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1,1′-bis(di-*tert*-butylphosphino) ferrocene copper(I) complex catalyzed C-H activation and carboxylation of terminal alkynes

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Four copper(I) complexes [CuBr(dtbpf)] (**1**), [CuI(dtbpf)] (**2**), [$Cu_4(\mu_2$-I)$_2(\mu_3$-I)$_2(\mu$-dtbpf)$_2$] (**3**) and [$Cu_6(\mu_3$-I)$_6(\mu$-dtbpf)$_2$].2CH$_3$CN (**4**), were prepared using CuX (X= Br, I) and 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf). These complexes have been characterized by elemental analyses, IR, ^{1}H and ^{31}P NMR, ESI-MS and electronic absorption spectroscopy. Molecular structures of the complexes **2** and **4** were determined crystallographically. Complex **2** is the first monomeric isolated Cu(I) complex of dtbpf with largest P-Cu-P bite angle (120.070(19)°) to date. Complex **4** shows a centrosymmetrical dimeric unit with two [$Cu_3(\mu_3$-I)$_3$] motifs bridged by two bidentate dtbpf ligands in κ^1-manner. Each [$Cu_3(\mu_3$-I)$_3$] motifs unites to form a pyramid with one copper atom at the apex and one of the triangular faces capped by an iodine atom. All the complexes were found to be efficient catalysts for the conversion of terminal alkynes into propiolic acids with CO_2. Owing to the excellent catalytic activity, the reactions proceed at atmospheric pressure and ambient temperature (25°C). The catalytic products were obtained in moderate to good yields (80-96%) by using complex loading to 2 mol%. To the best of our knowledge, this is the first example of an active ferrocenyl diphosphines Cu(I) catalyst for the carboxylation of terminal alkynes with CO_2.

Introduction

Ferrocenyl diphosphines have received considerable attention because of their extensive applications as ligands for a wide variety of transition metal catalyzed transformations.[1] There are many different types of ferrocenyl diphosphines, the most common are 1,1′-bis(diphenylphosphino) ferrocene (dppf)[2] and 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf).[2i,3] These ligands have significant advantages over other diphosphines which contain alkyl rather than metallocene-backbones.[4] The advantage of these ligands is that they are capable of stabilizing the metal centre in a variety of states of charge and geometries due to their numerous possible modes of coordination. Recently it has been reported that dtbpf is superior to dppf for the Pd-catalyzed α-arylation of ketones and for certain Pd-catalyzed Suzuki couplings.[5,6] Various Cu(I) complexes containing phosphine, *N*-heterocyclic carbene, imidazole, triazole, hybrid nitrogen-sulfur ligands have been found to be versatile catalysts.[7]

Currently, an urgent issue of our decade is the emission of

CO_2 which causes global warming and a consequent series of environmental problems.[8] One of the ways to mitigate this problem is to use carbon dioxide as an C_1 building block in organic synthesis because it is an abundant, renewable carbon source and an environmentally friendly chemical reagent.[9] The utilization, as opposed to the storage of CO_2, is indeed more attractive especially if the conversion process to useful bulk products is an economical one. Significant efforts have been devoted towards exploring the technologies for CO_2 transformation, whereby harsh and severe reaction conditions are one of the major limitations for their practical applications.[9,10] Therefore, the development of efficient catalyst systems for CO_2 utilization under mild conditions is highly desired, especially for real world applications.

One of the best strategies for CO_2 conversion is the synthesis of propiolic acids through the C-H bond activation of terminal alkynes with CO_2 as a C_1 building block[11] because the alkynyl carboxylic acid products can serve as an important synthetic intermediates[12] for further applications in medicinal chemistry as well as organic synthesis[13] to give coumarins, flavones, aminoalkynes, alkynylarenes, and arylidene oxindoles.[14] Several procedures and catalysts, including both homo-[11c-e,15] and heterogeneous catalytic[11a,16] systems, have been developed in this area, but either reusability problems or synthetic complications limit further application of these catalytic systems. The design and synthesis of efficient, inexpensive, and easily prepared catalysts for this type of reactions are only at the beginning and urgently require further developments. In the past decades, several interesting systems

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have been reported for metal-mediated reductive carboxylation of alkynes[17], allenes[18], and alkyenes[19] with CO_2 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 CO_2 is by direct C-H bond activation and carboxylation. Recently, Nolan's group reported a gold-catalyzed CO_2 carboxylation of C-H bonds of highly activated arenes and heterocycles.[20] The state of the art for the carboxylation of terminal alkynes has recently been published by Gooßen *et al.*.[11] This article suggests that it is possible to perform carboxylations of terminal alkynes with various copper and silver complexes, even at ppm loadings. This motivated us to study the application of these compounds in carbon dioxide fixation reaction. Because of our interests in the area of copper chemistry, we decided to investigate the interaction of CuX (X=Br, I) complexes with 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf). Herein, we also report copper(I) complexes containing 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf) catalyzed transformation of CO_2 to carboxylic acids through C-H bond activation and carboxylation of terminal alkynes. To the best of our knowledge, this is the first example of an active ferrocenyl diphosphines Cu(I) catalyst for the carboxylation of terminal alkynes with CO_2. Various propiolic acids were synthesized in good to excellent yields under ambient conditions. This catalytic system is a simple and economically viable protocol with great potential for practical applications.

Experimental section

Materials and Physical Measurements

All the synthetic manipulations were performed under nitrogen atmosphere. The solvents were dried and distilled before use by following the standard procedures.[21] Copper(I) iodide, Copper(I) bromide, 1,1′-bis(di-*tert*-butylphosphino) ferrocene, Phenylacetylene, 1-Chloro-4-ethynylbenzene, 4-Ethynylanisole, cyclohexylacetylene, Ethynyltrimethylsilane, 4-Ethynyltoluene (all Aldrich) and 4-Nitrophenylacetylene (TRC) were used as received. Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N was within ±0.4% of calculated values. IR(KBr) was recorded using Perkin-Elmer FT-IR spectrophotometer. Electronic and emission spectra for **1**, **2** and **4** were recorded on a Perkin Elmer Lambda-35 and Horiba Jobin Yvon Fluorolog 3 spectrofluorometer, respectively. ^{1}H and ^{31}P NMR spectra were recorded on a JEOL AL-400 FTNMR instrument using tetramethylsilane and phosphoric acid as an internal standard, respectively. Mass spectral data were recorded using a Waters micromass LCT Mass Spectrometer/Data system. Electrochemical properties of the complexes **1**, **2** and **4** were investigated using cyclic voltammetry. Platinum was used as the working electrode and tetrabutylammonium perchlorate (0.1 M) in dichloromethane solution was used as supporting electrolyte in 0.001 M solution of complexes **1**, **2** and **4**. The

measurements were performed against Fc^+/Fc couple 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, 2 and 4

Complexes **1**, **2** and **4** were prepared as follows: 1 mmol of 1,1′-bis(di-*tert*-butylphosphino) ferrocene was dissolved in CH_3OH (15 mL), and CH_2Cl_2 (15 mL) and a copper(I) bromide/iodide (For complex **1** & **2** (1 mmol); **4** (6 mmol)) was then added. The resulting solution was refluxed for 24 hours. The resulting solution was filtered and saturated with hexane/CH_3CN and left for slow evaporation.

Orange block crystals for complex **2** and **4** suitable for X-ray studies were obtained after three days.

Synthesis of [CuBr(dtbpf)] (1). Yield: (0.432 g, 70%). Anal. Calc. for $C_{26}H_{44}BrP_2CuFe$: C, 50.56; H, 7.13. Found: C, 50.88; H, 7.15. IR(cm^{-1}, KBr): ν = 3420, 3100, 3080, 2940, 2920, 2890, 2860, 2360, 2340, 2120, 1720, 1470, 1453, 1380, 1360, 1302, 1180, 1150, 1060, 1040, 938, 898, 850, 829, 810, 740, 630, 601, 580, 548, 490, 471, 440. ^{1}H NMR (δ ppm, 400 MHz, CDCl$_3$, 298K): δ 5.27 (s, 4H, C$_5$H$_4$), 4.44 (s, 4H, C$_5$H$_4$), 1.31 (m, 36H, CH$_3$). ^{31}P{^{1}H}: δ 36.04 (s) (sharp). UV/Vis: λ_{max} (ε[dm^3 mol^{-1} cm^{-1}]) = 367(12770), 240(14620). ESI-MS (m/z): 537.6 (M$^+$).

Synthesis of [CuI(dtbpf)] (2). Yield: (0.531 g, 80%). Anal. Calc. for $C_{26}H_{44}IP_2CuFe$: C, 46.98; H, 6.62. Found: C, 47.02; H, 6.85. IR (cm^{-1}, KBr): ν = 3410, 3098, 2940, 2880, 1640, 1455, 1390, 1360, 1180, 1160, 1040, 940, 815, 591, 540, 491, 460, 438. ^{1}H NMR (δ ppm, 400 MHz, CDCl$_3$, 298K): δ 4.41 (s, 4H, C$_5$H$_4$), 4.40 (s, 4H, C$_5$H$_4$), 1.46 (m, 36H, CH$_3$). ^{31}P{^{1}H}: δ 19.85 (s) (sharp). UV/Vis: λ_{max} (ε[dm^3 mol^{-1} cm^{-1}]) = 364 (27666), 238(9505). ESI-MS (m/z): 537.2 (M$^+$).

Synthesis of [Cu$_4$(μ_2-I)$_2$(μ_3-I)$_2$(κ^1-*P*,*P*-dtbpf)$_2$] (3). This is prepared following our earlier reported method.[24d]

Synthesis of [Cu$_6$(μ_3-I)$_6$(μ-dtbpf)$_2$].2CH$_3$CN (4). Yield: (1.197 g, 85%). Anal. Calc. for $C_{56}H_{94}N_2P_4I_6Cu_6Fe_2$: C, 30.92; H, 4.32; N, 1.29 . Found: C, 31.03; H, 4.48; N, 1.30. IR (cm^{-1}, KBr): ν = 3410, 3098, 2940, 2880, 2860, 1630, 1460, 1385, 1361, 1180, 1160, 1040, 930, 817, 580, 544, 493, 470, 438. ^{1}H NMR (δ ppm, 400 MHz, CDCl$_3$, 298K): δ 4.73 (s, 8H, C$_5$H$_4$), 4.40 (s, 8H, C$_5$H$_4$), 1.36 (m, 72H, CH$_3$), 1.22(s, 6H, CH$_3$). ^{31}P{^{1}H}: δ 28.07 (s) (sharp). UV/Vis: λ_{max} (ε[dm^3 mol^{-1} cm^{-1}]) = 330(67129), 232 (18362). ESI-MS (m/z): 2173.2 (M$^+$).

X-ray structure determination

Intensity data sets for **2** and **4** were collected on a Bruker APEX II CCD area detector diffractometer using graphite monochromatized Mo-Kα radiation at 100(2) K. ApexII, and SAINT software packages were used for data collection and data integration for **2** and **4**.[22] The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-2014.[22] 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.[23]

General Experimental Procedure for Carboxylation of Terminal Alkynes

CuI/complex **1-4** (2 mol%) and Cs_2CO_3 (1.5 mmol) were added to DMF (5 mL) in the reaction tube (10 mL). A CO_2 (balloon) and 1 mmol of terminal alkynes were introduced into the reaction mixture under stirring. The progress of the reaction was monitored by TLC. After completion, 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, 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 afford the acid products.

Results and discussion

Synthesis

All the complexes [CuBr(dtbpf)] (**1**), [CuI(dtbpf)] (**2**), [$Cu_4(\mu_2$-I$)_2(\mu_3$-I$)_2(\mu$-dtbpf$)_2$] (**3**) and [$Cu_6(\mu_3$-I$)_6(\mu$-dtbpf$)_2$].2CH$_3$CN (**4**) were prepared in high yield by the reaction of CuX (X= Br, I) with 1,1′-bis(di-*tert*-butylphosphino) ferrocene ligand in a dichloromethane: methanol mixture (50:50 V/V) in 1:1, 2:1 and in excess (6: 1) under reflux (Scheme 1). Complex **3** was isolated in good yield following our earlier reported method.[24d] Complexes **1-4** were found to be air stable, non-hygroscopic solids and soluble in DMF, DMSO and halogenated solvents but insoluble in petroleum ether and diethyl ether. The positions of different peaks and overall fragmentation patterns in the ESI-MS of the respective complexes are consistent with their formulations. In ^{1}H NMR spectra of the complexes **1**, **2** and **4**, η^5-C_5H_4 protons of dtbpf ligand were observed as two broad singlets in the range of δ 5.27-4.40 ppm (See F-1 to F-3 supporting material). The *tert*-butyl protons of dtbpf were observed as a multiplet at 1.31-1.46 ppm. The ^{31}P NMR spectra of the complexes **1**, **2** and **4** showed a single resonance (δ 36.04(**1**), 19.85(**2**), 28.07 (**4**) ppm) for the dtbpf ligand which suggested that all the phosphorus atoms were chemically equivalent (See F-4 to F-6 supporting material). These chemical shifts were within the accepted range and are comparable to that of the chelating dtbpf ligands (δ_P for dtbpf is 28.2).[21] In the electronic absorption spectra all the complexes exhibited two bands at 328-367 nm and 230-241 nm in dichloromethane solution (Fig. 1). The lower-energy band can be assigned to the MLCT transition. The higher-energy band at 230-241 nm has been assigned to intraligand charge transfer. All the complexes were non emissive on excitation at 328-367 nm however, on excitation at 230-241 nm exhibited two broad emissions at 334-341 nm and 415-419 nm, respectively (Fig. 2). We tentatively assigned the emission of these complexes to XLCT, CC, and LC transitions as dtbpf ligand does not show luminescence in the range of 495-900 nm.
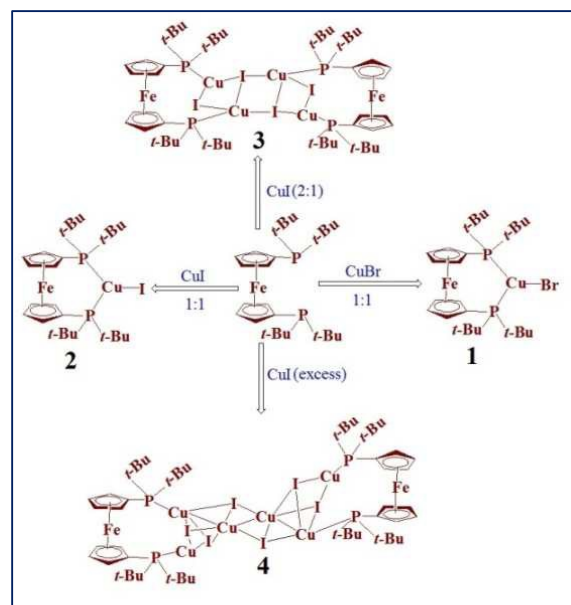
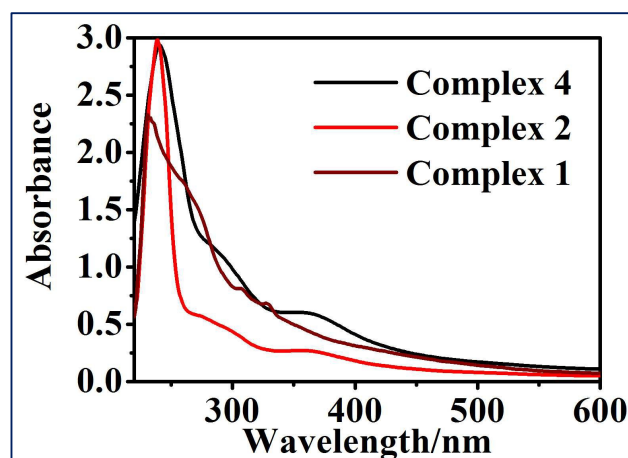Scheme 1. Synthetic routes for the complexes **1-4**.

Fig. 1. Electronic spectra for **1, 2** and **4** in CH_2Cl_2.

The electrochemical properties of the complexes **1, 2** and **4** were studied through cyclic voltammetry (CV) (Fig. 3) and the pertinent electrochemical data are presented in Table 1. The complex **1** exhibits two quasi-reversible redox waves while complexes **2** and **4** exhibit one quasi-reversible redox peak and one single reduction peaks with onset of -0.198 and -0.224 V, respectively with respect to Fc^+/Fc.

Description of the Crystal Structures

Two X-ray structures emerged from the current study. Structural data and refinement details for both the structures are summarized in Table 1 in the SI, and hydrogen bond parameters are presented in Table 2 in the SI, respectively.
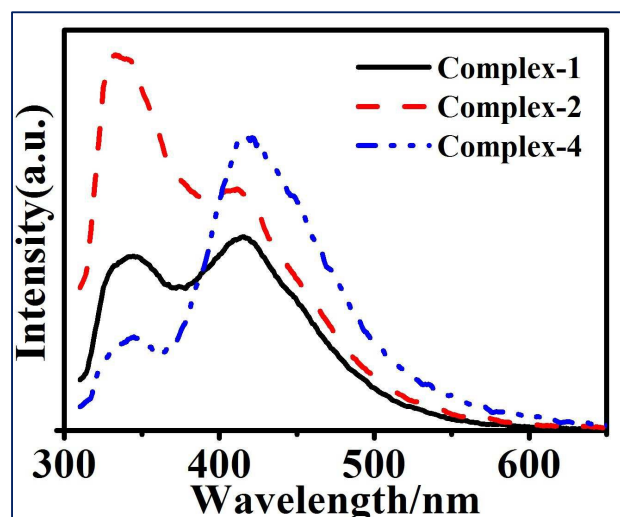
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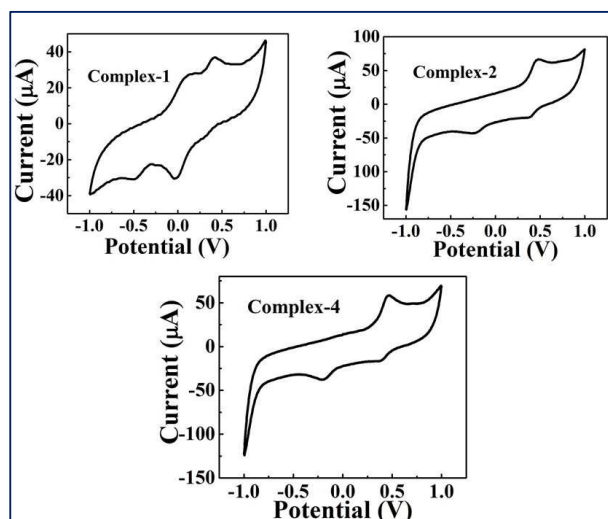
Fig. 2. Emission spectra for **1**, **2** and **4** in CH$_2$Cl$_2$.

Fig. 3. Cyclic voltammogram for the complexes **1**, **2** and **4** in CH$_2$Cl$_2$/0.1 M [NBu$_4$]ClO$_4$ at 100 mV s^{-1} scan rate.

Complex **2** crystallizes in the orthorhombic crystal system, and the structure was solved in space group Pna2$_1$ (Fig. 4).

Table 1. Electrochemical data for **1**, **2** and **4** in dichloromethane solution/0.1 M [NBu$_4$]ClO$_4$ at 298 K.

	Oxidation			Reduction	
	^{a}E$_{pa}$ (1), vs. Fc$^+$/Fc (in CH$_2$Cl$_2$)	^{a}E$_{pa}$ (2),/V		^{b}E$_{pc}$ (1), vs. Fc$^+$/Fc (in CH$_2$Cl$_2$)	^{b}E$_{pc}$ (2),/V
Complex-1	+0.106	+0.41	-	-0.498	-0.025
Complex-2	+0.462	-	-	+0.389	-0.198
Complex-4	+0.483	-	-	+0.373	-0.224
^{a}E$_{pa}$ is the anodic peak potential ; ^{b}E$_{pc}$ is the cathodic peak potential					

X-ray structure for **2** reveals that the copper(I) atom is bonded to two phosphorus atoms of the dtbpf ligand in a trigonal planar environment completed by an iodide [Cu(1)-I(1) 2.5293(3) Å]. The Cu-P distances [Cu(1)-P(1) 2.2540(5) Å, Cu(1)-P(2) 2.2584(5) Å] are slightly longer than those reported for

polynuclear copper(I) complexes with dtbpf ligand.[24c,24d] The bite angle for complex **2** [P(1)-Cu(1)-P(2)] is 120.070(19)°. The bite angle (β$_n$) of diphosphines is defined as the selective chelation angle (P-M-P bond angle) that is determined by the diphosphine ligand backbone (Fig. 5). The bite angle seems to be influenced by several factors such as the central metal atom of the metallocene, groups on the phosphorus atoms, and the complexing metal.
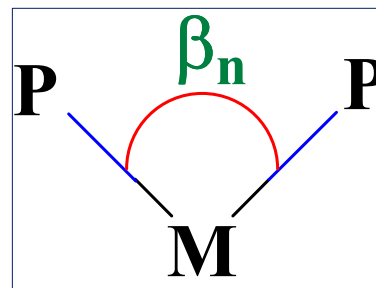

Fig. 5. Bite angle of a diphosphine ligand bound to metal.

A comparison of the P-M-P bite angle of several of these complexes is given in Table 2. To the best of our knowledge, this is the largest bite angle found to date in complexes containing different ferrocenyldiphosphines.[1c,1f,24,27-41] The plane of the bridge defined in **2** by the copper centre and the iodide atoms is almost perpendicular to the plane defined by the two phosphorus atoms. The dihedral angle between these two planes (β) is 89.95°. The two substituted Cp rings in the dtbpf ligand in **2** adopt the antiperiplanar staggered conformation [Cp(centroid)····Fe····Cp(centroid) = 176.97°]. Crystal packing in complex **2** is stabilized by C-H···I weak interactions (See F-7 supporting material). The contact distances for C-H···I interactions are in the range of 3.00-3.32Å. Complex **4** crystallized in the triclinic space group P $\bar{1}$. The structure of complex **4** exhibits a centrosymmetrical dimeric unit with two [Cu$_3$(μ_3-I)$_3$] units bridged by two bidentate dtbpf ligands in κ^1-manner (Fig. 6). Each [Cu$_3$(μ_3-I)$_3$] units forms a pyramid with one copper atom at the apex and one of the triangular faces capped by one iodine atom. Cu(2) is trigonally coordinated to the phosphorus donor [P(2)] of two bridging dtbpf ligands in κ^1-manner and two triple- bridging iodine atoms [I(1) and I(2)] whereas Cu(1) exhibits trigonal bipyramidal coordination and bonded to the phosphorus donor [P(1)] in κ^1-manner, three-bridging iodine atoms[I(1), I(2)and I(3)] and one Cu(3) atom. The Cu(3) atom is octahedrally bonded to four three-bridging iodine atoms[I(1), I(2), I(3)and I(3)$^{\#1}$] and two copper atoms [Cu(1) and Cu(3)]. The Cu-Cu distances are in the range of 2.6661(8) Å-2.9161(6) Å which are shorter than those found in 'cubane' [Cu$_4$X$_4$(PPh$_3$)$_4$] (X = I, Br or Cl)[25] [2.874(5)–3.164(4) Å] and 'step' [Cu$_4$X$_4$(PPh$_3$)$_4$] (X = I or Br) [2.835(3)-3.448(3) Å] and are comparable to [Cu$_4$(μ_2-I)$_2$(μ_3-I)$_2$(μ-dtbpf)$_2$].[24d] The Cu-I-Cu angles are comparable to those in the other similarly related complexes with step and cubane-like structures. The reason for small Cu-I-Cu angles could be due to van der Waals repulsions between the halogen atoms.

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Table 2. Bite angle of metal complexes of ferrocenyldiphosphines.

Complex	Bite angle(°)	Reference
[Cu$_2$(μ-Cl)$_2$(κ^2-P,P-B-dppf)$_2$]	111.24(4)/	1f, 27
	111.2(1)/ 111.26(4)	
[Cu$_2$(μ-Br)$_2$(κ^2-P,P-B-dppf)$_2$]	111.58(5)	27
[Cu$_2$(μ-I)$_2$(κ^2-P,P-B-dppf)$_2$]	111.06(5)	1f, 28
[Cu$_2$(μ-CN)$_2$(κ^2-P,P-B-dppf)$_2$]	115.85(3)	27
[Cu$_2$(μ-SCN)$_2$(κ^2-P,P-B-dppf)$_2$]	112.13(4)	1f, 29
[{Cu(μ-NO$_3$-O)(dppf-P,P')}$_2$]	117.8(1)	1f, 30
[{Cu(μ-O$_2$CH-O,O$'$)(dppf-P,P')}$_2$]	110.8(1)°	1f, 30
[PdCl$_2$(dppf)]	97.98(4)	1d, 31
[PdCl$_2$(dppr)]	100.02(2)	1d, 32
[PdCl$_2$(dppo)]	101.29(4)	1d, 33
[PdCl$_2$(dmpf)]	98.95(9)/99.64(9)	1d, 34
[PdCl$_2$(depf)]	97.74(3)	1d, 33
[PdCl$_2$(dippf)]	103.59(4)	1d, 35
[PtCl$_2$(dippf)]	103.78(5)	1d, 36
[ZnCl$_2$(dippf)]	109.98(2)	1d, 36
[PdCl$_2$(dcypf)]	102.45(3)	1d, 37
[PdCl$_2$(dtbpf)]	104.22(5)	1d, 38
[PdBr(4-CN-C$_6$H$_4$)(dtbpf)]	104.28(5)	1d, 39
[Rh(NBD)(dtbpf)][ClO$_4$]	103.75(5)	1d, 40
[Cu$_2$(μ_2-SCN)$_2$(k^2-P,P-dppdtbpf)$_2$]	112.82(3)	41
[Cu(k^2-P,P-dppdtbpf)(CH$_3$CN)$_2$]PF$_6$	116.36(8)	41
[Pd(k^2-P,P-dppdtbpf)Cl$_2$]	101.37(3)	41

Fig. 6. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: I(1)-Cu(2) 2.5665(4), I(1)-Cu(3) 2.7372(4), I(1)-Cu(1) 2.7647(4), I(2)-Cu(2) 2.5984(4), I(2)-Cu(1) 2.7130(4), I(2)-Cu(3) 2.7160(4), I(3)-Cu(3) 2.6596(4), I(3)-Cu(1) 2.8190(4), Cu(1)-P(1) 2.2402(7), Cu(1)-Cu(3) 2.5969(5), Cu(1)-Cu(2) 2.9161(6), Cu(2)-P(2) 2.2182(8), P(1)-C(11) 1.887(3), P(1)-C(15) 1.896(3), P(2)-C(19) 1.885(3), P(2)-C(23) 1.888(3), C(1S)-N(1S) 1.137(6), C(1S)-C(2S) 1.457(6), Cu(2)-I(1)-Cu(3) 75.241(12), Cu(2)-I(1)-Cu(1) 66.202(13), Cu(3)-I(1)-Cu(1) 56.326(11), Cu(2)-I(2)-Cu(1) 66.562(13), Cu(2)-I(2)-Cu(3) 75.105(13), Cu(1)-I(2)-Cu(3) 57.155(12), Cu(3)$^{\#1}$-I(3)-Cu(3) 61.350(15), Cu(3)-I(3)-Cu(1) 56.499(11), P(1)-Cu(1)-Cu(3) 174.12(3), P(1)-Cu(1)-I(2) 120.48(2), P(1)-Cu(1)-I(1) 122.51(2), I(2)-Cu(1)-I(1) 97.066(14), I(2)-Cu(1)-I(3) 99.118(13), I(1)-Cu(1)-I(3) 97.146(12), P(1)-Cu(1)-Cu(2) 114.06(2), Cu(3)-Cu(1)-Cu(2) 71.731(15), P(2)-Cu(2)-I(1) 127.48(2), P(2)-Cu(2)-I(2) 126.46(2), I(1)-Cu(2)-I(2) 105.262(15), I(3)-Cu(3)-I(2) 103.126(14), I(3)-Cu(3)-I(1) 101.743(14), I(2)-Cu(3)-I(1) 97.653(13), N(1S)-C(1S)-C(2S) 179.7(6).

The comparative catalytic activities of the CuI and Cu(I) complexes (**1-4**) were determined for the fixation of CO$_2$ with terminal alkynes into propiolic acids.In the initial investigation, the carboxylation of phenylacetylene was selected as a model reaction to study the influence of various solvents, loadings and reaction time on the reaction. It can be seen that, without copper source, the system was inefficient (Table 3, entry 1). We have also found that no reaction occurred in the presence of dtbpf ligand (entry 2). Table 3 shows the generation of 3-phenylpropiolic acid from CO$_2$ (1 atm) and phenylacetylene at room temperature in the presence of CuI as well as complex **1-4**. The yield in DMF was found to be higher in comparison to that obtained in DMSO, CH$_3$CN, chloroform, and NMP (entry 4, 7-10). We have also checked the effect of catalyst loadings on the outcome of the reaction in the presence of 1, 2, 3 and 5 mol% of CuI (entry 3-6). For 2 mol% of CuI, 3-phenylpropiolic acid was obtained in good yields (50%). However, no significant increase was observed with increase in the catalyst amount to 5 mol%. The plot of yield *vs.* time for fixation of CO$_2$ with phenylacetylene with complex **2** is presented in Fig. 7. As shown in Table 3, complexes **1-4** exhibited higher catalytic activity compared to CuI. The catalytic activity decreased in the following order: **2**>**4**>**3**>**1**. The high product yields observed in **2** as compared to others may be due to larger bite angle which suggests
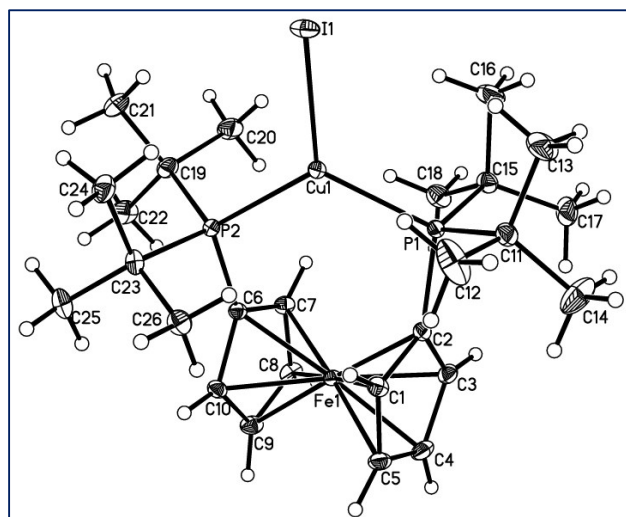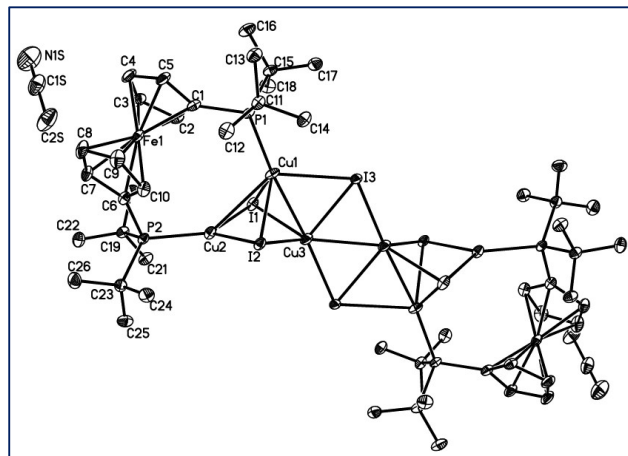

Fig. 4. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: I(1)-Cu(1) 2.5293(3), Cu(1)-P(1) 2.2540(5), Cu(1)-P(2) 2.2584(5), P(1)-C(15) 1.8895(19), P(1)-C(11) 1.898(2), P(2)-C(23) 1.8901(19), P(2)-C(19) 1.8903(19), P(1)-Cu(1)-P(2) 120.070(19), P(1)-Cu(1)-I(1) 119.785(15), P(2)-Cu(1)-I(1) 120.135(15).

The two substituted Cp rings in the dtbpf ligand in **4** adopt the antiperiplanar staggered conformation. Crystal packing in complex **4** is stabilized by C-H···I and C-H···N weak interactions (See F-11 supporting material).

Catalytic Performances for the conversion of terminal alkynes into propiolic acids with CO$_2$

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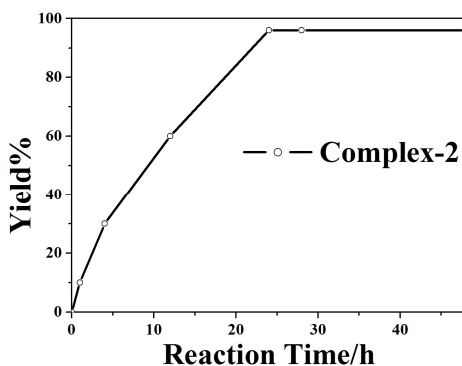Fig. 7. Plots of 3-phenylpropiolic acid yield *vs.* time for the CO_2 fixation reaction of phenylacetylene and CO_2 in the presence of complex **2** as the catalyst.

that the P-Cu-P bite angle plays a crucial role in catalytic activity. The yield dropped to 30% when the base was changed to K_2CO_3 under similar conditions (entry 16).

Table 3. Synthesis of 3-phenylpropiolic acid from CO_2 and Phenylacetylene with catalysts CuI and complexes **1-4**.[a]

Entry	Catalyst	Solvent	Yield (%)[b]
1.	No catalyst	DMF	0
2.	Dtbpf	DMF	0
3.	1 mol% CuI	DMF	21
4.	2 mol% CuI	DMF	50
5.	3 mol% CuI	DMF	50
6.	5 mol% CuI	DMF	52
7.	2 mol% CuI	CH_3CN	20
8.	2 mol% CuI	DMSO	35
9.	2 mol% CuI	NMP	10
10.	2 mol% CuI	$CHCl_3$	10
11.	2 mol% complex **1**	DMF	80
12.	2 mol% complex **2**	DMF	96
13.	2 mol% complex **3**	DMF	90
14.	2 mol% complex **4**	DMF	92
[c]15.	2 mol% complex **4**	DMF	0
[d]16	2 mol% complex **4**	DMF	65

[a]Reaction conditions: Phenylacetylene (1.0 mmol), catalyst, Cs_2CO_3 (1.5 mmol), CO_2 (1.0 atm), 25°C, solvent (5 mL), 24 h. [b]Yield of isolated product. [c]In absence of CO_2. [d]K_2CO_3.

This indicate that Cs_2CO_3 is a superior base for this direct carboxylation reaction of terminal alkynes with CO_2. With the optimized conditions (1.5 equiv Cs_2CO_3, 1 atm CO_2, DMF, 2 mol% catalyst, 25°C) in hand, several typical alkyne substrates were subjected to this carboxylation reaction (Table 4). Under the standard conditions, the corresponding products were obtained in excellent yields (80-96%) when aromatic alkynes with either electron-donating ($-CH_3$, $-OCH_3$) or electron-withdrawing ($-Cl$, $-NO_2$) substituent's were employed. However, for non-phenylacetylene-based alkynes such as cyclohexylacetylene or ethynyltrimethylsilane, the desired yield was 85-90%.

It is known that copper acetylide is the key intermediate for copper-catalyzed C-H activation of terminal alkynes and the Cu-C bond is active for CO_2 insertion.[26]

Table 4. Synthesis of propiolic acid derivatives from CO_2 and terminal alkynes with complex **2**.

Entry	Alkyne	Product	Yield (%)[b]
1.			94
2.			95
3.			96
4.			90
5.			80
6.			85
7.			90

[a]Reaction conditions: alkyne (1.0 mmol), complex **2** (2 mol%), Cs_2CO_3 (1.5 mmol), CO_2 (1.0 atm), 25°C, DMF (5 mL), 24 h. [b]Yield of isolated product.

A possible reaction mechanism for copper-catalyzed carboxylation of terminal alkynes with CO_2 is proposed in F-18, supporting material. The copper center activates the terminal alkyne with a base to form the copper acetylide intermediate. Afterwards CO_2 inserts into the C-Cu bond to form the carboxylic acid products, as previously proposed.[11c,11e]

Conclusions

In summary, we have synthesized and characterized four Cu(I) complexes containing dtbpf ligand in the solid as well as in solution state. We have successfully developed a process where

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copper(I) complexes containing dtbpf ligand catalyze the transformation of CO_2 to carboxylic acids through C-H bond activation of terminal alkynes. Various propiolic acids were synthesized in good to excellent yields under ambient conditions. The most remarkable advantage of this mild reaction system is its tolerance toward a wide substrate scope. This protocol opens up access to a pool of highly functionalized propiolic acids from CO_2.

Acknowledgements

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