[*N*-Alkyl-(2-pyridyl)methanimine]copper(I) Complexes: Characterisation and Application as Catalysts for Atom-Transfer Polymerisation

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The synthesis and characterisation of a series of novel bis(imine)copper(I) complexes and their use in atom-transfer polymerisation of methyl methacrylate is described. Several *N*-alkyl-(2-pyridyl)methanimines (alkyl = *n*-butyl, isobutyl, *sec*-butyl, *n*-propyl) and *N*-(*n*-propyl)-1-(2-pyridyl)ethanimine as ligands have been fully characterised. Three bis[*N*-alkyl-(2-pyridyl)methanimine]copper(I) complexes, $[Cu\{(C_5H_4N)CH=N(iBu)\}_2][BF_4]$, $[Cu\{(C_5H_4N)C(CH_3)=N(nPr)\}_2][PF_6]$, and $[Cu\{(C_5H_4N)CH=N(sBu)\}_2][BF_4]$ have been structurally characterised; all having a distorted tetrahedral arrangement of co-ordinating nitrogen atoms surrounding the metal centre. All of the catalysts were found to be effective atom-transfer polymerisation catalysts for the polymerisation of MMA in hydrocarbon solution. However, it was discovered that the performance of the catalysts containing *n*-alkyl substituents was superior to those containing branched alkyl substituents. The presence of branching in the alkyl substituent results in a reduction of reaction rate and a corresponding broadening of the polydispersity index.

Introduction

Copper complexes containing chelating bis(imine) ligands are used increasingly as catalysts for a wide range of synthetic organic reactions.[1] Chiral ligands, in particular, are finding use in asymmetric organic catalysis,[2] such ligands being simply prepared from commercially available, and enantiomerically pure, primary amines. Atom-transfer addition, ATA, a technique used to effect organic transformation reactions, utilises transition-metal complexes[3] to promote carbon−carbon bond formation.[4] Transition-metal complexes able to function as halogen carriers with an available $n+1$ oxidation state, e.g. Cu^{I}/Cu^{II} are typical catalysts for ATA.

Recently, this chemistry has been extended and modified for use in polymerisation reactions. The groups of Matyjaszewski[5a][5b][5c][5d] and Sawamoto,[5e][5f][5g][5h] working independently from each other have reported the use of transition-metal-mediated polymerisation derived from the ATA reaction. It is believed that the mechanism of atom-transfer polymerisation depends upon the formation of a favourable equilibrium, shown in Scheme 1, where: R_n-X represents both the initiator and dormant polymer chain, X and X′ halogen atoms, L_m an unspecified, *m*, number of donor ligands and $R^{\bullet}$ represents both the initiating species and the propagating polymeric radical. The position of the equilibrium is pivotal to the control of the polymerisation reaction; easily oxidised complexes, i.e. catalysts having a too stable $n+1$ oxidation state, cause a movement to the right of the equilibria, ultimately resulting in a relatively high concentration of free radicals. At high free-radical concentration termination occurs by radical−radical combination and/or disproportionation, which results in a lack of control over the polymerisation and results in polymer having an increased polydispersity index, PDI, and ultimately loss of the linear relationship between the number-average molecular mass, M_n, and the ratio of monomer to initiator which is observed for *living polymerisation*. Conversely, if the metal complex is unable to increase its oxidation number then the equilibria will lie far to the left and the rate of polymerisation reaction will be too slow to lead to useful products on a sensible time-scale. Propagation of the polymerisation takes place from, an as yet, undetermined active centre. The active centre is either a carbon-centred free radical or a metal-complexed radical, or insertion at the metal centre takes place. At present a free-radical process is preferred by most authors but the exact mechanism is proving very difficult to determine unequivocally.

Scheme 1

$$R_n-X + [L_mCu(I)X'] \rightleftharpoons [R_n\ldots X\ldots CuL_mX'] \rightleftharpoons R_n^{\bullet} + [XCuL_mX']$$

The ligand choice is considered crucial in controlling the position of the equilibrium either by acting as electron donors, or acceptors, to the metal centre. In systems where copper(I) halides are used the ligand also serves to solubilise the particularly insoluble copper salt, and perhaps more importantly, the low-lying LUMO π* orbital, present in the conjugated π system (N=C-C=N) of the ligand, is able to accept electron density from the metal centre, which is

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thought to be central to the action of these particular atom-transfer polymerisation catalysts.

Recently, we have reported on the use of a series of *N*-alkyl-(2-pyridyl)methanimine ligands which, when complexed with copper halides, give rise to highly effective atom-transfer polymerisation catalysts.[6] We have been interested in examining the structure of atom-transfer catalysts with a view to further understanding the mechanism of the reaction. Ultimately, we believe this to help in the optimisation of the ligands/catalysts for each monomer system thus giving greater control over this rapidly emerging polymerisation chemistry. The mode of co-ordination of this type of Schiff base ligand to metal centres in both the solution and solid state has been reported to vary depending upon many variables. Indeed in the case of copper(I) complexes, a simple change in the counter-ion can dramatically alter the nature of the predominant species[7]. Thus, structural determinations may play an important role in elucidating the mechanism of atom-transfer polymerisation. The results presented in this paper show how increasing the steric hindrance in the alkyl group of the imine ligand affects the kinetics of the polymerisation and the dramatic effects these apparently small changes in ligand have on the molecular mass control and molar mass distribution of the resulting poly(methyl methacrylate). Three of the catalysts used in this work have been fully characterised by single-crystal X-ray diffraction. Similar "*living*" polymerisation systems mediated by transition-metal complexes have been reported by a range of other research groups[8].

Results and Discussion

The *N*-alkyl-(2-pyridyl)methanimine ligands, **L1**−**L5** (see Scheme 2), were prepared from the condensation of 2-pyridinecarboxaldehyde (or 2-acetylpyridine in the case of **L5**) with the respective primary amine. Figure 1(a) shows the ^{1}H-NMR spectrum of **L1**, and Figure 1(b) shows the spectrum of the complex between **L1** and CuBr, **C1** (see Scheme 3)[9]. The assignments were made using NOE difference experiments by irradiating at H^6 so as to determine H^4 long−range COSY and ^{1}H-^{13}C heteronuclear correlation. The remaining ring protons were assigned by further decoupling experiments. In solution the ligand can exist in the *trans* conformation; however, on complexation to copper(I) we observe changes in the spectrum associated with the ligand adopting a *cis* conformation. The signal of the imine proton H^6 shifts approximately 0.6 ppm downfield on complexation. Figures 2(a) and 2(b) show the ^{13}C{^{1}H}-NMR spectrum of **L1** and **C1**, respectively. The assignments were made using heteronuclear shift-correlated 2D-NMR experiments. The pair C^5/C^1 changes its relative position whilst C^6 remains at highest field. These proton and carbon ring assignments are applicable to all ligands used in this study.

Scheme 2

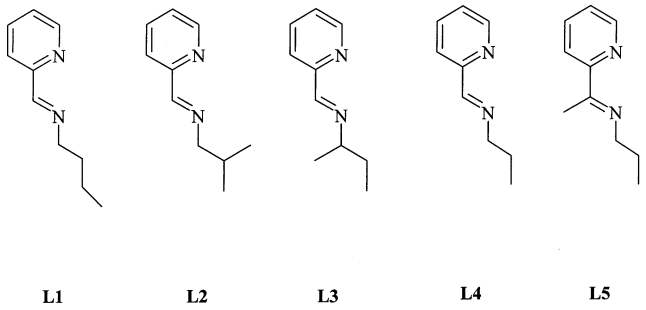
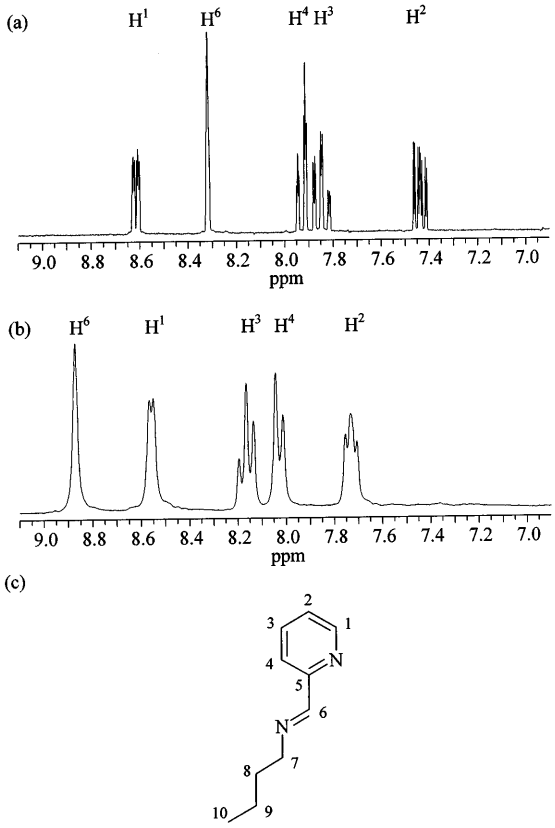
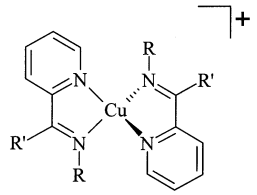


Figure 1. ^{1}H-NMR spectrum of (a) the free ligand **L1** and (b) the complex **C1** in [D_6]DMSO; (c) peak assignments



Scheme 3

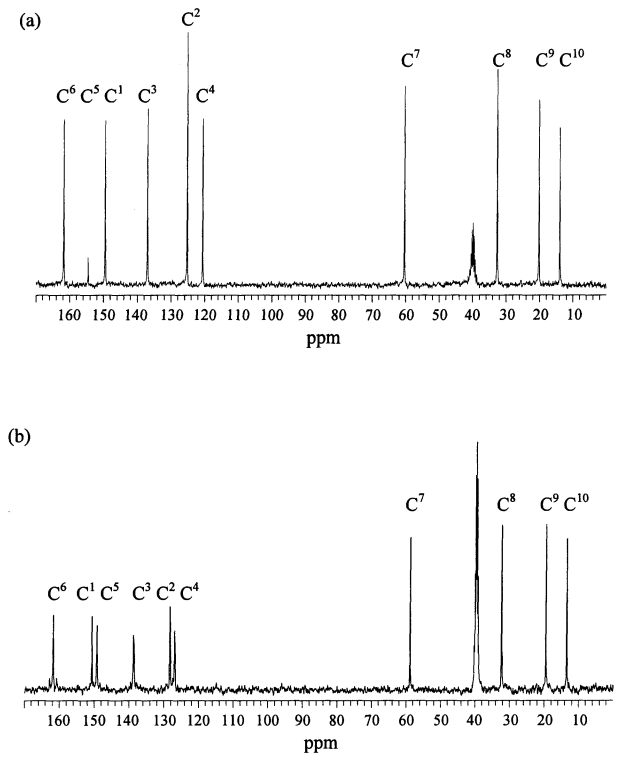


C1: R = *n*Bu, R′ = H; **C2**: *i*Bu, R′ = H; **C3**: R = *s*Bu, R′ = H; **C4**: R = *i*Pr, R′ = H; **C5**: R = *n*Pr; R′ = Me.

Polymerisation of Methyl Methacrylate Using C1 to C5 as Atom-Transfer Polymerisation Catalysts

Methyl methacrylate was polymerised in xylene solution at 90°C using ethyl 2-bromoisobutyrate as initiator in the

Figure 2. $^{13}C\{^1H\}$-NMR spectrum of (a) the free ligand **L1** and (b) the complex **C1** in [D_6]DMSO; the assignments were made using heteronuclear shift-correlated 2D-NMR experiments; for peak assignments see Figure 1(c)



The effectiveness of the catalysts **C1**−**C5** for promoting controlled atom-transfer polymerisation was determined in three ways: (1) the relationship between the number-average molecular weight (M_n) and conversion to polymer. Living polymerisation processes lead to a linear increase in M_n with conversion.[6b] (2) The polydispersity index, PDI, of the polymer, free-radical polymerisation of methyl methacrylate has a PDI larger than 1.5. (3) The appearance of a first-order rate plot. For a living polymerisation a plot of $\ln [M]_0/[M]$ against time gives a linear plot with the gradient equal to the pseudo first-order rate coefficient, k^{app}, which gives an indication of the rate of reaction. k^{app} is defined by Equation 1, where [M] is the monomer concentration, $[M]_0$ is the initial monomer concentration, k_p is the propagation rate coefficient, $[R^\bullet]$ is the concentration of active species, and t is time.

$$\ln [M]_0/[M] = k_p[R^\bullet]t = k^{app}t \quad (1)$$

Figure 3 shows the dependence of the number-average molecular weight (M_n) on polymer conversion for the catalysts **C1**−**C5**. In all cases, M_n increases approximately linearly with conversion, as is expected for a *living* polymerisation. The actual values of M_n are slightly higher than the theoretical line, which suggests that the initiator efficiency is less than unity i.e. the initiator is involved in secondary, as yet undetermined reactions such as coupling of carbon-centred radicals in the initial stages of the reaction. The presence of **C1**−**C5** catalysts (see Scheme 3). The catalysts were prepared in situ by the addition of ligands **L1**−**L5**, respectively, to CuBr in the xylene reaction solution. Polymer conversion and molecular weight data are listed in Table 1.

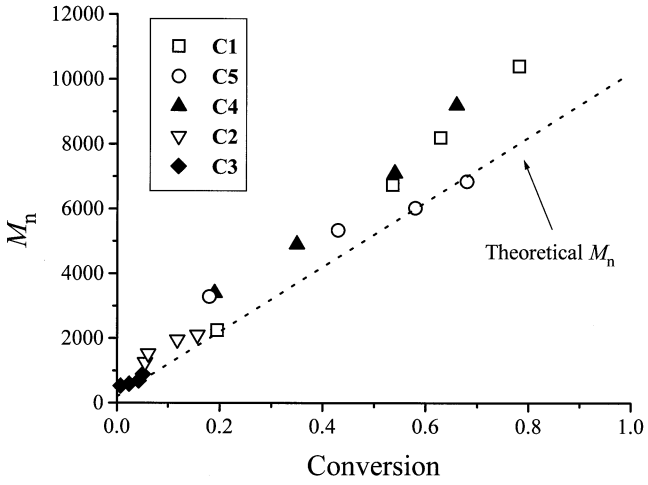
Table 1. Conversion and molecular-weight data for polymerisations using **C1**−**C5**

Catalyst	Time [min]	Conversion	M_n[a]	M_w[b]	PDI[c]	$M_{n,theo}$[d]	Initiator[e] efficiency	k^{app} [s^{-1}][f]
C1	60	0.195	2250	5000	2.22	1950	0.87	$1.00 \cdot 10^{-4}$
	120	0.536	6740	10000	1.49	5370	0.80	
	180	0.629	8200	12300	1.5	6300	0.77	
	240	0.782	10400	13800	1.33	7830	0.75	
C2	60	0.055	1250	1950	1.56	550	0.44	$1.15 \cdot 10^{-5}$
	120	0.061	1520	2450	1.61	610	0.40	
	180	0.118	1950	2930	1.5	1180	0.60	
	240	0.157	2100	3300	1.57	1570	0.75	
C3	60	0.007	530	689	1.3	70	0.13	$3.67 \cdot 10^{-6}$
	120	0.024	590	714	1.21	240	0.41	
	180	0.043	690	876	1.27	430	0.62	
	240	0.051	890	1230	1.38	510	0.57	
C4	60	0.19	3390	4510	1.33	1900	0.56	$7.15 \cdot 10^{-5}$
	120	0.35	4900	6320	1.29	3500	0.71	
	180	0.54	7100	8870	1.25	5400	0.76	
	240	0.66	9200	10900	1.19	6610	0.72	
C5	60	0.18	3290	4570	1.39	1800	0.55	$7.85 \cdot 10^{-5}$
	120	0.43	5340	7580	1.42	4300	0.81	
	180	0.58	6030	9280	1.54	5810	0.96	
	240	0.68	6850	10900	1.59	6810	0.99	

[a] Number-average molecular weight.− [b] Weight-average molecular weight. − [c] Polydispersity index = M_w/M_n. − [d] $M_{n,theo}$ = Conversion · [Monomer]/[Initiator]. − [e] Initiator efficiency = $M_{n,theo}/M_n$. − [f] Pseudo first-order rate coefficient determined from the slope of the line of best fit in Figure 4.

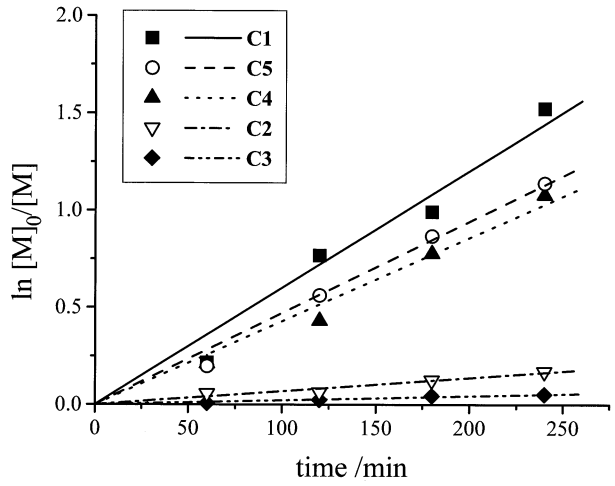
PDIs (Table 1) are narrower for polymer produced using catalysts **C1**, **C3**, and **C4**, than catalysts **C2** and **C5**, which are quite broad for a *living* polymerisation (> 1.5). In general the PDI becomes narrower during the course of the reaction.

Figure 3. Dependence of the number-average molecular weight, M_n, on conversion for polymerisations using catalysts **C1**−**C5**



The first-order rate plots are shown in Figure 4. The lines through the data represent the best fit and correspond to the pseudo first-order rate coefficient, k^{app}. These plots are characteristic of *living* polymerisation;[6b] in all cases the plots are linear, indicating that the number of active species is constant and effects from termination of growing polymer chains by combination/disproportionation or chain transfer are not significant. It is immediately obvious, from Figure 4 and Table 1, that the catalysts **C2** and **C3** give a significantly lower rate of polymerisation (approximately one order of magnitude) than when **C1**, **C4**, and **C5** are used as catalysts . Thus, the catalysts using branched substituents at either the α or β positions in the ligand give significantly lower rates of polymerisation.

Figure 4. First-order log plots for polymerisations using catalysts **C1**−**C5**



Overall, **C1** and **C4** show the best performance as atom-transfer polymerisation catalysts, giving both narrow PDI polymer and acceptable rates of reaction. Catalyst **C3** gives reasonable PDI but has a very low rate of reaction, **C5** gives good rate but broad PDI and **C2** is the least effective catalyst in this series, yielding both a low rate of reaction and broad PDI.

Single-Crystal X-ray Structural Study of Copper Complexes with L2, L3, and L5

X-ray structural studies were carried out for the compounds $Cu[BF_4]\cdot(\mathbf{L2})_2$, $Cu[BF_4]\cdot(\mathbf{L3})_2$, and $Cu[PF_6]\cdot(\mathbf{L5})_2$ which were isolated as crystalline salts from slowly cooled (5°C) solutions in methanol. Compounds formed from the reaction of $Cu(CH_3CN)_4[BF_4]$ with the ligands **L1** and **L4**, however, could not be isolated as crystals of suitable quality for X-ray analysis.

The compounds $Cu[BF_4]\cdot(\mathbf{L2})_2$, $Cu[BF_4]\cdot(\mathbf{L3})_2$, and $Cu[PF_6]\cdot(\mathbf{L5})_2$ all have the same basic distorted tetrahedral arrangement of co-ordinating nitrogen atoms which sur-

Figure 5. The crystal structure of $Cu[BF_4]\cdot(\mathbf{L2})_2$ (BF_4 counter ion not shown for clarity)

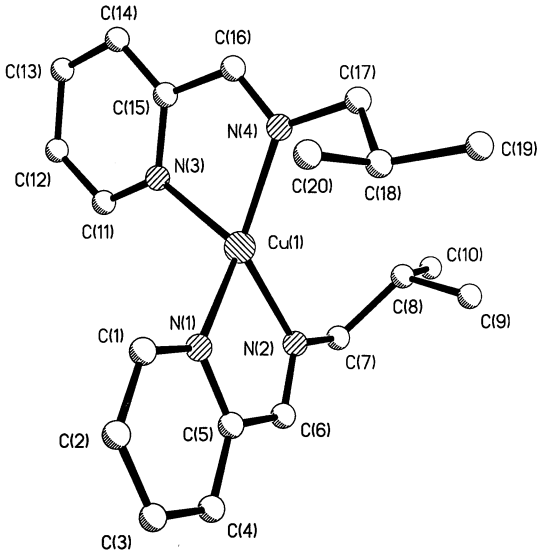


Figure 6. The crystal structure of $Cu[BF_4]\cdot(\mathbf{L3})_2$ (BF_4 counter ion not shown for clarity)

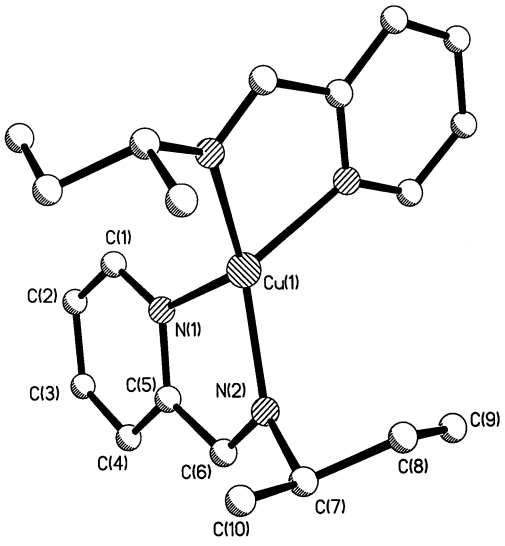
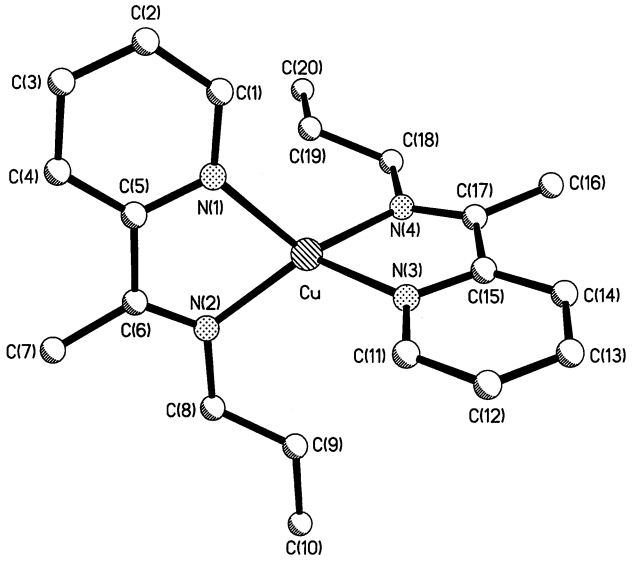


Figure 7. The crystal structure of $Cu[PF_6]\cdot(\mathbf{L5})_2$ (PF_6 counter ion not shown for clarity)



round the metal centre. Table 2 compares angles and average bond lengths to other similar published structures. The interligand dihedral angle between the mean planes defined by the central copper ion and each pair of chelating nitrogen atoms is 86.8° for $Cu[BF_4]\cdot(\mathbf{L2})_2$, 86.5° for $Cu[BF_4]\cdot(\mathbf{L3})_2$, and 85.3° for $Cu[PF_6]\cdot(\mathbf{L5})_2$ these values fall between 68° for the tetramethylbipyridine complex (entry 8) and 89.7° for the *N*-(α-methylbenzyl)-(2-pyridyl)methanimine complex (entry 4). The Cu−N bond lengths for $Cu[BF_4]\cdot(\mathbf{L2})_2$ are in the range of Cu(1)−N(1) = 2.080(3) Å, Cu(1)−N(2) = 2.005(2) Å, Cu(1)−N(3) = 2.047(3) Å, and Cu(1)−N(4) = 2.013(3) Å, for $Cu[BF_4]\cdot(\mathbf{L3})_2$ the Cu−N bond lengths are similar, with Cu(1)−N(1) = 2.092(2) Å and Cu(1)−N(2) = 2.008(2) Å. The Cu−N distances for $Cu[PF_6]\cdot(\mathbf{L5})_2$, tend to be, in most cases, somewhat shorter than those seen for $Cu[BF_4]\cdot(\mathbf{L2})_2$ and $Cu[BF_4]\cdot(\mathbf{L3})_2$, with Cu−N(1) = 2.028(2) Å, Cu−N(2) = 2.011(3) Å, Cu−N(3) = 2.034(3) Å, and Cu−N(4) = 2.001(2) Å. From Table 2 it can be seen that the average Cu−N bond lengths for $Cu[BF_4]\cdot(\mathbf{L2})_2$ and $Cu[BF_4]\cdot(\mathbf{L3})_2$ lie within the values measured for other $[CuL_2]^+$-type complexes, the average Cu−N distance for $Cu[PF_6]\cdot(\mathbf{L5})_2$ falling slightly below the other measured values. The N−Cu−N angles for $Cu[BF_4]\cdot(\mathbf{L2})_2$, $Cu[BF_4]\cdot(\mathbf{L3})_2$, and $Cu[PF_6]\cdot(\mathbf{L5})_2$ are similar and differ by only 0.37° at most, these values being comfortably within the estimated standard deviations.

Conclusion

A series of *N*-alkyl-(2-pyridyl)methanimines have been fully characterised. The bis[*N*-alkyl-(2-pyridyl)methanimine]copper(I) complexes characterised exhibit a distorted tetrahedral arrangement of co-ordinating nitrogen atoms surrounding the metal centre in the solid state. All of the catalysts tested were found to polymerise MMA effectively in hydrocarbon solution by an atom-transfer polymerisation process. Catalysts which contain *n*-alkyl substituents are more efficacious than those containing branched alkyl substituents in the imine group. The presence of branching in the alkyl substituent results in a loss of control over the polymerisation manifested by a slowing of the reaction rate and a broadening of the polydispersity index. The cause of these efffects of branching at the α-carbon atom of the imine on the final polymer properties is currently not known and is under further investigation in our laboratory.

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Table 2. Comparison of average bond-length and -angle data for $[Cu^I(L)_2]^+$ complexes

Ligand	Counter ion	C−$N_{acyclic}$	C−N_{cyclic}	C−C bond length [Å]	Cu−N	N−Cu−N angle [°]	Dihedral angle [°]	Ref.
L2	BF_4^-	1.277(4)	1.357(4)	1.457(5)	2.009	81.20(10)	86.8	This
		1.278(4)	1.344(4)	1.460(5)	2.064	80.97(10)		work
L3	BF_4^-	1.273(3)	1.654(3)	1.463(3)	2.08(2)	81.12(8)	86.2	This
					2.092(2)			work
L5	PF_6^-	1.279(4)	1.351(4)	1.479(5)	2.006	80.86(10)	85.3	This
		1.280(4)	1.353(4)	1.489(4)	2.031	80.64(11)		work
N-(α-methylbenzyl)-(2-pyridyl)methanimine[a][b]	BF_4^-	1.282	1.341	1.457	2.040	81.8	89.7	[10]
		1.273	1.370	1.456	2.030	82.3	85.1	
N-(*tert*-Butyl)-(2-pyridyl)methanimine	BF_4^-	1.270(4)	1.349(4)	1.467(5)	2.035	81.89(10)	81.9	[11]
1,4-Di-(*tert*-butyl)-1,4-diaza-1,3-butadiene	Br^-	1.263(4)	1.352(4)	1.470(4)	2.035	81.84(10)		
2,2′-Bipyridine	ClO_4^-	1.268(7)	1.290(7) [c]	1.453(8)	2.025(4)	82.2(2)	89.5	[11]
4,4′,6,6′-Tetramethyl-2,2′-bipyridine[b]	Cl^-	1.325(14)	1.385(15)	1.440(15)	2.021(11)	81.5(4)	75.2	[12]
1,10-Phenanthroline[b]	$CuBr_2^-$	1.347	1.360	1.488	2.040	81.35	68	[13]
2,9-Dimethyl-1,10-phenanthroline[b]	NO_3^-	1.366	1.352	1.428	2.039	82.2	76.8	[14]
		1.360	1.361	1.450	2.063	83.4	85.7	[15]

[a] There are two molecules in the asymmetric unit. − [b] Lengths are averaged for cyclic C−N (no estimated standard deviations for averaged data). − [c] Second acyclic bond.

Experimental Section

General Remarks: The reagents 2-pyridinecarboxaldehyde (Avocado, 99%), 2-acetylpyridine (Avocado, 98%), *n*-butylamine (Acros, 99.5%), isobutylamine (Avocado, 99%), *sec*-butylamine (Avocado, 99%), *n*-propylamine (Avocado, 99%), ethyl 2-bromoisobutyrate (Aldrich, 98%), xylene (Fisons, 99.8%), diethyl ether (BDH, 98%), and magnesium sulfate (Philip Harris) were used as received. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff[10]. Methyl methacrylate (Aldrich, 99%) was purified by passing through a column of activated basic alumina to remove the inhibitor 4-methoxy phenol. All manipulations were performed using standard Schlenk line and syringe techniques under nitrogen.

NMR spectra were recorded using a Bruker WH 400 spectrometer. X-ray crystallographic data was collected with a Siemens R3m diffractometer.

Polymer conversions were determined by gravimetry and molecular-weight distributions were measured using size-exclusion chromatography (SEC), with a system equipped with a guard column, one 30-cm mixed E column (Polymer Laboratories) and a differential refractive-index detector, using tetrahydrofuran at 1 ml min^{-1} as the eluent. Poly(methyl methacrylate) standards in the range ($6 \cdot 10^4$ to 200 g mol^{-1}, Polymer laboratories) were used to calibrate the SEC.

N-Alkyl-(2-pyridyl)methanimine Ligands **L1**−**L4**: A solution of 2-pyridinecarboxaldehyde (15 g, 0.140 mol) in 100 ml of diethyl ether was placed into a 250-ml flask under dry nitrogen together with 2−3 g of anhydrous $MgSO_4$. The appropriate amount of amine was added dropwise to this solution. (**L1** *n*$BuNH_2$, **L2** *i*$BuNH_2$, **L3** *s*$BuNH_2$: 10.22 g, 0.140 mol; **L4** *n*$PrNH_2$: 8.26 g, 0.140 mol), with gentle cooling of the flask with iced water. After the addition of amine was complete, the reaction was stirred for ca. 3 h, after which time the solvent was removed by rotary evaporation and the residual oil further purified by vacuum distillation (**L1**, **L2**, **L3**, **L4**). The products were isolated as pale yellow liquids, yields were typically 94%.

L1: B.p. 105−106°C at 1.2 Torr. − IR: $\tilde{\nu}$ = 1649 cm^{-1} (C=N). − ^{1}H NMR (250 MHz, 298 K, $CDCl_3$): δ = 8.50 (d, *J* = 4.92 Hz, 1 H), 8.26 (s, 1 H), 7.86 (d, *J* = 7.72 Hz, 1H), 7.57 (t, *J* = 8.08 Hz, 1 H), 7.14 (m, *J* = 6.32 Hz, 1 H), 3.17 (t, *J* = 7.00 Hz, 2 H), 1.50 (quint, *J* = 7.00 Hz, 2 H), 1.13 (sext, *J* = 7.36 Hz, 2 H), 0.72 (t, *J* = 7.36 Hz, 3 H). −^{13}C{^{1}H} NMR (250 MHz, 298 K, [D_6]DMSO): δ = 161.57, 154.62, 149.29, 136.39, 124.47, 121.07, 61.15, 32.70, 20.34, 13.79. − MS (+EI); *m/z*: 163 [M^+].

L2: B.p. 179°C at 5.0 Torr. − IR: $\tilde{\nu}$ = 1636 cm^{-1} (C=N). − ^{1}H NMR (250 MHz, 298 K $CDCl_3$): δ = 8.53 (d, *J* = 4.53 Hz, 1 H), 8.25 (s, 1 H), 7.90 (d, *J* = 7.72 Hz, 1 H), 7.61 (t, *J* = 7.68 Hz, 1 H), 7.18 (m, *J* = 4.92 Hz, 1 H), 3.39 (d, *J* = 6.32 Hz, 2 H), 1.95 (sept, *J* = 6.68 Hz, 1 H), 0.87 (d, *J* = 6.68 Hz, 6 H). − ^{13}C{^{1}H} NMR (250 MHz, 298 K, $CDCl_3$): δ = 159.51, 154.56, 149.13, 136.22, 124.28, 121.13, 67.84, 30.30, 21.95. − MS (+EI): *m/z*: 163 [M^+].

L3: B.p. 74°C at 5.0 Torr. − IR: $\tilde{\nu}$ = 1630 cm^{-1} (C=N). − ^{1}H NMR (250 MHz, 298 K, $CDCl_3$), δ = 8.50 (d, *J* = 4.56 Hz, 1 H), 8.24 (s, 1 H), 7.86 (d, *J* = 7.68 Hz, 1 H), 7.57 (t, *J* = 7.36 Hz, 1H), 7.14 (dd, *J* = 4.92, 6.32 Hz, 1 H), 3.17 (sext, *J* = 6.32 Hz, 1 H), 1.50 (m, *J* = 7.72 Hz, 2H), 1.13 (d, *J* = 6.28 Hz, 3 H), 0.72 (t, *J* = 7.36 Hz, 3 H). −^{13}C{^{1}H} NMR (250 MHz, 298 K, $CDCl_3$): δ = 161.60, 154.49, 149.16, 136.29, 124.38, 120.96, 69.36, 29.27, 22.50.10.90. − MS (+EI); *m/z*: 163 [M^+].

L4: B.p. 50° at 0.2 Torr. − IR: $\tilde{\nu}$ = 1650 cm^{-1} (C=N). − ^{1}H NMR (250 MHz, 298 K, $CDCl_3$): δ = 8.44 (d, *J* = 4.24 Hz, 1 H), 8.20 (s, 1 H), 7.80 (d, *J* = 7.72 Hz, 1 H), 7.57 (t, *J* = 7.72 Hz, 1 H), 7.10 (t, *J* = 4.92 Hz, 1 H), 3.45 (t, *J* = 7.00 Hz, 2 H), 1.56 (sext, *J* = 7.00 Hz, 2 H), 0.77 (t, *J* = 7.36 Hz, 3 H). − ^{13}C{^{1}H} NMR (250 MHz, 298 K, $CDCl_3$): δ = 161.53, 154.50, 149.21, 136.29, 124.37, 120.97, 63.11, 23.58,11.65. − MS (+EI); *m/z*: 149 [M^+ + 1], 133 [M^+ − Me].

N-(n-Propyl)-1-(2-pyridyl)ethanimine (**L5**): A solution of 2-acetylpyridine (10 g, 0.0825 mol) in 60 ml of diethyl ether was placed in a 250-ml flask under dry nitrogen, together with 2−3 g of $MgSO_4$. The flask was cooled gently in iced water whilst *n*-propylamine (8 ml, 0.0973 mol) was added dropwise with stirring. After addition of the amine, the reaction was allowed to warm up to room temperature and the solution stirred overnight. After this time, the solvent was removed by rotary evaporation and the residual oil purified further by vacuum distillation. − B.p. 60°C at 0.4 Torr. − IR: $\tilde{\nu}$ = 1639 cm^{-1} (C=N). − ^{1}H NMR (250 MHz, 298 K, [D_6]DMSO): δ = 8.64 (d, *J* = 4.88 Hz, 1 H), 8.00 (d, *J* = 4.88 Hz, 1 H), 7.59 (m, *J* = 8.28, 7.33 Hz, 1 H), 7.16 (m, *J* = 7.33, 8.23 Hz, 1 H), 3.40 (t, *J* = 7.03 Hz, 2 H), 2.27 (s, 2 H), 1.70 (m, *J* = 7.33, 7.03 Hz, 2 H), 0.94 (t, *J* = 7.33 Hz, 2 H). − ^{13}C{^{1}H} NMR (250 MHz, 298°C, $CDCl_3$): δ = 166.51, 158.32, 148.48, 136.68, 124.28, 121.10, 54.58, 24.39,12.52, 14.21. − MS (+EI); *m/z*: 163 [M^+ + 1], 106 [M^+ − Et].

Bis[N-(isobutyl)-(2-pyridyl)methanimine]copper(I) Tetrafluoroborate ($Cu[BF_4]\cdot$(**L2**)$_2$; [Cu{(C_5H_4N)CH=N(*i*Bu)}$_2$][BF_4]): To a slurry of [$Cu(CH_3CN)_4$][BF_4][9b] (1.0 g, 3.22 mmol) in degassed methanol (30 ml) was added **L2** (1.008 g, 6.22 mmol) under nitrogen. The solution was stirred at room temperature overnight, filtered, and concentrated to ca. 10 ml. Slow cooling to 5°C resulted in the formation of red crystalline $Cu[BF_4]\cdot$(**L2**)$_2$ (75%). − IR: $\tilde{\nu}$ = 1622 cm^{-1} [ν(C=N)]. − ^{1}H NMR (250 MHz, 298 K $CDCl_3$): δ = 8.63 (s, 1 H), 8.39 (d, 1 H), 8.05 (t, 1 H), 7.92 (d, 1 H), 7.61 (m, 1 H), 3.63 (d, 2 H), 2.00 (m, 1 H), 0.87 (d, 6 H). − ^{13}C{^{1}H} NMR (250 MHz, 298 K, $CDCl_3$) δ = 161.32, 150.66, 149.28, 138.93, 128.71, 127.42, 67.62, 30.20, 20.28. − MS (+EI) *m/z* : 387 [M^+], 225 [M^+ − **L2**].

Bis[N-sec-butyl)-(2-pyridyl)methanimine]copper(I) Tetrafluoroborate ($Cu[BF_4]\cdot$(**L3**)$_2$; [Cu{(C_5H_4N)CH=N(*s*Bu)}$_2$][BF_4]): An identical procedure to that used for $Cu[BF_4]\cdot$(**L2**)$_2$, using **L3**, was followed yielding red crystals of $Cu[BF_4]\cdot$(**L3**)$_2$ (70%). − IR: $\tilde{\nu}$ = 1620 cm^{-1} [ν(C=N)]. − ^{1}H NMR (250 MHz, 298 K, $CDCl_3$): δ = 8.72 (s, 1 H), 8.30 (d, 1 H), 7.96 (m, 2 H), 7.54 (m, 1 H), 3.71 (m, 1 H), 1.44 (br., 2 H), 1.13 (br., 3 H), 0.77 (t, 3 H). −^{13}C{^{1}H} NMR (250 MHz, 298 K, $CDCl_3$): δ = 159.68, 150.67, 148.39, 138.41, 127.79, 126.91, 66.65, 30.81, 22.50, 10.83. − MS (+EI); *m/z*: 387 [M^+], 225 [M^+ − **L3**].

Bis[N-(n-propyl)-1-(2-pyridyl)ethanimine}]copper(I) Hexafluorophosphate ($Cu[PF_6]\cdot$(**L5**)$_2$; [Cu{(C_5H_4N)C(CH_3)=N(*n*Pr)}$_2$]-[PF_6]): To a slurry of [$Cu(CH_3CN)_4$][PF_6][9b] (1.5 g, 4.839 mmol) in degassed methanol (40 ml) was added **L5** (1.568 g, 9.678 mmol) under nitrogen. The resulting red solution was stirred at room temperature overnight, filtered and concentrated to ca. 15 ml. Slow cooling to 5°C resulted in the formation of red crystalline $Cu[PF_6]\cdot$(**L5**)$_2$ (65%). − IR: $\tilde{\nu}$ = 1591 cm^{-1} [ν(C=N)]. − ^{1}H NMR (250 MHz, 298 K, $CDCl_3$): δ = 8.37 (s, 1 H), 8.00 (br., 2 H), 7.55 (m, 1 H), 3.55 (br., 2 H), 2.42 (s, 3 H), 1.50 (m, 2 H), 0.74 (m, 3 H). − ^{13}C{^{1}H} NMR (250 MHz, 298 K, $CDCl_3$): δ = 164.5, 151.63, 147.60,137.41, 126.69, 123.59, 54.34, 23.34, 23.66, 14.26, 10.94. − MS (+EI); *m/z*: 387 [M^+], 225 [M^+ − **L5**].

Table 3. Summarized crystallographic data

(a) Crystal parameters	$Cu[BF_4]\cdot(\mathbf{L2})_2$	$Cu[BF_4]\cdot(\mathbf{L3})_2$	$Cu[PF_6]\cdot(\mathbf{L5})_2$
Formula	$C_{20}H_{28}BCuF_4N_4$	$C_{20}H_{28}BCuF_4N_4$	$C_{20}H_{28}PCuF_6N_4$
M	474.81	474.81	532.97
Crystal system	Monoclinic	Monoclinic	Monoclinic
spyace group	$P2_1/c$	$P2/n$	$P2_1/c$
a [Å]	8.850(2)	11.8712(6)	16.600(3)
b [Å]	23.609(5)	7.5742(4)	8.3920(2)
c [Å]	11.889(2)	12.4059(6)	17.300(4)
β [°]	107.02(3)	90.1050(10)	111.20(3)
V [Å^3]	2375.3(8)	1115.47(10)	2388.3(8)
Z	4	2	4
Crystal dimensions [mm]	0.4 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.30 × 0.20 × 0.20
Colour	Red	Red	Red
D_c [g·cm^{-3}]	1.328	1.414	1.482
μ(Mo-K_α) [mm^{-1}]	0.963	1.025	1.043
T [K]	200(2)	200(2)	200(2)
(b) Data collection[a]			
Data collected h	−9 to 11	−15 to 13	−21 to 21
(index ranges) k	−18 to 30	−9 to 10	−11 to 11
l	−10 to 11	−15 to 16	−9 to 22
Reflections collected	6291	6654	14624
Independent reflections	3484	2614	5612
Independent observed reflections [$F_o \leq 4\sigma(F_o)$]	2547	2182	4067
θ range [°]	1.73 to 26.49	2.37 to 28.59	1.32 to 28.59
F(000)	984	492	1096
Decay	< 1%	< 1%	< 1%
(c) Refinement			
R[b]	0.0387	0.0440	0.0543
$wR2$[c]	0.1007	0.1144	0.1491
Absorption correction	SADABS	SADABS	SADABS
S	0.994	1.079	1.090
Δ [e·Å^{-3}] (max, min)[d]	0.524, −0.420	0.475, −0.489	0.450, −0.417
Transmission max, min	1.000, 0.862	1.000, 0.1575	0.8552, 0.8464
Weighting scheme a, b[e]	0.0544, 0.000	0.0431, 0.7160	0.0588, 2.1880

[a] X-ray data collected with a Siemens 3-circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated radiation Mo-K_α radiation (λ = 0.71073 Å). Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters U = 0.08 Å^3. − [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o \geq 4\sigma(F_o)$]. − [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data. − [d] Peaks of unsassigned residual electron density. − [e] $w^{-1} = \sigma^2(F_o^2) + aP + bP$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, where $\max(F_o^2,0)$ indicates that the larger of F_o^2 or 0 is taken, a and b are values set by the program.

Polymerisation Reactions: 0.134 g of CuBr ($9.35\cdot10^{-4}$ mol) was placed in a Schlenk tube, containing a magnetic stirring bead, and pumped/filled three times with nitrogen to remove air from the apparatus. Deoxygenated MMA (10 ml, 0.0935 mol) and deoxygenated xylene (20 ml) were added via syringe to the Schlenk tube at room temperature, followed by the appropriate ligand (2 molar equivalents on CuBr, $1.87\cdot10^{-3}$ mol). The Schlenk tube was then placed into an oil bath at 90°C with stirring, followed by the addition of the initiator, ethyl 2-bromoisobutyrate (0.137 ml, $9.35\cdot10^{-4}$ mol). Periodically, 1−2-ml samples were removed for conversion and molecular-weight analysis.

Crystal-Structure Determinations: Crystallographic data for complexes $Cu[BF_4]\cdot(\mathbf{2})_2$, $Cu[BF_4]\cdot(\mathbf{3})_2$, and $Cu[PF_6]\cdot(\mathbf{5})_2$ are summarised in Table 3. The corresponding molecular structures are shown in Figures 5−7. Suitable crystals were quickly glued to quartz fibres, coated with dry nujol, and cooled in the cold nitrogen gas stream of the diffractometer. The structures were solved by direct methods. Anisotropic thermal parameters were used for all non-H atoms, whilst hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters (U = 0.08 Å^3), riding on the supporting atom. The structure solutions were carried out using SHELXTL[16a] version 5 software with a Silicon Graphics Indy workstation, refinements were carried out using SHELX 96[16b] software, minimising on the weighted R factor $wR2$. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101884, -101885, -101886. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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