Insertion of Benzylisocyanide into a Zr-P bond and Rearrangement. Atom-Economical Synthesis of a Phosphaalkene

Samantha N. MacMillian  
*Vassar College*, samacmillan@gmail.com

Joseph M. Tanski  
*Vassar College*, jotanski@vassar.edu

Rory Waterman  
*University of Vermont*, rory.waterman@uvm.edu

Follow this and additional works at: [https://scholarworks.uvm.edu/casfac](https://scholarworks.uvm.edu/casfac)

This Article is brought to you for free and open access by the College of Arts and Sciences at ScholarWorks @ UVM. It has been accepted for inclusion in College of Arts and Sciences Faculty Publications by an authorized administrator of ScholarWorks @ UVM. For more information, please contact donna.omalley@uvm.edu.
Insertion of Benzylisocyanide into a Zr–P bond and Rearrangement. Atom-Economical Synthesis of a Phosphaalkene

Samantha N. MacMillan, Joseph M. Tanski and Rory Waterman

Reaction of (N₃N)ZrPHPh (1; N₃N = N(CH₂CH₂NSiMe₃)₃) with PhCH₂N≡C affords the 1,1-insertion product (N₃N)Zr[C(PhP)=NCH₂Ph] (2), which thermally rearranges to the phosphaalkene-containing complex, (N₃N)Zr[NI(CH₃)₂C(H)=PPh] (3).

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

Reaction of (N₃N)ZrPHPh (1; N₃N = N(CH₂CH₂NSiMe₃)₃, eqn 1) with 1 equiv of benzylisocyanide in benzene solution at ambient temperature afforded the 1,1-insertion product, (N₃N)Zr[C(PhP)=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, Jₚₚ = 259 Hz, compared to other (N₃N)Zr-species containing a phenylphosphide moiety. This assignment was confirmed by observation of equivalent P–H coupling in the ³¹P NMR spectrum of 2. Additionally, νₚₚ = 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 n-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 δₚₚ = 1705 cm⁻¹ in the infrared and an imine carbon resonance at δ 163.2 with no primary P–H scalar coupling observed.

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'[η²-N(Ph)=CP(SiMe₃)₂], that Hey-Hawkins reported (vida supra), was not observed, possibly due to the η₂-coordination of the imine or the lower propensity of substituents other than hydride to engage in migrations.

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[NI(CH₃)₂C(H)=PPh] (3, eqn 2). Complex 3 was prepared directly by reaction of phosphido 2 with benzylisocyanide 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'²ZrCl[η²-N(Ph)=CP(SiMe₃)₂], that Hey-Hawkins reported (vida supra), was not observed, possibly due to the η₂-coordination of the imine or the lower propensity of substituents other than hydride to engage in migrations.

Spectroscopic properties of 3 support the formulation given. Notably, the phosphaalkene carbon resonates at δ 193.1 with Jₚₚ = 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 (∆ν₁/₂ ~ 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-d₈ solution revealed a dynamic process with an activation barrier ∆G°‡ = 15.1 kcal/mol. At lower (<280 K) and higher (>320 K) temperatures, the P–H coupling becomes resolved (Jₚₚ ~ 12 Hz).
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 phosphaalkene displays similar bond lengths. There are several common routes to amine-substituted phosphaalkenes, which are facile syntheses evolved. There are several common routes to amine-substituted phosphaalkenes, which are facile syntheses evolved.1, 4, 5 There are several common routes to amine-substituted phosphaalkenes, which are facile syntheses evolved. There are several common routes to amine-substituted phosphaalkenes, which are facile syntheses evolved. There are several common routes to amine-substituted phosphaalkenes, which are facile syntheses evolved.

Interestingly, complex 3 is a rare instance of metal complex containing a phosphaalkene moiety that is not involved in coordination to the metal center.

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 phosphaalkenes 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 phosphaalkenes 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.

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

This work was supported by the University of Vermont and the U.S. National Science Foundation (Grant # 0521237 to JMT). The authors thank Prof. John Protasiewicz for helpful discussions.

Notes and references

1 Experimental data: (N,N)Zr[(P(HPh)=NCH2Ph] (2). A 6 mL benzene solution of (N,N)Zr[HPh] (86 mg, 0.154 mmol) was cooled to 5 °C, and a 2 mL benzene solution of PhCH2NH (36 mg, 0.309 mmol) was added. The resultant orange solution was then frozen, and the benzene removed by lyophilization to give a pale orange powder (98 mg, 0.309 mmol) which 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 a 3 mL benzene solution of (N3N)Zr[PC(Ph)(HPh)=NCH2Ph] (2). A 6 mL benzene solution of (N,N)Zr[HPh] (86 mg, 0.154 mmol) was cooled to 5 °C, and a 2 mL benzene solution of PhCH2NH (36 mg, 0.309 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 (CD3OH, 500.1 MHz): 6.735 (t, JCD3OH = 7.55 Hz), 7.543 (br, CD3OH, 7.543 Hz). The phosphaalkene is in the E configuration in the phenyl substituent of 2 F. Ozawa and M. Yoshifuji, Carbon–Heterocyclic Chemistry: The Rise of a New Domain, Copyright 2006, D. P. Gates. This work was supported by the University of Vermont and the U.S. National Science Foundation (Grant # 0521237 to JMT). The authors thank Prof. John Protasiewicz for helpful discussions.


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)°.

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

This work was supported by the University of Vermont and the U.S. National Science Foundation (Grant # 0521237 to JMT). The authors thank Prof. John Protasiewicz for helpful discussions.

Notes and references

1 Experimental data: (N,N)Zr[(P(HPh)=NCH2Ph] (2). A 6 mL benzene solution of (N,N)Zr[HPh] (86 mg, 0.154 mmol) was cooled to 5 °C, and a 2 mL benzene solution of PhCH2NH (36 mg, 0.309 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 (CD3OH, 500.1 MHz): 6.735 (t, JCD3OH = 7.55 Hz), 7.543 (br, CD3OH, 7.543 Hz). The phosphaalkene is in the E configuration in the phenyl substituent of 2 F. Ozawa and M. Yoshifuji, Carbon–Heterocyclic Chemistry: The Rise of a New Domain, Copyright 2006, D. P. Gates. This work was supported by the University of Vermont and the U.S. National Science Foundation (Grant # 0521237 to JMT). The authors thank Prof. John Protasiewicz for helpful discussions.


10 Photochemical E/Z isomerization energies have been measured recently for m-terphenyl-supported phosphaalkenes: Gudimetla, V. B.; Rheingold, A. L.; Payton, J. L.; Peng, H.-L.; Simpson, M. C.; Protasiewicz, J. D. Inorg. Chem. 2006, 45, 4895–4901.


Reaction of (N₃N)ZrPHPh (1) with PhCH₂N≡C gave the 1,1-insertion product (N₃N)Zr[C(PHPh)=NCH₂Ph] (2), which thermally rearranges to the structurally characterized phosphaalkene-containing complex, (N₃N)Zr[N(CH₂Ph)C(H)=PPh] (3), with perfect atom economy.