

Electronic Supplementary Information

Insertion of Sodium Phosphaethynolate, Na[OCP], into a Zirconium-Benzyne Complex

Jerod M. Kieser,^a Robert J. Gilliard Jr.,^{a,b} Arnold L. Rheingold,^c Hansjörg Grützmacher^b and John D. Protasiewicz^a

^a Department of Chemistry, Case Western Reserve University, 2080 Adelbert Rd., Cleveland, Ohio, 44106 (USA)

^b Department of Chemistry and Applied Biosciences, ETH-Hönggerberg, 8093 Zürich (Switzerland)

^c Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, 92093 (USA)

E-mail: protasiewicz@case.edu; gruetzmacher@inorg.chem.ethz.ch

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1. General

All reactions were performed under an atmosphere of rigorously dry and oxygen-free nitrogen using either an MBraun glove box or standard Schlenk line techniques. Unless otherwise stated, all chemicals were purchased from commercial sources and used without further purification. Tetrahydrofuran was purified using an MBraun solvent purification system. Benzene was distilled over sodium benzophenone ketyl prior to use. Chloroform-d and dichloromethane-d₂ were dried over alumina or 3 Å molecular sieves and degassed prior to use. [Cp₂Zr(C₆H₄)(PMe₃)] (**1**)¹ and Na[OCP]² were prepared following literature procedures. Solution NMR spectra were recorded on a Bruker AVANCE III 500 or Varian Inova 400 spectrometers and chemical shifts referenced to residual solvent signal (¹H and ¹³C) or to 85% H₃PO₄ (³¹P). Unless otherwise stated, ¹³C and ³¹P NMR spectra were ¹H-decoupled. Solid-state ³¹P MAS NMR spectrum was recorded on a Bruker AVANCE III 800 spectrometer using a 2.5 mm rotor with a spinning rate of 30 kHz and chemical shift (δ) referenced to Na₂HPO₄ as an external standard (2.3 ppm).³ Elemental Analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ).

2. Experimental Procedures

Compound **2**

To a solution of Na[OCP]·Dioxane_{2.5} (1.70 g, 5.6 mmol) in 50 mL THF was added a solution of **1** (2.11 g, 5.6 mmol) in 5 mL THF. The resulting dark red solution was stirred at room temperature for 24 hours. During this time, **2** precipitated from solution and was collected by filtration through a fine porosity filter funnel. The precipitate was washed with additional THF and dried under reduced pressure to give a bright red insoluble solid (1.26 g, 43%). Single crystals were obtained by carefully layering a solution of Na[OCP] in THF on top of a solution of **1** in THF in a thin glass tube and allowing to sit undisturbed for 24 hours. ³¹P MAS NMR (324 MHz): δ 50.6.

Compound **3**

To a suspension of **2** (0.47 g, 0.45 mmol) in 25 mL THF was added trimethylchlorosilane (0.12 mL, 0.95 mmol) which slowly formed a cloudy red-orange solution upon stirring for 30 minutes. Removal of volatiles under reduced pressure produced a bright orange powder. Crude product was dissolved in 50 mL THF, filtered, and filtrate evaporated under reduced pressure to afford a bright orange powder (0.37 g, 96%). Analytically pure single crystals were produced through recrystallization from benzene. ¹H NMR (CDCl₃, 500 MHz): δ 0.47 (s, 18H), 5.90 (s, 20H), 6.93-6.95 (m, 4H), 7.19-7.22 (m, 4H). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 1.77 (s), 105.53 (s), 119.66 (t, J_{PC} = 6.55 Hz), 122.14 (s), 124.09 (s), 141.46 (s), 152.18 (t, J_{PC} = 5.43 Hz), 186.16 (t, J_{PC} = 6.26 Hz), 209.10 (d, J_{PC} = 21.02 Hz). ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ 193.97. Anal. Calcd. for C₄₀H₄₆O₂P₂Zr₂: C, 55.91; H, 5.40. Found: C, 55.79; H, 5.28.

Compound 4

A) To a suspension of **2** (36 mg, 0.034 mmol) in 1 mL dichloromethane- d_2 was added a solution of HCl in Dioxane (0.21 mmol). After mixing, the reaction mixture was filtered to yield a bright yellow solution containing **4** and Cp_2ZrCl_2 . 1H NMR (CD_2Cl_2 , 500 MHz): δ 4.20 (d, $^1J_{PH} = 219.6$ Hz, 2H), 6.48 (Cp_2ZrCl_2 , s, 10H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 7.7$ Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 126 MHz): δ 116.65 (Cp_2ZrCl_2), 127.97 (d, $J_{PC} = 5.04$ Hz), 129.29, 134.31, 140.50 (d, $J_{PC} = 27.47$ Hz), 211.93 (d, $J_{PC} = 30.10$ Hz). ^{31}P NMR 1H Coupled (CD_2Cl_2 , 202 MHz): δ -107.90 (t, $^1J_{PH} = 219.7$ Hz).

B) To a suspension of **3** (29 mg, 0.034 mmol) in 1 mL CD_2Cl_2 was added H_2O (2 μL , 0.1 mmol). The bright orange suspension slowly turned to a clear, light orange solution and after 30 minutes was analyzed by multinuclear NMR. Spectra show complete conversion of **3** to **4** as well as unidentified byproducts containing zirconocene or trimethylsilyl functionality. 1H NMR (CD_2Cl_2 , 500 MHz): δ 4.22 (d, $J = 219.7$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.86 (d, $J = 7.6$ Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 126 MHz): δ 127.98 (d, $J_{PC} = 5.07$ Hz), 129.31, 134.33, 140.51 (d, $J_{PC} = 27.40$), 212.02, (d, $J_{PC} = 30.13$). ^{31}P NMR 1H Coupled (CD_2Cl_2 , 202 MHz): δ -107.74 (t, $J_{PC} = 219.7$ Hz).

3. NMR Spectra

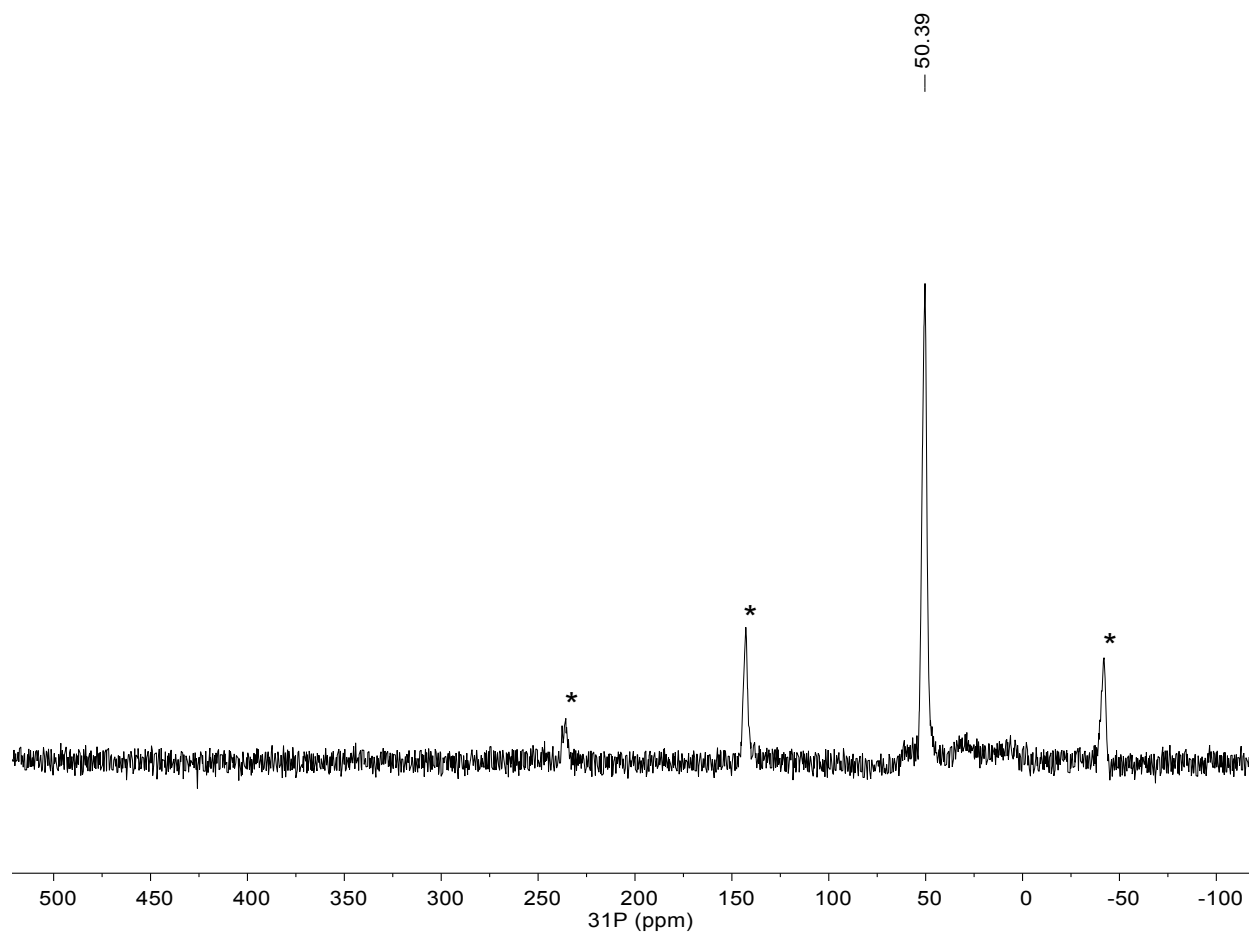


Figure S1. ^{31}P MAS NMR (324 MHz) spectrum of **2** at 30 kHz spinning rate, spinning sidebands marked.

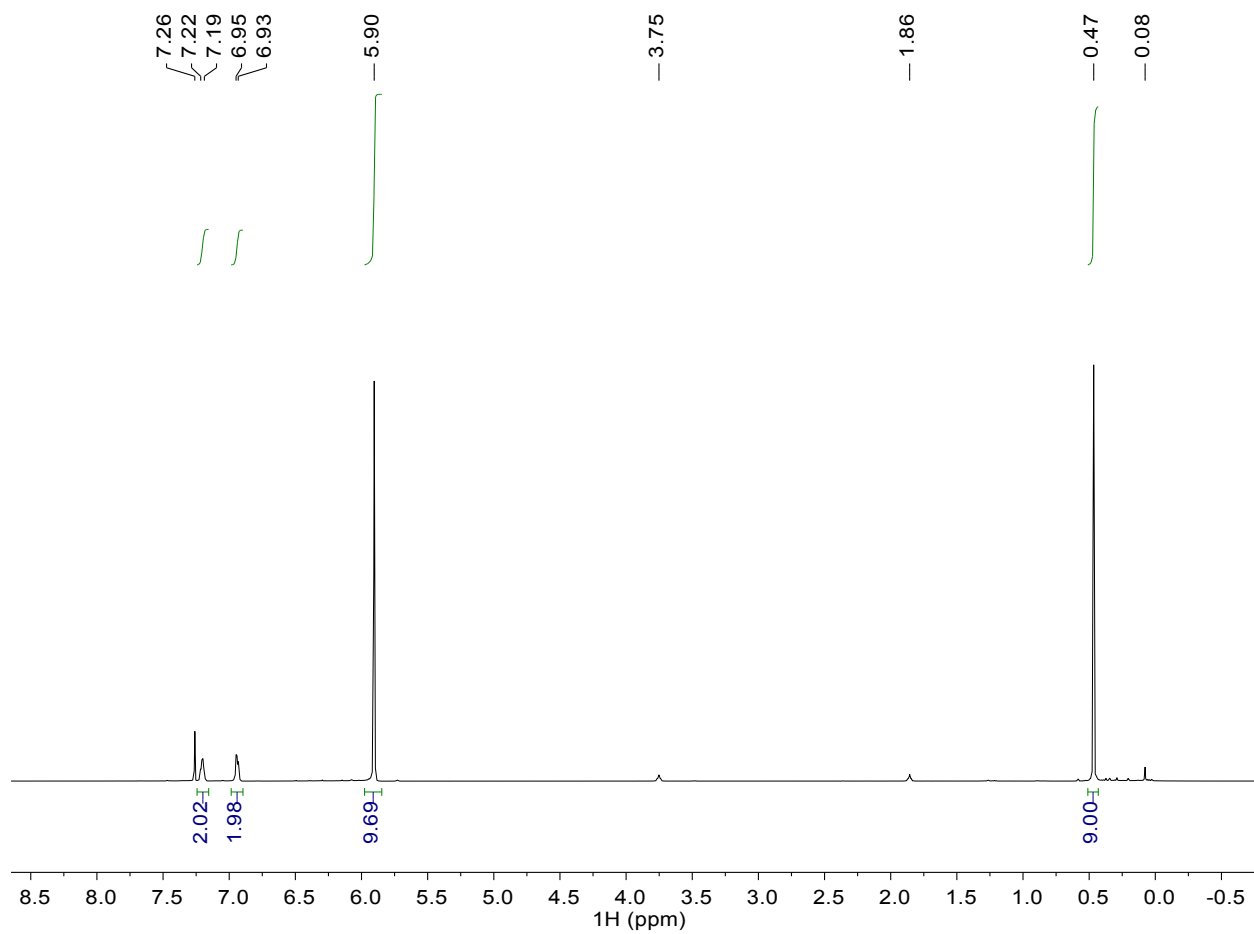


Figure S2. ^1H NMR (500 MHz, CDCl_3) spectrum of bulk **3**.

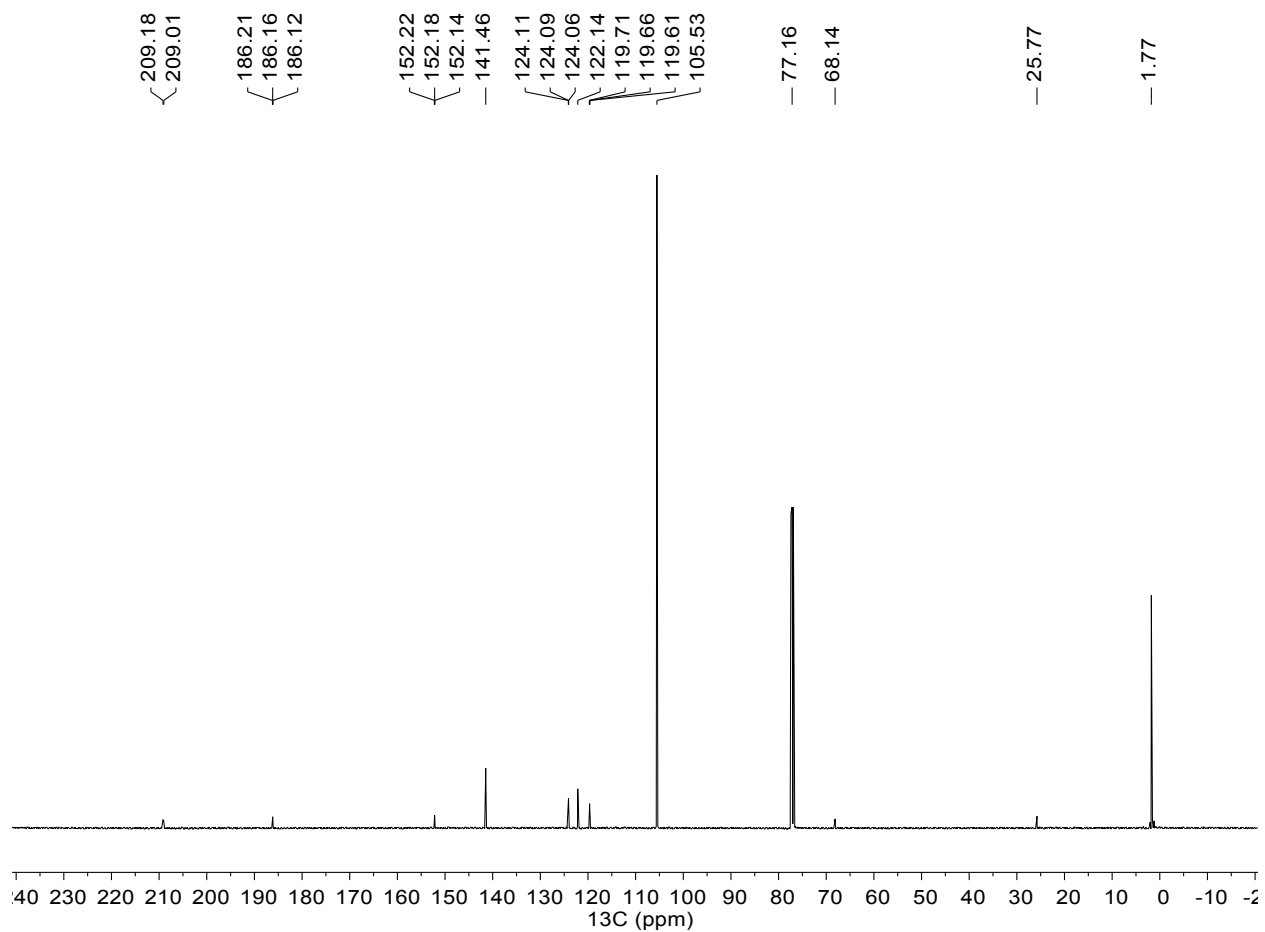


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) spectrum of bulk **3**.

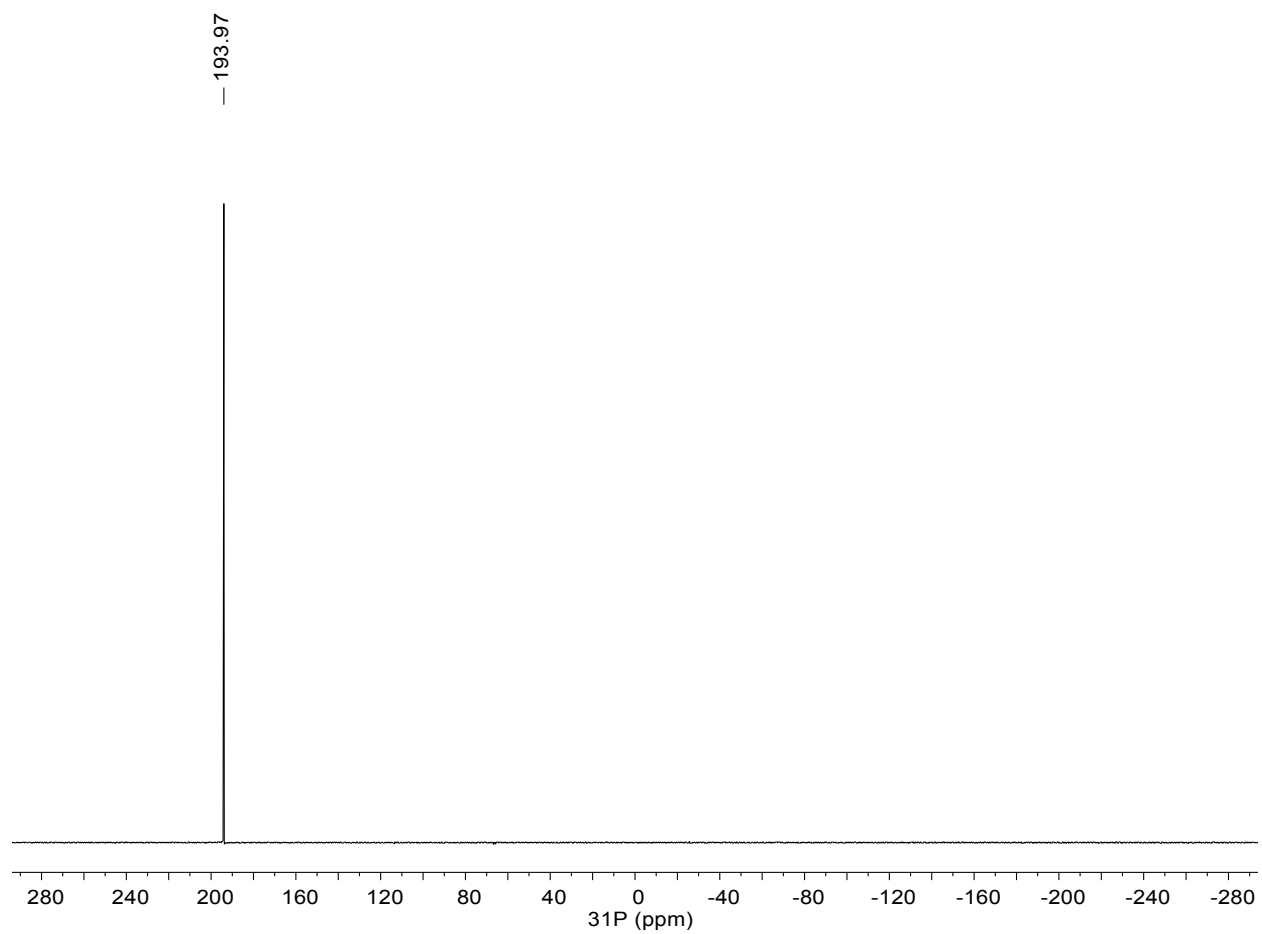


Figure S4. ^{31}P NMR (202 MHz, CDCl_3) spectrum of bulk **3**.

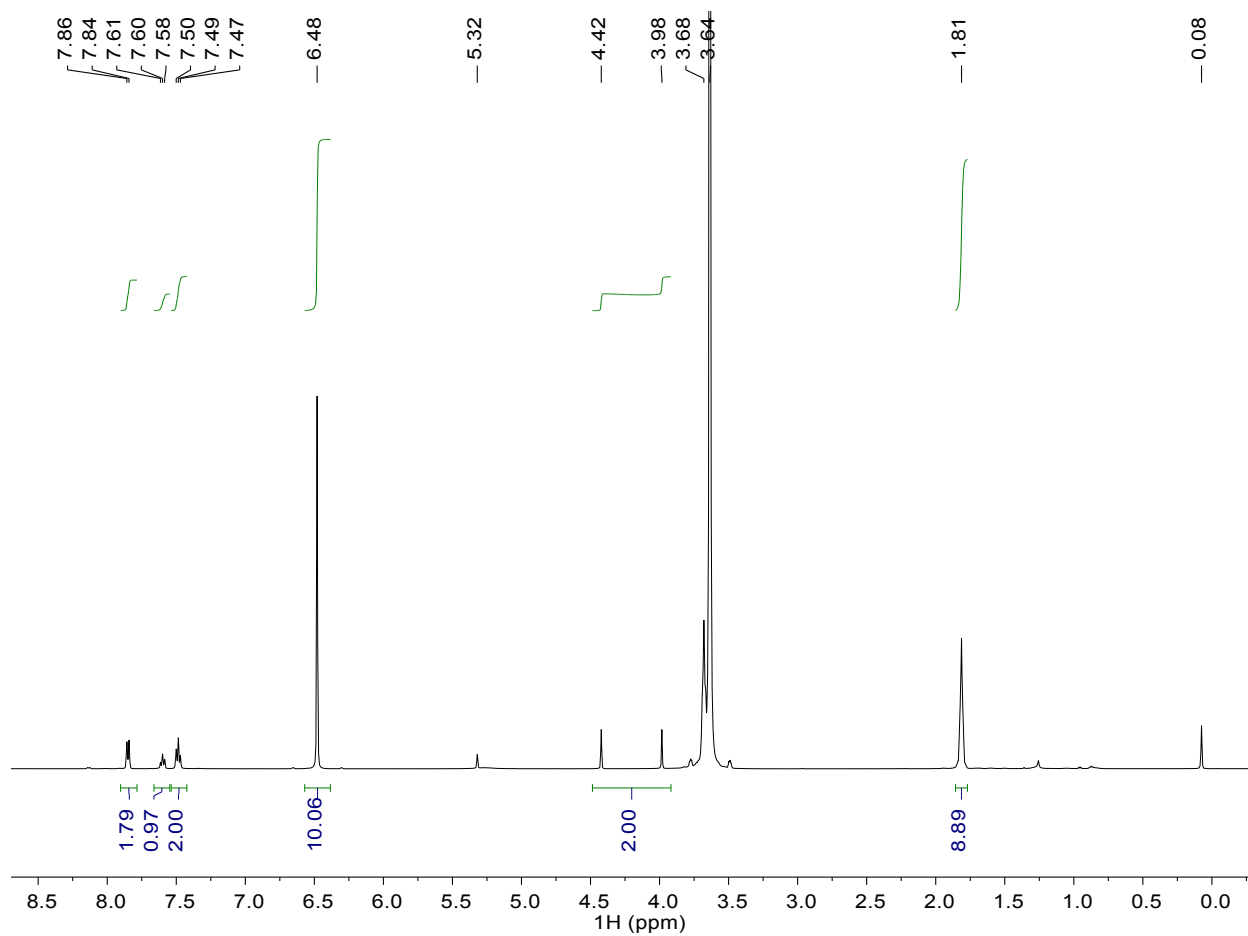


Figure S5. ^1H NMR (500 MHz, CD_2Cl_2) spectrum of reaction mixture containing **4** and Cp_2ZrCl_2 using procedure **A**.

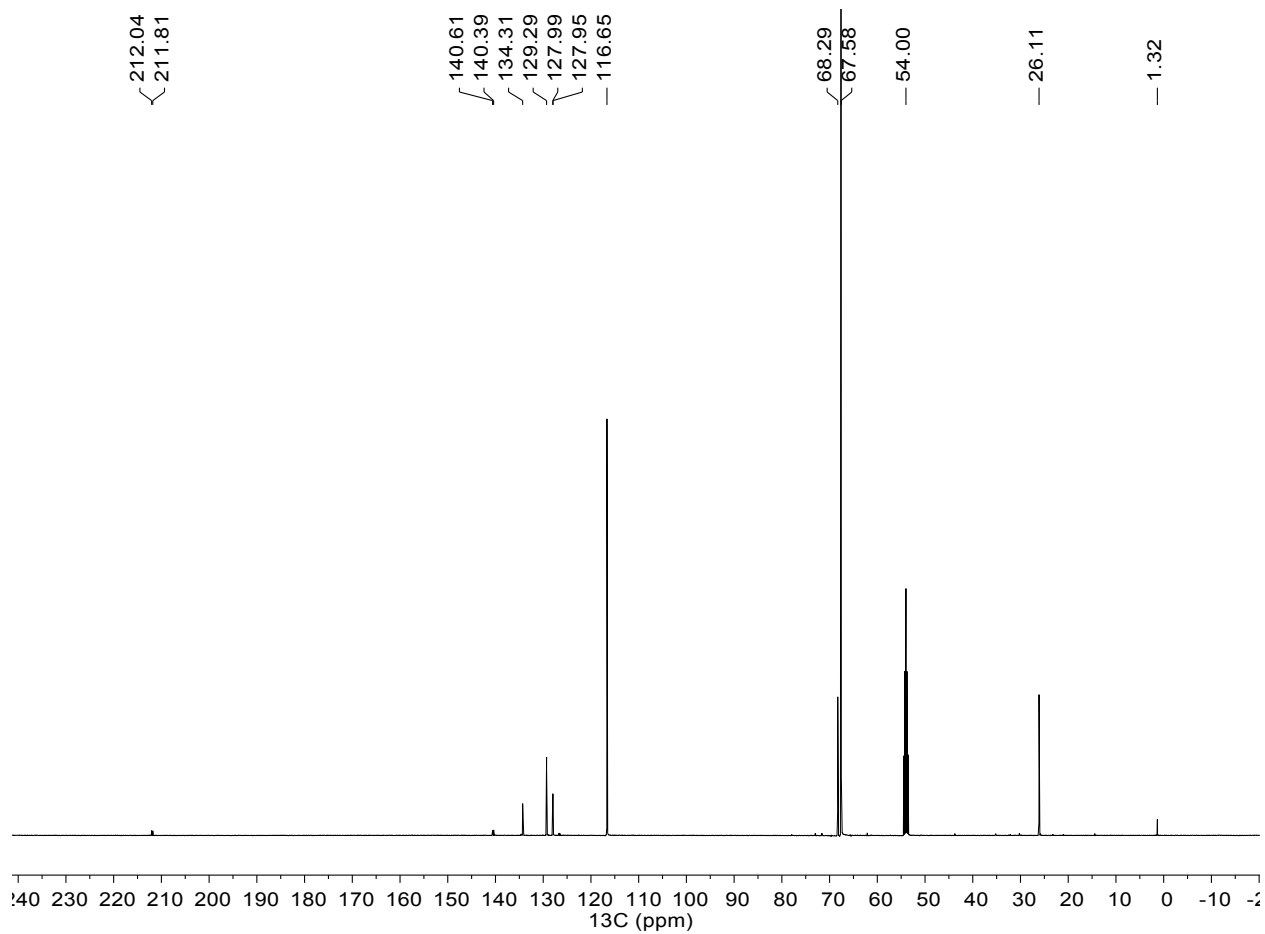


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) spectrum of reaction mixture containing **4** and Cp_2ZrCl_2 using procedure **A**.

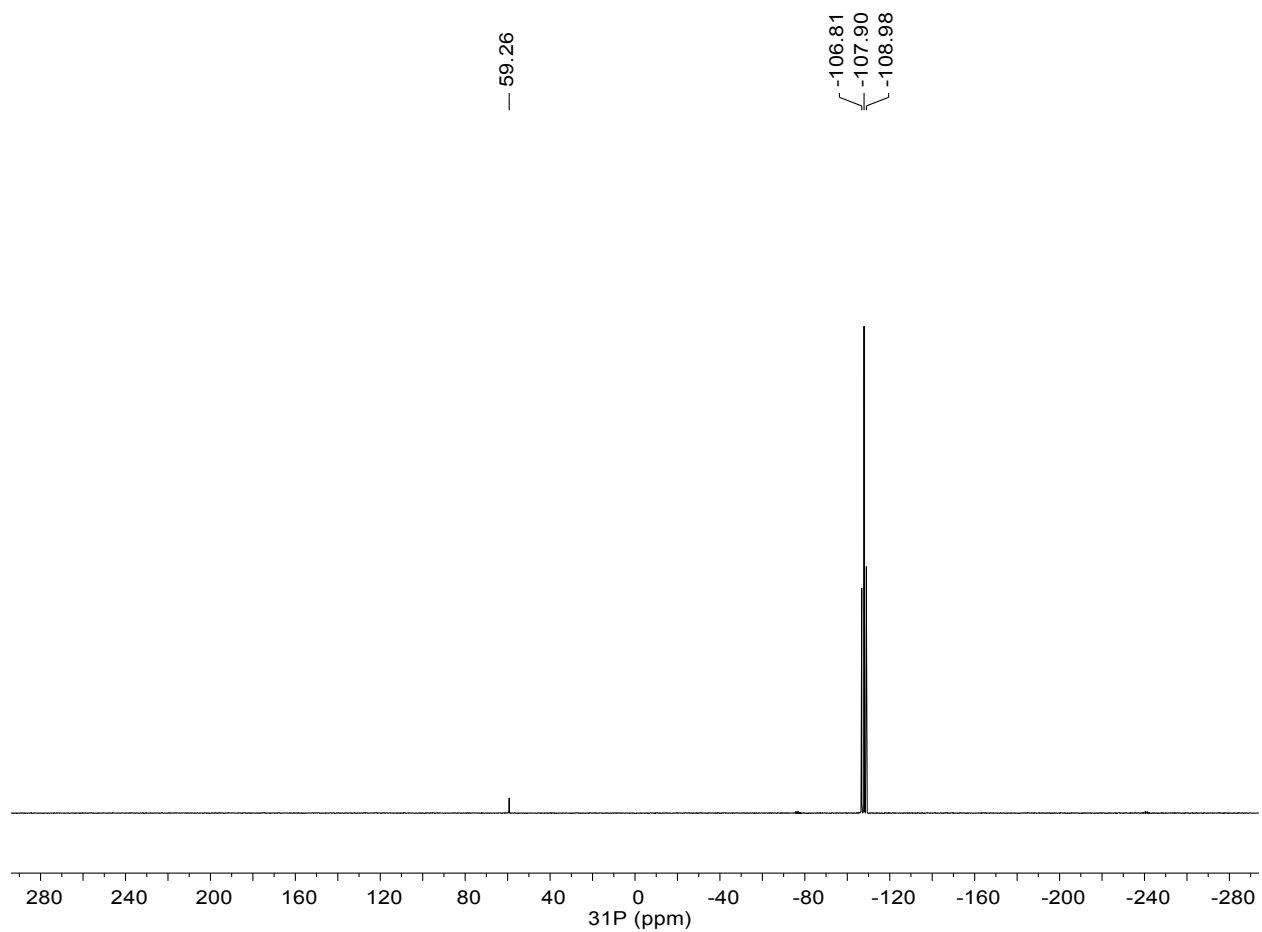


Figure S7. ^{31}P NMR (202 MHz, CD_2Cl_2) spectrum of reaction mixture containing **4** and Cp_2ZrCl_2 using procedure **A**.

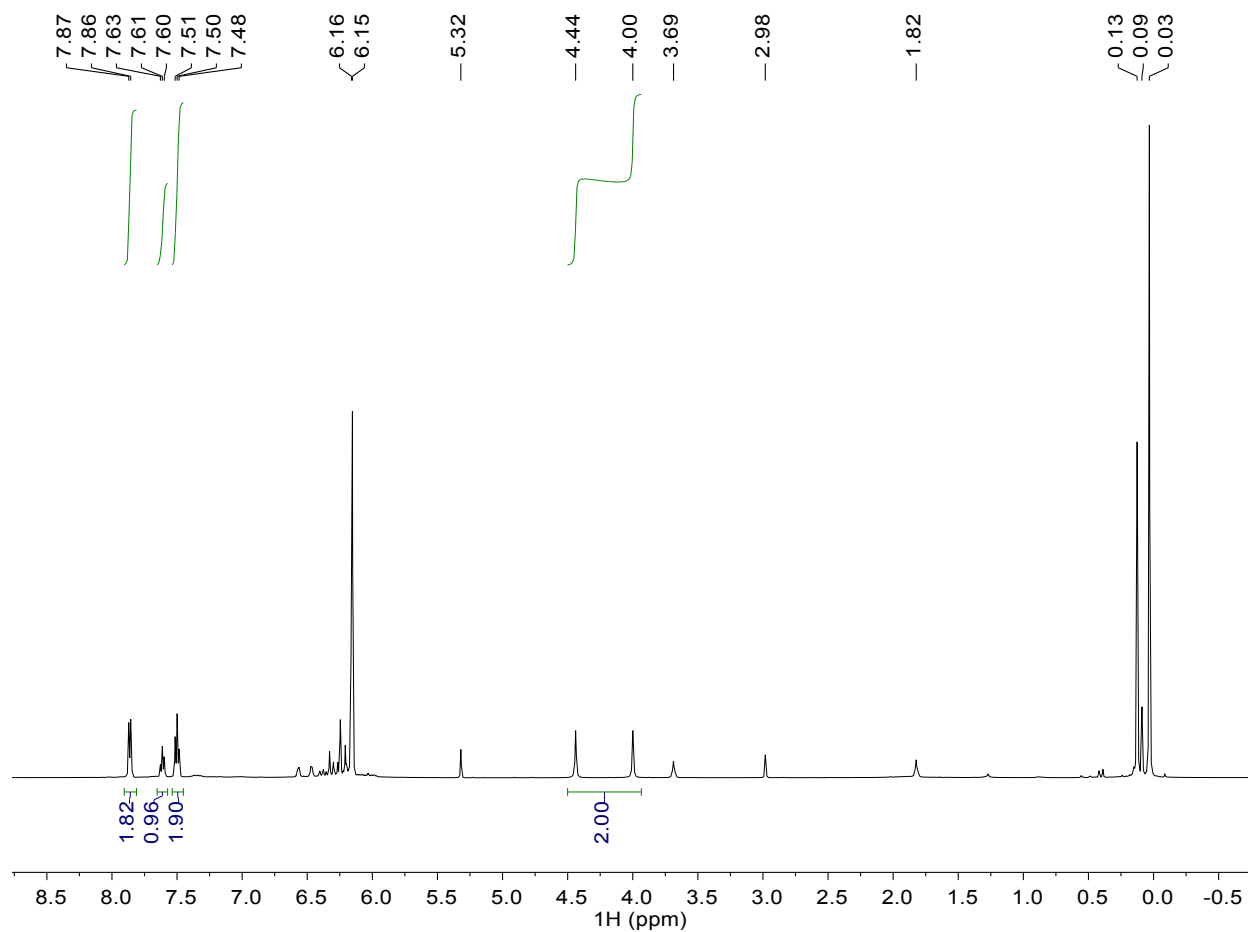


Figure S8. ^1H NMR (500 MHz, CD_2Cl_2) spectrum of reaction mixture containing **4** using procedure **B**.

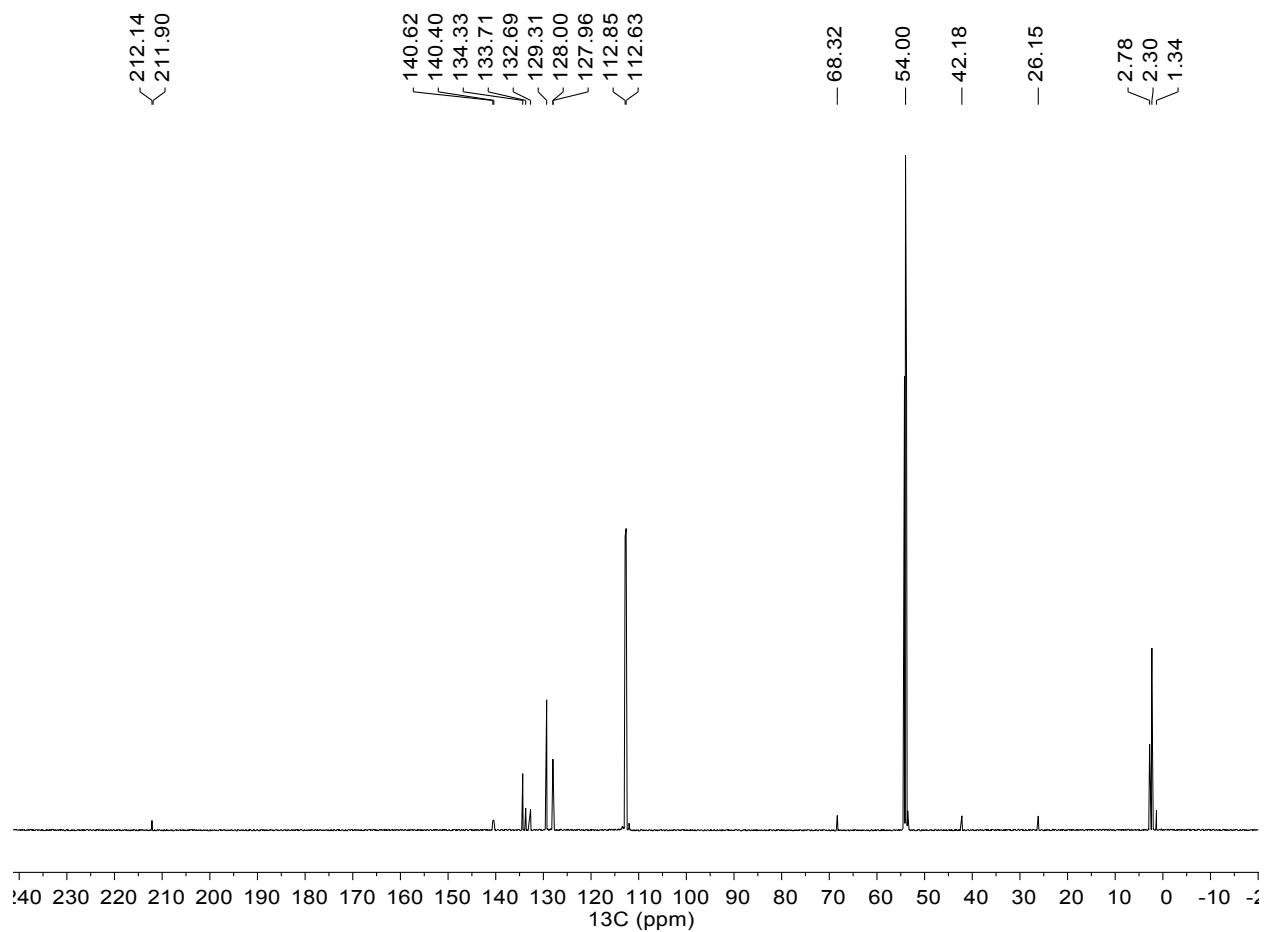


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) spectrum of reaction mixture containing **4** using procedure **B**.

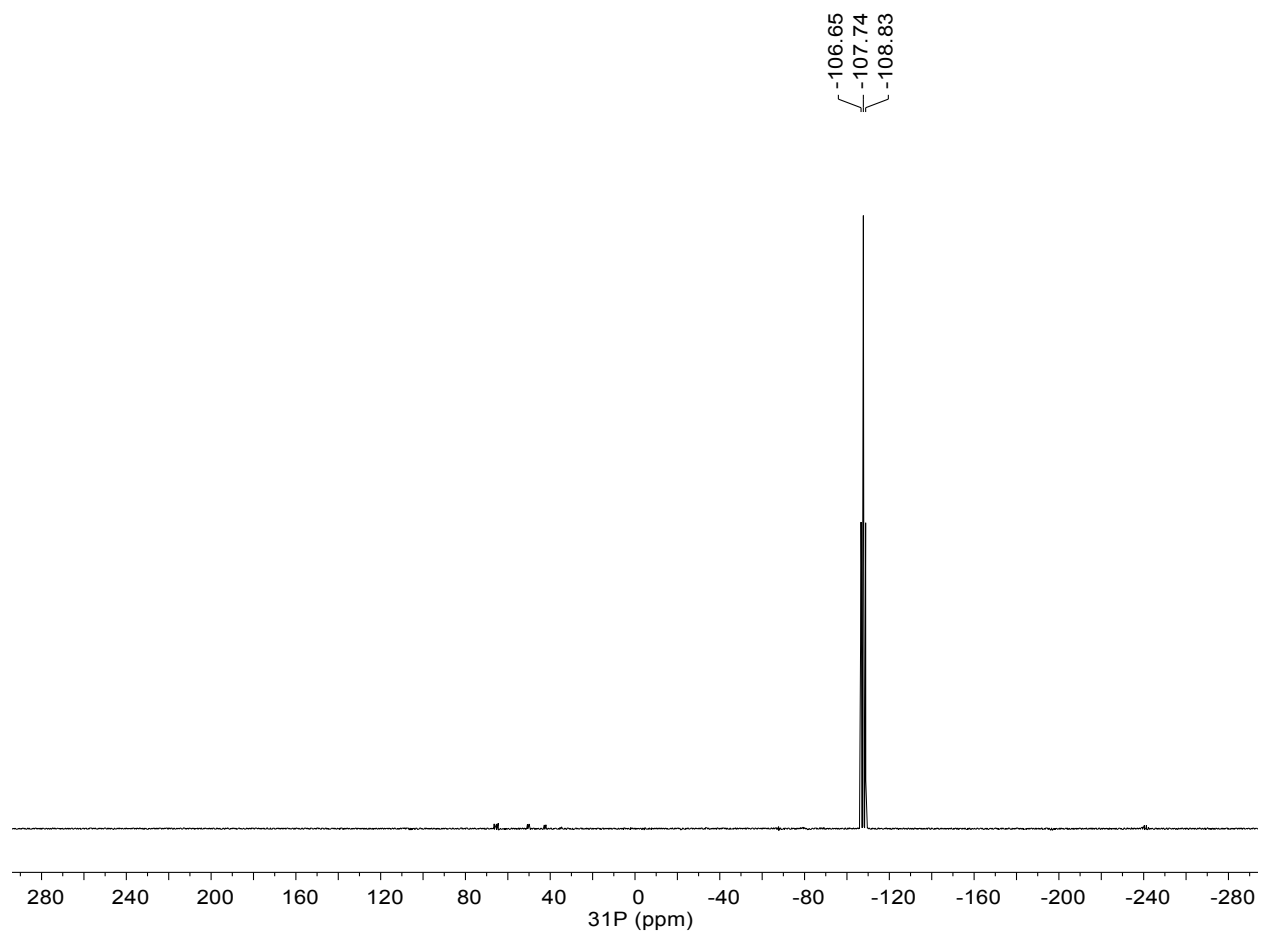


Figure S10. ^{31}P NMR ^1H Coupled (202 MHz, CD_2Cl_2) spectrum of reaction mixture containing **4** using procedure **B**.

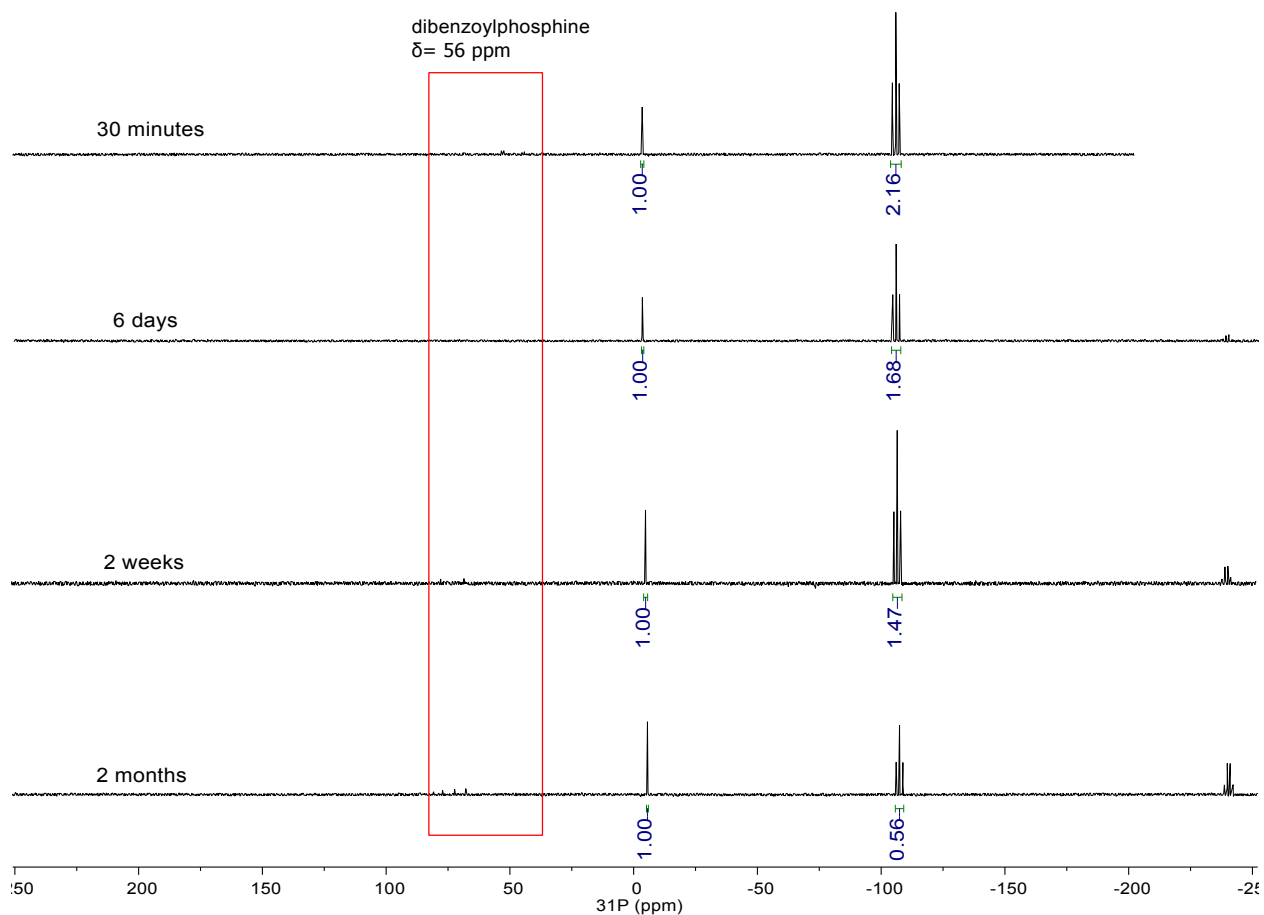


Figure S11. ^{31}P NMR ^1H Coupled (162 MHz, CH_2Cl_2) spectra of sealed tube containing reaction mixture of **4** using procedure **B**, sample tube stored in ambient conditions for 2 months. Half-life was calculated to be approximately 35 days, however lack of concurrent formation of dibenzoylphosphine suggests decomposition was due to imperfect seal on tube resulting in hydrolysis to benzoic acid and phosphane.

4. X-Ray Crystal Structure Analysis

Single crystals of **2** were grown by carefully layering a solution of Na[OCP] in THF on top of a solution of **1** in THF and allowing to stand undisturbed for 24 hours. Single crystals of **3** were obtained from recrystallization in benzene. Crystallographic data for both **2** and **3** are collected in Table 1. For both, data were collected with a Bruker Ultra rotating-anode system equipped with microfocus optics using Mo radiation. All procedures employed are part of Bruker APEX3 software systems (Bruker XRD, Madison, WI). Structure refinement without restraint employed OLEX2 software.⁴

Table S1. Crystal Data and Structure Refinement

Compound	2	3
Empirical Formula	C ₂₉ H ₃₈ NaO ₄ PZr	C ₄₀ H ₄₆ O ₂ P ₂ Si ₂ Zr ₂
Formula Weight	595.77	859.33
Temperature	100.0 K	100.0 K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P 21/n
a	10.3925(15) Å	10.6157(18) Å
b	16.372(2) Å	17.277(2) Å
c	16.948(3) Å	10.7644(16) Å
α	93.428(5)°	90°
β	100.442(4)°	105.752(5)°
γ	98.703(4)°	90°
Volume	2792.0(7) Å ³	1900.1(5) Å ³
Z, Z'	4	2, 0.5
Density (calculated)	1.417 Mg/m ³	1.502 Mg/m ³
Absorption Coefficient	0.499 mm ⁻¹	0.730 mm ⁻¹
F (000)	1240	880
Crystal Size	0.22 x 0.16 x 0.14 mm ³	0.32 x 0.29 x 0.26 mm ³
Theta range for data collection	1.680 to 24.999°	2.292 to 28.320°
Index Ranges	-12≤h≤12, -19≤k≤19, -20≤l≤20	-13≤h≤14, -23≤k≤22, -14≤l≤14
Reflections Collected	43409	17868
Independent Reflections	9838 [R(int) = 0.0554]	4720 [R(int) = 0.0683]
Completeness to Theta = 24.999°	99.9 %	99.9 %
Absorption Correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min. Transmission	0.0926 and 0.0666	0.2627 and 0.2064
Refinement Method	Full-matrix least-squares on F ²	Full-matrix least squares on F ²
Data / Restraints / Parameters	9838 / 0 / 649	4720 / 0 / 220
Goodness-of-fit on F ²	1.098	1.063
Final R Indices [I>2σ(I)]	R1 = 0.0596, wR2 = 0.1531	R1 = 0.0363, wR2 = 0.0946
R indices (all data)	R1 = 0.0847, wR2 = 0.1745	R1 = 0.0402, wR2 = 0.0986
Largest Diff. Peak and Hole	1.544 and -0.637 e.Å ⁻³	0.909 and -0.534 e.Å ⁻³

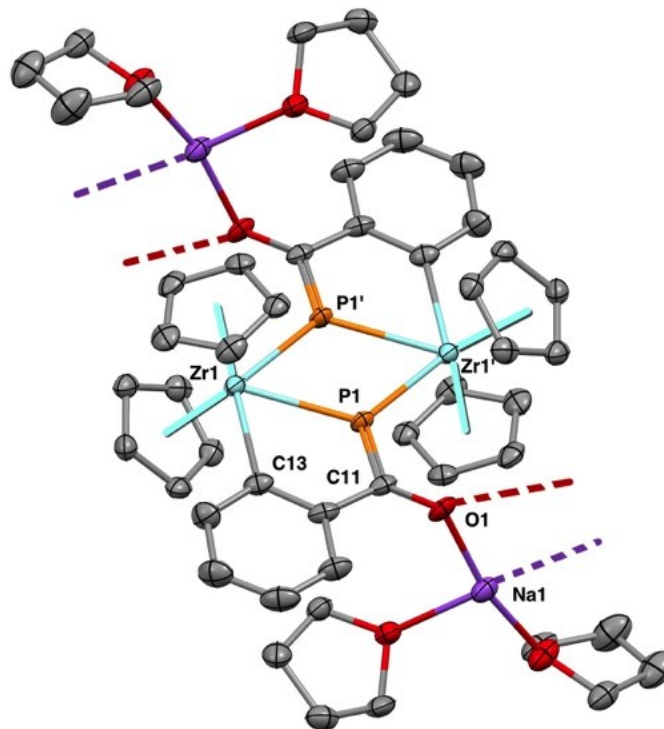


Figure S12. Molecular structure of **2** (ellipsoids set at 50% probability; hydrogen atoms, co-crystallized THF, and second coordination polymer chain omitted for clarity).

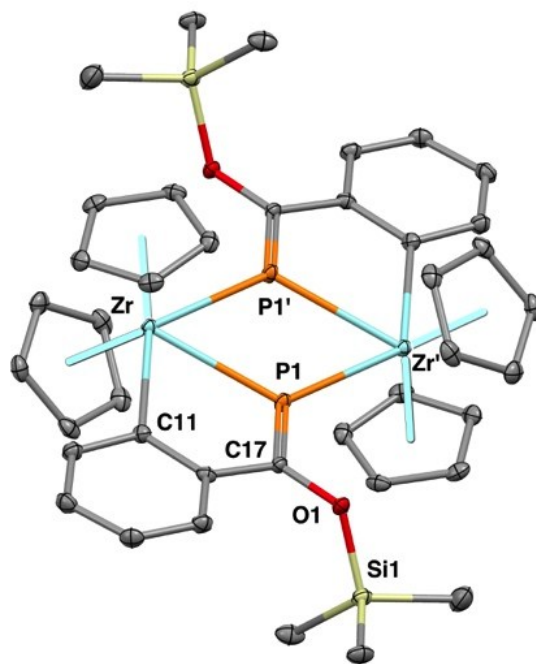


Figure S13. Molecular structure of **3** (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity).

5. References

1. S. L. Buchwald, B. T. Watson and J. C. Huffman, *J. Am. Chem. Soc.* **1986**, *108*, 7411-7413.
2. F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H. F. Grutzmacher and H. Grutzmacher, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420-8423.
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4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.