

Copper(I)-arene complexes with a sterically hindered trispyrazolylborate ligand

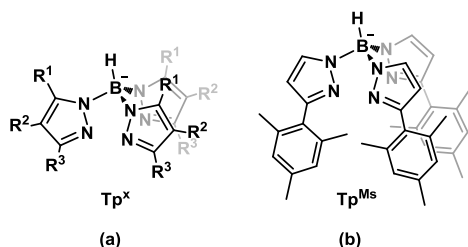
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Dedication ((optional))

Abstract: A series of arene copper(I) complexes bearing the hydrotris(3-mesityl-pyrazolyl)borate ligand (Tp^{Ms}) of general formulae $\text{Tp}^{\text{Ms}}\text{Cu}(\text{arene})$ (arene = toluene, **1**; nitrobenzene, **2**; chlorobenzene, **3**; and iodobenzene, **4**) has been structurally characterized. Complexes **1-3** shows a η^2 -arene coordination mode to the copper centre whereas the iodobenzene ligand in **4** is coordinated to Cu by the iodine atom. In the absence of excess of arene, these compounds undergo arene loss and formation of the dinuclear complex $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$ (**5**), that has also been structurally characterized. Given the number of catalytic systems described in which the Tp^{Cu} core display the main role, the observation of these adducts assesses their presence in those catalytic systems, a feature not described to date.

Introduction

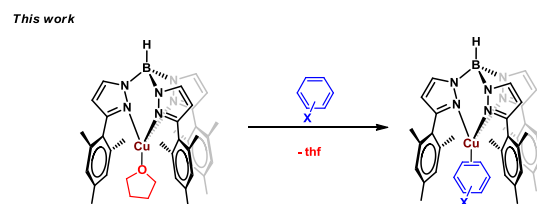
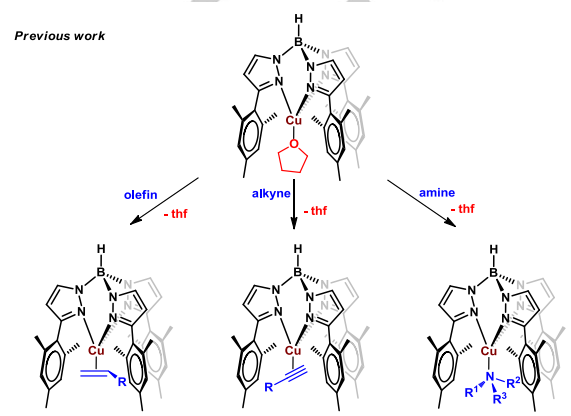
Since Trofimenko described the preparation of the first trispyrazolylborate ligand (Tp^{x} , Scheme 1)^[1] in 1966, an



Scheme 1. (a) Generic trispyrazolylborate ligand. (b) The Tp^{Ms} ligand.

increasing number of members of the series have appeared in the literature, currently surpassing two hundred. Most of the transition metals have been employed in the synthesis of Tp^{x} -containing complexes.^[2] Among the areas in which these ligands have been employed, that of catalysis has probably been the most developed in the last decade.^[3] This is a consequence of the versatility of these ligands, given the large number of

combinations available upon variation of the R^1 - R^3 groups.



Scheme 2. The synthesis of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{I})$ adducts: previous examples and the formation of arene complexes described in this work.

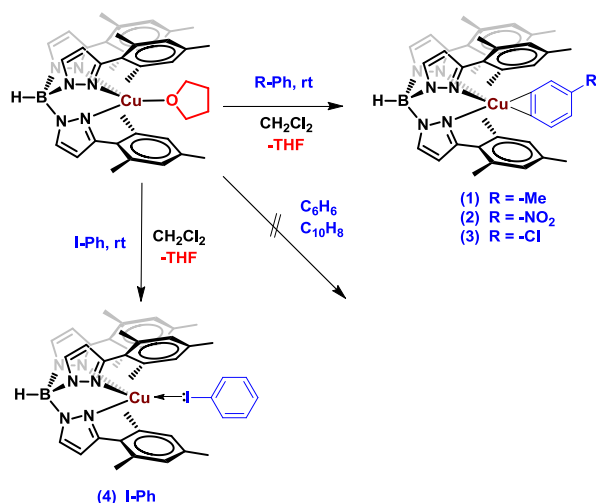
Particularly, the substituent R^3 exerts a crucial effect in the steric protection around a metal centre when coordinated to a Tp^{x} ligand. In this sense, the bulky Tp^{Ms} ligand (Tp^{Ms} = hydrotris(3-mesityl-pyrazolyl)borate, Scheme 1) bearing a mesityl substituent, originates a sort of “aromatic wall” that restricts the size of the potential catalytic pocket around the metal. The complex $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ was described by Tolman and co-workers twenty years ago,^[4] and in our hands it has shown a remarkable catalytic activity toward the preferential *cis*-cyclopropanation of olefins with copper as the metal.^[5] Moreover, the use of the $\text{Tp}^{\text{Ms}}\text{Cu}$ core has been crucial in the detection of copper-carbene complexes^[6] and in the synthesis and isolation of alkene-, alkyne- or amine- adducts.^[7] At variance with this reactivity, we are not aware of any report on structurally characterized $\text{Tp}^{\text{x}}\text{Cu}$ -arene complexes. Such adducts could be relevant in the context of the catalytic systems based on the $\text{Tp}^{\text{x}}\text{Cu}$ core in those transformations with arenes as substrates, In this contribution we describe the structural characterization of several $\text{Tp}^{\text{Ms}}\text{Cu}(\text{arene})$ complexes, showing a dihapto coordination of the aromatic ring to the copper centre. Structural data collected have provided evidences for the presence of π -aromatic bonding interactions between the arene ligand and the mesityl rings of the Tp^{Ms} ligand.

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Results and Discussion

The reaction of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ with arenes. The parent complex $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ described by Tolman and co-workers^[4] has been employed as the starting material, following previous work from this laboratory toward the isolation of alkene, alkyne or amine adducts.^[7] The experimental procedure consisted of the dissolution of this copper complex in dichloromethane followed by the addition of 30 equiv of the corresponding arene: toluene, nitrobenzene, chlorobenzene, iodobenzene, benzene or naphthalene. After 30 min of stirring at room temperature, pentane was added and the mixture was cooled overnight at $-30\text{ }^{\circ}\text{C}$, affording crystalline materials that were filtered off, dried under a nitrogen stream and investigated by NMR spectroscopy. Surprisingly, in all cases the spectra were constituted by a set of resonances identical to those observed by Tolman when the starting material $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ was analyzed by NMR. Only in



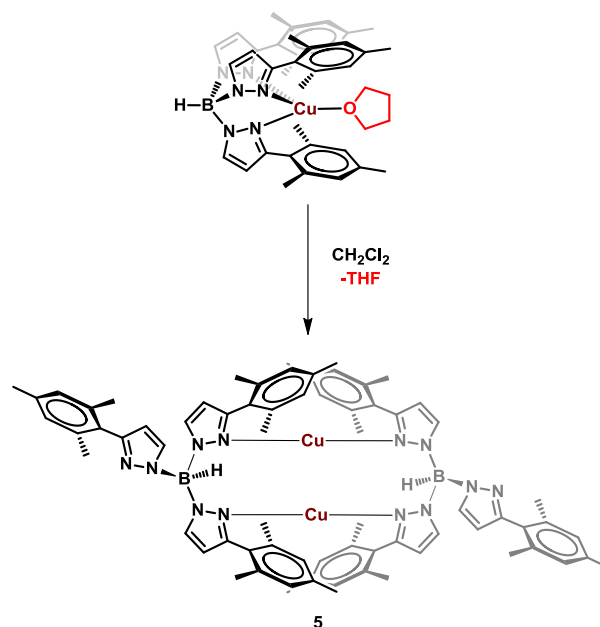
Scheme 2. Complexes formed upon reaction of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ and several arenes

the cases of nitrobenzene and iodobenzene the resonances of the coordinated Tp^{Ms} ligand were accompanied by other group of signals, attributable to one equiv of the free, non-coordinated arene. At a first sight, this behavior demonstrates the inexistence of any arene coordination to the $\text{Tp}^{\text{Ms}}\text{Cu}$ core. However, the exact presence of one equiv of free arene in the aforementioned cases could not be just a coincidence, but perhaps the result of de-coordination of the arene ligand when the isolated complex was dissolved. On this basis, we repeated the experiments and analyzed the crystalline materials by X-ray diffraction, using crystals directly taken from the crystallization liquor. To our delight, four complexes were characterized (Scheme 2) with composition $\text{Tp}^{\text{Ms}}\text{Cu}(\eta^2\text{-toluene})$ (1), $\text{Tp}^{\text{Ms}}\text{Cu}(\eta^2\text{-nitrobenzene})$ (2), $\text{Tp}^{\text{Ms}}\text{Cu}(\eta^2\text{-chlorobenzene})$ (3) and $\text{Tp}^{\text{Ms}}\text{Cu}(\kappa^1\text{-iodobenzene})$ (4). When benzene or naphthalene were employed, no arene adduct could be obtained, but the dinuclear compound $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$ (5), that was also structurally characterized.

Crystals of complexes 1 and 3 loss the arene during the workup, either under vacuum or just a nitrogen stream, evidencing the weakness of the arene-copper linkage. In the

cases of 2 or 4, the complexes could be isolated after filtration and drying, allowing elemental analysis, but crystallinity was lost. However, as mentioned above, NMR experiments showed the immediate dissociation of the arene. In addition, attempts to detect 1-4 by in situ NMR also failed.

The formation of the dinuclear complex 5 can be observed when the volume of the crystallization liquor is reduced to a minimum or when adding a larger amount of pentane. In these



Scheme 3. The synthesis of the dinuclear complex $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$ (5).

cases, crystalline 5 was formed, no matter the arene employed. This compound was already mentioned by Tolman and co-workers in their seminal work,^[4] being described as $[\text{Tp}^{\text{Ms}}\text{Cu}]_n$. Its NMR spectra is indistinguishable from that obtained upon dissolving pure $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$, a fact also mentioned in that work as the result of fluxional processes in solution. Fortunately, we have now been able to characterize this complex by X-ray diffraction studies. It can be obtained as single crystals not only from those concentrated solutions but also when treating pure $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ to several cycles of solution-evaporation to eliminate the THF ligand, and finally crystallization from dichloromethane. Other $[\text{Tp}^{\text{X}}\text{Cu}]_2$ complexes^[8,9,10] have been described with several substituents at the pyrazolyl ring, albeit the structure of the mesityl derivative has remained undiscovered until now.

X-ray structures of complexes 1-4. Figure 1 displays the solid-state structures of complexes 1-4. The toluene (1), nitrobenzene (2) and chlorobenzene (3) derivatives present a similar structure with the Tp^{Ms} ligand bonded in a κ^3 fashion to the metal centre, whereas the arene rings were coordinated in a dihapto manner through the C3-C4 bond relative to the carbon bearing the substituent. Complex 4 did not show such coordination mode, the arene being coordinated to the copper by the iodine atom.

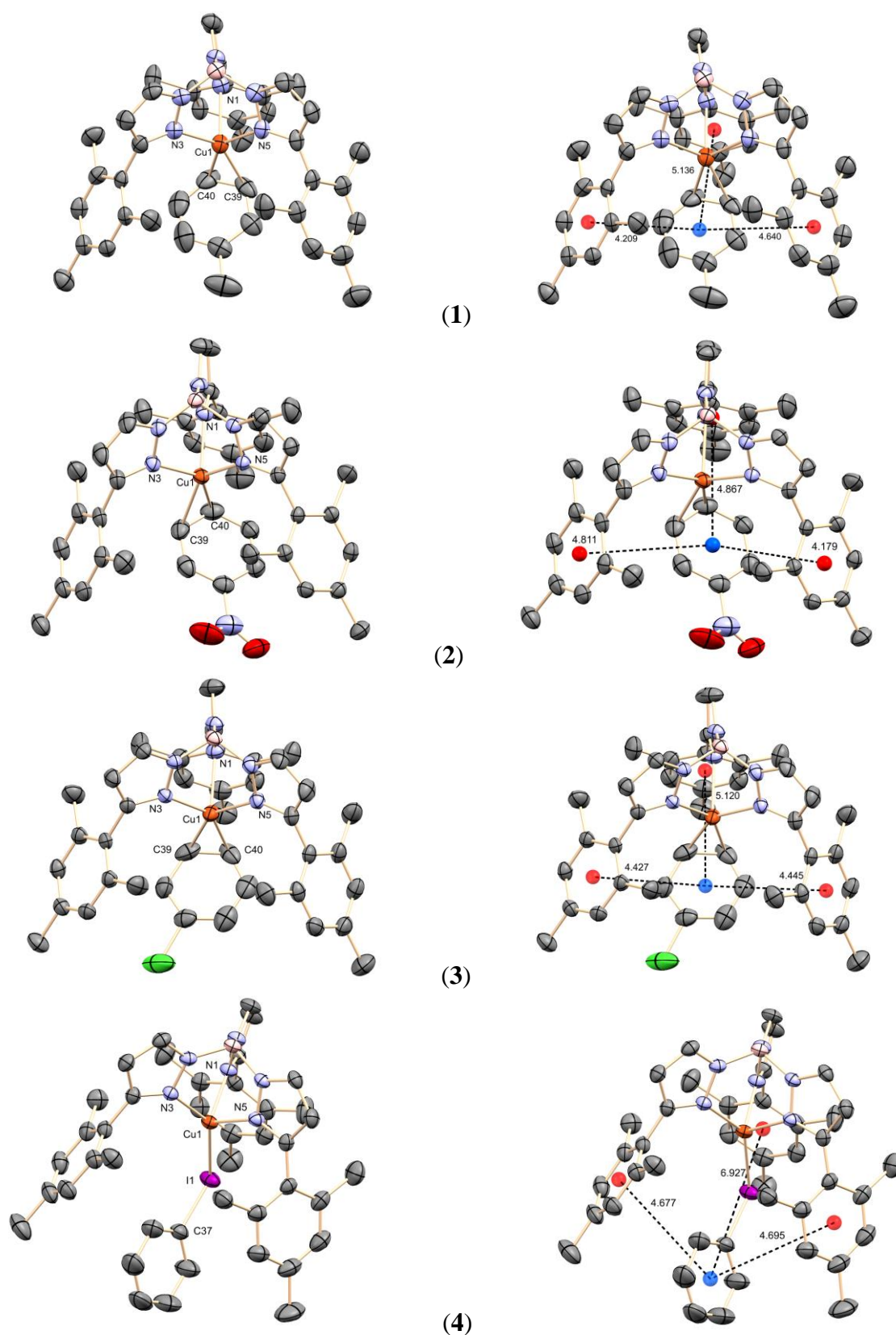


Figure 1. ORTEP view of the molecule of complexes 1-4. Left: relevant atoms labelling. Right: distances (in Å) correspond to the separation between the centroids of the mesityl aryl rings of the Tp^M ligand and that of the arene ligand. Hydrogen atoms have been omitted for clarity.

Crystallographic data for **1** show the copper centre embedded in a distorted pseudo-tetrahedral geometry (Figure 1). The Cu-N distances display the commonly observed pattern in complexes of type Tp^xCuL ,^[4,7] with one of them being slightly longer than the other two (Table 1). The Cu-C_{sp²} distances are similar (2.189(5) Å for Cu-C39 and 2.182(5) Å for Cu-C40, Table 1), in agreement with other Cu-arene complexes with bidentate ancillary ligands.^[11] The C39-C40 distance of 1.389(8) Å for the coordinated arene bond is very close to that found in free toluene (1.38 Å).^[12] This feature has been observed in our previous work with the olefin adducts,^[7a] and reflects the weakness of the copper-arene bond. Compounds **2** and **3** display similar structural parameters, regarding the coordination mode of the arene (η^2 -C3-C4, with imperceptible difference in that distance relative to free arene).

Table 1. Selected distances [Å] and angles [°] for structures in compounds **1-4**.

	1	2	3	4
Cu-N(1)	2.178(4)	2.1147(17)	2.198(3)	2.043(2)
Cu-N(3)	2.065(4)	2.0723(2)	2.051(2)	2.054(2)
Cu-N(5)	2.090(4)	2.1112(17)	2.078(2)	2.090(2)
Cu-C(39)	2.189(5)	2.175(2)	2.214(4)	
Cu-C(40)	2.182(5)	2.179(2)	2.102(3)	
C39-C40	1.389(8)	1.397(4)	1.409(8)	1.364(6)
Cu-I(1)				2.4850(3)
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N(1)-Cu-I(1)				109.40(6)
C(37)-I(1)-Cu				112.45(8)
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N(3)-Cu-C(40)	118.2(2)	137.37(9)	146.66(11)	
N(5)-Cu-C(39)	107.91(19)	139.08(8)	148.33(12)	
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<i>d</i> _{centroids}	4.209	4.179	4.427	4.677
	4.640	4.811	4.445	4.695
	5.136	4.867	5.120	6.927

[a] Defined as the distance between the centroid of the arene ligand and each of the three mesityl rings of the Tp^{Ms} ligand

Data collected from the solid-state structures of these new complexes point toward the existence of aromatic interactions between the coordinated arene ring and those of the mesityl fragments of the Tp^{Ms} ancillary ligand. This is inferred from the observed distances between their centroids (Table 1), which appear in the range 4.1-6.9 Å. In each complex **1-4**, two of those

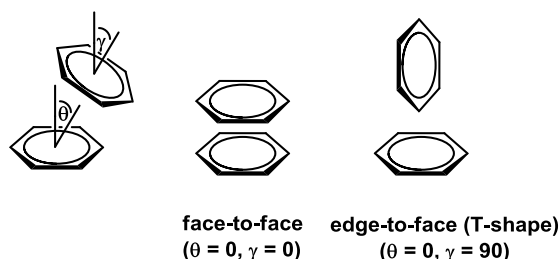


Figure 2. General π - π interactions between aromatic rings.

distances are below 5 Å, clearly in the range previously ascribed to π -aromatic interactions.^[13] Compounds **1-3** display T-shape interactions (Figure 2), with the arene ring pointing toward the mesityl rings, as well as a second π - π interaction that maybe classified as a distorted face-to-face type. In the case of complex **4**, there is a nearly parallel interaction (face-to-face) between the arene ligand and one mesityl ring.

X-ray structure of complex 5. As mentioned above, Tolman and co-workers found that recrystallization of complex $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ in the absence of THF or just upon exposing it to vacuum led to materials of analytical composition " $\text{Tp}^{\text{Ms}}\text{Cu}$ ", which could not be characterized.^[4] In our hands, we have obtained single crystals of such complex and characterized by X-ray studies as the dinuclear complex shown in Figure 3. Each copper centre displays linear coordination to two pyrazolyl N-donor atoms from two different Tp^{Ms} ligands. Thus, the latter acts as a bridge between two copper ions, whereas these are bridges between two Tp^{Ms} ligands. A third pyrazolyl ring remains as non-coordinated. The structure is similar to those reported for the Tp^{tBu} and $\text{Tp}^{\text{tBu,Me}}$ [Tp^xCu]₂ complexes by Tolman^[9] and Parkin,^[10] respectively. It is worth mentioning that the Cu-Cu distance of 3.659 Å found in **5**, slightly higher than those observed for the analogs Tp^{tBu} , and $\text{Tp}^{\text{tBu,Me}}$ (3.300(5) and 3.284(8) Å) demonstrates the lack of metal-metal bond interaction (van der Waals radius of Cu = 1.40 Å).^[14]

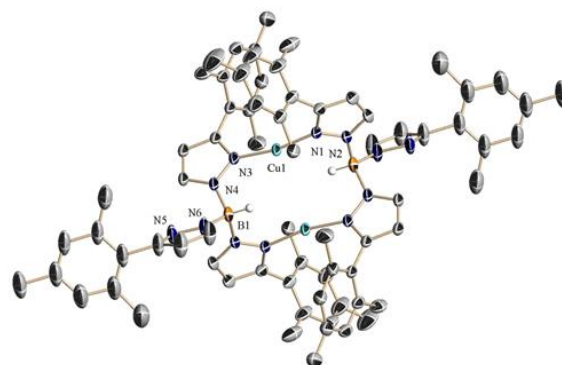
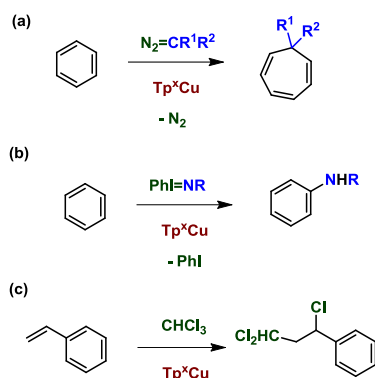


Figure 3. ORTEP view of the molecules of complex **5**. Hydrogen atoms have been omitted for clarity.

Relevance of the $\text{Tp}^{\text{Ms}}\text{Cu}(\text{arene})$ complexes in catalytic systems. In the last decades our group and others have employed Tp^xML ($M = \text{Cu}, \text{Ag}$) complexes as catalyst precursors for several transformations, some of them involving aromatic substrates.^[15] This is the case, for example, of the carbene transfer reaction from diazocompounds (Scheme 4a),^[16] the nitrene transfer from iminoiodonanes (Scheme 4b)^[17] or the atom transfer radical addition of halomethanes to styrenes (Scheme 4c).^[18] In all these catalytic systems, the arene is present at a very large concentration relative to that of the catalyst (20-500 fold). The formation of arene adducts **1-3** must

be interpreted as a proof of the generation of similar species in all those catalytic systems, a fact that should be considered when analyzing the overall amount of the catalyst involved in a cycle, e. g. in kinetic studies. The formation of complex **4** is quite relevant due to the formation of one equiv of PhI in the catalytic transfer of a nitrene unit from PhI=NTs (Scheme 4), with the concomitant potential generation of complexes of formula $\text{Tp}^{\text{Ms}}\text{Cu}(\kappa^1\text{-IPh})$. Fortunately, for catalytic purposes, the lability of the Cu-arene or Cu-halogen bond affords copper-unsaturated species that promote the desired catalytic transformation.



Scheme 4. $\text{Tp}^{\text{Ms}}\text{Cu}$ -catalyzed transformations involving substrates with arene rings.

Conclusions

We have described the formation of complexes of composition $\text{Tp}^{\text{Ms}}\text{Cu}(\text{arene})$ (arene = toluene, **1**; nitrobenzene, **2**; chlorobenzene, **3**; iodobenzene, **4**) when solutions of $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ were exposed to excess of the arene in dichloromethane solutions. The complexes could be characterized by X-ray crystallography. In the absence of a large excess of arene, the complexes dissociate the arene ligand and form the dinuclear complex $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$, that has also been structurally characterized. Complexes **1-3** display the arene bonded to the copper centre in a η^2 -fashion whereas **4** contains the arene bonded to the metal in a κ^1 -iodine manner. Crystallographic data allow proposing the existence of π - π interactions between the arene ligand and the mesityl rings of the ancillary Tp^{Ms} ligand. The demonstration of the existence in solution of these complexes has impact in a number catalytic systems that employ the $\text{Tp}^{\text{Ms}}\text{Cu}$ core, since a certain amount of the catalyst would be resting on those NMR-undetectable intermediates.

Experimental Section

All reactions and manipulations were performed in a M-Braun glovebox under an inert atmosphere of dinitrogen or using standard Schlenk techniques. All substrates were purchased from Sigma-Aldrich and used without further purification. Solvents were dried degassed before use.

The $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ complex was prepared according to literature methods.^[4] NMR spectra were recorded on an Agilent 500 DD2, ^1H and ^{13}C NMR shifts were measured relative to deuterated solvents peaks but are reported relative to tetramethylsilane. FT-IR spectra were collected on a Nicolet IR200 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400.

General synthetic protocol for complexes $\text{Tp}^{\text{Ms}}\text{Cu}(\text{arene})$ (1-4**).** To a solution of complex $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ (0.1 g, 0.14 mmol) in dichloromethane (20 mL) 30 equiv of the arene were added. After 1 h of stirring, 5 mL of pentane were added and the solution was evaporated under reduced pressure until cloudiness. Cooling at $-30\text{ }^\circ\text{C}$ yielded microcrystalline materials of **1-4**, that were directly taken from the liquor for X-ray determination. Isolated yields of 60-80% for **2** and **4** were found, whereas the reactions with toluene and chlorobenzene led to similar yields into **5** due to loss of arene ligand during drying.

$\text{Tp}^{\text{Ms}}\text{Cu}(\text{NO}_2\text{C}_6\text{H}_5)$ (**2**). Anal. Calcd for $\text{C}_{42}\text{H}_{45}\text{BCuN}_7\text{O}_2$: C, 66.88; H, 6.01; N, 13.00. Found: C, 66.98; H, 6.54; N, 12.30. IR(KBr): $\nu(\text{B-H})$, 2452 cm^{-1} .

$\text{Tp}^{\text{Ms}}\text{Cu}(\text{IC}_6\text{H}_5)$ (**4**). Anal. Calcd for $\text{C}_{41}\text{H}_{45}\text{BCuIN}_6$: C, 60.41; H, 5.43; N, 10.06. Found: C, 60.19; H, 5.37; N, 10.07. IR(KBr): $\nu(\text{B-H})$, 2468 cm^{-1} .

Synthesis of $[\text{Tp}^{\text{Ms}}\text{Cu}]_2$ (5**).** Complex $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ (0.22 g, 0.31 mmol) was dissolved in dichloromethane (15 mL). After 5 min of stirring the solution was taken to dryness, this procedure being repeated twice to ensure THF elimination. Then the solid was washed with petroleum ether (15 mL) and dried under vacuum. Recrystallization from dichloromethane afforded complex **5** as white crystals. Yields: 0.175 g, 90%. Anal. Calcd for $\text{C}_{72}\text{H}_{80}\text{B}_2\text{Cu}_2\text{N}_{12}$: C, 68.53; H, 6.34; N, 13.34. Found: C, 68.82; H, 6.44; N, 13.39. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.84 (s, 18H, CH_3 mesityl), 2.34 (s, 9H, CH_3 mesityl), 6.13 (d, 3H, $J = 2\text{ Hz}$, $\text{CH}_{\text{pyrazol}}$), 6.79 (s, 6H, $\text{CH}_{\text{mesityl}}$), 7.92 (d, 3H, $J = 2\text{ Hz}$, $\text{CH}_{\text{pyrazol}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2): δ 20 (CH_3 mesityl), 20.9 (CH_3 mesityl), 106.1 ($\text{CH}_{\text{pyrazol}}$), 127.8 ($\text{CH}_{\text{mesityl}}$), 130.1 ($\text{C}_{\text{qmesityl}}$), 135.8 ($\text{CH}_{\text{pyrazol}}$), 137.1 ($\text{C}_{\text{qmesityl}}$), 137.3 ($\text{C}_{\text{qmesityl}}$), 152.5 ($\text{C}_{\text{qpyrazol}}$).

Crystal X-Ray structure analysis for **1, **2**, **3**, **4** and **5**.** Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream ($T = 100\text{ K}$) to the goniometer head. Data collection was performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation $\lambda(\text{Mo K}\alpha) = 0.71073\text{ \AA}$, by means of ω and ϕ scans with a width of 0.50 degree. The data were reduced (SAINT)^[19] and corrected for absorption effects by the multi-scan method (SADABS).^[20] The structures were solved by direct methods (SIR-2002)^[21] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)^[22] minimizing $w[F_o^2 - F_c^2]^2$. All the non-hydrogen atoms were refined anisotropically, while C-H hydrogen atoms were placed in geometrically calculated positions using a riding model. Some geometric restraints (SADI and DFIX shelx instructions), the ADP restraint SIMU and the rigid bond restraint (DELU and ISOR) were used to make the geometric and ADP values of the disordered atoms more reasonable. A search for solvent accessible voids in the crystal structures **1** and **2** using PLATON,^[23] showed a potential solvent volume, impossible to model even with the most severe restraints. The corresponding CIF data represent SQUEEZE^[24] treated structure, with the undefined solvent excluded from the structural model. The SQUEEZE result was appended to the CIF. CCDC 1443481 (**1**), 1443482 (**2**), 1443483 (**3**), 1443484 (**4**) and 1821136 (**5**) contain the supplementary crystallographic data for this paper.

Acknowledgements

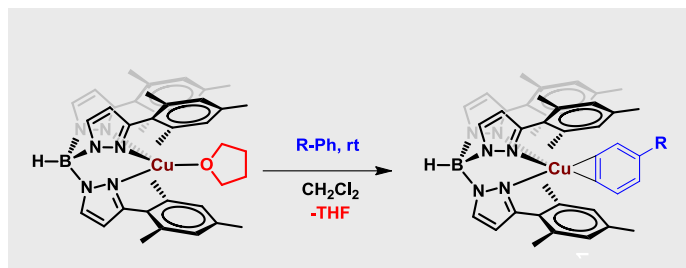
Support for this work was provided by MINECO (CTQ2014-52769-C3-1-R).

Keywords: Cu arene complexes • hindered trispyrazolylborate ligands • aromatic interactions • dihapto arene ligands copper catalysis

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FULL PAPER

**Key Topic***

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Copper(I)-arene complexes with sterically hindered trispyrazolylborate ligand

Copper(I)-arene complexes are generated when $\text{Tp}^{\text{Ms}}\text{Cu}(\text{THF})$ is exposed to excess of $\text{C}_6\text{H}_5\text{-R}$. The new compounds are unstable upon isolation, but their formation in solution is relevant in the context of $\text{Tp}^{\text{x}}\text{Cu}$ -mediated catalytic transformations.