Research paper

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A Novel Tetramer Copper(I) Complex Containing Diallylphosphine Ligands: Synthesis, Characterization and Catalytic Application in A^3-Coupling (Aldehyde-Amine-Alkyne) Reactions

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KEYWORDS: A^3-coupling reactions; propargylamine; diallylphosphine ligands; tetramer cobre(I) complex.

ABSTRACT: A novel tetrameric copper(I) complex containing tert-butyldiallylphosphine ligands, $[CuCl\{^tBu\text{-}P(CH_2CH{=}CH_2)_2\}]_4$ (**2**), has been synthesized and characterized by structural and spectroscopic methods. X-ray diffraction analysis showed that **2** has a cubane-like solid structure of formula $[CuCl\{\ ^1(P)\text{-}^tBu\text{-}P(CH_2CH{=}CH_2)_2\}]_4$. In solution, a dynamic behavior

generated by the cubane ⇌ chair isomerization was detected by variable temperature NMR analysis. DFT calculations have been performed to explain the observed dynamic equilibrium in solution. The use of copper(I) complex **2** as catalyst for the synthesis of propargylamines via A^3-coupling reactions has been tested. Complex **2** is capable of promoting A^3-coupling reactions of both aromatic and aliphatic aldehydes with cyclic secondary amines and phenylacetylene. The reaction proceeds under mild condition and absence of solvent.

1. Introduction

Propargylamines are generally used in organic chemistry as precursors and versatile building blocks for the preparation of various nitrogen-containing heterocyclic compounds as well as key intermediates for the synthesis of biologically active pharmaceuticals and natural products [1]. Furthermore, some propargylamines have been used for the treatment of neuropsychiatric disorders such as Parkinson's and Alzheimer's disease [2]. Because of their importance, many synthetic methods have been developed [3]. However, the most direct and efficient method for the preparation of propargylamines is through transition-metal catalyzed three-component coupling of an aldehyde, an amine and a terminal alkyne, which is known as an A^3 coupling reaction [4]. In recent years, various homogeneous and heterogeneous catalysts have been employed in the synthesis of propargylamine *via* A^3-coupling reaction, based on transition metals such as Zr [8], Mn [9], Re [10], Fe [11], Ru [12], Co [13], Ir [14], Ni [15], Pd [16] Cu [17], Ag [18], Au [19], Zn [20], Cd [21] and Hg [22]. Among the different transition metals, copper have been widely studied because of its abundance, low cost, low toxicity and high reactivity.

It is well-known that phosphines are versatile ligands capable of exerting a subtle control on the metal center, which leads to metal catalysts with improved reactivity and stability [23].

However, there are few reports that describe the use of copper(I) catalysts bearing phosphines as ligand in A^3-coupling reactions [24]. We have recently reported a study concerning to hemilabile properties of diallylphosphine ligands [25]. Ligands displaying this behavior enable to generate active sites on the metal center and to stabilize reactive intermediates, which are features that have been shown to enhance both activity and selectivity in catalytic reactions [26]. Now, we feel motivated to explore the synthesis and catalytic potential of copper complexes with diallylphosphine. Thus, herein we wish to report the synthesis of a novel tetrameric copper(I) complex containing diallylphosphine ligands and its use as catalyst in the synthesis of propargylamine *via* A^3-coupling reaction.

2. Experimental

2.1. General Information

All reactions and manipulations were carried out under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. The elemental analysis was performed (C, H, N) on a model EA1108 Fisons elemental analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with either Bruker Avance-300, Avance-500 or Avance-600 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR chemical shifts are expressed in ppm relative to 85 % H_3PO_4. tert-butyldiallylphosphine was prepared by reported method [27]. $[CuCl(Ph_3P)]_4$ (**3**) and $[CuCl(^{i}Pr_3P)]_4$ (**4**) complexes were prepared following the reported procedure by Churchill [28]. CuCl complex and other chemicals were purchased from Sigma–Aldrich Co.

*2.2. Preparation of $[CuCl\{^{t}Bu\text{-}P(CH_2CH{=}CH_2)_2\}]_4$ (**2**)*

To a solution of CuCl (200 mg, 2.02 mmol) in CH_2Cl_2 (20 mL) was added a solution of the *tert*-butyldiallylphosphine (**1**) (343.4 mg, 2.02 mmol) in 10 mL of CH_2Cl_2. The solution was stirred for 24 h at RT. The solution was evaporated to dryness to give a white solid, which was washed with pentane (15 mL) and dried under vacuum. Yield: 80% (435 mg) ^{1}H NMR (500.03 MHz, $CDCl_3$, 25 °C): δ 1.17 (d, $^3J_{PH}$= 14.0 Hz, 36H, $CH^t_{3\ Bu}$), 2.36-2.51 (m, 16H, PCH_2), 5.05 (m, 16H, $=CH_2$), 6.0 (br. s, 8H, CH=). ^{13}C {^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ 27.3 (d, $^2J_{CP}$ = 5.7 Hz, 12C, $CH^t_{3\ Bu}$), 28.1 (d, J_{CP} = 14.1 Hz, 8C, PCH_2), 30.3 (d, 4C, J_{CP} = 17.2 Hz, PC^t_{Bu}), 117.2 (br. s, 8C, $=CH_2$), 132.9 (br. s, 8C, CH=). ^{31}P {^{1}H} NMR (202.41 MHz, $CDCl_3$, 25 °C): δ 3.4 (br. s). Anal. Calcd for $C_{40}H_{76}P_4Cu_4Cl_4$: C, 44.61; H, 7.11. Found: C, 44.25; H, 7.08.

*2.3. General Procedure for A^3-Coupling Catalyzed by [CuCl{^{t}Bu-P(CH$_2$CH=CH$_2$)$_2$}]$_4$(**2**)*

Under argon atmosphere, catalyst [CuCl{^{t}Bu-P($CH_2CH=CH_2$)$_2$}]$_4$ **2** (2.7 mg, 0.0025 mmol, 0.5 mol%), aldehyde (0.5 mmol), amine (0.55 mmol) and alkyne (0.75 mmol) were loaded in a screw-cap test tube equipped with a stirring bar. The mixture was stirred at 50 °C for 6 h and kept in the dark until completed the time of reaction. Then, the mixture was cooled, extracted with ether (3x5 mL) and dried over $MgSO_4$. The mixture was filtrated, concentrated (^{1}H-NMR spectroscopy showed quantitative conversion of aldehyde) and the residue was purified by flash chromatography on silica gel (eluent: hexane/EtOAc= 3:1 V/V). The corresponding propargylamines were obtained as a racemic mixture in form of light-yellow oil. Reported yields are the average of at least two independent runs.

*N-(1,3-Diphenyl-2-propynyl)piperidine (**4a**)*: Following the general procedure from 53 mg of benzaldehyde, 47 mg of piperidina and 77 mg of phenylacetylene was obtained *N*-(1,3-Diphenyl-2-propynyl)piperidina (**4a**) (128 mg, 93%). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25ºC): = 1.49 (m, 2H, $NCH_2CH_2CH_2$), 1.65 (m, 4H, NCH_2CH_2), 2.62 (br. s, 4H, NCH_2CH_2),4.85 (s, 1H, N-CH),

7.35-7.40 (m, 6H, CH_{Ar}), 7.57 (m, 2H, CH_{Ar}), 7.69 (m, 2H, CH_{Ar}). $^{13}C\{^1H\}$ NMR (150.91 MHz, $CDCl_3$, 25ºC): = 24.43 (s, 1C, $NCH_2CH_2CH_2$), 26.17 (s, 2C, $NCH_2CH_2CH_2$), 50.68 (s, 2C, NCH_2), 62.37 (s, 1C, N-CH), 86.07 (s, 1C, C•*C*-Ph), 87.81 (s, 1C, *C*•C-Ph), 123.33 (s, 1C, C_{Ar}), 127.40, 128.01, 128.23, 128.49, 131.77 (5 x s, 10C, CH_{Ar}), 138.59 (s, 1C, C_{Ar}).

*N-(1,3-Diphenyl-2-propynyl)pyrrolidine (**4b**)*: Following the general procedure from 53 mg of benzaldehyde, 39 mg of pyrrolidine and 77 mg of phenylacetylene was obtained *N*-(1,3-Diphenyl-2-propynyl)pyrrolidine (**4b**) (118 mg, 90%). ^1H NMR (600.13 MHz, $CDCl_3$, 25ºC): = 1.79 (m, 4H, NCH_2CH_2), 2.69 (br. s, 4H, NCH_2), 4.88 (s, 1H, N-CH), 7.23-7.36 (m, 6H, CH_{Ar}), 7.48 (m, 2H, CH_{Ar}), 7.60 (m, 2H, CH_{Ar}). $^{13}C\{^1H\}$ NMR (150.91 MHz, $CDCl_3$, 25ºC): = 23.47 (s, 2C, NCH_2CH_2), 50.23 (s, 2C, NCH_2), 59.09 (s, 1C, N-CH), 86.67 (s, 1C, C•*C*-Ph), 86.89 (s, 1C, *C*•C-Ph), 123.21 (s, 1C, C_{Ar}), 128.04, 128.22, 128.25, 128.40, 129.16, 131.75 (6 x s, 10C, CH_{Ar}), 132.46 (s, 1C, C_{Ar}).

*N-(1,3-Diphenyl-2-propynyl)morpholine (**4c**)*: Following the general procedure from 53 mg of benzaldehyde, 48 mg of morpholine and 77 mg of phenylacetylene was obtained *N*-(1,3-Diphenyl-2-propynyl)morpholine (**4c**) (114 mg, 83%). ^1H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 2.65 (m, 4H, NCH_2CH_2), 3.75 (br. s, 4H, NCH_2), 4.81 (s, 1H, N-CH), 7.31-7.38 (m, 6H, CH_{Ar}), 7.54 (m, 2H, CH_{Ar}), 7.65 (m, 2H, CH_{Ar}). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25ºC): = 49.83 (s, 1C, N*C*H), 61.97 (s, 2C, NCH_2CH_2), 67.08 (s, 2C, CH_2CH_2O), 85.01 (s, 1C, C•*C*-Ph), 88.45 (s, 1C, *C*•C-Ph), 122.92 (s, 1C, C_{Ar}), 127.69, 128.15, 128.23, 128.50, 131.73 (5 x s, 10C, CH_{Ar}), 137.76 (s, 1C, C_{Ar}).

*N-(1,3-Diphenyl-2-propynyl)tetramethylpiperidine (**4d**)*: Following the general procedure from 53 mg of benzaldehyde, 77 mg of 2,2,6,6-tetramethylpiperidine and 77 mg of phenylacetylene. The analysis of crude mixture by ^1H-NMR spectroscopy did not reveal the formation of desired product.

*N-(1,3-Diphenyl-2-propynyl)di-isopropylamine (**4e**)*: Following the general procedure from 53 mg of benzaldehyde, 56 mg of di-isopropylamine and 77 mg of phenylacetylene was obtained *N*-(1,3-Diphenyl-2-propynyl)di-isopropylamine (**4e**) (22 mg, 15%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.05 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, CH_{3NiPr}), 1.30 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH_{3Nipr}), 3.20 (sept, $^{3}J_{HH}$ = 6.7 Hz, 2H, CH_{Nipr}), 5.02 (s, 1H, N-CH), 7.30-7.33 (m, 5H, CH_{Ar}), 7.46-7.49 (m, 3H, CH_{Ar}), 7.72-7.75 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 20.69 (s, 2C, CH_{3NiPr}), 23.84 (s, 2C, CH_{3NiPr}), 46.64 (s, 2C, CH_{NiPr}), 50.50 (s, 1C, N-CH), 85.90 (s, 1C, C•*C*-Ph), 91.96 (s, 1C, *C*•C-Ph), 123.94 (s, 1C, C_{Ar}), 126.76, 127.81, 127.88, 128.30, 131.33 (5 x s, 10C, CH_{Ar}), 142.19 (s, 1C, C_{Ar}).

*N-(1,3-Diphenyl-2-propynyl)N-methylaniline (**4f**)*: Following the general procedure from 53 mg of benzaldehyde, 59 mg of methylaniline and 77 mg of phenylacetylene was obtained *N*-(1,3-Diphenyl-2-propynyl)*N*-methylaniline (**4f**) (49 mg, 33%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 2.81 (s, 3H, NCH_3), 6.30 (s, 1H, N-CH), 6.86-6.91 (m, 1H, CH_{Ar}), 7.04 (m, 1H, CH_{Ar}), 7.07 (m, 1H, CH_{Ar}), 7.30-7.44 (m, 8H, CH_{Ar}), 7.48-7.51 (m, 2H, CH_{Ar}), 7.67 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 33.90 (s, 1C, N*C*H_3), 57.13 (s, 1C, N-CH), 85.84 (s, 1C, C•*C*-Ph), 87.08 (s, 1C, *C*•C-Ph), 115.39, 118.81 (2 x s, 3C, CH_{Ar}),123.01 (s, 1C, C_{Ar}),127.67, 127.80, 128.33, 128.50, 129.24, 131.90 (6 x s, 12C, CH_{Ar}), 138.64 (s, 1C, C_{Ar}), 150.37 (s, 1C, C_{Ar}).

*1-(1-propyl-3-phenyl-2-propynyl)piperidine (**4g**)*: Following the general procedure from 36 mg of butyraldehyde, 47 mg of piperidine and 77 mg of phenylacetylene was obtained 1-(1-propyl-3-phenyl-2-propynyl)piperidine (**4g**) (119 mg, 99%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 0.95 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, C*H*$_3$-CH_2), 1.44-1.79 (m, 10H, $NCH_2CH_2CH_2$, CH_3-CH_2CH_2), 2.49, 2.66 (2 x m, 4H, NCH_2), 3.48 (dd, $^{3}J_{HH}$ = 5.4 Hz, $^{2}J_{HH}$ = 9.2 Hz, 1H, N-CH), 7.27 (m, 3H, C*H*$_{Ar}$), 7.41 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (150.91 MHz, $CDCl_3$, 25ºC): = 13.94 (s, 1C, *C*H_3-CH_2), 20.18 (s,

1C, CH_3-*C*H_2), 24.64 (s, 2C, NH_2CH_2*C*H_2), 26.26 (s, 2C, NCH_2*C*H_2CH_2), 35.65 (s, 1C, CH_2-*C*H_2), 50.62 (s, 2C, NCH_2), 58.36 (s, 1C, NCH), 85.67 (s, 1C, C•*C*-Ph), 88.19 (s, 1C, *C*•C-Ph), 123.66 (s, 1C, C_{Ar}), 127.74, 128.20, 131.79 (3 x s, 3C, CH_{Ar}).

*1-(1-propyl-3-phenyl-2-propynyl)pyrrolidine (**4h**)*: Following the general procedure from 36 mg of butyraldehyde, 39 mg of pyrrolidine and 77 mg of phenylacetylene was obtained 1-(1-propyl-3-phenyl-2-propynyl)pyrrolidine (**4h**) (112 mg, 99%). ^{1}H NMR (600.13 MHz, $CDCl_3$, 25ºC): = 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H, C*H*$_3$-CH_2), 1.48 (sept, $^3J_{HH}$ = 7.2 Hz, 1H, CH_3-C*H*$_2$), 1.60 (sept, $^3J_{HH}$ = 7.1 Hz, 1H, CH_3-C*H*$_2$), 1.70 (dd, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2-C*H*$_2$), 1.78 (br. s, 4H, NCH_2C*H*$_2$), 2.68, 2.75 (2 x br. s, 4H, NCH_2), 3.67 (t, $^3J_{HH}$ = 7.4 Hz, 1H, N-CH), 7.25 (m, 3H, CH_{Ar}), 7.40 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (150.91 MHz, $CDCl_3$, 25ºC): = 13.89 (s, 1C, *C*H_3-CH_2), 19.95 (s, 1C, CH_3-*C*H_2), 23.49 (s, 2C, NCH_2*C*H_2), 37.18 (s, 1C, CH_2-*C*H_2), 49.69 (s, 2C, N*C*H_2), 50.84 (s, 1C, N-CH), 85.28 (s, 1C, C•C-Ph), 88.24 (s, 1C, *C*•C-Ph), 123.48 (s, 1C, C_{Ar}), 127.28, 128.18, 131.18 (3 x s, 3C, CH_{Ar}).

*1-(1-propyl-3-phenyl-2-propynyl)di-isopropylamine (**4i**)*: Following the general procedure from 36 mg of butyraldehyde, 77 mg of di-isopropylamine and 77 mg of phenylacetylene was obtained 1-(1-propyl-3-phenyl-2-propynyl)piperidine (**4i**) (39 mg, 30%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3H, C*H*$_3$-CH_2), 1.02 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH_{3NiPr}), 1.18 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH_{3Nipr}), 1.41-1.64 (m, 4H, CH_2-CH_2), 3.20 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, CH_{Nipr}), 3.60 (t, $^3J_{HH}$ = 7.4 Hz, 1H, N-CH), 7.25 (m, 3H, CH_{Ar}), 7.35 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 13.97 (s, 1C, *C*H_3-CH_2), 19.92 (s, 1C, CH_3-*C*H_2), 20.47, 24.16 (2 x s, 4C, CH_{3NiPr}), 37.18 (s, 1C, CH_2-*C*H_2), 45.86, (s, 1C, CH_{Nipr}), 46.42 (s, 1C, N-CH), 82.42 (s, 1C, C•*C*-Ph), 94.34 (s, 1C, *C*•C-Ph), 124.31 (s, 1C, C_{Ar}), 127.36, 128.17, 131.26 (3 x s, 3C, CH_{Ar}).

*N-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]pyrrolidine (**4j**)*: Following the general procedure from 68 mg of *p*-methoxybenzaldehyde, 39 mg of pyrrolidine and 77 mg of

phenylacetylene was obtained *N*-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]pyrrolidine (**4j**) (143 mg, 98%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.78 (m, 4H, NCH_2CH_2), 2.67 (m, 4H, NCH_2), 3.79 (s, 1H, OCH_3), 4.82 (s, 1H, N-CH), 6.87, 6.90 (2x br. s, 2H, CH_{Ar}), 7.29 (m, 3H, CH_{Ar}), 7.46-7.52 (m, 4H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 23.44 (s, 2C, NCH_2CH_2), 50.19 (s, 2C, NCH_2), 55.22 (s, 1C, N-CH), 58.48 (s, 1C, OCH_3), 86.65 (s, 1C, C•*C*-Ph), 87.00 (s, 1C, *C*•C-Ph), 113.55 (s, 2C, CH_{Ar}), 123.25 (s, 1C, C_{Ar}), 127.98, 128.19, 129.33, 131.71 (4 x s, 7C, CH_{Ar}), 132,44 (s, 1C, C_{Ar}), 159.02 (s, 1C, C_{Ar}).

*N-[1-(4-Bromophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4k**)*: Following the general procedure from 93 mg of *p*-bromobenzaldehyde, 39 mg of pyrrolidine and 77 mg of phenylacetylene was obtained *N*-[1-(4-Bromophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4m**) (136 mg, 80%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.84 (br. s, 4H, NCH_2CH_2), 2.72 (br. s, 4H, NCH_2), 4.92 (s, 1H, N-CH), 7.35 (m, 4H, CH_{Ar}), 7.53 (m, 5H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 23.52 (s, 2C, NCH_2CH_2), 50.07 (s, 2C, NCH_2), 58.37 (s, 1C, N*C*H), 85.82 (s, 1C, C•*C*-Ph), 87.40 (s, 1C, *C*•C-Ph), 121.47 (s, 1C, C_{Ar}), 122.92 (s, 1C, C_{Ar}), 128.23, 128.27, 128.39, 129.15, 129.94, 131.31, 131.76 (7 x s, 9C, CH_{Ar}), 138.51 (s, 1C, C_{Ar}).

*N-[1-(3-Chlorophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4l**)*: Following the general procedure from 70 mg of *m*-chlorobenzaldehyde, 39 mg of pyrrolidine and 77 mg of phenylacetylene was obtained *N*-[1-(3-Chlorophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4l**) (123 mg, 83%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.85 (br. s, 4H, NCH_2CH_2), 2.74 (m, 4H, NCH_2), 4.94 (s, 1H, N-CH), 7.35 (m, 5H, CH_{Ar}), 7.54 (m, 3H, CH_{Ar}), 7.68 (m, 1H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 23.61 (s, 2C, NCH_2CH_2), 50.16 (s, 2C, NCH_2), 58.53 (s, 1C, N-CH), 85.72 (s, 1C, C•*C*-Ph), 87.56 (s, 1C, *C*•C-Ph), 122.98 (s, 1C, C_{Ar}), 126.45, 127.80, 128.32, 128.35, 128.39, 129.53, 131.86 (7 x s, 9C, CH_{Ar}), 134.22 (s, 1C, C_{Ar}), 141.66 (s, 1C, C_{Ar}).

*N-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4m**)*: Following the general procedure from 70 mg of *p*-chlorobenzaldehyde, 39 mg of pyrrolidine and 77 mg of phenylacetylene was obtained *N*-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4m**) (133 mg, 90%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.80 (br. s, 4H, NCH_2CH_2), 2.67 (m, 4H, NCH_2), 4.87 (s, 1H, N-CH), 7.32 (m, 5H, CH_{Ar}), 7.50 (m, 4H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 23.61 (s, 2C, NCH_2CH_2), 50.17 (s, 2C, NCH_2), 58.42 (s, 1C, N-CH), 86.11 (s, 1C, C•*C*-Ph), 87.41 (s, 1C, *C*•C-Ph), 123.07 (s, 1C, C_{Ar}), 128.28, 128.36, 128.43, 129.63, 131.84 (5 x s, 9C, CH_{Ar}), 133.34 (s, 1C, C_{Ar}), 138.23 (s, 1C, C_{Ar}).

*N-[1-(2-Chlorophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4n**)*: Following the general procedure from 70 mg of *o*-chlorobenzaldehyde, 39 mg of pyrrolidine and 77 mg of phenylacetylene was obtained *N*-[1-(2-Chlorophenyl)-3-phenyl-2-propynyl]pyrrolidine (**4n**); (59 mg, 40%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.78 (br. s, 4H, NCH_2CH_2), 2.72 (m, 4H, NCH_2), 5.29 (s, 1H, N-CH), 7.30 (m, 5H, CH_{Ar}), 7.45 (m, 3H, CH_{Ar}), 7.77 (m, 1H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 23.54 (s, 2C, NCH_2CH_2), 50.42 (s, 2C, NCH_2), 55.65 (s, 1C, N-CH), 86.50 (s, 1C, C•*C*-Ph), 86.56 (s, 1C, *C*•C-Ph), 123.12 (s, 1C, C_{Ar}), 126.71, 128.21, 128.30, 128.85, 129.69, 130.17, 131.83 (7 x s, 9C, CH_{Ar}), 133.86 (s, 1C, C_{Ar}), 137.26 (s, 1C, C_{Ar}).

*N-(1,3-Diphenyl-2-propynyl)N-butylamine (**4o**)*: Following the general procedure from 53 mg of benzaldehyde, 40 mg of N-butylamine and 77 mg of phenylacetylene was obtained *N*-(1,3-Diphenyl-2-propynyl)*N*-butylamine (**4o**) (33 mg, 25%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 0.86 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3-CH_2), 1.38 (m, 2H, CH_3-CH_2), 1.53 (m, 2H, N-CH_2-CH_2), 1.82 (br, 1H, N-H), 2.72 (m, 1H, N-CH_2), 2.82 (m, 1H, N-CH_2), 4.79 (s, 1H, N-CH), 6.86-6.91 (m, 1H, CH_{Ar}), 7.04 (m, 1H, CH_{Ar}), 7.07 (m, 1H, CH_{Ar}), 7.30-7.44 (m, 8H, CH_{Ar}), 7.24-7.59 (m, 10H, CH_{Ar}) ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 13.96 (s, 1C, CH_3-CH_2), 20.49 (s, 1C, CH_3-CH_2), 32.07 (s, 1C, N-CH_2-CH_2), 47.01 (s, 1H, N-CH_2), 54.71 (s, 1C, N-CH), 85.33 (s, 1C, C•*C*-

Ph), 89.51 (s, 1C, *C*•C-Ph), 123.22 (s, 1C, C_{Ar}), 127.59, 127.69, 128.08, 128.22, 128.48, 131.69 (6 x s, 10C, CH_{Ar}), 140.54 (s, 1C, C_{Ar}).

*1-(1-phenylhept-2-yn-1-yl)pyrrolidine (**4p**)*: Following the general procedure from 53 mg of benzaldehyde, 39 mg of pyrrolidine and 62 mg of 1-hexyne was obtained 1-(1-phenylhept-2-yn-1-yl)pyrrolidine (**4p**) (62 mg, 51%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 0.91 (t, $^{3}J_{HH}$= 7.2 Hz, 3H, CH_3); 1.50 (m, 4H, $CH_2CH_2CH_3$), 1.76 (m, 4H, NCH_2CH_2), 2.27 (m, 2H, C•C-CH_2), 2.60 (m, 4H, NCH_2), 4.60 (t, J_{HH}= 2.0 Hz, 1H, N-CH), 7.24-7.31 (m, 3H, CH_{Ar}), 7.50 (m, 1H, CH_{Ar}), 7.53 (m, 1H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 13.57 (s, 1C, CH_3), 18.44 (s, 1C, C•C-CH_2), 21.96 (s, 1C, CH_2CH_3), 23.40 (s, 2C, NCH_2CH_2), 31.06 (s, 1C, C•C-CH_2CH_2), 50.11 (s, 2C, NCH_2), 58.74 (s, 1C, N-CH), 76.81 (s, 1C, C•C-CH_2), 87.03 (s, 1C, C•C-CH_2), 127.31, 128.05, 128.22 (3 x s, 5C, CH_{Ar}), 139.96 (s, 1C, C_{Ar}).

*7-phenyl-7-(pyrrolidin-1-yl)hept-5-ynenitrile (**4q**)*: Following the general procedure from 53 mg of benzaldehyde, 39 mg of pyrrolidine and 70 mg of 5-hexynenitrile was obtained 7-phenyl-7-(pyrrolidin-1-yl)hept-5-ynenitrile (**4q**) (91 mg, 72%). ^{1}H NMR (300.20 MHz, $CDCl_3$, 25ºC): = 1.73 (m, 4H, NCH_2CH_2), 1.85 (m, 2H, N•C-CH_2), 2.44 (m, 4H, C•C-CH_2CH_2), 2.54 (m, 4H, NCH_2), 4.54 (t, J_{HH}= 2.0 Hz, 1H, N-CH), 7.24-7.33 (m, 3H, CH_{Ar}), 7.45 (m, 1H, CH_{Ar}), 7.48 (m, 1H, CH_{Ar}). ^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$, 25ºC): = 18.00 (s, 1C, C•C-CH_2), 17.76 (s, 1C, C•C-CH_2CH_2), 23.20 (s, 2C, NCH_2CH_2), 24.62(s, 1C, N•C-CH_2), 50.21 (s, 2C, NCH_2), 58.62 (s, 1C, N-CH), 79.18 (s, 1C, C•C-CH_2), 83.63 (s, 1C, C•C-CH_2), 119.00 (s, 1C, N•C-CH_2), 127.36, 127.89, 128.04 (3 x s, 5C, CH_{Ar}), 139.47 (s, 1C, C_{Ar}).

2.4. X-Ray Crystallography

One single crystal was mounted on a glass fiber and the crystallographic data were collected at 298(2) K on a Rigaku diffractometer, AFC-7, Mercury CCD-detector, Mo-K (= 0.71073 Å)

radiation. Additionally, data collection using and scan was performed. Non-hydrogen atoms are located from the difference *E*-maps by means of starting models for structure refinement were found using direct methods with *SHELXS* program [29] (*SHELXL-NT* suite software [30]), and the structural data were refined by full-matrix least-squares methods on F^2 using the *SHELXL* program [29] (*SHELXL-NT* suite software) [31]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The H atoms on the C atoms were included in calculated positions. The H atoms on water molecules can be found from the weak residual electron peaks. For distances and angles bonds and coordination sphere analysis was done with the *PLATON* package of crystallographic software [32]. CCDC 1453471 for compound **2**, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic Parameters for 2

Crystal data	
Chemical formula	$C_{40}H_{76}Cl_4Cu_4P_4$
M_r	1076.85
Crystal system, space group	Tetragonal, *I-4* (No. 82)
Temperature (K)	295
a, *c* (Å)	14.130 (6), 13.268 (5)
V (Å^3)	2649 (19)
Z	2
Radiation type	Mo *K* , λ = 0.71070 Å
μ (mm^{-1})	1.93
Crystal size (mm)	0.17 × 0.15 × 0.10
Data collection	
Diffractometer	Rigaku AFC7S Mercury diffractometer
Absorption correction	Multi-scan methods
T_{min}, T_{max}	0.478, 0.521
No. of measured, independent and observed [I > 2 (I)] reflections	7160, 2540, 2299
R_{int}	0.025
(sin /)$_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\ (F^2)]$, $wR(F^2)$, *S*	0.036, 0.082, 1.11
No. of reflections	2540
No. of parameters	1118
H-atom treatment	H-atom parameters constrained
$_{max}$, $_{min}$ (e Å^{-3})	0.21, –0.29
Absolute structure	Flack parameter [33]
Absolute structure parameter	-0.003 (17)

2.5. Theoretical calculations.

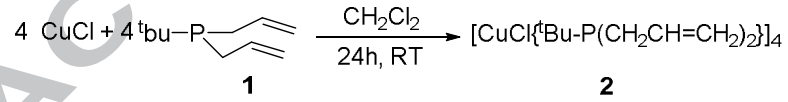
Structures were optimized using DMol[3] [34]. This DFT based program permits determination of the relative stability of all studied species based on their electronic structure. The calculations were performed using the Kohn–Sham Hamiltonian with the Perdew–Wang 1991 gradient correction [35] and the double-zeta plus (DNP) numerical basic set [34], which provides good accuracy at a relatively low computational cost. The All Electron core treatment was used for all the atoms. Frequency calculations of the structures showed that all frequencies were positive indicating that all structures are real minima.

3. Results and discussion

*3.1. Synthesis and characterization of [CuCl{^{t}Bu-P($CH_2CH=CH_2$)$_2$}]$_4$ (**2**)*

The reaction 1:1 of CuCl and tert-butyldiallylphosphine (**1**), in dichloromethane, resulted in the formation of tetramer copper(I) complex [CuCl{^{t}Bu-P($CH_2CH=CH_2$)$_2$}]$_4$ (**2**), which was isolated as an off-white crystalline powder in 80% yield (Scheme 1).

Scheme 1. Synthesis of copper(I) complex [CuCl{^{t}Bu-P($CH_2CH=CH_2$)$_2$}]$_4$ (**2**)



$^{31}P\{^1H\}$ NMR spectrum at RT for **2** showed a broad signal slightly shifted to downfield with respect to the free ligand [25] (Table 2). Meanwhile, ^1H and $^{13}C\{^1H\}$ NMR spectra at RT reveal the $^1(P)$ coordination mode of the diallylphosphine ligand, as indicated by broad resonances for olefin protons and carbons of the allyl groups, which exhibit similar values to those observed for

free ligand [25, 27c] (Table 2). Moreover, elemental analysis for **2** revealed a stoichiometric ratio Cu/R_3P 1:1.

Table 2. Spectral data for **2**[a]

Compounds	δ ^{31}P{^{1}H}	δ ^{1}H (=CH)	δ ^{1}H (=CH_2)	δ ^{13}C{^{1}H} (=CH)	δ ^{13}C{^{1}H} (=CH_2)
1	-1.9	5.7	4.9	135.3	115.8
2	3.4	6.0	5.05	132.9	117.2

[a] Taken in $CDCl_3$ at RT.

Copper(I) complex **2** was successfully isolated from concentrated pentane solution at RT as white crystals, and the molecular structure was confirmed by X-ray diffraction analysis (Figure 1). Complex **2** has a tetrameric structure, which crystallizes in tetragonal space groups I-4 (No. 82) with asymmetric units containing [CuCl{ ^{1}(*P*)-^{t}Bu-P($CH_2CH{=}CH_2$)$_2$}]$_4$.

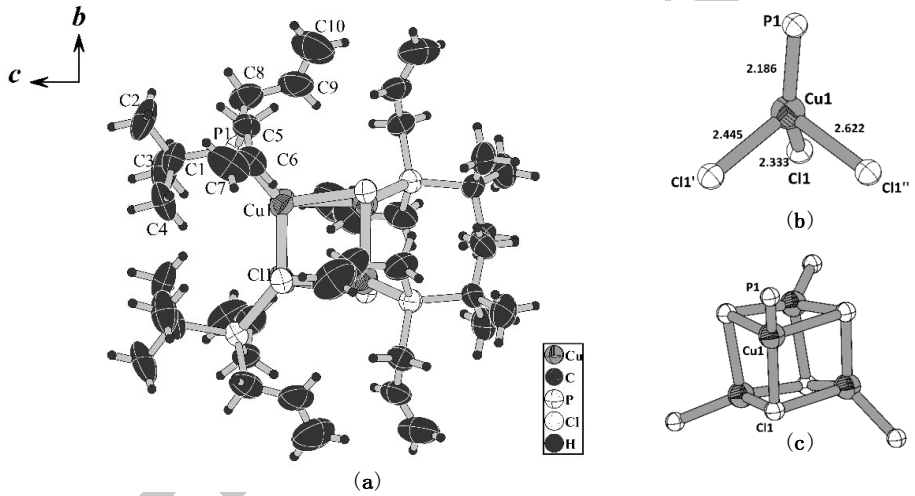


Figure 1. (**a**) Molecular structure of complex **2**, with selected atom labeling scheme and ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): Cu1—P1 2.186(1), Cu1—Cl1^i 2.333(1), Cu1—Cl1^{ii} 2.622(2), Cu1—Cl1^{iii} 2.445(1); P1—Cu1—Cl1^i 133.46(4), P1—Cu1—Cl1^{ii} 105.37(4), P1—Cu1—Cl1^{iii} 119.71(4), Cl1^i—Cu1—Cl1^{ii} 98.92(3), Cl1^i—Cu1—Cl1^{iii} 98.50(3), Cl1^{ii}—Cu1—Cl1^{iii} 91.13(3). (**b**) Coordination sphere surrounded of Cu1 ion. (**c**) The "cubane-like" framework [CuCl{ ^{1}(*P*)-^{t}Bu-P($CH_2CH{=}CH_2$)$_2$}]$_4$.

Complex **2** has one crystallographically independent Cu(I) ion, surrounded by one phosphorus atom (Cu1—P1 bond length 2.186 (1) Å) and three chlorine ligands (Cu1—Cl1, Cu1—Cl1^i, and Cu1—Cl1^{ii} bond length 2.333 (1) Å, 2.622 (2) Å, and 2.445 (1) Å, respectively). This environment describes a coordination sphere of a distorted tetrahedral for Cu1, as is shown in the

Figure 2b. The bond angle values range from 91.13° to 98.92° for Cl—Cu—Cl and from 105.37° to 133.46° for P—Cu—Cl. In addition, each chlorine ion joins another Cu1 ion to form an distorted "cubane-like" structure, as is shown in Figure 2c. The deformation of the Cu_4Cl_4 core is evidenced by bond angles values Cl—Cu—Cl (ranging from 91.13° to 98.92°) and Cu—Cl—Cu (ranging from 81.26° to 87.64°), which describe well the deviation from ideal cubane-like structures. This cubane-like structure is in agreement with stoichiometric ratio Cu/L 1:1 and confirms the monodentate coordination mode of tert-butyldiallylphosphine in **2**. In addition, cubane-like solid structures are well-known for phosphine copper(I) complexes. In fact, this motif is present in 11 structures reported on the CSD data base [36]. A comparative analysis indicates that bond distances and angles found for complex **2** are consistent with those in similar reported structures.

Because of width of the signal in $^{31}P\{^1H\}$ NMR spectrum at RT, NMR analysis at variable temperature was performed (Figure 2). This spectroscopic analysis revealed the existence of a dynamic equilibrium in solution between two copper(I) species (labeled as **2'** and **2''**). In $^{31}P\{^1H\}$ NMR spectra at variable temperature, the single broad signal around 3.4 ppm becomes into two signals at 4.6 ppm (for **2'**) and - 3.2 ppm (for **2''**) by decreasing the temperature from 35°C to -90°C, whereas it remain unchanged by increasing from 25 °C to 75°C (Figure 2). Meanwhile, ^1H NMR spectrum at -90 °C (Figure S7 in supporting information) show the signals corresponding to allyl protons for the two copper(I) species [6.04 for CH=; 4.94 ($^3J_{HH}$ = 9.3 Hz) and 5.01 ($^3J_{HH}$ = 16.7 Hz) for $=CH_2$] for **2''** and [5.8 for CH=; 5.17 and 4.41 ($^3J_{HH}$ = 16.7 Hz) for $=CH_2$] for **2'**.

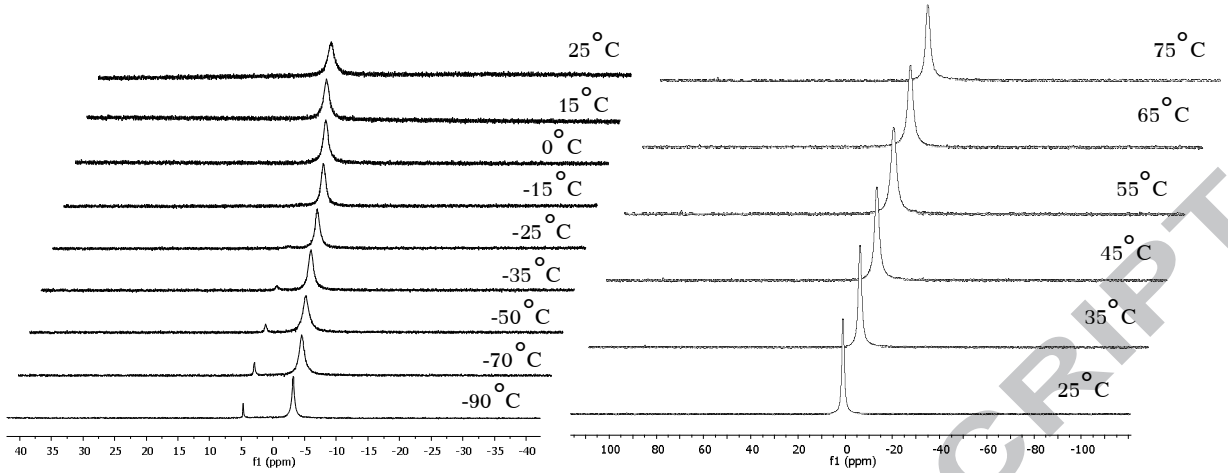


Figure 2. $^{31}P\{^{1}H\}$ NMR spectra at variable temperature for **2**: from -90°C to 25°C in CD_2Cl_2 (left) and from 25°C to 75°C in toluene-d_8 (right).

As we have mentioned above, cubane-like structure has been found to be the most common for tetrameric phosphine copper(I) halides, however, open chair-like (or step) structure has been also observed in several cases [28, 37]. Indeed, it has been established that the cube-like structure is destabilized relative to the chair structure when large halogen atoms are accompanied by bulky phosphine on the metal atom, thereby $[Ph_3PCuBr]_4$ and $[Ph_3PCuI]_4$ were isolated as chair-like structures in solid state while $[Ph_3PCuCl]_4$ as a cubane-like structure. In addition, Teo and Calabrese [38] have found that $[Ph_3PAgI]_4$ is capable of existing in both a highly distorted cubane-like configuration and a chair-like structure in solid state. These authors have analyzed steric interaction in $(R_3Y)_4M_4X_4$ (Y= P, As; M= Cu, Ag; X= Cl, Br, I) tetramers and concluded: "As the steric hindrance among the ligands increases, the following stereochemical variation inevitably occurs symmetrical cubane • distorted cubane • (cubane $\rightleftharpoons$ chair isomerization) • chair ". Therefore, observed dynamic equilibrium in solution for **2** can be ascribable to the cubane $\rightleftharpoons$ chair isomerization as consequence of the low stability of the cube-like structure caused by the strain of the Cu_4Cl_4 core for steric reasons. In order to deep on this hypothesis we have performed DFT calculations. Theoretical calculations indicates that the experimentally isolated tetrameric structure **2''** is destabilized relative to the chair-like structure

2' by barely ca. 0.73 Kcal/mol (Figure 3). This result confirms that dynamic equilibrium is generated by the isomerization of tetramer $[CuCl\{ {}^{1}(P)\text{-}{}^{t}Bu\text{-}P(CH_2CH{=}CH_2)_2\}]_4$ to give both the cubane and the chair forms in solution.

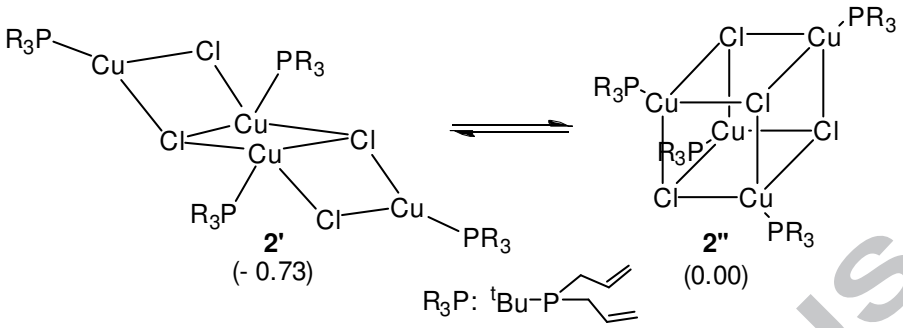


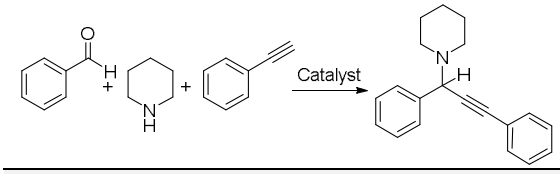
Figure 3. Relative energies (kcal/mol) calculated for **2'** and **2''** using Dmol[3] are given in parentheses.

3.2. Catalytic Studies

We have examined the catalytic activity of copper(I) complex **2** in the A^3-coupling reaction of aldehyde, amine and alkyne for the preparation of propargylamines. In order to find optimized reaction conditions, the coupling of benzaldehyde, piperidine and phenylacetylene was chosen as model reaction in molar ratio 1:1.1:1.5 respectively. The results are summarized in Table 2. The reaction was initially carried out under solvent free conditions at 25°C and 50°C. Almost total conversion (96%) into desired product was achieved at 50°C within 6 hour using 0.5 mol% of **2** (Table 3, entries 8 and 9). When catalyst loading was decreased to 0.25 and 0.125 mol%, the conversion was significantly lowered (Table 3. entries 8, 10 and 11). Meanwhile, solvents such as toluene, petroleum ether, $CHCl_3$, CH_3OH, THF, CH_3CN and water gave conversion lower than that obtained under solvent free conditions (Table 3, entries 1-8). Thus, using **2** (0.5 mol%) at 50°C under solvent-free conditions (Table 3, entry 8) was selected as the optimum conditions for the A^3-coupling reaction of aldehyde, amine and alkyne.

Under the above optimized conditions, the model A^3-coupling reaction was carried out using analogous copper(I) complexes containing homofunctional phosphine $[CuCl(Ph_3P)]_4$ (**3**) and $[CuCl(^iPr_3P)]_4$ (**4**) as catalyst (Table 2, entries 8, 12 and 13). The results indicate that complex **2** shows higher catalytic activity than **3** and **4** (Table 3, entries 8, 12 and 13), which suggests that tert-butyldiallylphosphine ligand might have a notable effect on the reactivity of copper(I) chloro complexes involved in the A^3-coupling reaction. However, to date we have not found any evidence that correlates the best catalytic performance of complex **2** with the hemilabile behavior of the ligand tert-butyldiallylphosphine.

Table 3. Optimization studies [a]



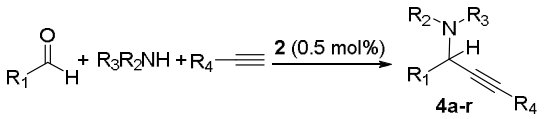
Entry	Catalyst	Solvent	[Cu] (mol%)	Temperature (°C)	Time (h)	Conversion (%)[b]
1	**2**	Ph-CH_3	0.5	50	6	48
2	**2**	Petroleum ether	0.5	50	6	69
3	**2**	$CHCl_3$	0.5	50	6	67
4	**2**	CH_3OH	0.5	50	6	70
5	**2**	THF	0.5	50	6	59
6	**2**	CH_3CN	0.5	50	6	73
7	**2**	water	0.5	50	6	51
8	**2**	neat	0.5	50	6	96
9	**2**	neat	0.5	25	24	49
10	**2**	neat	0.25	50	6	74
11	**2**	neat	0.125	50	6	51
12	$[CuCl(Ph_3P)]_4$ (**3**)	neat	0.5	50	6	70
13	$[CuCl(^iPr_3P)]_4$ (**4**)	neat	0.5	50	6	71

[a] All the reactions were carried out by using benzaldehyde (0.5 mmol), piperidine, (0.55 mmol) and phenylacetylene (0.75 mmol) in various solvent (0.5 mL). [b] Conversions were determined by ^{1}H-NMR spectroscopy of the crude reaction and are average of at least two independent runs.

In order to examine the scope of the reaction, we extended our investigation to different combinations of aldehydes, amines and alkynes as depicted in Table 4. Initially, we studied the

reactivity of aromatic and aliphatic aldehydes with cyclic secondary amines and phenylacetylene under the optimized reaction conditions (Table 4, entries 1-3, 7 and 8). Coupling of aromatic benzaldehyde and aliphatic butyraldehyde using piperidine and pyrrolidine led to corresponding propargylamines **4a**-**b** and **4g**-**h** in excellent yields. For a cyclic amine less nucleophilic as morpholine, the corresponding propargylamine (**4c**) was obtained in good yield but at longer reaction time than piperidine and pyrrolidine (Table 4, entry 3). It is interesting to note that for the bulky 2,2,6,6-tetramethylpiperidine the expected reaction product was not obtained and starting material remained intact (Table 4, entry 4).

Table 4. A^3-coupling reactions catalyzed by [CuCl{^{t}Bu-P($CH_2CH{=}CH_2)_2$}]$_4$ catalyst (2)[a]



Entry	Aldehyde	Amine	Alkyne	Product	yield (%)[b]
1	C_6H_5CHO	Piperidine	phenylacetylene	4a	93
2	C_6H_5CHO	Pyrrolidine	phenylacetylene	4b	90
3	C_6H_5CHO	Morpholine	phenylacetylene	4c	83[c]
4	C_6H_5CHO	2,2,6,6-Tetramethylpiperidine	phenylacetylene	4d	NR[d]
5	C_6H_5CHO	$^i Pr_2NH$	phenylacetylene	4e	15[c]
6	C_6H_5CHO	Methylaniline	phenylacetylene	4f	33[c]
7	$CH_3(CH_2)_2CHO$	Piperidine	phenylacetylene	4g	99
8	$CH_3(CH_2)_2CHO$	Pyrrolidine	phenylacetylene	4h	99
9	$CH_3(CH_2)_2CHO$	$^i Pr_2NH$	phenylacetylene	4i	30[c]
10	4-$MeOC_6H_5CHO$	Pyrrolidine	phenylacetylene	4j	98
11	4-BrC_6H_5CHO	Pyrrolidine	phenylacetylene	4k	80
12	3-ClC_6H_5CHO	Pyrrolidine	phenylacetylene	4l	83
13	4-ClC_6H_5CHO	Pyrrolidine	phenylacetylene	4m	90
14	2-ClC_6H_5CHO	Pyrrolidine	phenylacetylene	4n	40
15	C_6H_5CHO	n-Butylamine	phenylacetylene	4o	25
16	C_6H_5CHO	Pyrrolidine	1-hexyne	4p	51
17	C_6H_5CHO	Pyrrolidine	5-hexynenitrile	4q	72[c]

[a] All the reactions were carried out by using aldehyde (0.5 mmol), amine, (0.55 mmol), phenylacetylene (0.75 mmol) and 2 mol% of catalyst **2** under free solvent conditions at 50°C for 6h. [b] Isolated yield based on aldehyde. [c] Reactions were carried out at 50°C for 24h. [d] Verified by ^{1}H-NMR spectroscopy of the crude reaction.

We also studied the influence of electron–donating or –withdrawing groups on the aromatic ring of aldehyde. Aromatic aldehyde containing electron donating group as CH_3O– at *para*–

position returned the corresponding product **4j** in excellent yield (Table 4, entry 10). Also, aromatic aldehydes possessing electron withdrawing groups such as Cl– and Br– at either *meta*– and *para*–position gave good yields of the desired products **4k**-**4m** (Table 4. entries 10-13). However, aromatic aldehyde with chloro group at *ortho*–position gave low yield of the corresponding product **4n** (Table 4, entry 14). Subsequently, we screened additional secondary amines such as isopropylamine and methylaniline with benzaldehyde and phenylacetylene, which gave the desired products **4e** and **4f** in low yields (Table 4, entries 5 and 6). With butyraldehyde, the reaction yield also resulted to be low (Table 4, entry 9). We then studied the reactivity of the primary amine butylamine under the optimized reaction conditions, which led to propargylamine **4o** with only 25% yield (Table 4, entry 15).

Finally, we also evaluated the reactivity of aliphatic alkynes such as 1-hexyne and 5-hexynenitrile with benzaldehyde and pyrrolidine under the optimized reaction conditions. The use of 1-hexyne results in the formation of propargylamine **4p** in 51% yield but in case of 5-hexynenitrile, moderate yield of the corresponding propargylamine **4q** was obtained after longer reaction time (Table 4, entries 16 and 17).

Our catalyst **2** offer some advantages over previously reported Cu(I) catalysts bearing phosphine-based ligands [24]. For instance, catalyst **2** operates under solvent free conditions, moderate reaction temperature and lower catalyst loading.

4. Conclusions

In summary, we have synthesized and characterized a new copper(I) complex with tert-butyldiallylphosphine ligands. X-ray crystallographic study confirmed the cubane-like structure of the copper complex of formula $[CuCl\{ {}^{1}(P)\text{-}{}^{t}Bu\text{-}P(CH_2CH{=}CH_2)_2\}]_4$. However, spectroscopic data at variable temperature indicated the existence of a dynamic behavior in solution generated by the cubane $\rightleftharpoons$ chair isomerization as consequence of the low stability of the cube-like structure caused by the strong strain of the Cu_4Cl_4 core for steric reasons. DFT calculations

indicates that the experimentally isolated tetrameric structure is destabilized relative to the chair-like structure. Catalytic ability of complex **2** was tested in A^3-coupling reaction of aldehydes, amines and alkynes. We found that complex **2** is an efficient catalyst for A^3-coupling reactions of both aromatic and aliphatic aldehydes with cyclic amine and phenylacetylene under mild reaction condition and absence of solvent.

ASSOCIATED CONTENT

Supporting Information

Theoretical calculation, spectroscopic and crystallographic data. This material is available free of charge via the Internet at https://www.journals.elsevier.com/inorganica-chimica-acta.

AUTOR INFORMATION

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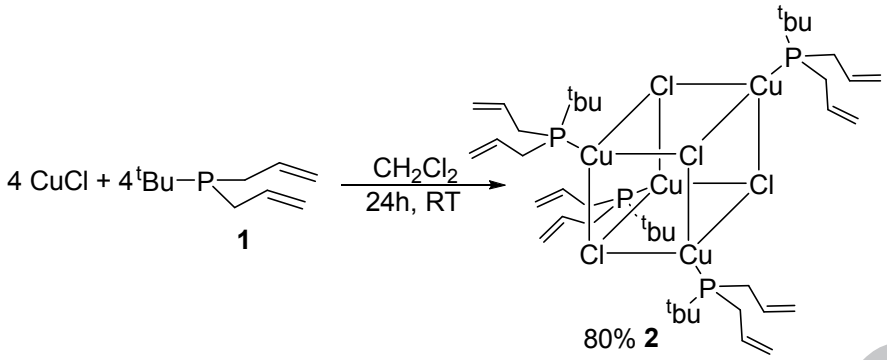
GraphicalAbstract #1



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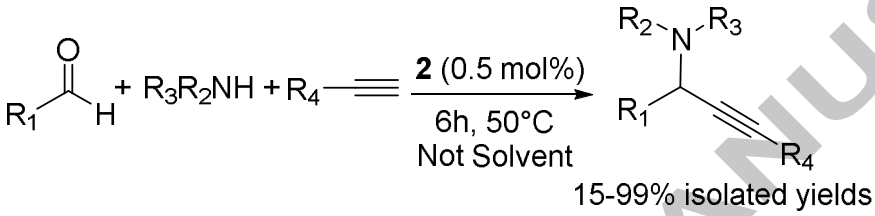

Highlights:

A tetramer copper(I) complex with tert-butyldiallylphosphine has been synthesized and characterized.

Tetramer copper(I) complex shows a cubane-like structure in solid state.

Isomerization of tetramer copper(I) complex was observed in solution.

A^3-Coupling (Aldehyde-Amine-Alkyne) Reaction catalyzed by tetramer copper(I) complex.