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Insertion of Benzyliisocyanide into a Zr–P bond and Rearrangement. Atom-Economical Synthesis of a Phosphaalkene[†]

Samantha N. MacMillan,^a Joseph M. Tanski^a and Rory Waterman^{*b}

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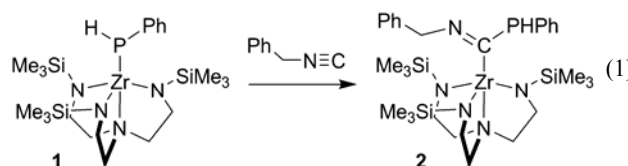
Reaction of (N₃N)ZrPPh (1; N₃N = N(CH₂CH₂NSiMe₃)₃³⁻) with PhCH₂N≡C afford the 1,1-insertion product (N₃N)Zr[C(PPh)=NCH₂Ph] (2), which thermally rearranges to the phosphaalkene-containing complex, (N₃N)Zr[N(CH₂Ph)C(H)=PPh] (3).

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

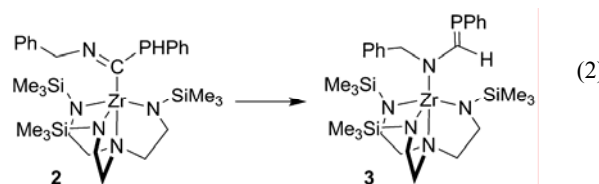
Reaction of (N₃N)ZrPPh (1; N₃N = N(CH₂CH₂NSiMe₃)₃³⁻) with 1 equiv of benzyliisocyanide in benzene solution at ambient temperature afforded the 1,1-insertion product, (N₃N)Zr[C(PPh)=NCH₂Ph] (2, eqn 1).[‡] Complex 2 was isolated as a pale-orange powder by lyophilization of the benzene solution and characterized by NMR (¹H, ¹³C, and ³¹P) 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*_{PH} = 259 Hz, compared to other (N₃N)Zr-species containing a phenylphosphide moiety.⁶ This assignment was confirmed by observation of equivalent P–H coupling in the ³¹P NMR spectrum of 2. Additionally, ν_{PH} = 2280 cm⁻¹ 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_{CN} = 1705 cm⁻¹ in the infrared and an imine carbon resonance at δ 263.2 with *J*_{PC} = 99.5 Hz in the ¹³C 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*HfCl₂(P^tBu₂), by Bercaw and coworkers.⁷ More recently, Hey-Hawkins and coworkers have reported the

insertion of phenylisocyanide into the Zr–P bond of Cp^zZrClP(SiMe₃)₂ (Cp^z = C₅MeH₄)⁸. Insertion reactions of other unsaturated substrates into Zr–P bonds have also appeared.⁹



Complex 2 exhibits limited thermal stability and gradually decomposes even as a solid when stored in the dark at –30 °C under N₂. The decomposition of 2 is significantly accelerated in solution and is qualitatively more rapid in polar solvents such as Et₂O rather than benzene or toluene. The product of the decomposition, in all cases, is the phosphaalkene-containing complex, (N₃N)Zr[N(CH₂Ph)C(H)=PPh] (3, eqn 2). Complex 3 was prepared directly by reaction of phosphido 2 with benzyliisocyanide in benzene followed by heating.[‡] Observation of the reaction by ¹H and ³¹P NMR showed quantitative conversion to 3, which was isolated in 78% yield as analytically pure, pale-yellow crystals from a concentrated Et₂O solution. A similar rearrangement of the phenylisocyanide insertion product, Cp^zZrCl[η²-N(Ph)=CP(SiMe₃)₂], 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.⁸



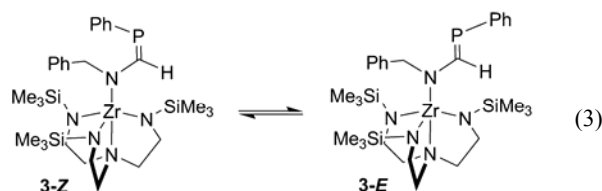
Spectroscopic properties of 3 support the formulation given. Notably, the phosphaalkene carbon resonates at δ 193.1 with *J*_{PC} = 55.6 Hz in the ¹³C NMR spectrum, and the phosphorus nucleus resonates at δ 91.9 with no primary P–H scalar coupling in the ³¹P NMR spectrum of 3—values consistent with a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

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[†] 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).¹⁰



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 1.⁸ 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 sp²-hybridized phosphorus center and delocalization. The P–C bond length of 1.716(2) Å is somewhat long compared to other structurally characterized phosphoalkenes.^{4,5} 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.¹¹ Interestingly, complex **3** is a rare instance of metal complex containing a phosphoalkene moiety that is *not* involved in coordination to the metal center.¹²

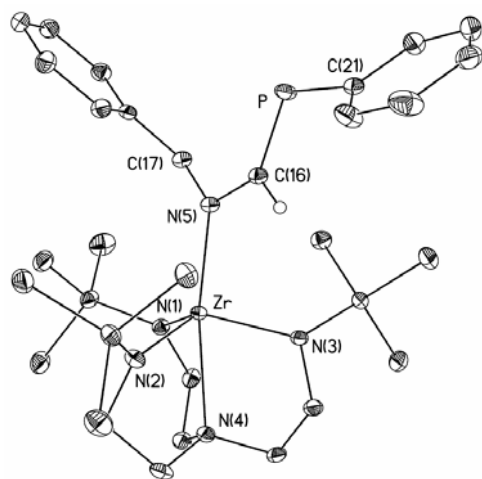


Figure 1. Perspective view of the molecular structure of **3** with hydrogen atoms except H(16) omitted for clarity. Thermal ellipsoids shown at the 35% probability level. Selected metrical parameters: N(5)–C(16) = 1.362(2), N(5)–C(17) = 1.465(2), P–C(16) = 1.716(2), P–C(21) = 1.831(2), C(16)–H(16) = 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.^{1,4–5} There are several common routes to these molecules including 1,2-elimination, condensation, and rearrangement reactions.⁴ 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.¹³

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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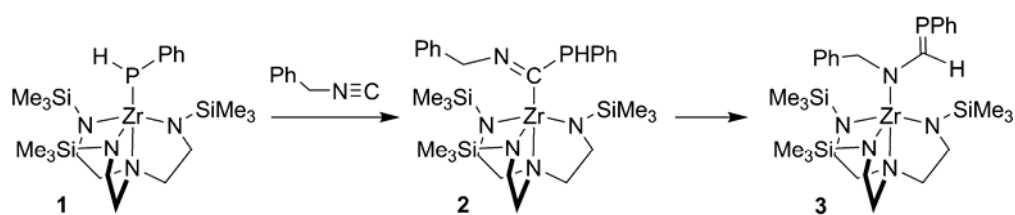
Notes and references

[†] *Experimental data:* (N₃N)Zr[C(PhPh)=NCH₂Ph] (**2**). A 6 mL benzene solution of (N₃N)ZrPPh (86 mg, 0.154 mmol) was cooled to ca. 5 °C, and a 2 mL benzene solution of PhCH₂N≡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%). ¹H (C₆D₆, 500.1 MHz): δ 7.750 (t, C₆H₆, 2 H), 7.554 (d, C₆H₆, 2 H), 7.202 (t, C₆H₆, 2 H), 7.102 (m, C₆H₆, 4 H), 6.038 (d, PH, J_{PH} = 259 Hz), 4.903 (s, CH₂, 2 H), 3.287 (br s, CH₂, 6 H), 2.484 (s, CH₂, 6 H), 0.090 (s, CH₃, 27 H). ¹³C (C₆D₆, 125.8 MHz): δ 263.21 (d, C=N, J_{PC} = 99.5 Hz), 137.93 (s, Ph), 135.75 (d, Ph, J_{PC} = 16.6 Hz), 129.34 (s, Ph), 129.01 (s, Ph), 128.68 (s, Ph), 128.66 (d, Ph, J_{PC} = 6.9 Hz), 128.48 (s, Ph), 126.56 (s, Ph), 63.27 (d, CH₂, J_{PC} = 19.4 Hz), 61.21 (s, CH₂), 47.45 (s, CH₂), 2.19 (s, CH₃). ³¹P{¹H} (C₆D₆, 202.4 MHz): –39.98 (s). IR (KBr, Nujol): 2280 s (ν_{PH}), 1705 s (ν_{CN}) cm^{–1}. (N₃N)Zr[N(CH₂Ph)C(H)=PPh] (**3**). A 3 mL benzene solution of (N₃N)ZrPPh (173 mg, 0.309 mmol) and PhCH₂N≡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 Et₂O. The orange solution was filtered then cooled to –30 °C to yield pale yellow crystals in several crops (163 mg, 0.241 mmol, 78%). ¹H (C₆D₆, 500.1 MHz): 10.291 (br s, CH, 1 H), 7.836 (br, C₆H₆, 2 H), 7.543 (br, C₆H₆, 2 H), 7.260 (t, C₆H₆, 2 H), 7.092 (m, C₆H₆, 2 H), 7.045 (m, C₆H₆, 2 H), 5.207 (s, CH₂, 2 H), 3.204 (s, CH₂, 6 H), 2.278 (s, CH₂, 6 H), 0.170 (s, CH₃, 27 H). ¹³C (C₆D₆, 125.8 MHz): δ 193.12 (d, C=N, J_{PC} = 55.6 Hz), 138.76 (s, Ph), 133.35 (s, Ph), 132.88 (d, Ph, J_{PC} = 16.6 Hz), 128.46 (s, Ph), 128.28 (s, Ph), 126.71 (s, Ph), 126.37 (s, Ph), 65.73 (s, CH₂), 64.46 (s, CH₂), 46.78 (s, CH₂), 1.38 (s, CH₃), one phenyl carbon resonance was not observed, presumably obscured by solvent. ³¹P{¹H} (C₆D₆, 202.4 MHz): 91.85 (s). Anal. Calcd for C₂₉H₅₂N₅PSi₃Hf: C, 51.43; H, 7.74; N, 10.34. Found: C, 51.54; H, 7.44; N, 10.63.

⁸ *Crystal data:* For **3**, C₂₉H₅₂N₅PSi₃Zr, *M* = 677.22, monoclinic, *P*2₁/*c*, *a* = 16.5616(8), *b* = 10.9871(5), *c* = 21.170(1) Å, β = 110.889(1)°, *Z* = 4, *V* = 3598.9(3) Å³, *T* = 125(2) K, μ(Mo-Kα) = 0.475 mm^{–1}. Of 49757 total reflections (pale yellow block, 1.35 = θ = 30.45°), 10366 were independent (*R*_{int} = 3.51%). The structure was solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures on *F*². 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.

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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