Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION OF SYNTHESIS, STRUCTURES, and COMPUTATIONS

Synthesis of $P_2C_2O_2$ and P_2CO via NHC-Mediated Coupling of the Phosphaethynolate Anion

Robert J. Gilliard, Jr., Riccardo Suter, Erik Schrader, Zoltan Benko, Arnold Rheingold, Hansjörg Grutzmacher,* John D. Protasiewicz*

To whom correspondance should be addressed.
email: protasiewicz@case.edu, hgruetzmacher@ethz.ch

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General Information

All reactions were performed under an atmosphere of rigorously dry and oxygen-free nitrogen using either an MBraun glovebox or standard Schlenk line techniques. Unless otherwise stated, all chemicals were purchased from commercial sources and used without further purification. Tetrahydrofuran, toluene, and hexanes were purified using an MBraun solvent purification system. Benzene-d_6 was distilled over sodium prior to use. [NHC][Cl] (**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 (^{1}H and ^{13}C) or to 85% H_3PO_4 (^{31}P). Elemental Analysis was performed by Complete Analysis Laboratories, 1259 Route 46, Building #4/C, Parsippany, NJ 07054-4909.

Experimental Procedures, NMR Data, and Elemental Analysis

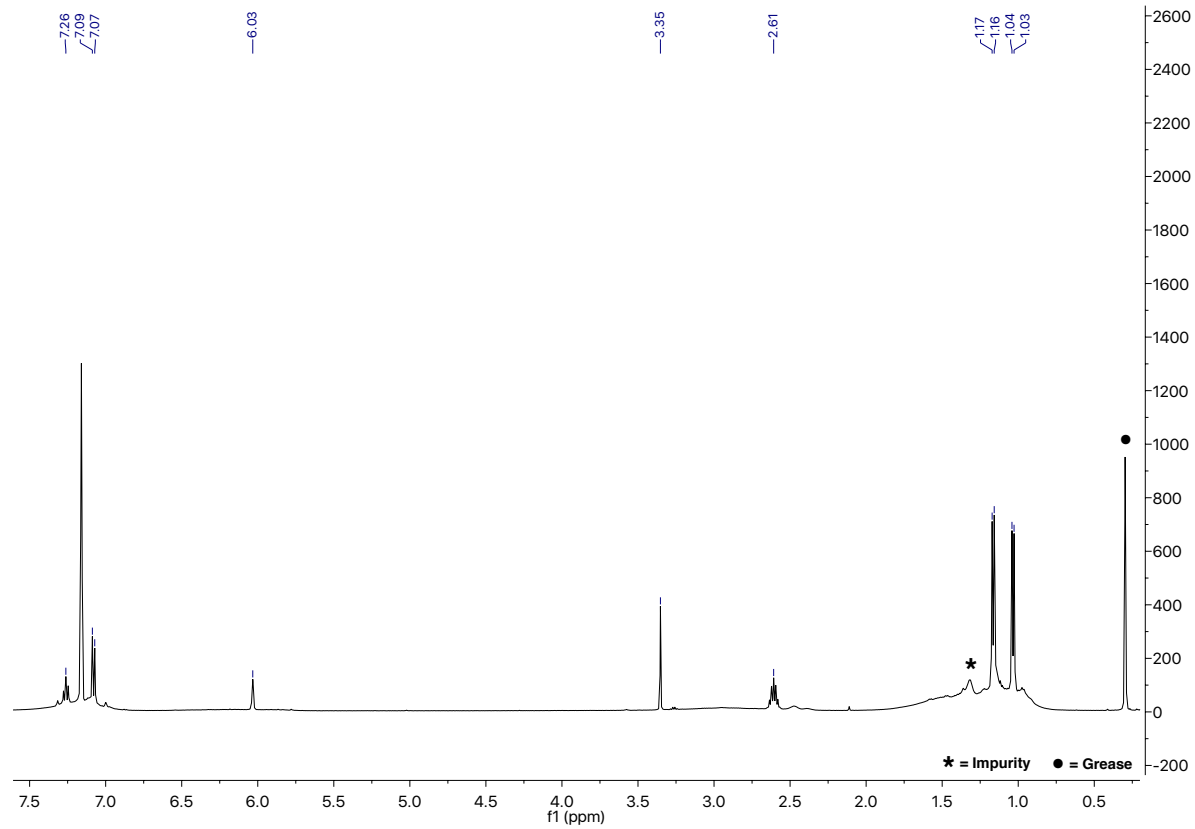
Synthesis of Compound **2**:

At –78 °C, a 30 mL dry THF solution of Na[OCP]•(dioxane)$_{2.5}$ (3.13 g, 10.4 mmol) was added to a suspension of chloroimidazolium chloride salt **1** (2 g, 4.7 mmol) in 20 mL of dry THF in a 100 mL Schlenk flask. The reaction was allowed to warm to room temperature and stirring was continued for 16 hours. All volatiles were removed in vacuo and the residue was extracted with 2 X 50 mL of dry toluene leaving a reddish brown solution. The toluene extracts were combined, all volatiles were removed and the solid was washed with 2 X 60 mL of hexanes to yield compound **2** as an air- and moisture-sensitive red solid (0.57 g, 24% yield). Red crystals suitable for X-ray diffraction studies were obtained from a 5:1 THF:toluene mixed solvent at –35 °C. NMR data for Compound **2**•(dioxane)$_x$: ^{1}H NMR (C_6D_6, 500 MHz): δ = 1.03 [d, 12H, CH(CH_3)$_2$], 1.16 [d, 12H, CH(CH_3)$_2$], 2.61 [m, 4H, CH(CH$_3$)$_2$], 3.35 [$C_4H_8O_2$], 6.03 [s, 2H, NCH], 7.07 [d, 4H, Ar-H], 7.26 [t, 2H, Ar-H]. ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ = 290.0 [d, $^1J_{p,p}$ = 484 Hz], 74.6 [d, $^1J_{p,p}$ = 484 Hz]. Due to the poor solubility of compound **2** in solvents in which it does not react, no sufficiently resolved ^{13}C NMR data could be obtained.

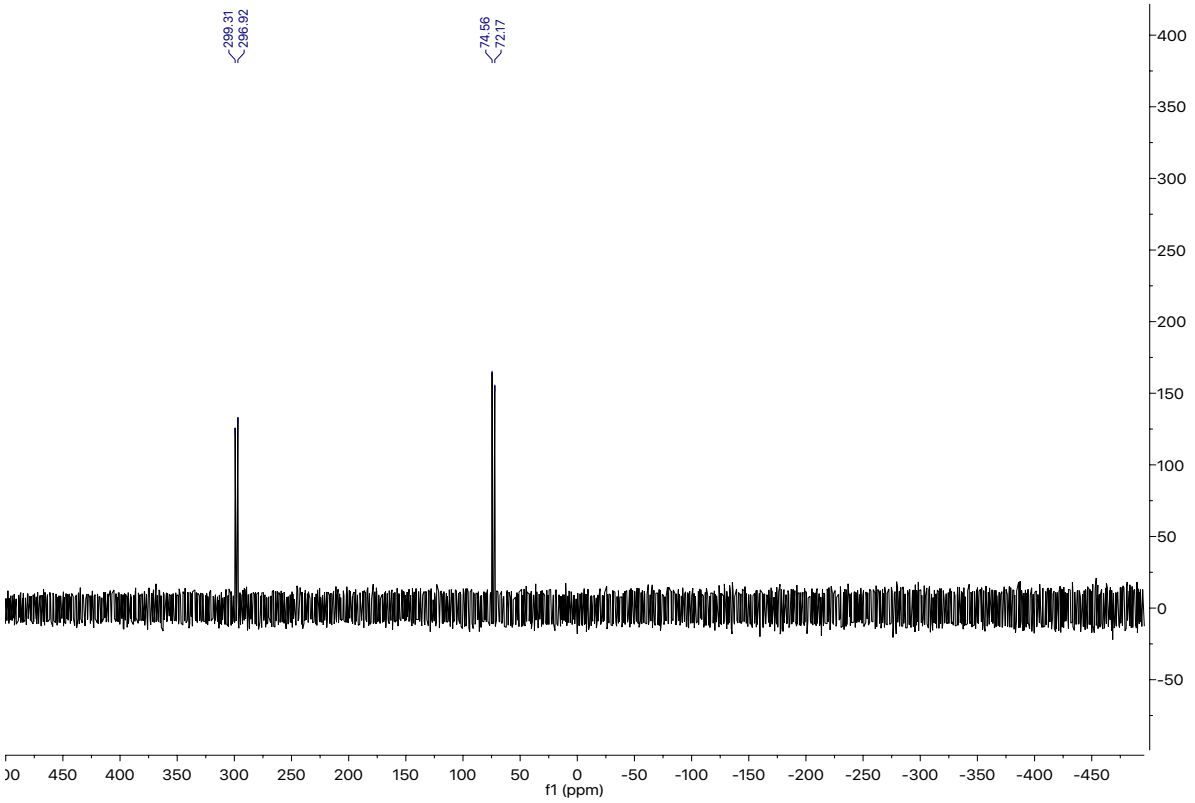
Synthesis of Compounds **2** and **3**:

At room temperature, Na[OCP]•(dioxane)$_{2.5}$ (3.13 g, 10.4 mmol) and chloroimidazolium chloride salt **1** (2 g, 4.7 mmol) were combined in a 100 mL Schlenk flask. With stirring, 20 mL of dry THF was added to the mixture and the reaction was allowed to stir for 16 hours. All volatiles were removed in vacuo and the residue was extracted with 2 X 50 mL of dry toluene to give a dark brown solution. The toluene extracts were combined and all volatiles were removed to afford a dark reddish brown solid. The solid was washed with 3 X 60 mL of hexanes. The residue was dried to afford compound **2** as a red solid (1.92 g, 62 % yield). The hexanes portions were combined and all volatiles were removed to yield compound **3** as a green solid (0.265 g, 13 % yield). Green crystals suitable for X-ray diffraction studies were obtained from hexanes at –35 °C. Compound **3** NMR data: ^{1}H NMR (C_6D_6, 500 MHz): δ = 1.02 [d, 12H, CH(CH_3)$_2$], 1.13 [d, 12H, CH(CH_3)$_2$], 1.23 [d, 12H, CH(CH_3)$_2$], 1.28 [d, 12H, CH(CH_3)$_2$], 2.68 [m, 4H, CH(CH$_3$)$_2$], 3.07 [m, 4H, CH(CH$_3$)$_2$], 3.35 [$C_4H_8O_2$], 5.89[s, 2H, NCH], 6.04 [s, 2H, NCH], 6.96 [d, 4H, Ar-H], 6.98 [d, 4H, Ar-H], 7.26 [t, 2H, Ar-H], 7.26 [t, 2H, Ar-H. ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ = 153.5 [d, $^1J_{p,p}$ = 304 Hz], –5.09 [d, $^1J_{p,p}$ = 3044 Hz]. Note: Compound **3** is extremely air- and moisture-sensitive, changing from green to orange upon decomposition. Therefore, it must be handled under rigorously dried inert gas. Due to the very similar solubility of free NHC and compound **3**, it has proved difficult to completely separate the two compounds on a preparative scale. Therefore, no sufficiently resolved ^{13}C NMR data could be obtained on the bulk sample. Elemental analysis on a sample of **3** isolated from a hexanes solution at –35 °C, Anal. Calculated(Experimental): $C_{55}H_{73}N_4P_2$•(dioxane) C = 74.11%(74.19%), H = 8.52%(8.50%), N = 5.86(6.20).

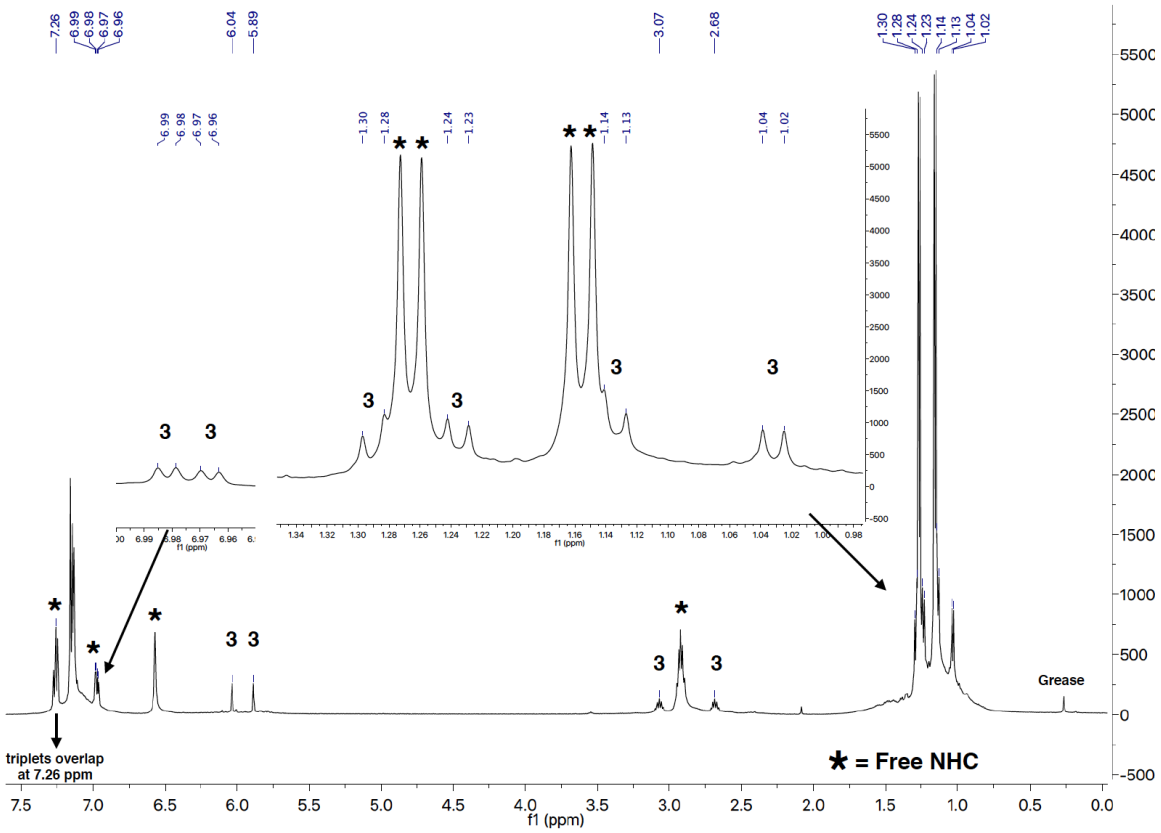
^{1}H NMR of Bulk **2**:



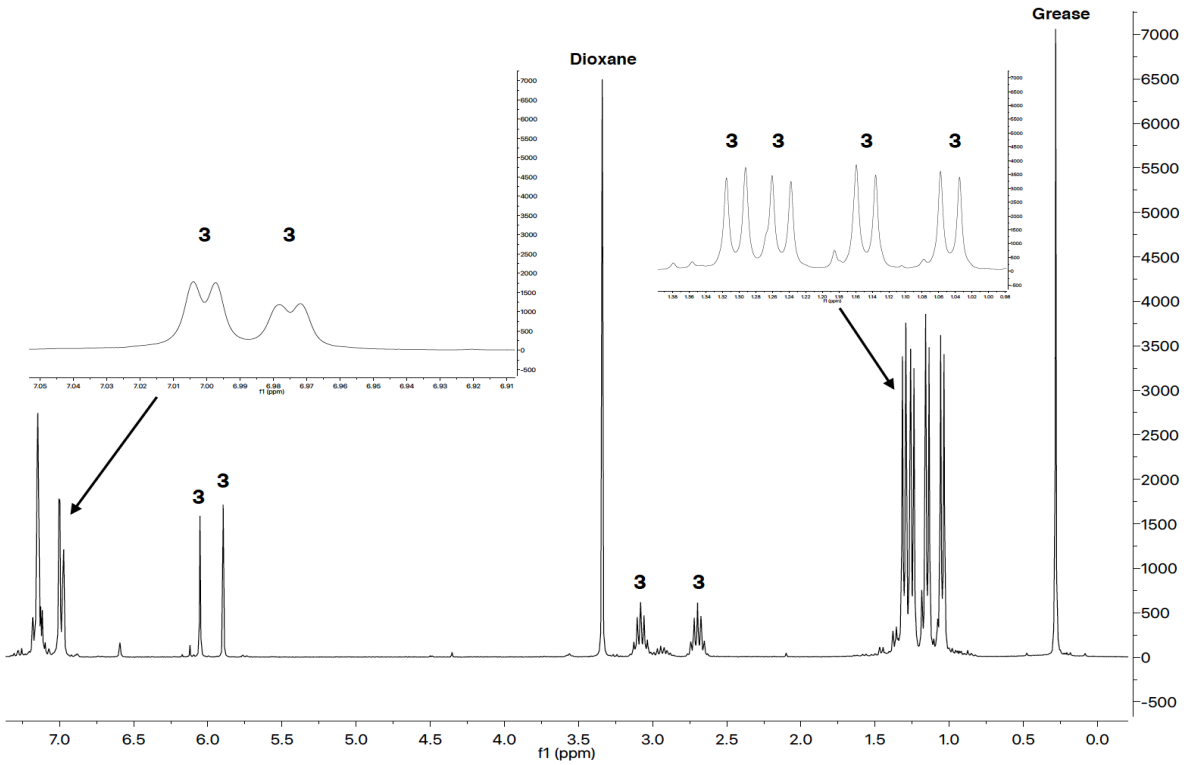
^{31}P NMR of Bulk **2**:



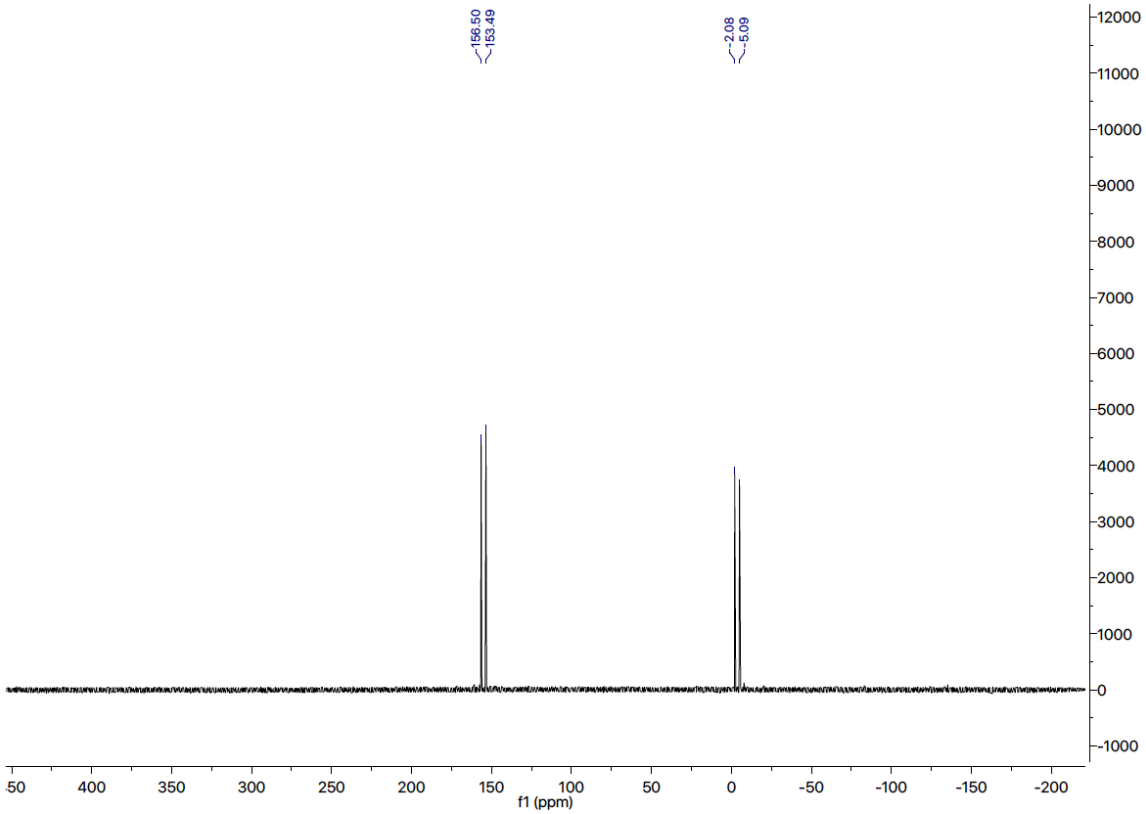
^{1}H NMR of Bulk **3** After Separation (with free NHC contaminant):



^{1}H NMR of **3** (after multiple recrystallizations):

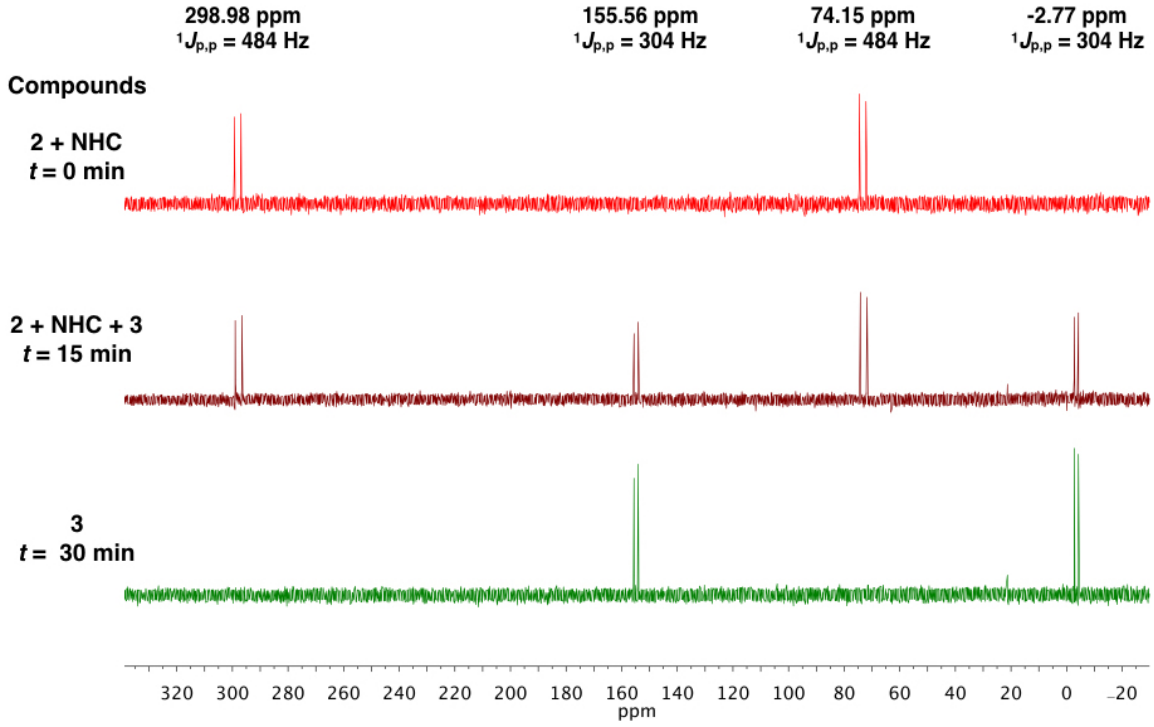


^{31}P NMR of **3** (after recrystallization):



$^{31}P\{^{1}H\}$ NMR Observations for the Conversion of Compound **2** to **3**:

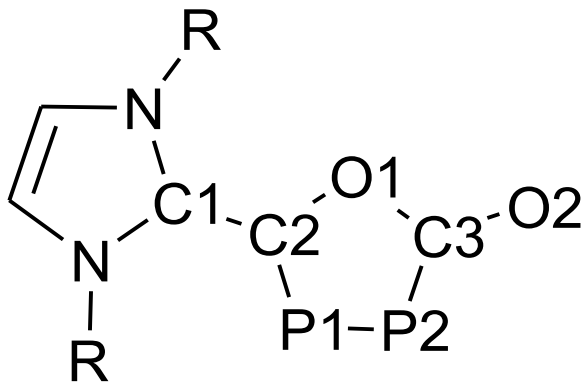
Compound **2** (100 mg, 0.197 mmol) and free NHC ligand (77 mg, 0.198 mmol) were combined in a vial and 1 mL of C_6D_6 was added to the vial and mixed to dissolve the two compounds. Then, the mixture was transferred to a J Young NMR tube. The mixture was heated to 60 °C over a period of 30 min to observe the conversion of compound **2** to **3** by ^{31}P NMR spectroscopy. Spectra were record at 0 min of heating (red), 15 min of heating (brown), and 30 min of heating (green). Note that a separate sample of compound **2** in C_6D_6, without free NHC, was heated at 80 °C for 3 hours, however, compound **3** was not observed.



Computational Analysis

Compound **2**

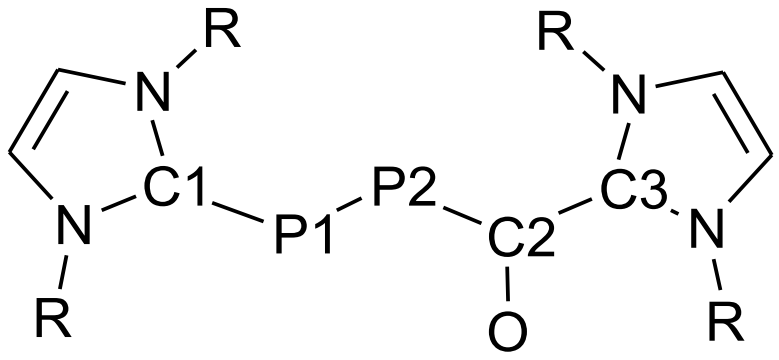
Bond lengths (d in Å), Wiberg bond indices (WBI), electron densities (ρ) and ellipticity values at the bond critical points for selected bonds at the ωB97XD/aug-cc-pVDZ level of theory.



		d	WBI	ρ	ε
Compound **2**	C1-C2	1.419	1.26	0.291	0.306
	C2-P1	1.742	1.27	0.158	0.137
	P1-P2	2.088	1.45	0.137	0.599
	P2-C3	1.836	1.08	0.143	0.124
	C3-O2	1.208	1.69	0.413	0.076
	C2-O1	1.370	0.94	0.128	0.114
	O1-C3	1.393	0.90	0.261	0.057

Compound **3**

Bond lengths (d in Å), Wiberg bond indices (WBI), electron densities (ρ) and ellipticity values at the bond critical points for selected bonds at the ωB97XD/aug-cc-pVDZ level of theory.



		d	WBI	ρ	ε
Compound **3**	C1-P1	1.784	1.28	0.141	0.485
	P1-P2	2.197	1.04	0.118	0.199
	P2-C2	1.754	1.35	0.159	0.439
	C2-O	1.255	1.41	0.272	0.055
	C2-C3	1.501	1.01	0.251	0.086
For Comparison:					
H_3CCH_3	C-C	1.527	1.04	0.240	0.000
H_2CCH_2	C=C	1.332	2.04	0.338	0.355
H_3CPH_2	C-P	1.868	0.98	0.144	0.142
H_2CPH	C=P	1.671	1.96	0.176	0.385
H_2PPH_2	P-P	2.239	1.04	0.114	0.019
HPPH	P=P	2.031	2.04	0.149	0.414
H_3COH	C-O	1.419	0.94	0.242	0.001
H_2CO	C=O	1.203	1.91	0.409	0.024

X-Ray Crystal Structure Analysis

Summary of Data from CCDC 1536982 (Compound **2**) and 1536982 (Compound **3**)

All procedures employed are part of Bruker APEX3 software systems (Bruker XRD, Madison, WI) or Oxford Diffraction Xcailber S program. Structure refinement without restraint employed OLEX2 software.[3]

Compound	**2**	**3**
Empirical Formula	C33 H43 N2 O3 P2	C59 H80 N4 O3 P2
Formula Weight	577.63	955.21
Temperature	100.0 K	100.0 K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Orthorhomic
Space Group	P 21/n	P 2_1 2_1 2_1
a	9.6328(5) Å	12.4060(5)Å
b	23.1916(9) Å	14.2364(4)Å
c	15.9848(7) Å	31.2334(17) Å
α	90°	90°
β	97.856(3)°	90°
γ	90°	90°
Volume	3537.5(3) $Å^3$	5516.4(4)$Å^3$
Z, Z'	4	4, 0
Density (calculated)	1.085 Mg/m^3	1.150 Mg/m^3
Absorption Coefficient	0.154 mm^{-1}	0.125 mm^{-1}
F (000)	1236	2064
Crystal Size	0.28 x 0.24 x 0.2 mm^3	0.22 x 0.18 x 0.18 mm^3
Theta range for data collection	2.177 to 24.998°	3.2740 to 25.4240°
Index Ranges	-11<=h<=9, -27<=k<=27, -18<=l<=18	-5≤h≤13, -15≤k≤15, -32≤l≤23
Reflections Collected	21551	13695
Independent Reflections	6220 [R(int) = 0.0302]	6985 [R(int) = 0.0460]
Completeness to Theta = 24.999°	99.9 %	93.61%
Absorption Correction	Semi-emperical from equivalents	Semi-emperical from equivalents
Max. and Min. Transmission	0.0644 and 0.0406	0.96448 and 1.00000
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least squares on F^2
Data / Restraints / Parameters	6220 / 0 / 369	6985 / 0 / 599
Goodness-of-fit on F^2	1.052	1.051
Final R Indices [I>2sigma(I)]	R1 = 0.0658, wR2 = 0.1757	R1 = 0.0790, wR2 = 0.2062
R indices (all data)	R1 = 0.0788, wR2 = 0.1890	R1 = 0.0961, wR2 = 0.2221
Largest Diff. Peak and Hole	1.424 and -0.509 e.$Å^{-3}$	1.497 and -0.702e.$Å^{-3}$

*For compound **2** there is one molecule of THF and one toluene disordered on an inversion center. This was treated using SQUEEZE.

References

1. D. Mendoza-Espinosa, B. Donnadieu, and G. Bertrand, *J. Am. Chem. Soc.* 2010, **132**, 7264-7265.

2. F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H. F. Grützmacher and H. Grützmacher., *Angew. Chem. Int. Ed.*, 2011, **50**, 8420-8423.

3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst. **2009**, *42*, 339-341.