DALTON
FULL PAPER

Copper diimine complexes: the synthesis and crystal structures of $[Cu(C_{10}H_{14}N_2)_2(MeOH)][BF_4]$, $[Cu(C_{10}H_{20}N_2)_2]Br$, $[\{(C_{10}H_{14}N_2)CuBr(\mu\text{-}OMe)\}_2(MeOH)]$ and $[\{(C_{10}H_{20}N_2)CuBr(\mu\text{-}OMe)\}_2]$

David M. Haddleton,*,† Andrew J. Clark, David J. Duncalf, Alex M. Heming, Dax Kukulj and Andrew J. Shooter

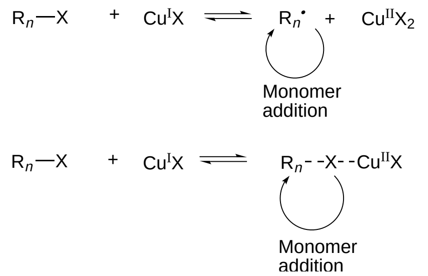
Chemistry Department, University of Warwick, Gibbet Hill Road, Coventry, UK CV4 7AL

The synthesis and structural characterisation of related novel copper-(I) and -(II) diimine complexes have been described and their application as catalysts for atom transfer polymerisation is noted. The unexpected formation of a methoxy bridged copper(II) diimine complex $[\{(C_{10}H_{14}N_2)CuBr(\mu\text{-}OMe)\}_2(MeOH)]$ **3** from the reaction of a copper(I) diimine complex with phenol is described. Compounds **3** and $[\{(C_{10}H_{20}N_2)CuBr(\mu\text{-}OMe)\}_2]$ **4** appear to be examples of a rare class of alkoxy bridged Cu^{II} complexes, with very few similar examples being crystallographically characterised previously.

Copper complexes containing chelating diimine ligands are finding increasing use as catalysts for a wide range of synthetic organic reactions.[1] For example, the use of chiral N-donor ligands is proving to be particularly attractive in asymmetric organic catalysis,[2] such ligands being simply prepared using commercially available, and enantiomerically pure, amine starting material. For example, copper(I) bis(oxazoline) complexes have been utilised in the enantioselective carbenoid addition to organochalcogen atoms.[2c] Atom transfer addition, ATA, a technique that uses transition-metal complexes[3] to promote carbon–carbon bond formation has found many applications in organic synthesis.[4] Transition metals able to function as halogen carriers, with an available $n + 1$ oxidation state, such as the Cu^I–Cu^{II} couple, are useful as catalysts for ATA (Scheme 1).

Recently, two groups, independently from each other, Matyjaszewski and co-workers[5] and Sawamoto and co-workers,[6] reported the use of atom transfer polymerisation (ATP) derived from the ATA reaction. The chemistry of ATP may be described by the equilibria shown in Scheme 1, in this case $R_n^{\bullet}$ represents both the initiating species and the propagating polymeric radical depending on whether the halogen atom is released, following homolytic bond cleavage of R_n–X, or if the halogen remains within the co-ordination sphere of the propagating polymer. The position of the equilibrium in Scheme 1 is pivotal to the control of the polymerisation reaction. If the complex is too easily oxidised, *i.e.* the $n + 1$ oxidation state is too stable, then the equilibrium may lie too far to the right resulting in a relatively large concentration of free radicals leading to termination by radical–radical combination and disproportionation. This ultimately results in an increase in molecular weight distribution, MWD, and loss of the linear relationship between number average molecular mass (M_n) and the ratio of monomer to initiator as is observed for *living polymerisation*. Conversely, if the metal is not able to increase its oxidation number the equilibrium lies too far to the left and no polymerisation occurs.

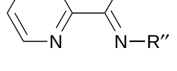
Sawamoto and co-workers[6] described a $RuCl_2(PPh_3)_3$–CCl_4 based system for the polymerisation of methyl methacrylate, $CH_2{=}C(Me)CO_2Me$. However, in order to achieve reasonable reaction rates the addition of a co-catalyst, *e.g.* $Al(OPr^i)_3$, is required, thus precluding the use of certain solvents and functional monomers which are able to react with aluminium alkoxides and aryloxides. Matyjaszewski and co-workers[5] have described the use of copper(I) complexes of 2,2′-bipyridine (bpy) as catalysts for ATP, the active species being described as 'CuBr·bpy', this system being effective for the living polymerisation of styrene, acrylates and methacrylates. This work has subsequently been developed to use 4,4′-disubstituted bpy which solubilises the active copper(I) giving truly homogeneous reactions in polymers with decreased MWD.[5c]



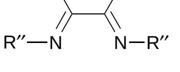
Scheme 1

The choice of ligand is crucial in controlling the position of the equilibrium by acting as either electron donors or acceptors to the metal. In the systems where copper(I) halides are used in conjunction with bpy the bpy ligand serves to solubilise the CuBr by forming tetrahedral $[Cu^I(bpy)_2]Br$, copper(I) halides being very insoluble in organic solvents. More importantly, the low lying LUMO π* orbital, present in the conjugated π system of bpy, is able to accept electron density from the metal and hence serves to stabilise low oxidation states, in this case Cu^I.

We have previously reported that bipyridines may be replaced with other α-diimines having the N=C–C=N skeleton,[7] *e.g.* ligands of type **A** and **B**, where R′ and R″ = H, alkyl, aryl, substituted alkyl/aryl. Both **A** and **B** have the capability of accepting electron density into their low lying π* orbital and they have been reported to be superior to bpy in stabilising and solubilizing Cu^I halides.[8]



A

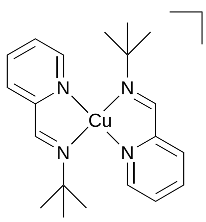


B

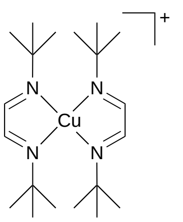
---

† E-Mail: msrgs@csv.warwick.ac.uk

We have recently reported that copper(I) diimine complexes similar to **1** and **2** (see below) and other alkyl substituted



1



2

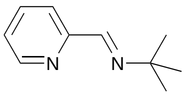
derivatives are effective, when used in conjunction with an appropriate initiator [*e.g.* ethyl 2-bromoisobutyrate, $Me_2C(Br)CO_2Et$], as catalysts for ATP of methyl methacrylate.[7] Our studies have furnished much information on the rates of such reactions and have shown the existence, in our system, of an initial induction period under certain conditions.[7b] We believe that during this time the necessary equilibrium conditions (Scheme 1) are being established, *i.e.* the formation of Cu^I and Cu^{II} species in the appropriate ratio for effective propagation. We have identified that when phenol, or certain substituted phenols, are added to the polymerisation reaction the induction period is either completely removed or considerably reduced.

These results have prompted us to investigate the synthesis of well defined copper diimine complexes as potential polymerisation catalysts using *N*-alkyl-*N*-[(2-pyridyl)methylidene]amine (type **A**) and *tert*-butyl substituted diazabutadiene (type **B**) ligands and in an attempt to understand the role of phenols when used in conjunction with copper(I) diimines in ATP. Although the copper(II) complexes isolated and characterised in this present work were from solutions designed to reproduce ATP reaction conditions the role, if any, of the copper(II) species is not yet identified. It would be envisaged that copper(II) complexes would not act as effective ATP catalysts and if anything might deactivate the system.

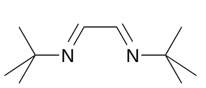
The ease by which a wide variety of alkyl-substituted (pyridylmethylidene)amine (PCA) and diazabutadiene (DAB) derivatives may be prepared, *via* modification to the alkyl group, makes such ligands particularly suited for the preparation of well defined copper complexes, which then find use in mechanistic studies of the polymerisation reaction.

Results and Discussion

The *N*-(*tert*-butyl)-*N*-[(2-pyridyl)methylidene]amine (Bu^t-PCA) ligand, **C** (shown below), is easily prepared *via* the condensation of 2-pyridinecarbaldehyde with Bu^tNH_2. Water produced in this reaction is removed by the addition of excess $MgSO_4$ allowing isolated yields of at least 95% to be routinely achieved. 1,4-Di-*tert*-butyl-1,4-diazabuta-1,3-diene, **D** (shown below), is also very easily prepared, in high yield, *via* the reaction of glyoxal with Bu^tNH_2.



C



D

Compound **1**, Fig. 1, was prepared by the addition of 2 equivalents of **C** to a slurry of $[Cu(MeCN)_4][BF_4]$ in methanol, subsequent concentration of the solution followed by slow cooling to ≈5 °C yielding deep red crystals in good yield. Complex **2**, Fig. 2, was prepared in an analogous fashion *via* the reaction of CuBr with 2 equivalents of **D** in methanol.

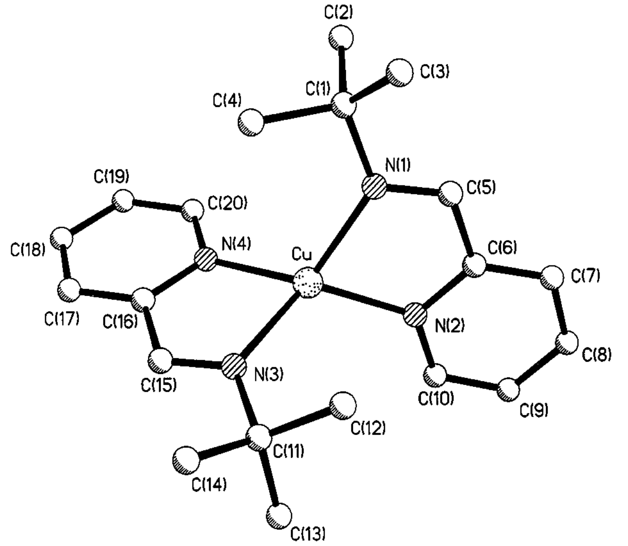


Fig. 1 The crystal structure of $[Cu(C_{10}H_{14}N_2)_2(MeOH)][BF_4]$ **1** (solvent molecule and BF_4 anion not shown)

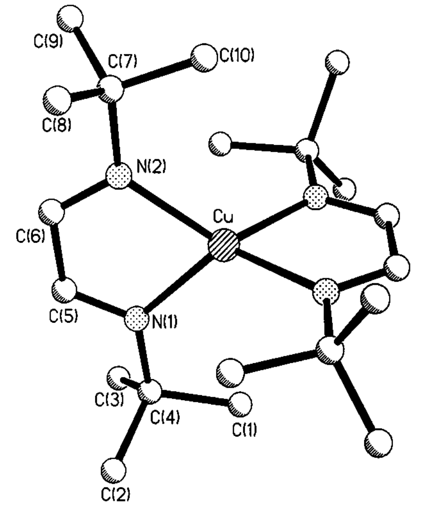


Fig. 2 The crystal structure of $[Cu(C_{10}H_{20}N_2)_2]Br$ **2** (Br^- counter ion not shown)

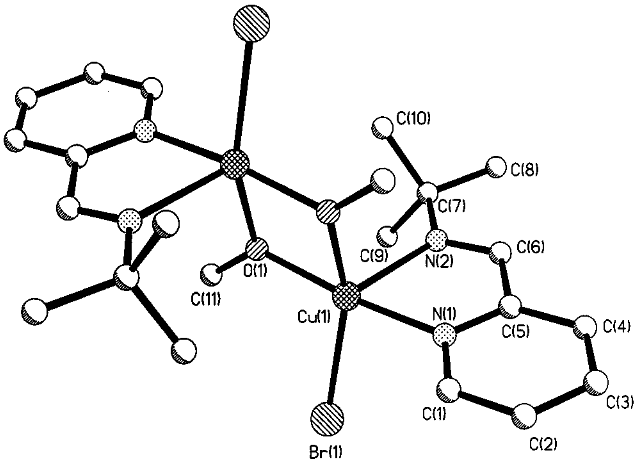


Fig. 3 The crystal structure of $[\{(C_{10}H_{14}N_2)CuBr(\mu\text{-}OMe)\}_2(MeOH)]$ **3** (solvent molecule not shown)

The methoxide bridged compounds, **3**, Fig. 3, and **4**, Fig. 4, despite their structural similarity were synthesised by somewhat different routes. The bright green Cu^{II} complex **3** was prepared *via* the reaction of Cu^IBr with 2 equivalents of **C** and 2 equivalents of phenol in methanol; presumably phenol acted as an oxidising agent, with likely formation of phenoxide ligands, which were then substituted for methoxide during crystallisation. It is interesting to note that if the same reaction is carried

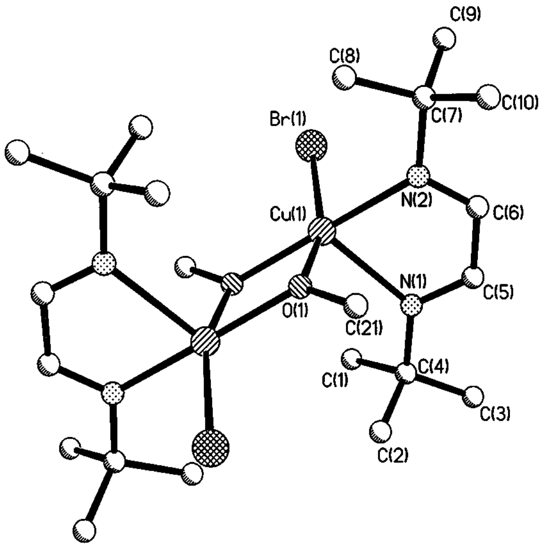
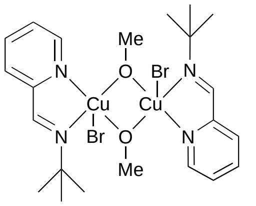
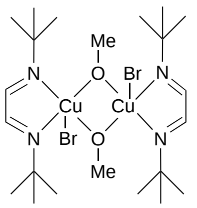


Fig. 4 The crystal structure of $[\{(C_{10}H_{20}N_2)CuBr(\mu\text{-}OMe)\}_2]$ **4**

out in the absence of phenol, only the red Cu^I bromide salt of compound **1** can be isolated. In contrast, the bright green Cu^{II} complex **4** was synthesised by the reaction of $CuBr_2$ with 2 equivalents of **D** in methanol. In this case the methoxide ligands are most likely being formed *via* substitution of Br^- for MeO^- together with elimination of HBr.



3



4

In compound **1** the ligands are arranged such that the coordinating nitrogen atoms surround the metal centre in a distorted tetrahedral arrangement, the same basic geometry also being observed for **2**. The intraligand dihedral angle between the mean planes defined by the central copper ion and each pair of chelating nitrogen atoms is 81.9° for **1** and 89.5° for **2** with **2** having the crystallographic symmetry C_2. The Cu–N bond lengths for **1** range from 2.021(4) to 2.038(4) Å and for **2** range from 2.016(4) to 2.035(4) Å, the N(1)–Cu–N(2) and N(3)–Cu–N(4) angles for **1** at 81.89(10) and 81.84(10)° being similar to the N(1)–Cu–N(2) angle observed in **2** at 82.2(2)°. Table 1 gives a comparison of average bond parameters reported for $[CuL_2]^+$ type complexes. It can be seen that average Cu–N bond lengths for **1** and **2** are similar to those seen for the unsubstituted bpy complex; the Cu–N bond lengths for complexes using tetramethyl-substituted bpy or phenanthroline based ligands being somewhat longer. The N–Cu–N bond angles range from 80.6(4)°, for the 4,4′,6,6′-tetramethyl-2,2′-bipyridine complex, to 83.4°, for the 2,9-dimethyl-1,10-phenanthroline complex, with complexes **1** and **2** positioned toward the midpoint of this range. The intraligand dihedral angles for the compounds given in Table 1 exhibit quite a large range from 68°, in the case of the 4,4′,6,6′-tetramethyl-2,2′-bipyridine complex, to 89.5° for **2**.

Compounds **3** and **4** appear to be examples of a rare class of alkoxy-bridged Cu^{II} complexes, with very few similar examples being crystallographically characterised.[13,14] The arrangement of ligated atoms around the metal centres is described as square-based pyramidal. Interestingly, the nitrogen atoms of the chelating ligands adopt basal *and* apical positions. In compound **3** the apical N(2)–Cu(1) distance, 2.289(5) Å (Table 2), is much longer than the basal Cu(1)–N(1) distance, 2.010(5) Å. The remaining basal positions, O(1), O(1′), Br(1) have bond lengths to Cu(1) of 1.912(4), 1.972(4), and 2.4331(9) Å respectively. The unit cell of **3** contains only one formula unit and the complex is centrosymmetrical. A similar situation exists for **4** whereby the apical Cu(1)–N(1) distance at 2.300(5) Å is longer than the basal Cu(1)–N(2) distance, 2.084(5) Å. The other basal distances from Cu(1) to O(1), O(1′) and Br(1) are 1.955(4), 1.956(4) and 2.4336(10) Å respectively. The N(1)–Cu(1)–N(2) angle for **3**, 77.3(2)°, compares well with 77.0(2)° observed for **4**. Compound **4** contains two symmetrically independent, centrosymmetrical complexes in the unit cell.

Conclusion

This study has demonstrated that phenol can react with copper(I) diimine complexes to form dimeric Cu^{II} compounds. We believe that phenol has a similar effect on the Cu^I catalysts when used in polymerisation reaction mixtures, and that Cu^{II} complexes similar to **3** and **4** are formed. In this way the equilibrium shown in Scheme 1 is established more quickly in the presence of phenol, and that this process removes or reduces the induction period which is observed in the absence of phenol.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out using standard Schlenk-line techniques under an atmosphere of argon or nitrogen. All solvents were purified by distillation, degassed by bubbling nitrogen through them, and dried over molecular sieves. Deuteriated solvents were stored under argon, and kept dry over molecular sieves. Nuclear magnetic resonance spectra were recorded using a Bruker AC-250

Table 1 Comparison of average bond length and angle data for $[Cu^IL_2]^+$ complexes

Ligand	Counter ion	Cu–N bond length/Å	N–Cu–N angle/°	Dihedral angle/°	Ref.
Bu^{t}PCA	BF_4^-	2.030(4)	81.86(10)	81.9	This work
Bu^{t}DAB	Br^-	2.025(4)	82.2(2)	89.5	This work
2,2′-Bipyridine	ClO_4^-	2.021(11)	81.5(4)	75.2	9
4,4′,6,6′-Tetramethyl-2,2′-bipyridine	ClO_4^-	2.057(1)	80.6(4)	68	10
1,10-Phenanthroline	$CuBr_2^-$	2.039(8)	82.2(3)	76.8	11
2,9-Dimethyl-1,10-phenanthroline	NO_3^-	2.063	83.4	85.7	12

Table 2 Selected bond length and angle data for compounds **3** and **4**

Compound	Cu–N$_{apical}$/Å	Cu–N$_{basal}$/Å	N–Cu–N/°	Cu–O/Å	Cu–O′/Å	Cu–Br/Å
3	2.289(5)	2.010(5)	77.3(2)	1.912(4)	1.972(4)	2.4331(9)
4	2.300(5)	2.084(5)	77.0(2)	1.955(4)	1.956(4)	2.4336(10)

Table 3 Summarised crystallographic data for compounds **1**–**4**

	1	**2**	**3**	**4**
Crystal parameters				
Formula	$C_{21}H_{32}BCuF_4N_4O$	$C_{20}H_{40}BrCuN_4$	$C_{23}H_{38}Br_2Cu_2N_4O_3$	$C_{22}H_{46}Br_2Cu_2N_4O_2$
M	506.86	480.01	705.47	1371.06
Crystal system	Orthorhombic	Tetragonal	Triclinic	Triclinic
Space group	*Pbca*	$I4_1/acd$	$P\bar{1}$	$P\bar{1}$
a/Å	17.5311(5)	28.137(4)	9.0441(2)	10.6185(2)
b/Å	15.9486(5)	28.137(4)	8.9112(2)	10.9060(2)
c/Å	17.5691(5)	12.451(3)	10.4037(2)	14.5347(3)
α/°			110.7680(10)	69.8450(10)
β/°			93.6260(10)	88.1580(10)
γ/°			101.6830(10)	72.01210(10)
Reflections for cell determination	5189	2103	2651	3835
U/Å^3	4912.3(3)	9858(3)	759.35	1497.74
Z	8	16	4	2
Dimensions/mm	0.15 × 0.1 × 0.1	0.1 × 0.1 × 0.2	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.1
D_c/g cm^{-3}	1.371	1.294	1.541	1.520
μ(Mo-Kα)/mm^{-1}	0.939	2.518	4.059	4.111
T/K	220	240(2)	180	180
Data collection[a]				
Data collected h, k, l	−22 to 23, −21 to 11, −22 to 22	−37 to 37, −23 to 36, −13 to 16	−11 to 8, −11 to 11, −13 to 13	−14 to 7, −13 to 14, −18 to 18
Total reflections	29 478	26 360	4671	7537
Independent reflections	6028	2997	3373	5134
Independent observed reflections [$F_o \geqslant 4\sigma(F_o)$]	3797	1690	2269	3321
θ Range/°	2.08–28.77	1.45–28.29	2.12–28.40	1.50–25.00
F(000)	2112	4032	355	700
Refinement				
R[b]	0.0593	0.0834	0.0590	0.0503
$wR2$[c]	0.1484	0.1470	0.1739	0.1148
S	1.057	1.190	1.008	0.963
Δ/e Å^{-3} (maximum, minimum)[d]	0.384, −0.388	0.502, −0.357	1.956, −0.662	0.831, −0.764
T maximum, minimum[e]	0.9276, 0.9320	0.9103, 0.6320	1.000, 0.5182	1.000, 0.0373
Weighting scheme a, b[f]	0.0489, 6.1212	0.0234, 80.1867	0.140, 0.000	0.457, 0.000

[a] Data collected on a Siemens three-circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o \geqslant 4\sigma(F_o)$]. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data. [d] Peaks of unassigned residual electron density. [e] By SADABS.[19] [f] $w^{-1} = \sigma^2(F_o^2) + aP + bP$, 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.

MHz instrument. Spectra were referenced using the resonances of residual protons in the deuteriated solvents. Ligands were prepared *via* suitable modifications to the published procedure, *N*-(*tert*-butyl)-*N*-[(2-pyridyl)methylidene]amine by the method of Bähr and Thamlitz,[15] 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene by that of Emmons.[16]

Preparations

$[Cu(C_{10}H_{14}N_2)_2(MeOH)][BF_4]$ 1. To a slurry of $[Cu(CH_3CN)_4][BF_4]$ (1.0 g, 3.22 mmol) in degassed methanol (30 ml) was added *N*-(*tert*-butyl)-*N*-[(2-pyridyl)methylidene]amine (1.046 g, 6.44 mmol) under nitrogen. The solution was stirred at room temperature overnight, filtered and concentrated to *ca.* 10 ml. Slow cooling to 5 °C gave 1.2 g of red crystalline **1** (79% yield). ^1H NMR $[(CD_3)_2CO$, 250 MHz, 298 K] δ 9.36 (s, 1 H, $C_5H_4NC\mathit{H}{=}NBu^t$), 9.05, 8.57, 8.53, 8.14 (m, 4 H, $C_5\mathit{H}_4N$), 1.81 (s, 9 H, Bu^t); ^{13}C-{H} NMR $[(CD_3)_2CO$, 250 MHz, 298 K] δ 159.03 (s, $C_5H_4N\mathit{C}H{=}NBu^t$) 152.92, 150.10, 139.675, 129.33, 128.75 (s, C_5H_4N), 60.76 [s, $\mathit{C}(CH_3)_3$], 30.85 [s, $C(\mathit{C}H_3)_3$]; mass spectrometry (FAB, NH_3) *m*/*z* 387 [M^+], 225 [M^+ − (Bu^tPCA)] [Found (Calc.): C, 49.31 (49.76); H, 6.01 (6.36); N, 10.20 (11.05)%]; IR ν(C=N) 1619 cm^{-1}.

$[Cu(C_{10}H_{20}N_2)_2]Br$ 2. To a slurry of CuBr (1.0 g, 6.97 mmol) in degassed methanol (20 ml) was added a solution of 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (2.20 g, 13.94 mmol, in 10 ml degassed methanol) under nitrogen. The solution was stirred overnight at room temperature, filtered and concentrated to *ca.* 10 ml. Slow cooling to 5 °C gave 2.5 g of red crystalline **2** (78% yield). ^1H NMR $[(CD_3)_2CO$, 250 MHz, 298 K] δ 8.48 [br, 2 H, $(Bu^tN{=}C\mathit{H})_2$], 1.69 (s, 18 H, Bu^t); ^{13}C-{H} NMR $[(CD_3)_2CO$, 250 MHz, 298 K] δ 158.20 [br, $(Bu^tN{=}\mathit{C}H)_2$], 60.40 [s, $\mathit{C}(CH_3)_3$], 30.41 [s, $C(\mathit{C}H_3)_3$]; mass spectrometry (FAB, NH_3) *m*/*z* 399 [M^+], 231 [M^+ − (Bu^tDAB)] [Found (Calc.): C, 51.20 (50.04); H, 7.69 (8.40); N, 12.65 (11.67)%]; IR ν(C=N) 1623 cm^{-1}.

$[\{(C_{10}H_{14}N_2)CuBr(\mu\text{-}OMe)\}_2(MeOH)]$ 3. To a slurry of CuBr (1.0 g, 6.97 mmol) in degassed methanol (20 ml) was added a solution of *N*-(*tert*-butyl)-*N*-[(2-pyridyl)methylidene]amine (2.26 g, 13.94 mmol in 10 ml degassed methanol) under nitrogen. Phenol (1.31 g, 13.94 mmol) was then added and the solution stirred at room temperature overnight. Filtration and concentration of the solution, followed by slow cooling to 5 °C yielded 1.8 g of green crystals of **3** (77% yield, based on Cu) [Found (Calc.): C, 39.56 (39.16); H, 6.29 (5.43); N, 8.51 (7.94)%]; IR ν(C=N) 1637 cm^{-1}.

$[\{(C_{10}H_{20}N_2)CuBr(\mu\text{-}OMe)\}_2]$ 4. To a slurry of $CuBr_2$ (1.0 g, 4.46 mmol) in degassed methanol (20 ml) was added 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (1.41 g, 8.92 mmol, in 10 ml degassed methanol). The solution was stirred overnight, filtered and concentrated to *ca.* 10 ml. Slow cooling to 5 °C afforded 1.2 g of green crystals of **4** (yield 79%, based on Cu) [Found (Calc.): C, 39.36 (38.55); H, 7.12 (6.76); N, 9.20 (8.17)%]; IR ν(C=N) 1602 cm^{-1}.

Crystal structure determinations

Crystallographic data for complexes **1** to **4** are summarised in Table 3. The molecular structures of **1**–**4** are shown in Figs. 1–4 respectively. Suitable crystals were quickly glued to quartz fibres, coated in 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[17] version 5.0 software on a Silicon Graphics Indy workstation, refinements were carried out using SHELXL 96[18] software, minimising on the weighted *R* factor *wR*2. Selected bond lengths and angles for **1** and **2** are given in Table 1, Table 2 lists selected bond lengths and angles for **3** and **4**.

CCDC reference number 186/810.

References

1 A. Togni and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 497; D. A. Evans, K. A. Woerpel and M. J. Scott, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 430; F. O. H. Pirrung, H. Hiemstra, W. N. Speckamp, B. Kaptein and H. Schoemaker, *Tetrahedron Lett.*, 1994, **50**, 12 415.

2 (*a*) I. W. Davies, C. H. Senanayake, R. D. Carsen, T. R. Verhoeven and P. J. Reider, *Tetrahedron Lett.*, 1996, **37**, 1725; (*b*) R. Lowenthal and S. Masamune, *Tetrahedron Lett.*, 1991, **32**, 7373; (*c*) Y. Nishibayashi, K. Ohe and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 1995, 1245; (*d*) F. O. H. Pirrung, H. Hiermstra, W. N. Speckamp, B. Raptein and H. E. Schoemaker, *Synthesis*, 1995, 465.

3 G. M. Lee and S. M. Weinreb, *J. Org. Chem.*, 1990, **55**, 1281; H. Nagashima, H. Wakamatsu and K. Itoh, *J. Chem. Soc., Chem. Commun.*, 1984, 652; H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama and K. Itoh, *J. Org. Chem.*, 1993, **58**, 464.

4 B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon, New York, 1988; J. Iqbal, B. Rhatia and N. K. Nayyar, *Chem. Rev.*, 1994, **94**, 519.

5 (*a*) J.-S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614; (*b*) T. Grimaud and K. Matyjaszewski, *Macromolecules*, 1997, **30**, 2216; (*c*) K. Matyjaszewski, T. E. Patten and J. Xia, *J. Am. Chem. Soc.*, 1997, **119**, 674.

6 M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1995, **28**, 1721.

7 (*a*) D. M. Haddleton, C. B. Jasieczek, M. J. Hannon and A. J. Shooter, *Macromolecules*, 1997, **30**, 2190; (*b*) D. M. Haddleton, A. J. Clark, M. C. Crossman, D. J. Duncalf, A. M. Hemings, S. R. Morsley and A. J. Shooter, *Chem. Commun.*, 1997, 1173; (*c*) D. M. Haddleton, C. Waterson, P. J. Derrick, C. Jasieczek and A. J. Shooter, *Chem. Commun.*, 1997, 683.

8 G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 157.

9 M. Munakata, S. Kitagawa, A. Asahara and H. Masuda, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1927.

10 J. Foley, S. Tyagi and B. J. Hatheway, *J. Chem. Soc., Dalton Trans.*, 1984, 1.

11 P. C. Healy, L. M. Englehardt, V. A. Patrick and A. White, *J. Chem. Soc., Dalton Trans.*, 1985, 2451.

12 R. Haemaelaeinen, M. Ahlgren and U. Terpeinen, *Finn. Chem. Lett.*, 1978, 199.

13 R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 1970, **74**, 3497.

14 L. Menabue and M. Saladini, *J. Chem. Soc., Dalton Trans.*, 1990, 1581.

15 Von G. Bähr and H. Thamlitz, *Z. Anorg. Allg. Chem.*, 1955, **282**, 3.

16 W. D. Emmons, *J. Am. Chem. Soc.*, 1957, **79**, 5739.

17 G. M. Sheldrick, SHELXTL, Siemens Analytical Instruments, Madison, WI, 1994.

18 G. M. Sheldrick, SHELXL 96, University of Göttingen, 1996.

19 G. M. Sheldrick, SADABS, Empirical Absorption Corrections Program, University of Göttingen, 1997.

Received 16*th September* 1997; *Paper* 7/06722D