View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Trivedi, J. R. Smreker, G. Singh, A. Kumar and N. P. Rath, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ03038J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

YAL SOCIETY CHEMISTRY

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Manoj Trivedi,^{*a**} Jacob R. Smreker,^{*c*} Gurmeet Singh,^{*a**} Abhinav Kumar,^{*b*} Nigam P. Rath^{*c**}

The reaction of *cis*-1,2-bis(diphenylphosphino)ethylene (dppet) with CuX (X = CN, SCN) in 1:1 M molar ratio in DCM-MeOH (50:50 V/V) under refluxing condition gave two dimeric Cu(I) complexes *viz*. [Cu₂(μ -CN)₂(k^2 -*P*,*P*-dppet)₂] (**1**), and [Cu₂(μ_2 -SCN)₂(k^2 -*P*,*P*-dppet)₂] (**2**). These complexes have been characterized by elemental analyses, IR, ¹H and ³¹P NMR, electronic absorption spectroscopy and ESI-MS. The molecular structure of **2** was confined by single crystal X-ray diffraction which indicated that **2** exists as a centrosymmetric dimer in which the two copper centers are bonded to two dppet ligands and two bridging thiocyanate groups in μ_2 -manner. The electrochemical properties of **1** and **2** were studied by cyclic voltammetry. Both the complexes exhibited strong luminescence properties in the solution state at ambient temperature. Both the complexes were found to be efficient catalysts for the conversion of terminal alkynes into propiolic acids with CO₂. Owing to their excellent catalytic activity, the reactions proceed at atmospheric pressure and ambient temperature (25°C). The catalytic products were obtained in excellent yields (90-97%) by using the complex loading of 1 mol%.

Introduction

Bidentate diphosphines have received significant research interest due to their extensive applications as ligands for a wide variety of transition metal catalysed transformations.¹⁻³ In the presented, we have chosen the rigid diphosphine cis-1,2bis(diphenylphosphino) ethylene (dppet) ligand because transition metal complexes of cis-1,2-bis(diphenylphosphino) ethylene (dppet) had displayed novel and markedly different bonding properties when compared to complexes of other diphosphines complexes having saturated backbone.⁴ For dppet complexes, solution ³¹P NMR investigations⁵⁻⁷, solid state ¹⁹⁷Au Mossbauer⁸ and ³¹P CP-MAS NMR studies^{6,8} and single crystal X-ray structure determinations for [Cu(dppet)2]X for $X=PF_{6}^{5}$, BF_{4}^{9} , and $CuCl_{2}^{10}$; $[Ag(dppet)_{2}]X$ for X= SnPh₃(NO₃)₂¹¹, ClO₄¹², and BF₄¹²; $[Au(dppet)_{2}]X$ for $X=PF_{6}^{6}$, I⁸, BF₄¹³, Cl¹³, Br¹³, and BPh₄¹³ support the formation of stable tetrahedral bis(chelated) cations in both solid as well as in solution state. Recently another incentive to study cis-1,2-

^{b.} Department of Chemistry, University of Lucknow, Lucknow-226007, INDIA

New Journal of Chemistry Accepted Manuscript

^{a.} Department of Chemistry, University of Delhi, Delhi-110007, INDIA. Email: manojtri@gmail.com;gurmeet123@yahoo.com

⁶ Department of Chemistry & Biochemistry and Centre for Nanoscience, University of Missouri-St. Louis, One University Boulevard, St. Louis, MO 63121-4499, USA. Email: rathn@umsl.edu

[†] Electronic supplementary information (ESI) available: full crystallographic data; additional crystal structure figures. CCDC 1543220 for 2, respectively. For ESI and crystallographic data in CIF or other electronic format see OI: 10.1039/b0000000x/

bis(diphenylphosphino) ethylene copper(I) complexes has emerged from the finding that little had been explored in respect to the binuclear structural form of its complexes with simple salts, particularly copper(I) salts and their application in catalysis¹⁴. Previous reports of simple CuX: dppet (1:1) adducts comprises of: CuI: dppet (1:1) (of the form $[Cu_2(\mu-I)_2(\kappa^2-P,P$ dppet)₂] and [CuI(dppet)(CH₃CN)]¹⁵ but no structural report had been published till date dealing with CuX: dppet (1:1) (X= CN, SCN, Cl, Br). Similar adducts for HAuCl₄: dppet (1.5:1) had been reported by Eggleston and co-workers.¹⁶ Various Cu(I) complexes containing phosphine, N-heterocyclic carbene, imidazole, triazole, hybrid nitrogen-sulfur ligands have been found to be the versatile catalysts.¹⁷ Currently, the serious issue of our generation is the emission of CO₂ which causes global warming and as a consequence imposes serious environmental problems.¹⁸ One of the ways to mitigate this problem is by using carbon dioxide as C₁ building block in organic synthesis because it is an abundant, renewable carbon source and an environmentally friendly chemical reagent.¹⁹ Significant efforts have been devoted towards exploring the technologies for CO₂ transformation, but harsh and severe reaction condition is one of the major limitations to implement these technologies for practical applications.^{19,20} Therefore, the development of efficient catalysts systems for CO₂ utilization under mild conditions is highly desired, especially for real world applications. One of the best strategies for CO₂ conversion is the synthesis of propiolic acids through the C-H bond activation of terminal alkynes with CO₂ as a C₁ building block²¹ because the alkynyl carboxylic acid products can serve as important

ARTICLE

synthetic intermediates²² for further applications in medicinal chemistry as well as in organic synthesis²³ to give coumarins, flavones, aminoalkynes, alkynylarenes, and arylidene oxindoles.24 Several procedures and catalysts, including both homogenous^{21c-e,25} and heterogeneous catalytic^{21a,26} systems, have been developed in this area, but either the reusability problems or synthetic complications limits further application of these catalytic systems. Therefore design and syntheses of efficient, inexpensive, and easy to prepare catalysts for these types of reactions are urgently required. In the past decades, several interesting systems have been reported for metalmediated reductive carboxylation of alkynes²⁷, allenes²⁸, and alkyenes²⁹ with CO₂ to form carboxylic acids or esters. However, most of those systems need either a stoichiometric amount of transition metals as reactants or an excess amount of organometallic reagents for transmetallation processes. An alternative possibility to achieve the catalytic synthesis of carboxylic acid from CO₂ is by direct C-H bond activation and carboxylation. Recently, Nolan's group had reported a goldcatalyzed CO₂ carboxylation of C-H bonds of highly activated arenes and heterocycles.³⁰ The state of the art for the carboxylation of terminal alkynes has recently been published by Gooßen et al..21b which suggests that it is possible to perform carboxylation of terminal alkynes with various copper and silver complexes, even at ppm loadings. Because of our interest in the area of copper chemistry³¹, we decided to investigate the catalytic transformation of CO₂ to carboxylic acids through C-H bond activation and carboxylation of terminal alkynes in the presence copper(I) complexes containing cis-1,2-bis(diphenylphosphino) ethylene (dppet) The results of these investigations are presented herein.

Experimental section

Materials and Physical Measurements

All the synthetic manipulations were performed under oxygen free nitrogen atmosphere. The solvents were purified and dried before use by adopting the standard procedures.³² Copper(I) cyanide, Copper(I) thiocyanate and cis-1.2bis(diphenylphosphino)ethylene (all Aldrich) were used as received. Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyser and data for C, H, N and S are within ±0.4% of calculated values. Infrared spectra were recorded using Perkin-Elmer FT-IR spectrophotometer. Electronic and emission spectra of the complexes were obtained on a Perkin Elmer Lambda-35 and Horiba Jobin Yvon Fluorolog-3 spectrofluorometer, respectively. ¹H, and ³¹P{¹H} NMR spectra were recorded on a JEOL AL-400 FTNMR instrument using tetramethylsilane and phosphoric acid as internal standards, respectively. Mass spectral data were using a Waters micromass recorded LCT Mass Spectrometer/Data system. Electrochemical property of the complexes were measured by cyclic voltammetry using platinum as working electrode and the supporting electrolyte was [NBu₄]ClO₄ (0.1 M) in dichloromethane solution of 0.001

M of complex versus Ag/AgCl at a scan rate of 100 mVs⁻¹. GCMS studies were done with the Shimadzu-2010 instrument containing a DB-5/RtX-5MS-30Mt & 60Mt column of 0.25mm internal diameter. M^+ is the mass of the cation.

Syntheses of the complexes 1 and 2

Complexes 1, and 2 were prepared as follows: 1 mmol of *cis*-1,2-bis(diphenylphosphino)ethylene (dppet) was dissolved in CH₃OH (15 mL), and CH₂Cl₂ (15 mL) and a copper cyanide/thiocyanate (1 mmol) was then added. The resulting solution was refluxed for 24 hours. The resulting solution was filtered and left for slow evaporation. Yellow colour powder and needle shaped crystals for complex 1 and 2 were obtained. Synthesis of $[Cu_2(\mu-CN)_2(\kappa^2-P,P-dppet)_2]$ (1).

Synthesis of $[Cu_2(\mu-CN)_2(\kappa-P,P-dppet)_2]$ (1).

Yield: (0.776 g, 80%). Anal. Calc. for $C_{54}H_{44}N_2P_4Cu_2$: C, 66.74; H, 4.53; N, 2.88. Found: C, 66.82; H, 4.65; N, 2.92. IR (cm⁻¹, nujol):v = 2960, 2923, 2873, 2112 (CN), 1990, 1733, 1650, 1545, 1457, 1437, 1379, 1338, 1314, 1259, 1215, 1172, 1120, 1102 1069, 1025, 926, 879, 800, 746, 691, 662. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 298 K): 7.16-7.39 (m, 40H, J=3.0 Hz, Ph), 7.45-7.62 (m, 2H, CH=CH). ³¹P{¹H}: δ 11.23 (s) (broad). UV/Vis: λ_{max} (ϵ [dm³ mol⁻¹ cm⁻¹]) = 284 (8777), 241 (5028). ESI-MS (m/z): 971.63 (M⁺).

Synthesis of $[Cu_2(\mu$ -SCN)₂(κ^2 -*P*,*P*-dppet)₂] (2).

Yield: (0.725g, 70%). Anal. Calc. for $C_{54}H_{44}N_2P_4S_2Cu_2$: C, 62.55; H, 4.25; N, 2.70; S, 6.18. Found: C, 62.79; H, 4.35; N, 2.78; S, 6.32. IR (cm⁻¹, nujol):v = 3734, 2373, 2341, 2109 (SCN), 2066, 2042, 1652, 1540, 1474, 1431, 1304, 1259, 1182, 1091, 1023, 996, 727, 687, 608. ¹H NMR (δ ppm, 400 MHz, CDCl₃, 298 K): 7.00-7.40 (m, 40H, J=6.8 Hz, Ph), 7.53-7.83 (m, 2H, CH=CH). ³¹P{¹H}: δ 30.03 (s) (sharp). UV/Vis: λ_{max} (ϵ [dm³ mol⁻¹ cm⁻¹]) = 313 (28641), 241 (6017). ESI-MS (m/z): 1035.78 (M⁺).

X-ray structure determination

Intensity data sets for **2** was collected on a Bruker APEX II CCD area detector diffractometer using a graphite monochromated Mo-K α radiation at 100(2) K. ApexII, and SAINT software packages were used for data collection and data integration for **2**.³³ The structure was solved by direct method using SHELXS-97, and refined by full matrix least-squares with SHELXL-2014.³³ The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were treated using appropriate riding models. PLATON was also used for analyzing the intermolecular interactions and stacking distances.³⁴

Structure **2** (CCDC 1543220): $C_{54}H_{44}N_2P_4S_2Cu_2$, M = 1035.99, monoclinic, a = 28.3225(15), b= 9.7812(5), c = 18.6050(9) Å, U = 4820.8(4) Å³, T = 100(2) K, space group C2/c, Z = 4, 70850 reflections measured, 11709 unique (Rint = 0.0719), which were used in all calculations. The final w*R*(*F*²) was 0.0960 (all data).

General Experimental Procedure for Carboxylation of Terminal Alkynes

CuX(X=CN, SCN)/complexes 1-2 (1 mol%) and Cs_2CO_3 (1.5 mmol) were added to DMF (5 mL) in a reaction tube (10 mL). A CO_2 (balloon) and 1 mmol of terminal alkynes were

Published on 04 October 2017. Downloaded by University of Newcastle on 11/10/2017 08:54:41

introduced into the reaction mixture under stirring. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with water (15 mL) and the solid residue was separated *via* centrifugation. The mixture was washed with CH_2Cl_2 and the aqueous layer was acidified with concentrated HCl to pH=1 at low temperature and then extracted with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried over Na_2SO_4 and filtered. The solvent was removed in vacuum to obtain the carboxylic acid products.

Results and discussion

Synthesis

The reactions of CuX (X= CN, SCN) with *cis*-1,2bis(diphenylphosphino)ethylene (dppet) ligand in a dichloromethane: methanol mixture (50:50 V/V) in equimolar ratio under refluxing conditions gave neutral bimetallic complexes with the formulations $[Cu_2(\mu-X)_2(\kappa^2-P,P-dppet)_2]$ (X= CN(1), SCN(2)) in good yield (Scheme 1).



Scheme 1. Synthetic Routes to Complexes 1-2

These complexes are air-stable, non-hygroscopic solids and soluble in dimethylformamide, dimethylsulfoxide and halogenated solvents but insoluble in petroleum ether and diethyl ether. Infrared spectrum of complex 1 exhibited characteristic band corresponding to $\nu C \equiv N$ of the bridging cyanide group at 2112 cm⁻¹ (Fig. S-1, ESI[†]). The appearance only one $\nu C \equiv N$ band indicated the presence of only one type of cyanide bridge between copper(I) centers.³⁵ In 2 the band associated with bridging SCN group appeared at 2109 cm⁻¹ (Fig. S-2, ESI[†]) which is in accordance with those reported in literature for bridging pseudohalide groups.35 In ¹H NMR spectra of the complexes 1, and 2, the -CH=CH protons of dppet ligands resonated as a multiplet in the range of δ 7.45-7.83 ppm. The phenyl ring protons of dppet ligands resonated as a multiplets at δ 7.00-7.40 ppm (Fig. S-3 and S-4, ESI[†]). In the ${}^{31}P{}^{1}H$ NMR spectra of both the complexes showed a single resonance (δ 11.23(1), 30.03(2) ppm) for dppet ligands indicating that all the phosphorus atoms were chemically equivalent (Fig. S-5 and S-6, ESI[†]). This occurs downfield compared to the ^{31}P NMR signal of the free ligand (δ_P for dppet is -21.95 ppm).⁴ The ³¹P-^{63/65}Cu couplings were not resolved.

These chemical shifts are within the range and are comparable to copper(I) complexes containing chelating dppet ligands.⁶ The NMR data for 1 and 2 are consistent with structure showing four equivalent phosphorus atoms. This means that the two different diphosphine bridges indicated in the X-ray structure of 2 (*vide infra*) become chemically similar in solution at room temperature. The electronic absorption spectroscopy in dichloromethane solution shows that both complexes exhibit two bands at 284-313 nm and 241 nm in dichloromethane solution (Fig. 1) which may be attributed to the charge transfer transitions.

DOI: 10.1039/C7NJ03038J

ARTICLE



Fig. 1. UV-Vis spectra of the complexes 1 and 2 in 10⁻³ DCM solution.

Both the complexes were non emissive when excited at 241 nm However, on excitation at 284-313 nm the complexes exhibited one broad emissions at 363-398 nm (Fig. 2). Consistent with the previously reported copper(I) complexes³⁶, we tentatively assigned the emission of these Cu(I) complexes as being a combination of a XLCT, and CC. But LC transitions may be ruled out since metal-metal bonding is negligible and cyanide and thiocyanide has a fairly large band gap. Pike et al.36b reported that the emission band at 392 nm for CuCN should be ascribed to invoke MC transitions of the type $3d \rightarrow (4p, 4s)$. They also reported that the peak broadening for (CuCN)₂₀(pip)₇ (pip = piperazine), compared to that of CuCN, were due to the incorporation of pip ligands and a heterogeneous array of copper(I) centers. Taking the position and broad shape into account, the emission of 1 and 2 may also be reasonable and consistent with the MC transitions influenced by the existence of dppet ligands.³⁶ The redox behaviour of the complexes were studied through cyclic voltammetry (Fig. 3). The cyclic voltammograms of both the complexes were first compared with that of their respective ligand to identify whether any redox phenomenon is arising specifically from the ligand and not from the copper(I) center. The complex 1 shows four quasireversible oxidations at -1.03, -0.574, 0.081 and 1.88 V, respectively. Complex 2 exhibits similar behaviour with four distinct and separate oxidation couples at -0.995, -0.655, 0.760 and 1.55 V. The oxidation wave at 1.55 to 1.88 V corresponds to the copper(I/II) oxidation. The rest of the oxidation waves are arising because of the structure of the chelating ligand which possess C=C π bonds.

Published on 04 October 2017. Downloaded by University of Newcastle on 11/10/2017 08:54:41

DOI: 10.1039/C7NJ03038J Journal Name



Fig. 2. Emission spectra of complexes 1 and 2 in DCM at 284 to 313 nm.



Fig. 3. Cyclic voltammogram for the complexes 1, and 2 in DCM/0.1 M [NBu₄]ClO₄ at 100 mV s^{-1} scan rate.

Crystal Structure

The molecular structure of complex 2 with atomic numbering scheme is presented in Fig. 4. Complex 2 crystallizes in monoclinic system with C2/c space group. The molecular structure of 2 revealed a centrosymmetric dimeric unit with the two thiocyanate groups bridging the two copper centers. The structural chemistry of this copper(I) complex can be compared with that of the analogous copper(I) complexes [Cu(dppet)₂]X for $X=PF_6^5$, BF_4^9 , $CuCl_2^{10}$, $[Cu(\mu-I)(dppet)]_2^{15}$ and others polymorphs of this compound.³⁷ The tetrahedral coordination around the copper atoms is defined by two P atoms of the chelating dppet ligand [Cu-P bond lengths = 2.2520(4) and 2.2495(4) Å] and two thiocyanate groups [S(1)-C(3)= 1.6472(16) Å, N(1)-C(3)= 1.1575(19) Å]. The P1-Cu-P2 bite angle is 90.936(15)°, which is marginally larger than those found in Cu(I) complexes containing dppet ligand.^{5,6,9,10,15} The other bond angles in 2 are rather distorted [N(1)-Cu(1)-

 $P(1)=125.05(4)^{\circ}$, $N(1)-Cu(1)-P(2)=111.35(4)^{\circ}$, P(2)-Cu(1)- $S(1)^{\#1}=118.442(18)^{\circ}$, P(1)-Cu(1)-S(1)^{#1}=104.955(16)^{\circ}]. This is because of the strained four-membered Cu₂(SCN)₂ ring and due to steric hindrance of the dppet ligand.^{5,6,9,10,15} The Cu-S, Cu-N and Cu-P bond distances are 2.3561(4) Å, 1.9524(13) Å and 2.2520(4)-2.2495(4) Å, respectively and are comparable with other copper derivatives with dppet ligand.5,6,9,10,15 The S-C-N bond angle is 179.17(16) which confirmed that thiocyanate groups are linearly coordinated to each copper(I) center. The S-C and C-N bond distances fall in the range of 1.6472(16) Å and 1.1575(19) Å, respectively. These distances are within the reported range.³⁸ The C-C distance in the ethylene bridge is 1.327(2) Å and is within the range reported for the cisethylene bridged structure.^{39,16} The PCH=CHP planes are orthogonal to the copper centers. The dppet ligands adopts essentially the same conformation with a pseudo twofold axis of symmetry lying in the PCH=CHP plane and is perpendicular to C=C. Crystal packing in complex 2 is stabilised by C-H···S hydrogen bond interactions. The contact distance for C-H···S interactions is 3.131Å (See S-10, ESI[†]).



 $\begin{array}{l} \textbf{Fig. 4. Molecular structure of 2. Selected bond lengths [Å] and angles [°]: Cu(1)-N(1) \\ 1.9524(13), Cu(1)-P(2) 2.2495(4), Cu(1)-P(1) 2.2520(4), Cu(1)-S(1)^{il} 2.3561(4), S(1)-Cu(1)^{il} 2.3561(5), S(1)-C(3) 1.6472(16), N(1)-C(3) 1.1575(19), C(1)-C(2) 1.327(2), \\ N(1)-Cu(1)-P(2) 111.35(4), N(1)-Cu(1)-P(1) 125.05(4), P(2)-Cu(1)-P(1) 90.936(15), \\ N(1)-Cu(1)-S(1)^{il} 106.43(4), P(2)-Cu(1)-S(1)^{il} 118.442(18), P(1)-Cu(1)-S(1)^{il} 104.955(16), N(1)-C(3)-S(1) 179.17(16). \end{array}$

Catalytic Performances for the conversion of terminal alkynes into propiolic acids with CO₂

The comparative catalytic activities of the CuX (X=CN, SCN) and Cu(I) complexes (1 and 2) were assessed for CO_2 fixation with terminal alkynes into propiolic acids. In the initial investigation, the carboxylation of phenylacetylene as a model reaction had been performed to study the influence of various solvents, loadings, bases and reaction times on the reaction. It can be seen that, without copper source, no reaction taken place (Table 1, entry 1). Also no reaction occurred in the presence of isolated dppet and dppe ligands (entry 2 & 3). Table 1 shows the generation of 3-phenylpropiolic acid from CO₂ (1 atm) and phenylacetylene at room temperature in the presence of CuX (X = CN, SCN) as well as complexes 1 and 2. The yield in DMF was found to be higher in comparison to those obtained in DMSO, CH₃CN, chloroform, NMP, 1,4-dioxane (entry 4, 8-12). We have also checked the effects of catalyst loadings on the outcome of the reaction in the presence of 1, 2, 3 and 5

Journal Name

mol% of CuCN (entry 4-7). For 1 mol% of CuCN, 3phenylpropiolic acid was obtained in good yields (50%). However, significant decrease in yield was observed with increase in the catalyst amount to 5 mol%. As shown in Table 1, complexes 1 and 2 exhibited higher catalytic activity in comparison to CuX (X=CN, SCN). Furthermore, the catalytic performance of CuX (X=CN, SCN) containing 1,2bis(diphenylphosphino)ethane (dppe) was evaluated under identical conditions. Interestingly, the CuX (X=CN, SCN) containing dppe showed lower catalytic activity (entry 13 & 14). The catalytic activity of 1 was relatively inferior in comparison to 2. The yield dropped to 27% when the base was changed to K₂CO₃ under similar conditions (entry 18). The other bases screened, NaOH, KOH, CsOH·H₂O, and Na₂CO₃, resulted in poor yields (entry 19 to 22). This indicates that Cs₂CO₃ is a superior base for this direct carboxylation reaction of terminal alkynes with CO₂. With the optimized conditions (1.5 equiv Cs₂CO₃, 1 atm CO₂, DMF, 1 mol% catalyst, 25°C) in hand, several typical alkyne substrates were subjected to this carboxylation reaction (Table 2).

Table 1. Synthesis of 3-phenylpropiolic acid from CO_2 and Phenylacetylene with catalysts CuX(X=CN, SCN) and complexes 1-2.^a

	$\rightarrow = + \operatorname{CO}_2 \frac{\operatorname{CuX/Complex 1-2}}{\operatorname{HCl}}$		Соон
Entry	Catalyst	Solvent	Yield (%) ^b
1.	No catalyst	DMF	0
2.	dppet	DMF	0
3.	dppe	DMF	0
4.	1 mol% CuCN	DMF	50
5.	2 mol% CuCN	DMF	40
6.	3 mol% CuCN	DMF	25
7.	5 mol% CuCN	DMF	20
8.	1 mol% CuSCN	CH ₃ CN	20
9.	1 mol% CuSCN	DMSO	35
10.	1 mol% CuSCN	NMP	10
11.	1 mol% CuSCN	Dioxane	5
12.	2 mol% CuSCN	CHCl ₃	10
13.	1 mol% CuCN/1 equiv. dppe	DMF	25
14.	1 mol% CuSCN/1 equiv. dppe	DMF	30
15.	1 mol% complex 1	DMF	91
16.	1 mol% complex 2	DMF	97
°17.	1 mol% complex 2	DMF	0
^d 18	1 mol% complex 2	DMF	70
°19	1 mol% complex 2	DMF	5
^f 20	1 mol% complex 2	DMF	4
^g 21	1 mol% complex 2	DMF	4
^h 22	1 mol% complex 2	DMF	3

^aReaction conditions: Phenylacetylene (1.0 mmol), catalyst, Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 25°C, solvent (5 mL), 12 h. ^bYield of isolated product. ^cIn absence of CO₂. ^dK₂CO₃. ^cNaOH. ^fKOH. ^gNa₂CO₃. ^hCsOH.H₂O

Under standard conditions, the corresponding products were obtained in excellent yields (91-97%) when aromatic alkynes with either electron-donating ($-CH_3$, $-OCH_3$) or electron-withdrawing (-Cl, -F, $-NO_2$) substituent's were employed. With non-phenylacetylene-based alkynes such as

cyclohexylacetylene, ethynyltrimethylsilane, 1-heptyne and 1-hepten-6-yne, the desired yield was 91-95%. In comparison to the previously reported carboxylation methods for catalysis of the carboxylation of terminal alkynes,^{40.41} the present Cu(I) complexes (1 and 2) appear to be more efficient than diPhPhen-Cu(PPh₃)₂NO₃^{40a} and P(NHC)_{0.5}(NHC-CuCl)_{0.5}^{40b}.

Table 2. Synthesis of propiolic acid derivatives from $\rm CO_2$ and terminal alkynes with complex 2.



^aReaction conditions: alkyne (1.0 mmol), complex **2** (1 mol%), Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 25°C, DMF (5 mL), 12 h. ^bYield of isolated product.

It is known that copper acetylide is the key intermediate for copper-catalyzed C-H activation of terminal alkynes and the

DOI: 10.1039/C7NJ03038J

Journal Name

ARTICLE

Cu-C bond is active for CO₂ insertion.⁴⁰⁻⁴¹ A possible reaction mechanism for copper-catalyzed carboxylation of terminal alkynes with CO₂ is proposed in Fig. 5. The copper center activates the terminal alkyne with a base to form the copper acetylide intermediate. Afterwards CO2 inserts into the C-Cu bond to form the carboxylic acid products, as previously proposed.21c,21e



Fig. 5. The proposed reaction mechanism for Cu(I) complex catalyzed C-H activating carboxylation of terminal alkynes with CO₂

Conclusions

Published on 04 October 2017. Downloaded by University of Newcastle on 11/10/2017 08:54:41

In summary, we have synthesized and characterized two Cu(I) complexes containing dppet ligand and successfully established the reaction conditions where copper(I) complexes comprising of dppet ligand catalysed the transformation of CO2 to carboxylic acids through C-H bond activation of terminal alkynes. Various propiolic acids were synthesized in excellent yields under ambient conditions. The most remarkable advantage of this mild reaction system is its tolerance towards a wide substrate scope. This protocol opens up the access to a pool of highly functionalized propiolic acids from CO₂.

Acknowledgements

This project was financially supported by the Department of Science and Technology, New Delhi, India (Grant No. SR/FT/CS-104/2011). We acknowledge funding from the National Science Foundation (CHE0420497) for the purchase of the APEX II diffractometer. The authors sincerely thank the reviewers for their valuable suggestions and Prof. Pedro Valerga from Universidad de Cádiz, Spain for his kind encouragement.

Notes and references

- F.A. Cotton, K.R. Dunbar, M.G. Verbruggen, J. Am. Chem. 1 Soc. 1987, 109, 5498.
- 2 R.J. Puddephatt. Chem. Soc. Rev. 1983. 12, 99.
- 3 R.V. Kiress, R. Eisenberg, Inorg. Chem. 1989, 28, 3372.

- E.M. Mothi, H. Stoeckli-Evans, K. Panchanatheswaran, Synth. React. Inorg. Met-Org. Nano-Met. Chem. 2016, 46, 1371
- 5 S.J. Berners-Price, C. Brevard, A. Pagelot, P.J. Sadler, Inorg. Chem. 1985, 24, 4278.
- S.J. Berners-Price, L.A. Colquhoun, P.C. Healy, K.A. Byriel, 6 J.V. Hanna, J. Chem. Soc., Dalton Trans. 1992, 3357.
- S.J. Berners-Price, P.J. Sadler, Inorg. Chem. 1986, 25, 3822.
- P.C. Healy, B.T. Loughrey, G.A. Bowmaker, J.V. Hanna, Dalton Trans. 2008, 3723.
- P.C. Healy, B.T. Loughrey, M.L. Williams, Acta Crystallogr. 2009, E65, m500.
- 10 P.C. Healy, J.C. McMurtrie, J. Bouzaid, Acta Crystallogr. 2010, E66, m493.
- D. Franzoni, G. Pelizza, G. Predieri, P. Tarasconi, C. Pellizi, 11 Inorg. Chim. Acta 1988, 150, 279.
- 12 C. Pettinari, A. Marinelli, A. Pizzabiocca, Effendy, B.W. Skelton, A.H. White, Inorg. Chem. Commun. 2009, 12, 55.
- 13 P.C. Healy, B.T. Loughrey, M.L. Williams, P.G. Parsons, J. Inorg. Biochem. 2010, 104, 625.
- 14 (a) P.T. Maragh, Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., 2009, 105, 416; (b) M. Akita, M. Hashimoto, S. Hikichi. Moro-oka Organometallics 2000, 19, 3744; (c) A. Correa, Ni- and Fe-Based Cross-Coupling Reactions. (Ed.), 2017.
- 15 P. Aslanidis, P.J. Cox, S. Divanidis, P. Karagiannidis,
- Inorganica Chimica Acta, 2004, **357**, 1063. 16 D.S. Eggleston, J.V. McArdle, G.E. Zuber, J. Chem. Soc. Dalton Trans. 1987.677.
- 17 (a) V. Rampazzi, A. Massard, P. Richard, M. Picquet, P.L. Gendre, J.-C. Hierso, ChemCatChem 2012, 4, 1828; (b) A.J. Blake, N.R. Brooks, N.R. Champness, L.R. Hanton, P. Hubberstey, Martin Schröder, Pure and Appl. Chem., 1998, 70, 2351; (c) S.-Q. Bai, J.Y. Kwang, L.L. Koh, D.J. Young, T.S. Andy Hor, Dalton Trans. 2010, 39, 2631; (d) S.-Q. Bai,L. Jiang, J.-L. Zuo, T.S. Andy Hor, Dalton Trans. 2013, 42, 11319; (e) S.-Q. Bai, A.M. Yong, J.J. Hu, D.J. Young, X. Zhang, Y. Zong, J. Xu, J.-L. Zuo, T.S. Andy Hor, CrystEngComm, 2012, 14, 961;(f) M. Beaupérin, E. Fayad, R. Amardeil, H. Cattey, P. Richard, S. Brandès, P. Meunier, J.-C. Hierso, Organometallics 2008, 27, 1506; (g) M. Beaupérin, E. Fayad, R. Amardeil, H. Cattey, P. Richard, S. Brandès, P. Meunier, J.-C. Hierso. Organometallics 2008, 27, 1506.
- 18 M. Pervaiz, M. M. Sain, Resour. Conserv. Recycl. 2003, 39, 325.
- 19 (a) R. Zevenhoven, S. Eloneva, S. Teir, Catal. Today, 2006, 115, 73; (b) M. Aresta, A. Dibenedetto, I. Tommasi, Energy Fuels, 2001, 15, 269; (c) P. Tundo, M. Selva, Acc. Chem. Res. 2002, 35, 706; (d) G.A. Olah, Angew Chem., Int Ed. 2005, 44, 2636; (e) T. Aida, S. Inoue, Acc. Chem. Res. 1996, 29, 39; (f) S.N. Riduan, Y. Zhang, Dalton Trans. 2010, 39, 3347.
- 20 (a) H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G. J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 2001, 101, 953; (b) T. Sakakura, J.C. Choi, H. Yasuda, Chem. Rev. 2007, 107, 2365; (c) D.J. Darensbourg, Chem. Rev. 2007, 107, 2388; (d) N. Eghbali, C.-J. Li, Green Chem. 2007, 9, 213; (e) S.N. Riduan, Y. Zhang, J.Y. Ying, Angew Chem. Int. Ed. 2009, 48, 3322; (f) T. Sakakura, K. Kohon, Chem. Commun. 2009, 1312; (g) L. Gu, Y. Zhang, J. Am. Chem. Soc. 2010, 132, 914; (h) T. Kubota, I. Hayakawa, H. Mabuse,

6 | J. Name., 2012, 00, 1-3

This journal is C The Royal Society of Chemistry 20xx

K. Mori, K. Ushikoshi, T. Watanabe, Masahiro Saito, *Appl. Organomet. Chem.* 2001, **15**, 121; (*i*) I. Omae, *Catal. Today*, 2006, **115**, 33.

- 21 (a) D.Y. Yu, M.X. Tan, Y.G. Zhang, Adv. Synth. Catal. 2012, 354, 969; (b) F. Manjolinho, M. Arndt, K. Gooßen, L.J. Gooßen, ACS Catal. 2012, 2, 2014; (c) M. Arndt, E. Risto, T. Krause, L.J. Gooßen, ChemCatChem 2012, 4, 484; (d) D.Y. Yu, Y.G. Zhang, Green Chem. 2011, 13, 1275; (e) X. Zhang, W.Z. Zhang, X. Ren, L.L. Zhang, X.B. Lu, Org. Lett. 2011, 13, 2402; (f) K. Inamoto, N. Asano, K. Kobayashi, M. Yonemoto, Y. Kondo, Org. Biomol. Chem. 2012, 10, 1514; (g) W. Zhang, W. Li, X. Zhang, H. Zhou, X.B. Lu, Org. Lett. 2010, 12, 4748; (h) Y. Fukue, S. Oi, Y. Inoue, J. Chem. Soc. Chem. Commun. 1994, 2091; (i) Z. Wu, L. Sun, Q. Liu, X. Yang, X. Ye, Y. Hub, Y. Huang, Green Chem., 2017,19, 2080; (i) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, Angew. Chem., Int. Ed., 2011, 50, 8510; (k) H. Cheng, B. Zhao, Y. Yao, C. Lu, Green Chem., 2015, 17, 1675; (1) J. Jover, F. Maseras, J. Org. Chem., 2014, 79. 11981.
- 22 (a) A. Correa, R. Martin, Angew. Chem. Int. Ed. 2009, 48, 6201-6204; Angew. Chem. 2009, 121, 6317; (b) F. Lehmann, L. Lake, E.A. Currier, R. Olsson, U. Hacksell, K. Luthman, Eur. J. Med. Chem. 2007, 42, 276; (c) D. Bonne, M. Dekhane, J. Zhu, Angew. Chem. Int. Ed. 2007, 46, 2485; Angew. Chem. 2007, 119, 2537; (d) D.M. D_Souza, A. Kiel, D.P. Herten, F. Rominger, T.J.M_ller, Chem. Eur. J. 2008, 14, 529.
- 23 (a) J. Moon, M. Jeong, H. Nam, J. Ju, J.H. Moon, H.M. Jung,
 S. Lee, Org. Lett. 2008, 10, 945; (b) J. Moon, M. Jang, S.
 Lee, J. Org. Chem. 2009, 74, 1403; (c) W. Jia, N. Jiao, Org.
 Lett. 2010, 12, 2000.
- 24 (a) B.M. Trost, F.D. Toste, K. Greenman, J. Am. Chem. Soc. 2003, 125, 4518; (b) T. Kitamura, Eur. J. Org. Chem. 2009, 1111; (c) M. Bararjanian, S. Balalaie, F. Rominger, B. Movassagh, H.R. Bijanzadeh, J. Org. Chem. 2010, 75, 2806; (d) A.V. Dubrovskiy, R.C. Larock, Org. Lett. 2010, 12, 3117.
- 25 (a) L.J. Gooßen, N. Rodríguez, F. Manjolinho, P.P. Lange, Adv. Synth. Catal. 2010, **352**, 2913; (b) D.Y. Yu, Y.G. Zhang, Proc. Natl. Acad. Sci. USA 2010, **107**, 20184.
- 26 X.-H. Liu, J.-G. Ma, Z. Niu, G.-M. Yang, P, Cheng, Angew. Chem. Int. Ed. 2015, 54, 988.
- 27 (a) M. Aoki, M. Kaneko, S. Izumi, K. Ukai, N. Iwasawa, *Chem. Commun.* 2004, 2568; (b) J. Louie, J.E. Gibby, M.V. Farnworth, T.N. Tekavec, *J. Am. Chem. Soc.* 2002, **124**, 15188.
- 28 (a)M. Takimoto, Y. Nakamura, K. Kimura, M. Mori, J. Am. Chem. Soc. 2004, **126**, 5956; (b) C.M. Williams, J.B. Johnson, T. Rovis, J. Am. Chem. Soc. 2008, **130**, 14936.
- 29 J. Takaya, N. Iwasawa, J. Am. Chem. Soc. 2008, 130, 15254.
- 30 I.I.F. Boogaerts, S.P. Nolan, J. Am. Chem. Soc. 2010, 132, 8858.
- 31 (a) M. Trivedi, G. Singh, A. Kumar, N.P. Rath, *Dalton Trans.* 2015, **44**, 20874;(b) M. Trivedi, Bhaskaran, A. Kumar, G. Singh, A. Kumar, N.P. Rath, *New J. Chem.* 2016, **40**, 3109.
- 32 B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell, 4th Edn., *Vogel,s Textbook of Practical Organic Chemistry*, Longman, London, 1978.
- 33 G.M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112.
- 34 (a) G.M. Sheldrick, SHELX-97; Programme for Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany, 1997; (b) PLATON, A.L. Spek, Acta Cryst. 1990, 46A, C34.
- 35 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edn., Wiley, New York 1981.
- 36 (a) P.C. Ford, E. Čariati, J. Bourassa, *Chem. Rev.* 1999, **99**, 3625; (b) R.D. Pike, K.E. deKrafft, A.N. Ley, T.A. Tronic, *Chem. Commun.* 2007, 3732;(c) A. Hiromi, T. Kiyoshi, S.

Yoichi, I. Shoji, K. Noboru, *Inorg. Chem.* 2005, **44**, 9667; (*d*) C. Kutal, *Coord. Chem. Rev.* 1990, **99**, 213; (*e*) W.F. Fu, X. Gan, C.M. Che, Q.Y. Cao, Z.Y. Zhou, N.N.Y. Zhu, *Chem. Eur. J.* 2004, **10**, 2228; (*f*) S. Hu, A.-J. Zhou, Y.-H. Zhang, S. Ding, M.-L. Tong, *Crystal Growth & Design*, 2006, **6**, 2543.

- 37 (a) G.A. Bowmaker, J.V. Hanna, R.D. Hart, B.W. Skelton, A.H. White, *Dalton Trans.*, 2008, 5290; (b) C. Pettinari, C.d. Nicola, F. Marchetti, R. Pettinari, B.W. Skelton, N. Somers, A.H. White, W.T. Robinson, M.R. Chierotti, R. Gobetto, C. Nervi, *Eur. J. Inorg. Chem.* 2008, 1974; (c) S.K. Chawla, M. Arora, K. Nättinen, K. Rissanen, *Polyhedron*, 2006, **25**, 627.
- 38 C.d. Nicola, C. Pettinari, M. Ricciutelli, B.W. Skelton, N. Somers, A.H. White, *Inorg. Chim. Acta* 2005, **358**, 4003.
- 39 P.G. Jones, Acta Crystallogr., Sect. B, 1980, 36, 2775.
- 40 (a) L.J. Gooßen, N. Rodríguez, F. Manjolinho, P.P. Lange, Adv. Synth. Catal., 2010, 352, 2913;(b) D. Yu, Y. Zhang, Proc. Natl. Acad. Sci. U. S. A., 2010, 107, 20184; (c) J.-N. Xie, B. Yu, Z.-H. Zhou, H.-C. Fu, N. Wang, L.-N. He, Tetrahedron Letters 2015, 56, 7059;(d) S. Wang, G. Dua, C. Xi, Org. Biomol. Chem., 2016, 14, 3666.
- 41 (a) G.W. Ebert, W.L. Juda, R.H. Kosakowski, B. Ma, L. Dong, K.E. Cummings, M.V.B. Phelps, A.E. Mostafa, J. Luo, J. Org. Chem. 2005, 70, 4314; (b) A.S. Hay, J. Org. Chem. 1962, 27, 3320; (c) Y. Fukue, S. Oi, Y. Inoue, Chem. Commun. 1994, 2091-2091; (d) T. Tetsuo, U. Kazuo, S. Takeo, Chem. Commun. 1974, 380; (e) S. Adimurthy, C.C. Malakar, U. Beifuss, J. Org. Chem. 2009, 74, 5648.

Graphical Abstract: Synopsis and Pictogram

Copper(I) complexes $[Cu_2(\mu-CN)_2(\kappa^2-P,P-dppet)_2](1)$, and $[Cu_2(\mu-SCN)_2(\kappa^2-P,P-dppet)_2]$ (2), were prepared using CuX (X= CN, SCN) and *cis*-1,2-bis(diphenylphosphino)ethylene (dppet) in 1:1 molar ratio in DCM-MeOH (50:50 V/V) under reflux. Complexes 1-2 were shown to be efficient catalysts in comparison to CuCN/CuSCN for the conversion of terminal alkynes into propiolic acids with CO₂ at room temperature.

