Short Note

Cyclo-tetrakis(μ-diphenylphosphido)-1,5-bis(tri-*tert*-butylphosphine-tetracopper(I)

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Abstract: Copper phosphido cluster $Cu_4(\mu\text{-}PPh_2)_4(P^tBu_3)_2$ was synthesized by three synthetic methods and structurally characterized by X-ray diffraction and ^1H, ^{31}P, ^{13}C and ^{31}P HMBC NMR spectroscopy. $Cu_4(\mu\text{-}PPh_2)_4(P^tBu_3)_2$ was also demonstrated to be a hydrophosphination pre-catalyst.

Keywords: copper; hydrophosphination; phosphido; X-ray diffraction

1. Introduction

Metal phosphido compounds are important synthetic intermediates in organophosphorus chemistry [1-3]. Most copper phosphido compounds characterized by X-ray crystallography have oligomeric structures [4-15] with a few notable exceptions [16, 17]. We have been studying these types of compounds as intermediates in copper catalyzed hydrophosphination [18]. During our study, we isolated the novel bridging phosphido copper cluster, $Cu_4(\mu\text{-}PPh_2)_4(P^tBu_3)_2$ (**1**) and were able to determine its molecular structure using X-ray diffraction (Figure 1). We also demonstrate that **1** is an active hydrophosphination pre-catalyst.

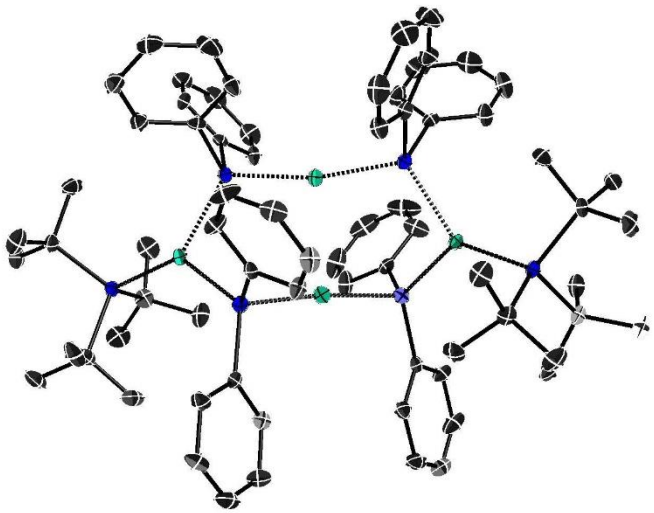


Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and two non-coordinated THF molecules of solvation are omitted for clarity.

2. Results and Discussion

Treatment of a THF solution of copper(I) chloride with potassium diphenylphosphide in the presence of tri-*tert*-butylphosphine at -30 °C results in the formation of compound **1** (eq. 1) as determined by single crystal X-ray diffraction, ^1H, ^{31}P, ^{13}C NMR, and ^{31}P HMBC NMR spectroscopy. Compound **1** can also be synthesized by treatment of mesitylcopper(I) with diphenylphosphine in the presence of tri-*tert*-butylphosphine (eq.

2) or by treatment of $Cu(acac)_2$ with three equivalents of diphenylphosphine in the presence of tri-*tert*-butylphosphine (eq. 3). The ^{1}H and ^{31}P NMR spectra of products from these three methods are equivalent.

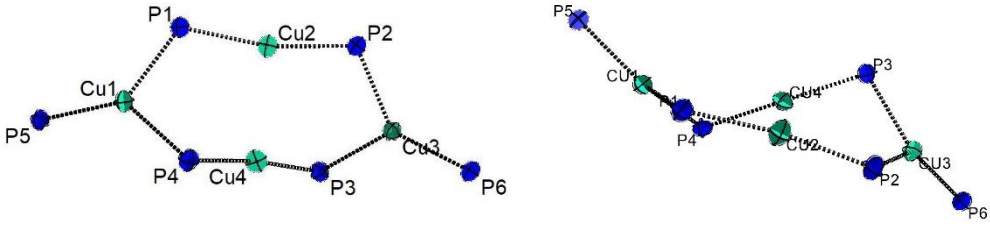
$$Cu(I)Cl + KPPh_2 + P^tBu_3 \xrightarrow{THF} Cu_4(\mu\text{-}PPh_2)_4(P^tbu_3)_2 \quad \text{Eq. 1}$$

$$MesCu + Ph_2PH + P^tBu_3 \xrightarrow{THF} \mathbf{1} \quad \text{Eq. 2}$$

$$Cu(acac)_2 + 3\ Ph_2PH + P^tBu_3 \xrightarrow{Toluene} \mathbf{1} \quad \text{Eq. 3}$$

Compound **1** prepared via eq. 1 forms as yellow prismatic crystals that vary in length from plates to columns from a mixture of greater than 99 : 1 pentane : THF when stored at -30 °C. Two co-crystalized THF molecules per asymmetric unit could be localized with **1**.

The molecular core of **1** consists of an eight-membered Cu_4P_4 ring that is capped by a P^tBu_3 (P5 and P6) on Cu1 and Cu3 (Figure 2a). Formally, **1** has 2-fold symmetry but does not crystalize with symmetry intact. Instead, **1** adopts a chair-like configuration (Figure 2b) in which the greatest deviations from a least-squares plane of best fit of the eight atoms in the Cu_4P_4 core is -1.0453 (0.0007) and 0.9814 (0.0007) Å, for P3 and P4 respectively. The greatest distance from a plane of best fit consisting of the four copper atoms is -1.2939 (0.0009) Å for P3.The copper atoms in **1** have alternating coordination numbers. Two-coordinate Cu2 and Cu4 are approaching linear geometry P2–Cu2–P1 = 167.32(3), P3–Cu4–P4 = 173.43(2), whereas Cu1 and Cu3 have a nearly trigonal planar geometry (P5–Cu1–P4 = 129.66(3), P5–Cu1–P1 = 130.14(4), P6–Cu3–P2 = 132.84(3), P6–Cu3–P3 = 127.65(3). The influence of the electron rich P^tBu_3 manifests in the increased bond length between Cu1 and P1 (2.3076 (10) Å) versus that of Cu2 and P1 (2.2.2272 (12) Å). Both values are within the range of previously reported μ_2- Cu-P bonds[5, 17]. The closest copper–copper distances are between Cu2 and Cu4, (2.8612(13)), larger than the sum of covalent radii (2.64 Å) [8].



(**a**) (**b**)

Figure 2. Cu_4P_4 ring that is capped by a P^tBu_3 in compound **1**: (**a**) view from above the ring (**b**) view from the side.

Table 2. Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Cu1–P5	2.2738(10)	P5–Cu1–P1	130.14(4)
Cu1–P1	2.3076(10)	P4–Cu1–P1	98.75(4)
P1–Cu2	2.2272(12)	Cu2–P1–Cu1	115.59(4)
Cu2–Cu4	2.8612(13)	P2–Cu2–P1	167.32(3)
		P2–Cu2–Cu4	96.16(2)

The structure of **1** resembles $Cu_4(\mu\text{-}PPh_2)_4(PHPh_2)_4$ (**2**) described by Fenske [5]. However, in compound **2**, Cu1 and Cu3 adopt tetrahedral geometry resulting from the coordination of two Ph_2PH molecules per copper. The increased steric bulk of the P^tBu_3 versus that of Ph_2PH provides a rationale for the observed three coordinate trigonal planar geometry as only one P^tBu_3 can coordinate to copper. The closest Cu–Cu distance in **2** is 3.17(6) Å which is larger than the corresponding distance in **1**. This may be a result of **2** having a closer to linear structure than **1** with no deviations greater than 0.2 Å from the best fit plane of the Cu_4P_4 ring. Compound **1** also resembles $Cu_4(\mu\text{-}PPh_2)_4(dppm)_2$ **(3)** (dppm = bis(diphenylphosphino)methane) [9] that has a Cu_4P_4 core but is not capped at Cu1 and Cu3 but is instead supported by two dppm bridges between Cu1–Cu2 and Cu3–Cu4. Sulfide cluster $(CuS^tBu)_4(Ph_3P)_2$ **(4)** [7] is also related, consisting of a Cu_4S_4 core that is capped by PPh_3 on Cu1 and Cu3. Similar to **1**, both **3** and **4** adopt a chair-like conformation with maximum deviations of 1.52 and 1.55 Å respectively, from a plane of best fit consisting of the four copper atoms.

Compound **1** displays evidence for dynamic behavior in solution by ^{1}H NMR and ^{31}P NMR spectroscopy. The *tert*-butyl substituents in the ^{1}H spectrum of **1** are split into several overlapping multiplets centered around δ = 1.11 and 1.28. To confirm that the multiple alkyl peaks were features of **1** in solution, and not

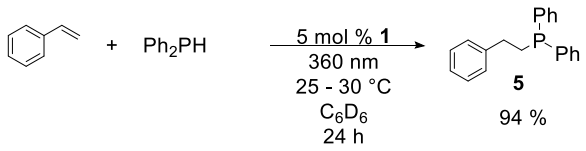
Compound **1** displays evidence for dynamic behavior in solution by ^{1}H NMR and ^{31}P NMR spectroscopy. The *tert*-butyl substituents in the ^{1}H spectrum of **1** are split into several overlapping multiplets centered around δ = 1.11 and 1.28. To confirm that the multiple alkyl peaks were features of **1** in solution, and not impurities, a variable temperature (VT) NMR experiment was performed in which ^{1}H NMR spectra were taken at 25 °C, 35 °C, and 45 °C. A coalescing of the alkyl peaks was observed upon increasing the temperature from 25 °C to 45 °C. This behavior is consistent with hindered bond rotation, slow conformational change or a derivative speciation of **1** in solution under rapid exchange on the NMR time scale [19].

Similarly, ^{31}P NMR spectra of **1** have features that show evidence of dynamic behavior. A spectrum obtained at 25 °C initially appears to have two broad singlets, but closer inspection by enlarging the peaks reveals multiplets at δ = -19.5, 60.1, and 62.3 that integrate in a 1 : 0.15 : 1 ratio. This is unexpected because compound **1** has a 2 : 1 ratio of (μ-PPh_2) : (P^tBu_3) atoms. A second VT NMR experiment was undertaken to confirm that these features were a result of dynamic behavior. Upon heating a benzene-d_6 solution of **1** to 45 °C, the signal changes from the initial 1 : 0.15 : 1 ratio to 0.67 : 0.07 : 1. Several new broad peaks also appear in the baseline of the spectrum obtained at 45 °C. Upon the solution returning to 25 °C the original features return in the same 1 : 0.15 : 1 ratio. This result suggests that the multiplets are features of a derivative speciation of **1** in solution under rapid exchange on the NMR time scale. Furthermore, the 1 : 0.15 : 1 ratio was preserved across three trials and repeated crystallizations.

Finally, a ^{31}P HMBC NMR spectrum of **1** confirmed the shift at δ = -19.53 is the signal for the bridging phosphido as it is correlated only with aromatics. The signals at δ = 62.3

and 60.1 are correlated with multiple alkyl peaks which identifies them as belonging to P^tBu_3 ligand.

Compound **1** was found to be an active hydrophosphination catalyst. Treatment of a benzene-d_6 solution of styrene, diphenylphosphine, and 6 mol% of **1** under 360 nm irradiation resulted in a 94% NMR conversion to the hydrophosphination product, diphenyl(2-phenylethyl)-phosphine (**5**), after 24 h (eq. 4). We did not purse further hydrophosphination reactivity given this derivative compound showed no improvement in reactivity compared to $Cu(acac)_2$ [18].



Eq. 4

3. Experimental details

3.1. General considerations

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Tetrahydrofuran was dried over sodium/benzophenone and vacuum transferred. Benzene-d_6 was purchased and then degassed and dried over 3 and 4 Å molecular sieves. Diphenylphosphine [20], copper(I)chloride [21], and mesitylcopper(I) [22], were synthesized according to literature procedures and stored under an inert atmosphere of N_2. Potassium diphenylphosphine was made by a modified literature procedure [23] in which Ph_2PH was deprotonated by KH in THF and then filtered through celite, and concentrated to dryness by vacuum. All other reagents were acquired from commercial sources and dried by conventional means, as necessary. ^1H, ^{13}C, ^{31}P and ^{31}P HMBC NMR spectra were recorded with a Bruker AXR 500 MHz spectrometer. All 1-D ^{31}P NMR spectra were ^1H decoupled. Resonances in ^1H NMR spectra are referenced to the residual solvent resonance (C_6D_6 = δ 7.16). Reported ^{31}P NMR resonances are relative to external 85% H_3PO_4. Spectral data for diphenyl(2-phenylethyl)-phosphine is consistent with literature reports [24].

3.2. Synthesis of Compound 1

Method A*:* In an N_2 filled glovebox, $P(^tBu)_3$ (51 mg, 0.25 mmol), Cu(I)Cl (25 mg, 0.25 mmol) and 5 mL of cold THF (stored at -30 °C and removed immediately before use) were stirred in a scintillation vial. After 30 seconds, a $KPPh_2$ (56 mg, 0.25 mmol) solution in 5 mL of cold THF was added dropwise resulting in a color change to yellow. The solution was stirred for 30 min at ambient temperature, then concentrated to a yellow residue under reduced pressure. The crude product was redissolved pentane and filtered through a bed of Celite. The filtrate was immediately pipetted into a scintillation vial and placed in a freezer at -30 °C. Crystals suitable for X-ray crystallography precipitated overnight. To isolate the product for NMR the mother liquor was decanted from the precipitate, and the precipitate was washed with 2 mL of cold pentane and dried in vacuo. Yield 57 mg (65%). ^1H NMR (500 MHz, C_6D_6) δ 7.97 – 7.35 (m), 7.15 – 6.75 (m), 1.36 (d, J = 11.8 Hz), 1.32 – 1.25

(m), 1.11 (d, J = 11.8 Hz). ^{31}P NMR (202 MHz, C_6D_6) δ 62.207 (m), 60.07 (m), -19.53 (m). ^{13}C NMR (126 MHz, C_6D_6) δ 142.26 (s), 135.75 (s), 135.51 (s), 126.09 (s), 125.83 (s), 125.51 (s), 36.01 (s), 32.26 (s), 32.20 – 31.48 (m).

Method B: In an N_2 filled glovebox, P(^{t}Bu)$_3$ (166 mg, 0.824 mmol) and mesitylcopper(I) (150 mg, 0.824 mmol) were dissolved in 2-3 mL of cold THF (-30 °C). Neat Ph_2PH (153 mg, 143 μl, 0.824 mmol) was added dropwise. The resulting yellow solution was stirred for 24 h. (Note: subsequent trials with less concentrated solutions monitored by ^{31}P NMR indicate that full conversion is reached after 4 h). The solution was then layered with ~8 mL of pentane and placed in a freezer at -30 °C. After decanting the mother liquor, 107 mg (37 % yield) of **2** was recovered upon washing the precipitate with cold pentane and drying.

Method C: In an N_2 filled glovebox, 31.5 mg Ph_2PH (29.5 μl, 0.170 mmol) was added dropwise at -30 °C to a scintillation vial containing a toluene solution of 15 mg (0.057 mmol) $Cu(acac)_2$ and 11.5 mg (0.057 mmol) of P(^{t}Bu)$_3$. The solution allowed to warm to ambient temperature and stirred for 24 h. Then the solvent was removed under reduced pressure, the residue was taken up in pentane, filtered through a bed of Celite, and placed in a freezer at -30 °C. The resultant precipitate was dissolved in a minimum amount of THF ~ 1 mL and layered with three mL of pentane and placed in the freezer again. The 10.6 mg (53% yield) of solid was isolated by decanting the mother liquor, washing with cold pentane, and drying. The ^{1}H and ^{31}P NMR spectra of the compound obtained by this method matched methods A and B.

Catalytic experiment: In an N_2 filled dry box, 8 mg (.023 mmol, 6 mol %) of **1**, 70.7 mg (66 μl, 0.38 mmol) diphenylphosphine and 39.5 mg (43.5 μl, 0.38 mmol) of styrene was measured and mixed in 0.6 mL benzene-d_6. This solution was transferred to an NMR tube. Initial ^{1}H and ^{31}P NMR spectra were obtained before placing the tube in a photoreactor containing a Rexim G23 UV-A (9W) lamp at ambient temperature. The temperature of the 360 nm photoreactor was measured to be 25–30 °C, depending on how long it had been in use. No efforts to control the temperature between this range were undertaken. Periodic ^{1}H and ^{31}P NMR spectra were collected. Conversions were determined by integration of ^{1}H and ^{31}P NMR spectra to starting materials.

3.3 X-Ray structure determinations

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα (λ = 0.71073 Å)) at 150(2) K. A suitable yellow prismatic plate crystal of $Cu_4(\mu\text{-}PPh_2)_4(P^tBu_3)_2$, was mounted on a MiTeGen Micromount 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 F2 with using the Bruker SHELXTL Software Package [25, 26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model.

Crystal Data for $C_{72}H_{94}Cu_4P_6$, $2(C_4H_8O)$ (M = 1543.65 g/mol): monoclinic, space group $P2_1/n$ (14), a = 17.127(10) Å, b = 19.946(11) Å, c = 23.841(14) Å, β = 105.715(7)°, V = 7840(8) Å^3, Z = 4, ρ_{calc} = 1.308 g/cm^3, 90959 reflections measured (3.32° ≤ 2Θ ≤ 55.01°) (0.77 Å) , 17898 unique (R_{int} = 0.0881, R_{sigma} = 0.0587), which were used in all calculations. The final R_1 was 0.032 ($I > 2\sigma(I)$) and wR_2 was 0.0839 (all data). Full crystallographic information (as CIF file) and CheckCIF report are given in the supplementary materials.

4. Conclusions

Compound **1** has been synthesized by three methods and characterized by X-ray diffraction and ^{1}H, ^{31}P, ^{13}C and ^{31}P HMBC NMR spectroscopy. **1** has been demonstrated to be a hydrophosphination pre-catalyst under photocatalytic conditions. Mechanistic work on a monomeric copper phosphido for hydrophosphination is underway.

Supplementary Materials: The following are available online: ^{1}H, ^{31}P, ^{13}C and ^{31}P HMBC NMR spectra of **1**, ^{1}H and ^{31}P NMR spectra of a catalytic hydrophosphination experiment, crystallographic information file (CIF) and CheckCIF report for compound **1.**

Author Contributions: Conceptualization, S.D. and R.W.; methodology, S.D. and R.W.; formal analysis, S.D.; investigation, S.D.; resources, R.W.; data curation, S.D. and R.W.; writing—original draft preparation, S.D.; writing—review and editing, R.W.; visualization, S.D.; supervision, R.W.; All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: CCDC 2131210 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk. All other data in this study can be found in **Supplementary Materials** and at https://www.uvm.edu/~waterman/pubs.html.

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Conflicts of Interest: The authors declare no conflict of interest.

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Graphical abstract: