Inorg. Chem. **2007**, *46*, 7725–7730

Inorganic Chemistry
Article

Copper–Homoscorpionate Complexes as Active Catalysts for Atom Transfer Radical Addition to Olefins

José María Muñoz-Molina,[†] Ana Caballero,[†] M. Mar Díaz-Requejo,[†] Swiatoslaw Trofimenko,[‡] Tomás R. Belderraín,[*,†] and Pedro J. Pérez[*,†]

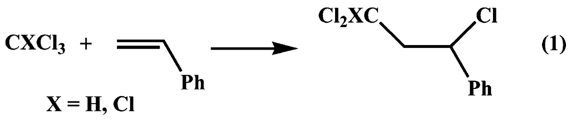
Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Campus de El Carmen s/n, Universidad de Huelva, 21007-Huelva, Spain, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received February 13, 2007

Cu(I) complexes containing trispyrazolylborate ligands efficiently catalyze the atom transfer radical addition (ATRA) of polyhalogenated alkanes to various olefins under mild conditions. The catalytic activity is enhanced when bulky and electron donating Tp^x ligands are employed. Kinetic data have allowed the proposal of a mechanistic interpretation that includes a Cu(II) pentacoordinated species that regulates the catalytic cycle.

Introduction

Known for more than half a century, the Kharasch reaction constitutes one effective method for the generation of carbon−carbon bonds in a catalytic manner.[1,2] This process consists of the addition of a polyhalogenated saturated hydrocarbon to an alkene (eq 1) and requires either a radical initiator (original Kharasch reaction) or a transition metal catalyst. It has not been until the mid-90s that the latter has emerged due to its relevance with another process: atom-mediated olefin radical polymerization. Early reports in this area by Sawamoto[3] and Matyjazewski[4] showed the similarities between both transformations in such a way that the polymerization process was named atom transfer radical polymerization (ATRP) following that of the metal-catalyzed Kharasch reaction, the atom transfer radical addition (ATRA).[5] ATRP is currently one of the areas of interest in polymer chemistry,[6] and it is well-established that knowledge from ATRA can be directly applied to ATRP processes.



(1)

Scheme 1 displays the commonly accepted mechanism for ATRA reactions.[5] A metal center with accessible, consecutive oxidation states is required. The cycle initiates with the metal-induced homolytic cleavage of the carbon−halogen bond that generates a metal−halide and a carbon-centered radical. The latter species interacts with the olefin to afford another radical that is more reactive than the former, inducing the abstraction of the halogen from the metal−halide in a step in which the metal is reduced to the initial oxidation state and the desired addition product is formed. It seems clear that the choice of the metal must be related to its capabilities to undergo the reversible oxidation−reduction process. In addition, a subtle balance in the relative concentrations of both oxidation states present in the reaction mixture is also crucial: if one of them is too stable, then it constitutes a thermodynamic sink from which the cycle cannot restart. Several metals have been described to catalyze this transformation that is known for both the inter- and intramolecular versions. Among them, ruthenium-[7] and nickel-based[8] catalysts have provided the

---

[*] To whom correspondence should be addressed. E-mail: perez@dqcm.uhu.es (P.J.P.), trodri@dqcm.uhu.es (T.R.B).

[†] Universidad de Huelva.

[‡] University of Delaware. Deceased February 2007.

(1) (a) Kharasch, M. S.; Engelmann, H.; Mayo, F. R. *J. Org. Chem.* **1938**, *2*, 288. (b) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102*, 128.

(2) (a) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423. (b) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. (c) Curran, D. P. *Synthesis* **1988**, 417. (d) Bellus, D. *Pure Appl. Chem.* **1985**, *57*, 1827. (e) Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

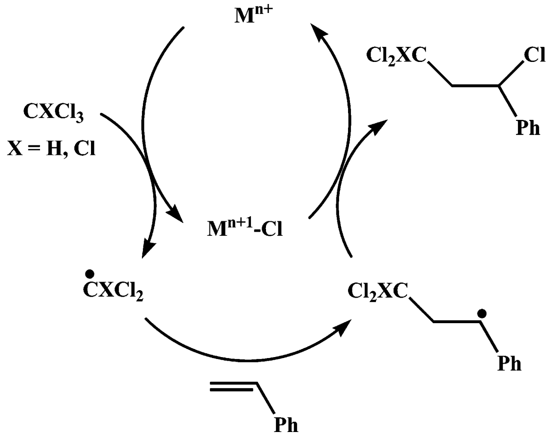
(4) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(5) Matyjaszewski, K. L. *Curr. Org. Chem.* **2002**, *6*, 67.

(6) (a) Matyjaszewski, K.; Davis; T. P., Ed. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, NJ, 2002. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (c) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.

10.1021/ic0702872 CCC: $37.00

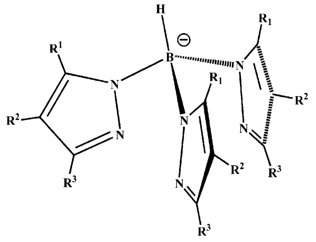
Scheme 1. General Mechanism for Atom Transfer Radical Addition to Styrene



best values for the intermolecular version, whereas the use of copper has been mainly restricted to intramolecular atom transfer radical cyclization (ATRC).[9] Only a few examples of its use in ATRA have been reported to date.[10]

In the past decade, we have been involved in the use of polypyrazolylborate[11]−copper complexes as catalysts for the transfer of carbene,[12] nitrene,[13] and oxo[14] groups to hydrocarbons. We have now turned our attention to the use of this family of complexes of the general formulas Tp^{x}Cu(NCMe) or Tp^{x}Cu in ATRA processes. The availability of a number of different Tp^x ligands that exert distinct steric and electronic effects in the metal center has provided an excellent tool to tune these compounds toward its catalytic activity in ATRA reactions. The results we report in this Article show that these Tp^{x}Cu catalysts (Table 1) display a remarkable activity that surpasses those of other previous Cu-based catalysts. Interesting mechanistic information has also been collected, providing insight for the design of future, more active catalysts.

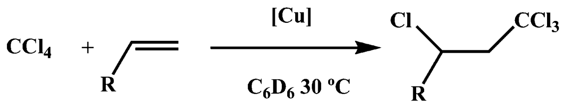
Table 1. Homoscorpionate Ligands Employed in This Work



Tp^x	R^1	R^2	R^3
Tp*	Me	H	Me
Tp$^{tBu, Me}$	Me	H	^{t}Bu
Tp^{Cy,4Br}	H	Br	C_6H_{11}
Tp^{Br3}	Br	Br	Br
Tp^{Ms}	H	H	$C_6H_2Me_3$

Results and Discussion

Addition of CCl_4 and $CHCl_3$ to Olefins Catalyzed by Tp^{x}Cu Complexes. In a typical procedure, a 4.6 mM solution (C_6D_6) of the Tp^{x}Cu complex, containing 300 equiv of the olefin (styrene, methyl methacrylate, or 1-hexene) and 1200 equiv of CCl_4, was maintained at 30 °C for 24 h and then was investigated by ^{1}H NMR. The final mixtures contained the desired product (eq 2) as well as an excess of CCl_4 and olefin. As shown in Table 2, the conversions observed after that time were clearly dependent on the catalyst employed. The best conversions were obtained with those catalysts containing the Tp^{tBu,Me} and Tp^{Cy,4Br} ligands, whereas those with Tp* or Tp^{Ms} provided low conversions. On the other hand, the use of Tp^{Br3}Cu(NCMe) has proven ineffective for this transformation even at temperatures as high as 80 °C. In the case of **5** as the catalyst, the low conversions observed at 30 °C could be increased upon heating at 70 °C, being comparable to those with **2** or **3** at 30 °C. In the experiment carried out with MMA and **1** as the catalyst, minor amounts of polymeric material were



(2)

---

(7) (a) Quebatte, L.; Thommes, K.; Severin, K.; Severin, K. *J. Am. Chem. Soc.* **2006**, *128*, 7440. (b) Quebatte, L.; Solari, E.; Scopelliti, R.; Severin, K. *Organometallics* **2005**, *24*, 1404−1406. (c) Quebatte, L.; Scopelliti, R.; Severin, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1520. (d) Lee, B. T.; Schrader, T. O.; Martín-Matute, B.; Kauffman, C. R.; Zhang, P.; Snapper, M. L. *Tetrahedron* **2004**, *60*, 7391. (e) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2003**, *44*, 8421. (f) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830. (g) Opstal, T.; Verpoort, F. *New J. Chem.* **2003**, *27*, 257. (h) De Clercq, B.; Verpoort, F. *J. Organomet. Chem.* **2003**, *672*, 11. (i) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Eur. J. Org. Chem.* **2001**, 2689. (j) Tallarico, J. A.; Malnick, L. M.; Snapper, M. L. *J. Org. Chem.* **1999**, *64*, 344. (k) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2000**, *41*, 6071.

(8) (a) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423. (b) van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985. (c) Kleij, A. W.; Gossage, R. A.; Klein Gebbink, R. J. M.; Brinkmann, N.; Reijerse, E. J.; Kragl, U.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 12112.

(9) Clark, A. J. *Chem. Soc. Rev.* **2002**, *31*, 1.

(10) (a) Hajek, M.; Kotora, M.; Davis, R.; Fischer, C.; Joshu, W. A. C. *Collect. Czech. Chem. Commun.* **1996**, *61*, 774. (b) Davies, R.; Stephens, K.; Hajek, M. *J. Mol. Catal. A* **1994**, *92*, 269. (c) Villemin, D.; Sauvaget, F.; Hajek, M. *Tetrahedron Lett.* **1994**, *35*, 3537. (d) Kotora, M.; Hajek, M. *J. Fluorine Chem.* **1993**, *64*, 101. (e) Kotora, M.; Hajek, M.; Dobler, C. *Collect. Czech. Chem. Commun.* **1992**, *57*, 2622. (f) Kotora, M.; Hajek, M. *J. Mol. Catal. A* **1992**, *77*, 51. (g) Hajek, M.; Silhavy, P. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1710. (h) Hajek, M.; Silhavy, P.; Malek, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 3502.

(11) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: River Edge, NJ, 1999.

(12) (a) Caballero, A.; Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 1446. (b) Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 896. (c) Díaz-Requejo, M. M.; Caballero, A.; Belderrain, T. R.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 978. (d) Díaz-Requejo, M. M.; Belderrain, T. R.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 3167.

(13) (a) Fructos, M. R.; Trofimenko, S.; Díaz-Requejo, M. M.; Pérez, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 11784. (b) Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 12078. (c) Mairena, M. A.; Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. *Organometallics* **2004**, *23*, 253−256.

(14)) Díaz-Requejo, M. M.; Belderrain, T. R.; Pérez, P. J. *Chem. Commun.* **2000**, 1853.

Table 2. Conversions (%)/Yields (%) Observed for the Reaction[a] of Olefins and CCl_4 in the Presence of Tp^{x}Cu(I) as the Catalyst

olefin	Tp*C (**1**)	Tp^{tBu,Me}Cu (**2**)	Tp^{Cy,4Br}Cu(NCMe) (**3**)	Tp^{Br3}Cu(NCMe) (**4**)	Tp^{Ms}Cu[b] (**5**)
MMA	15/11	95/95	82/82	nr[c]	18 (95)/18 (68)
styrene	40/40	85/85	>99/>99	nr[c]	0 (>99)/0 (>99)
1-hexene	10/10	47/47	50/50	nr[c]	8 (75)/8 (75)

[a] [catalyst]/[olefin]/[CCl_4] = 1:300:1200; [catalyst] = 4.6 mM; solvent is benzene-d_6; temp = 30 °C. The conversions were determined by ^{1}H NMR spectroscopy after 24 h. [b] Parentheses contain conversions and yields at 70 °C. [c] No reaction observed at 30 °C or at 70 °C.

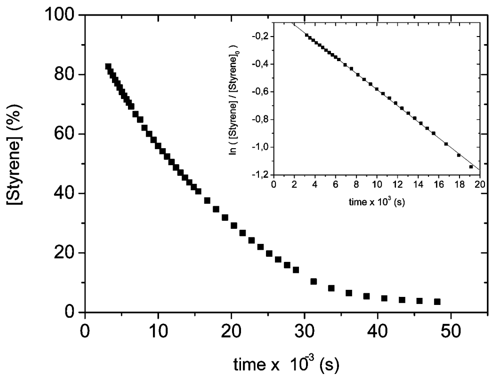


Figure 1. Consumption of styrene with time in the reaction with CCl_4 using Tp^{Cy,4Br}Cu(NCMe) (**3**) as the catalyst. Inset: initial first-order kinetics from which k_{obs} is obtained.

Table 3. Values of k_{obs} (s^{-1}) for the Reaction[a] of Olefins and CCl_4 in the Presence of Tp^{x}Cu(I) as the Catalyst

olefin	Tp*Cu (**1**)	Tp^{tBu,Me}Cu (**2**)	Tp^{Cy,4Br}Cu(NCMe) (**3**)	Tp^{Ms}Cu[b] (**5**)
MMA	1.9×10^{-5}	72.1×10^{-5}	5.5×10^{-5}	21.2×10^{-5}
styrene	3.2×10^{-5}	24.2×10^{-5}	14.3×10^{-5}	5.8×10^{-5}
1-hexene	nd[c]	16.7×10^{-5}	3.8×10^{-5}	2.9×10^{-5}

[a] [catalyst]/[olefin]/[CCl_4] = 1:300:1200; [catalyst] = 4.6 mM; solvent is benzene-d_6; temp = 30 °C. [b] Reactions performed at 70 °C. [c] Not determined.

observed by NMR, accounting for the difference between the conversion (olefin consumed) and yield (addition product formed).

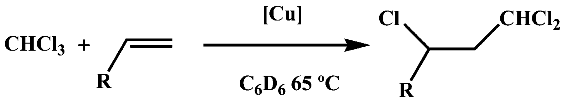
We have monitored the consumption of the olefin with time for these catalysts, with the obvious exception of the Tp^{Br3}-containing one. Figure 1 shows the decay of the concentration of styrene in the reaction of this olefin with CCl_4 using Tp^{Cy,4Br}Cu(NCMe) as the catalyst. The initial reaction rate could be estimated since the experimental data could be fitted into a first-order kinetic equation. This behavior was observed for the four catalysts and the three olefins employed, leading to the set of k_{obs} values shown in Table 3. The sequence for the k_{obs} values is identical for the three olefins studied: Tp^{tBu,Me}Cu > Tp^{Cy,4Br}Cu(NCMe) > Tp*Cu > Tp^{Ms}Cu (the latter operates at 70 °C).

Copper halides have been employed as catalysts for atom transfer radical cyclization, i.e., the intramolecular version of the ATRA reaction.[9] However, the intermolecular transformation finds very few examples of copper-based catalytic systems. Hajek and co-workers reported[10] the use of several in situ generated Cu(I) complexes for the addition of polyhalogenated substrates to olefins. The maximum conversions were about 90%, but temperatures of 80 °C or higher were required. Another Cu(I) system, described by Zazybin et al., requires heating at 120 °C to add CCl_4 to alkenes with moderate yields.[15a] ATRA-based polymer grafting has also been reported[15b] using Cu(I)−TREN catalysts in a process carried out at 60 °C. To the best of our knowledge, no reports about the use of copper catalysts for ATRA at a temperature as low as 30 °C have been reported to date with the degrees of conversions shown in Table 2. Moreover, the initial TOF (turnover frequency) (5 min) calculated for Tp^{tBu,Me}Cu of 730 h^{-1} for MMA (methyl methacrylate) exceeds those reported with Ni-based catalysts[8b] (400 h^{-1} at 25 °C). In the case of ruthenium, conversions of 1500 h^{-1} at 40 °C have been reported for styrene, first by Demonceau and co-workers[7e] and later by Severin and co-workers.[7a] Data in Tables 2 and 3 indicate that our copper catalysts display activities comparable to those known with nickel but not as much as those based on ruthenium.

Table 4. Conversions (%)/Yields (%) Observed for the Reaction[a] of Olefins and $CHCl_3$ in the Presence of Tp^{x}Cu(I) as the Catalyst

olefin	Tp^{tBu,Me}Cu (**2**)	Tp^{Cy,4Br}Cu(NCMe) (**3**)
MMA	77/55	32/15
styrene	73/70	11/11
1-hexene	23/23	5/5

[a] [catalyst]/[olefin]/[$CHCl_3$] = 1:100:400; [catalyst] = 13.8 mM; solvent is benzene-d_6; temp = 65 °C. The conversions were determined by ^{1}H NMR spectroscopy after 24 h.



(3)

We have also employed chloroform as the halogenated substrate with the three olefins (MMA, styrene, 1-hexene) using the more efficient catalysts **2** and **3**. Since $CHCl_3$ is less reactive than CCl_4, the experiments were carried out at 65 °C to give the product formed by an ATRA mediated reaction (eq 3). As shown in Table 4, complex **2** induced the best conversions affording the addition product in good yields for MMA and styrene. However, these Cu-catalysts are not as efficient as those based on ruthenium reported by Severin,[7b,c] for which the reactions are performed at 40 °C. It is worth mentioning that the conversion/yield difference is due to the formation of some PMMA (poly(methylmethacrylate)) with both **2** and **3** as the catalyst.

---

(15) (a) Zazybin, A.; Osipova, O.; Khusnutdinova, U.; Aristov, I.; Solomonov, B.; Sokolov, F.; Babashkina, M.; Zabirov, N. *J. Mol. Catal. A* **2006**, *253*, 234. (b) Camerlynk, S.; Cormack, P. A. G.; Sherrington, D. C. *Eur. Polym. J.* **2006**, *42*, 3286.

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

(17) (a) Imai, S.; Fujisawa, K.; Kobayashi, T.; Shirasawa, N.; Fujii, H.; Yoshimura, T.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3066. (b) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, *263*, 357.

(18) Unpublished results from this laboratory.

(19) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, *120*, 11408.

Table 5. ν(CO) Values for $Tp^xCu(CO)$ and Cone Angles for the Tp^x Ligands Employed in This Work

Tp^x	ν(CO) (cm^{-1})	cone angle[11]
Tp*	2056[16]	239
$Tp^{tBu,Me}$	2061[17]	243
$Tp^{Cy,4Br}$	2068[18]	273
Tp^{Ms}	2079[19]	nr[a]
Tp^{Br3}	2107[12a]	234

[a] Not reported.

Effect of the Tp^x Ligand: Electronics vs Sterics. As shown in Tables 2 and 3, the catalytic activity of this family of complexes is strongly dependent on the homoscorpionate Tp^x ligand, the order of activity decreasing in the sense $Tp^{tBu,Me} > Tp^{Cy,4Br} > Tp^{Ms} > Tp^* \gg Tp^{Br3}$. Demonceau and co-workers have reported[7e] that for the ruthenium phosphine-containing catalyst, the Ru(II) center is more easily oxidized when electron rich ligands are coordinated to the metal center. Such effect induces a higher activity of the catalysts for the ATRA reaction. In the case of Tp^xCu complexes, the electronic effects can be rationalized using the ν(CO) frequencies of the carbonyl adducts $Tp^xCu(CO)$, shown in Table 5. In good accord with the need of an electron rich metal center, there is a clear correlation between the values of the carbonyl stretching frequencies for **2**−**5** and the above order of catalytic activity: the higher is the ν(CO), the lower is the electron density at copper and, subsequently, the lower is the catalytic activity. The case of Tp*Cu seems to be an exception, since it presents the lowest ν(CO) value and therefore the highest density at the copper center, but its catalytic activity is lower than expected if electronic effects would explain per se the nature of this transformation.

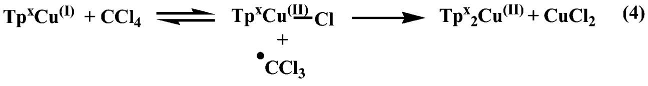
The oxidation of Cu(I) to Cu(II) with hydrotrispyrazolylborate ligands may also lead to the formation of compounds of the formula Tp^x_2Cu (eq 4)[11] that would suppose a dead-end in the catalytic cycle. This deactivation is only feasible with Tp^x ligands with relatively small groups at R^3.[20] When bulky groups occupy this position, as in the case of $Tp^{tBu,Me}$,$Tp^{Cy,4Br}$, or Tp^{Ms}, it has already been reported the lack of formation of such Tp^x_2Cu compounds,[11] and therefore the Tp^xCuCl species is stable enough[21] during the catalytic cycle. The reaction of $Tp^{tBu,Me}Cu$ with CCl_4 at 30 °C (eq 5), in the absence of olefin, originates the already reported $Tp^{tBu,Me}CuCl$.[22a] In addition, the product derived from the homocoupling of the radical $^{\bullet}CCl_3$ is also detected by ^{13}C NMR (see Experimental Section).

As observed in Table 5, the values of the cone angles reported for the Tp^x ligands employed in this study correlate with the catalytic activities: bulkier Tp^x ligands stabilize the Tp^xCuCl intermediate. The low activity of **1** can be explained in terms of the formation of Tp^*_2Cu, whereas that of **5** is related to the low electronic density at the metal induced by the Tp^{Br3} ligand. Therefore, a subtle balance between the electronic density at copper as well as the steric hindrance exerted by the subtituents at the Tp^x ligand seems to govern this transformation. The design of a more active catalyst of this family of compounds must account for these two factors: (a) the enhancement of the electronic donation and (b) the avoiding of the formation of dinuclear Tp^x_2Cu species.

Table 6. Effect of Added Donors in the ATRA of CCl_4 to Styrene Using **2** as the Catalyst[a]

entry	additive	conversion (%)	yield (%)	k_{obs} (s^{-1})
1	none	85	85	24.1×10^{-5}
2	20 equiv of MeCN	>99	>99	14.1×10^{-5}
3	CD_3CN as solvent	0	0	0
4	ethyl acetate (50 equiv)	>99	>99	4.4×10^{-5}
5	ethyl benzoate (50 equiv)	83	83	23×10^{-5}

[a] [catalyst]/[olefin]/[CCl_4] = 1:300:1200; [catalyst] = 4.6 mM; solvent is benzene-d_6; temp = 30 °C. The conversions were determined by ^1H NMR spectroscopy after 24 h.



$$Tp^xCu^{(I)} + CCl_4 \rightleftharpoons Tp^xCu^{(II)}\text{—}Cl + {}^{\bullet}CCl_3 \longrightarrow Tp^x_2Cu^{(II)} + CuCl_2 \quad (4)$$

$$2\ Tp^{tBu,Me}Cu + 2\ CCl_4 \longrightarrow 2\ Tp^{tBu,Me}CuCl + Cl_3CCCl_3 \quad (5)$$

Effect of Additives. Separate reports by Tolman[23] and Fujisawa[24] described that copper(I)−acetonitrile complexes of the formula $Tp^xCu(NCMe)$, with hindered Tp^x ligands, exhibit a reversible redox behavior in solution after the addition of some MeCN. Since such a property is greatly desired in the case of ATRA catalytic cycles, we have investigated the effect of added MeCN in the reaction of styrene and CCl_4 using the more active catalyst $Tp^{tBu,Me}Cu$ (**2**). Thus, the addition of 20 equiv of MeCN to the reaction mixture induced the complete transformation of styrene at 30 °C (Table 6, entry 2) although the value of k_{obs} is about 50% of that without nitrile added (Table 6, entry 1). These data are in accord with an easier Cu(I)/Cu(II) reversible process in the presence of acetonitrile and also with the existence of a MeCN dissociation pre-equilibrium. Accordingly, when the reaction is carried out using CD_3CN as the solvent (instead of C_6D_6), no conversion is observed (Table 6, entry 3), since no significant amounts of the unsaturated, 16 e$^-$ Tp^xCu species are available in solution to react with CCl_4. The observance of an increase in the yields is not restricted to the addition of MeCN. When ethyl acetate was incorporated into the reaction mixture, quantitative conversions were also observed, again a dramatic decrease in the reaction rate constant being observed. The use of ethyl benzoate did not induce any change in the conversion nor in the reaction rate: it seems reasonable to assume that the bulkiness of this additive prevents its coordination to the metal center and, therefore, that the effect of the additives must be related to its coordination to copper at any stage of the catalytic cycle.

Influence of the CCl_4 Concentration on the Reaction Rates Using 2 as the Catalyst. The use of different CCl_4

---

(20) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3210.

(21) Chia, L. M. L.; Radojevic, S.; Scowen, I. J.; McPartlin, M.; Halcrow, M. A. *J. Chem. Soc., Dalton Trans.* **2000**, 133.

(22) (a) Analytical and spectroscopic data were identical to those reported in the reference 22b. (b) Yoon, K.; Parkin, G. *Polyhedron* **1995**, *14*, 811.

(23) Carrier, S. M.; Ruggiero, C. E.; Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1993**, *32*, 4889.

(24) Fujisawa, K.; Ono, T.; Ishikawa, Y.; Amir, N.; Miyashita, Y.; Okamoto, K.-i.; Lehnert, N. *Inorg. Chem.* **2006**, *45*, 1698.

Table 7. Effect of [CCl$_4$] in the Reaction with Styrene Using **2** as the Catalyst

[**2**]/[styrene]/[CCl$_4$]	conversion (%)	yield (%)	k_{obs} (s^{-1})
1:300:10	>99	>99	0.5×10^{-5}
1:300:60	>99	>99	5×10^{-5}
1:300:300	85	85	17×10^{-5}
1:300:600	85	85	21×10^{-5}
1:300:1200	85	85	24×10^{-5}

concentrations in a set of experiments in which the concentrations of **2** and styrene remained constant has provided valuable information about the initiation step in the catalytic cycle. Table 7 contains the values of conversions and of k_{obs} for five different [CCl$_4$], and Figure 2 shows the plot of the rate constants vs the concentration of CCl$_4$. A typical saturation kinetic behavior is observed, in a similar manner to that previously described by van Koten and co-workers for a nickel-based catalyst,[8b] that attributed such a curve to the formation of an adduct radical. In our case, such an adduct would correspond to a species such as [Tp^{x}Cu−Cl]···[$^•$CXCl$_2$], in good accord with the work by Nondek et al.[25] about the interaction of polyhalogenated substrates with Cu(I) complexes that proposed the formation of these types of adducts as the previous step in the generation of free $^•$CX$_3$ radicals.

Mechanistic Proposal. Scheme 2 shows a mechanistic proposal based on all the data collected. The real catalyst is the species Tp^{x}Cu that equilibrates with the 18 e$^-$ adduct Tp^{x}CuL in the presence of a donor L (acetonitrile from the initial complex, olefin, or added donors).[26] This equilibrium drives the available amounts of Tp^{x}Cu in solution, therefore controlling the k_{obs} values.[27] The rate determining step is the oxidation of Cu(I) to Cu(II) and the concomitant formation of Tp^{x}CuCl and $^•$CCl$_3$ through the already commented on radical adduct (**A**). Species $^•$CCl$_3$ will interact with the olefin forming a second, more reactive radical of the type Cl$_3$CCH$_2$(H)(R)C$^•$. In the absence of olefin, $^•$CCl$_3$ undergoes homocoupling to yield C$_2$Cl$_6$.

The isolation of Tp^{tBu,Me}CuCl by reaction of Tp^{tBu,Me}Cu and CCl$_4$ supports the participation of Tp^{x}CuCl (**B**) in the catalytic cycle. We believe that this intermediate reacts with a given L donor (olefin, acetonitrile, ester) affording a pentacoordinated complex Tp^{x}CuX(L) (**C**). This is based on the previous isolation,[20,28] for hindered trispyrazolylborate ligands, of such compounds. The formation of this species could be crucial for this catalytic system. Fujisawa and co-workers have established that these complexes are unable to keep their tetrahedral geometry after oxidation to copper(II) and pentacoordination provides additional stability. Besides, pentacoordinated complexes have been described as intermediates in ATPR by Matyjaszewski.[6] In our system, the formation of the pentacoordinated intermediate would favor the necessary reversible redox reaction for the ATRA reaction. Collapse of such an intermediate with the Cl$_3$CCH$_2$(H)(R)C$^•$ radical provides the desired product and closes the cycle.

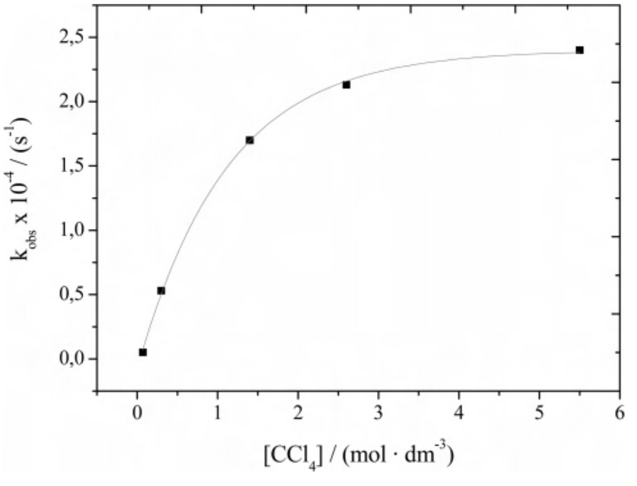
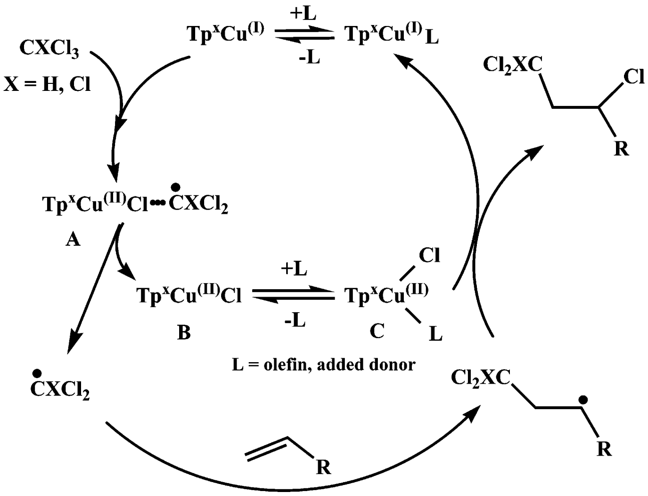


Figure 2. Variation of the reaction rate constant with varying [CCl$_4$] and with [**2**] = 4.6 mM in C$_6$D$_6$.

Scheme 2. Mechanistic Proposal for ATRA Reactions Catalyzed by Tp^{x}Cu Complexes



Conclusions

We have found that Tp^{x}Cu complexes efficiently catalyze the atom transfer radical addition of CCl$_4$ or CHCl$_3$ to olefins under mild conditions (30 °C). The Tp^x ligand exerts a strong effect on the catalytic activity. The more active catalysts are those with hindered as well as electron-donating Tp^x ligands. Particularly, the complex Tp^{tBu,Me}Cu (**2**) induces the highest catalytic activity under mild conditions for any known copper-based catalyst reported to date. A mechanistic proposal has been presented on the basis of kinetic data, where the participation of a pentacoordinated intermediate seems to be relevant in the ATRA process. In view of these findings and their good activity/cost ratio, the development of more active copper-based catalysts and their application

---

(25) Nondek, L.; Hun, L.-G.; Wichterlová, B.; Krupicka, S. *J. Mol. Catal.* **1987**, *42*, 51.

(26) Such equilibrium has already been proposed for Tp^{x}Cu complexes: see ref 12c. We have also synthesized the styrene adducts Tp^{Br3}Cu(CH$_2$=CHPh) and Tp^{Ms}Cu(CH$_2$=CHPh) by direct reaction of Tp^{Br3}Cu(NCMe) and Tp^{Ms}Cu with styrene, respectively.

(27) Addition of amounts of Tp^{tBu,Me}CuCl should decrease the reaction rate. In good accord with this, an experiment carried out as that in Table 6, entry 2, with 1 equiv of Tp^{tBu,Me}CuCl added led to a decrease in k_{obs} from 14.1×10^{-5} to 10.0×10^{-5} s^{-1}. In the absence of the Cu(I) complex, Tp^{tBu,Me}CuCl did not induce any ATRA reaction.

(28) Siemer, C. J.; Meece, F. A.; Armstrong, W. H.; Eichhorn, D. M. *Polyhedron* **2001**, *20*, 2637.

in the ATRC and ATRP related process are now under investigation.

Experimental Section

General Information. All preparations were carried out in a glovebox, placed into a thick walled pressure NMR tube, and sealed with a Teflon screw cap under nitrogen. Starting materials and reagents were purchased from Aldrich and were purified as follows: carbon tetrachloride and chloroform were distilled, and olefins (styrene, methyl methacrylate, 1-hexene) were filtered on alumina columns prior to use. The homoscorpionate ligands were prepared according to literature methods as well as the complexes Tp^xCu.[11−14] NMR experiments were run in a Varian Mercury 400 MHz spectrometer.

General Procedure for the ATRA of CCl_4 to Olefins. A solution of the olefin (1.23 mmol), the corresponding Tp^xCu complex (0.0410 mmol from a stock solution), and CCl_4 (476 μL) was dissolved in the required amount of C_6D_6 to a total volume of 900 μL. The final concentrations were [catalyst] = 4.6 mM, [olefin] = 1.38 M, and $[CCl_4]$ = 5.52 M. The solution was transferred into a pressure NMR tube and sealed with a Teflon screw cap. The tube was removed from the glovebox and placed in an oil bath at 30 °C. The conversions were monitored by ^1H NMR spectroscopy at the desired times. The reactions with additives (acetonitrile, ethyl acetate, or ethyl benzoate) were done in a similar manner, with the appropriate amounts of the additive at the beginning of the reaction.

General Procedure for the ATRA of $CHCl_3$ to Olefins. The procedure was identical to that described above for CCl_4. A solution with a final volume of 745 μL was prepared with 0.041 mmol of the Tp^xCu complex, 1.03 mmol of the olefin, 330 μL of $CHCl_3$, and C_6D_6 to reach the final volume. The final concentrations were [catalyst] = 13.8 mM, [olefin] = 1.38 M, $[CHCl_3]$ = 5.52 M. The solution was transferred into a pressure NMR tube and sealed with a Teflon screw cap. The tube was removed from the glovebox and placed in an oil bath at 65 °C. The conversions were monitored by ^1H NMR spectroscopy at the desired times.

Reaction of 2 with CCl_4. A toluene solution (30 mL) of complex **2** (0.13 mmol) and CCl_4 (200 mmol) was stirred for 4 h. A red-brown solution is obtained. The volatiles were removed under vacuum, and the residue was extracted with diethyl ether. The resulting solution was concentrated under reduced pressure. Crystallization at −30 °C afforded a red crystalline solid, for which the IR, NMR, and analytical data were identical to those reported for $Tp^{tBu,Me}CuCl$.[22b]

Reaction of 2 with CCl_4 in C_6D_6. A solution of $Tp^{tBu,Me}Cu$ (**2**) (0.13 mmol) and CCl_4 (200 mmol) in C_6D_6 was introduced into a NMR tube and was analyzed by $^{13}C\{^1H\}$ NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum showed a resonance at 104.8 ppm assigned to Cl_3CCCl_3.

Acknowledgment. We thank the MEC for financial support (Project CTQ2005-00324BQU). J.M.M.-M. thanks the Universidad de Huelva for a research fellowship, A.C. thanks the MEC for a research fellowship, and M.M.D.-R. thanks the Ramon y Cajal Program (MEC) for financial support.

Supporting Information Available: NMR spectra of reaction mixtures and kinetic plots and data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0702872