Insertion of benzyl isocyanide 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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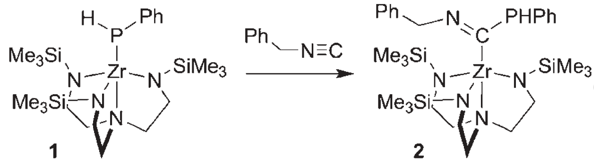
Reaction of $(N_3N)ZrPHPh$ (1, $N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$) with $PhCH_2N{\equiv}C$ affords the 1,1-insertion product $(N_3N)Zr[C(PHPh){=}NCH_2Ph]$ (2), which thermally rearranges to the phosphaalkene-containing complex, $(N_3N)Zr[N(CH_2Ph)C(H){=}PPh]$ (3).

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.

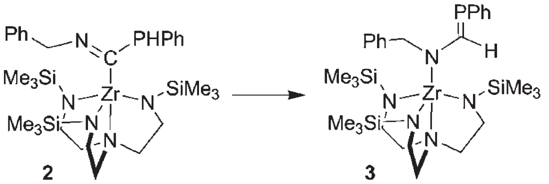
Reaction of $(N_3N)ZrPHPh$ (**1**; $N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$)[6] with 1 equiv. of benzyl isocyanide in benzene solution at ambient temperature afforded the 1,1-insertion product, $(N_3N)Zr[C(PHPh){=}NCH_2Ph]$ (**2**, eqn (1)).‡ Complex **2** was isolated as a pale-orange powder by lyophilization of the benzene solution and characterized by NMR (^1H, ^{13}C and ^{31}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_{PH} = 259 Hz, compared to other $(N_3N)Zr$-species containing a phenylphosphide moiety.[6] This assignment was confirmed by observation of equivalent P–H coupling in the ^{31}P 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 ^{13}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 $Cp^*HfCl_2(P^tBu_2)$, by Bercaw and co-workers.[7] More recently, Hey-Hawkins and co-workers have reported the insertion of phenyl isocyanide into the Zr–P bond of $Cp'_2ZrClP(SiMe_3)_2$ ($Cp' = C_5MeH_4^-$).[8] Insertion reactions of other unsaturated substrates into Zr–P bonds have also appeared.[9]



(1)

Complex **2** exhibits limited thermal stability and gradually decomposes even as a solid when stored in the dark at −30 °C under N_2. The decomposition of **2** is significantly accelerated in solution and is qualitatively more rapid in polar solvents such as Et_2O rather than benzene or toluene. The product of the decomposition, in all cases, is the phosphaalkene-containing complex, $(N_3N)Zr[N(CH_2Ph)C(H){=}PPh]$ (**3**, eqn (2)). Complex **3** was prepared directly by reaction of phosphido **2** with benzyl isocyanide in benzene followed by heating.‡ Observation of the reaction by ^1H and ^{31}P NMR showed quantitative conversion to **3**, which was isolated in 78% yield as analytically pure, pale-yellow crystals from a concentrated Et_2O solution. A similar rearrangement of the phenyl isocyanide insertion product, $Cp'_2ZrCl[\eta^2\text{-}N(Ph){=}CP(SiMe_3)_2]$, reported by Hey-Hawkins and co-workers (*vida supra*), was not observed, possibly due to the η^2 coordination of the imine or the lower propensity of substituents other than hydride to engage in migrations.[8]



(2)

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 ^{13}C NMR spectrum, and the phosphorus nucleus resonates as a broadened singlet at δ 91.9 ($\Delta\nu_{1/2}$ = 45 Hz) with no primary P–H scalar coupling in the ^{31}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 ($\Delta\nu_{1/2}$ ~40 Hz) at ambient temperature in the ^1H NMR spectrum. Investigation of this complex by variable-temperature ^1H and ^{31}P NMR spectroscopy (215–320 K) in toluene-d_8 solution revealed a dynamic process with an activation barrier $\Delta G^{\ddagger}$ = 15.1 kcal mol^{-1}. At lower (<280 K) and higher (>320 K) temperatures, the P–H coupling becomes resolved (J_{PH} ~12 Hz),

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[a] *Department of Chemistry, Vassar College, Poughkeepsie, NY, 12604, USA*
[b] *Department of Chemistry, University of Vermont, Burlington, VT, 05405, USA. E-mail: rory.waterman@uvm.edu; Fax: 01 802 656-8705; Tel: 01 802 656-0278*

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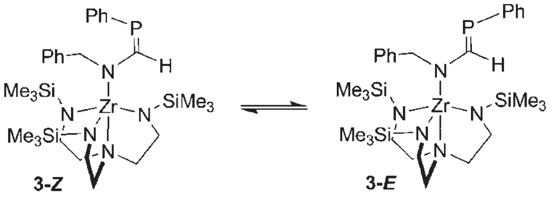
suggesting that the process is a thermal *E*/*Z* isomerization of the phosphaalkene (eqn (3)).[10]



(3)

The structure of **3** was confirmed by a single-crystal X-ray diffraction study, and a perspective view of the complex is shown in Fig. 1.§ The phosphaalkene is in the *E* configuration in the solid state, and P, C(16), H(16) and C(21) (the *ipso* carbon of the phenyl ring on P) are coplanar, which is implicit of an sp^2-hybridized phosphorus center. The P–C bond length of 1.716(2) Å is somewhat long compared to other structurally characterized phosphaalkenes, despite the relatively small hydrogen and phenyl substituents.[4,5] The slightly elongated P–C bond 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 of **3** is slightly shorter than expected for a C–N single bond.[11] Additionally, N is coplanar with the phosphaalkene fragment, which is also consistent with delocalization. Known amine-substituted phosphaalkenes display similar bond lengths.[12] Interestingly, complex **3** is a rare instance of metal complex containing a phosphaalkene moiety that is *not* involved in coordination to the metal center.[13]

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.[14]

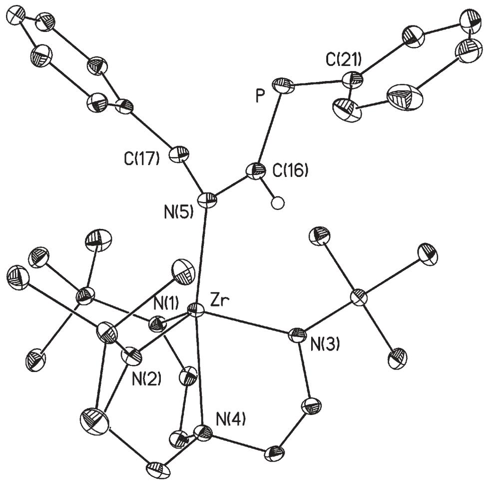


Fig. 1 Perspective view of the molecular structure of **3** with hydrogen atoms except H(16) omitted for clarity. Thermal ellipsoids shown at the 35% probability level. Selected metrical parameters: N(5)–C(16) 1.362(2), N(5)–C(17) 1.465(2), P–C(16) 1.716(2), P–C(21) 1.831(2), C(16)–H(16) 0.96(2), Zr–N(1) 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 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 benzyl isocyanide. 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*: $(N_3N)Zr[C(PHPh){=}NCH_2Ph]$ (**2**). A 6 mL benzene solution of $(N_3N)ZrPHPh$ (86 mg, 0.154 mmol) was cooled to *ca.* 5 °C, and a 2 mL benzene solution of $PhCH_2N{\equiv}C$ (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 NMR (C_6D_6, 500.1 MHz): δ 7.750 (t, C_6H_6, 2 H), 7.554 (d, C_6H_6, 2 H), 7.202 (t, C_6H_6, 2 H), 7.102 (m, C_6H_6, 4 H), 6.038 (d, PH, J_{PH} = 259 Hz), 4.903 (s, CH_2, 2 H), 3.287 (br s, CH_2, 6 H), 2.484 (s, CH_2, 6 H), 0.090 (s, CH_3, 27 H). ^{13}C NMR (C_6D_6, 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, CH_2, J_{PC} = 19.4 Hz), 61.21 (s, CH_2), 47.45 (s, CH_2), 2.19 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.4 MHz): −39.98 (s). IR (KBr, Nujol): 2280s (ν_{PH}), 1705s (ν_{CN}) cm^{-1}. $(N_3N)Zr[N(CH_2Ph)C(H){=}PPh]$ (**3**). A 3 mL benzene solution of $(N_3N)ZrPHPh$ (173 mg, 0.309 mmol) and $PhCH_2N{\equiv}C$ (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_2O. 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 NMR (C_6D_6, 500.1 MHz): 10.291 (br s, CH, 1 H), 7.836 (br, C_6H_6, 2 H), 7.543 (br, C_6H_6, 2 H), 7.260 (t, C_6H_6, 2 H), 7.092 (m, C_6H_6, 2 H), 7.045 (m, C_6H_6, 2 H), 5.207 (s, CH_2, 2 H), 3.204 (s, CH_2, 6 H), 2.278 (s, CH_2, 6 H), 0.170 (s, CH_3, 27 H). ^{13}C NMR (C_6D_6, 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, CH_2), 64.46 (s, CH_2), 46.78 (s, CH_2), 1.38 (s, CH_3), one phenyl carbon resonance was not observed, presumably obscured by solvent. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.4 MHz): 91.85 (s). Anal. Calc. for $C_{29}H_{52}N_5PSi_3Hf$: C, 51.43; H, 7.74; N, 10.34. Found: C, 51.54; H, 7.44; N, 10.63%.

§ *Crystal data* for **3**, $C_{29}H_{52}N_5PSi_3Zr$, $M = 677.22$, monoclinic, $P2_1/c$, $a = 16.5616(8)$, $b = 10.9871(5)$, $c = 21.170(1)$ Å, $\beta = 110.889(1)°$, $Z = 4$, $V = 3598.9(3)$ Å^3, $T = 125(2)$ K, μ(Mo-Kα) = 0.475 mm^{-1}. Of 49757 total reflections (pale yellow block, $1.35 \leqslant \theta \leqslant 30.45°$), 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 phosphaalkene 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 651742. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709506f

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., Int. Ed. Engl.*, 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., Int. 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., Int. Ed.*, 2006, **45**, 7271–7274; V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates,

J. Am. Chem. Soc., 2006, **128**, 8836–8844; R. C. Smith and 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*, ed. M. Regitz and O. J. Scherer, 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, *Inorg. Chem.*, 2007, DOI: 10.1021/ic7013144, in press.

7 D. M. Roddick, B. D. Santarsiero and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 4670–4678.

8 F. Lindenberg, J. Sieler and E. Hey-Hawkins, *Polyhedron*, 1996, **15**, 1459–1464.

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 phosphaalkenes: V. B. Gudimetla, A. L. Rheingold, J. L. Payton, H.-L. Peng, M. C. Simpson and J. . Protasiewicz, *Inorg. Chem.*, 2006, **45**, 4895–4901.

11 The C–N bond of methylamine is ~1.474 Å: A. Streitwieser, C. H. Heathcock and E. M. Kosower, *Introduction to Organic Chemistry*, MacMillan Publishing Company, New York, 4th edn, 1992, p. 726.

12 K. Paasch, M. Nieger and E. Niecke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2369–2370.

13 L. Weber, *Coord. Chem. Rev.*, 2005, **249**, 741–763; J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327–1362.

14 R. Appel, J. Peters and R. Schmitz, *Z. Anorg. Allg. Chem.*, 1981, **475**, 18–26.