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PAPER

Atom transfer radical addition (ATRA) catalyzed by copper complexes with tris[2-(dimethylamino)ethyl]amine (Me_6TREN) ligand in the presence of free-radical diazo initiator AIBN†

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In this article, we focus on the evaluation of tris[2-(dimethylamino)ethyl]amine (Me_6TREN) ligand in copper catalyzed ATRA in the presence of free-radical diazo initiator AIBN (2,2′-azobis(2-methylpropionitrile)). The addition of carbon tetrachloride to 1-hexene, 1-octene and *cis*-cyclooctene proceeded efficiently to yield 89, 85 and 85% of monoadduct, respectively, using the catalyst to alkene ratio of 1 : 2500. For alkenes that readily undergo free radical polymerization, such as methyl acrylate, catalyst loadings as high as 0.4 mol-% were required. Furthermore, modest yields of the monoadduct were obtained with less active alkyl halides (chloroform and bromoform) using 250 : 1 and 500 : 1 ratios of alkene to copper(II). Interestingly, the addition of carbon tetrachloride to *cis*-cyclooctene produced only 1-chloro-4-(trichloromethyl)-cyclooctene, while carbon tetrabromide yielded 1,2 and 1,4-regioisomers in 75 : 25 ratio. The activity of $[Cu^{II}(Me_6TREN)X][X]$ (X = Br^- and Cl^-) complexes in ATRA in the presence of AIBN was additionally probed by adding excess free ligand, source of halide anions and triphenylphosphine. The results indicated that disproportionation is a likely cause for lower activity of Me_6TREN as compared to TPMA (tris(2-pyridylmethyl)amine).

Introduction and background

Discovered by Kharasch in 1945, atom transfer radical addition (ATRA) is a fundamental reaction for the formation of carbon–carbon bonds starting from alkyl halides and alkenes.[1–6] The reaction is typically initiated by peroxides, diazo compounds or light. Initially, ATRA was limited to the addition of polyhalogenated alkanes to alkenes that do not readily undergo free radical polymerization such as α-olefins. However, the realization that transition metal complexes could act as better halogen atom transfer agents than alkyl halides, and additionally catalyze ATRA through a reversible redox process, expanded the scope of this relatively simple organic transformation.[7–11] These catalysts provided better selectivity towards the monoadduct by reducing the overall radical concentration, thus suppressing side reactions such as radical termination and oligomerization/polymerization. Complexes of Cu, Fe, Ru, and Ni were found to be particularly active for a variety of alkyl halides and alkenes.[12–27] However, metal-mediated ATRA systems required large concentrations of the catalyst in order to obtain high yields of the monoadduct (typically between 5 and 30 mol% relative to alkene). This was mostly due to radical termination reactions, which resulted in accumulation of the deactivator (transition metal complex in the higher oxidation state). Similar problems were also encountered in a synthetically more useful intramolecular version of ATRA, also commonly known as atom transfer radical cyclization (ATRC).[28–38] The use of solid supported catalysts[30,39,40] and biphasic fluorous systems[41] was examined as solutions to catalyst recycling and recovery, but met with only limited success.

Although the catalyst in such systems could be easily separated from the reaction mixture, the problem of recycling due to the accumulation of the deactivator species still remained.

One of the most effective methods of diminishing catalyst concentration in ATRA is that of *in situ* catalyst regeneration in the presence of free radical diazo initiators (*e.g.* 2,2′-azobis(2-methylpropionitrile) (AIBN)) or magnesium. This method was originally developed for mechanistically similar atom transfer radical polymerization (ATRP),[42–45] and was subsequently applied first to Ru[46–54] and then Cu[55–69] based ATRA. In all of these processes, the deactivator (transition metal complex in the higher oxidation state) is continuously reduced to the activator (transition metal complex in the lower oxidation state). The proposed mechanism for copper catalyzed ATRA in the presence of free radical diazo initiator AIBN is shown in Scheme 1. Radicals generated from thermal decomposition of AIBN partially reduce copper(II) to the corresponding copper(I) complex. The copper(I) complex starts a catalytic cycle by homolytically cleaving an alkyl

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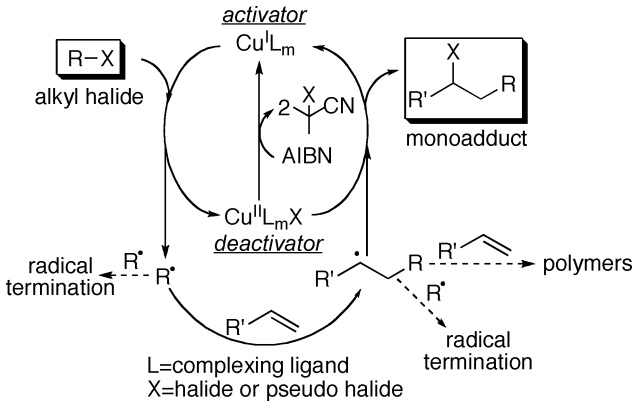
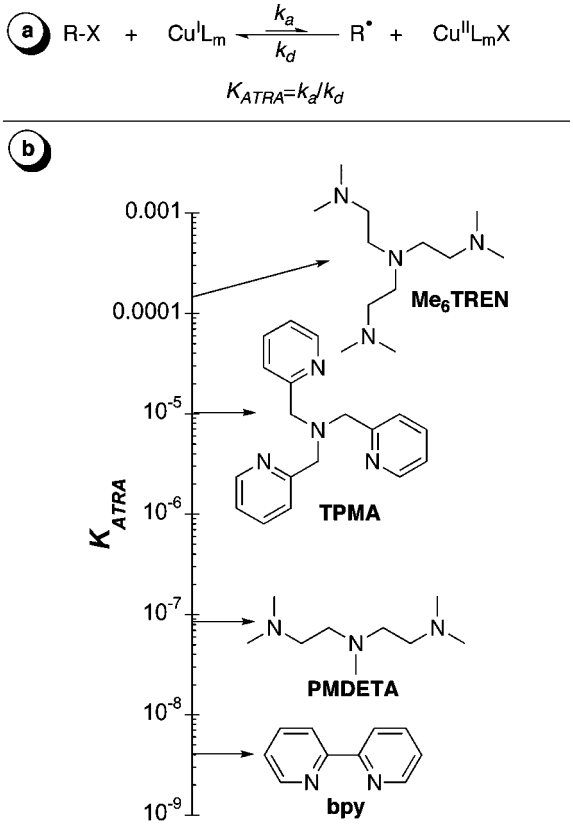


Scheme 1 Proposed mechanism for copper catalyzed ATRA in the presence of free radical diazo initiator AIBN.

halide bond to produce an alkyl radical that adds across a carbon–carbon double bond of an alkene. The generated secondary radical then irreversibly abstracts halogen atom from the copper(II) complex to form a desired monoadduct. This step regenerates the activator or copper(I) complex, completing the catalytic cycle. As indicated in Scheme 1, the competing side reactions in this process include radical terminations by coupling or disproportionation, as well as repeating radical additions to alkene to form oligomers/polymers.

Catalyst regeneration has been shown to be highly successful when used in copper mediated ATRA systems, producing the highest turn-over-numbers (TON) observed for this process.[59,62,64] Using [Cu^{I}(TPMA)Cl] (TPMA = tris(2-pyridylmethyl)amine) and AIBN, TONs as high as 7200 were achieved in the addition of CCl_4 to 1-hexene,[58] and even more notable results were obtained with [Cu^{II}(TPMA)Br][Br] in the addition of CBr_4 to methyl acrylate and styrene with TONs of 162 000 and 190 000 respectively.[57] Controlling the single addition to highly reactive alkenes (vinyl acetate, methyl methacrylate, methyl acrylate, and styrene), which polymerize rapidly in the presence of free radical initiators, has historically been a challenge for ATRA. By performing the reactions at room temperature using 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) and [Cu^{II}(TPMA)X][X] (X = Cl or Br), the addition of polyhalogenated methanes proceeded efficiently with $[Cu^{II}]_0 \ll 0.1$ mol% relative to alkene.[63] Copper(I) complexes with anionic trispyrazolyl-borate (homoscorpionate) ligands were also recently shown to be effective in ATRA systems without the use of reducing agents. In this case, small amounts of acetonitrile were used to coordinatively saturate copper in the lower oxidation state, suppressing the oxidation by alkyl halide.[68,69] This process reduced the overall radical concentration and thus minimized accumulation of the deactivator (copper(II) complex). The methodology for catalyst regeneration in the presence of reducing agents was also extended towards more complex organic synthesis with the addition of CCl_4 to 1,6-heptadiene derivatives followed by sequential ATRC to yield substituted cyclopentanes in a single step with the lowest catalyst loadings reported so far.[65,67] Recently, monoadducts formed *via* Ru mediated ATRA and ATRC in the presence of magnesium powder as a reducing agent were utilized in a second reaction to synthesize cyclopropane rings *via* dehalogenation.[50] These examples are a visible indicator that this methodology is on a trajectory to potentially become a "greener" alternative to currently available synthetic processes for such organic transformations.

The success of ATRA in the presence of reducing agents using copper complexes with TPMA encouraged us to seek more active complexing ligands for this process. According to the well established correlation between the equilibrium constant for atom transfer ($K_{ATRA} = k_a/k_d$) and activity in ATRP,[70,71] tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was projected to be an even more active ligand in copper catalyzed ATRA (Scheme 2). Me_6TREN was first introduced to copper catalyzed ATRP of acrylates, enabling well controlled polymerization even at ambient temperature.[44,72,73] Subsequently, its use was extended to ATRC reactions of bromoacetimides with excellent results when compared to other neutral nitrogen-based ligands.[29,74]



Scheme 2 ATRA equilibrium (a) and typical nitrogen based ligands commonly used in copper catalyzed ATRA/ATRP (b). The equilibrium constant (K_{ATRA}) was measured for ethyl 2-bromoisobutyrate in the presence of $Cu^{I}Br$ in CH_3CN at 22 °C.[70]

In this article, we describe the use of [Cu^{II}(Me_6TREN)X][X] (X = Br^- and Cl^-) complexes in ATRA of polyhalogenated methanes to various alkenes in the presence of free radical diazo initiator AIBN. Furthermore, the activity of copper complexes in the presence of excess free ligand, source of halide anions and triphenylphosphine is examined.

Table 1 ATRA of polyhalogenated methanes to various alkenes catalyzed by $[Cu^{II}(Me_6TREN)X][X]$ (X = Cl^- or Br^-) in the presence of free-radical diazo initiator AIBN

Entry[a]	Alkene	$[Alkene]_0 : [Cu]_0$	R-X	Conv. (%)/Yield (%)[b]
1	1-Hexene	1000 : 1	CCl_4	100/100
2	1-Hexene	2500 : 1	CCl_4	89/89
3	1-Octene	1000 : 1	CCl_4	99/99
4	1-Octene	2500 : 1	CCl_4	85/85
5	*cis*-Cyclooctene	1000 : 1	CCl_4	95/95[c]
6	*cis*-Cyclooctene	2500 : 1	CCl_4	85/85[c]
7	Methyl Acrylate	250 : 1	CCl_4	100/67
8	1-Hexene	250 : 1	$CHCl_3$	51/51
9	1-Octene	250 : 1	$CHCl_3$	46/46
10	*cis*-Cyclooctene	250 : 1	$CHCl_3$	26/26[c]
11	Styrene	250 : 1	$CHCl_3$	77/40
12	Methyl Acrylate	250 : 1	$CHCl_3$	100/32
13	1-Hexene	500 : 1	$CHBr_3$	46/46
14	1-Octene	500 : 1	$CHBr_3$	39/39
15	*cis*-Cyclooctene	500 : 1	$CHBr_3$	37/37[c]
16	Styrene	250 : 1	$CHBr_3$	98/80
17	Styrene	500 : 1	$CHBr_3$	93/69
18	Methyl Acrylate	250 : 1	$CHBr_3$	100/51
19	Methyl Acrylate	1000 : 1	CBr_4	100/87

[a] T = 60 °C, time = 24 h, solvent = CH_3CN, $[Alkene]_0 : [R\text{-}X]_0 : [AIBN]_0$ = 1 : 1.1 : 0.05, $[Alkene]_0$ = 1.34 M (CCl_4, $CHCl_3$ and $CHBr_3$) or 1.13 M (CBr_4). [b] Yield is based on the formation of monoadduct and was determined using ^1H NMR spectroscopy. [c] 1,4-regioisomer resulting from a 1,5-hydrogen shift.

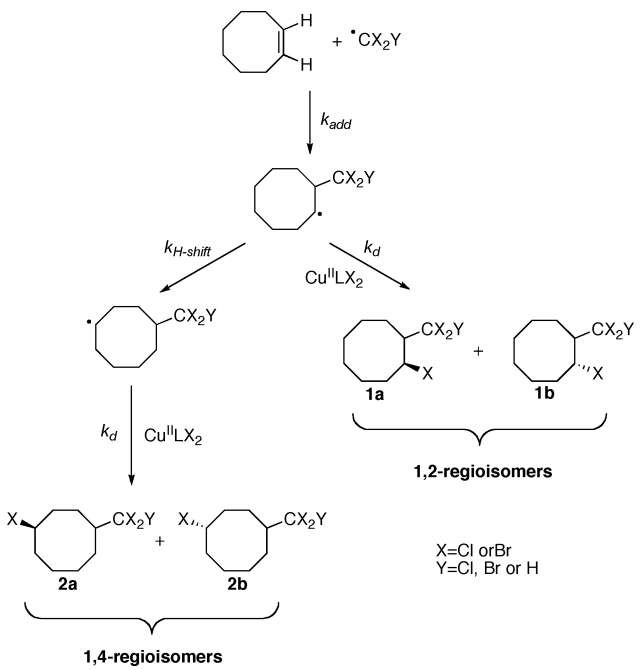
Results and discussion

ATRA catalyzed by copper complexes with Me_6TREN ligand

The activity of copper complexes with Me_6TREN ligand was first evaluated in ATRA of polychlorinated and polybrominated methanes to a variety of alkenes (Table 1). Overall, $[Cu^{II}(Me_6TREN)X][X]$ (X = Br^- or Cl^-) complex in the presence of AIBN was found to be less active than its pyridyl counterpart, tris(2-pyridylmethyl)amine (TPMA). At alkene to catalyst ratios of 2500 : 1, ATRA of CCl_4 to 1-hexene, 1-octene, and *cis*-cyclooctene proceeded efficiently to yield between 85 and 89% of monoadduct (entries 2, 4, and 6). Much higher yields of monoadduct were obtained at higher catalyst loadings (entries 1, 3, and 5). Poor control was attained in the case of the addition of CCl_4 to methyl acrylate, which required a catalyst loading as high as 0.4 mol-% in order to suppress competing free radical polymerization initiated by AIBN (entry 7). As expected, the additions of chloroform to all alkenes produced significantly lower yields of the monoadduct (entries 8–12). This was presumably due to a slower activation rate constant, as a result of stronger C–Cl bonds.[75] The discrepancy between conversion and percent yield of the monoadduct in the case of styrene (entry 11) and methyl acrylate (entry 12) can be attributed to AIBN-initiated free radical polymerization. Similar results were also obtained in the case of bromoform (entries 13–18), with the exception of styrene which yielded 80% of the monoadduct (entry 16).

Due to the large chain transfer constant of carbon tetrabromide, ATRA reactions with most alkenes proceeded efficiently in the absence of copper catalyst, with the exception of methyl acrylate which polymerized rapidly, affording only 12% yield of the monoadduct. However, in the presence of $[Cu^{II}(Me_6TREN)Br][Br]$ (0.10 mol-%), the yield increased to 87% (entry 19).

The addition of CCl_4, $CHCl_3$, and $CHBr_3$ to *cis*-cyclooctene produced predominantly 1,4-regioisomers, resulting from a 1,5-hydrogen shift occurring before the radical trapping by copper(II) complex (Scheme 3). For the molecular structure of *cis*-1-chloro-4-(trichloromethyl)-cyclooctane, see supporting information. Clearly, with these alkyl halides, the rate of 1,5-hydrogen shift ($k_{H\text{-}shift}[R^\bullet]$) exceeded the rate of radical trapping ($k_d[Cu^{II}][R^\bullet]$), consistent with previous studies in which initiation was achieved by either thermal or photoinitiated means.[76,77] Taking into account the ratio of 1,4- to 1,2-regioisomers (~98 : 2), copper(II) concentration (~5.0×10^{-3} M), and approximate deactivation rate constant for copper(II) complex ($k_d \approx 5.0 \times 10^7$ $M^{-1}s^{-1}$),[55,56] the rate constant for 1,5-hydrogen shift can be estimated to be on the order of $k_{H\text{-}shift} \approx 1.2 \times 10^7$ s^{-1}. This value is in good agreement with literature values for similar substrates involving 1,2- and 1,5-hydrogen shifts.[78,79] Certainly, the control over product distribution could be achieved by increasing the copper concentration in the system. For example, at copper(II) loadings as high as 10 mol-% (relative to alkene), the ratio of 1,4- to 1,2-regioisomers is expected to decrease to approximately 65 : 35. Similar effects were previously observed in ruthenium catalyzed ATRA reactions.[80]



Scheme 3 Formation of 1,2- and 1,4-regioisomers during copper catalyzed ATRA of CX_3Y (X = Cl or Br, Y = Cl, Br or H) to *cis*-cyclooctene.

The situation with carbon tetrabromide is expected to be quite different because of the well known fact that it is an excellent halogen atom transfer agent.[81,82] Indeed, ATRA reactions proceeded efficiently in the presence of AIBN only, affording nearly quantitative yields of the monoadduct. However, the addition of CBr_4 favored the formation of 1,2-regioisomers (75%), with the remaining 25% being attributed to products resulting from the 1,5-hydrogen shift. Following the analogy discussed above and assuming that $k_{H\text{-}shift} \approx 1.2 \times 10^7$ s^{-1}, the rate constant for halogen atom transfer from CBr_4 to cyclooctene radical can be approximated to be on the order of 3.2×10^7 $M^{-1}s^{-1}$.

Each regioisomer in the addition of CBr_4 to *cis*-cyclooctene consisted of approximately 50 : 50 ratio of diastereomers, which is typical for radical addition reactions. The molecular structures of *cis* and *trans* 1,4-regioisomers obtained by slow evaporation from chloroform at −10 °C are shown in Fig. 1.

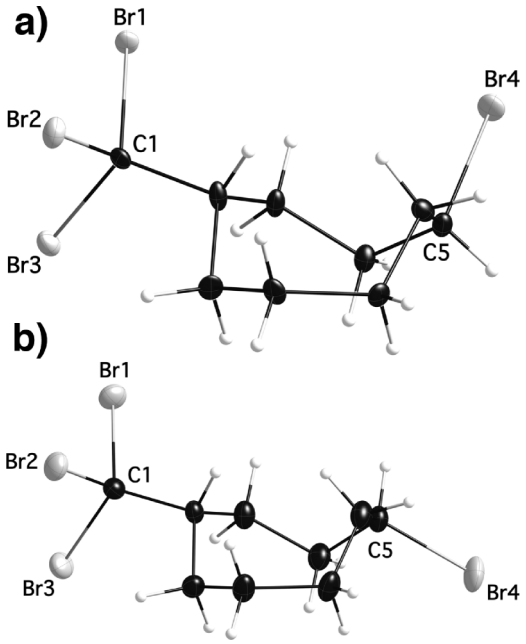


Fig. 1 Molecular structures of *cis*-1-bromo-4-(tribromomethyl)-cyclooctane (a) and *trans*-1-bromo-4-(tribromomethyl)cyclooctane (b) collected at 150 K, shown with 50% probability displacement ellipsoids. Selected bond distances [Å] for (a) Br1–C1 1.951(7), Br2–C1 1.942(7), Br3–C1 1.954(7), Br4–C5 1.992(7). For (b) Br1–C1 1.958(2), Br2–C1 1.960(2), Br3–C1 1.944(2), Br4–C5 1.988(2).

The drastic differences in product distribution between CCl_4, $CHBr_3$ and CBr_4 can clearly be attributed to different halogen atom transfer rate constants. To test this observation further, $CBrCl_3$ was used in ATRA to *cis*-cyclooctene in the absence of copper catalyst. This substrate should have a deactivating ability (*i.e.* halogen atom transfer rate constant) between that of CCl_4 and CBr_4. Indeed, the product distribution in this case consisted of a 52 : 48 ratio of 1,2- to 1,4-regioisomers. For the molecular structure of *cis*-1-bromo-4-(trichloromethyl)-cyclooctane see supporting information.

Optimization of [Cu(Me$_6$TREN)Cl][Cl] mediated ATRA reactions

Available electrochemical and kinetic data on copper complexes with Me_6TREN indicate that they should be considerably more active than corresponding complexes with TPMA ligand.[70,71,83,84] Possible reasons for this lack of activity could include: (a) ligand dissociation, (b) halide anion dissociation, (c) disproportionation of copper(I) to copper(II and 0), and/or (d) alkene coordination.[85] Aliphatic amine ligands are well known to have weaker binding constants to copper when compared to pyridine based ligands,[86,87] so ligand dissociation was investigated first. By adding excess of Me_6TREN, the equilibrium of dissociation could be shifted towards the complexed and more active copper(I) complex. No significant effects on the alkene conversion and the overall product yield were observed in the case of CCl_4 and 1-octene when up to 20 equivalents of excess Me_6TREN were added to the reaction mixture (Fig. 2a and 2b). Reactions of styrene and CCl_4 showed a very slight decrease in yield with increasing free ligand concentration. Interestingly, in the case of methyl acrylate, a significant decrease in both the alkene conversion and monoadduct yield was observed on addition of excess Me_6TREN. For example, with 20 eq. of ligand, the conversion and product yield after 24 h decreased from 100 to 76 and 65 to 32%, respectively. Most likely, Me_6TREN acts as a radical inhibitor when present in large excess. Furthermore, precipitation of amino halide salts was also observed, likely arising from a reaction with alkyl halide (see supporting information).

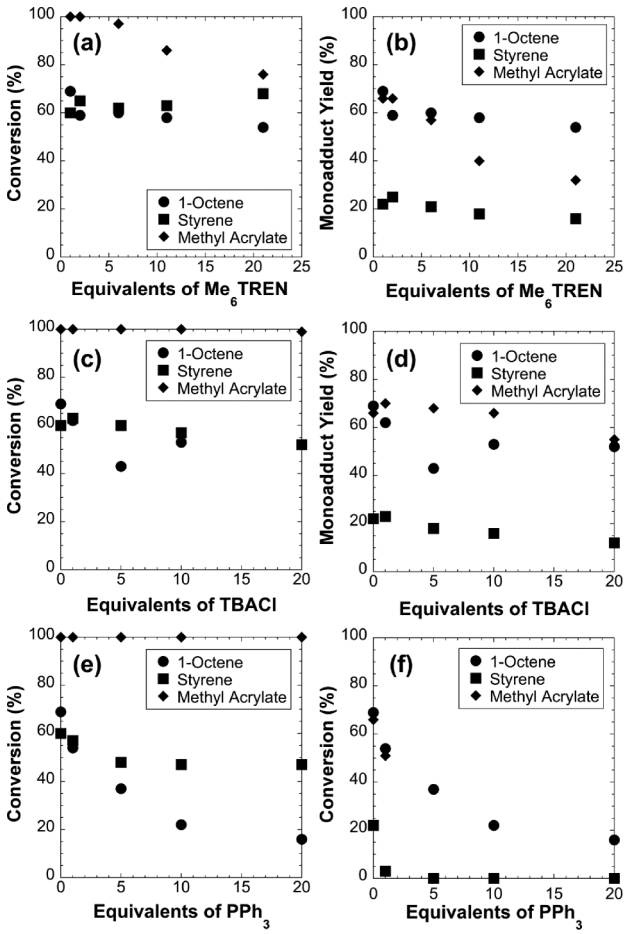


Fig. 2 Effect of added Me_6TREN ligand, tetrabutylammonium chloride (TBACl), and triphenylphosphine (PPh_3) on [Cu^{II}(TPMA)Cl][Cl] catalyzed ATRA reactions. T = 60 °C, time = 24 h, solvent = CH_3CN, $[Alkene]_0 : [R\text{-}X]_0 : [AIBN]_0$ = 1 : 1.1 : 0.05, $[Alkene]_0$ = 1.34 M, $[Alkene]_0 : [Cu^{II}]_0$ = 5000 : 1 (1-octene), 250 : 1 (styrene and methyl acrylate).

In order to additionally examine the effect of free Me_6TREN ligand, the conversion of 1-octene (which does not undergo free radical polymerization in the presence of AIBN at 60 °C) was monitored as a function of time. The results for 0, 5, and 20 equivalents of free ligand relative to [Cu^{II}(Me_6TREN)Cl][Cl] are shown in Fig. 3. As expected, in the presence of 0 equiv. of Me_6TREN, the first order kinetic plot was linear confirming constant radical concentration in the system ($d[1\text{-octene}]/dt = -k_{add}[R^{\bullet}][1\text{-octene}]$).[55,56,62] However, significant deviations were

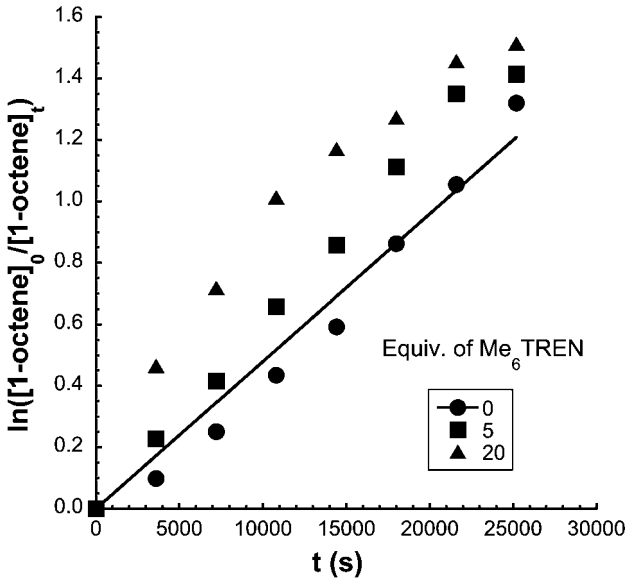


Fig. 3 First order kinetic plots for ATRA of 1-octene to CCl_4 catalyzed by [Cu^{II}(Me_6TREN)Cl][Cl] in the presence of 0 (●), 5 (■), and 20 (▲) equivalents of free Me_6TREN. T = 60 °C, solvent = CH_3CN, [1-octene]$_0$: [CCl_4]$_0$: [AIBN]$_0$: [Cu^{II}]$_0$ = 5000 : 5500 : 250 : 1, [1-octene]$_0$ = 1.34 M.

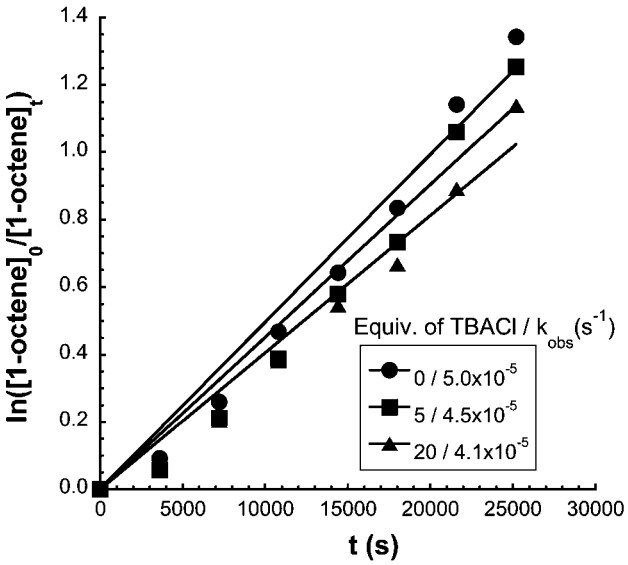


Fig. 4 First order kinetic plots for ATRA of 1-octene to CCl_4 catalyzed by [Cu^{II}(Me_6TREN)Cl][Cl] in the presence of 0 (●), 5 (■), and 20 (▲) equivalents of TBACl. T = 60 °C, solvent = CH_3CN, [1-octene]$_0$: [CCl_4]$_0$: [AIBN]$_0$: [Cu^{II}]$_0$ = 5000 : 5500 : 250 : 1, [1-octene]$_0$ = 1.34 M.

observed in the case of 5 and 20 equiv., which also showed faster reaction rates. The acceleration in the latter two cases can be attributed to increased copper(I) concentrations in the system, indicating that free Me_6TREN might act as an additional reducing agent (apart from radicals generated by thermal decomposition of AIBN).[88] To test this hypothesis, UV-Vis spectroscopy was employed to monitor the ratio of equilibrium concentrations of copper(II) and copper(I) complexes in the presence of AIBN at 60 °C. Without externally added free ligand, only 10% of [Cu^{II}(Me_6TREN)Cl][Cl] was reduced to Cu^{I}(Me_6TREN)Cl, even after six days. However, upon the addition of 20 equivalents of Me_6TREN, most of the copper(II) complex was found to be reduced to copper(I) (see supporting information). These results further indicate that free Me_6TREN can indeed act as reducing agent in these systems.

The possibility of chloride anion dissociation from [Cu^{II}(Me_6TREN)Cl][Cl] was also examined by the addition of tetrabutylammonium chloride (TBACl, Fig. 2c and 2d). Overall, the addition of TBACl was found to have a slightly negative effect on the conversion of alkene and the yield of monoadduct. In the ATRA of 1-octene to CCl_4, the yield decreased from 69% to 52% in the presence of 20 equivalents of TBACl. Similarly, decrease in the conversion of styrene from 66% to 52% was accompanied by a decrease in the monoadduct yield from 22% to 12%. Lastly, in the addition of CCl_4 to methyl acrylate in the presence of 20 equiv. of TBACl, nearly quantitative conversions were observed as a result of free radical polymerization initated by AIBN. However, the yield of the desired monoadduct decreased from 66% to 55%. Generally, the addition of TBACl to ATRA reactions catalyzed by [Cu^{II}(Me_6TREN)Cl][Cl] in the presence of AIBN resulted in slower reaction rates. This is demonstrated in Fig. 4 which shows the first order kinetic plots for the ATRA of CCl_4 to 1-octene in the presence of 1,5 and 20 equivalents of TBACl. The decreased activity is most likely due to the formation of complexes that are not active in ATRA systems. Such complexes can be formed by multiple halide substitutions resulting in the formation of higher order halocuprates, which are well known and documented in the literature.[85]

Having probed the ligand and/or halide anion dissociation from [Cu^{II}(Me_6TREN)Cl][Cl], our studies have focused on disproportionation, which is known to occur readily with copper(I) complexes with Me_6TREN ligand. Neutral phosphines, such as PPh_3 and $P(OBu)_3$, have been shown to stabilize copper(I) complexes and suppress this side reaction. However, their coordination to copper complexes might result in significantly lower ATRA activity. Both phosphines were found to produce very similar results when added to ATRA reactions involving 1-octene, styrene, and methyl acrylate. Therefore, only data with PPh_3 will be discussed. The yield of monoadduct in the case of 1-octene was found to drastically decrease in the presence of more than 10 equivalents of PPh_3 (Fig. 2e and 2f). Under such conditions, the results mimicked non-metal catalyzed Kharasch addition, indicating the complete inactivity of the copper complexes to catalyze ATRA. Product yields for both styrene and methyl acrylate were also reduced to negligible amounts by the addition of more than 10 equivalents of PPh_3 relative to copper(II). The reason for this decreased yield is clearly the formation of ATRA inactive copper complexes. Therefore, although auxiliary ligands such as PPh_3 or $P(OBu)_3$ might suppress disproportionation of copper(I) to copper(II) and copper(0), their use in ATRA catalysis should be avoided.

Aside from CH_3CN, ATRA reactions were also performed in DMF, MeOH, and MeOH–H_2O mixtures. Disproportionation is known to occur more rapidly in polar solvents,[87] and would thus have a more noticeable effect on ATRA. This was indeed observed experimentally. Using 0.2 mol-% of [Cu^{II}(Me_6TREN)Cl][Cl] (relative to alkene), 1-octene was previously shown to produce quantitative yields of monoadduct in CH_3CN. However, the yield

decreased to 50% in both MeOH and DMF. A further decrease was also observed on the addition of small amounts of H_2O. A similar trend was noted for methyl acrylate, which showed complete conversion in each solvent, but the yields of monoadduct decreased from 67% in CH_3CN, to 52% and 37% in MeOH and DMF respectively. Clearly, the increased polarity of the reaction medium decreases the yield of the desired monoadduct as a result of disproportionation. Disproportionation decreases the overall copper(I) concentration in the system, resulting in slower activation rates ($Cu^I + RX \rightarrow Cu^{II}\text{-}X + R^{\bullet}$). Additionally, polar protic media might favor halide anion dissociation from $[Cu^{II}(Me_6TREN)Cl][Cl]$, which would result in even further decrease in product selectivity.[87]

The results presented thus far indicate that copper complexes with Me_6TREN ligand can be used in ATRA reactions in the presence of free-radical diazo initiator AIBN. However, despite higher equilibrium constant for atom transfer (Fig. 1), their activity appears to be approximately 10 times lower than with TPMA analogue.[57,58] This decrease can be attributed to concurrent side reactions associated with the catalyst such as ligand and/or halide anion dissociation and disproportionation. Based on the above studies, the latter one was found to have the most significant effect in lowering the product selectivity.

Structural characterization of copper complexes with Me_6TREN ligand

The copper(II) complexes, $[Cu^{II}(Me_6TREN)Cl][Cl]$ (**1**) and $[Cu^{II}(Me_6TREN)Br][Br]$ (**2**), were synthesized by reacting $Cu^{II}Cl_2$ or $Cu^{II}Br_2$ with stoichiometric amounts of Me_6TREN. The same complexes can alternatively be prepared by oxidizing $Cu^{I}(Me_6TREN)Cl$ or $Cu^{I}(Me_6TREN)Br$ with excess CCl_4 or CBr_4, respectively. **1** and **2** were found to be distorted trigonal bipyramidal in geometry with crystallographically imposed C_3 symmetry (Fig. 5). Each complex was coordinated by four nitrogen atoms from Me_6TREN ligand and either a chloride (**1**) or bromide (**2**) anion. The axial Cu^{II}–N bond lengths in both complexes were approximately 2.05 Å, and the equatorial bonds were slightly longer (~2.15 Å, Table 2). The Cu^{II}–Cl and Cu^{II}–Br bond lengths were found to be 2.2589(5) and 2.4016(4) Å, respectively. All of the angles in the coordination sphere of both complexes were close to a trigonal bipyramidal geometry. This was also confirmed by a τ factor which was calculated to be 1.00 for both complexes (trigonal bipyramidal (τ = 1) and square pyramidal (τ = 0)).[85] The structures reported herein were in close agreement with

Table 2 Selected bond distances (Å) and angles (°) for $[Cu^{II}(Me_6TREN)Cl][Cl]$ (**1**) and $[Cu^{II}(Me_6TREN)Br][Br]$ (**2**)[a]

	1	2
Bond distances		
Cu–N1	2.0545(15)	2.046(2)
Cu–N2	2.1489(9)	2.1527(13)
Cu–X	2.2589(5)	2.4016(4)
Bond angles		
N1–Cu–N2	84.62(3)	84.81(4)
N2–Cu–X	95.38(3)	95.19(4)
N2–Cu–N2^i	119.132(8)	119.191(11)
N1–Cu–X	180.00(2)	180.00(4)

[a] X = Cl for **1** and Br for **2**.

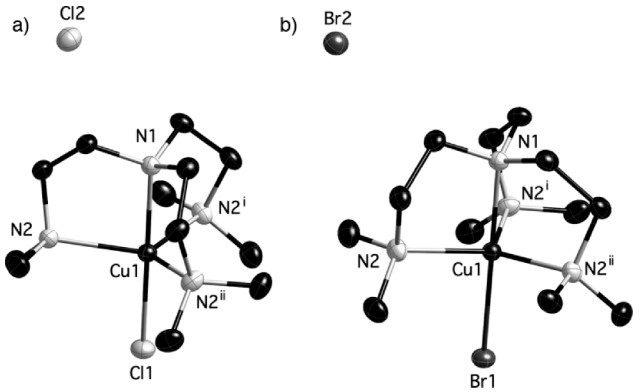


Fig. 5 Molecular structures of $[Cu^{II}(Me_6TREN)Cl][Cl]$ (a) and $[Cu^{II}(Me_6TREN)Br][Br]$ (b) collected at 150 K, shown with 50% probability displacement ellipsoids. H-atoms have been omitted for clarity, [symmetry codes: (i) –z + 3/2,–x + 1,y + 1/2, (ii) –y + 1,z – 1/2,–x + 3/2 for (a) and (i) y,z,x, (ii) z,x,y for (b)].

previously reported structures for $[Cu^{II}(Me_6TREN)Br][Br]$[85,89] and $[Cu^{II}(Me_6TREN)Cl_{0.63}/Br_{0.37}][Br]$[90] at room temperature. Additionally, the structural features of **1** and **2** were also similar to other copper(II) complexes with tetradentate neutral nitrogen based ligands.[57,58,60,85]

Only a few examples of copper(I) complexes with Me_6TREN ligand have known molecular structures.[91,92] This is mostly due to their oxidative instability and propensity to disproportionate in a variety of solvents. To prevent this, a single equivalent of PPh_3 was added to a solution of $[Cu^{I}(CH_3CN)_4][ClO_4]$ in CH_3CN before the addition of Me_6TREN. Salt metathesis with $NaBPh_4$ resulted in the formation of $[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ (**3**). No disproportionation was observed during the reaction and the resulting complex was relatively air stable. The copper(I) center in **3** was distorted tetrahedral in geometry as a result of displacement of one arm of Me_6TREN ligand by PPh_3 (Fig. 6). The remaining three nitrogen atoms from Me_6TREN were found to be coordinated

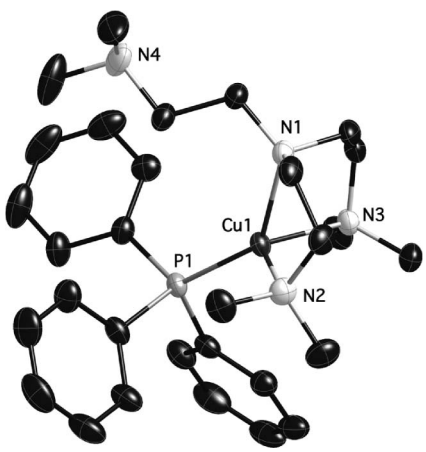


Fig. 6 Molecular structure of $[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ (**3**) collected at 150 K, shown with 50% probability displacement ellipsoids. H-atoms and counterion BPh_4^- have been omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1–N1 2.1450(14), Cu1–N2 2.1753(17), Cu1–N3 2.1865(18), Cu1–P1 2.1910(5), N1–Cu1–N2 85.79(6), N1–Cu1–N3 83.87(6), N2–Cu1–N3 113.40(8), N1–Cu1–P1 136.92(4), N2–Cu1–P1 111.80(6), N3–Cu1–P1 119.80(4).

at distances of 2.1450(14), 2.1753(17) and 2.1865(18) Å. Finally, the tetrahedral geometry was completed by the coordination of a phosphorus atom from PPh_3 at the distance of 2.1910(5) Å. The arm displacement from Me_6TREN, induced by the steric bulk of PPh_3, was previously observed in structurally related copper(I) complexes with tetradentate tris(2-pyridylmethyl)amine (TPMA) ligand.[60,93]

From the solid-state structure of **3**, Me_6TREN is clearly acting as a tridentate ligand, similar to *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine (PMDETA). Therefore, the solution structure was probed by variable temperature ^{1}H NMR spectroscopy. At room temperature, only a single resonance was observed for the methyl protons of the ligand at 2.20 ppm and two signals for the methylene ones at 3.04 and 2.68 ppm (Fig. 7). All three proton resonances showed a downfield shift relative to free Me_6TREN (2.56 and 2.31 ppm for methylene and 2.16 ppm for methyl protons), consistent with coordination to copper(I). Upon cooling, the resonances for Me_6TREN significantly broadened until finally at 170 K the signals for the methylene protons coalesced and the singlet for the methyl protons at 2.09 ppm became very broad. Resonances corresponding to PPh_3 (7.57–7.55 ppm and 7.49–7.44 ppm) and BPh_4^- anion (7.33, 6.92, and 6.77 ppm) were observed to show very little change as a result of cooling. The observed broadening and shifting of Me_6TREN resonances in **3** towards free ligand can be best explained as the result of rapid dissociation/association of at least one ligand arm. We ruled out the possibility for complete ligand dissociation because experiments in the presence of **3** and one equivalent of free Me_6TREN clearly indicated resonances for both free and complexed ligand in the temperature range 298–180 K. Furthermore, the ligand exchange occurred only at temperatures above 360 K (see supporting information). Therefore, the solution structure of **3** is consistent with the solid state (Fig. 6).

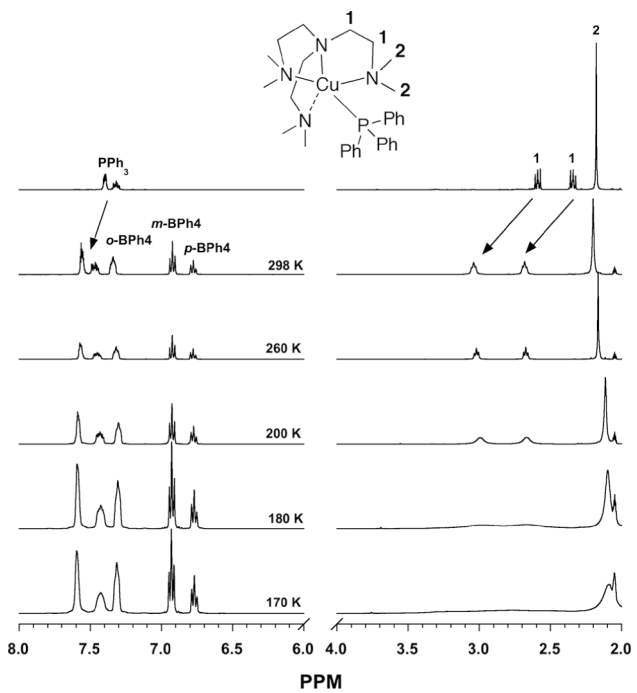


Fig. 7 Variable temperature ^{1}H NMR (400 MHz, acetone-d_6) of [Cu^I(Me_6TREN)PPh_3][BPh_4] (**3**).

Conclusions

Copper(II) complexes with the Me_6TREN ligand were thoroughly investigated as catalysts for ATRA in the presence of free-radical diazo initiator AIBN. These complexes were found to catalyze the addition of CCl_4, $CHCl_3$, CBr_4, and $CHBr_3$ to a series of alkenes with good efficiency, albeit lower than expected due to their large ATRA equilibrium constants. Attempts were made to increase their activity towards ATRA by addressing ligand/halide anion dissociation and disproportionation equilibria. Catalytic activity could not be increased, and disproportionation of Cu^I(Me_6TREN)X to Cu^0 and [Cu^{II}(TPMA)X][X] (X = Br^- or Cl^-) was found to be the most likely cause.

The reactions of CCl_4 to *cis*-cyclooctene were found to produce solely the 1-chloro-4-(trichloromethyl)cyclooctane, as a result of intramolecular 1,5-hydrogen transfer. Interestingly, CCl_3Br and CBr_4 produced both the 1,2- and 1,4-regioisomers in 48 : 52 and 75 : 25 ratios, respectively. These results were attributed to different halogen atom transfer constants of alkyl halides.

The molecular structures of [Cu^{II}(Me_6TREN)Cl][Cl] and [Cu^{II}(Me_6TREN)Br][Br] were determined and found to be nearly isostructural with distorted trigonal bipyramidal geometries and perfect C_3 symmetry. A rare example of a copper(I) complex with Me_6TREN was prepared using PPh_3 to stabilize the complex against disproportionation. The molecular structure of [Cu^I(Me_6TREN)PPh_3][BPh_4] was found to be distorted tetrahedral as a result of the dissociation of a single arm of Me_6TREN ligand. Variable temperature ^{1}H NMR studies confirmed that the structure in solution was consistent with the solid state.

Experimental section

Materials

All chemicals were purchased from commercial sources and used as received. Tetrakis(acetonitrile)copper(I) perchlorate[94] was synthesized according to literature procedures. *Warning*: *Although we have experienced no problems, perchlorate metal salts are potentially explosive and should be handled with care.* All manipulations involving copper(I) complexes were performed under argon in the dry box (<1.0 ppm O_2 and <0.5 ppm H_2O) or using standard Schlenk line techniques. Solvents (pentane, acetonitrile, acetone, and diethyl ether) were degassed and deoxygenated using an Innovative Technology solvent purifier. Methanol was vacuum distilled and deoxygenated by bubbling argon for 30 min prior to use. The corresponding copper(II) complexes were synthesized under ambient conditions.

Instrumentation

^{1}H NMR spectra were obtained using Bruker Avance 400 and 500 MHz spectrometers and chemical shifts are given in ppm relative to residual solvent peaks [$CDCl_3$ δ 7.26 ppm; $(CD_3)_2CO$ δ 2.05 ppm]. iNMR software was used to generate the images of NMR spectra. Temperature calibrations were performed using a pure methanol sample.

The X-ray intensity data were collected at 150 K using graphite-monochromated Mo-*K* radiation (0.71073 Å) with a Bruker Smart Apex II CCD diffractometer. Data reduction included absorption corrections by the multi-scan method using SADABS.[95] Structures were solved by direct methods and refined by full matrix least squares using the SHELXTL 6.1 bundled software package.[96]

The H-atoms were positioned geometrically (aromatic C–H 0.93, methylene C–H 0.97, and methyl C–H 0.96) and treated as riding atoms during subsequent refinement, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The methyl groups were allowed to rotate about their local threefold axes. ORTEP-3 for Windows[97] and Crystal Maker 7.2 were used to generate molecular graphics. For detailed crystallographic data tables refer to supporting information. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with Cambridge Crystallographic Data Centre (CCDC) as supplementary publications nos. CCDC 808280–808287. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax(+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

IR spectra were recorded in the solid state using a Nicolet Smart Orbit 380 FT-IR spectrometer (Thermo Electron Corporation). Elemental analyses for C, H, and N were obtained from Midwest Microlabs, LLC. UV-Vis spectra were recorded using a Beckman DU-530 spectrometer in 1.0 cm path-length airtight quartz cuvettes.

General procedures for ATRA reactions

0.033 g AIBN (0.20 mmol), *p*-dimethoxybenzene (internal standard), 4.03 mmol alkene (630 μL 1-octene, 525 μL *cis*-cyclooctene, 500 μL 1-hexene, 462 μL styrene, 362 μL methyl acrylate), and 4.43 mmol alkyl halide (430 μL CCl_4, 355 μL $CHCl_3$, 387 μL $CHBr_3$, 1.470 g CBr_4) were combined in a vial. Additives, such as tetrabutylammonium chloride (TBACl), PPh_3, or Me_6TREN, were added as solutions (32.2 mM for 1-octene and 645.0 mM for styrene and methyl acrylate). Solvent was then added (acetonitrile, methanol, or dimethylformamide) in order to maintain a constant volume of 2.20 mL for 1-hexene, 1-octene, and *cis*-cyclooctene or 1.39 mL for styrene and methyl acrylate. The reaction mixture was then divided equally into 5 NMR tubes (439 μL for 1-hexene, 1-octene and *cis*-cyclooctene and 278 μL for styrene and methyl acrylate). A 0.01 M solution of $[Cu^{II}(Me_6TREN)X][X]$ (X = Cl^- or Br^-) in acetonitrile, methanol, or dimethylformamide was then added to accommodate various catalyst loadings (250 : 1–322 μL, 500 : 1–161 μL, 1000 : 1–81 μL, 2500 : 1–32 μL, 5000 : 1–16 μL, and 10 000 : 1–8 μL). The total volume in the NMR tube was then adjusted by the addition of solvent so that the total concentration of alkene was maintained at 1.34 M. Reaction tubes were flushed with argon for 30 s, sealed with a plastic NMR tube cap, wrapped with Teflon tape, and placed in an oil bath thermostated at 60 °C for 24 h.

Synthesis of tris(2-dimethylaminoethyl)amine (Me_6TREN)

Tris((2-dimethylamino)ethyl)amine was synthesized according to published procedures.[98,99] Density was experimentally determined to be 0.860 g mL^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ2.52 (dd, J = 8.7 Hz, 6.2 Hz, 6H), δ2.29 (dd, J = 8.7 Hz, 6.1 Hz, 6H), δ2.14 (s, 18H). ^{13}C NMR (101 MHz; $CDCl_3$, 298 K): δ57.1, 52.7, 45.6.

Synthesis of $[Cu^{II}(Me_6TREN)Cl][Cl]$ (1)

$Cu^{II}Cl_2$ (0.50 g, 3.71 mmol) was dissolved in methylene chloride and Me_6TREN (0.860 g, 1 mL, 3.71 mmol) added. The blue solution was stirred at ambient temperature for 15 min. The complex was precipitated by the addition of 50 mL of petroleum ether. The blue powder was collected by filtration and dried under vacuum (yield = 1.33 g, 98%). UV-Vis (CH_3CN): λ_{max} = 938 nm, ε_{max} = 451 $Lmol^{-1}cm^{-1}$. Anal. Calcd. for $C_{12}H_{30}N_4CuCl_2$ (364.85): C, 39.50; H, 8.29; N, 15.36. Found: C, 38.81; H, 7.97; N, 14.98.

Synthesis of $[Cu^{II}(Me_6TREN)Br][Br]$ (2)

$Cu^{II}Br_2$ (0.83 g, 3.71 mmol) was dissolved in methylene chloride and Me_6TREN (0.860 g, 1 mL, 3.71 mmol) added. The green solution was stirred at ambient temperature for 15 min. The complex was precipitated by the addition of 50 mL of petroleum ether. The green powder was collected by filtration and dried under vacuum (yield = 1.63 g, 96%). UV-Vis (CH_3CN): λ_{max} = 973 nm, ε_{max} = 426 $Lmol^{-1}cm^{-1}$. Anal. Calcd. for $C_{12}H_{30}N_4CuBr_2$ (453.75): C, 31.76; H, 6.66; N, 12.35. Found: C, 31.40; H, 6.46; N, 12.20.

Synthesis of $[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ (3)

$[Cu^{I}(CH_3CN)_4][ClO_4]$ (100 mg, 0.306 mmol) and PPh_3 (80 mg, 0.306 mmol) were dissolved in 3.0 mL of MeOH. Me_6TREN (70 mg, 82 μL, 0.306 mmol) was then added, followed by $NaBPh_4$ (105 mg, 0.306 mmol). A colorless powder began to precipitate immediately. The solution was left at –35 °C overnight to complete precipitation. The methanol was removed and the powder was redissolved in 3.0 mL acetone. The complex was crystallized by slow diffusion of diethyl ether (yield = 0.213 g, 80%). ^{1}H NMR (400 MHz, acetone-d_6, 298 K): δ7.57–7.55 (m, 9H), δ7.49–7.44 (m, 6H), δ7.36–7.32 (m, 8H), δ6.92 (t, J = 7.4 Hz, 8H), δ6.79–6.76 (m, 4H), δ3.04 (t, J = 5.4 Hz, 6H), δ2.68 (t, J = 5.6 Hz, 6H), δ2.20 (s, 18H). Anal. Calcd. for $C_{54}H_{65}BCuN_4P$ (875.45): C, 74.08; H, 7.48; N, 6.40. Found: C, 74.09; H, 7.65; N, 6.87.

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