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# Insertion of Benzylisocyanide into a Zr–P bond and Rearrangement. Atom-Economical Synthesis of a Phosphaalkene<sup>†</sup>

Samantha N. MacMillan,<sup>a</sup> Joseph M. Tanski<sup>a</sup> and Rory Waterman<sup>\*.b</sup>

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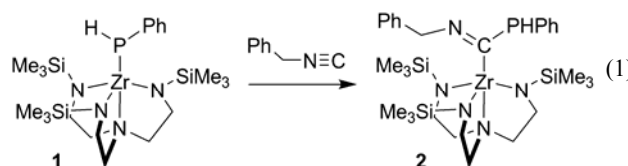
Reaction of (N<sub>3</sub>N)ZrPPh (1; N<sub>3</sub>N = N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub><sup>3-</sup>) with PhCH<sub>2</sub>N≡C afford the 1,1-insertion product (N<sub>3</sub>N)Zr[C(PPh)=NCH<sub>2</sub>Ph] (2), which thermally rearranges to the phosphaalkene-containing complex, (N<sub>3</sub>N)Zr[N(CH<sub>2</sub>Ph)C(H)=PPh] (3).

An intensified interest in phosphaalkenes has emerged due to the advantageous properties the P=C bond displays as a synthetic precursor,<sup>1</sup> transition-metal ligand,<sup>2</sup> and part of conjugated materials.<sup>3</sup> In typical syntheses of phosphaalkenes, transmetalation or elimination reactions are commonly employed,<sup>4</sup> and steric protection is often required to kinetically trap the P=C bond.<sup>5</sup> As part of our on-going interest in developing new metal-mediated reactions that form phosphorus–element bonds,<sup>6</sup> we wish to report an unusual transformation that forms a new phosphalkene with perfect atom-economy.

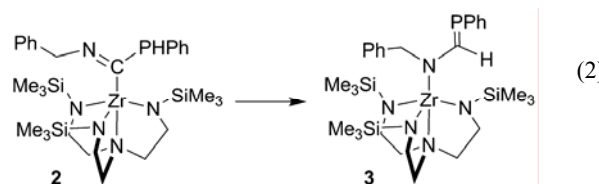
Reaction of (N<sub>3</sub>N)ZrPPh (1; N<sub>3</sub>N = N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub><sup>3-</sup>)<sup>6</sup> with 1 equiv of benzylisocyanide in benzene solution at ambient temperature afforded the 1,1-insertion product, (N<sub>3</sub>N)Zr[C(PPh)=NCH<sub>2</sub>Ph] (2, eqn 1).<sup>‡</sup> Complex 2 was isolated as a pale-orange powder by lyophilization of the benzene solution and characterized by NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P) and infrared spectroscopy. The phosphine proton of 2 displays a significantly downfield shifted resonance at δ 6.038 and a large coupling to phosphorus, *J*<sub>PH</sub> = 259 Hz, compared to other (N<sub>3</sub>N)Zr-species containing a phenylphosphide moiety.<sup>6</sup> This assignment was confirmed by observation of equivalent P–H coupling in the <sup>31</sup>P NMR spectrum of 2. Additionally, ν<sub>PH</sub> = 2280 cm<sup>-1</sup> was observed in the infrared. The strong P–H scalar coupling may arise from increased s-character of the P–H bond resulting from some delocalization of the phosphorus lone pair into the imine π-system, a feature that may also be responsible for the downfield chemical shift of the phosphorus proton. Other spectroscopic features support the formulation given, including an imine ν<sub>CN</sub> = 1705 cm<sup>-1</sup> in the infrared and an imine carbon resonance at δ 263.2 with *J*<sub>PC</sub> = 99.5 Hz in the <sup>13</sup>C NMR spectrum of 2.

Insertion of unsaturated organic molecules into metal-phosphido bonds is well known since the first example, insertion of CO into the Hf–P bond of Cp\*HfCl<sub>2</sub>(P<sup>t</sup>Bu<sub>2</sub>), by Bercaw and coworkers.<sup>7</sup> More recently, Hey-Hawkins and coworkers have reported the

insertion of phenylisocyanide into the Zr–P bond of Cp<sup>z</sup>ZrClP(SiMe<sub>3</sub>)<sub>2</sub> (Cp<sup>z</sup> = C<sub>5</sub>MeH<sub>4</sub><sup>-</sup>).<sup>8</sup> Insertion reactions of other unsaturated substrates into Zr–P bonds have also appeared.<sup>9</sup>



Complex 2 exhibits limited thermal stability and gradually decomposes even as a solid when stored in the dark at –30 °C under N<sub>2</sub>. The decomposition of 2 is significantly accelerated in solution and is qualitatively more rapid in polar solvents such as Et<sub>2</sub>O rather than benzene or toluene. The product of the decomposition, in all cases, is the phosphaalkene-containing complex, (N<sub>3</sub>N)Zr[N(CH<sub>2</sub>Ph)C(H)=PPh] (3, eqn 2). Complex 3 was prepared directly by reaction of phosphido 2 with benzylisocyanide in benzene followed by heating.<sup>‡</sup> Observation of the reaction by <sup>1</sup>H and <sup>31</sup>P NMR showed quantitative conversion to 3, which was isolated in 78% yield as analytically pure, pale-yellow crystals from a concentrated Et<sub>2</sub>O solution. A similar rearrangement of the phenylisocyanide insertion product, Cp<sup>z</sup>ZrCl[η<sup>2</sup>-N(Ph)=CP(SiMe<sub>3</sub>)<sub>2</sub>], that Hey-Hawkins reported (*vide supra*), was not observed, possibly due to the eta-2 coordination of the imine or the lower propensity of substituents other than hydride to engage in migrations.<sup>8</sup>



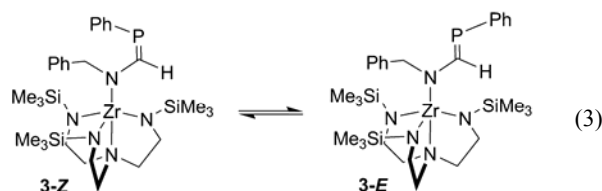
Spectroscopic properties of 3 support the formulation given. Notably, the phosphaalkene carbon resonates at δ 193.1 with *J*<sub>PC</sub> = 55.6 Hz in the <sup>13</sup>C NMR spectrum, and the phosphorus nucleus resonates at δ 91.9 with no primary P–H scalar coupling in the <sup>31</sup>P NMR spectrum of 3—values consistent with a phosphaalkene moiety. The hydrogen atom of the phosphaalkene carbon resonates at δ 10.29 and is broad (Δν<sub>1/2</sub> ~ 40 Hz) at ambient temperature in the <sup>1</sup>H NMR spectrum. Investigation of this complex by variable temperature <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (215 – 320 K) in toluene-*d*<sub>8</sub> solution revealed a dynamic process with an activation barrier Δ*G*<sup>‡</sup> = 15.1 kcal/mol. At lower (<280 K) and higher (>320 K) temperatures, the P–H coupling becomes resolved (*J*<sub>PH</sub> ~ 12

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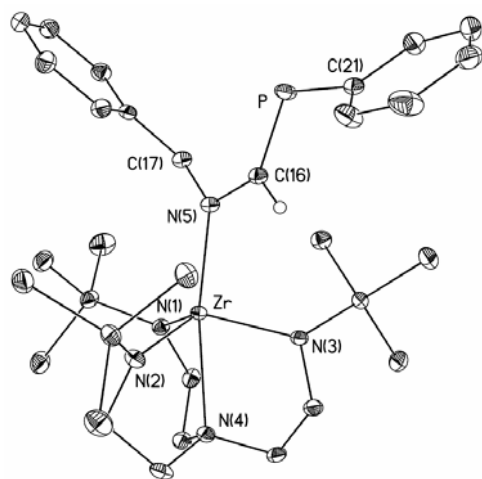
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<sup>†</sup> Electronic Supplementary Information (ESI) available: Complete experimental, spectroscopic, and analytical details and X-ray data for 3 (CCDC number: XX). See <http://dx.doi.org/10.1039/b000000x/>

Hz), suggesting that the process is a thermal *E/Z* isomerization of the phosphoalkene (eqn 3).<sup>10</sup>



The structure of **3** was confirmed by a single crystal X-ray diffraction study, and a perspective view of the complex is shown in Figure 1.<sup>8</sup> The phosphoalkene is in the *E* configuration in the solid state, N and C(16) are planar, and the phenyl substituent of phosphorus is coplanar with P and C(16), implicit of an sp<sup>2</sup>-hybridized phosphorus center and delocalization. The P–C bond length of 1.716(2) Å is somewhat long compared to other structurally characterized phosphoalkenes.<sup>4,5</sup> This feature may result from a zwitterionic resonance contributor where there is some C–N double bond character and a delocalized system. In support of this hypothesis, the C–N bond length of 1.362(2) Å is slightly shorter than expected for a C–N single bond. Known amine-substituted phosphoalkenes display similar bond lengths.<sup>11</sup> Interestingly, complex **3** is a rare instance of metal complex containing a phosphoalkene moiety that is *not* involved in coordination to the metal center.<sup>12</sup>



**Figure 1.** Perspective view of the molecular structure of **3** with hydrogen atoms except H(16) omitted for clarity. Thermal ellipsoids shown at the 35% probability level. Selected metrical parameters: N(5)–C(16) = 1.362(2), N(5)–C(17) = 1.465(2), P–C(16) = 1.716(2), P–C(21) = 1.831(2), C(16)–H(16) = 0.96(2), Zr–N(1) = 2.064(1), Zr–N(3) = 2.071(1), Zr–N(2) = 2.081(1), Zr–N(5) = 2.187(1), Zr–N(4) = 2.498(1) Å; C(16)–N(5)–C(17) = 114.3(1), C(16)–N(5)–Zr = 121.75(9), C(17)–N(5)–Zr = 122.12(9), N(5)–C(16)–P = 126.4(1), N(5)–C(16)–H(16) = 114.2(1), P–C(16)–H(16) = 119.3(1), C(16)–P–C(21) = 101.63(7) °.

A rich reaction chemistry has developed around phosphoalkenes as facile syntheses evolved.<sup>1,4–5</sup> There are several common routes to these molecules including 1,2-elimination, condensation, and rearrangement reactions.<sup>4</sup> Synthesis of phosphoalkenes by a 1,2-hydride migration appears not to have been previously reported. However, the most related reaction in the literature is a 1,2-phenyl migration from a P(V) intermediate.<sup>13</sup>

This synthesis, insertion of an organic isocyanide in to the Zr–P bond of a primary phosphido complex followed by rearrangement, takes advantage of phenylphosphine as the phosphorus source and commercially available benzyliocyanide. Such a strategy avoids salt elimination and exhibits perfect atom economy. We are currently expanding this novel transformation into a general synthesis.

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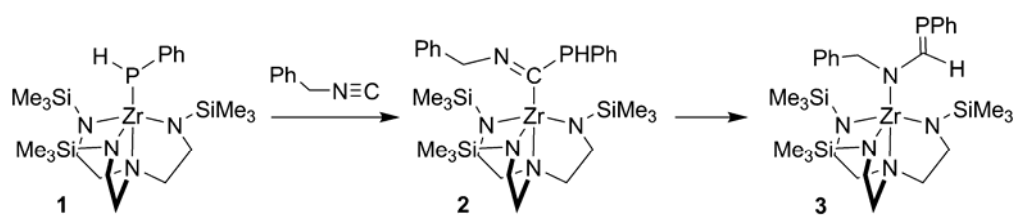
## Notes and references

<sup>†</sup> *Experimental data:* (N<sub>3</sub>N)Zr[C(PhPh)=NCH<sub>2</sub>Ph] (**2**). A 6 mL benzene solution of (N<sub>3</sub>N)ZrPPh (86 mg, 0.154 mmol) was cooled to ca. 5 °C, and a 2 mL benzene solution of PhCH<sub>2</sub>N≡C (18 mg, 0.154 mmol) was added. The resultant orange solution was then frozen, and the benzene removed by lyophilization to give a pale orange powder (98 mg, 0.144 mmol, 94%). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 500.1 MHz): δ 7.750 (t, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.554 (d, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.202 (t, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.102 (m, C<sub>6</sub>H<sub>6</sub>, 4 H), 6.038 (d, PH, J<sub>PH</sub> = 259 Hz), 4.903 (s, CH<sub>2</sub>, 2 H), 3.287 (br s, CH<sub>2</sub>, 6 H), 2.484 (s, CH<sub>2</sub>, 6 H), 0.090 (s, CH<sub>3</sub>, 27 H). <sup>13</sup>C (C<sub>6</sub>D<sub>6</sub>, 125.8 MHz): δ 263.21 (d, C=N, J<sub>PC</sub> = 99.5 Hz), 137.93 (s, Ph), 135.75 (d, Ph, J<sub>PC</sub> = 16.6 Hz), 129.34 (s, Ph), 129.01 (s, Ph), 128.68 (s, Ph), 128.66 (d, Ph, J<sub>PC</sub> = 6.9 Hz), 128.48 (s, Ph), 126.56 (s, Ph), 63.27 (d, CH<sub>2</sub>, J<sub>PC</sub> = 19.4 Hz), 61.21 (s, CH<sub>2</sub>), 47.45 (s, CH<sub>2</sub>), 2.19 (s, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 202.4 MHz): –39.98 (s). IR (KBr, Nujol): 2280 s (ν<sub>PH</sub>), 1705 s (ν<sub>CN</sub>) cm<sup>–1</sup>. (N<sub>3</sub>N)Zr[N(CH<sub>2</sub>Ph)C(H)=PPh] (**3**). A 3 mL benzene solution of (N<sub>3</sub>N)ZrPPh (173 mg, 0.309 mmol) and PhCH<sub>2</sub>N≡C (36 mg, 0.309 mmol) was heated to 90 °C for 3 h. The orange solution was then frozen, and the benzene removed by lyophilization to give an orange powder, which was extracted into ca. 3 mL Et<sub>2</sub>O. The orange solution was filtered then cooled to –30 °C to yield pale yellow crystals in several crops (163 mg, 0.241 mmol, 78%). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 500.1 MHz): 10.291 (br s, CH, 1 H), 7.836 (br, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.543 (br, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.260 (t, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.092 (m, C<sub>6</sub>H<sub>6</sub>, 2 H), 7.045 (m, C<sub>6</sub>H<sub>6</sub>, 2 H), 5.207 (s, CH<sub>2</sub>, 2 H), 3.204 (s, CH<sub>2</sub>, 6 H), 2.278 (s, CH<sub>2</sub>, 6 H), 0.170 (s, CH<sub>3</sub>, 27 H). <sup>13</sup>C (C<sub>6</sub>D<sub>6</sub>, 125.8 MHz): δ 193.12 (d, C=N, J<sub>PC</sub> = 55.6 Hz), 138.76 (s, Ph), 133.35 (s, Ph), 132.88 (d, Ph, J<sub>PC</sub> = 16.6 Hz), 128.46 (s, Ph), 128.28 (s, Ph), 126.71 (s, Ph), 126.37 (s, Ph), 65.73 (s, CH<sub>2</sub>), 64.46 (s, CH<sub>2</sub>), 46.78 (s, CH<sub>2</sub>), 1.38 (s, CH<sub>3</sub>), one phenyl carbon resonance was not observed, presumably obscured by solvent. <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 202.4 MHz): 91.85 (s). Anal. Calcd for C<sub>29</sub>H<sub>52</sub>N<sub>5</sub>PSi<sub>3</sub>Hf: C, 51.43; H, 7.74; N, 10.34. Found: C, 51.54; H, 7.44; N, 10.63.

<sup>8</sup> *Crystal data:* For **3**, C<sub>29</sub>H<sub>52</sub>N<sub>5</sub>PSi<sub>3</sub>Zr, *M* = 677.22, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 16.5616(8), *b* = 10.9871(5), *c* = 21.170(1) Å, β = 110.889(1)°, *Z* = 4, *V* = 3598.9(3) Å<sup>3</sup>, *T* = 125(2) K, μ(Mo-Kα) = 0.475 mm<sup>–1</sup>. Of 49757 total reflections (pale yellow block, 1.35 = θ = 30.45°), 10366 were independent (*R*<sub>int</sub> = 3.51%). The structure was solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures on *F*<sup>2</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model except the hydrogen atom on the phosphoalkene carbon, H(16), which was located in the Fourier difference map and refined. *R*(*F*) = 2.89%, *R*(*wF*) = 6.78%, *GoF* = 1.033. CCDC reference number XXXX.

- 1 F. Mathey, *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Pergamon: Amsterdam, 2001; E. Niecke, A. Fuchs, F. Baumeister, M. Nieger and W. W. Schoeller, *Angew. Chem., Intl. Ed.* **1995**, *34*, 555–557; J. I. Bates and D. P. Gates, *J. Am. Chem. Soc.*, **2006**, *128*, 15998–15999; D. Martin, F. S. Tham, A. Baceiredo and G. Bertrand, *Chem.–Eur. J.*, **2006**, *12*, 8444–8450.
- 2 F. Ozawa and M. Yoshifuji, *Dalton Trans.*, **2006**, *42*, 4987–4995; M. Yoshifuji, *Pure Appl. Chem.*, **2005**, *77*, 2011–2020.
- 3 I. Manners, *Angew. Chem., Intl. Ed.*, **2007**, *46*, 1565–1568; T. Baumgartner and R. Reau, *Chem. Rev.*, **2006**, *106*, 4681–4727; K. J. T. Noonan and D. P. Gates, *Angew. Chem., Intl. Ed.* **2006**, *45*, 7271–7274; V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates, *J.*

- 170 *Am. Chem. Soc.*, **2006**, *128*, 8836–8844; R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.*, **2004**, *126*, 2268–2269.
- 4 H. W. Kroto and J. F. Nixon, *ACS Symp. Ser.*, **1981**, *171*, 383–390; L. N. Markovski and V. D. Romanenko, *Tetrahedron*, **1989**, *45*, 6019–6090; R. Appel *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; M. Regitz, and O. J. Scherer, Eds.; Thieme Verlag: Stuttgart, Germany, 1990, p. 157; F. Mathey, *Acc. Chem. Res.*, **1992**, *25*, 90–96.
- 5 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*; John Wiley & Sons: New York, 1998, p. 88; P. P. Power, *Chem. Rev.*, **1999**, *99*, 3463–3504; M. Yoshifuji, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2002**, *177*, 1827–1831; M. Yam, C.-W. Tsang and D. P. Gates, *Inorg. Chem.*, **2004**, *43*, 3719–3723.
- 6 R. Waterman, *Organometallics*, **2007**, *26*, 2492–2494; A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *submitted*.
- 7 D. M. Roddick, B. D. Santarsiero, J. E. Bercaw, *J. Am. Chem. Soc.* 185 **1985**, *107*, 4670–4678; Insertion of CO<sub>2</sub> into the Hf–P bond of Cp\*<sub>2</sub>HfH(PPh<sub>2</sub>): G. A. Vaughan, G. L. Hillhouse, A. L. Rheingold, *Organometallics*, **1989**, *8*, 1760–1765.
- 8 F. Lindenberg, J. Sieler and E. Hey-Hawkins, *Polyhedron*, **1996**, *15*, 1459–1471.
- 190 9 D. W. Stephan, *Angew. Chem. Int. Ed* **2000**, *39*, 314–329 and references therein.
- 10 Photochemical *E/Z* isomerization energies have been measured recently for *m*-terphenyl-supported phosphalkenes: Gudimetla, V. B.; Rheingold, A. L.; Payton, J. L.; Peng, H.-L.; Simpson, M. C.; 195 Protasiewicz, J. D. *Inorg. Chem.* **2006**, *45*, 4895–4901.
- 11 K. Paasch, M. Nieger and E. Niecke, *Angew. Chem., Intl. Ed.* **1995**, *34*, 2369–2370.
- 12 J. F. Nixon, *Chem. Rev.*, **1988**, *88*, 1327–1362.
- 13 R. Appel, J. Peters, and R. Schmitz, *Z. Anorg. Allg. Chem.*, **1981**, 200 *475*, 18–26.



Reaction of  $(N_3N)ZrPPh$  (**1**) with  $PhCH_2N\equiv C$  gave the 1,1-insertion product  $(N_3N)Zr[C(PPh)=NCH_2Ph]$  (**2**), which thermally rearranges to the structurally characterized phosphalkene-containing complex,  $(N_3N)Zr[N(CH_2Ph)C(H)=PPh]$  (**3**), with perfect atom economy.

## Graphical Contents Entry