Inorg. Chem. **2007**, *46*, 7428–7435

Inorganic Chemistry
Article

Effects of the Substituents in the Tp^{x}Cu Activation of Dioxygen: An Experimental Study

Miguel A. Mairena,[†] Juan Urbano,[†] José Carbajo,[†] J. Joaquín Maraver,[†] Eleuterio Alvarez,[‡] M. Mar Díaz-Requejo,*,[†] and Pedro J. Pérez*,[†]

Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales,
Unidad Asociada al CSIC, and Departamento de Ingeniería Química, Química Física y Química
Orgánica, Campus de El Carmen s/n, Universidad de Huelva, 21007 Huelva, Spain, and
Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla, Avda. Américo Vespucio 49,
41092 Sevilla, Spain

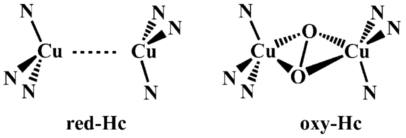
Received April 13, 2007

A series of Tp^{x}Cu(I) complexes (Tp^x = homoscorpionate ligand) have been reacted in solution with dioxygen at room temperature. Two different behaviors have been observed: the already described reaction with O_2 or the lack of any transformation. The trend has been correlated with the electronic density at the metal center, and that has been evaluated by means of cyclic voltammometry studies as well as by IR studies with the Tp^{x}Cu(CO) complexes. The data collected indicate that the former could serve as a better tool to predict such transformation, establishing a limit above which the complexes are stable under oxygen in solution. Catalytic tests carried out under oxygen have demonstrated that the use of an inert atmosphere is not a requirement in some cases.

Introduction

The activation of dioxygen in nature by copper-containing macromolecules is a well-known process.[1,2] The active sites of the hemocyanine (Hc) are known to be formed by a dicopper center, with three imidazole residues bonded to each metal ion (Scheme 1). This reduced[3] form of Hc can accommodate an oxygen molecule in the so-called oxyHc form,[4] in a process in which O_2 undergoes a two-electron reduction to afford a peroxide ion ligated to both copper centers in a μ-η^2:η^2 fashion. Since the geometry of the Hc half-core resembles that of the Tp^{x}Cu(I) complexes (Tp^x = homoscorpionate ligand), these compounds have been commonly accepted as models for that copper protein.[2] Seminal work by Kitajima, Moro-Oka, and co-workers[5] showed the capabilities of several Tp^{R_2}Cu complexes to react with molecular oxygen at low temperature (Scheme 2, reaction i). In good accord with the expectation for a model complex, this interaction led to the characterization of μ-η^2:η^2-peroxo binuclear copper complexes (similar to that of the active site of Hc) that spontaneously decomposed upon warming toward μ-oxo dinuclear species (Scheme 2, reaction ii),[6] in a process in which a first-order kinetic behavior was observed for oxygen evolution. The oxo species could be trapped with carbon dioxide (Scheme 2, reaction iii), leading to the characterization of a μ-carbonato dinuclear species.[7] Reaction

Scheme 1. Simplified Representation of the Reduced and Oxidized Forms of Hemocyanine



---

* To whom correspondence should be addressed. E-mail: perez@dqcm.uhu.es (P.J.P), mmdiaz@dqcm.uhu.es (M.M.D.R.).

[†] Universidad de Huelva.

[‡] CSIC-Universidad de Sevilla.

(1) (a) Klinman, J. P. *Chem. Rev.* **1996**, *96*, 2541. (b) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563.

(2) (a) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013. (b) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047.

(3) (a) Hazes, B.; Magnus, K. A.; Bonaventura, V.; Dauter, Z.; Kalk, K. H.; Hol, W. G. J. *Protein Sci.* **1993**, *2*, 597. (b) Magnus, K. A.; Ton-That, H.; Carpenter, J. E. *Chem. Rev.* **1994**, *94*, 727.

(4) (a) Magnus, K.; Ton-That, H. *J. Inorg. Biochem.* **1992**, *47*, 20. (b) Magnus, K. A.; Hazes, B.; Ton-That, H.; Bonaventura, C.; Bonaventura, J.; Hol, W. G. J. *Proteins: Struct., Funct., Genet.* **1994**, *19*, 302. (c) Cuff, M. E.; Miller, K. I.; Vanholde, K. E.; Hendrickson, W. A. *J. Mol. Biol.* **1998**, *278*, 855.

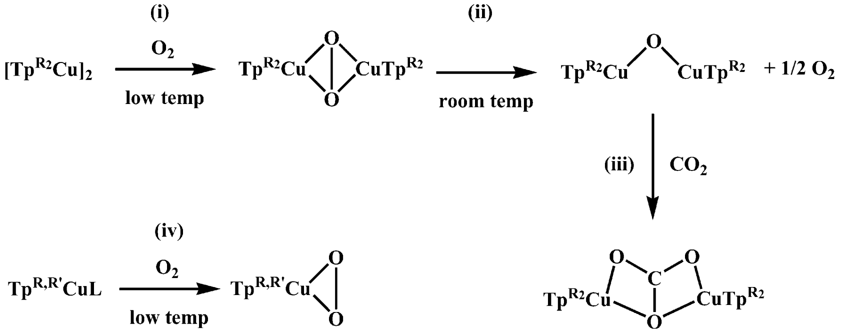
(5) (a) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8975. (b) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitakawa, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 151.

(6) Kitajima, N.; Koda, T.; Iwata, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8833.

(7) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitakawa, T.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664.

10.1021/ic7007073 CCC: $37.00

Scheme 2. Reaction Patterns Reported for Tp^{x}Cu Complexes and Molecular Dioxygen



i at Scheme 2 has been observed with several Tp^{x}Cu complexes (Tp*, Tp^{iPr_2}Cu, and Tp^{Ph_2}Cu).[5−7,8] Interestingly, when Tp^{CF_3,CH_3}Cu was employed by Gorun and co-workers,[9] the formation of the resulting μ-η^2:η^2-peroxo binuclear copper was reversible at room temperature (r.t.), in contrast with the aforementioned low-temperature stability of these species. This behavior has also been reported for other non-Tp^x-based copper systems.[10] It is also worth mentioning that the use of Tp^{tBu,iPr}Cu led to the formation of the mononuclear superoxocopper(II) species,[11] due to the steric hindrance of the *t*-Bu group located at the C3 position in the pyrazolyl rings (Scheme 2, equation iv).

Despite the interest of this oxygen reduction process by copper(I) centers, only a few Tp^{x}Cu complexes have been tested to date. Most of them were restricted to alkyl-containing subtituents in the pyrazolyl rings, i.e., electron donating groups, and in all cases, the peroxo species were formed. The only report of electron-withdrawing groups was that of the already-mentioned CF$_3$-substituted ligand[9] that provided the rare example, for Tp^{x}Cu complexes, of reversible oxygen binding and remarkable stability. This atypical behavior was explained in terms of the existence of a dramatic effect of fluorination in oxygen chemistry that involved a certain degree of encapsulation of the oxygen moiety by the fluorine atoms. A recent, very elegant theoretical work by Aullón and co-workers[12] supported this explanation, although most of the work referred to yet nondescribed Tp^x ligands. We have recently been attracted by the nature of the interaction between Tp^{x}Cu and oxygen, since for the past decade, we have employed Tp^{x}Cu(I) complexes as catalysts for several transformations.[13] During these studies, we have observed a distinct behavior of the Tp^{x}Cu complexes toward the existence of adventitious oxygen in the reaction medium. Because of this, we decided to investigate the reaction of molecular oxygen and a series of Tp^{x}Cu complexes with different substituents in the pyrazolyl rings of the Tp^x ligands. This study has led to the finding of the existence of a strong electronic effect in this transformation, in such a way that the oxidation of the copper center can be *completely inhibited* using the appropriated electron-withdrawing groups at the Tp^x ligands. In view of these results, we have now found that previously reported Tp^{x}Cu-catalyzed reactions can be performed under an open-air atmosphere instead of under inert nitrogen.

Results and Discussion

Reaction of Tp^{x}Cu Complexes with O$_2$. The reaction of a MTp^x salt (M = Na, Tl) with CuI in acetonitrile or methylene chloride is a well-known procedure for the synthesis of Tp^{x}Cu complexes. This procedure affords materials of analytical composition Tp^{x}Cu, although mono- or dinuclear structures have been reported depending of the steric hindrance of the R^3 groups in the pyrazolyl rings.[14] When the reaction is carried out in acetonitrile, mononuclear, acetonitrile adducts of formula Tp^{x}Cu(NCMe) are usually obtained when crystallized from the same solvent. Crystallization from other solvents led to the loss of coordinated acetonitrile. We have applied this strategy for the synthesis of a series of these compounds (Table 1) to be further reacted with dioxygen.

Once these compounds have been prepared and isolated as crystalline materials, we have studied the effect of the exposure of their solutions to an oxygen atmosphere. As a general strategy, 0.1 mmol of Tp^{x}CuL (L = CH$_3$CN) or Tp^{x}Cu has been dissolved in acetonitrile or methylene chloride (50 mL) in a 0.25 L Schlenk flask. The atmosphere was removed under vacuum, and the flask was then filled with pure oxygen. The mixture was stirred at room temperature for 1 h, and then the UV−vis spectrum was recorded. At that point, the flask was again purged and filled with CO$_2$. After 4 h of stirring, the volatiles were removed and the

---

(8) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Koda, T.; Moro-oka, Y.; Hashimoto, S.; Kitakawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.

(9) (a) Hu, Z.; Williams, R. D.; Tran, D.; Spiro, T. G.; Gorun, S. M. *J. Am. Chem. Soc.* **2000**, *122*, 3556. (b) Hu, Z.; George, G. N.; Gorun, S. M. *Inorg. Chem.* **2001**, *40*, 4812.

(10) (a) Hayashi, H.; Fujinami, S.; Nagatomo, S.; Ogo, S.; Suzuki, M.; Uehara, A.; Watanabe, Y.; Kitakawa, T. *J. Am. Chem. Soc.* **2000**, *122*, 2124. (b) Kodera, M.; Katayama, K.; Tachi, Y.; Kano, K.; Hirota, S.; Fujinami, S.; Suzuki, M. *J. Am. Chem. Soc.* **1999**, *121*, 11006.

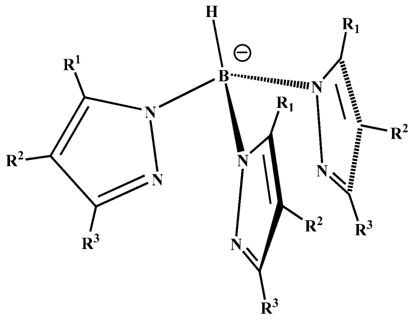
(11) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *126*, 12079.

(12) Aullón, G.; Gorun, S. M.; Alvarez, S. *Inorg. Chem.* **2006**, *45*, 3594.

(13) See for example: (a) Díaz-Requejo, M. M.; Caballero, A.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 978. (b) Díaz-Requejo, M. M.; Belderrain, T. R.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 3167. (c) Caballero, A.; Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 1446. (d) Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 896. (e) For a review, see: Díaz-Requejo, M. M.; Pérez, P. J. *J. Organomet. Chem.* **2005**, *690*, 5441.

(14) Trofimenko, S. *Scorpionates, The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

Table 1. Homoscorpionate[a] Ligands and Copper Complexes Employed in This Work

	Tp^x	R^1	R^2	R^3	complex
	Tp* (or Tp^{Me_2})	Me	H	Me	Tp*Cu
	Tp^{Cy}	H	H	C_6H_{11}	$Tp^{Cy}Cu(NCMe)$
	Tp^{cbu}	H	Br	cyclobutyl	$Tp^{cbu}Cu$
	Tp^{cpe}	H	Br	cyclopentyl	$Tp^{cpe}Cu$
	$Tp^{*,Br}$	Me	Br	Me	$Tp^{*Br}Cu$
	$Tp^{Cy,4Br}$	H	Br	C_6H_{11}	$Tp^{Cy,4Br}Cu(NCMe)$
	Tp^{p-An}	H	H	p-$MeOC_6H_4$	$Tp^{p-An}Cu\cdot{}^1/_2CH_2Cl_2$
	$Tp^{Ph,4Pr}$	H	n-Pr	C_6H_5	$Tp^{Ph,4Pr}Cu\cdot{}^1/_2CH_2Cl_2$
	Tp^{Ms}	H	H	$C_6H_2Me_3$	$Tp^{Ms}Cu$
	Tp^{Ph}	H	H	C_6H_5	$Tp^{Ph}Cu(NCMe)$
	$Tp^{3Bo7tBu}$	H	H	Bo7Bu	$Tp^{3Bo7tBu}Cu$
	Tp^{Br_3}	Br	Br	Br	$Tp^{Br_3}Cu(NCMe)$

[a] Abbreviations for Tp^x follow the accepted nomenclature. See ref 14. [b] Key: 3Bo7*t*Bu: 7-*t*-butylindazol.

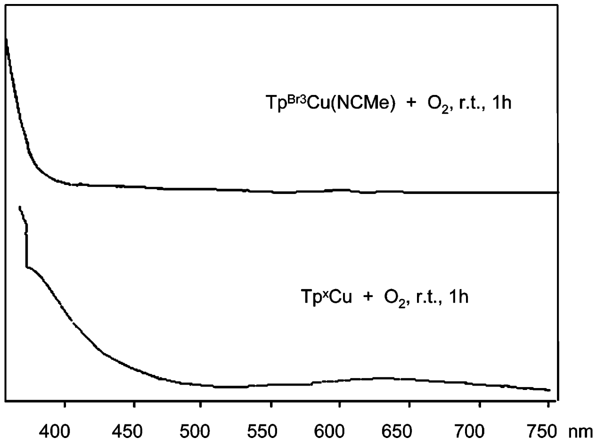


Figure 1. UV−vis spectra of a solution of Tp^xCu in CH_2Cl_2 after 1 h under an oxygen atmosphere.

residue was investigated by IR. Two distinct behaviors have been observed following the previous procedure. When an acetonitrile or methylene chloride solution of Tp*Cu was exposed to an oxygen atmosphere at room temperature, an immediate change from colorless to purple took place, which was then followed by the change into a greenish color after a few minutes. On the other hand, the solutions of $Tp^{Br_3}Cu$(NCMe) did not undergo any change in color. Figure 1 displays the UV−vis spectra of both experiments carried out after 1 h of stirring under O_2. In the case of $Tp^{Br_3}Cu(NCMe)$, the lack of any absorption in the 550−700 cm^{-1} range or in the 350−450 cm^{-1} region associated with the activation of dioxygen in any of its already-reported forms is clearly observable,[2] as observed in the Tp*Cu case. This lack of reactivity could be associated to the existence of the acetonitrile ligand that would block a coordination site for the initial bonding of the dioxygen molecule. However, other acetonitrile adducts such as $Tp^{Cy}Cu(NCMe)$, $Tp^{cbu}Cu$, or $Tp^{cpe}Cu$ readily react with oxygen, giving greenish solutions after a few minutes of exposure. In addition, we prepared the related $Tp^{Br_3}Cu$ complex in the absence of acetonitrile, using methylene chloride as the solvent, and no reaction with O_2 was observed. A series of the 12 Cu(I) complexes shown in Table 1 have been reacted and studied using the above protocol (0.1 mmol of Tp^xCuL dissolved in 50 mL of solvent). We have found that in some cases, the initial colorless solution becomes green along the reaction time (1 h, r.t.), whereas in other cases, the solution remained unchanged for that time. The analysis of the UV−vis spectra appeared inefficient in its ability to unambiguously assess whether or not the copper complex had reacted with oxygen, since in some cases the bands were not as intense as in the Tp*Cu case. According to previous literature,[6−8] it is quite probable that the species we have in solution at room temperature corresponds to an oxo complex (Scheme 2) that is known to react with carbon dioxide to yield a dinuclear carbonato complex. Therefore, we have employed carbon dioxide to trap those oxo complexes, the carbonato absorptions in the IR spectrum being later employed as the probe to establish the initial oxidation of the copper center with oxygen. Five out of the 12 Tp^xCu complexes studied have verified this reaction sequence, leading to the isolation of $[Tp^xCu]_2(\mu\text{-}CO_3)$: those with the Tp*, Tp^{Cy}, Tp^{cbu}, Tp^{cpe}, and $Tp^{*,Br}$ ligands. In good accord with the work by Kitajima and co-workers,[7] reporting a value of 1592 cm^{-1} for the CO_3^{2-} absorption in $[Tp^*Cu]_2(\mu\text{-}CO_3)$, similar bands were observed at 1585, 1585, 1586, and 1599 cm^{-1} for Tp^{Cy}, Tp^{cbu}, Tp^{cpe} and $Tp^{*,Br}$, respectively (eq 1). On the other hand, the complexes Tp^xCu with $Tp^x = Tp^{Cy,4Br}$, Tp^{p-An}, $Tp^{Ph,4Pr}$, Tp^{Ms}, Tp^{Ph}, $Tp^{3Bo7tBu}$ and Tp^{Br_3} did not show any variation of their solutions when exposed to an oxygen atmosphere. Further reaction with carbon dioxide, at room temperature, did not suppose any change either, and the material isolated after this procedure did not show any absorptions attributable to CO_3^{2-}. Actually, the ^1H NMR spectrum of the final residue was identical to that of the starting material.

$$Tp^xCu \xrightarrow[\text{(2) } CO_2\text{, r.t.}]{\text{(1) } O_2\text{, r.t.}} {}^1/_2[Tp^xCu]_2(\mu\text{-}CO_3) \qquad (1)$$

$$Tp^x = Tp^*, Tp^{cbu}, Tp^{cpe}, Tp^{Cy}, Tp^{*,Br}$$

To ascertain the nature of the final products after this O_2/CO_2 treatment, we have isolated, crystallized, and structurally characterized some of them. We first studied the already-reported system with the Tp* ligand. At the end of the reaction with carbon dioxide, slow evaporation of the methylene chloride solutions led to the isolation of crystalline material containing two types of crystals, green and blue in color. X-ray studies revealed the formation of the carbonato-bridged complex $[Tp^*Cu]_2(\mu\text{-}CO_3)$ (blue) as well

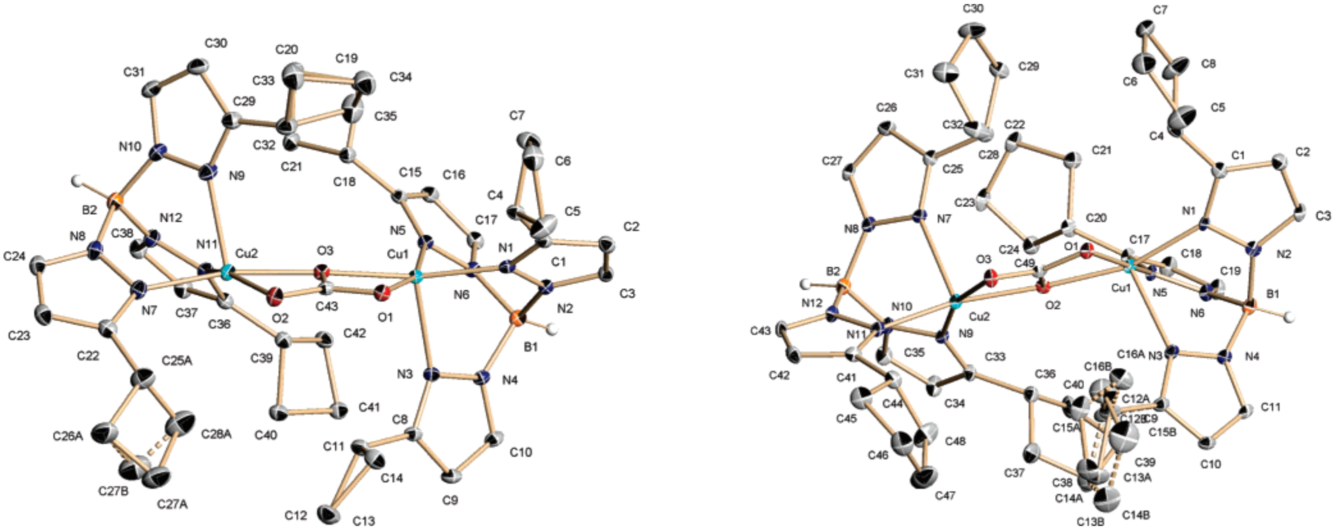
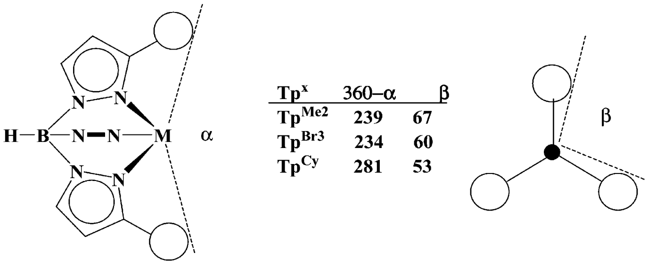


Figure 2. Molecular structures of [Tp^{cbu}Cu]$_2$(μ-CO$_3$)] (left) and [Tp^{cpe}Cu]$_2$(μ-CO$_3$)] (right). Thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

as Tp*$_2$Cu (green).[15] The latter appeared as a consequence of some decomposition during the already-described[6] peroxo → oxo transformation shown in Scheme 2. Once it was demonstrated that the protocol employed led to the carbonato compounds, we also tried to grow single crystals of the final products for the other reactive Tp^{x}Cu complexes, and we have succeeded in the case of Tp^{cbu} and Tp^{cpe}, for which only the carbonato complexes [Tp^{x}Cu]$_2$(μ-CO$_3$)] have been isolated. Figure 2 shows the molecular structure of both complexes, where the existence of two Tp^{x}Cu units and the carbonato group acting as a bridge between them is clearly observable. The lack of observation of homoleptic Tp$^x{}_2$Cu complexes for these two ligands must be explained in terms of the volume of the cycloalkyl groups located at the C3 position in the pyrazolyl ring of the Tp^x ligand.[14] These groups would collapse in a structure of this type; in fact, the carbonato groups could be defined as spacers in the structures shown in Figure 2, separating both Tp^{x}Cu cores to a distance in which the cycloalkyl groups can be accommodated. The geometries around the metal are similar to those already reported[7] for [Tp*Cu]$_2$(μ-CO$_3$) and deserve no additional comment.

We can conclude at this stage that the complexes Tp^{x}CuL, frequently claimed as models for oxygen activation, display a dual behavior toward O$_2$, in such a way that the appropriate election of the Tp^x ligand can promote or prevent the oxidation of the copper center.

Scheme 3. Cone (left) and Wedge (right) Angles for Tp^x Ligands



Tp^x	360−α	β
Tp^{Me2}	239	67
Tp^{Br3}	234	60
Tp^{Cy}	281	53

Role of the Tp^x Ligand in the Oxidation of Cu(I) by O$_2$. The observed distinct behavior of the Tp^{x}Cu complexes when reacted with O$_2$ is obviously induced by the nature of the Tp^x ligand. It is well-known that the R^1−R^3 groups at the pyrazolyl rings provide the steric and electronic properties of the ligand,[14] and it is not easy to establish the contribution of each effect in a given process. The steric hindrance at the metal center is mainly given by the R^3 groups. The cone (360-α) and wedge (β) angles of several Tp^x ligands (as thalium complexes) have been reported[14] (Scheme 3) in an effort to quantify the volume of these ligands when bonded to a metal. Although the calculated values for 360-α and β are limited in number, and they only apply when coordinated to thallium, they provide a trend that can be used for our purposes. Thus, the data in Scheme 3 indicate that the Tp* and Tp^{Br_3} ligands display similar values for α and β, implying that they are isosteric. However, the reactivity with dioxygen of the copper complexes containing those ligands is completely different, as mentioned above. A second example comes from the comparison of the very bulky Tp^{Cy} and Tp* ligands: both react with oxygen despite the large difference in volume. Unfortunately, values for 360-α and β for aryl-containing Tp^x ligands have not yet been reported. We could assume that a phenyl ring located at the R^3 position in Tp^{Ph} would have, at maximum, a similar steric effect to that of a cyclohexyl group. In any case, no reaction of Tp^{Ph}Cu(NCMe) with dioxygen has been observed. It has been reported that the use of bulky groups such *t*-Bu in R^3 avoids the formation of dinuclear species but does not preclude the reaction with dioxygen: instead of peroxo species, Cu(II)−superoxo complexes have been obtained.[11] This is at variance with our results, for which no reaction at all was observed for several Tp^{x}Cu complexes with a bulky aryl group at R^3.

Since no trend can be extracted from the experimental data to propose that the volume of the Tp^x ligand drives this reaction, we have turned to an examination of electronic effects. A well-known tool to estimate electron density at a

---

(15) Although these structures have been reported, they are included in the Supporting Information to unambiguously demonstrate the nature of the isolated products.

Table 2. Values of E_{pa} (mv) for Tp^{x}Cu and ν(CO) (cm^{-1}) for Tp^{x}Cu(CO) Complexes

	Tp*	Tp^{Cy}	Tp^{cbu}	Tp^{cpe}	Tp^{*,Br}	Tp^{Cy,4Br}
ν(CO)	2056	2061	2064	2065	2073	2068
E_{pa}	472	n.d.[a]	515	n.d.[a]	537	n.d.[a]

	Tp^{p-An}	Tp^{Ph,4Pr}	Tp^{Ms}	Tp^{Ph}	Tp^{3Bo7tBu}	Tp^{Br_3}
ν(CO)	2072	2074	2079	2080	2090	2107
E_{pa}	612	644	603	680	745	834

[a] Key: n.d. = not determined

metal center consists of the study of ν(CO) values for metal−carbonyl complexes.[16] In the case of Tp^{x}Cu complexes, the monocarbonyl adducts Tp^{x}Cu(CO) are readily generated upon bubbling of CO throughout their methylene chloride or acetonitrile solutions. We have generated in situ the carbonyl adducts of the series of Tp^{x}Cu complexes employed in this study, leading to the series of ν(CO) values shown in Table 2. It is clearly observable that a certain correlation exists between the reactivity toward the oxygen of the Tp^{x}Cu complexes and the observed ν(CO) values of Tp^{x}Cu(CO). The group of reactive complexes correspond to those with lower carbonyl frequencies, i.e., those with higher electron density at the metal center. On the other hand, electron-withdrawing Tp^{x} ligands disfavor the reaction with oxygen, since they induce a decrease in the electron density at the copper center.

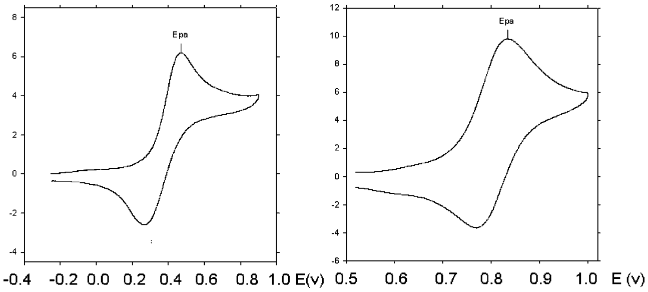


Figure 3. Cyclic voltammograms of Tp*Cu (left) and Tp^{Br_3}Cu(NCMe) (right).

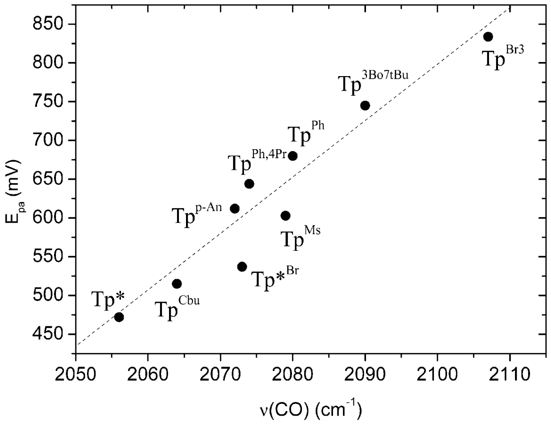


Figure 4. Correlation between ν(CO) values in Tp^{x}Cu(CO) complexes and the redox potentials (E_{pa}) of the corresponding Tp^{x}Cu complexes.

It could be thought that on the basis of the previous discussion, the reactivity of the complexes Tp^{x}Cu with dioxygen is not dependent on the steric pressure exerted by the Tp^{x}, but on the electronic density at copper, mainly due to the donating or withdrawing capabilities of the Tp^{x} ligand. However, this could be an extremely simple explanation. The transformation studied in this work consists of the oxidation of a Cu(I) center, and therefore, a parameter related to this process should be helpful. A recent work by Fujisawa and co-workers has proposed[16] that this redox process is also influenced by the steric hindrance of the ligands. Therefore, we have carried out a series of cyclic voltammetry experiments that would lead to the values of potentials that are due to the overall effect of the ligand (electronic and steric) on the redox process. As an example, Figure 3 contains the cyclic voltammograms of the two limiting cases, those of Tp*Cu and Tp^{Br_3}Cu(NCMe), in acetonitrile, in what can be considered reversible redox processes. The E_{pa} values are significantly distinct: 472 mv for Tp*Cu and 834 mv for Tp^{Br_3}Cu(NCMe). The rest of the complexes displayed E_{pa} values within that range, as shown in Table 2. A plot of ν(CO) vs E_{pa}, shown in Figure 4, reveals a correlation between both magnitudes, although the general trend does not apply when comparing case by case. For example, the Tp^{Ph}Cu(CO) and the Tp^{Ms}Cu(CO) cases only differ by one wavenumber (2080 and 2079 cm^{-1}, respectively) but differ by 77 mV in regards to their potentials (680 vs 603 mV). This behavior, also observed in other cases in a lesser extension, can be explained by assuming that the oxidation potential is mainly influenced by the electronic density at metal (measured by ν(CO) values) but that steric factors can somehow alter the purely electronic order. In the set of experiments of these Tp^{x}Cu complexes with dioxygen, those with Tp^{x} = Tp*, Tp^{Cy}, Tp^{cbu}, Tp^{cpe}, and Tp^{*Br} underwent oxidation whereas those with Tp^{x} = Tp^{Cy,Br}, Tp^{p-An}, Tp^{Ph,4Br}, Tp^{Ms}, Tp^{Ph}, Tp^{3Bo7tBu}, and Tp^{Br_3} remained unaltered. Thus, it seems that the complex Tp^{*BrCu}(NCMe) establishes the upper limit, with E_{pa} = 537 mV, for these compounds to undergo reaction with molecular oxygen. Those with higher values of E_{pa} should be stable toward O_2 in solution at room temperature. The ν(CO) values could also serve as a probe to predict such transformation, taking into account that some deviation could exist. In this case, a value around 2073 cm^{-1} could be established as the upper limit. As an example of the restrictions of this approach, the Tp^{Cy,4Br}Cu(NCMe) complex does not react with O_2, the carbonyl adduct having a ν(CO) of 2068 cm^{-1}, lower than that of the Tp^{*,Br}-containing complex. To the best of our knowledge, the examples reported in the literature of Tp^{x}Cu complexes reacting with molecular oxygen correspond to complexes with ν(CO) values below those 2073 cm^{-1} and/or 537 mV limits.[2] But there is one unique case that largely surpasses the former and *undergoes* a room-temperature reaction with O_2. It is the already mentioned fluorine-containing [Tp^{CF_3,CH_3}Cu]$_2$ complex described by Gorun and co-workers[9] that reversibly bonds dioxygen at room temperature. Tolman and co-

---

(16) DTF calculations have recently shown that C−O stretching vibrations in these compounds correlate with the electron density in copper. See: Fujisawa, K.; Ono, T.; Ishikawa, Y.; Amir, N.; Miyashita, Y.; Okamoto, K.; Lehnert, N. *Inorg. Chem.* **2006**, *45*, 1698.

workers[17a] reported the carbonyl adduct $Tp^{CF_3,CH_3}Cu(CO)$ with a ν(CO) value of 2109 cm^{-1}, nearly identical to that of $Tp^{Br_3}Cu(CO)$. However, we have not been able to induce any reaction of $Tp^{Br_3}Cu(NCMe)$ or $Tp^{Br_3}Cu$ (obtained when prepared in CH_2Cl_2) with molecular oxygen at room temperature or at 80 °C for several hours in 1,2-dichloroethane. Our study has reflected that ligand electronic deficiency disfavors the reaction with O_2. Gorun et al.[9a] proposed that the presence of fluorine atoms is the key feature to explain this "abnormal" behavior that is in contrast with the previous results by others as well as with the study reported herein. A recent work by Aullon et al.[12] reported DFT calculations that accounted, to some extent, for the behavior of the CF_3-containing copper complex.

It is worth mentioning that the correlation between ν(CO) and E_{pa} is not followed by other families of complexes relevant to bioinspired dioxygen activation. Electrochemical studies carried out with the well-known Cu(I)−TACN (TACN = triazacyclononane) system developed by Tolman and co-workers[17b] have shown the lack of this correlation when comparing the values of $E_{1/2}$ and ν(CO).

Reaction of $Tp^{Br_3}Cu(NCMe)$ and Hydrogen Peroxide. Given the stability of this Cu(I) complex under dioxygen, we decided to investigate its reactivity toward a strong oxidant such as H_2O_2. The addition of 5 equiv of this peroxide to a CH_2Cl_2 solution of $Tp^{Br_3}Cu(NCMe)$ at room temperature induced an immediate change of the initial colorless solution to green. Slow evaporation of the solvent led to the formation of green, single crystals of a compound of analytical composition $(Tp^{Br_3})_2Cu$. To ascertain the structure of this Cu(II) complex, an X-ray diffraction study was carried out, the molecular structure of which is shown in Figure 5. The more interesting feature of this structure is its similarity with that of the related $Tp^*{}_2Cu$ complex.[18] Both are triclinic, and the geometry around the metal center consists of a slightly distorted octahedron. The Cu−N distances of 2.0120(9), 2.0755(8), and 2.3859(9) Å found in $Tp^*{}_2Cu$ compare well with those in $(Tp^{Br_3})_2Cu$ of 2.038(6), 2.163(8), and 2.217(8) Å, respectively. The trans N−Cu−N groups display nearly ideal angles of 180° in both structures, whereas the cis N−Cu−N angles, within the same Tp ligand, show a minor deviation that is higher in the $Tp^*{}_2Cu$ case. The similarities between these two compounds are in good agreement with the already-commented isostericity of both ligands and with the correspondence of their cone and wedge angle values.

Catalytic Activity of Tp^xCu Complexes under Oxygen. As pointed out above, our initial aim was to understand the stability of this family of copper(I) complexes under oxygen in order to apply such knowledge to the catalytic systems based on them. Once we learned that above a certain limit of E_{pa} and/or ν(CO) the complexes are stable in solution under a dioxygen atmosphere, we ran a few catalytic experiments to demonstrate whether or not an inert atmosphere was required any longer. We have chosen the styrene cyclopropanation reaction with ethyl diazoacetate, EDA (Table 3), a transformation that is known to be efficiently catalyzed by these $Tp^xCu(I)$ complexes.[13a,b] Under an inert atmosphere, a methylene chloride solution of styrene (2.5 mmol) and the catalyst (0.05 mmol of Tp^xCu, $Tp^x = Tp^{cbu}$, Tp^{Br_3}) was prepared, and 0.5 mmol of EDA was added in one portion. After 45 min of stirring, the mixtures were investigated by GC, showing that all the EDA had been consumed in both cases, leading to a mixture of the cis and trans cyclopropanes and also some diethyl fumarate and maleate. A second series of experiments was carried out, with identical reactants, ratios, and solvent, but *under an oxygen atmosphere*. Again, after 45 min, the mixtures were investigated by GC. The reaction performed with $Tp^{Br_3}Cu$ showed identical results to those of the reaction carried out under nitrogen. However, in the case of $Tp^{cbu}Cu$, most of the EDA was yet unreacted. Upon stirring for 24 h, at least 50% of the EDA was yet unconsumed. This is the result of the oxidation of a large amount of the catalyst to Cu(II) that is not active for this reaction. On the other hand, the further addition of several 0.5 mmol portions of EDA to the flask containing the $Tp^{Br_3}Cu$ catalyst, under oxygen, yielded more cyclopropanes, demonstrating that the catalyst was still active. The same experiment has been performed with other Tp^xCu complexes above the limit of stability (E_{pa} = 537 mV) toward oxygen, with substituents such as Tp^{Ph} or Tp^{Ms}, showing that their catalytic activities are not influenced by the presence of atmospheric oxygen.

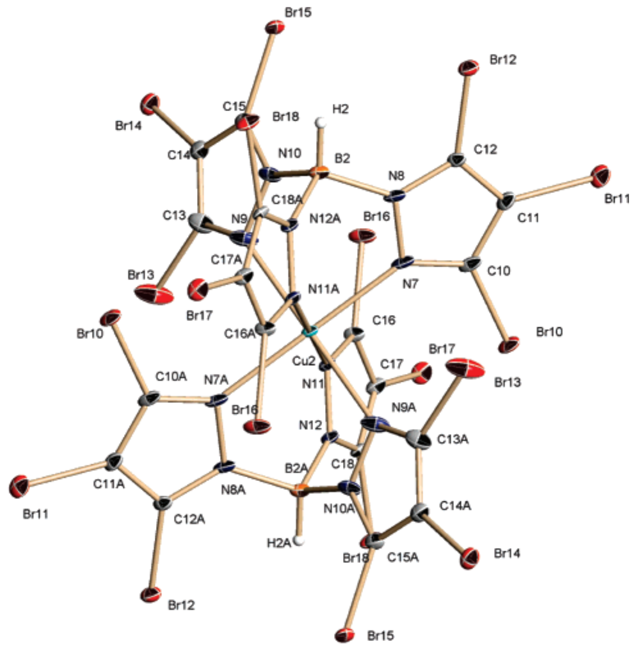


Figure 5. Molecular structure of $(Tp^{Br_3})_2Cu$. Thermal ellipsoids are drawn at the 50% probability level.

Conclusion

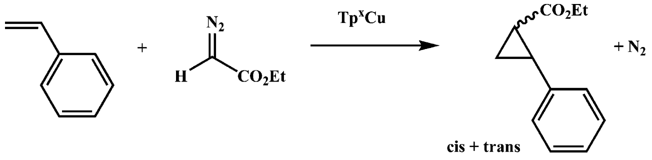
The complexes Tp^xCu or $Tp^xCu(NCMe)$ display two distinct behaviors in solution (CH_2Cl_2 or CH_3CN) under an

---

(17) (a) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Soc. Soc.* **1998**, *120*, 11408. (b) Lam, B. M. T.; Halfen, J. A.; Young Jr., V. G.; Hagadorn, J. R.; Holland, P. L.; Lledós, A.; Cucurull-Sánchez, L.; Novoa, J. J.; Álvarez, S.; Tolman, W. B. *Inorg. Chem.* **2000**, *39*, 4059.

(18) Wang, J. L.; Wang, D. W.; Miao, F.-M. *Acta Chim. Sin.* **1992**, *50*, 122.

Table 3. Effect of the Atmosphere in the Catalytic Cyclopropanation of Styrene Using $\mathrm{Tp^xCu}$ Complexes



catalyst/atmosphere	conversion (%)^a/ time (min or h)	yield cyclopropanes^b	cis/trans
$\mathrm{Tp^{Br_3}Cu(NCMe)/N_2}$	>99/45 min	87	62:48
$\mathrm{Tp^{cpe}Cu/N_2}$	>99/45 min	89	73:27
$\mathrm{Tp^{Br_3}Cu(NCMe)/O_2}$	>99/45 min	92	62:48
$\mathrm{Tp^{cpe}Cu/O_2}$	<50/24 h	89	66:34

oxygen atmosphere, being readily oxidized at room temperature or remaining unreacted, even at 80 °C. We have found that the redox potential is a better tool than the analysis of ν(CO) to predict such reactivity and that for these complexes, those with an E_{pa} value higher than ca. 537 mV should be stable under oxygen (in the absence of any additional variable such as the existence of fluorine). This knowledge has been applied to the use of these compounds as catalysts for the olefin cyclopropanation reaction, showing that in the case of oxygen-stable complexes, the use of an inert atmosphere is not yet a requirement.

Experimental Section

Solvents were rigorously dried and degassed previously to their use. All substrates and reagents were purchased from Aldrich. The $\mathrm{Tp^x}$ ligands were prepared according to literature procedures,[14] as well as the Tp*Cu[19] and $\mathrm{Tp^{Ms}Cu}$[17a] complexes. NMR experiments were run in a Varian Mercury 400 MHz spectrometer. GC data were collected with a Varian GC-3900 instrument. The IR spectra were recorded on a Nicolet FTIR 200 spectrophotometer, and the UV−vis spectra were recorded on a Thermo Helios spectrophotometer. Elemental analyses were performed by the Analytical Service of the Universidad de Huelva. Voltammetric curves were recorded on a Autolab (Eco Chemie model PGSTAT 20) instrument. A platinum electrode with an area of 7 mm^2 was used as the working electrode and a glassy-carbon rod was used as the counter electrode. All potentials were measured against Ag/AgCl/NaCl (3 M).

Synthesis of the Complexes $\mathrm{Tp^xCu}$. As a general procedure, equimolar amounts of CuI (190.5 mg, 1 mmol) and the thalium or sodium salt of the $\mathrm{Tp^x}$ ligand were dissolved in 40 mL of acetonitrile. The corresponding thalium or sodium iodide salt precipitated out of the solution during the reaction. After 8 h of stirring, the salts were filtered, and the clear, colorless solution was taken to dryness. The residue was extracted with a mixture of solvents (methylene chloride/diethyl ether or diethyl ether/petroleum ether, 5:1 v/v in all cases). Partial evaporation followed by cooling at −20 °C afforded crystalline materials of analytical purity, with yields in the range of 70−90%. In some cases, an acetonitrile molecule was coordinated to the copper center whereas in others the $\mathrm{Tp^xCu}$ unit crystallized alone or with methylene chloride. Complete characterization including ^{1}H and ^{13}C NMR, IR, and analytical data are given in the Supporting Information.

Reaction of $\mathrm{Tp^xCu(L)}$ with Oxygen and Carbon Dioxide. The amount of 0.1 mmol of $\mathrm{Tp^xCu}$ was dissolved in acetonitrile or methylene chloride (50 mL) in a Schlenk flask. The atmosphere was removed under vacuum, and the flask was then filled with oxygen. The mixture was stirred at room temperature for 1 h, and then the UV−vis spectrum was recorded. The flask was then purged and filled with CO_2. After 4 h of stirring, the volatiles were removed and the residue was investigated by IR. The addition of methylene chloride and the slow evaporation of the solvent led to the formation of single crystals when $\mathrm{Tp^x} = \mathrm{Tp^{cbu}}$ or $\mathrm{Tp^{cpe}}$.

Reaction of $\mathrm{Tp^{Br_3}Cu(NCMe)}$ with Hydrogen Peroxide. The amount of 0.1 mmol of $\mathrm{Tp^{Br_3}Cu(NCMe)}$ was dissolved in 20 mL of methylene chloride, and 5 equiv of H_2O_2 was added (from a commercial solution of H_2O_2 20% w/w in water). The colorless solution became green immediately. After 1 h of stirring, the volatiles were removed. No relevant information could be extracted from the IR spectrum of the residue. The addition of methylene chloride and the slow evaporation gave green single crystals suitable for X-ray studies. No other copper complexes were identified from the reaction mixture. Yield: 30%.

Catalytic Experiments. To a solution of 0.02 mmol of the copper complex in 10 mL of methylene chloride, 125 equiv of styrene (2.5 mmol) and 25 equiv of ethyl diazoacetate (0.5 mmol) were added in one portion. The mixture was stirred at room temperature for 1 h and then analyzed by GC. The products in the catalytic reactions were characterized as in previous work from this laboratory.[13a,b]

Cyclic Voltammetry Experiments. A 2.5 mM stock solution was prepared for each copper complex in acetonitrile. The final, 1 mM solution was prepared by successive dilution (0.5 mM solutions were used in the case of $\mathrm{Tp^{Cbu}}$ and $\mathrm{Tp^{*Br}}$ and a 0.1 mM solution was used for $\mathrm{Tp^{Ms}}$, due to their low solubility). In all cases, the ionic strength was kept at 0.1 M due to the addition of tetrabutylammonium perchlorate. Voltammetric curves were recorded for each complex, varying the scan rate from 0.05 up to 1 V/s. A reproducibility study involving 10 independent runs at different sweep rates (0.1, 0.2, and 0.5 V/s) produced a variation coefficient of 1% for the potential peak.

Structure Determination. Crystal data for $[\mathrm{Tp^{cbu}Cu}]_2(\mu\text{-}CO_3)$: $C_{45}H_{59}B_2Cu_2N_{13}O_3$ [$C_{43}H_{56}B_2Cu_2N_{12}O_3$, C_2H_3N], $M_w = 978.75$, a single crystal of suitable size, green prism (0.33 × 0.23 × 0.20 mm^3) from CH_2Cl_2−acetonitrile, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream, 100(2) K, to the goniometer head. Characteristics: Monoclinic, space group $P2_1/c$ (No. 14), $a = 13.3060(9)$ Å, $b = 14.5130(11)$ Å, and $c = 24.3521(18)$ Å, $\beta = 103.797(2)°$, $V = 4566.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.423$ g cm^{-3}, λ(Mo Kα_1) = 0.71073 Å, $F(000) = 2048$, $\mu = 0.988$ mm^{-1}. A total of 94 246 reflections were collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range $5.62 < 2\theta < 61.22°$, and 13 714 independent reflections [R(int) = 0.0482] were used in the structural analysis. The data

---

(19) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711.

were reduced (*SAINT*) and corrected for Lorentz polarization effects and absorption by the multiscan method applied by *SADABS*.[20,21] The structure was solved by direct methods (*SIR-2002*)[22] and refined against all F^2 data by full-matrix least-squares techniques (*SHELXL97*)[23] converged to final values of $R_1 = 0.0430$ [$I > 2\sigma(I)$] and $R_2 = 0.1196$ for all data, with a goodness-of-fit on F^2, $S = 1.051$, and 595 parameters.

Crystal data for $[\mathrm{Tp^{cpe}Cu}]_2(\mu\text{-}\mathrm{CO_3})$: $C_{49}H_{68}B_2Cu_2N_{12}O_3$, $M_w = 1021.85$, a single crystal of suitable size, green plate ($0.55 \times 0.49 \times 0.49$ mm^3) from CH_2Cl_2−acetonitrile, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream, 100(2) K, to the goniometer head. Characteristics: monoclinic, space group $P2_1/n$ (No. 14), $a = 12.310(4)$ Å, $b = 24.837(7)$ Å, and $c = 16.479(5)$ Å, $\beta = 103.257(9)°$, $V = 4904(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.384$ g cm^{-3}, $\lambda(\mathrm{Mo\ K\alpha_1}) = 0.71073$ Å, $F(000) = 2152$, $\mu = 0.923$ mm^{-1}. A total of 20 971 reflections were collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range $4.68 < 2\theta < 59.96°$, and 13 679 independent reflections [$R(\mathrm{int}) = 0.0608$] were used in the structural analysis. Data reduction, solving, and refinement was performed likewise, as above, converging to final values of $R_1 = 0.0735$ [$I > 2\sigma(I)$] and $R_2 = 0.2128$ for all data, with a goodness-of-fit on F^2, $S = 1.044$, and 658 parameters.

Crystal data for $(\mathrm{Tp^{Br_3}})_2\mathrm{Cu}$: $C_{19}H_4B_2Br_{18}Cl_2CuN_{12}$ [$C_{18}H_2B_2Br_{18}CuN_{12}$, CH_2Cl_2], $M_w = 1994.78$, a single crystal of suitable size, green prism ($0.23 \times 0.22 \times 0.19$ mm^3) from CH_2Cl_2-acetonitrile, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream, 100(2) K, to the goniometer head. Characteristics: triclinic, space group $P\bar{1}$ (No. 2), $a = 12.5043(10)$ Å, $b = 13.0229(12)$ Å, and $c = 15.5065(15)$ Å, $\alpha = 69.468(2)°$, $\beta = 75.945(2)°$, $\gamma = 69.019(2)°$, $V = 2188.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.028$ gcm^{-3}, $\lambda(\mathrm{Mo\ K\alpha_1}) = 0.71073$ Å, $F(000) = 1810$, $\mu = 17.094$ mm^{-1}. A total of 53 197 reflections were collected from a Bruker-Nonius X8Apex-II CCD diffractometer in the range $2.84 < 2\theta < 61.18°$ and 13 197 independent reflections [$R(\mathrm{int}) = 0.0557$] were used in the structural analysis. Data reduction, solving, and refinement was performed likewise, as above, converging to final values of $R_1 = 0.0588$ [$I > 2\sigma(I)$] and $R_2 = 0.1642$ for all data, with a goodness-of-fit on F^2, $S = 1.070$, and 490 parameters.

Acknowledgment. Financial support of this work from the MEC (CTQ2005-00324/BQU) is acknowledged. The Universidad de Huelva (Plan Propio de Investigación) and the Junta de Andalucía (JU) are also acknowledged.

Supporting Information Available: Characterization of the copper complexes as well as X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7007073

---

(20) *Bruker Apex 2*, version 2.1; Bruker AXS, Inc.: Madison, WI, 2004 .

(21) *SAINT* and *SADABS*; Bruker AXS, Inc.: Madison, WI, 2001.

(22) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *SIR2002: The Program*; *J. Appl. Crystallogr.* **2003**, *36*, 1103.

(23) Sheldrich, G. M. *SHELXL97*; University of Göttingen, Göttingen, Germany, 1997.