Short Note

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

Steven G. Dannenberg and Rory Waterman *

Department of Chemistry, University of Vermont, Burlington, Vermont 05405-0125, United States.
Steven.Dannenberg@UVM.edu

* Correspondence Rory.Waterman@UVM.edu; Tel.: +1 (802) 656-0278

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.

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 compound~luster~, $Cu_4(\mu\text{-}PPh_2)_4(P^tBu_3)_2$ (**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.
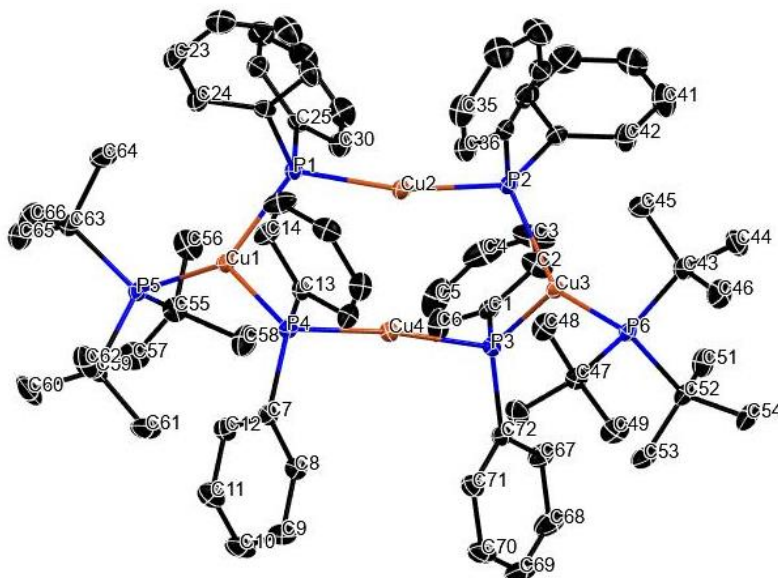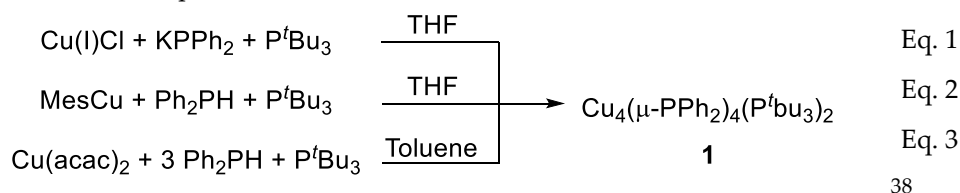
Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and two non-coordinated THF molecules of solvation are omitted for clarity. Full labeling scheme is shown in the supplemental information.

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, ^{1}H, ^{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.

$$Cu(I)Cl + KPPh_2 + P^tBu_3 \xrightarrow{\text{THF}} \qquad \text{Eq. 1}$$

$$MesCu + Ph_2PH + P^tBu_3 \xrightarrow{\text{THF}} Cu_4(\mu\text{-}PPh_2)_4(P^tbu_3)_2 \qquad \text{Eq. 2}$$

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

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$_4$P$_4$ ring that is capped by a P^{t}Bu$_3$ (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$_4$P$_4$ 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^{t}Bu$_3$ 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].
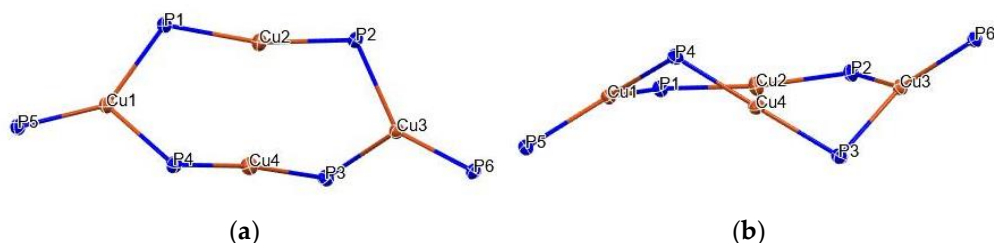

Figure 2. Cu$_4$P$_4$ ring that is capped by a P^{t}Bu$_3$ in compound **1**: (**a**) view from above the ring (**b**) view from the side.

Table 2. Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1** 61

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)

A complete table is provided in the supplemental information

62

The structure of **1** resembles $Cu_4(\mu\text{-}PPh_2)_4(PHPh_2)_4$ (**2**) described by Fenske [5]. How- 63
ever, in compound **2**, Cu1 and Cu3 adopt tetrahedral geometry resulting from the coordi- 64
nation of two Ph_2PH molecules per copper. The increased steric bulk of the P^tBu_3 versus 65
that of Ph_2PH provides a rationale for the observed three coordinate trigonal planar geom- 66
etry as only one P^tBu_3 can coordinate to copper. The closest Cu–Cu distance in **2** is 3.17(6) 67
Å which is larger than the corresponding distance in **1**. This may be a result of **2** having a 68
closer to linear structure than **1** with no deviations greater than 0.2 Å from the best fit plane 69
of the Cu_4P_4 ring. Compound **1** also resembles $Cu_4(\mu\text{-}PPh_2)_4(dppm)_2$ **(3)** (dppm = bis(di- 70
phenylphosphino)methane) [9] that has a Cu_4P_4 core but is not capped at Cu1 and Cu3 but 71
is instead supported by two dppm bridges between Cu1–Cu2 and Cu3–Cu4. Sulfide clus- 72
ter $(CuStBu)_4(Ph_3P)_2$ **(4)** [7] is also related, consisting of a Cu_4S_4 core that is capped by PPh_3 73
on Cu1 and Cu3. Similar to **1**, both **3** and **4** adopt a chair-like conformation with maximum 74
deviations of 1.52 and 1.55 Å respectively, from a plane of best fit consisting of the four 75
copper atoms. 76

Compound **1** displays evidence for dynamic behavior in solution by ^{1}H NMR and 77
^{31}P NMR spectroscopy. The *tert*-butyl substituents in the ^{1}H spectrum of **1** are split into 78
several overlapping multiplets centered around δ = 1.11 and 1.28. To confirm that the mul- 79
tiple alkyl peaks were features of **1** in solution, and not 80

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several overlapping multiplets centered around δ = 1.11 and 1.28. To confirm that the mul- 83
tiple alkyl peaks were features of **1** in solution, and not impurities, a variable temperature 84
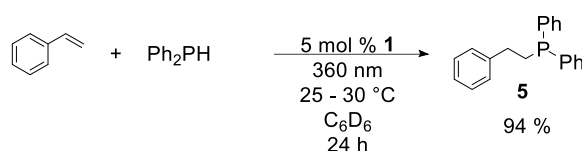(VT) NMR experiment was performed in which ^{1}H NMR spectra were taken at 25 °C, 35 °C, 85
and 45 °C. A coalescing of the alkyl peaks was observed upon increasing the temperature 86
from 25 °C to 45 °C. This behavior is consistent with hindered bond rotation, slow confor- 87
mational change or a derivative speciation of **1** in solution under rapid exchange on the 88
NMR time scale [19]. 89

Similarly, ^{31}P NMR spectra of **1** have features that show evidence of dynamic behav- 90
ior. A spectrum obtained at 25 °C initially appears to have two broad singlets, but closer 91
inspection by enlarging the peaks reveals multiplets at δ = -19.5, 60.1, and 62.3 that inte- 92
grate in a 1 : 0.15 : 1 ratio. This is unexpected because compound **1** has a 2 : 1 ratio of (μ- 93
PPh_2) : (P^tBu_3) atoms. A second VT NMR experiment was undertaken to confirm that these 94
features were a result of dynamic behavior. Upon heating a benzene-d_6 solution of **1** to 95
45 °C, the signal changes from the initial 1 : 0.15 : 1 ratio to 0.67 : 0.07 : 1. Several new 96

broad peaks also appear in the baseline of the spectrum obtained at 45 °C. Upon the solu-   97
tion returning to 25 °C the original features return in the same 1 : 0.15 : 1 ratio.   This result   98
suggests that the multiplets are features of a derivative speciation of **1** in solution under   99
rapid exchange on the NMR time scale. Furthermore, the 1 : 0.15 : 1 ratio was preserved   100
across three trials and repeated crystallizations.   101

Finally, a ^{31}P HMBC NMR spectrum of **1** confirmed the shift at δ = -19.53 is the signal   102
for the bridging phosphido as it is correlated only with aromatics. The signals at δ = 62.3   103
and 60.1 are correlated with multiple alkyl peaks which identifies them as belonging to   104
P^{t}Bu$_3$ ligand.   105

Compound **1** was found to be an active hydrophosphination catalyst. Treatment of   106
a benzene-d_6 solution of styrene, diphenylphosphine, and 6 mol% of **1** under 360 nm irra-   107
diation resulted in a 94% NMR conversion to the hydrophosphination product, diphe-   108
nyl(2-phenylethyl)-phosphine (**5**), after 24 h (eq. 4). We did not purse further hydrophos-   109
phination reactivity given this derivative compound showed no improvement in reactivity   110
compared to Cu(acac)$_2$ [18].   111

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$$\text{styrene} + \text{Ph}_2\text{PH} \xrightarrow[\substack{360 \text{ nm} \\ 25 - 30\ °C \\ C_6D_6 \\ 24\ h}]{5 \text{ mol \% } \mathbf{1}} \mathbf{5} \quad 94\ \%$$ Eq. 4

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3. Experimental details   116

3.1. General considerations   117

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-   118
free solvents using an M. Braun glovebox or standard Schlenk techniques. Tetrahydrofu-   119
ran was dried over sodium/benzophenone and vacuum transferred. Benzene-d_6 was pur-   120
chased and then degassed and dried over 3 and 4 Å molecular sieves. Diphenylphosphine   121
[20], copper(I)chloride [21], and mesitylcopper(I) [22], were synthesized according to liter-   122
ature procedures and stored under an inert atmosphere of N$_2$. Potassium diphe-   123
nylphosphine was made by a modified literature procedure [23] in which Ph$_2$PH was   124
deprotonated by KH in THF and then filtered through celite, and concentrated to dryness   125
by vacuum. All other reagents were acquired from commercial sources and dried by con-   126
ventional means, as necessary. ^{1}H, ^{13}C, ^{31}P and ^{31}P HMBC NMR spectra were recorded with   127
a Bruker AXR 500 MHz spectrometer. All 1-D ^{31}P NMR spectra were ^{1}H decoupled. Reso-   128
nances in ^{1}H NMR spectra are referenced to the residual solvent resonance (C$_6$D$_6$ = δ 7.16).   129
Reported ^{31}P NMR resonances are relative to external 85% H$_3$PO$_4$. Spectral data for diphe-   130
nyl(2-phenylethyl)-phosphine is consistent with literature reports [24].   131

3.2. Synthesis of Compound 1   132

Method A: In an N$_2$ filled glovebox, P(^{t}Bu)$_3$ (51 mg, 0.25 mmol), Cu(I)Cl (25 mg, 0.25 mmol)   133
and 5 mL of cold THF (stored at -30 °C and removed immediately before use) were stirred   134
in a scintillation vial. After 30 seconds, a KPPh$_2$ (56 mg, 0.25 mmol) solution in 5 mL of   135
cold THF was added dropwise resulting in a color change to yellow. The solution was   136

stirred for 30 min at ambient temperature, then concentrated to a yellow residue under 137
reduced pressure. The crude product was redissolved pentane and filtered through a bed 138
of Celite. The filtrate was immediately pipetted into a scintillation vial and placed in a 139
freezer at -30 °C. Crystals suitable for X-ray crystallography precipitated overnight. To 140
isolate the product for NMR the mother liquor was decanted from the precipitate, and the 141
precipitate was washed with 2 mL of cold pentane and dried in vacuo. Yield 57 mg (65%). 142
^{1}H 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 – 1.25 143
(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 144
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), 145
36.01 (s), 32.26 (s), 32.20 – 31.48 (m). 146

Method B: In an N_2 filled glovebox, P(^{t}Bu)$_3$ (166 mg, 0.824 mmol) and mesitylcopper(I) 147
(150 mg, 0.824 mmol) were dissolved in 2-3 mL of cold THF (-30 °C). Neat Ph_2PH (153 mg, 148
143 μl, 0.824 mmol) was added dropwise. The resulting yellow solution was stirred for 24 149
h. (Note: subsequent trials with less concentrated solutions monitored by ^{31}P NMR indi- 150
cate that full conversion is reached after 4 h). The solution was then layered with ~8 mL 151
of pentane and placed in a freezer at -30 °C. After decanting the mother liquor, 107 mg (37 152
% yield) of **2** was recovered upon washing the precipitate with cold pentane and drying. 153

Method C: In an N_2 filled glovebox, 31.5 mg Ph_2PH (29.5 μl, 0.170 mmol) was added drop- 155
wise at -30 °C to a scintillation vial containing a toluene solution of 15 mg (0.057 mmol) 156
Cu(acac)$_2$ and 11.5 mg (0.057 mmol) of P(^{t}Bu)$_3$. The solution allowed to warm to ambient 157
temperature and stirred for 24 h. Then the solvent was removed under reduced pressure, 158
the residue was taken up in pentane, filtered through a bed of Celite, and placed in a 159
freezer at -30 °C. The resultant precipitate was dissolved in a minimum amount of THF ~ 160
1 mL and layered with three mL of pentane and placed in the freezer again. The 10.6 mg 161
(53% yield) of solid was isolated by decanting the mother liquor, washing with cold pen- 162
tane, and drying. The ^{1}H and ^{31}P NMR spectra of the compound obtained by this method 163
matched methods A and B. 164

Catalytic experiment: In an N_2 filled dry box, 8 mg (.023 mmol, 6 mol %) of **1**, 70.7 mg (66 166
μl, 0.38 mmol) diphenylphosphine and 39.5 mg (43.5 μl, 0.38 mmol) of styrene was meas- 167
ured and mixed in 0.6 mL benzene-*d*$_6$. This solution was transferred to an NMR tube. Ini- 168
tial ^{1}H and ^{31}P NMR spectra were obtained before placing the tube in a photoreactor con- 169
taining a Rexim G23 UV-A (9W) lamp at ambient temperature. The temperature of the 360 170
nm photoreactor was measured to be 25–30 °C, depending on how long it had been in use. 171
No efforts to control the temperature between this range were undertaken. Periodic ^{1}H 172
and ^{31}P NMR spectra were collected. Conversions were determined by integration of ^{1}H 173
and ^{31}P NMR spectra to starting materials. 174

3.3 X-Ray structure determinations 175

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffracto-meter (Mo Kα (λ = 0.71073 Å)) at 150(2) K. A suitable yellow prismatic plate crystal of Cu$_4$(μ-PPh$_2$)$_4$(P^{t}Bu$_3$)$_2$, was mounted on a MiTeGen Micromount with Paratone-N cryopro-tectant 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 aniso-tropically. Hydrogen atoms on carbon were included in calculated positions and were re-fined using a riding model.

Crystal Data for C$_{72}$H$_{94}$Cu$_4$P$_6$, 2(C$_4$H$_8$O) (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 > 2σ(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 dif-fraction 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.

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Graphical abstract:
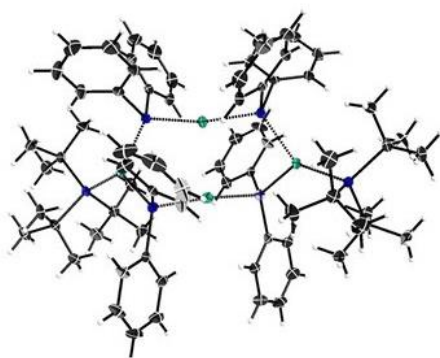
$Cu_4(\mu\text{-}PPh_2)_4(P^tBu_3)_2$

- X-ray structure
- Three synthetic methods
- Hydrophosphination catalyst