

Supporting Information for:

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

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Experimental Section

General Considerations. All manipulations were performed under an atmosphere of dry nitrogen using Schlenk or high vacuum techniques and/or in a M. Braun glovebox. Dry, oxygen-free solvents were employed throughout. C₆D₆ and toluene-*d*₈ were purchased from Cambridge Isotope Laboratory then degassed and dried over NaK alloy. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker AXR or Varian 500 MHz NMR spectrometers and are reported with reference to residual solvent resonances (C₆H₅, δ 7.16 and δ 128.0) or external H₂PO₄. PTFE = polytetrafluoroethylene.

(N₃N)ZrPPh (**1**)¹ was prepared according to the literature protocol.² All other chemicals were used as received from commercial sources.

(N₃N)Zr[C(PHPh)=NCH₂Ph] (**2**). A round bottom flask was charged with (N₃N)ZrPPh (86 mg, 0.154 mmol), and the solid was dissolved in 6 mL of benzene. The yellow solution was cooled to ca. 5 °C, and a 2 mL benzene solution of benzylisocyanide (18 mg, 0.154 mmol) was added to the zirconium solution resulting in an immediate color change to orange. The solution was stirred for 30 min then frozen, and the benzene removed by lyophilization to give a pale orange powder (98 mg, 0.144 mmol, 94%). Attempts to crystallize the complex gave a mixture of pure and rearranged products. The product converts slowly to (N₃N)Zr[N(CH₂Ph)C(H)=PPh] even in the solid state at –30 °C. 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}), 1592 s, 1582 s, 1529 s, 1479 m, 1452 s, 1376 s, 1349 w, 1243 s, 1184 w, 1146 m, 1061 s, 1025 m, 940 s, 910 s, 838 s, 786 s, 738 s, 696 s, 678 m, 624 w, 566 m, 498 s, 439 m cm^{–1}.

(N₃N)Zr[N(CH₂Ph)C(H)=PPh] (**3**). A PTFE-valved reaction flask was charged with (N₃N)ZrPPh (173 mg, 0.309 mmol) and 3 mL of benzene. Benzylisocyanide (36 mg, 0.309

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mmol) was and the flask was sealed and 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 and 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 (br s, Δv_{1/2} = 45 Hz). IR (KBr, Nujol): 1603 m, 1581 s, 1494 s, 1464 s, 1444 s, 1377 s, 1341 w, 1330 w, 1267 s, 1245 s, 1184 m, 1143 w, 1122 w, 1058 s, 1023 s, 979 m, 925 s, 897 m, 834 s, 783 s, 736 s, 694 m, 678 m, 623 w, 585 w, 565 s, 486 m, 459 s, 432 w cm⁻¹. Anal. Calcd for C₂₉H₅₂N₅Si₃PHf: C, 51.43; H, 7.74; N, 10.34. Found: C, 51.54; H, 7.44; N, 10.63.

¹H (C₆D₆, 500.1 MHz) at 340 K: 10.167 (d, CH, J_{PH} = 11.6 Hz, 1 H), 7.774 (t, C₆H₆, 2 H), 7.523 (d, C₆H₆, 2 H), 7.221 (t, C₆H₆, 2 H), 7.104 (m, C₆H₆, 2 H), 7.032 (m, C₆H₆, 2 H), 5.156 (s, CH₂, 2 H), 3.247 (s, CH₂, 6 H), 2.371 (s, CH₂, 6 H), 0.153 (s, CH₃, 27 H).

¹H (toluene-*d*₈, 500.1 MHz) at 215 K: 10.251 (d, CH, J_{PH} = 12.68 Hz, 1 H), 7.739 (t, C₆H₆, 2 H), 7.365 (d, C₆H₆, 2 H), 7.134 (t, C₆H₆, 2 H), 6.976 (m, C₆H₆, 2 H), 6.818 (m, C₆H₆, 2 H), 5.109 (s, CH₂, 2 H), 3.799 (s, CH₂, 6 H), 1.909 (s, CH₂, 6 H), 0.339 (s, CH₃, 27 H).

Activation barrier measurement. Coalescence of the phosphalkene proton coupling to phosphorus of complex **3** in toluene-*d*₈ was monitored by variable temperature NMR spectroscopy (¹H and ³¹P) over a range of 215–320 K. Analysis of the coalescence parameters (T, Δv) gave an activation barrier ΔG[‡] = 15.1(4) kcal/mol for a coalescence temperature of 292 K with slow exchange coupling of 12.5 Hz.³

X-ray Structure Determination:

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα (λ = 0.71073 Å)) at 125 K. A suitable orange crystal of (N₃N)Zr[N(CH₂Ph)C(H)=PPh], grown by cooling a concentrated Et₂O solution to -30 °C, was mounted in a nylon loop with Paratone-*N* cryoprotectant oil. The structure was solved using direct methods and standard difference map techniques and was refined by full-matrix least-squares procedures on *F*² with SHELXTL (Version 6.14).⁴ 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 phosphalkene carbon, H(16), which was located in the Fourier difference map and refined. Crystal data and refinement details are presented in Table 1.

Table 1. Crystal data and structure refinement for (N₃N)Zr[N(CH₂Ph)C(H)=PPh] (**3**).

Identification code	rw431zr
Empirical formula	C ₂₉ H ₅₂ N ₅ PSi ₃ Zr
Formula weight	677.22
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /c
Unit cell dimensions	a = 16.5616(8) Å α = 90° b = 10.9871(5) Å β = 110.889(1)° c = 21.170(1) Å γ = 90°
Volume	3598.9(3) Å ³
Z, Calculated density	4, 1.250 Mg/m ³
Absorption coefficient	0.475 mm ⁻¹
F(000)	1432
Crystal size	0.22 x 0.25 x 0.19 mm
Theta range for data collection	1.35 to 30.45°
Limiting indices	-23 ≤ h ≤ 23, -15 ≤ k ≤ 15, -29 ≤ l ≤ 29
Reflections collected / unique	49757 / 10366 [R _{int} = 0.0351]
Completeness to theta = 30.45°	94.7 %
Absorption correction	Empirical
Max. and min. transmission	0.9152 and 0.8905
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10366 / 0 / 365
Goodness-of-fit on F ²	1.033
Final R indices [I > 2σ(I)]	R ₁ = 0.0289, wR ₂ = 0.0678
R indices (all data)	R ₁ = 0.0394, wR ₂ = 0.0724
Largest diff. peak and hole	0.476 and -0.352 eÅ ⁻³

References

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