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Towards understanding monomer coordination in atom transfer radical polymerization: synthesis of [Cu^I(PMDETA)(π-M)][BPh_4] (M = methyl acrylate, styrene, 1-octene, and methyl methacrylate) and structural studies by FT-IR and ^{1}H NMR spectroscopy and X-ray crystallography

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Abstract

Cu^I complexes of the form [Cu^I(PMDETA)(π-M)][BPh_4] (where PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, and M = vinyl monomer) were synthesized and isolated from solution as crystals with methyl acrylate (MA), styrene (Sty), and 1-octene (Oct). The interaction of the C═C double bond of the vinyl monomer with Cu^I was characterized via FT-IR and ^{1}H NMR spectroscopy and single crystal X-ray crystallography. A fourth complex with methyl methacrylate (MMA) was synthesized and characterized spectroscopically, but no crystals suitable for X-ray structure analysis could be obtained. In all complexes, PMDETA acts as a tridentate ligand, while the pseudotetrahedral coordination geometry around Cu^I is completed by a π-interaction with the C═C double bond of M in the presence of a non-coordinating counter-ion. A decrease in C═C IR stretching frequencies of $\Delta\nu(C{=}C) = -110, -80, -109$, and $-127\ cm^{-1}$ for complexes with MA, Sty, Oct, and MMA, respectively, was observed upon coordination. No significant change in C═C bond length was seen in the crystal structure for complexes with MA and Oct while a slight lengthening was observed for the Sty complex. The upfield shift of the vinyl proton resonances indicated the presence of significant π-back-bonding.

Keywords: Copper(I) complexes; π-Coordination; X-ray structure; ^{1}H NMR; FT-IR; ATRP

1. Introduction

The potential to dramatically improve or modify the physical properties of polyolefins through the incorporation of functional groups has fueled the search for new polymerization catalysts capable of copolymerizing polar functional monomers with simple α-olefins [1,2]. Recent advances toward the copolymerization of polar monomers and alkenes were made in the field of coordination polymerization with the introduction of rationally designed Pd- and Ni-based diimine polymerization catalysts [3]. However, while these compounds were employed to successfully copolymerize as much as 25 mol% of methyl acrylate with ethylene and higher α-olefins, increasing the incorporation of functional groups into the copolymer required increasing the fraction of polar monomer in the monomer feed, which in turn resulted

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in a loss of activity of the catalyst [4]. Controlling the reaction still remains a challenge, and detailed mechanistic studies concerning olefin coordination to transition metals will be necessary for any further advances made in this field. Olefin-transition metal complexes have been the subject of numerous reviews [5–10]. According to the widely accepted model proposed by Dewar [11] and by Chatt and Duncanson [12], the metal–olefin bond has both σ and π components; which component dominates depends on the direction of transfer of electron density (from the metal to the olefin π^*-orbital, or from the olefin π-orbital to the vacant σ-type metal orbital).

Radical polymerization represents a different approach to the goal of copolymerizing polar monomers with α-olefins. The tolerance that radical polymerization shows toward polar functional groups, as opposed to traditional coordination and ionic polymerization, makes this technique attractive for polymerizing polar monomers. Nevertheless, a number of well-known drawbacks, including the inability to control molecular weight distribution or chain end functionality and develop well-defined complex structures, make conventional radical polymerization less than ideal. Atom transfer radical polymerization (ATRP) has emerged in the last decade as a powerful technique for the synthesis of macromolecules with well defined compositions, architectures and functionalities [13–18]. This controlled living radical polymerization technique has produced a plethora of polymeric materials with predictable molecular weights and narrow molecular weight distributions [19–23].

However, while radical polymerization techniques are well suited for polar monomers, α-olefins typically do not polymerize via a radical mechanism as they are subject to degradative chain transfer in the presence of a reactive propagating radical [24]. Recent publications have reported that while degradative chain transfer does occur, the copolymerization of methyl acrylate with various 1-alkenes under ATRP conditions is possible under mild conditions [25–27]. Well-controlled polymers of methyl acrylate constituting approximately 25 mol% of 1-octene have since been reportedly attained using ATRP [28]. However, increasing the level of incorporation of the olefin into the copolymer by increasing its fraction in the monomer feed resulted in low overall conversion, plausibly due to the irreversible deactivation of growing chains by formation of un-reactive alkyl halide chain ends derived from α-olefins. The unfavorable reactivity ratios of these monomers in radical polymerizations have made statistical copolymers with a high degree of olefin incorporation difficult to attain and a high conversion difficult to reach.

This project has a threefold purpose. First, the study of the coordination of various polar and non-polar olefins to Cu^I complexes will provide valuable insight into the nature of the Cu^I-olefin bonding. Several π-coordinated complexes of methyl acrylate and methyl methacrylate have been extensively studied with other transition metals, including Ru [29], Rh [30], Pt [31], and Ni [32]. However, little is known about the coordination of methyl acrylate with Cu^I [33,34], and there are no literature reports to date of π-coordination of methyl methacrylate to Cu^I. Information on the nature of this bonding will be necessary to later study the change in reactivity of a monomer in a radical polymerization upon coordination to a transition metal. Potentially, the altered reactivity could allow for an increased incorporation of α-olefin into a copolymer with polar functional monomers. Second, concurrent reactions that may occur during the ATRP and will affect its efficiency warrant further examination. Disproportionation of the Cu^I catalyst in aqueous media [35], transfer reactions associated with the complexing ligand [36–38], and solvent coordination [39] to the active catalyst have already been documented in this polymerization system. $[Cu^I(PMDETA)X]$ (X = Cl or Br) is successfully used as an ATRP catalyst [40], but these complexes could not be isolated with coordinated monomer. $[Cu^I(PMDETA)^+][BPh_4^-]$, for which the counter-ion does not compete with monomer for coordination to Cu^I, was thus studied in an effort to address the side reaction of monomer coordination to the Cu^I catalyst. Third, correlating reaction parameters including activation, deactivation, initiation, overall reaction rate constants, and evolution of molecular weight distribution [41–48] with catalyst, alkyl halide, and monomer structure, solvent composition and temperature should ultimately lead to the development of more active catalysts and are crucial to any future developments of ATRP [49–54]. This paper will address the nature of the bonding in these Cu^I complexes, and subsequent publications will address the quantification of this coordination process under various conditions and with $Cu^I(PMDETA)Br$, the effect that coordination has on the reactivity of the monomer, and the performance of the catalyst in polymerization.

2. Results and discussion

2.1. X-ray crystallography

The $[Cu^I(PMDETA)(\pi\text{-M})]^+$ cations and $[BPh_4]^-$ anions (where M = MA (**1**), Sty (**2**), Oct (**3**), and MMA (**4**)) build up the crystal structures of **1**–**3**; no interactions are observed between these respective counterions. PMDETA acts as a tridentate ligand, while the pseudotetrahedral coordination geometry around Cu^I is completed by a π-interaction with the C=C double bond of the coordinated monomer. Figs. 1–3 show the molecular structures of the respective cations of complexes

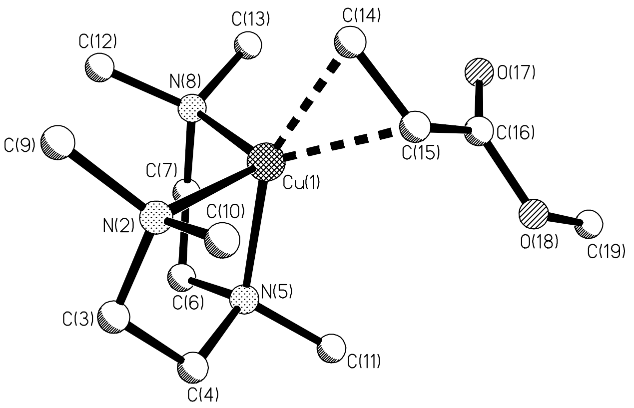


Fig. 1. Molecular structure of complex **1** cation. Hydrogen atoms have been removed for clarity.

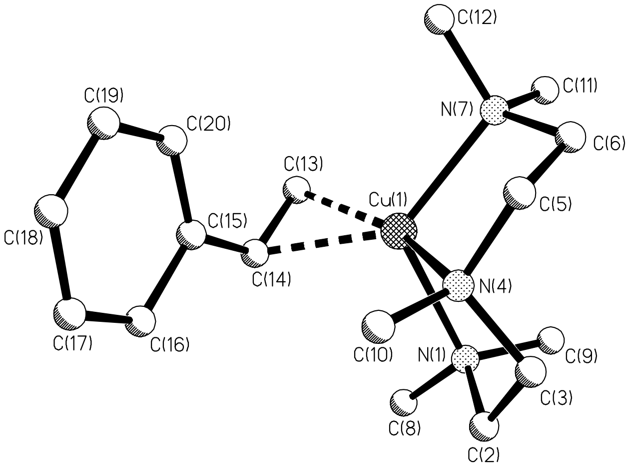


Fig. 2. Molecular structure of complex **2** cation. Hydrogen atoms have been removed for clarity.

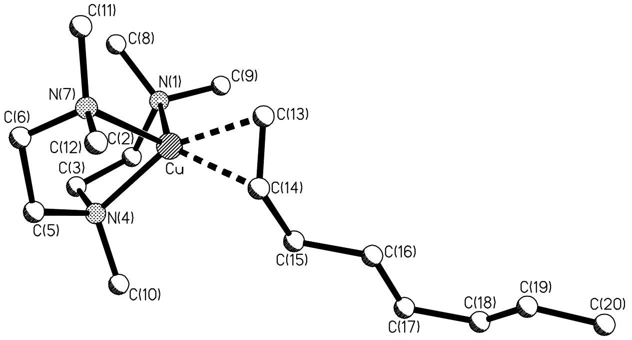


Fig. 3. Molecular structure of complex **3** cation. Hydrogen atoms have been removed for clarity.

1–**3** with their atomic numbering schemes. Selected bond lengths and angles are given in Table 1. While crystals of **4** suitable for X-ray analysis could not be obtained, the complex was studied by FT-IR and ^{1}H NMR spectroscopy (vide infra).

In the coordinated PMDETA ligand, the angles between the central nitrogen atom (N″), the $\mathrm{Cu^I}$ atom, and the terminal nitrogen atoms (N, N″) range from 84.07(6)° to 87.35(13)° while the N–$\mathrm{Cu^I}$–N bond angles range from 113.13(12)° to 114.93(6)° in complexes **1**–**3**. This deviation from tetrahedral geometry has been documented in the structurally related [$\mathrm{Cu^I}$(dien)(1-hex)][$\mathrm{BPh_4}$] (dien = diethylenetriamine), where the equivalent bond angles in the coordinated dien ligand are 83.2(7)°, 83.5(6)°, and 127.4(9)° [55]. The $\mathrm{Cu^I}$-N and $\mathrm{Cu^I}$–N″ bond lengths in the coordinated PMDETA ligand in **1**–**3** are significantly longer than the length of the $\mathrm{Cu^I}$–N′ bond (Table 1). While an elongation has been observed in the copper-nitrogen bonds of [$\mathrm{Cu^I}$(dien)(1-hex)][$\mathrm{BPh_4}$] and [$\mathrm{Cu^I}$(dien)(norbornene)][$\mathrm{BPh_4}$] [56], the elongation occurred at the central nitrogen rather than the terminal nitrogen atoms.

The two $\mathrm{Cu^I}$–C distances for the coordinated monomers are not equal; the $\mathrm{Cu^I}$ atom is always closer to the unsubstituted carbon atom ($\mathrm{C_\beta}$) than the substituted carbon atom ($\mathrm{C_\alpha}$) in **1**–**3**. This result is typical of metal–carbon bonds for a variety of metals and alkenes; the $\mathrm{C_\alpha}$–metal bond is invariably longer than the $\mathrm{C_\beta}$–metal bond [57]. In complex **1**, the $\mathrm{C_\beta}$-$\mathrm{Cu^I}$ distance is 2.021(4) Å and the $\mathrm{C_\alpha}$–$\mathrm{Cu^I}$ distance is 2.067(4) Å. In **2**, those respective distances are 2.052(4) Å and 2.108(4) Å, and in **3** 2.028(4) Å) and 2.094(4) Å. This difference between the two $\mathrm{Cu^I}$–C distances is fully consistent with the chemical shifts in the ^{1}H NMR spectrum of the complexes as will be discussed. The vinyl double bond length of coordinated MA in **1** was determined to be 1.360(6) Å, compared to 1.355 Å estimated for free MA [58]. The C=C distance of coordinated Sty in **2** was determined to be 1.367(3) Å, which is longer than 1.325(2) Å observed for the vinyl double bond in a crystal structure of free Sty at 83° K [59], and also longer than 1.358(10) Å observed for the vinyl double bond length in the structurally similar [$\mathrm{Cu^I}$(bipy)(π-Sty)]$\mathrm{ClO_4}$ [60] compound where Sty was π-coordinated to $\mathrm{Cu^I}$. The C=C distance of coordinated Oct in **3** was determined to be 1.354(3) Å; no significant lengthening was observed in comparison with the value commonly reported for free olefins of 1.34 Å [61] and that known for other 1-alkenes of 1.35 Å [58]. Additionally, complex **3** exists as two optical isomers which cocrystallize in equal amounts. The coordinated double bond in **3** occupied positions of C14 and C14A. The $\mathrm{Cu^I}$–(14A) and C(13)–(C14A) bond lengths for this optical isomer are 2.077(9) and 1.346(15) Å, respectively. The carbons found in positions C(14) and C(14A) would be approximately 1.017(14) Å from each other and make an angle C(14)–C(13)–C(14A) of 44.3°.

2.2. ^{1}H NMR spectroscopy

The ^{1}H NMR solution spectra of complexes **1**–**4** are fully consistent with the X-ray structures of the crystalline complexes discussed above. The proton resonances

Table 1
Selected bond distances (Å) and angles (°) for **1**–**3**

1		**2**		**3**	
Distances					
Cu(1)–N(2)	2.220(3)	Cu(1)–N(1)	2.2255(16)	Cu(1)–N(1)	2.251(3)
Cu(1)–N(5)	2.043(3)	Cu(1)–N(4)	2.1275(16)	Cu(1)–N(4)	2.061(3)
Cu(1)–N(8)	2.110(3)	Cu(1)–N(7)	2.1282(17)	Cu(1)–N(7)	2.177(3)
Cu(1)–C(14)	2.021(4)	Cu(1)–C(13)	2.052(2)	Cu(1)–C(13)	2.028(4)
Cu(1)–C(15)	2.067(4)	Cu(1)–C(14)	2.108(2)	Cu(1)–C(14)	2.094(8)
C(14)–C(15)	1.360(6)	C(13)–C(14)	1.367(3)	C(13)–C(14)	1.354(11)
Angles					
N(2)–Cu(1)–N(5)	85.58(12)	N(1)–Cu(1)–N(4)	84.07(6)	N(1)–Cu(1)–N(4)	84.98(11)
N(5)–Cu(1)–N(8)	87.35(13)	N(4)–Cu(1)–N(7)	85.80(6)	N(4)–Cu(1)–N(7)	85.48(13)
N(8)–Cu(1)–N(2)	113.65(12)	N(7)–Cu(1)–N(1)	114.93(6)	N(7)–Cu(1)–N(1)	113.13(12)
C(14)–Cu(1)–N(2)	111.64(13)	C(13)–Cu(1)–N(1)	109.86(8)	C(13)–Cu(1)–N(1)	110.1(2)
C(14)–Cu(1)–N(5)	156.15(17)	C(13)–Cu(1)–N(4)	153.29(8)	C(13)–Cu(1)–N(4)	156.23(18)
C(14)–Cu(1)–N(8)	108.26(16)	C(13)–Cu(1)–N(7)	107.14(8)	C(13)–Cu(1)–N(7)	104.1(2)
C(15)–Cu(1)–N(2)	103.52(15)	C(14)–Cu(1)–N(1)	102.84(8)	C(14)–Cu(1)–N(1)	131.6(3)
C(15)–Cu(1)–N(5)	117.33(15)	C(14)–Cu(1)–N(4)	117.43(9)	C(14)–Cu(1)–N(4)	118.0(3)
C(15)–Cu(1)–N(8)	129.55(14)	C(14)–Cu(1)–N(7)	137.76(9)	C(14)–Cu(1)–N(7)	110.8(3)
C(14)–Cu(1)–C(15)	38.84(16)	C(13)–Cu(1)–C(14)	38.65(9)	C(13)–Cu-C(14)	38.3(3)
Cu(1)–C(14)–C(15)	72.4(2)	Cu(1)–C(13)–C(14)	68.46(14)	Cu(1)–C(13)–C(14)	73.5(4)
Cu(1)–C(15)–C(14)	68.8(2)	Cu(1)–C(14)–C(13)	72.89(14)	Cu(1)–C(14)–C(13)	68.2(4)
C(14)–C(15)–C(16)	119.94(4)	C(13)–C(14)–C(15)	127.2(2)	C(13)–C(14)–C(15)	127.0(9)

associated with the $[BPh_4]^-$ anion do not change in any of the four Cu^I complexes and are the same as in $Na[BPh_4]$, indicating an absence of interaction between the ions. The downfield shift of approximately 0.5 ppm in the proton resonances of the PMDETA ligand upon coordination to Cu^I is typical of nitrogen based ligands complexing with a Cu^I center [33,62–64]. Furthermore, when coordination of the C=C double bond to Cu^I is relatively strong, π-back-donation from Cu^I to the olefin bond can be expected to shift the proton signals of the complexing PMDETA ligand further downfield. This effect is most pronounced in the case of **1** where the complexing monomer has strong electron withdrawing groups and π-back-donation from Cu^I is the strongest of complexes **1**–**4** (as evident by the extent of the upfield shift in C=C proton signals which will be further discussed). Relative to $[Cu^I(PMDETA)][BPh_4]$, the PMDETA proton resonances of **1** are further shifted downfield approximately 0.1 ppm (Fig. 4).

The upfield shift of the C=C proton resonances of the monomer upon coordination indicates π-back-donation where the olefin occupies one coordination site around the Cu^I center [11,12,65]. Because the complexes undergo fast monomer exchange on the NMR time scale at room temperature at the given concentration of dissolved complex (0.02 M), the average signal of the free and coordinated C=C protons is observed. The proton spectra were thus taken at sufficiently low temperatures where distinct signals for the free and coordinated monomers could be seen. Table 2 shows the change in chemical shift of the C=C protons for complexes **1**–**4**. The shielding effect is most pronounced in the case of coordinated unsaturated esters, which indicates that the contribution from π-back-bonding in **1** and **4** is stronger than in **2**, which in turn is more pronounced than in **3**. This result is expected since the $COOCH_3$ group is more electron withdrawing than the Ph group in styrene and the alkyl chain in 1-octene. Thus, the contribution from π-back bonding increases in **1** and **4** because the electron density around the double bond is lower. Basicity of the nitrogen based ligands is another factor that can effect the relative contribution from π-back-bonding [5,6]. The vinyl protons of **2** (designated in Table 2 as H_A, H_B, and H_C) shift upfield approximately 1.11, 0.68, and 0.96 ppm relative to free styrene.

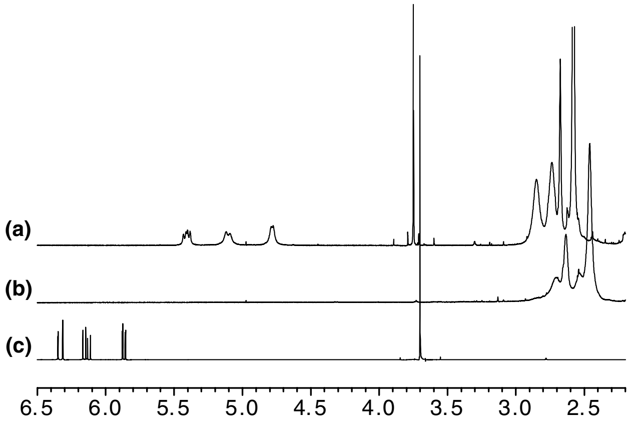
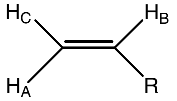


Fig. 4. Comparison of 500 MHz ^1H NMR spectra at 30 °C of 0.02 M **1** (a), 0.02 M $[Cu^I(PMDETA)][BPh_4]$ (b), and MA (c).

Table 2
Chemical shifts (300 MHz, $(CD_3)_2CO$) of vinyl protons in coordinated monomers



Complex	δH_A ($\Delta\delta H_A$)[a]	δH_B ($\Delta\delta H_B$)	δH_C ($\Delta\delta H_C$)
1[b]	4.59 (1.76)	5.09 (1.09)	4.32 (1.61)
2[b]	4.78 (1.11)	6.07 (0.68)	4.28 (0.96)
3[b]	4.10 (0.87)	5.10 (0.67)	4.15 (0.74)
4[c]	4.52 (1.52)		4.40 (1.30)

[a] $\Delta\delta H_A = \delta H_A$ (free MA) – δH_A (observed), ppm.
[b] –60 °C.
[c] –80 °C.

Comparatively, the vinyl protons of the $[Cu^I(2,2'\text{-bipyridine})(\pi\text{-}CH_2CH(C_6H_5)][ClO_4]$ complex [66] are less shielded and the upfield shift of 0.16, 0.03, and 0.19 ppm is less pronounced. Explained in terms of ligand basicity, the PMDETA ligand, being more basic than 2,2'-bipyridine, increases the electron density around Cu^I which results in a higher contribution from π-back bonding and thus stronger shielding.

The presence of π-back bonding in complexes **1**–**4** is further demonstrated by unequal shielding of the vinyl protons in the coordinated monomers. In the single crystal X-ray structures of **1**–**3**, the C_α was 0.046, 0.056, and 0.066 Å, respectively, further away from the Cu^I coordination sphere than was the C_β. Because π-back-donation will have a stronger influence on the chemical shifts of the protons closer to Cu^I, the shielding effect is expected and observed to be the weakest in all the complexes (Table 2) at the C_α ($\Delta\delta H_B(MA) = 1.09$, $\Delta\delta H_B(Sty) = 0.68$, $\Delta\delta H_B(Oct) = 0.67$). This unequal shielding of vinyl protons was also observed in the aforementioned $[Cu^I(2,2'\text{-bipyridine})(\pi\text{-}CH_2CH(C_6H_5))][ClO_4]$ [66] complex.

2.3. FT-IR spectroscopy

The coordinated C=C bonds in complexes **1**–**4** were further examined by IR spectroscopy. The C=C stretching frequency of Sty decreases from 1630 cm^{-1} to 1550 cm^{-1} ($\Delta\nu(C{=}C) = -80\ cm^{-1}$) upon coordination, and that of Oct decreases from 1642 cm^{-1} to 1533 cm^{-1} ($\Delta\nu(C{=}C) = -109\ cm^{-1}$). As indicated in the literature, both σ-donation from the monomer and π-back bonding from the metal (the latter which results in the occupation of the π^* orbitals of the coordinated monomer) weaken the C=C bond and decrease its stretching frequency [33,65,67]. This decrease in frequency is a result of the π-bond formation between vinyl monomer and the Cu^I center leading to a decrease in the double bond character of the coordinated C=C [68] and has been observed previously in Cu^I olefin complexes [69].

The complexation of MA in **1** results in a decrease in C=C IR stretching frequencies from 1634 cm^{-1} to 1524 cm^{-1} ($\Delta\nu(C{=}C) = -110\ cm^{-1}$), and the coordination of MMA in **4** similarly results in a decrease from 1638 cm^{-1} to 1511 cm^{-1} ($\Delta\nu(C{=}C) = -127\ cm^{-1}$). Additionally, the frequencies of vibration of the carbonyl group in both MA and MMA decrease from 1730 cm^{-1} to 1710 cm^{-1} ($\Delta\nu(C{=}O) = -20\ cm^{-1}$) and from 1726 cm^{-1} to 1720 cm^{-1} ($\Delta\nu(C{=}O) = -6\ cm^{-1}$), respectively, upon coordination to Cu^I (Fig. 5). This negative shift can be attributed to the increased electron density at the C=C double bond, due to the back-donation from the metal center. (The NMR analyses of the complexes (vide supra) demonstrate that this back donation indeed predominates over the monomer-to-metal electron density donation.) Similar changes in the carbonyl group frequency upon altering the electron density at a π-electron substituent in conjugated carbonyl compounds have been observed in many instances. The Δν value in m- or p-substituted benzoic acids [70] or methyl benzo-

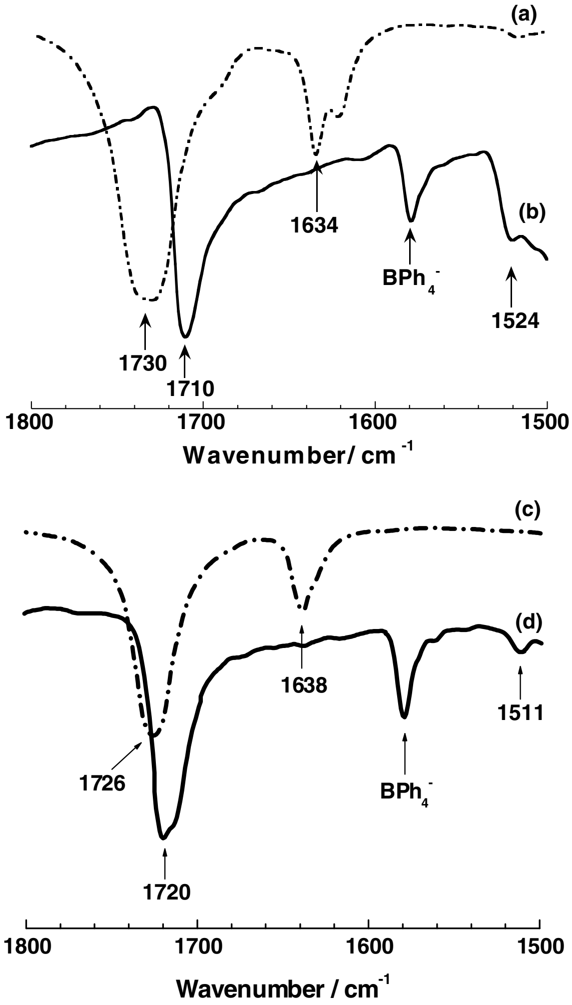


Fig. 5. Comparison of FT-IR spectra of MA (**a**), **1** (nujol) (**b**), MMA (**c**), and **4** (KBr pellet) (**d**).

ates [71] has been correlated to the electron-donating ability of the substituent attached to the benzene ring (Hammet's σ-parameter). The carbonyl group frequencies in β-substituted ethyl acrylates similarly decrease as the electron-releasing ability (either via inductive or resonance effect) of the substituent increases, i.e., in the order CF_3 (1737 cm^{-1}) > H (1727 cm^{-1})>Me (1722 cm^{-1}) > EtO (1711 cm^{-1}) [72].

The thermal and photo-stability of these complexes is currently being investigated. Detailed studies concerning the equilibrium between free and coordinated monomers and the effect of coordination on the reactivity of these monomers in free radical polymerizations and ATRP are currently being carried out.

3. Conclusions

Investigating the nature of the Cu^I-olefin bonding of the four novel Cu^I complexes **1**–**4** was the primary objective in this paper. PMDETA acts as a tridentate ligand, while the pseudotetrahedral coordination geometry around Cu^I is completed by a π-interaction with the C=C double bond of the coordinated olefin. No interactions are observed between the respective counterions. No significant lengthening of the C=C vinyl double bond in MA or Oct upon coordination is observed, while the C=C bond length in Sty increases from 1.325(2) to 1.367(3) Å. Coordination of the monomers to Cu^I results in a decrease in C=C IR stretching frequencies of $\Delta\nu(C{=}C) = -110$, -80, -109, and -127 $cm^{-1}$for complexes **1**–**4**, respectively. The extent to which the coordinated C=C proton resonances for all four complexes are shifted upfield, as compared to the shift in resonances of similar literature compounds, is indicative of significant π-back-bonding.

4. Experimental

4.1. General remarks

All reagents used in this study were obtained from commercial sources and used without further purification. Solvents were distilled and deoxygenated by purging with nitrogen for at least one hour prior to usage. All compounds were prepared under a nitrogen atmosphere using standard Schlenk techniques or in a dry box, unless otherwise noted. All ^1H NMR spectra were obtained in $(CD_3)_2CO$ using Bruker Avance DMX-500 (operating at 500.13 MHz) and Bruker Avance AV-300 (operating at 300.13 MHz) variable temperature spectrometers and chemical shifts are given in ppm relative to the residual acetone solvent peak. IR spectra were obtained with KBr pellets or nujol mulls using an FTIR-NIR Spectrometer (Mattson ATI Affinity 60AR).

4.2. Preparation of Cu^I complexes

4.2.1. Synthesis

Cu^IBr (0.0800 g, 5.58×10^{-4} mol) was added to a deoxygenated methanol (10.0 mL)/acetone (2.0 mL) solution containing (PMDETA) (0.0968 g, 5.58×10^{-4} mol) at room temperature. The addition of Cu^IBr resulted in the formation of a light blue homogeneous solution. One equivalent of monomer was added before the introduction of one equivalent of $NaBPh_4$ (0.1910 g, 5.58×10^{-4} mol). Storage in a −18 °C freezer resulted in the formation of a precipitate which was filtered and washed with 15.0 mL of cold methanol and dried under vacuum for 12 h. Similar procedures were used for the synthesis of all four complexes.

4.2.2. $Cu^I(PMDETA)(\pi\text{-}MA)][BPh_4]$ (**1**)

The Cu^I(PMDETA)Br solution changed color to a light yellow upon the addition of one equivalent of MA (0.0502 g, 5.58×10^{-4} mol). The introduction of $NaBPh_4$ at RT resulted in the formation of a yellow precipitate, which was dissolved by warming the solution to 40 °C. When cooled in an H_2O/ice bath, yellow crystalline needles were obtained in one hour to yield 0.272 g (76.1%) of complex **1**. ^1H NMR (300 MHz, $(CD_3)_2CO$, RT, 0.02 M): δ 7.35 (m, 8 *o*-H, BPh_4^-), 6.93 (broad td, $J_{ortho} = 7.3$ Hz, 8 *m*-H, BPh_4^-), 6.78 (tt, $J_{ortho} = 7.3$ Hz, $J_{meta} = 1.4$ Hz, 4 *p*-H, BPh_4^-), 5.38 (dd, $J_{trans} = 15.4$ Hz, $J_{cis} = 9.2$ Hz, 1H, CHCOOMe), 5.07 (broad dd, overlapping, 1H, CHH_{trans}=CHCOOMe), 4.75 (broad dd, overlapping, 1H, CHH_{cis}=CHCOOMe), 3.75 (s, 3H, $COOCH_3$), 2.90 – 2.30 (br, 23H, PMDETA). FT-IR (nujol): $\nu(C{=}O) = 1712$ cm^{-1}, $\nu(C{=}C_{arom.}, BPh_4^-) = 1579$ cm^{-1}, $\nu(C{=}C) = 1524$ cm^{-1}.

4.2.3. $Cu^I(PMDETA)(\pi\text{-}Sty)][BPh_4]$ (**2**)

The Cu^I(PMDETA)Br solution remained a light homogeneous blue upon the addition of one equivalent of Sty (0.0639 g, 5.58×10^{-4} mol). The addition of $NaBPh_4$ did not form a precipitate, but when the solution was stored in a −18 °C freezer for one hour, white crystalline needles were obtained to yield 0.253 g (68.7%) of complex **2**. ^1H NMR (300 MHz, $(CD_3)_2CO$, RT, 0.02 M): δ 7.55 (broad dt, $J_{ortho} = 7.2$ Hz, 2 *o*-H, CH_2=CHPh), 7.36 (broad td, $J_{ortho} = 7.2$ Hz, 2 *m*-H, CH_2=CHPh), 7.33 (m, 9 H, 1 *p*-H CH_2=CHPh and 8 *o*-H BPh_4^-), 6.93 (broad tt, $J_{ortho} = 7.3$ Hz, 8 *m*-H, BPh_4^-), 6.78 (tt, $J_{ortho} = 7.3$ Hz, $J_{meta} = 1.4$ Hz, 4 *p*-H, BPh_4^-), 6.32 (dd, $J_{trans} = 16.4$ Hz, $J_{cis} = 10.0$ Hz, 1 H, CHPh), 5.18 (broad dd, overlapping, 1H, CHH_{trans}=CH), 4.63 (broad dd, overlapping, 1H, CHH_{cis}=CH), 2.90–2.30 (br, 23H, PMDETA). FT-IR (nujol): $\nu(C{=}C_{arom.}, BPh_4^-) = 1579$ cm^{-1}, $\nu(C{=}C,\ CH_2{=}CH\text{–}) = 1550$ cm^{-1}.

4.2.4. *Cu^{I}(PMDETA)(π-Oct)][BPh_4]* (**3**)

No color change from light homogeneous blue was observed in the Cu^{I}(PMDETA)Br solution upon the addition of one equivalent of Oct (0.0639 g, 5.58×10^{-4} mol). The introduction of $NaBPh_4$ did not form a precipitate, but when the solution was stored in a −18 °C freezer for one hour, off-white crystalline needles were obtained to yield 0.205 g (55.0%) of complex **3**. ^1H NMR (300 MHz, $(CD_3)_2CO$, RT, 0.02 M): δ 7.35 (m, 8 *o*-H, BPh_4^-), 6.93 (broad td, $J_{ortho} = 7.3$ Hz, 8 *m*-H, BPh_4^-), 6.78 (tt, $J_{ortho} = 7.3$ Hz, $J_{meta} = 1.4$ Hz, 4 *p*-H, BPh_4^-), 5.39 (m, 1H, =CH–), 4.48 (broad dd, $J_{trans} = 17.1$ Hz, 1H, CHH_{trans}=CH), 4.47 (broad dd, $J_{cis} = 9.9$ Hz, 1H, CHH_{cis}=CH), δ 3.00–2.40 (br, 23H, PMDETA), δ 2.07 (dd, J = 14.6, 7.3 Hz, 2H, =CH$CH_2$$CH_2$–), 1.43 (m, 2H, =CH$CH_2$$CH_2$), 1.32 (m, 6H, –$(CH_2)_3$$CH_3$), 0.90 (t, $J = 7.0$ Hz, 3H, –CH_3). FT-IR (KBr): ν(C=Carom., BPh_4^-) = 1579 cm^{-1}, ν(C=C) = 1533 cm^{-1}.

4.2.5. *Cu^{I}(PMDETA)(π-MMA)][BPh_4]* (**4**)

The Cu^{I}(PMDETA)Br solution turned a light green upon the addition of one equivalent of MMA (0.0597 g, 5.58×10^{-4} mol). The addition of $NaBPh_4$ did not result in the formation of a precipitate, but when the solution was stored in a −18 °C freezer over night, a light green-yellow solid precipitate was obtained to yield 0.180 g (49.1%) of complex **4**. Crystals suitable for X-ray analysis could not be obtained. ^1H NMR (300 MHz, $(CD_3)_2CO$, RT, 0.02 M): δ 7.35 (m, 8 *o*-H, BPh_4^-), 6.93 (broad td, $J_{ortho} = 7.3$ Hz, 8 *m*-H, BPh_4^-), 6.78 (tt, $J_{ortho} = 7.3$ Hz, $J_{meta} = 1.4$ Hz, 4 *p*-H, BPh_4^-), 5.89 (m, 1H, CHH_{trans}=CMe), 5.57 (m, 1H, CHH_{cis}=CMe), 3.70 (s, 3H, OCH_3), δ 2.80–2.20 (br, 23H, PMDETA), δ 1.90 (dd, J = 1.5, 1.0 Hz, 3H, CH_2=CCH_3). FT-IR (KBr): ν(C=O) = 1720 cm^{-1}, ν(C=Carom., BPh_4^-) = 1579 cm^{-1}, ν(C=C) = 1511 cm^{-1}.

4.3. X-ray crystal structure analysis

The X-ray data were collected at room temperature for **1** and **3** and at 153 K for **2** on a Bruker-AXS SMART diffractometer with an APEX CCD area detector. Graphite-monochromated Mo K_α radiation (71.073 pm) was used for all measurements. The nominal crystal-to-detector distance was 5.00 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied [73]. The cell dimensions were refined with all unique reflections.

Table 3
Crystal data and structure refinement for **1**–**3**

Empirical formula	[$C_{74}H_{96}B_2Cu_2N_6O_4$]	[$C_{41}H_{51}BCuN_3$]	[$C_{41}H_{54}BCuN_3$]
Formula weight	1282.27	660.20	663.22
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*P2(1)/c*	*Pbca*	$P\bar{1}$
Unit cell dimensions			
a (Å)	22.593(2)	17.479(3)	11.0904(12)
b (Å)	9.9506(11)	18.046(3)	11.7655(13)
c (Å)	31.989(4)	22.761(4)	16.7262(19)
α (°)	90	90	80.841(2)
β (°)	100.047(3)	90	89.442(3)
γ (°)	90	90	64.862(2)
Volume ($Å^3$)	7081.1(13)	7180(2)	1946.5(4)
Z	4	8	2
T/K	294(2)	153(2)	298(2)
Calculated density (g cm^{-3})	1.203	1.222	1.132
Absorption coefficient (mm^{-1})	0.651	0.641	0.591
F(000)	2728	2816	710
Crystal size (mm)	0.80 × 0.70 × 0.06	0.36 × 0.28 × 0.10	0.33 × 0.27 × 0.22
Θ range for data collection (°)	1.71–24.72	1.79–28.28	2.47–23.26
Limiting indices	$-21 \leqslant h \leqslant 26$	$-23 \leqslant h \leqslant 23$	$-12 \leqslant h \leqslant 12$
	$-11 \leqslant k \leqslant 11$	$-14 \leqslant k \leqslant 24$	$-13 \leqslant k \leqslant 13$
	$-37 \leqslant l \leqslant 28$	$-30 \leqslant l \leqslant 30$	$-14 \leqslant l \leqslant 18$
Total reflections	36231	48069	9174
Independent reflections	12048 [*R*(int) = 0.0484]	8898 [*R*(int) = 0.0447]	5558 [*R*(int) = 0.0207]
Goodness-of-fit on F^2	1.012	1.023	1.044
R indicies (all data)	0.0903	0.0653	0.0721
Final *R* indices [$I > 2\sigma(I)$]	0.0539	0.0396	0.0581
R_w indicies (all data)	0.1565	0.1097	0.1594
Final R_w indices [$I>2\sigma(I)$]	0.1352	0.0960	0.1490
Largest diff. peak and hole [A^{-3}]	0.725 and −0.537	1.246 and −0.428	0.378 and −0.219

The structure was solved by direct methods (SHELXS97). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom (see Table 3).

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 209614, 246778, and 246779 for complexes **1**–**3**, respectively. Copies of the data can be obtained, free of charge, from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk.).

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