Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION OF SYNTHESIS, STRUCTURES, and COMPUTATIONS

An Isolable Magnesium Diphosphaethynolate Complex

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Table of Contents

General Information

All reactions were performed under an atmosphere of rigorously dry and oxygen-free nitrogen using an MBraun glovebox. Tetrahydrofuran was purified using an MBraun solvent purification system or distilled over sodium/benzophenone. Magnesium chloride was used as received from Sigma Aldrich. Sodium phosphaethynolate, Na(OCP)•(dioxane)$_{2.5}$, was prepared according to literature procedures.[1] All other chemicals were purchased from commercial sources and used without further purification. Solution ^{31}P NMR spectra were recorded on a Bruker AVANCE III 500 or Varian Inova 400 spectrometers and chemical shifts referenced to 85% H_3PO_4.

Experimental Procedure and NMR Spectra

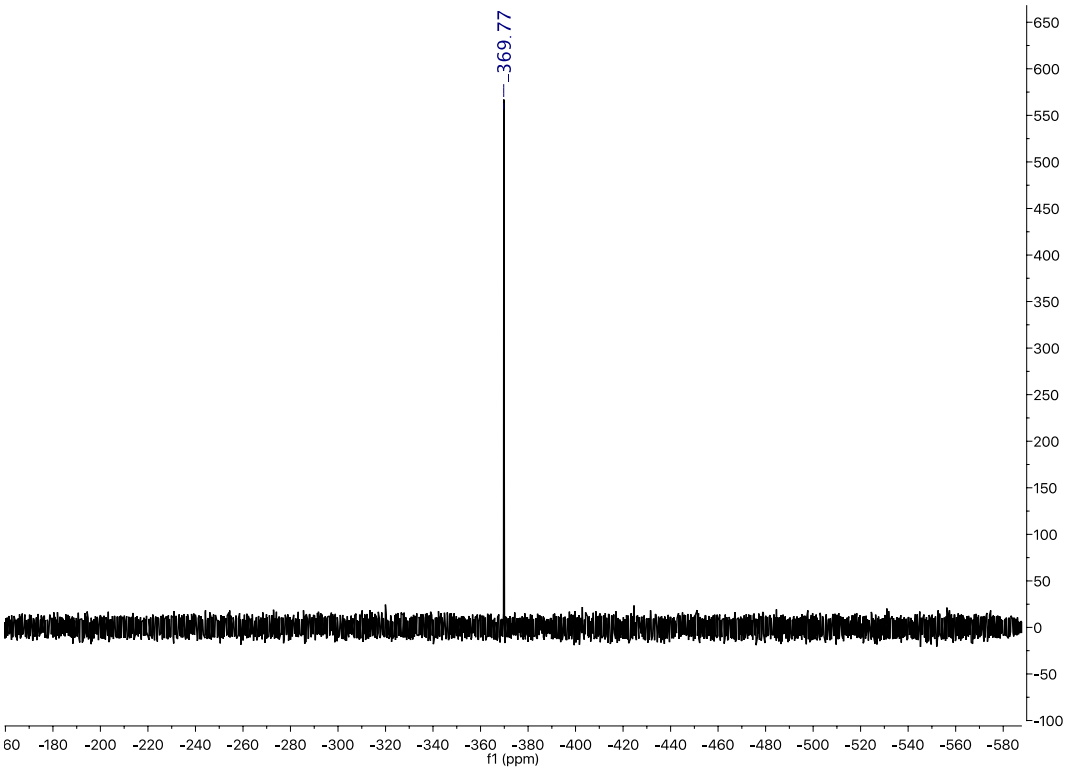
Synthesis of Compounds **2** and **3**:

A THF solution (15 mL) of sodium phosphaethynolate [Na(OCP)•$(dioxane)_{2.5}$] (1 g, 3.31 mmol) was added in segments by slow dropwise addition to a slurry of anhydrous magnesium chloride powder (157 mg, 1.65 mmol) rapidly stirring in 15 mL of a 5:1 THF:toluene mixture. After the addition of 1 eq of sodium phosphaethynolate (half the volume of the solution) was complete, a ^{31}P NMR spectrum of the reaction mixture revealed a singlet at δ = −369.8 ppm. This was assigned to the MgCl(OCP) complex **2**, which was not isolated. Continued dropwise addition of 0.5 eq of sodium phosphaethynolate (half the remaining volume of the solution) to the reaction mixture resulted in a slight color change from pale yellow to pale pink. A ^{31}P NMR spectrum of the reaction mixture revealed two singlets at δ = −369.5 ppm and δ = −367.9 ppm. The new peak at δ = −367.9 was attributed to the formation of the magnesium diphosphaethynolate complex **3**. Continued dropwise addition of 0.5 eq of sodium phosphaethynolate (the remaining volume of the solution) resulted in a slight darkening of the color. Analysis by ^{31}P NMR spectroscopy showed only the magnesium diphosphaethynolate complex **3** at δ = −367.9 ppm. The reaction mixture was filtered and concentrated to approximately one-fourth of the original volume to give a solid precipitate. The off-white solid was collected by filtration (medium porosity frit, inside the glovebox) and immediately transferred to a Schlenk pressure tube containing 15 mL of THF. The slurry was heated at reflux and additional THF was added until the solid completely dissolved. The heat was turned off, and after 24 hours, large colorless block-shaped X-ray quality crystals of **3** were isolated (690 mg, 97% yield). Note that slow dropwise addition of Na(OCP) is critical and the reaction must be worked up immediately or the yield of compound **3** is compromised, with the formation of a dark colored precipitate. The crystalline material is stable (in an inert atmosphere) at room temperature for ca. two months. However, to extend the shelf life it is recommended that compound **3** be stored at −35 °C to prevent loss of the coordinating solvent molecules. IR ν [cm^{-1}] = 1759 (vs) [$\nu_{asym.}$ $(OCP)^-$].

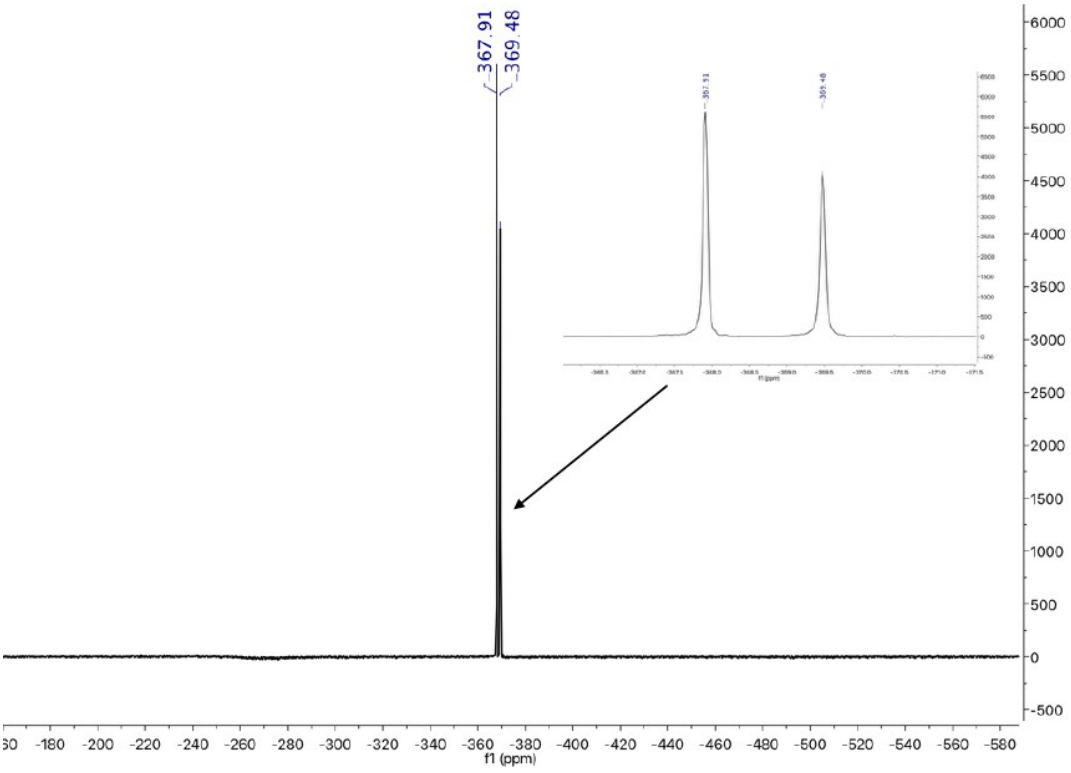
Synthesis of Compound **4:**

A solution of [Na(OCP)$(dioxane)_{2.5}$] (0.11g, 0.36 mmol) in THF (10 mL) was added dropwise at room temperature to a suspension of dibenzo-18-crown-6 (0.13 g, 0.36 mmol) in THF (10 mL). The reaction mixture was stirred for 12 hours at room temperature. Subsequently, the organic solvent was removed under reduced pressure and the reaction product was dried *in vacuo* yielding an off-white powder. Yield: 0.155 g (97%) ^{31}P NMR (THF-d_8, 162 MHz, 298 K): δ (ppm) = −388 (s). IR ν [cm^{-1}] = 1765 (vs) [overlapping peak: $\nu_{asym.}$ $(OCP)^-$ and crown ether]

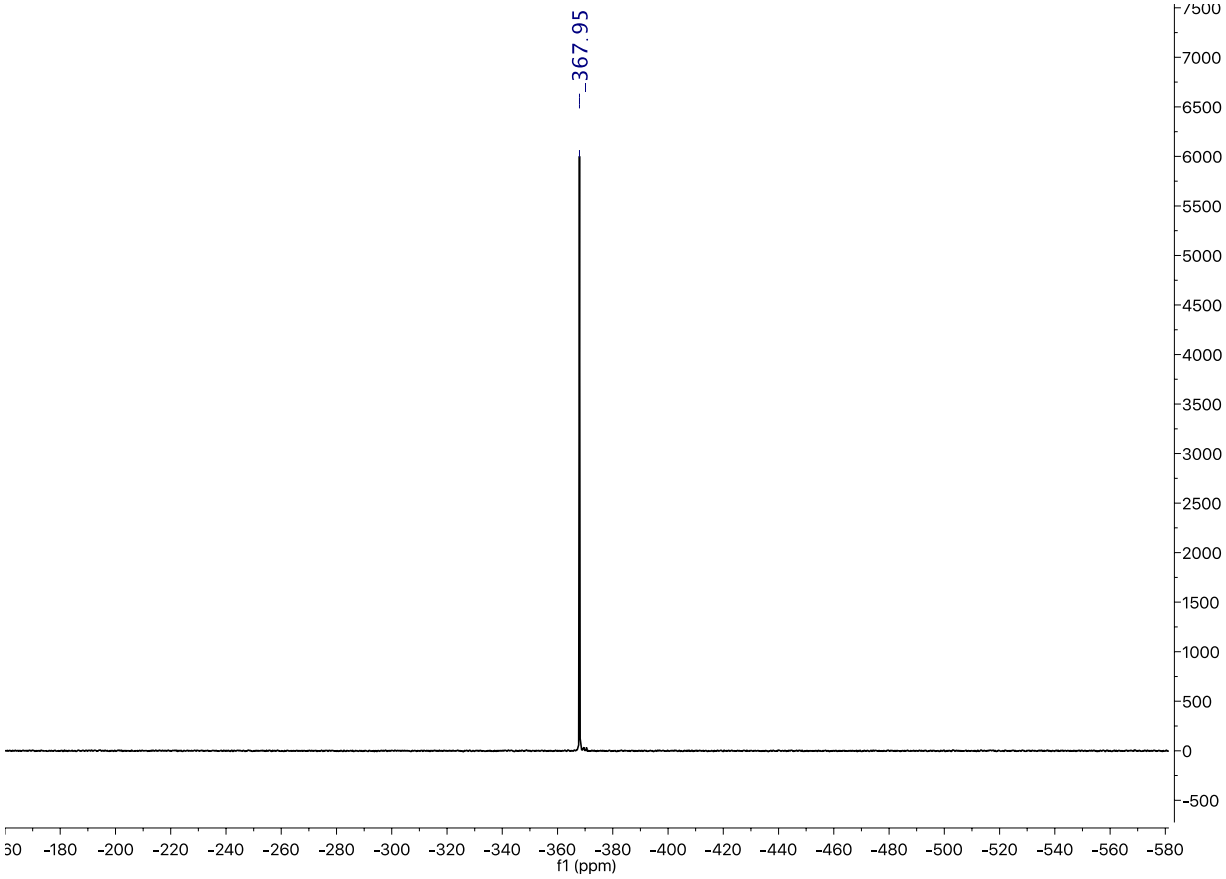
$MgCl_2$ + 1 eq Na(OCP)•$(dioxane)_{2.5}$:



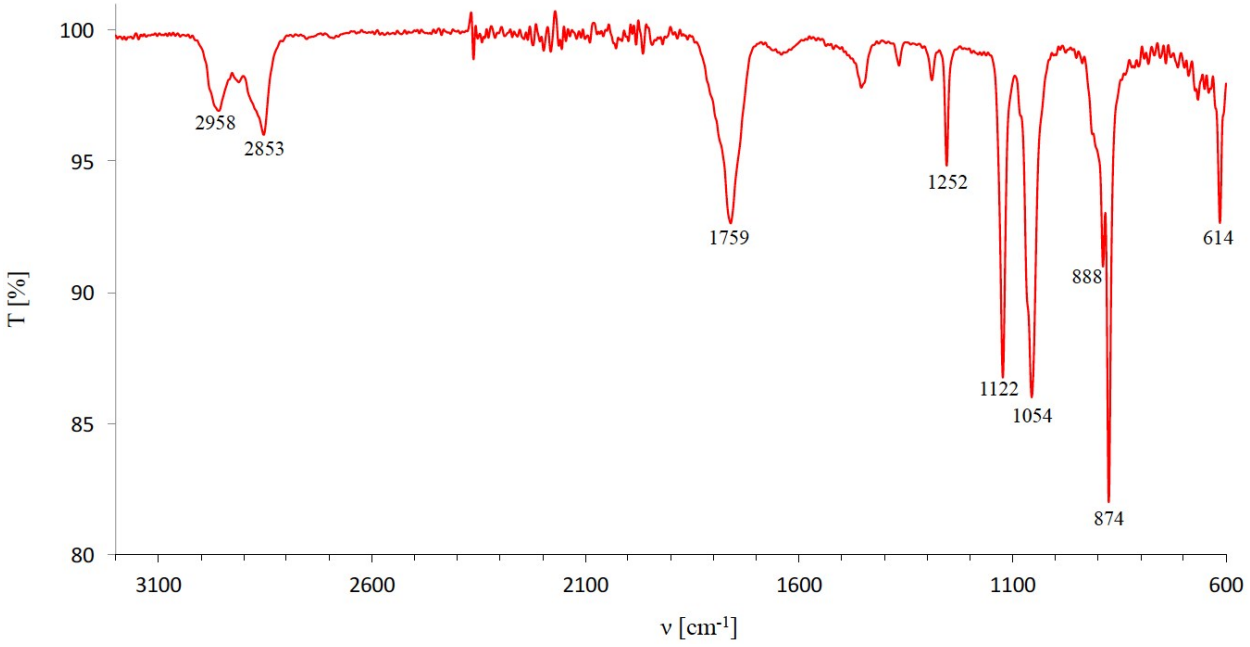
$MgCl_2$ + 1.5 eq Na(OCP)•$(dioxane)_{2.5}$:



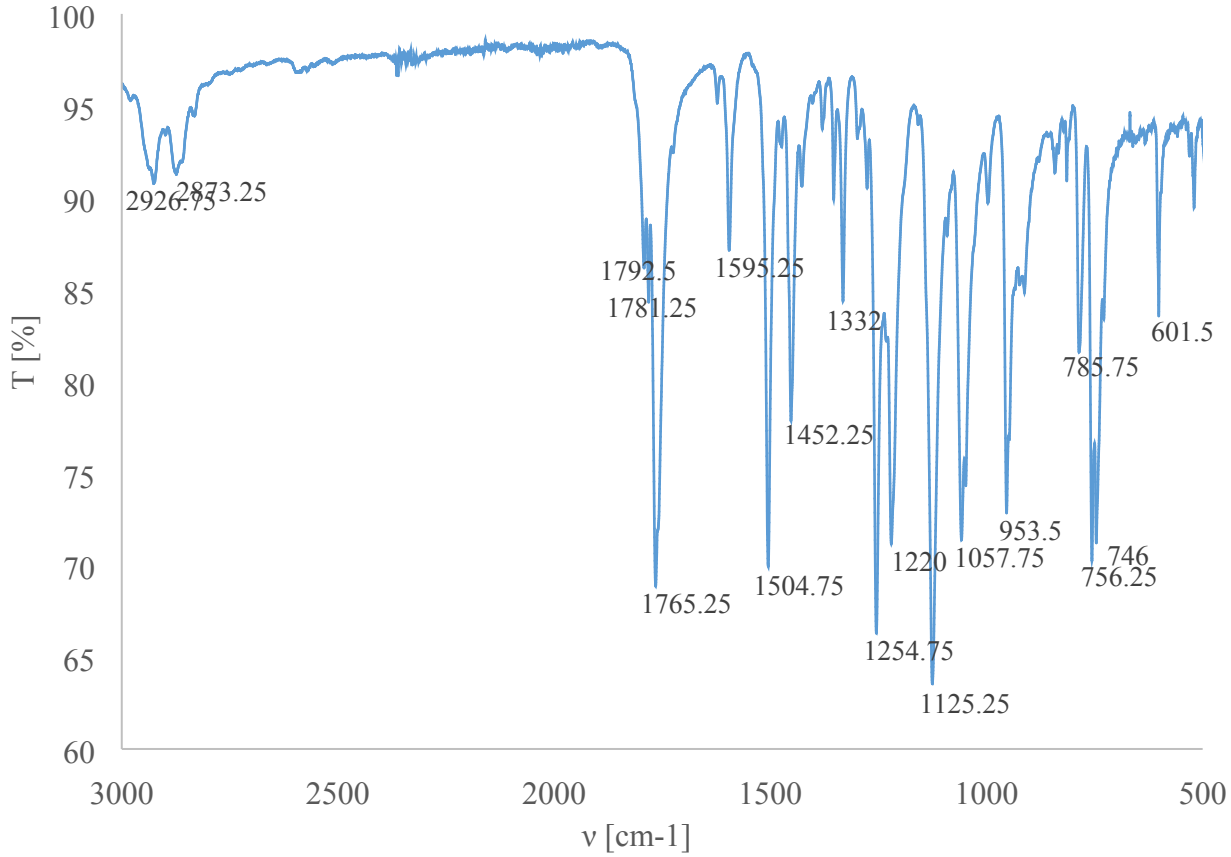
$MgCl_2$ + 2 eq Na(OCP)•$(dioxane)_{2.5}$:



IR Spectrum of 3



IR Spectrum of 4



Computational Data

	(OCP) **5M**	$Na(OCP)(THF)_5$ **4M**	$Mg(OCP)_2(THF)_4$ **3**
d(OC)	1.199	1.219	1.238
d(PC)	1.625	1.601	1.584
q(O)	-0.67	-0.79	-0.88
q(C)	+0.11	+0.03	-0.04
q(P)	-0.44	-0.18	-0.01
q(metal)	-	+0.89	+1.77

Table 1. OC and PC bond lengths (d, in Å) and partial charges (q, in e) at the M06-2X level.

References

1. 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.