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PAPER

Hydrotris(3-mesitylpyrazolyl)borato-copper(I) alkyne complexes: synthesis, structural characterization and rationalization of their activities as alkyne cyclopropenation catalysts†‡

Carmen Martín,[a] Marta Sierra,[a] Eleuterio Alvarez,[b] Tomás R. Belderrain*[a] and Pedro J. Pérez*[a]

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The use of the bulky hydrotris(3-mesitylpyrazolyl)borate anionic ligand has allowed the synthesis of stable $Tp^{Ms}Cu$(alkyne) complexes (alkyne = 1-hexyne, **1**, phenylacetylene, **2**, and ethyl propiolate, **3**). The spectroscopic and structural features of these compounds and their relative reactivity have been examined, indicating the existence of a low π back-bonding from the copper(I) centre to the alkyne. Ligand exchange experiments have shown that terminal alkyne adducts are more stable than internal alkyne analogues. In good accordance with this, the previously reported alkyne cyclopropenation reaction catalysed by the $Tp^{x}Cu$ complexes can be rationalized and correlated with their relative stability.

Introduction

Group 11 metals complexes containing alkynes are involved in important transformations, such as the addition of alkynes to heteroatom–hydrogen bonds,[1] cycloaddition,[2] cyclopropenation[3] and coupling reactions.[4] Copper–alkyne adducts are also employed as volatile metal precursors for chemical vapour deposition (CVD) of high-purity copper films.[5] Furthermore, these alkyne adducts have been proposed as reaction intermediates, providing insights into the mechanisms of catalytic processes.[6] But surprisingly, since the first report of an X-ray diffraction structure of an acetylene complex[7] by Thompson and Whitney nearly three decades ago, only a few mononuclear alkyne copper complexes have been isolated and structurally characterized.[6a,8] Therefore, the synthesis of coinage metal complexes containing metal–alkyne bonds constitutes an important area of interest.

Copper–alkyne bonding can be described by the Dewar–Chatt–Duncanson model in a similar manner to metal–alkene bonding.[9] The bond is explained as a consequence of a synergistic metal←acetylene σ-donation from the occupied π-orbital of the alkyne into the empty d(σ) atomic orbital of the metal, and metal→acetylene π-back-donation from the occupied d(π) orbital of the metal into the empty π* orbital of the ligand. However, theoretical studies have shown that the metal–alkyne interaction in cationic complexes of group 11 elements have more electrostatic than covalent character. Nevertheless, the covalent contributions to the bonding is mainly due to the metal←acetylene σ donation.[10]

Recently, we have reported the synthesis and characterization of several $Tp^{Ms}Cu$(olefin) complexes (Fig. 1).[11] The experimental as well as theoretical data collected were relevant to the nature of the copper–olefin bond. Thus, the impact of steric factors had a higher effect on the stability of those complexes than that of the electronic ones: small olefins, as ethylene, afforded more stable complexes than styrene or cyclohexene. We proposed that the three aromatic "walls" of mesityl substituents of pyrazolyl rings provide a somewhat protective pocket for the olefin. In addition, we showed that the stability of the olefin adducts clearly influenced the catalytic capabilities of the complex $Tp^{Ms}Cu$ for the transfer of the carbene moiety $:CHCO_2Et$ from ethyl diazoacetate (N_2CHCO_2Et, EDA), to olefins in the cyclopropanation reactions. On the basis of the aforementioned interest of copper–alkyne complexes and our previous study with copper–olefin complexes, we decided to study a series of terminal and internal alkyne complexes: 1-hexyne, phenylacetylene, ethyl propiolate and 3-hexyne. Herein, we describe the synthesis and characterization of $Tp^{Ms}Cu$(alkyne) complexes as well as the study of their relative stabilities and reactivities.

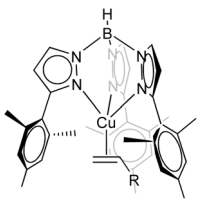

Fig. 1 $Tp^{Ms}Cu$(alkene) complexes.

[a]*Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Centro de Investigación en Química Sostenible (CIQSO), Universidad de Huelva, Campus de El Carmen, 21007 Huelva, Spain. E-mail: perez@dqcm.uhu.es, trodri@dqcm.uhu.es*
[b]*Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla, Avenida Américo Vespucio 49, 41092 Sevilla, Spain*

† In memoriam to Prof. Purificación Escribano

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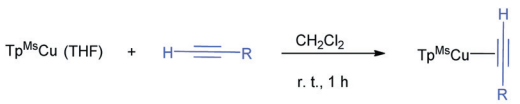
Results and discussion

Synthesis and spectroscopic characterization of $Tp^{Ms}Cu$(alkyne) complexes

$Tp^{Ms}Cu$(alkyne) adducts (alkyne = 1-hexyne, **1**, HC≡CPh, **2**, and HC≡CCO_2Et, **3**) were synthesized using the procedure previously reported for the $Tp^{Ms}Cu$(olefin) complexes.[11] An excess of alkyne was added to a solution of $Tp^{Ms}Cu$(THF) in CH_2Cl_2 to give the corresponding copper–alkyne adducts in 80–90% yields (eqn (1)). All three compounds were stable under vacuum and in the air in the solid state. Internal alkynes such as 3-hexyne have also been employed, but isolation of pure compounds has been elusive, although the adducts have been detected in solution. Indeed, the addition of 2 equiv of 3-hexyne to a solution of $Tp^{Ms}Cu$(THF) in C_6D_6 did not lead to complete conversion to the alkyne adduct and a mixture of THF and alkyne adducts was observed in a 1 : 5 ratio (see ^{1}H NMR spectrum in the ESI),‡ whereas that equilibrium is totally shifted to the formation of the alkyne complex in the case of 1-hexyne with only 1 equiv of alkyne added. Similarly to the $Tp^{Ms}Cu$(olefin) case,[11] the stability $Tp^{Ms}Cu$(alkyne) might be controlled by steric factors (see below).



(1)

R	Complex
C_4H_9	**1**
Ph	**2**
CO_2Et	**3**

Selected spectroscopic NMR and IR data of complexes **1–3** are shown in Table 1. In the ^{1}H NMR spectra of these three compounds the corresponding C≡C*H* acetylenic proton resonances appear at lower fields than those corresponding to the free alkynes. The alkyne chain hydrogens are affected by the presence of the π system of the mesityl ring of the ligand, with their signals shifted to higher fields than those for free 1-hexyne, as described for the adduct of 1-hexene.[11] Interestingly, the C≡C*H* resonance shifts found for **1–3** are small ($\Delta\delta$ = 1.0–1.3 ppm) compared with those described for other copper–terminal alkyne complexes. For example, the chemical shifts of the acetylene protons in the complexes [Cu{$NH(C_5H_4N)_2$}(HC≡CH)]BF_4,[7b] [(phen)Cu(CH≡CPh)]ClO_4[8a] and [H_2B(3,5-$(CF_3)_2$Pz)$_2$]Cu(CH≡CPh)[6a] appear at δ 5.21, 5.14 and 4.60 ppm, respectively. The smaller values found for **1–3** could be a consequence of the anisotropy generated by the π-systems of the mesityl aromatic rings which avoid the downfield shift of those resonances. However, in the ^{13}C{^{1}H} NMR spectra of **1–3** the chemical shifts of acetylenic carbons *C*≡*C* of the coordinated alkyne are similar to those of the above examples, with small differences in the chemical shifts of alkyne carbon atoms for coordinated and free alkyne molecule. This is at variance with d^{10} metal–alkyne complexes of group 10 elements, where the $\Delta\delta$(C≡C) is considerably higher.[12] The ν(C≡C) values observed in **1–3** have also provided useful information about the metal–alkyne interaction.[6a,8,13] Such absorptions appear at 1957, 1923, 1901 cm^{-1} for **1**, **2** and **3**, respectively, differing from those of the free alkynes (2120, 2110 and 2115 cm^{-1}, respectively), and resembling data already reported for other copper–alkyne adducts. Thus, the 1-pentyne complex [Cu(bpy)(HC≡$CCH_2CH_2CH_3$)]$^+$,[13a] shows the ν(C≡C) band at 1932 cm^{-1}, similar to the value observed for **1**. The reported value of ν(C≡C) for the complex [(phen)Cu(HC≡CPh)]ClO_4[13b] (1921 cm^{-1}) is close to the value of complex $Tp^{Ms}Cu$(HC≡CPh), **2**. The $\Delta\nu$(C≡C) between the free and the coordinated alkyne in complexes **1–3** is smaller than that for other alkyne adducts of other low oxidation state metals like Pt, Ni, Ir, Nb and W, which show much higher $\Delta\nu$(C≡C) values (around 410–540 cm^{-1}).[14] This fact could be related to the existence of a lower metal→alkyne π back-donation contribution in these $Tp^{Ms}Cu$(alkyne) complexes. In the case of $Tp^{Ms}Cu$(ethyl propiolate) (**3**) $\Delta\nu$(C≡C) = 214 cm^{-1} is slightly higher than in **1** or **2**, assessing a higher degree of such interaction in this compound due to the presence of the electron attracting substituent –CO_2Et.

Table 1 Selected NMR and IR data for **1–3**[a,b]

$Tp^{Ms}Cu$(alkyne)	δ(^{1}H) C≡C*H*	δ(^{13}C) R*C*≡*C*H	ν(C≡C)
$Tp^{Ms}Cu$(1-hexyne), **1**[c]	2.79 (1.75)	70.1 (68.5) 93.4 (83.9)	1957 (2120)
$Tp^{Ms}Cu$(phenylacetylene), **2**[c]	3.94 (2.66)	79.0 (77.9) 94.2 (83.9)	1923 (2110)
$Tp^{Ms}Cu$(ethyl propiolate), **3**[d]	3.89 (2.92)	85.4 (74.7) 87.1 (75.0)	1901 (2115)

[a] Chemical shift in ppm, at room temperature, and IR data in cm^{-1}. [b] Values for metal-free alkynes are given in brackets. [c] C_6D_6. [d] $CDCl_3$.

Structural characterization of complexes 1–3

The structures of complexes **1–3** were confirmed by means of single-crystal X-ray diffraction studies (Fig. 2). In the three compounds the Tp^{Ms} ligand is coordinated in a κ^3-*N*,*N*,*N* fashion and the alkyne molecules are bonded to the metal in a η^2 mode, the two Cu–C_α and Cu–C_β distances being slightly different (Table 2). The unit cell contains more than one independent molecule, as well as alkyne crystallization molecules that have been omitted in Fig. 2 (see ESI for complete ORTEP).‡

The Cu–C_{alkyne} bond distances found for **1–3** are similar to those reported for other copper complexes of the same alkynes For example, Cu–C(37) and Cu–C(38) bond lengths in **2**, 1.967 (2) and 2.0284(18) Å, respectively, compare well with those published for Bp^{CF_3,CF_3}Cu(HC≡CPh)[6a] (1.936(4) and 2.003(4) Å), [ClCu(HC≡CPh)][14b] (1.999(4) and 2.066(3) Å) and [(phen)Cu(HC≡CPh)]ClO_4[14b] (1.922(12) and 1.995(10) Å). In the case of complex **3** the Cu–C(78) and Cu–C(79) distances, 1.956(4) and 1.964(4), are slightly longer than those found for the complex [(phen)(CuHC≡CCO_2Et)]ClO_4,[8a] 1.925(9) and 1.934(7) Å.

The values of the C≡C–C angle for **1**, **2** and **3** are 163.5(2)°, 159.9(2)° and 151.9(4)°, respectively, with a deviation from linearity in each case of 16.5°, 20.1° and 28.1°. These data can be related with the degree of π back-bonding contribution, and, consequently, in good agreement with spectroscopic data, the

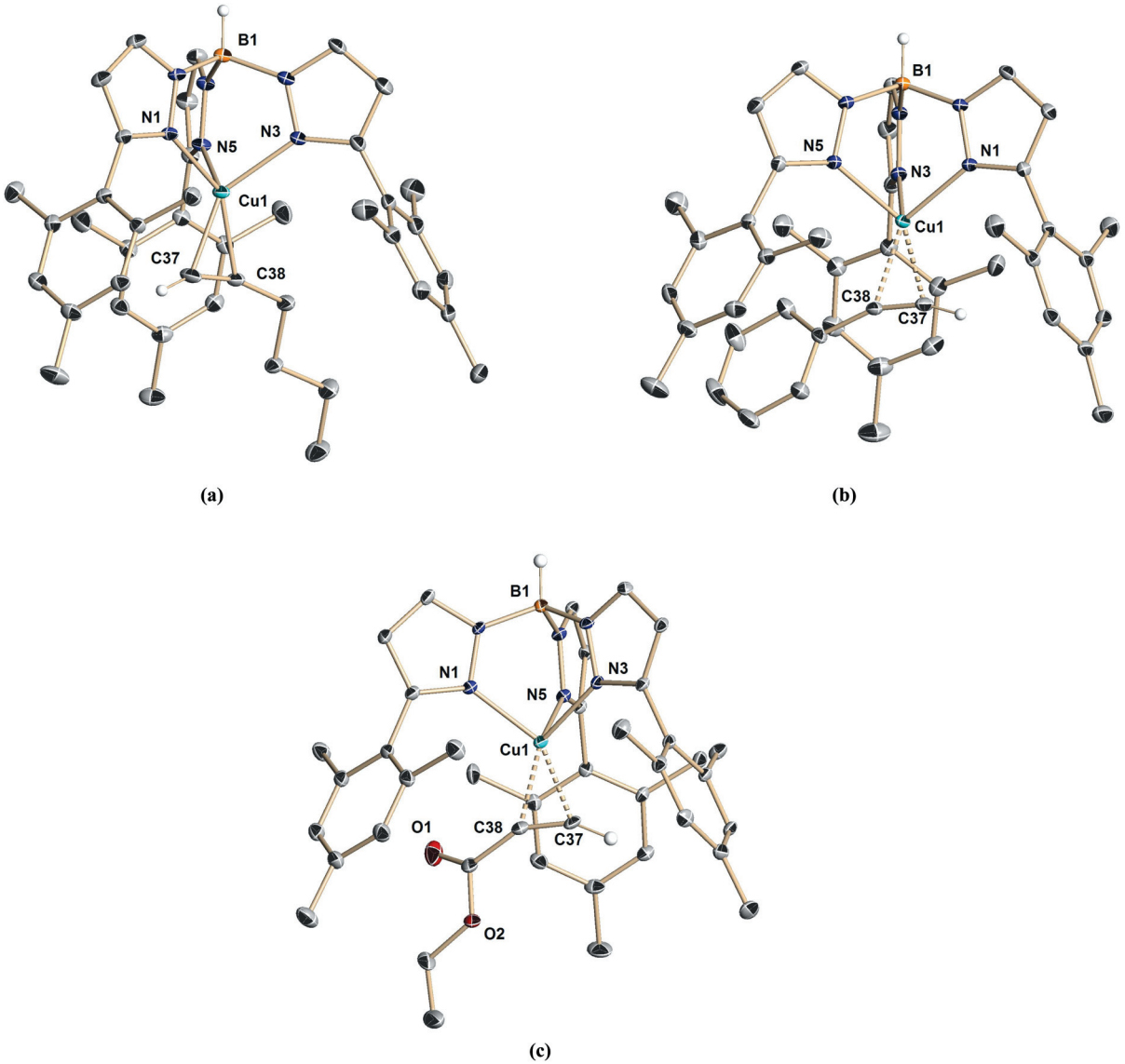


Fig. 2 The molecular structures of complexes (a) $Tp^{Ms}Cu$(1-hexyne), **1**, (b) $Tp^{Ms}Cu$(phenylacetylene), **2**, and (c) $Tp^{Ms}Cu$(ethyl propiolate), **3** (30% displacement ellipsoids; hydrogen atoms have been omitted except for the acetylenic one and that bound to the boron atom; crystallization solvent has been also omitted for clarity).

Table 2 Selected bond parameters for complexes $Tp^{Ms}Cu$(alkyne), **1–3**

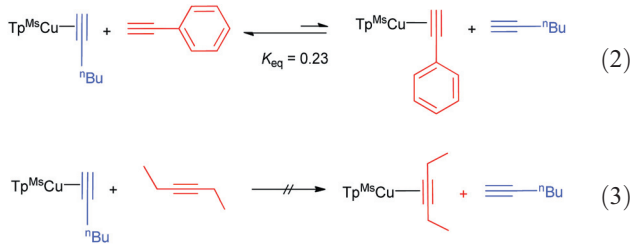
	Bond lengths (Å)			Angles (°)	
Complex	C≡C	Cu–C_α	Cu–C_β	C≡C–H	C≡C–C
1	1.213 (3)	1.991(2)	2.0127(18)	162.3 (18)	163.5 (2)
2	1.218 (3)	1.967(2)	2.0284(18)	161.4 (15)	159.9 (2)
3	1.212 (6)	1.956 (4)	1.964 (4)	166 (3)	151.9 (4)

greatest deviation is observed for the HC≡CCO_2Et adduct. As already mentioned, theoretical studies have indicated that the copper–acetylene interaction occurs mainly through the component σ, with a rather low Cu^+–HC≡CH π contribution.[10] Accordingly, the C≡C distance found for **2**, 1.218(3) Å, is only slightly longer than that for free phenylacetylene, 1.19(2) Å.[8a]

Alkyne exchange reactions

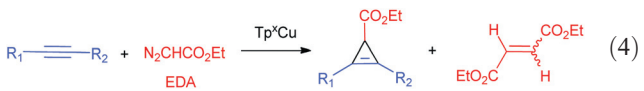
Experimental data obtained for the olefin exchange reactions in $Tp^{Ms}Cu$(olefin) indicated that the relative stability of such adducts depends mainly on steric factors.[11] With the aim of examining the role of those effects in the stability of alkyne complexes, we decided to study the related exchange reactions with alkynes. Thus, the addition of 1 equiv of phenylacetylene to a solution of the complex $Tp^{Ms}Cu$(1-hexyne) (**1**) in C_6D_6 led to an equilibrium mixture of **1** and **2** immediately (eqn (2)). The equilibrium constant K_{eq} has been estimated by ^{1}H NMR as 0.23(1) at room temperature by the integration of the coordinated acetylenic protons signals. The K_{eq} value indicates that **1** is more stable than **2**, and suggests, once again, that steric interactions between substituents of the acetylene and mesityl groups of the Tp^{Ms} control the stability of the adduct: reducing the size of the alkyne ligand confers a certain stability to the copper adduct. As

expected from that, when 1 equiv of 3-hexyne was added to a solution of complex $Tp^{Ms}Cu$(1-hexyne) (**1**) no formation of the internal alkyne adduct was observed (eqn (3)).



Rationalization of catalyst activity in the alkyne cyclopropenation reactions

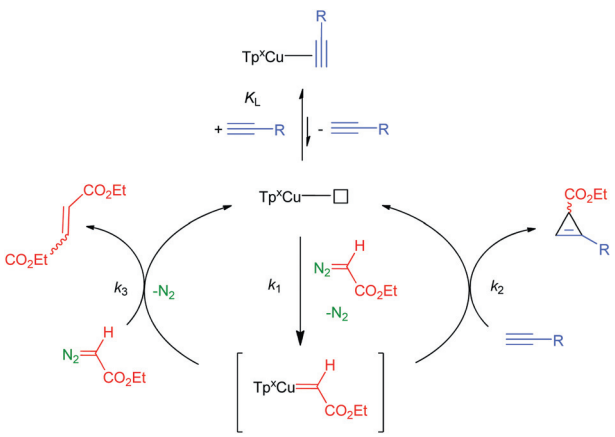
The reaction of diazo compounds and alkynes catalysed by transition metal complexes has been employed in the synthesis of cyclopropenes (eqn (4)).[3,15] In such processes there exists a side reaction, the carbene dimerization, that competes with the cyclopropenation reaction. In our group we have previously reported that a series of $Tp^{x}Cu$ complexes efficiently catalyses this transformation,[16,17]



using ethyl diazoacetate (EDA) as the carbene source, with excellent results for both internal and terminal alkynes. However, some exceptions were found: the complexes $Tp^{Ms}Cu$, $Tp^{Ph}Cu$ and $Tp^{\alpha\text{-}Nt}Cu$ (Tp^{Ph} = hydrotris(3-phenylpyrazolyl) borate; $Tp^{\alpha\text{-}Nt}$ = hydrotris(3-α-naftylpyrazolyl)borate) did not provide good yields. The behaviour of these complexes in the case of terminal alkynes can be explained by means of the existence of an equilibrium of the alkyne adducts and the real catalytic species, $Tp^{x}Cu$, in the reaction mixture (Scheme 1). In the case of high K_L (equilibrium constant of alkyne adduct formation) values a very stable adduct would be formed and the reaction rate would significantly decrease. On the other hand, very active catalysts for carbene transfer in cyclopropenation such as $Tp^{Br3}Cu(NCCH_3)$,[17] with low steric hindrance, do not form alkyne adducts.

With the aim of comparing the catalytic capabilities of $Tp^{Ms}Cu$, $Tp^{Br3}Cu$ and $Tp^{Ph}Cu$ complexes, we have carried out the cyclopropenation reactions of 1-hexyne and 3-hexyne using EDA as a carbene source. Table 3 displays the reaction outcome, showing substituted cyclopropene yields and the time required in each case for the total consumption of EDA. It is worth mentioning that these experiments have been carried out adding both the alkyne and the diazo in one portion, the use of slow addition devices would infer higher conversions. For the sake of comparison of activities, it is preferable to operate at moderate conversions. The reaction of EDA with the terminal alkyne, 1-hexyne using $Tp^{Ms}Cu$ as the catalyst is significantly slower for $Tp^{Ms}Cu$, followed by $Tp^{Ph}Cu$ and $Tp^{Br3}Cu$, the latter inducing a similar yield only in 1 h. This is the order of stabilities of the corresponding $Tp^{x}Cu$(1-hexyne) adducts, and therefore it is in good agreement with the proposal shown in Scheme 1: those complexes favouring the formation of alkyne adducts will display lower catalytic activities as the result of a certain decrease of the concentration of the catalytic species $Tp^{x}Cu$. For 3-hexyne as the substrate, reaction times were considerably shorter for the three complexes employed. These data can be reasoned in terms of the less favoured formation of internal alkyne adducts due to the steric interaction between the substituents of the Tp^{x} ligand and those of the alkyne.

The bulkiness of the Tp^{x} ligand also influences the catalyst chemoselectivity. Thus, in the 1-hexyne cyclopropenation reaction catalysed by $Tp^{Ms}Cu$, although slow, cyclopropene was obtained in moderate yields (49%), whereas for 3-hexyne diethyl fumarate and maleate (92%), from the dimerization reaction of



Scheme 1 Proposed mechanism for the cyclopropenation reactions catalysed by $Tp^{x}Cu$ complexes.

Table 3 Cyclopropenation of 1-hexyne and 3-hexyne with EDA using $Tp^{x}Cu$ complexes[a]

		Catalyst		
Substrate	Product	$Tp^{Ms}Cu$	$Tp^{Ph}Cu$	$Tp^{Br3}Cu$
1-Hexyne		49%/48 h	29%/24 h	50%/1 h
3-Hexyne		8%/1 h	18%/2 h	43%/1 h

[a] Catalyst : EDA : alkyne ratio of 1 : 30 : 90, 0.1 mmol of $Tp^{x}Cu$ employed. Percentage of cyclopropenes and reaction time required for total consumption of EDA. The remaining initial EDA was converted in mixtures of diethyl fumarate and maleate.

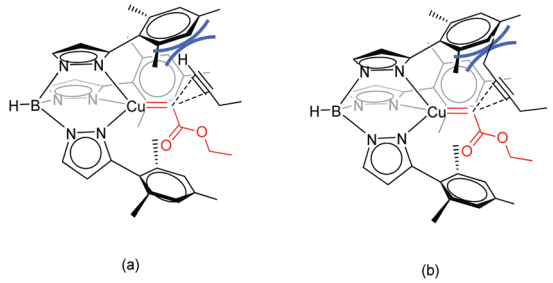


Fig. 3 Steric interactions between the mesityl groups of the Tp^{Ms} ligand and the alkyne during the carbene transfer step: (a) 1-hexyne; (b) 3-hexyne.

EDA, were obtained as the major products (Table 3). This behaviour may be due to steric repulsions between the mesityl groups of the Tp^{Ms} ligand and 3-hexyne, which would prevent the approach of the alkyne to the carbene ligand and hindering the process of carbene transfer (Fig. 3b). For internal alkynes the formation of diethyl fumarate and maleate is faster (k_3, Scheme 1) than the cyclopropenation reaction (k_2, Scheme 1), even in the presence of an excess of alkyne. In good agreement with this proposal, for 3-hexyne the yields of the cyclopropene derivative increase as the steric effect of the ligand decreases, in the order $Tp^{Ms} < Tp^{Ph} < Tp^{Br3}$. In the case of 1-hexyne, cyclopropenation using $Tp^{Ms}Cu(THF)$ as catalyst, the less bulky alkyne molecule can approximate more easily to the carbenic moiety since the steric repulsion with the mesityl groups is reduced (Fig. 3a), and, consequently, the cyclopropenation step rate becomes comparable or even higher than the EDA dimerization process, with the corresponding enhancement of cyclopropene products.

Conclusion

We have prepared and characterized a series of $Tp^{Ms}Cu$(alkyne) complexes. Data collected indicate that steric interactions between the mesityl groups and the substituents of the alkyne clearly influences the stability of the adducts. Thus, terminal alkyne adducts are more stable that internal alkyne analogues. This is an important issue when using these compounds as catalyst precursors in the alkyne cyclopropanation reaction with ethyl diazoacetate as the carbene source. Under catalytic conditions, metal centres with a low steric hindrance (such as $Tp^{Br3}Cu$) do not form alkyne adducts and display high catalytic activities. In the opposite case, stable alkyne adducts can be formed and the reaction rate lowered. This study provides the information to choose the appropriate Tp^{x} ligand for a given alkyne to be converted into cyclopropenes.

Experimental

General

Solvents were dried and deoxygenated before use. All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere with standard Schlenk techniques. $Tp^{Ms}Cu(THF)$,[18] $Tp^{Ph}Cu(NCCH_3)$[19] and $Tp^{Br3}Cu(NCCH_3)$[20] complexes were prepared according to the reported methods. All other chemicals were purchased from the Sigma-Aldrich Chemical Co. and purified before use. NMR spectra were recorded on a 400 MHz Varian Mercury. Infrared spectra were recorded on a Nicolet FTIR 200 spectrophotometer. Elemental analyses were performed in Unidad de Análisis Elemental at the Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla.

General synthesis of $Tp^{Ms}Cu$(alkyne) adducts

30 mmol of the alkyne were added to a solution of 0.10 g of complex $Tp^{Ms}Cu(THF)$ (0.14 mmol) in 10 mL of dichloromethane. After 1 h, the solvent was removed under vacuum and a solid was obtained. The complexes were purified by recrystallization using a mixture of CH_2Cl_2–alkyne. All complexes were isolated as crystalline solids in 80–90% yields.

$Tp^{Ms}Cu$(1-hexyne), 1. ^{1}H NMR (400 MHz, C_6D_6) δ 7.66 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 6.67 (s, 6H, $CH_{mesityl}$), 5.92 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 2.79 (t, ^3J(HH) = 2.3 Hz, 1H, $CH_{acetylene}$), 2.58 (s, 18H, $CH_{3(mesityl)}$), 2.05 (s, 9H, $CH_{3(mesityl)}$), 0.76–0.87 (m, 4H, CH_2), 0.57–0.71(m, 4H, CH_2), 0.65 (t, ^3J(HH) = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6) δ 151.24 ($C_{pyrazol}$), 137.81 ($C_{mesityl}$), 137.06 ($C_{mesityl}$), 135.35 ($CH_{pyrazol}$), 132.27 ($C_{mesityl}$), 128.01 ($CH_{mesityl}$), 104.92 ($CH_{pyrazol}$), 92.73 (HC≡C), 69.40 (HC≡C)), 32.09 (CH_2), 21.31(CH_2), 20.93 ($CH_{3(mesityl)}$), 20.82 ($CH_{3(mesityl)}$), 13.64 (CH_3). IR (KBr, cm^{-1}): 2443 [ν(BH)], 1957 [ν(C≡C)]. Anal. Calcd. for $BC_{42}H_{50}N_6Cu$: 70.75 C, 7.02 H, 11.79 N. Found: 70.91 C, 7.01 H, 11.94% N.

$Tp^{Ms}Cu$(phenylacetylene), 2. ^{1}H NMR (400 MHz, C_6D_6) δ 7.71 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 6.69 (t, ^3J(HH) = 7.4 Hz, 1H, $CH_{p\text{-phenyl}}$), 6.59 (t, ^3J(HH) = 7.7 Hz, 2H, $CH_{m\text{-phenyl}}$), 6.47 (s, 6H, $CH_{mesityl}$), 6.43 (d, ^3J(HH) = 7.1 Hz, 2H, $CH_{o\text{-phenyl}}$), 5.96 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 3.94 (s, 1H, $CH_{acetylene}$), 2.06 (s, 18H, $CH_{3(mesityl)}$), 1.90 (s, 9H, $CH_{3(mesityl)}$). ^{13}C NMR (100 MHz, C_6D_6) δ 151.84 ($C_{pyrazol}$), 137.32 ($C_{mesityl}$), 136.83 ($C_{mesityl}$), 135.36 ($CH_{pyrazol}$), 131.54 ($C_{mesityl}$), 131.38 ($CH_{o\text{-phenyl}}$), 128.04 ($CH_{mesityl}$), 126.98 ($CH_{p\text{-phenyl}}$), 126.07 ($CH_{m\text{-phenyl}}$), 122.76 (C_{phenyl}), 105.44 ($CH_{pyrazol}$), 94.05 (HC≡C), 78.82 (HC≡C), 21.22 ($CH_{3(mesityl)}$), 20.84 ($CH_{3(mesityl}$). IR (KBr, cm^{-1}): 2440 [ν(B-H)], 1923 [ν(C≡C)]. Anal. Calcd. for $BC_{44}H_{46}N_6Cu.^2/_3HC{\equiv}C\text{-}Ph$: 74.00 C, 6.25 H, 10.50 N. Found: 73.93 C, 6.28 H, 10.12% N.

$Tp^{Ms}Cu$(ethyl propiolate), 3. ^{1}H NMR (400 MHz, C_6D_6) δ 7.77 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 6.76 (s, 6H, $CH_{mesityl}$), 6.02 (d, ^3J(HH) = 2.1 Hz, 3H, pyrazol CH), 3.81 (s, 1H, $CH_{acetylene}$), 3.61 (q, ^3J(HH) = 7.1, 2H, CH_2), 2.02 (s, 9H, $CH_{3(mesityl)}$), 1.91 (s, 18H, $CH_{3(mesityl)}$), 0.98 (t, ^3J(HH) = 7.1, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6) 153.09 ($CO_{propiolate}$), 151.58 ($C_{pyrazol}$), 137.82 ($C_{mesityl}$), 137.38 ($C_{mesityl}$), 135.20 ($CH_{pyrazol}$), 131.28 ($C_{mesityl}$), 127.85 (mesityl CH), 105.32 ($CH_{pyrazol}$), 86.68 (HC≡C), 86.06 (HC≡C), 61.35 (CH_2), 21.29 ($CH_{3(mesityl)}$), 20.85($CH_{3(mesityl}$), 14.05 (CH_3). IR (KBr, cm^{-1}): 2447 [ν(B-H)], 1901 [ν(C≡C)], 1727 [ν(C=O)]. Anal. Calcd. for $BC_{40}H_{44}N_6O_2Cu$: 67.10 C, 6.16 H, 11.75 N. Found: 66.84 C, 5.84 H, 11.71% N.

In situ preparation of $Tp^{Ms}Cu$(3-hexyne), 4.

3.8 μL of 3-hexyne (0.032 mmol) was added to a solution of 10 mg of $Tp^{Ms}Cu$ (0.016 mmol) in 0.7 mL of C_6D_6. ^1H NMR (400 MHz, C_6D_6) δ 7.71 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 6.75 (s, 6H, $CH_{mesityl}$), 5.93 (d, ^3J(HH) = 2.1 Hz, 3H, $CH_{pyrazol}$), 2.11 (s, 18H, $CH_{3(mesityl)}$)), 2.07 (s, 9H, $CH_{3(mesityl)}$), 1.14 (q, ^3J(HH) = 7.3, 4H, CH_2), 0.52 (t, ^3J(HH) = 7.2, 6H, CH_3).

General procedure for the study of exchange equilibrium between alkynes

1 equiv of $HC{\equiv}CR^2$ was added to a solution of the adduct $Tp^{Ms}Cu(HCH{\equiv}CR^1)$ in 0.6 mL of C_6D_6. The solution was transferred to an NMR tube that was sealed with a Teflon stopper. The reaction mixture was monitored by ^1H NMR spectroscopy. The equilibrium was reached immediately. Accounting for the relative concentrations of $HC{\equiv}CR^2$ and $HCH{\equiv}CR^1$ in solution afforded the equilibrium constant K_{eq} at room temperature for the exchange reaction below.

General procedure for the alkyne cyclopropenation reactions

4.5 mmol of alkyne (1-hexyne or 3-hexyne) and 1.5 mmol of EDA were simultaneously added to a solution of 0.05 mmol of the Tp^xCuL (L = THF or CH_3CN) in 20 mL of dichloromethane (ratio catalyst–EDA–alkyne 1 : 30 : 90). The reaction mixture was stirred at room temperature until the total consumption of diazo compounds was observed by IR and/or GC. The reaction time (1–48 h) depended on the substrate and catalyst used. Solvent was removed under vacuo and the reaction crude was analysed by ^1H NMR spectroscopy. The reaction products were identified by comparison with the reported data.[21] Reaction conversions and yields of the products were determined by using 1,4-dimethoxybenzene as internal standard.

X-ray structure determination

A single crystal, of each compound, of suitable size was mounted on a glass fiber using perfluoropolyether oil (FOMBLIN 140/13, Aldrich) in the cold N_2 stream of a low-temperature device attachment. Full crystallographic data and structure refinement are given in the ESI.‡ Intensity data were performed on a Bruker-AXS X8 Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator Mo Kα_1 (λ = 0.71073 Å) and a Bruker Cryo-Flex low-temperature device. The data collection strategy used in all instances was Φ and Ω scans with narrow frames. Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times, and no decay was observed. The data were reduced (SAINT)[22] and corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied (SADABS).[23] The structure was solved by direct methods (SIR-2002)[24] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.14)[25] minimizing $w[F_o^2-F_c^2]^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced into geometrically calculated positions and refined riding on the corresponding parent atoms.

Crystal data for 1. $C_{87}H_{106}B_2C_{l6}Cu_2N_{12}$, M = 1681.26, triclinic, $P\bar{1}$, a = 11.1908(5), b = 12.0506(5), c = 16.6731(7) Å, α = 77.7080(9)°, β = 83.1730(10)°, γ = 89.2120(10)°, V = 2181.19 (16) Å^3, Z = 1, D_c = 1.280 Mg m^{-3}, absorption coefficient 0.722 mm^{-1}, T = 173(2) K, colourless prisms; 13 139 independent measured reflections (R_{int} = 0.0266), F^2 refinement, final R indices [$I > 2\sigma(I)$] $R1$ = 0.0481, w$R2$ = 0.1287, R indices (all data) $R1$ = 0.0664, w$R2$ = 0.1437.

Crystal data for 2. $C_{52}H_{52}BCuN_6$ [$C_{44}H_{46}BCuN_6$, C_8H_6], M = 835.35, monoclinic, $P2_1/n$, a = 9.1406(6), b = 20.6632(15), c = 23.8733(17) Å, α = 90°, β = 97.186(2)°, γ = 90°, V = 4473.6 (5) Å^3, Z = 4, D_c = 1.240 Mg m^{-3}, absorption coefficient 0.531 mm^{-1}, T = 173(2) K, colourless prisms; 13 516 independent measured reflections (R_{int} = 0.0652), F^2 refinement, final R indices [$I > 2\sigma$ (I)] $R1$ = 0.0463, w$R2$ = 0.1001, R indices (all data) $R1$ = 0.0769, w$R2$ = 0.1142.

Crystal data for 3. : $C_{165}H_{186}B_4Cl_2Cu_4N_{24}O_8$ [4 ($C_{41}H_{46}BCuN_6O_2$), CH_2Cl_2], M = 3001.68, triclinic, $P\bar{1}$, a = 9.0009(7), b = 11.2392(9), c = 38.765(3) Å, α = 97.899(2)°, β = 97.186(2)°, γ = 90°, V = 3875.5(5) Å^3, Z = 1, D_c = 1.286 Mg m^{-3}, absorption coefficient 0.641 mm^{-1}, T = 100(2) K, colourless prisms; 23 921 independent measured reflections (R_{int} = 0.0544), F^2 refinement, final R indices [$I > 2\sigma$ (I)] $R1$ = 0.0776, w$R2$ = 0.1802, R indices (all data) $R1$ = 0.1021, w$R2$ = 0.1900.

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