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Copper-Catalyzed Synthesis of 1,2-Disubstituted Cyclopentanes from 1,6-Dienes by Ring-Closing Kharasch Addition of Carbon Tetrachloride

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Abstract: The reaction of carbon tetrachloride (CCl_4) with various 1,6-heptadienes catalyzed by copper homoscorpionate complexes affords cyclization products in moderate to high yields. The process involves the addition of the trichloromethyl radical to the diene followed by a 5-*exo*-*trig* cyclization reaction, resulting in the formation of the *cis*-3-chloromethyl-4-(2,2,2-trichloroethyl)cyclopentane isomers in a highly regiospecific and stereospecific manner. We have studied the use of magnesium (Mg) as reducing agent for the regeneration of copper(I) catalysts. This method has afforded heterocycles in high yields even in the cases of diallyl ether (DAE) and *tert*-butyl *N,N*-diallylcarbamate (TBDAC).

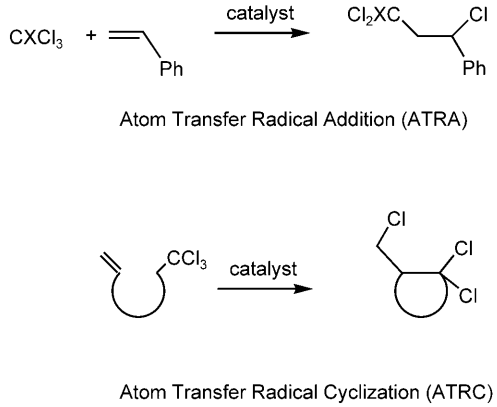
Keywords: atom transfer radical addiiton (ATRA); copper; Kharasch reaction; radical reactions; trispyrazolylborate ligands

Introduction

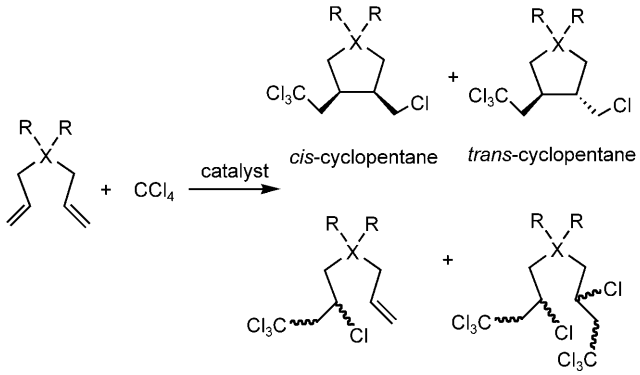
Ring-forming reactions, namely cyclization reactions, play a very important role in organic synthesis because many natural organic molecules possess carbo- and heterocyclic rings.[1] Over the past twenty years there has been high demand by the pharmaceutical and fine chemical industries for the development of different synthetic methods to cyclic compounds, particularly for five-membered rings (i.e., cyclopentanes, tetrahydrofurans, tetrahydropyrroles, etc).[2] Among them, the transition metal-catalyzed cyclization reactions of unsaturated substrates are undoubtedly one of the most useful synthetic procedures for the construction of five-membered ring systems.[3] Some of the more commonly encountered methods are based on oxidative addition,[4] radical cyclization,[5] cycloisomerization,[6] and olefin metathesis processes.[7]

Free-radical reactions provide an effective tool for the generation of carbon-carbon bonds, and, therefore, to obtain compounds by radical cyclization.[8] Organotin hydrides dominate these kinds of processes, in spite of the well-known drawback of the neurotoxicity of such reagents, that enforces the need for complex purification and separation steps.[9] This fact has led to the development of alternative methods for radical generation, i.e., the use of tris(trimethylsilyl)-silane,[10] manganese(III) acetate,[11] dimanganese decacarbonyl,[12] samarium(II) iodide,[13] copper[5,14] and ruthenium(II)[15] complexes, etc. Since the early reports by Matyjazewski[16] concerning the use of copper complexes as catalyst in atom transfer radical polymerization (ATRP), this catalytic system has emerged as one of the most important in radical-controlled transformations. ATRP processes involve a first step that consists on a metal-catalyzed Kharasch reaction,[17] also designated as atom transfer radical addition (ATRA, Scheme 1). The intramolecular version of the latter reaction, the so-called atom transfer radical cyclization (ATRC, Scheme 1), has been extensively studied over the last decade.[5]

An interesting transformation is the one leading to the formation of five-membered rings *via* consecutive Kharasch addition of CCl_4 to 1,6-heptadienes followed by radical cyclization (Scheme 2). This reaction has been shown to be catalyzed by dimanganese decacarbonyl,[12] rhenium,[18] ruthenium,[18,19,20] rhodium[20] and iridium.[20] This reaction usually affords a mixture of compounds from the cyclization (*cis* and *trans* isomers) or the simple ATRA reaction onto one or two double bonds. In spite of the well-known capabilities of several copper complexes to promote ATRP,



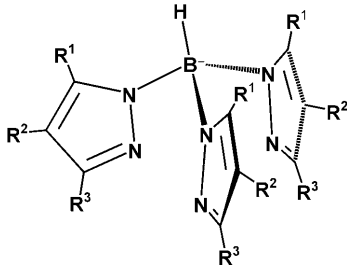
Scheme 1. ATRA and ATRC reactions.



Scheme 2.

ATRA or ATRC processes, to the best of our knowledge the use of this metal for this transformation remains unknown. We have recently reported that trispyrazolylborate copper complexes $Tp^xCu(I)$ (Table 1) display a remarkable activity in ATRA reactions,[21] that surpassed those of other previous Cu-based catalysts.[22] In this contribution we present the results obtained with these compounds as catalysts in the reaction of CCl_4 with 1,ω-dienes. Very high yields under mild conditions have been obtained in the first example of the use of copper in such transformations.

Table 1. Homoscorpionate ligands employed in this work.



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

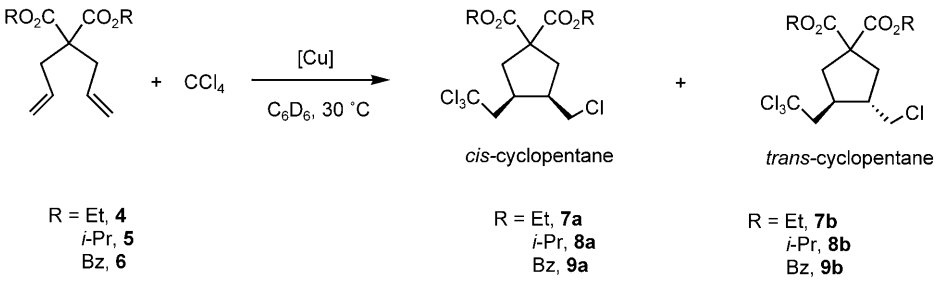
Results and Discussion

Addition of CCl_4 to 1,6-Hexadienes Catalyzed by Tp^xCu Complexes

As a probe reaction, we chose three different diallylmalonates as the substrates to be reacted with CCl_4 in the presence of catalytic amounts of complexes **1**–**3** (Scheme 3). Such substrates are usually employed in other metal-catalyzed cyclization processes, such as ring-closing metathesis[19c,23] or cycloisomerization.[6] A mixture of 100 equiv. of the corresponding diallylmalonate and 400 equiv. of CCl_4 in the presence of 1 equiv. of Tp^xCu in C_6D_6 (see Table 2) was maintained at 30 °C for 24 h and was then monitored by ^1H NMR. Table 2 displays the results of this series of nine experiments, from which it is clearly observable that complex **1**, containing the $Tp^{t\text{-Bu,Me}}$ ligand induced the highest conversions. Complex **2** induced a lower activity whereas the Tp^{Ms}-containing catalyst was inactive at 30 °C. However, yields improved up to 80–90% when carrying out the reaction at 70 °C. In all cases the *cis*-isomer was preferentially formed, with nearly no effect of the catalyst employed in the diastereoselectivity. It is also worth mentioning that this system provides exclusively products **7**–**9**, those corresponding to the simple ATRA addition to the double bonds or alternate cyclization to 6-membered ring products were not observed.

With the above results in hand, we decided to extend these studies to another three dienes: 1,6-heptadiene, **10**, diallyl ether (DAE), **11**, and *tert*-butyl *N*,*N*-diallylcarbamate (TBDAC), **12** (Table 2). For DAE and TBDAC, as for the diallylmalonate esters, only cyclization products are observed, but in the case of heptadiene, the linear addition products are obtained in 39, 16 and 12% yields for **1**, **2** and **3** as catalyst, respectively (Scheme 4).

The results shown in Table 2 are, to the best of our knowledge, the first example of copper-catalyzed cyclization reactions by this methodology, and compare well with other results reported in the literature, using other metal-based (Mn, Ru, Ir, Rh, Ru) catalysts.[12,18,19,20] Mild conditions (30 °C) without the need of irradiation[24] or heat for the generation of the radical species and relatively low charge of catalyst (1%) are employed in our system. After these findings, we focussed our attention in the understanding of this transformation in order to improve the catalytic conversions.



Scheme 3.

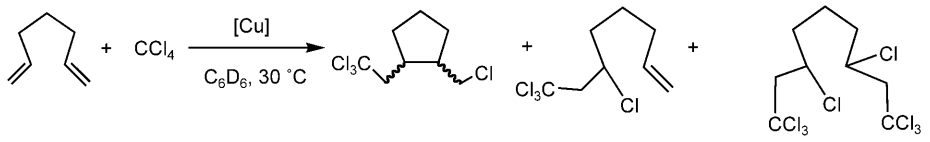
Table 2. Ring-closing Kharasch addition of CCl_4 to 1,ω-dienes catalyzed by $Tp^xCu(I)$ complexes.[a]

Entry	1,6-Diene	Tp^xCu	Conversion [%][b]	Yield [%][b]	*cis*:*trans*[b]	$k_{obs} \times 10^5$ [s^{-1}]
1	**4**	**1**	90	90	93:7	12.8
		2	58	58	90:10	6.7
		3	87 (<1)	87	91:9	9.9
2	**5**	**1**	83	83	88:12	17.0
		2	48	48	86:14	5.5
		3	90 (<1)	90	84:16	26.7
3	**6**	**1**	74	74	86:14	16.3
		2	45	45	84:16	7.9
		3	84 (<1)	84	84:16	39.2
4	**10**	**1**	98	59	87:13	n.d.[c]
		2	77	62	84:16	n.d.[c]
		3	93 (<1)	81	81:19	n.d.[c]
5	**11**	**1**	33	33	77:23	6.5
		2	23	23	70:30	1.0
		3	62 (<1)	62	71:29	2.6
6	**12**	**1**	41	41	68:32	3.9
		2	25	25	69:31	1.5
		3	88 (<1)	88	65:35	3.0

[a] [catalyst]:[diene]:[CCl_4] = 1:100:400; [cat] = 11.0 mM; solvent, benzene-d_6.
[b] Conversions, yields and *cis*:*trans* ratios were determined by ^{1}H NMR spectroscopy after 24 h. Reactions were carried out at 30 °C with complexes **1** and **2**, and 70 °C for **3** (parenthesis contain conversions at 30 °C).
[c] n.d.: not determined.

Mechanistic Insights

In our previous report about the use of copper-based catalysts for ATRA reactions,[21] we proposed the catalytic cycle shown in Scheme 5. The copper complex is responsible of the generation of the radical species that further interacts with the olefin with no participation, at this stage, of the metal center. In the case of the cyclization reaction, data in Table 1 show very similar diastereoselectivities independently of the catalyst employed. Additional evidence was gained upon carrying out the reaction of ethyl diallylmalonate and CCl_4 in the presence of Tp*Cu [Tp* = tris(3,5-dimethylpyrazolyl)borate], with the low sterically demanding Tp*. As previously described for the Kharasch addition reaction of CCl_4 to other olefins,[21] Tp*Cu only



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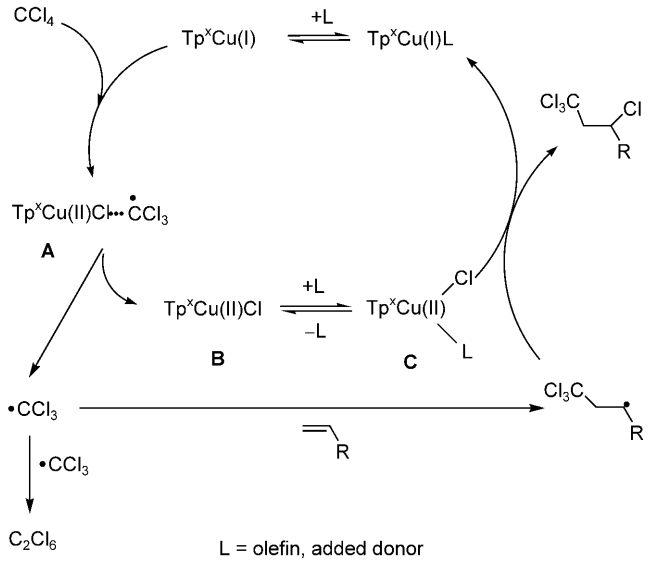
catalyst	13	14	15	cycliz./linear
1	59	15	25	1.5
2	62	12	4	3.9
3	81	7	5	6.7

Ratio of products were determined by ^{1}H NMR spectroscopy after 24 h

Scheme 4. Ring-closing Kharasch addition of CCl_4 to 1,ω-dienes catalyzed by $Tp^xCu(I)$ complexes.

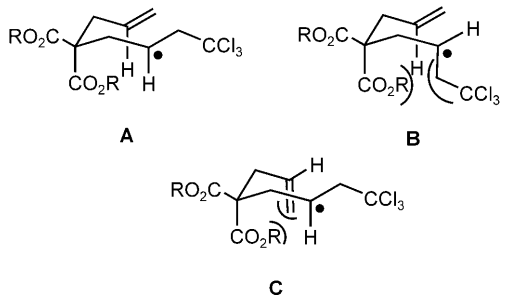


Scheme 5. Mechanistic proposal for ATRA reactions catalyzed by Tp^xCu complexes.

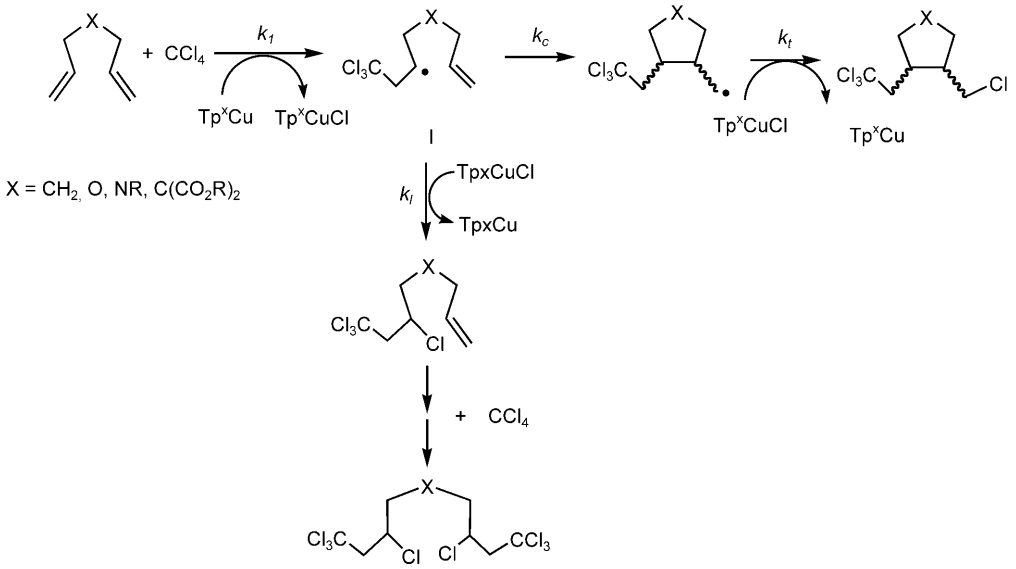
afforded low yields of the cyclization products (15%) and with the same diastereoselectivity as previously observed with complexes **1**–**3** (*cis:trans* ratio: 95:5). These results can be interpreted as a consequence of a similar pathway in which the copper complex is not involved in the cyclization steps, and only in the radical formation.

Various explanations have been developed to account for the regioselectivity of these radical cyclizations, i.e., the selective formation of 5-membered rings (5-*exo-trig* pathway), such as entropic,[25] steric[26] and stereoelectronic factors.[27] It is known that 1-substituted hex-5-enyl radicals give predominantly *cis*-1,2-disubstituted cyclopentene on cyclization.[28] Moreover, it has been also proposed that in substrates such as diallylmalonates the stereoselectivity could be due to steric effects in the transition states.[18] Thus, once the organic radical is formed, the less sterically demanding transition state **A** (Scheme 6) with CO_2R/H 1,3-pseudodiaxial interactions would lead to the *cis* isomer, whilst other possible transition states **B** and **C** with more severe interactions $CO_2R/CHCCl_3$ (**B**) or $CO_2R/CH{=}CH_2$, would afford the *trans* stereoisomer (Scheme 6).

As detailed above (Scheme 2), these reactions provide not only cyclopentane derivatives but, in some cases, products derived from the simple ATRA reaction into one or two double bonds, the latter being observed only in the case of 1,6-heptadiene with these copper-based catalysts. Once the radical (Scheme 7, I) is formed, two competitive reactions could occur: the cyclization reaction or the linear addition, the latter being induced by the reaction of the radical with Tp^xCuCl. The respective reaction rates for these processes are k_C and k_l, respectively. It has been already proposed for the organostannane-mediated[29] cyclization of 6-hepten-2-radicals that an oxygen-containing radical affords a higher k_C/k_l than the methylene one, and the former cyclizes much more rapidly than the later. This process seemed to be independent of the concentration of the species **I** but dependent of the nature of the radical. As shown in Table 2, the addition of CCl_4 to DAE or TBDAC, after 24 h, using **1** or **2** as catalyst provided moderate to low conversions and lower rates, possibly due to the coordination of the substrate to the metal center which then forbids the interaction with the CCl_4 to generate the $^{\bullet}CCl_3$ and to catalyst decomposition.



Scheme 6. Transition states for the cyclization reaction.



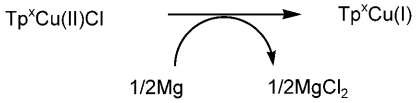
Scheme 7. Kharasch addition of CCl_4 to 1,ω-dienes catalyzed by $Tp^xCu(I)$ complexes.

The results found for the addition of CCl_4 to 1,6-heptadiene with our Cu-based catalyts seem to indicate that there is a relationship between the ratio of cyclization to linear addition products and the activity of the catalyst. Therefore, for the most active catalyst, $Tp^{t\text{-}Bu,Me}Cu$ (**1**), such a ratio was *ca.* 1.5, whereas for $Tp^{Cy,4Br}Cu$ (**2**) and $Tp^{Ms}Cu$ (**3**) respective values of *ca.* 3.9 and 6.7 were observed. We interpret these results in the following manner. The more active catalyst would generate a high concentration of **I** and this could favor the termination step by reaction with Tp^xCuCl. On the other hand, a less active catalyst would induce lower concentrations of **I**, allowing the intramolecular cyclization.

Enhanced Catalytic Activity by the Presence of Additives: the Magnesium Effect

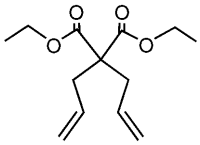
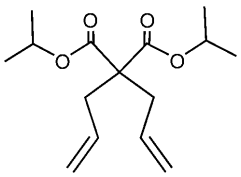
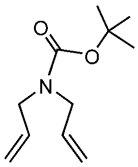
The main problem found with these catalysts for the ring-closing Kharasch addition of CCl_4 to 1,ω-dienes is the deactivation of the catalyst involving radical termination, disproportionation or oxidation reactions. This usually occurs due to a side reaction in which radicals collapse. In ATRA reactions, for instance (Scheme 5), CCl_3 radical undergoes homocoupling to give C_2Cl_6, that was detected in the absence of olefins. Such behavior leads to accumulation of the Cu(II) species, and therefore the initiating Cu(I) species cannot be regenerated, therefore diminishing the catalytic activity. This same proposal was made by Severin and co-worker[29] for a Ru(II)-based system for ATRA reactions, in which accumulation of Ru(III)–Cl complexes induced a decrease of the catalytic rates. This problem is also of relevance in copper-catalyzed ATRP systems, for which Matyjaszewski et al. have recently introduced the concept of initiators for continuous activator regeneration (ICAR).[30,31] This strategy is based in the use of a constant source of organic free radicals to regenerate the Cu(I) activator, which is otherwise consumed in termination reactions. After this report, Severin[32] and Pintauer[33] have employed the same technique in ATRA reactions catalyzed by ruthenium and copper complexes, respectively. One of the possible reducing agents is AIBN, but the use of this compound has some problems. For instance, the reactions have to be heated in order to make AIBN an efficient radical source, and at high temperature, it can initiate polymerization of the olefins. In case of Tp^xCu complexes, **1** and **2** catalyze the reaction at 30 °C, so it was important to try a reducing agent which works under mild conditions. A second agent reported by Severin and co-worker was metallic magnesium.[32] On the basis of these findings, we decided to try the use of Mg in the Kharasch addition of CCl_4 to a series of dienes (**4**, **5**, **11** and **12**), using **1** and **2** as catalyst (Scheme 8). Water was employed to activate the Mg surface.

The results are shown in Table 3, from which it can be observed that very high to quantitative conversions were observed in all cases, even for the case of DAE, making this strategy an alternative to others such cycloisomerization[6] or RCM.[23] The effect of Mg seems



Scheme 8.

Table 3. Ring-closing Kharasch addition of CCl_4 to 1,6-dienes catalyzed by $Tp^xCu(I)$[a] complexes in presence of Mg.[b]

Entry	1,6-Diene		Tp^xCu	Conversion [%][c]	Yield [%][c]	*cis*:*trans*[d]
1	**4**		**1**	>99	>99	93:7
			2	>99	>99	90:10
2	**5**		**1**	>99	>99	88:12
			2	96	96	87:13
3	**11**		**1**	>99	>99	86:14
			2	>99	>99	82:18
4	**12**		**1**	95	95	87:13
			2	90	90	83:13

[a] [catalyst]:[1,6-diene]:[CCl_4] = 1:100:400; [cat] = 11.0 mM; solvent, benzene-d_6; reactions were carried out at 30 °C.
[b] The reactions were performed in the presence of activated Mg powder in benzene-d_6 saturated with D_2O.
[c] Conversions and yields were determined by ^1H NMR spectroscopy after 24 h.
[d] *cis*:*trans* ratio determined from the ^1H and ^{13}C NMR spectra.

to be the reduction of Cu(II) to the Cu(I) active species for radical formation, avoiding the deactivation of the catalytic system. The diastereoselectivities are similar to those found in the absence of magnesium (Table 2) for **4** and **5**, but the *cis* diastereoselection increases for **11** and **12**. Once again there seems not to be an influence of the copper center during the cyclization process and the observed increase in the percentage of *cis* isomer for the later maybe due to coordination of the substrate to the magnesium during the reaction.[34]

Conclusions

We have described the use of the $Tp^xCu(I)$ complexes as good catalysts in ring-closing Kharasch addition of CCl_4 to 1,ω-dienes, affording the corresponding five-membered hetero- and carbocycles in yields which vary from moderate to high. In the case of 1,6-heptadiene only are linear addition products formed, the reaction being regioselective toward ring products with the other substrates. The *cis*:*trans* ratio is independent of the catalyst, but the regioselectivity between rings and linear products depends of the catalyst activity. The use of magnesium as co-catalyst has led to very high to quantitative conversions, under mild conditions. This Mg-Tp^xCu catalytic system displays a very good activity/cost ratio. We are currently extending these findings to other copper-catalyzed radical reactions.

Experimental Section

General Information

The homoscorpionate ligands were prepared according to literature methods as well as the complexes Tp^XCu[35] and diisopropyl and dibenzyl malonates, **5** and **6**.[36] All other starting materials and reagents were purchased from Aldrich, and were purified as follows: carbon tetrachloride was distilled and substrates were filtered on alumina columns prior to use. NMR experiments were run in a Varian Mercury 400 MHz spectrometer. All preparations were carried out in a glove box under nitrogen.

General Procedure for the Ring-Closing Kharasch Addition of CCl_4 to Diolefins

A solution of the diolefin (0.821 mmol), the corresponding Tp^xCu complex (8.21×10^{-3} mmol from a stock solution) and CCl_4 (3.285 mmol) were dissolved in the required amount of C_6D_6 to complete a total volume of 820 μL. The final concentrations were [catalyst] = 10.0 mM, [olefin] = 1.0 M, [CCl_4] = 4.0 M. The solution was transferred into a pressure NMR tube and sealed with a Teflon screw cap. The tube was removed from the glove box and placed in an oil bath

at 30 °C. The conversions were analyzed by ^{1}H NMR spectroscopy at the desired times.

General Procedure for the Ring-Closing Kharasch Addition of CCl_4 to Diolefins in the Presence of Mg

A solution of the diolefin (0.821 mmol), the corresponding Tp^xCu complex ($8.21 \cdot 10^{-3}$ mmol from a stock solution) and CCl_4 (3.285 mmol) were disolved in the required amount of C_6D_6 to complete a total volume of 820 μL. This solution was added to a vial that contained Mg powder (100 mg) and D_2O (20 μL). The mixture was stirred for 24 h (30 °C). After addition of 50 μL of dioxane (in order to avoid the coordination of magenesium to the products), a sample was removed from the final mixture, filtered on alumina column, and analyzed by ^{1}H NMR.

Kinetic Studies

The kinetic experiments were performed in a manner similar to that described for the standard catalytic system. The total volume of the solution was maintained at 820 μL by adding sufficient C_6D_6 (see Supporting Information).

Supporting Information

NMR data for the products, reaction NMR spectra of reaction mixtures and kinetic plots are available as Supporting Information.

Acknowledgements

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