 0.054 (0.061) for 410 refined parameters. The disordered diethyl ether molecule was given half-occupancy, and its carbon and oxygen atoms were allowed isotropic temperature factors.

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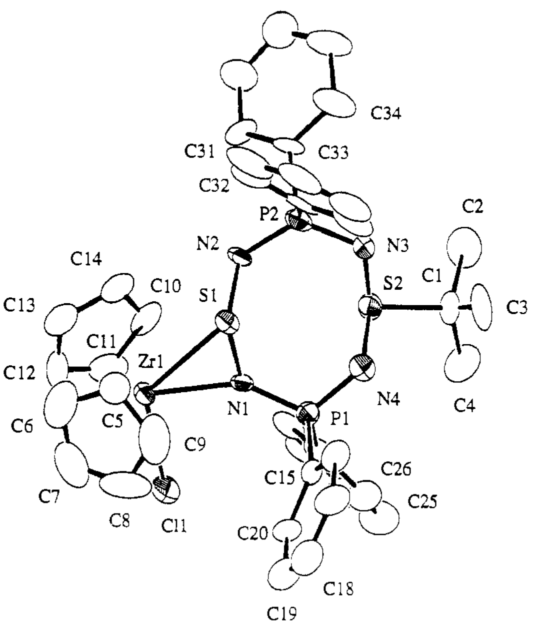
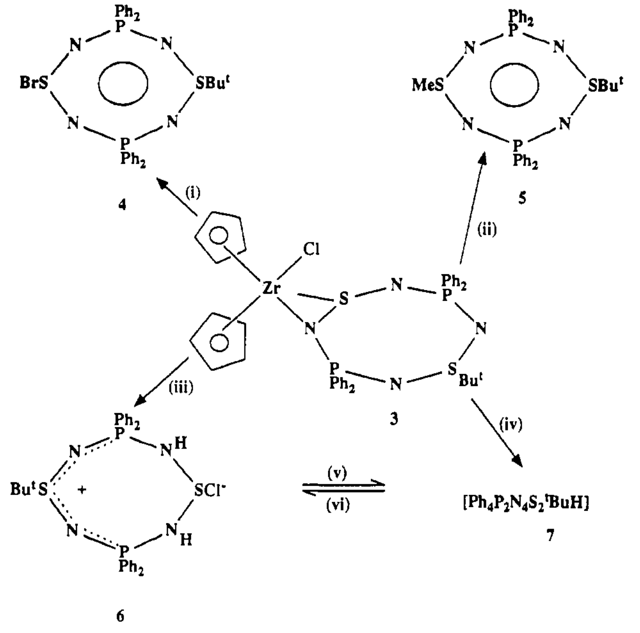


Figure 1. ORTEP diagram (50% probability ellipsoids) for [$Cp_2ZrCl(\eta^2-N,S-Ph_4P_2N_4S_2Bu^t)$] (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr–N(1), 2.206(5); Zr–S(1), 2.634(2); Zr–Cl, 2.530(2); N(1)–S(1), 1.697(6); N(1)–P(1), 1.648(5); S(1)–N(2), 1.650(5); N(2)–P(2), 1.615(2); P(1)–N(4), 1.603(6); P(2)–N(3), 1.600(7); N(3)–S(2), 1.618(7); N(4)–S(2), 1.640(5); Zr–S(1)–N(1), 56.4(2); Zr–N(1)–S(1), 83.8(2); S(1)–Zr–N(1), 39.8(1); Cl–Zr–N(1), 124.1(1); Cl–Zr–S(1), 84.4(1).

of the unusual nature of the heterocyclic ligand in **3** it is difficult to find appropriate complexes for structural comparisons. However, Zr–N distances in the range 2.105(4)–2.267(3) Å have been reported for complexes in which the imino moiety is acting as a one-electron donor.[2c,7] The $P_2N_4S_2$ ring adopts a distorted chair conformation in **3**.[8]

As indicated in Scheme 1, the Zr–S and Zr–N bonds in **3** are highly susceptible to cleavage by electrophiles. These reactions utilize the high halophilicity of the zirconyl moiety to facilitate the release of the functionalized heterocycle from the coordination sphere of the metal. For instance, the treatment of **3** with bromine in THF gives the *S*-bromo derivative **4**[5] (and $Cp_2ZrClBr$), which cannot be made cleanly by bromination of **2** (R = Bu^t).[9] Compound **3** also reacts smoothly with iodomethane to give **5**. The reaction of **3** with 2 molar equiv of gaseous HCl produces the diprotonated heterocycle $Ph_4P_2N_4S_2Bu^tH_2^+$ as the chloride salt (**6**).[5] An X-ray analysis of **6**[10] has established that the two protons are transferred regiospecifically to two vicinal nitrogens separated by a sulfur atom (see Figure 2).[8] The treatment of **6** with DBU removes 1 equiv of HCl to give the monoprotonated derivative [$Ph_4P_2N_4S_2Bu^tH$] (**7**),[5] which can also be obtained by the careful protonation of **3** with 1 molar equiv of HCl. The ^{31}P NMR spectrum of **7** exhibits a broad resonance at *ca.* 33 ppm. An X-ray analysis has established the structural framework of **7**, but the quality of the data did not allow a distinction between N–H and S–H isomers to be made. In view of the known structure of **6** (Figure 2), the N–H isomer seems more likely for **7**. A rapid [1,3] proton shift in solution could account for the broad ^{31}P NMR resonance.

Scheme 1. Reactions of [$Cp_2ZrCl(\eta^2-N,S-Ph_4P_2N_4S_2{}^tBu)$] (**3**) with Electrophiles[a]



[a] Key: (i) Br_2; (ii) MeI; (iii) 2HCl; (iv) HCl; (v) diazabicycloundecene (DBU); (vi) HCl.

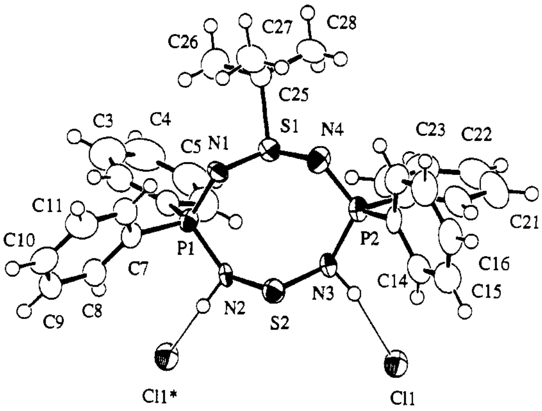


Figure 2. ORTEP diagram (50% probability ellipsoids) for [$Ph_4P_2N_4S_2Bu^tH_2$] Cl (**6**). Selected bond lengths (Å) and angles (deg): S(1)–N(1), 1.638(6); S(1)–N(4), 1.613(6); N(1)–P(1), 1.603(6); N(2)–P(1), 1.661(6); N(2)–S(2), 1.677(6); S(2)–N(3), 1.694(6); N(3)–P(2), 1.651(6); N(4)–P(2), 1.612(6); N(1)–S(1)–N(4), 106.2(3); N(4)–P(2)–N(3), 114.2(3); N(3)–S(2)–N(2), 102.6(3); N(2)–P(1)–N(1), 112.1(3); S(2)–N(3)–P(2), 122.7(4); S(2)–N(2)–P(1), 122.6(4). Compound **6** exists as a dimer in the solid state as a result of hydrogen bonding between NH protons and the Cl^- counterions. The asterisk indicates a symmetry-related atom.

In summary, the $Ph_4P_2N_4S_2Bu^{t-}$ anion engages in a novel (η^2-N,S) bonding mode with zirconium. The resulting zirconathiaziridene reacts more cleanly with electrophiles than the lithium derivative of this anion (**2**, R = Bu^t) to give $P_2N_4S_2$ rings with *S*-halogeno or N–H functionalities, which themselves should have an interesting reaction chemistry.

Acknowledgment. The financial support of the NSERC (Canada) is gratefully acknowledged.

Supplementary Material Available: Text giving X-ray experimental details and tables of crystal parameters, atomic coordinates and thermal parameters, bond lengths and angles, and anisotropic thermal parameters for **3** and **6** and a table of torsion angles for **6** (29 pages). Ordering information is given on any current masthead page.

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(7) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894.

(8) A more detailed discussion of the structures of **3** and **6** will be given in the full paper.

(9) By contrast, the reaction of **2** (R = Ph) with Br_2 gives high yields of $Ph_4P_2N_4S_2(Br)Ph$, which has been shown by X-ray crystallography to be an *S*-bromo derivative: Chivers, T.; Edwards, M.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. Presented at the 76th CSC Conference, Sherbrooke, Quebec, Canada, June 1993; Abstract 651.

(10) Colorless crystals of **6** were obtained from a CH_2Cl_2–Et_2O mixture at 23 °C. Crystallographic data for **6** at –73 °C: $C_{28}H_{31}N_4P_2S_2Cl$, $P\bar{1}$, $a = 12.797(4)$ Å, $b = 14.618(3)$ Å, $c = 8.276(5)$ Å, $\alpha = 90.48(3)°$, $\beta = 105.59(3)°$, $\gamma = 81.24(2)°$, $V = 1472(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.319$ g/cm^3, μ(Mo Kα) = 0.405 mm^{-1}, 5946 reflections, 1746 of which were observed. The structure was solved by Fourier techniques. Refinement converged at R (R_w) = 0.045 (0.033) for 334 refined parameters.