Inorganica Chimica Acta 380 (2012) 336–342

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Cu^{I} click catalysis with cooperative noninnocent pyridylphosphine ligands

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ARTICLE INFO

Article history:
Available online 17 October 2011

Young Investigator Award Special Issue

Keywords:
Cooperative catalysis
Copper
Pincer ligand
Click reaction
Ligand design
Hybrid ligand

ABSTRACT

We describe the synthesis and characterization of compound **L1H**, 2-di(*tert*-butyl)phosphinomethyl-6-methylpyridine, and the first dimeric Cu^{I} complex **3** with this novel bidentate NP^{tBu} ligand. We also demonstrate for the first time that this ligand scaffold exhibits noninnocent reactivity through dearomatization behavior, similar to its well-studied tridentate analog **L2H**, 2,6-bis((di-*tert*-butylphosphino)methyl)pyridine PNP^{tBu}. The molecular structure of $[Cu(CCPh)(\mathbf{L2H})]_2$ is reported, which is a rare case of a crystallographically characterized copper-acetylide dimer. We also demonstrate that copper(I) complexes with either ligand **L1H** or **L2H** or their dearomatized counterparts may act as active, cooperative catalysts for the [2+3] polar cycloaddition of azides and acetylenes. These results represent the first indications of selective Cu-based cooperative catalysis, using non-innocent lutidine-based PNP backbone and catalysts **2** and **5** could thus be termed all-inclusive systems for this reaction.

1. Introduction

Nature often employs cooperative substrate activation to enhance selectivity, reactivity or activity, and almost without exception first row transition metals are utilized in metalloenzyme active sites [1]. This activation can be roughly separated into two areas: redox-based reactivity and acid-base related reactivity. Traditionally, the general concept of cooperative interactions has been ignored in synthetic catalyst designs, where ligand and metal have strictly separated roles during the catalytic conversion of substrates, and this is the case for the majority of newly developed systems to facilitate both existing and new catalytic transformations. Only recently, some convincing examples of productive metal–ligand interplay during substrate orientation, activation and/or transformation have been demonstrated. However, there is a striking dichotomy in these literature examples, with first-row transition metals mainly involved in redox-based cooperativity [2], while various expensive second- or third-row transition metals have been involved in other types of substrate activation to an appreciable extent [3]. Hence, the combination of first-row metals and cooperative ligand systems is a relative barren field of research, with potential applications to replace existing processes based on scarce metals with benign, earth-abundant alternatives [4].

Pincer ligands have been around for a few decades now, but research on these well-defined, tridentate scaffolds is still blossoming. The majority of the developed classes of pincer compounds are strictly monoanionic frameworks, predominantly with a deprotonated pivot (heteroatom) donor atom [5–7]. Recently, neutral lutidine-based PNP and PNN pincer scaffolds, which are susceptible to selective deprotonation–rearomatization of the ligand backbone [8], have also been successfully applied in cooperative catalysis [9], mainly with Ru [10] and to a lesser extent with Rh [11] and Ir [12]. Upon dearomatization, the ligand system undergoes a reversible formal charge-switching from neutral to monoanionic. Compared to the varied chemistry detailed for the heavier congeners, strikingly little attention has been paid to the use of first row transition metals with these ligand frameworks to date [13].

Therefore, we started a research program to explore metal–ligand cooperative reactivity with specific focus on first row metals, utilizing *inter alia* cooperative PNP ligands as a reactive scaffold. We have described the stoichiometric reactivity of ligand $\mathbf{PNP^{tBu}}$(**L2H**) with Cu^{I}, whereby hemilabile coordination of the pyridine-nitrogen donor was observed on going from neutral species **1** to the T-shaped cationic complex **A** (Scheme 1) [14]. Complex **1** selectively reacted with strong bases at the ligand backbone [15], mirroring reactivity described for 2nd and 3rd row metals [10–12] and providing a platform for further investigations with first row metals. Deprotonation of the reactive CH_2-spacer of the **PNP**-backbone resulted in bright orange, neutral T-shaped Cu-complex **2**, featuring ligand scaffold **L2**, which was susceptible to electrophilic addition (C–C bond formation) reactions on the ligand backbone. Reprotonation of **2** with thiophenol and benzyl mercaptan (pK_a = 15.3 in DMSO) occurs smoothly and instantaneously at room temperature [16], while boiling this species in ethanol (pK_a = 29.8 in DMSO) did not induce any visual change, with the

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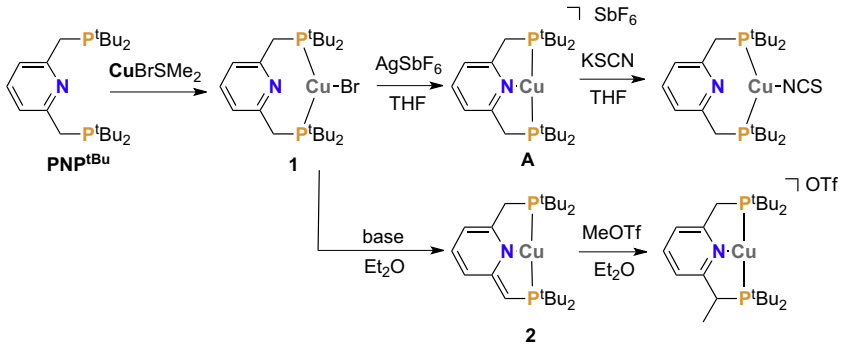
doi:10.1016/j.ica.2011.10.037



Scheme 1. Synthesis of Cu^{I} complex **2** featuring a dearomatized PN^{-}P-ligand and the structural resemblance to the cationic derivative **A**.

persistent bright orange color indicative of the intact dearomatized heterocycle.

Alternatively, a 1D coordination polymer based on **L2H** and with the overall formula $[Cu_2Br_2(\mathbf{L2H})]_n$ could be fabricated, which showed identical response to base-mediated deprotonation of the PNP backbone. Subsequent treatment with sufficiently acidic thiols resulted in the formation of unique dinuclear Cu^{I} complexes featuring bridging thiolate and PNP ligands [16].

Hence, the methodology of dearomatization–reprotonation offers a flexible and versatile route toward Cu^{I} species bearing functionalities that are otherwise difficult to install. We also reported on the chemistry of ligand **PNP^{tBu}** with nickel [17] and palladium [18], including a direct comparison of dearomatized Pd(alkyl)(**PN^{-}P^{tBu}**) species with their isoelectric PCP analogs in the Suzuki coupling of arylbromides and arylboronic acids.

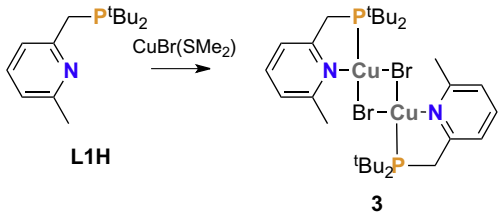
Besides tridentate ligands based on lutidine, also picoline and lutidine-derived NP^{R}-ligands as well as the closely related quinoline analogs have been employed quite extensively in the last decade [19], but the potential noninnocent character of these bidentate analogs of the PNP^{R} ligand class has been almost completely overlooked to date and practical application of this feature has not been reported so far [20]. Furthermore, very few reports on alkyl-substituted PN ligands have appeared. Given our recent explorations in the first row chemistry of cooperative but very bulky pincer ligands, it was deemed interesting to probe the cooperative reactivity with the sterically more accessible PN ligands while coordinated to Cu^{I} and thereby expand the toolbox of noninnocent, reactive ligands. We herein describe our initial efforts in this direction with the synthesis and application of Cu-complexes **3** and **4** for the (stoichiometric and catalytic) activation of acetylenes and azides. Furthermore, we have applied complexes **2** and **5**, featuring PNP ligand **L2** and **L2H**, respectively, in the same 'click-reaction'. This is the first example of cooperative copper catalysis with these noninnocent NP and PNP scaffolds.

2. Results and discussion

2.1. Ligand synthesis and Cu^{I} coordination chemistry

Ligand **L1H** is prepared in a straightforward manner [21] by careful monolithiation of one of the lutidine methyl-groups, followed by phosphorylation using ClP^{t}Bu$_2$ to give a white solid after recrystallization by slow vapor diffusion of hexane into a concentrated dichloromethane solution. The ^{31}P NMR signal appears at δ 35.3 ppm in acetone-d_6. The second, unreacted methyl-group can act both as a spectroscopic handle and as a steric (and electronic) tuning factor upon coordination [22]. By using a lutidine-scaffold instead of picoline, undesirable cyclometallation reactions at the 6-position of the pyridine ring are also efficiently avoided.

Upon combining ligand **L1H** with CuBr(SMe)$_2$ in diethyl ether a light-yellow solid was recovered (Scheme 2) after work-up that



Scheme 2. Synthesis of complex **3**.

showed a broad ^{31}P NMR signal at 26.6 ppm as well as the expected signals in the ^{1}H NMR spectrum for all types of hydrogen atoms present. IR spectroscopy indicated coordination of the pyridine N-atom to the Cu^{I} center, with two bands at ν 1590 and 1577 cm^{-1}. High resolution FAB-MS showed a peak at m/z 790.0530 for the parent molecule [M+] and a fragmentation pattern indicative of a dimeric structure, which was confirmed by an X-ray crystallographic analysis of single crystals, grown by slow vapor diffusion of pentane into an acetone-d_6 solution. The molecular structure for dimeric complex **3** in the solid state, with bridging bromide ligands, is depicted in Fig. 1.

The complex shows overall centrosymmetry and the geometry around the Cu^{I}-center is distorted tetrahedral, with a more acute Br1–Cu1–Br1^{i} angle of 103.783(9)° and large P–Cu–Br angles of 127.070(16)° and 118.207(16)°. The Cu–N and Cu–P bond distances are within the usual regions [14–16,23].

2.2. Cooperative click reactivity of Cu(PNP) complexes

It was reasoned that compound **2** might be a suitable starting material for the direct preparation of a precatalyst for the [2+3] polar cycloaddition [24] of phenyl acetylene, given that the pK_a of this reagent is 28.8 (in DMSO). Reconstitution of the aromatic pyridine heterocycle of the **PN^{-}P^{tBu}** backbone occurred instantaneously upon addition of one equiv phenylacetylene to an orange solution of **2** in diethyl ether, as evidenced by a color change to yellow, and NMR, IR spectroscopic and mass spectrometric analysis of the isolated light-yellow solid confirmed formation of species **5**. Evidently, proton transfer from the acidic phenylacetylene to the dearomatized **L2** backbone, concomitant with formation of the copper–phenylacetylide adduct proceeded smoothly and rapidly at room temperature, which is in contrast with the sluggish formation of a monomeric, two-coordinate Cu^{I}-phenylacetylide complex, reported by Gunnoe [25]. Reaction of the starting (NHC)CuMe-complex with PhCCH, eliminating methane concomitant with formation of the desired copper species, required heating to 60 °C for 22 h to enable complete conversion. This hints towards a different mechanism for both reactions, *i.e.* intermolecular proton-transfer followed by

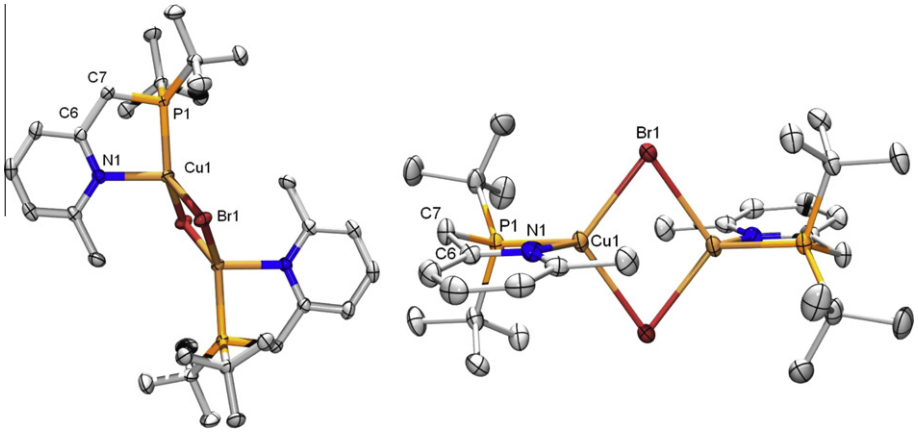
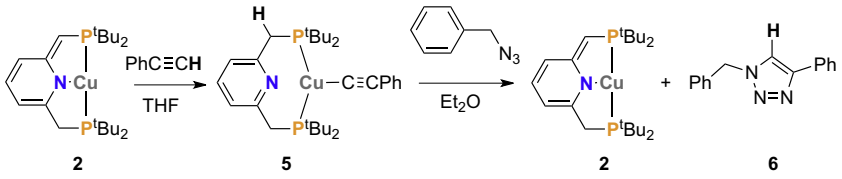


Fig. 1. ORTEP plot (50% probability displacement ellipsoids) of complex **3**, [Cu(μ-Br)(**L1H**)]$_2$; left – top view; right – side view. Hydrogen atoms and disordered solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–P1 2.2188(5); Cu1–N1 2.1505(15); Cu1–Br1 2.4580(3); Cu1–Br1^i 2.5198(3); P1–C7 1.8506(18); Cu1···Cu1^i 3.0725(4); P1–Cu1–N1 87.54(4); P1–Cu1–Br1 127.070(16); P1–Cu1–Br1^i 118.207(16); N1-Cu1-Br1 109.93(4); Cu1–Br1–Cu1^i 76.217(9); Br1–Cu1–Br1^i 103.783(9); P1–C7–C6–N1 29.2(2); Cu1–P1–C7–C6 −25.62(14). Symmetry operation i: 0.5 − *x*, 0.5 − *y*, −*z*.

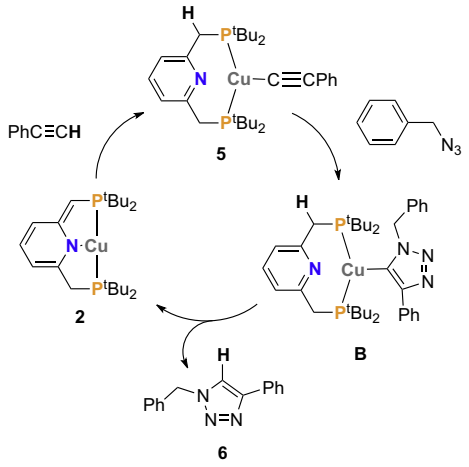


Scheme 3. Reaction of **2** toward phenyl acetylene and subsequent addition of benzyl azide to generate compound **6** via intermediacy of complex **5**.

nucleophilic addition in our case versus associative substitution via intramolecular proton-transfer in the literature case.

The instantaneous formation of an copper-acetylide species supported by a reprotonated PNP^{tBu} ligand (Scheme 3) was further verified by an independent synthesis of the complex Cu(C≡CPh)(**L2H**) by reaction of commercially available Cu(C≡CPh) with **PNP^{tBu}** in diethyl ether to yield a yellow-green solid. We have no definite proof for the monomeric or higher-ordered nature of **5**, – higher mass aggregates seem to be absent in the FAB mass spectrum (FAB+ 459.09 [M−{CCPh}]observed as major species). The ^{31}P NMR spectrum of proposed complex **5** showed a singlet at δ 42.1 ppm in d_4-methanol, similar to the starting CuBr(PNP) species **1** and markedly different than dearomatized intermediate **2**, indicating that reprotonation and coordination of the acetylide fragment was successful. We have modeled (DFT, PM3 level) a dimeric copper species with the acetylene σ-bonded to Cu_1 and π-bonded to Cu_2 – often proposed to be a likely constitution for the active species with less bulky ligands present – but this proved to lead to highly congested complexes. Similar evidence for the possibility of a mononuclear Cu-center to be an active 'click-catalyst' was recently provided by Straub, who showed that both Cu(NHC)(OAc) and Cu(NHC)(CCPh) are active CuAAC catalysts (CuAAC – copper-catalyzed azide–alkyne cycloaddition) [25].

In a subsequent experiment using complex **5** in the presence of an equimolar amount of benzyl azide, the orange color of complex **2** was regenerated, along with the product 1-benzyl-4-phenyltriazole **6** of the [2+3] polar cycloaddition reaction. Obviously, the intermediate copper triazolide adduct **B**, with a proposed structure analogous to the isolated compound reported by Straub [26], is basic enough (and also sterically hindered enough) to induce facile intramolecular proton transfer, *i.e.* deprotonation of the PNP-ligand backbone, to release triazole species **6**. This implies that the 'click' reaction can thus be performed without the need for additional base or buffered solution media. The regeneration of complex **2** was also confirmed by *in situ* ^{31}P NMR spectroscopy.



Scheme 4. Proposed catalytic cycle for the click-reaction of phenyl acetylene and benzyl azide catalyzed by 1 mol% of species **2** or **5**.

To run this reaction in a catalytic fashion we used 1 mol% **5** as catalyst and diethyl ether as reaction medium (Scheme 4); alternatively complex **2** could be employed as well. As expected, compound **6** was obtained in near quantitative yield after 16 h as a white solid precipitate from the reaction mixture, with NMR signatures as previously reported for this benchmark product. Furthermore, it may be anticipated that all-inclusive catalysts with a built-in reactive site may give rise to enhanced rates or unusual chemoselectivities compared to standard 'click' catalysts, as intramolecular proton-transfer could suppress side-reactions wherein the intermediate triazolide undergoes rearrangement. We are currently testing this hypothesis by extending our screening studies. Initial reactivity of **2** with benzoxazole confirms that C–H bond

activation may also occur with this heterocyclic compound, which is also under further investigation.

2.3. Cooperative reactivity of Cu(NP) complex **4**

Stimulated by the results obtained with complexes **2** and **5** in this cycloaddition reaction, we also tested the behavior of species **3** for dearomatization and subsequent interaction with phenylacetylene. Gratifyingly, upon addition of one equiv HCCPh to the orange solution obtained after treating **3** with strong base in diethyl ether (with presumable formation of a {Cu(**L1**)(solvent)} species), the color instantaneously faded to light yellow, indicative of reprotonation of the ligand-backbone, and after work-up a greenish-yellow solid was obtained for complex **4**. NMR spectroscopic analysis of the product indicated formation of the desired copper(PN)(acetylide) unit, with a broad signal at 32 ppm in the ^{31}P NMR spectrum and ^{13}C NMR signals indicative of the acetylenic fragment. FAB-MS spectrometry indicated the formation of dinuclear species, with the highest-intensity peak at *m/z* 729.3 for $[Cu_2(CCPh)(\mathbf{L1H})_2]^+$. IR spectroscopy indicated that the Cu–N bond remained intact, with bands apparent at ν 1592 and 1575 cm^{-1}. The existence of a bimetallic constitution for complex **7** was confirmed by an X-ray crystallographic analysis of single crystals obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution. The resulting molecular structure for complex [Cu(μ-CCPh)(**L1H**]$_2$ is depicted in Fig. 2.

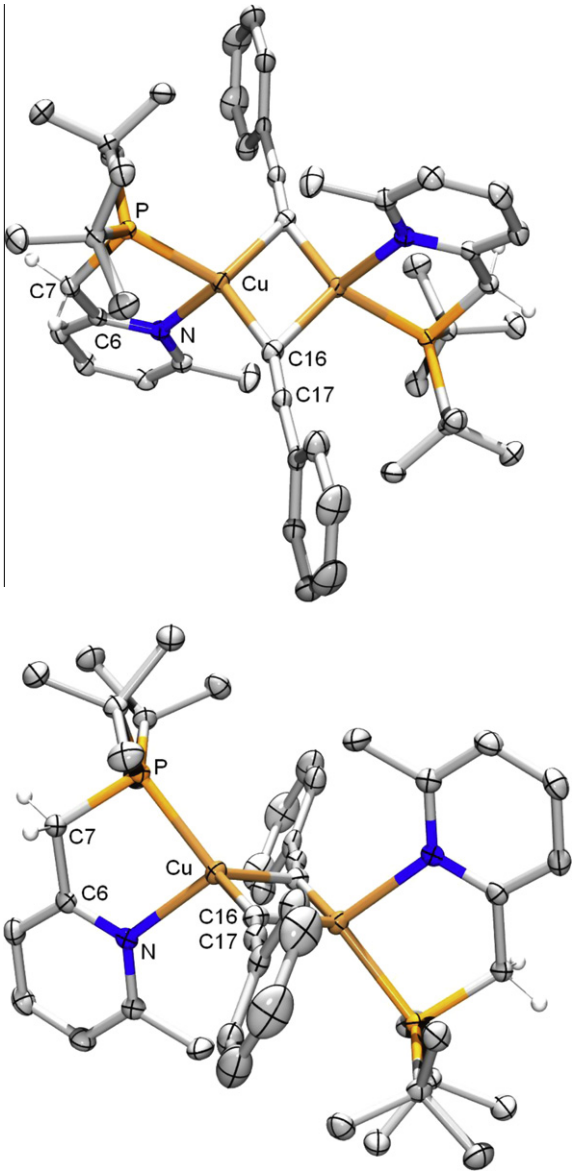


Fig. 2. ORTEP plot (50% probability displacement ellipsoids) of complex **4** [Cu(μ-CCPh)(**L1H**)]$_2$; top – top view; bottom – side view. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–P1 2.2735(4); Cu1–N1 2.2132(13); Cu1–C16 2.0147(16); Cu1–C16^i 2.1667(17); C16-C17 1.210(2); C17–C18 1.444(2); P1–C7 1.8438(16); Cu1···Cu1^i 2.4417(4); P1–Cu1–N1 84.46(4); P1–Cu1–C16 125.59(5); P1–Cu1–C16^i 115.99(4); N1–Cu1–C16 112.33(6); N1–Cu1–C16^i 105.51(6); C16–Cu1–C16^i 108.65(5); Cu1–C16–Cu1^i 71.35(5); C17–C16–Cu1 156.04(14); C17–C16-Cu1^i 132.60(13). Symmetry operation (i): 1 − *x*, 1 − *y*, 1 − *z*.

The geometry around the Cu^I metal centers is distorted tetrahedral with angles between 84.46(4)° and 125.59(5)°. The Cu1–C16–Cu1^i angle is acute with 71.35(5). As a consequence of the inversion symmetry of the complex, the Cu1–C16–Cu1^i–C16^i unit is planar. The acetylide group is approximately coplanar with this plane, but bent in the direction of one copper center. The C17–C16–Cu1 and C17–C16–Cu1^i angles are thus significantly different with 156.04(14)° and 132.60(13)°. The angle sum at C16 is 360.0(2)°. The bridging of the acetylide groups results in a short Cu1···Cu1^i contact of 2.4417(4) Å.

As a consequence, there is no side-on interaction of the respective Cu^I centers with either of the π-systems of the two triple bonds, which is also reinforced by the steric hindrance imparted by the *tert*-butyl groups. A search of the Cambridge Structural Database CSD revealed only a few published dimeric structures featuring related μ-CCR or μ-CCAr binding motifs [26]. The C16–C17 bond length of 1.210(2) Å is in the range of an C≡C bond [27].

Subsequent addition of an equimolar amount of benzyl azide regenerated an orange-colored solution in the course of 4 h, concomitant with formation of a white precipitate, which was identified by NMR spectroscopy as 1-benzyl-4-phenyltriazole, after comparison with an authentic sample [28].

3. Conclusions

In summary, we have reported the facile, selective and efficient coupling of azides and acetylenes (click-reaction) using an all-inclusive Cu^I complex with a cooperative diphosphinopyridine (PNP) framework. This reaction sequence relies on the reversible dearomatization of the PNP-scaffold combined with its affinity to activate sufficiently protic E–H bonds. The described intramolecular C–C coupling methodology is believed to provide a general route to induce selective formation of triazoles. We are currently investigating catalyst tuning by modifications on the ligand framework.

4. Experimental

All commercial starting materials were used as received. THF, pentane, hexane and diethyl ether were distilled from sodium benzophenone ketyl, CH_2Cl_2, isopropanol and methanol were distilled from CaH_2, and toluene was distilled from sodium under nitrogen. NMR spectra (^{1}H, ^{31}P and ^{13}C) were measured on a Varian INOVA 500 MHz or a Varian MERCURY 300 MHz. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. IR spectra were collected on a Bruker alpha-p FT-IR spectrometer with ATR module. Elemental analyses were carried out at Kolbe Mikroanalytisches Laboratorium in Mülheim an der Ruhr. CuBr(**PNP^{tBu}**) **1** and Cu(**PN$^-$P^{tBu}**) **2** were prepared following literature procedures [10,11]. Ligand **L1H** was prepared according to a literature procedure [21].

4.1. Complex **3** *[Cu(μ-Br)(**L1H**)]$_2$*

To a suspension of CuBr(SMe)$_2$ (374.9 mg, 1.82 mmol) in 20 mL diethyl ether was added a solution of **NP^{tBu}** (**L1H**) (458.5 mg,

1.82 mmol) in 10 mL diethyl ether. The light-yellow suspension is stirred for 16 h and all volatiles are removed *in vacuo* to leave a light-yellow solid. Yield: 716.7 mg, 0.91 mmol, 99.5%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.70 (t, J_H = 7.6 Hz, 1H, ArH), 7.36 (d, J_H = 7.2 Hz, 1H, ArH), 7.20 (d, J_H = 6.8 Hz, 1H, ArH), 3.39 (d, J_{PH} = 7.6 Hz, 2H, CH_2), 2.98 (s, 3H, CH_3), 1.31 (d, J_{PH} = 12.8 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, $(CD_3)_2CO$): δ 26.6 (br s). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 159.9 (d, J_{PC} = 17.1 Hz, 2C, Ar-C), 138.7 (s, 1C, Ar-CH), 122.7 (d, J_{PC} = 30 Hz, 2C, Ar-CH), 33.5 (d, J_{PC} = 7.8 Hz, 2C, ^{t}Bu-C), 31.1 (d, J_{PC} = 11 Hz, 1C, CH_2), 28.2 (d, J_{CH} = 10.8 Hz, 6C, ^{t}Bu-CH_3), 26.3 (s, 1C, CH_3). IR (ATR, Et_2O): ν 1592, 1575 cm^{-1}. HR-MS (FAB) calcd for $[M]^+$ $C_{30}H_{52}Br_2Cu_2N_2P_2$ 790.0530; found, 790.0530.

4.2. Complex **4** Cu(CCPh)(***L1H***)

To a suspension of $[CuBr(\mathbf{NP^{tBu}})]_2$ **3** (33.9 mg, 0.043 mmol) in 10 mL diethyl ether was added KO^{t}Bu (1 M solution in THF) (0.086 mg, 0.086 mmol). The solution immediately turned orange, indicating the formation of {Cu(**L1**)}. After stirring the reaction for 20 min., phenyl acetylene (8.8 mg, 0.086 mmol) was added by syringe, leading to a color change to dark yellow. After stirring for 2 h, the solution was filtered to remove salts and all volatiles removed *in vacuo* to leave a yellow solid. Isolated yield: 26.1% (9.3 mg, 0.086 mmol). Alternatively, complex **4** could be prepared by stirring a suspension of $\mathbf{NP^{tBu}}$ (329.0 mg, 1.31 mmol) and solid Cu(phenylacetylide) (215.6 mg, 1.31 mmol) in 25 mL toluene for 18 h at r.t. Yield: 93.6% (509.8 mg, 1.31 mmol). Single crystals were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.61 (t, J_H = 7.6 Hz, 1H, ArH), 7.52 (br s, 1H, ArH), 7.17 (m, 2H, ArH), 7.11 (m, 3H, ArH), 7.01 (m, 1H, ArH), 3.33 (d, J_{PH} = 4.8 Hz, 2H, CH_2), 2.81 (s, 3H, CH_3), 1.29 (d, J_{PH} = 12.4 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, $(CD_3)_2CO$): δ 32.0 (br s).^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 160.0 (d, J_{PC} = 4.5 Hz, 1C, pyC), 159.3 (d, J_{PC} = 9.1 Hz, 1C, pyC), 138.1 (s, 1C, pyCH), 131.6 (s, 2C, PhCH), 128.6 (s, 2C, PhCH), 125.7 (s, 1C, PhCH), 122.5 (d, J_{PC} = 3.8 Hz, 1C, pyCH), 122.1 (s, 1C, pyCH), 113.1 (s, 1C, PhC), 82.6 (d, J_{PC} = 3.7 Hz, 1C, Cu–C≡C), 75.2 (s, 1C, C≡C-Ph), 33.7 (d, J_{PC} = 2.7 Hz, 2C, ^{t}Bu-CH_3), 31.8 (d, J_{PC} = 7.4 Hz, 1C, CH_2), 30.1 (s, 6C, ^{t}Bu-CH_3), 26.0 (d, J_{PC} = 1.3 Hz, 1C, CH_3). IR (ATR, Et_2O): ν 2037, 1592, 1575 cm^{-1}. HR-MS (FAB) calcd for $[M-CCPh]^+$ $C_{23}H_{31}CuNP$ 314.1099; found, 314.1152.

4.3. Complex **5** Cu(CCPh)(***L2H***)

To a solution of CuBr($\mathbf{PNP^{tBu}}$) **1** (200 mg, 0.371 mmol) in 10 mL diethyl ether was added a solution of $NaN(SiMe_3)_2$ (68.4 mg, 0.371 mmol) in 7 mL THF. The solution immediately turned orange, indicating the formation of Cu($\mathbf{PN^-P^{tBu}}$) **2**. After stirring the reaction for 15 min, phenyl acetylene (37.9 mg, 0.371 mmol) was added by syringe, leading to a color change to light yellow. After stirring for 1 h, the solution was evaporated to dryness. The crude was then retaken in toluene, filtered over celite to separate salts, and toluene was then removed *in vacuo* to leave a light-yellow solid. Yield: 90 mg, 0.161 mmol, 43%. Alternatively, complex **3** can be prepared by stirring a suspension of $\mathbf{PNP^{tBu}}$ (130 mg, 0.329 mmol) and solid Cu(phenylacetylide) (54.1 mg, 0.329 mmol) in 20 mL toluene for 15 h at r.t. Yield: 84 mg, 0.150 mmol, 45%. ^{1}H NMR (400.13 MHz, CD_3OD): δ 7.87 (t, J_H = 7.6 Hz, 1H, ArH), 7.50 (d, J_H = 7.6 Hz, 2H, ArH), 7.10–7.47 (m, 5H, ArH), 1.33 (d, J_{PH} = 14.4 Hz, 36H, ^{t}Bu-H). ^{31}P NMR (CD_3OD, 161.98 MHz): δ 42.1 (br s). ^{13}C NMR (CD_3OD, 100.62 MHz): δ 141.4 (s, CH_{ar}), 133.0 (s, CH_{ar}), 129.7 (s, CH_{ar}), 129.5 (s, CH_{ar}), 123.6 (s, CH_{ar}), 34.0 (t, J_{PC} = 6.5 Hz, either $PC(CH_3)_3$ or PCH_2), 29.8 (t, J_{PC} = 3.9 Hz, $PC(CH_3)_3$. IR (ATR, solid): ν 2036 cm^{-1}. MS (FAB) 459.09 [M−CCPh].

5. Copper catalyzed azide alkyne cycloaddition

The appropriate catalyst was charged into a flame-dried Schlenk of 15 mL volume, together with 100 molar equiv of phenyl acetylene (182.3 mg) in 10 mL diethyl ether. To this yellow solution was added benzyl azide (237.7 mg, 100 mol. eq. to catalyst) and the reaction monitored in time. Progressive formation of a white precipitate signaled generation of triazole product. After 16 h the reaction mixture was filtered and the product analyzed. Yield: 170 mg, 0.723 mmol, 40%. The NMR spectroscopic features of the thus obtained product match that of *N*-benzyl-4-phenyltriazole [28].

6. X-ray crystal structure determination of complex 3

$C_{30}H_{52}Br_2Cu_2N_2P_2$ + disordered solvent, Fw = 789.58[*], pale yellow plate, 0.68 × 0.39 × 0.02 mm^3, monoclinic, *C*2/*c* (no. 15), *a* = 23.2103(15), *b* = 12.4802(7), *c* = 16.1383(9) Å, β = 123.830(4)°, *V* = 3883.3(4) Å^3, *Z* = 4, D_x = 1.351 g/cm$^{3[*]}$, μ = 3.26 mm$^{-1[*]}$. 29182 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150(2) K. Intensity data were integrated with the Eval14 software [29], taking a large anisotropic mosaicity about *hkl* = (0 1 0) into account. An analytical absorption correction and the scaling was performed with SADABS [30] (0.22–0.97 correction range). 4442 Reflections were unique (R_{int} = 0.025), of which 3808 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97 [31] and refined with SHELXL-97 [31] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. The crystal structure contains solvent accessible voids (655 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of PLATON [32] resulting in 153 electrons/unit cell). 179 Parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0230/0.0520. R_1/wR_2 [all reflections]: 0.0313/0.0555. *S* = 1.108. Residual electron density between −0.38 and 0.43 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program [32]. [*] derived values do not contain the contribution of the disordered solvent.

7. X-ray crystal structure determination of complex 4

$C_{46}H_{62}Cu_2N_2P_2$, Fw = 832.00, yellow plate, 0.21 × 0.15 × 0.08 mm^3, triclinic, $P\bar{1}$ (no. 2), *a* = 9.1681(4), *b* = 10.8102(4), *c* = 11.7608(5) Å, α = 96.7585(12), β = 112.5160(11), γ = 92.9488(12)°, *V* = 1063.33(8) Å^3, *Z* = 1, D_x = 1.299 g/cm^3, μ = 1.11 mm^{-1}. 22911 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150(2) K. Intensity data were integrated with the SAINT software [33]. An absorption correction based on multiple measured reflections and the scaling was performed with SADABS [30] (0.67–0.75 correction range). 4813 Reflections were unique (R_{int} = 0.025), of which 4105 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97 [31] and refined with SHELXL-97 [31] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 242 Parameters were refined with no restraints. R_1/wR_2[$I > 2\sigma(I)$]: 0.0259/0.0584. R_1/wR_2 [all reflections]: 0.0359/0.0618. *S* = 1.057. Residual electron density between −0.24 and 0.38 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program [32].

Acknowledgements

This research was funded by an VENI Innovative Research grant from the Netherlands' Organisation for Scientific Research – Chemical Sciences (NWO-CW Grant 700.56.403) to J.I.v.d.V., with further financial support from the University of Amsterdam. We thank Prof. Dr. Joost N.H. Reek for continuous interest in our work on first-row transition metal cooperative catalysis. Support from the EU-FP7 COST network CM0802 'PhoSciNet' is appreciated as well. Han Peeters is thanked for the HR-MS measurements and Dr. Evgeny A. Pidko (TU/e) for scientific discussions.

Appendix A. Supplementary material

CCDC 834114 and 846882 contain the supplementary crystallographic data for complexes **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.10.037.

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