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CHEMISTRY
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Copper catalysts

ADAP Ligands as surrogates of NHCs in copper catalysis (ADAP = alkoxydiaminophosphine)

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Abstract: A new family of phosphine ligands containing a five-member ring similar to the popular N-heterocyclic carbene ligands and an alkoxy third substituent has been developed. These alkoxydiaminophosphine ligands (ADAP) can be generated in one pot and reacted with a copper (I) source leading to the high yield isolation of complexes $[(ADAP)CuX]_2$ (X = Cl, Br). The dinuclear nature of these compounds has been established by means of X-ray studies and DOSY experiments. A screening of the catalytic properties of these complexes toward carbene transfer reactions from diazocompounds to C-H bonds (alkane, arene), olefins or N-H bonds, as well as in CuAAC or nitrene transfer reactions have shown a performance at least similar, if not better, than their (NHC)CuCl analogues, opening a new window in copper catalysis with these readily tunable ADAP ligands.

Introduction

Thirty years ago Arduengo reported the isolation of the first N-heterocyclic carbene (NHC), the 1,3-diadamantylimidazol-2-ylidene (Scheme 1).[1] Since then, NHCs emerged as one of the most employed ligands in organometallic chemistry, with implication in synthetic routes and catalytic transformations.[2] In the context of group 11 metals, complexes of type (NHC)MX have been prepared and widely employed as catalysts for a number of transformations.[3] In contrast, ligands containing a related five-member ring with two N bonded to a P donor and a third substituent have been much less studied. Several of those compounds bearing -OR as the third substituent at P have been directly employed as catalysts for several transformations.[4,5] However, there is a reduced number of examples in which such alkoxydiaminophosphines (ADAPs, Scheme 1) are incorporated as ligands in the coordination sphere of transition metals.[6] This is quite surprising since such molecules provide two different sites for steric tuning, i. e., both N-wingtips and –OR as well, the latter also allowing a certain degree of electronic tuning at the P-donor. Moreover, -OR groups also provide an opportunity to design chiral ligands upon employing the appropriate R* group. In the case of coinage metals, we are aware of just one example, a copper complex in which a diphosphine pincer ligand containing a phosphenium cation converts into an ADAP ligand upon reaction with tetrahydrofuran employed as solvent.[7]

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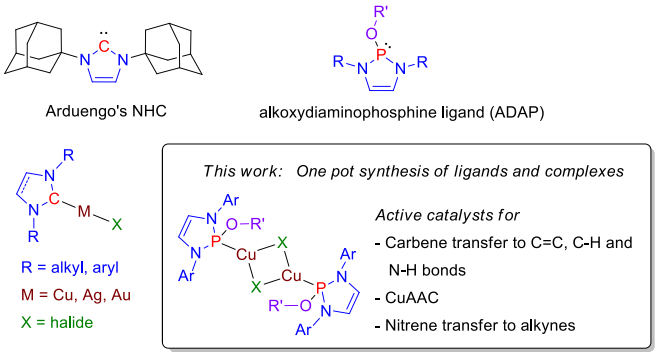


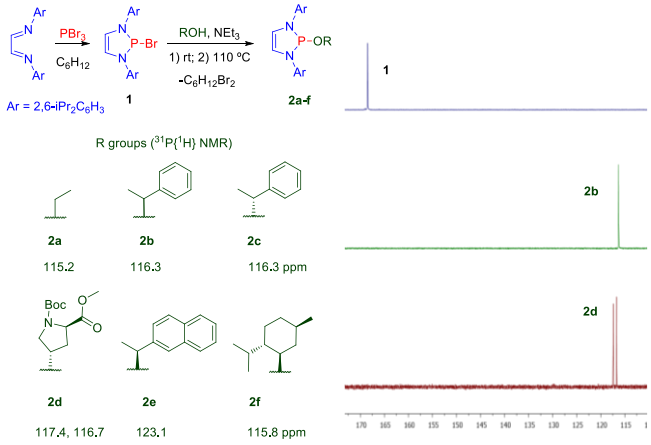
Scheme 1. Left: First NHC ligand isolated and the group 11 metal complexes described and employed as homogenous catalysts. Right: Alkoxydiaminophosphine ligands (ADAP) as surrogates of NHCs.

In view of the well-known catalytic capabilities of the (NHC)Cu moiety toward a series of catalytic transformations (click chemistry, C-H activation, multiple C=C bond activation or borylation reactions, among others),[2,3] we decided to focus on the development of a systematic route for the preparation of alkoxydiaminophosphines-copper complexes, and the screening of their potential use in catalysis. Herein we describe a general and straightforward methodology which allows the one pot preparation of tunable ADAP ligands and their corresponding Cu(I) complexes. Initial catalytic tests have shown that their catalytic properties are comparable to those shown by (NHC)-Cu complexes.

Results and discussion

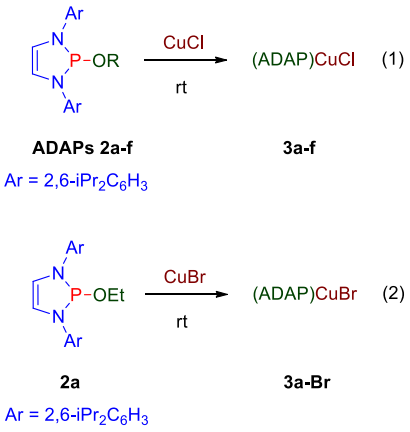
Synthesis of alkoxydiaminophosphine-containing copper(I) complexes. We first designed a strategy to generate a representative library of alkoxydiaminophosphine (ADAP) ligands to be further incorporated to the copper coordination sphere (Scheme 2). Following a procedure described in the literature for N-alkyl substituted ADAPs,[4a,c] we decided to employ 2,6-diisopropylphenyl at the N-wingtips, mimicking one of the most employed NHC ligands, IPr (1,3-bis(diisopropylphenyl)imidazol-2-

ylidene). From bromodiaminophosphine **1**, [8] such family of ADAP ligands **2a-f** can be directly prepared upon addition of several alcohols ROH in the presence of NEt_3 and gently stirring for 12 h at room temperature followed by one additional hour at 110 ºC. The reaction is monitored by $^{31}P\{^1H\}$ NMR spectroscopy, showing the disappearance of the signal of **1** at 168.5 ppm and the appearance of those of ADAPs **2** at higher chemical shifts within the range 116-123 ppm (Scheme 2). It is worth mentioning that for the proline derivative **2d** two singlets are observed, derived from the already reported restriction for nitrogen inversion,[9] leading to two different and observable isomers. The presence of two distinct forms is also detected in the $^{31}P\{^1H\}$ NMR spectrum of the starting alcohol.



Scheme 2. In situ generation of the alkoxydiaminophosphines (ADAPs) ligands **2a-f.**

Albeit the conversion is quantitative, decomposition during workup takes place at variable extent, precluding the isolation of these ligands in useful yields, with the exception of **2b/2c** which could be isolated and characterized by means of its NMR spectra, using short acquisition times to avoid decomposition. The ^1H NMR spectrum (see SI) shows four distinct methinic resonances for the four tertiary C-H bonds of the isopropyl groups of the N-substituted 2,6-diisopropylbenzene fragments, as well as eight



Scheme 3. Synthetic route for complexes (ADAP)CuX (X = Cl, Br).

doublets for the iPr methyl groups, evidencing the lack of any symmetry.

The above procedure allows the generation of clean solutions of ADAP ligands **2a-f**. From this point, we connected the second step in this synthetic sequence: the incorporation of the copper center. This was done by simply adding CuCl to that toluene solution (Scheme 3), stirring at room temperature for several hours, followed by workup leading to the isolation of complexes **3a-f** as off-white solids in 75-90% yields (Scheme 3).

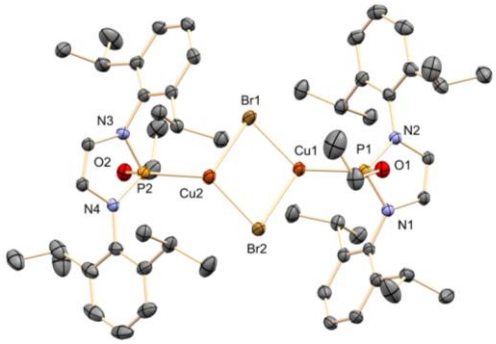


Figure 1. Molecular structure of complex **3a-Br**. Hydrogen atoms have been omitted for clarity.

Spectroscopic and analytical data agreed with the formulation (ADAP)CuCl (see SI). The $^{31}P\{^1H\}$ NMR spectra showed a singlet for complexes **3a-c** and **3e,f**, and two singlets for the proline derivative **3d**. Since attempts to obtain single crystals failed in all cases, we prepared **3a-Br**, the bromine analog of **3a**, which provided crystalline material suitable for X-ray diffraction studies. Figure 1 contains the solid-state structure of the molecules of **3a-Br**, being dinuclear in nature, with the bromine atoms acting as a bridge in a μ^2 fashion. The geometry around the copper center resembles that of the previously described complex $[(PCy_3)Cu(\mu^2\text{-}Br)_2Cu(PCy_3)]$.[10] In **3a-Br** each Cu displays two slightly different distances to both Br, averaging 2.366 and 2.426 Å, respectively. The Cu-P distance of 2.1601(10) Å compares well with that of the PCy_3 analogue (2.191(2) Å). The Cu-Cu distance of 2.9890(6) Å lies above the sum of the van der Waals radius for two copper centers (2.80 Å).

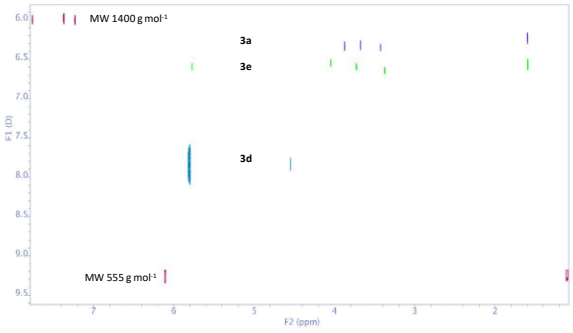
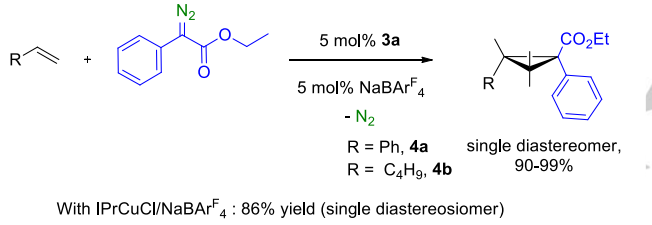


Figure 2. DOSY experiments carried out with **3a**, **3e** and **3d**. The signals in red above and below corresponds to molecular weight of ca. 1400 and 555 g mol^{-1}.

From the crystallographic data of **3a-Br** we have obtained the $\%V_{bur}$ of this ligand, a well-known measurement of the steric hindrance.[11] Using SambVCa software[12] (see SI), a value of $\%V_{bur} = 46$ has been obtained which is slightly smaller than that reported for the IPr ligand in IPrCuCl (47.6) and close to that of SIPr (46.4). in the corresponding SIPrCuCl complex.[13]

The observation of the dinuclear structure for **3a-Br** led us to re-evaluate the series of chloride complexes (ADAP)CuCl, since neither NMR data nor elemental analyses served to ascertain their nuclearity. Thus, we carried out several DOSY experiments in which **2b**, **2d** and **2e** were tested, separately, using two standards with molecular weights approaching those expected for mono- and dinuclear structures. Figure 2 shows the three experiments superimposed, from which it can be inferred that complexes **2b** and **2e** are also dinuclear in solution. The case of complex **2d** is rather distinct, since the observance of the signals in the central region must be interpreted as the consequence of an equilibrium between both mono- and dinuclear structures.

Catalytic behavior of copper complexes 3. With the aim of comparing complexes **3a-f** with their (NHC)CuCl analogues from a catalytic point of view, we have performed a screening of reactions in which the latter have been described as catalysts with noticeable success. It is the case of (a) the catalytic transfer of carbene groups from diazo compounds to unsaturated (olefins)[14] and saturated bonds such as N-H,[14] C_{sp2}-H[15] and C_{sp3}-H; [16] (b) the copper-catalyzed alkyne-azide cycloaddition,[17] and (c) the nitrene transfer to alkynes.[18]



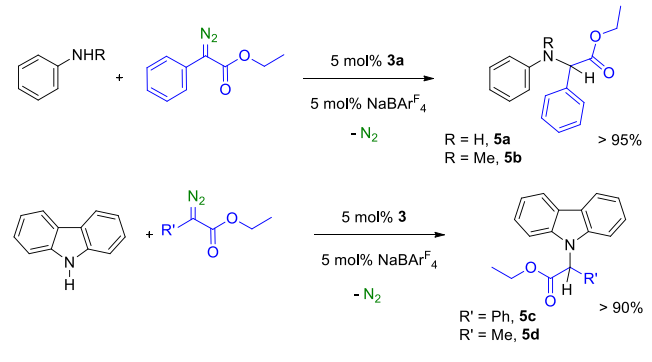
Scheme 4. Olefin cyclopropanation catalyzed by complex **3a**.

(a) Carbene transfer from diazo compounds. We first investigated the benchmark reaction of olefin cyclopropanation, using styrene and 1-hexene as representative alkenes and ethyl 2-diazo-2-phenylacetate (PhEDA) as the carbene source (Scheme 4). The reactions were carried out with complex **3a** as the catalyst, with one equiv of NaBAr$^F_4$ as the halide scavenger, and provided the corresponding cyclopropanes **4a-b** in high yields (90%-99% depending of the rate of diazo addition, see Experimental). Only the *cis*-diastereomer was formed, a feature also observed in previous catalytic systems with coinage metal-based catalysts.[19] The same reaction catalyzed by IPrCuCl gave 86% yield,[19a] with the same single diastereoisomer. Given the presence of one OR substituent at the ADAP ligand, a comparison with the catalytic behavior of a phosphite-containing complex should be made. In a previous work from our laboratory,[19a] the reaction shown in Scheme 4 was carried out with $[[(Ar\text{-}O)_3P]Cu(NCPh)]SbPF_6$ (Ar = 2,4-di-t-butylphenyl). In this case only a 58% yield into the cyclopropane derived from styrene was obtained, at variance with the nearly quantitative yields obtained with the ADAP-containing catalyst **3a**.

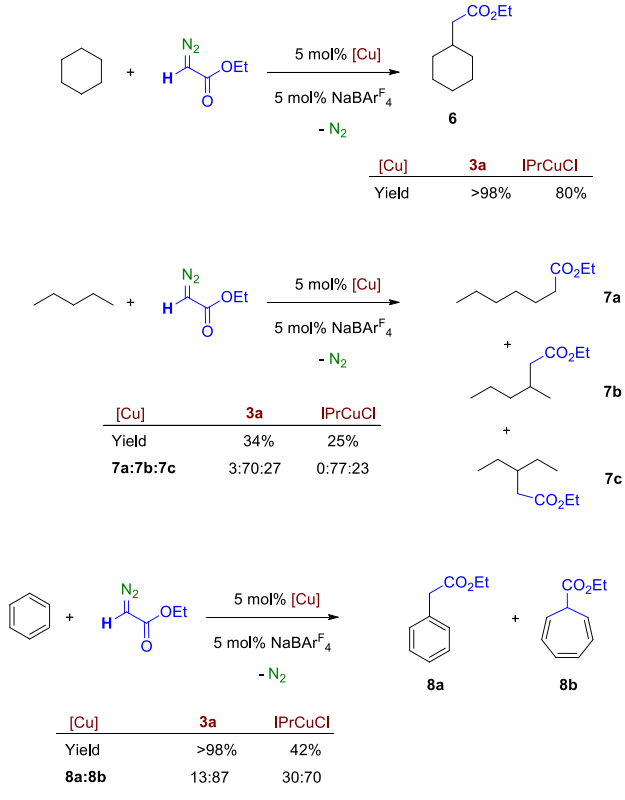
Table 1. Carbazol functionalization by carbene insertion[a]

Entry	Catalyst	R'[b]	% Yield[c]	ee(%)
1	**3a**	Ph	99(87)	-
2	**3a**	Me	96(85)	-
3	**3b**	Ph	99(92)	7
4	**3b**	Me	95(87)	5
5	**3c**	Ph	99(91)	5
6	**3c**	Me	97(81)	2
7	**3d**	Ph	99(87)	2
8	**3d**	Me	96(85)	0
9	**3f**	Ph	99(89)	6
10	**3f**	Me	99(83)	4

[a] Reaction conditions: 0.25 mmol of diazocompound, 1.2 equiv of carbazole, 5 mol % of catalyst, 5 mol % of NaBAr$^f_4$ in 3 mL of CH_2Cl_2 at rt. [b] As in Scheme 5. [c] Based in diazo reagent. Determined by ^{1}H NMR using benzaldehyde as internal standard. Isolated yields in brackets.



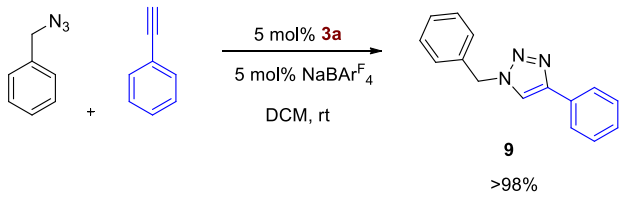
Scheme 5. Amine N-H functionalization by carbene insertion.



Scheme 6. Carbon-hydrogen bond functionalization by carbene insertion.

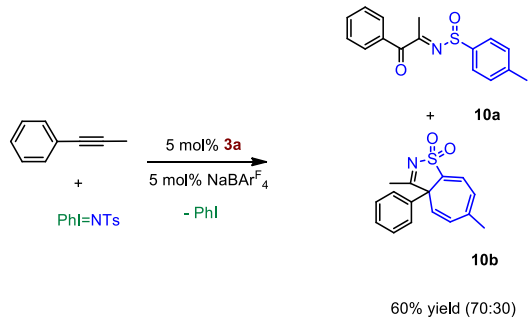
The insertion into N-H bonds of several amines has also been tested using three different substrates and **3a**/NaBAr$^F_4$ as the catalyst, in all cases the quantitative formation of the aminoacid derivatives **5a-c** being observed (Scheme 4). Such conversions are similar to those previously found catalyzed by IPrCuCl.[14] Given the chiral nature of complexes **3c-f**, and the formation of a stereocenter when a disubstituted diazo compound is employed, we used carbazole as the probe to investigate the enantioinduction capabilities of such copper-based catalysts. Using both PhEDA as well as ethyl 2-diazo-2-methylacetate (MEDA) as carbene precursors, the catalysts behaved well in terms of conversions (>90%), albeit very low enantiomeric excesses were observed. It is worth mentioning that the number of successful catalytic systems toward the enantioselective N-H functionalization by carbene insertion is yet quite reduced.[20] Moreover, in this context there are no reports on effective chiral induction using (NHC*)CuX (NHC* = chiral NHC ligand) complexes as catalysts for such transformation.

Carbon-hydrogen bonds have also been targeted with this strategy. The use of **3a**/NaBAr$^F_4$ as catalyst in the reaction of ethyl diazoacetate (EDA) with cyclohexane, pentane or benzene led to the products derived from the formal insertion of the carbene group into the corresponding C_{sp3}-H or C_{sp2}-H bond. Scheme 6 displays a comparison between the performances of **3a** and of IPrCuCl, both with NaBAr$^F_4$ as additive. As a first trend, it is observable that the ADAP-containing catalyst provided higher yields than the NHC analogue.[15,16] With cyclohexane and benzene only the functionalization products were observed using **3a**, whereas IPrCuCl gave 80 and 42% yields, the remaining of the initial EDA being converted in a mixture of diethyl fumarate and maleate, because of the catalytic dimerization of two carbene groups.[21] In the case of pentane, the yields are lower, 34% for **3a** and 25% for IPrCuCl, of the mixture of three products derived from the insertion reaction. The regioselectivity is similar regarding the secondary C-H bonds but **3a** provides low, but detectable amounts of the linear product, which it is not observed with the IPr-containing catalyst. Finally, the reaction with benzene originates a mixture of two products **8a** and **8b**, respectively derived from the formal insertion of the carbene group into the C_{sp2}-H bond[15,16] and the Buchner reaction.[22] The higher yields promoted by **3a** led to an enriched mixture into **8b**, the relative amount of the latter being lower with IPrCuCl as the catalyst.



Scheme 7. CuAAC reaction catalyzed by **3a**.

(b) Copper-catalyzed azide-alkyne cycloadditions (CuAAC). In view of the excellent results obtained in the field of CuAAC with copper (I) complexes containing NHC ligands, [23] particularly cationic [(NHC)$_2$Cu]$^+$X$^-$,[23d] we decided to employ our ADAP-containing complex **3a** toward that end, in the presence of halide scavengers to favor the in situ formation of a cationic species. The reaction of benzyl azide with phenyl acetylene was carried out at room temperature in dichloromethane leading to the exclusive formation of triazole **9** (Scheme 7) as the unique product detected by NMR after 4 h. This result is superior to the reported conversions for the same reaction using IPrCuCl (< 30%)[23] albeit it is of note that other (NHC)CuCl complexes also led to quantitative conversions.[23]]



Scheme 8. Alkyne functionalization by nitrene transfer catalyzed by **3a**.

*(b) Nitrene transfer to alkynes catalyzed by ADAP-containing **3a**.* In a recent work from our group we found that several copper-based complexes catalyzed the transfer of the nitrene NTs (Ts = p-toluenesulfonamide) to alkynes, leading to the formation of two main products, sulfinamides and isothiazoles.[18] A trispyrazolylborate copper catalyst gave the best results, although IPrCuCl also proved active in this transformation. With the probe reaction of 1-phenyl-1-propyne and PhI=NTs (Scheme 8) we have tested the capabilities of complex **3a**. A 60 % yield into a mixture of products **10a** and **10b** was obtained, with a respective 70:30 ratio. The use of IPrCuCl had led[18] to 42% yield and 80:20 ratio, thus **3a** being more productive in this case.

Conclusions

A novel protocol which provides the one-pot generation of a family of alkoxydiaminophosphine ligands (ADAP) and subsequent formation of copper complexes of formulae (ADAP)CuCl are reported. The ADAP ligands contain a tunable -OR substituent derived from any alcohol. The two other P-substituents correspond to a -N-CH=CH-N- skeleton which forms, along with P, a five-member ring resembling the well-known N-heterocyclic carbene ligand structure. The ligand is completed with the 2,6-iPr_2-C_6H_3 substituents at N to mimic the IPr analogue. The copper complexes have been tested as catalysts for several transformations in which (NHC)CuCl has demonstrated a superb behavior. From these experiments we have learnt that the new family of (ADAP)CuCl complexes display a catalytic behavior similar, at least, to that of the NHC-containing equivalents. We believe that in view of the extensive use of the latter, the complexes (ADAP)CuCl can be employed in several catalytic transformations with success. The possibility of employing any alcohol to tune the R position allows the potential availability of a plethora of members of this series, with the corresponding impact in the catalytic field.

Experimental Section

General. All reactions were carried out under an oxygen free nitrogen atmosphere by using an MBraun-Unilab glovebox containing dry argon or nitrogen or conventional Schlenk techniques. Anhydrous

solvents were dried using a solvent purification system (SPS). EDA, $NaBAr^F_4$, reagents and substrates were purchased from Sigma-Aldrich and used without previous purification. The bromodiaminophosphine **1**,[8] PhEDA[24] and MEDA[25] were prepared according to literature methods. Elemental analyses were performed on a PerkinElmer Series II CHNS/O Analyzer 2400. High Resolution Mass Spectroscopy (HRMS) experiments were carried out at the Centre of Research Technology and Innovation of the University of Seville (CITIUS). Enantiomeric excess was measured with a HPLC Waters 1525. X-Ray diffraction studies were performed in a BRUKER D8 FIXED-CHI diffractometer equipped with an Oxford Cryosystem low-temperature device.

Generation of alkoxydiamidophosphine ligands (ADAPs).

Under N_2 atmosphere, the alcohol (1 mmol) and Et_3N (1.2 mmol) were added to a solution of 1,3-bis[2,6-bis(1-methylethyl)phenyl]-2-bromo-2,3-dihydro-1H-1,3,2-diazaphospholene (**1**) (1 mmol) in toluene (5 mL). The reaction mixture was stirred for 12 h at room temperature and after this time the ammonium salt precipitates as a white solid. The reaction is heated at 110 ºC for 1 extra hour and the mixture cooled to room temperature. The solid was filtered and the solution was checked by $^{31}P\{^1H\}$ showing the formation of ADAP ligands **2a-f**. In the case of **2b/2c**, removal of volatiles gave a solid which could be characterized by $^{31}P\{^1H\}$ NMR using concentrated samples and employing a few minutes of acquisition.

Synthesis of the copper complexes (ADAP)CuCl (3a-f).

The in situ generated toluene solutions of ADAP ligands (**2a-2f**) were transferred via cannula into flame-dried Schlenk flask containing CuX (X = Cl, Br; 1mmol). After 4 hours, the mixture was filtered, and the filtrate was evaporated under reduced pressure. The solid residue was washed with hexane (2 x 20 mL) to afford the desired products **3a**-**3f** and **3a-Br** as off-white solids with analytical purity. Single crystals of **3a-Br** were grown from acetone solutions at -30 ºC. See SI for full characterization data. Crystallographic data has been deposited at CCDC with code number 1993132.

Carbene transfer reactions.

The catalyst (0.0125 mmol), $NaBAr^F_4$ (0.0125 mmol) and the olefin (0.7 mmol) were dissolved in DCM (4 mL). The diazocompound (0.5 mmol) was added portionwise (one portion of 12 μl every 30 min for 7 hours). The resulting mixture was stirred at room temperature for additional 12 h before reaction analysis. The experiments with amines, alkanes and benzene were carried out following a similar same procedure. See SI for details.

Copper-catalyzed Azide Alkyne Cycloaddition.

The copper complex (**3a**, 0.0125 mmol), $NaBAr^F_4$ (0.0125 mmol), the azide (0.125 mL) and phenylacetylene (0.11 mL) were dissolved in 4 mL of DCM. The resulting mixture was stirred at room temperature for 4 h. After this time, volatiles were removed under reduced pressure, and the residue investigated by NMR showing the exclusive formation of the expected triazole. See SI for details.

Reaction of 1-phenyl-1-propyne and PhI=NTs.

The copper complex (**3a**, 0.0125 mmol), $NaBAr^F_4$ (0.0125 mmol), the alkyne (2 mmol) were dissolved in 5 mL of DCM before PhI=NTs (0.2 mmol) was added. The resulting mixture was stirred at room temperature for 30 minutes. After this time, volatiles were removed and the residue investigate by NMR. See SI for details.

Acknowledgements

The authors would like to thank the financial support of the MINECO (CTQ2017-82893-C2-1-R), and PO FEDER 2014–2020, (UHU-1260216).

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkoxydiaminophosphine ligands • copper phosphine complexes • C-H activation • carbene and nitrene transfer • CuAAC

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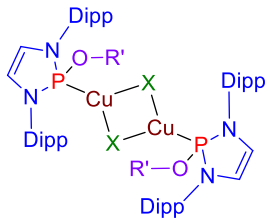
Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))



(ADAP)CuX

Similar catalytic properties to IPrCuCl

One pot procedure for ligands and complexes

Accesible tuning of R' (from any alcohol)

Remote Catalyst Tuning

Juan Diego Pizarro, Francisco Molina, Manuel R. Fructos and Pedro J. Pérez**

■■ – ■■

ADAP Ligands as surrogates of NHCs in copper catalysis (ADAP = alkoxydiaminophosphine)

A one-pot protocol to generate alkoxydiaminophosphine (ADAP) ligands and their copper (I) complexes is described. The (ADAP)CuX complexes show similar catalytic activity than the IPrCuCl complex toward several transformations.