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Synthesis and reactivity of copper(I) complexes containing a bis(imidazolin-2-imine) pincer ligand†

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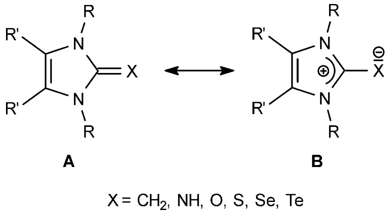
Received 2nd March 2007, Accepted 11th April 2007
First published as an Advance Article on the web 2nd May 2007
DOI: 10.1039/b703183a

The new pincer ligand 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine (TL^{tBu}) has been prepared in high yield from 2,6-bis(hydroxymethyl)pyridine (**1**) and 1,3-di-*tert*-butylimidazolin-2-imine (**3**). Reaction of TL^{tBu} with $[Cu(MeCN)_4]PF_6$ affords the highly reactive copper(I) complex $[(TL^{tBu})Cu]PF_6$, [**5**]PF_6, which forms the stable copper(I) isocyanide complexes [**6a**]PF_6 (ν_{CN} = 2179 cm^{-1}) and [**6b**]PF_6 (ν_{CN} = 2140 cm^{-1}) upon addition of *tert*-butyl or 2,6-dimethylphenyl isocyanide, respectively. For the cations **6a** and **6b**, DFT calculations reveal ground-state electronic structures of the type $[(TL^{tBu}\text{-}\kappa N^1{:}\kappa N^2)Cu(CNR)]$ with tricoordinate geometries around the copper atoms. Exposure of [**5**]PF_6 to the air readily leads to trapping of atmospheric CO_2 to form the square-planar complex $[(TL^{tBu})Cu(HCO_3\text{-}\kappa O)]PF_6$, [**7**]$PF_6$, with the bicarbonate ligand adopting a rarely observed monodentate coordination mode. In chlorinated solvents such as dichloromethane or chloroform, [**5**]PF_6 rapidly abstracts chloride by reductive dechlorination of the solvent to yield $[(TL^{tBu})CuCl]PF_6$, [**8**]PF_6 quantitatively. Reaction of TL^{tBu} with copper(I) bromide or chloride affords complexes **9a** and **9b**, respectively, for which X-ray diffraction analysis, low-temperature NMR experiments and DFT calculations reveal the presence of a κ^2-coordinated ligand of the type $[(TL^{tBu}\text{–}\kappa N^1{:}\kappa N^2)CuX]$. In solution, complex **9b** undergoes slow disproportionation forming the mixed-valence copper(II)/copper(I) system $[(TL^{tBu})CuCl][CuCl_2]$, [**8**]$CuCl_2$ with a linear dichlorocuprate(I) counterion.

Introduction

Ligands derived from the 1*H*-imidazole heterocycle currently play a major role in organotransition metal and coordination chemistry. In particular, *N*-heterocyclic carbenes of the imidazolin-2-ylidene type[1] are nowadays ubiquitous and indispensable to the development of diverse research areas such as homogeneous catalysis,[2] materials science[3] and medicinal chemistry.[4] The stability of these carbenes can be attributed *inter alia* to the capability of the imidazolium ring to stabilize a positive charge, leading to strongly basic and highly nucleophilic ligands. This behavior can be transferred to an exocyclic moiety X at the 2-position of the *N*-heterocycle, so that for species such as 2-methylen-, 2-imino- and 2-oxoimidazolines ($X = CH_2$, NH, O) a strong contribution from the ylidic mesomeric structure **B** (Scheme 1) must be considered.[5,6] The resulting build-up of negative charge at X affords compounds with considerably enhanced basicity and nucleophilicity. Accordingly, the heavier 2-chalcogenoimidazolines (X = S, Se, Te) have been regarded as neutral analogues of thiolate, selenolate and tellurolate ligands, respectively.[7]

We have exploited this concept in the synthesis of various novel 2-trimethylsilyliminoimidazolines ($X = NSiMe_3$) and have shown that these are suitable precursors for the synthesis of transition metal complexes incorporating ancillary imidazolin-2-iminato ligands ($X = N^-$).[8] Desilylation of these precursors allows access to imidazolin-2-imines (X = NH), which are strong bases that may well exhibit even stronger nucleophilic properties than related guanidine-type systems.[5,9] These imines are valuable ligands in their own right, and also useful building blocks for the design and preparation of novel multidentate poly(imidazolin-2-imine) ligands of type **L1** (Scheme 2).[10] The first example of an ethylene-bridged bis(imidazolin-2-imine) system of this type was introduced by Kuhn *et al.*,[11] however, their synthetic protocol is confined to the use of the ligand precursor 2-imino-1,3-dimethylimidazoline, obtained by a multi-step protocol from 2-aminoimidazole.[12] Related poly(guanidines) of type **L2** have recently found remarkable applications as "superbasic" proton sponges and as ligands for transition metal complexation, with particular emphasis on copper coordination chemistry.[13,14]



Scheme 1 Mesomeric structures of imidazole-based ligands.

With this contribution, we wish to present a new pyridine-bridged bis(imidazolin-2-imine) ligand TL^{tBu} along with an account of its copper coordination chemistry. Since TL^{tBu} can be described by the two limiting resonance structures **A** and **B** (Scheme 2), it can be regarded as a potentially more basic analogue of Schiff-base pyridine-2,6-diimine ligands. The latter are among

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† Electronic supplementary information (ESI) available: Details of the electronic structure calculations and presentations of all calculated molecular structures together with Cartesian coordinates of their atomic positions. See DOI: 10.1039/b703183a

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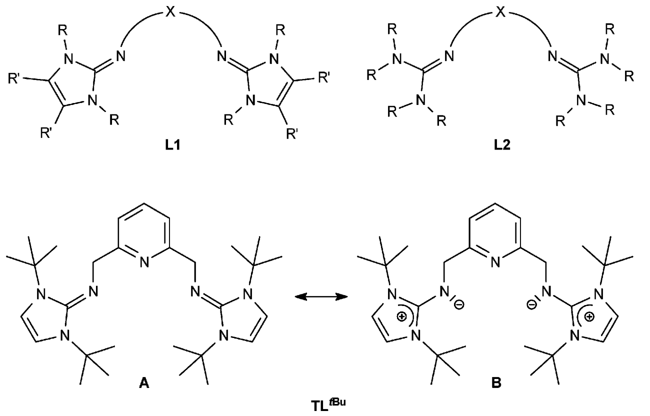


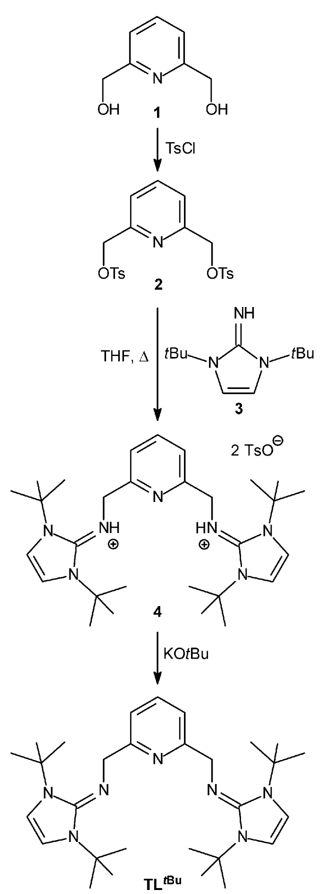
Scheme 2 Mesomeric structures of TL$^{t\mathrm{Bu}}$ (**A** and **B**), novel multidentate poly(imidazolin-2-imine) ligands of type **L1** and related poly(guanidines) of type **L2**.

the most popular pincer-type ligands,[15] in particular because of the unexpected discovery that their late transition metal complexes are exceptionally active olefin polymerization catalysts.[16] To date, only a limited number of reports on copper complexes containing pyridine-2,6-diimine ligands exist,[17] which is surprising in view of their potential use in dioxygen activation.[18] For instance, some unexpected results were reported upon reaction of copper(I) derivatives with 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine.[17b] In addition, it should be noted that copper(I) chloride and bromide complexes with related chelating *N*-donor ligands have been used as efficient catalysts in atom transfer radical polymerizations (ATRP).[19,20]

Results and discussion

Ligand synthesis

The synthesis of the ligand 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine (TL$^{t\mathrm{Bu}}$) is achieved starting from 2,6-bis(hydroxymethyl)pyridine (**1**), which can be converted into the corresponding diester **2** by reaction with *p*-toluenesulfonyl chloride.[21] Treatment of **2** with two equivalents of 1,3-di-*tert*-butylimidazolin-2-imine (**3**) affords the ditosylate [(TL$^{t\mathrm{Bu}}$H$_2$)(OTs)$_2$] (**4**) in high yield, from which the free ligand TL$^{t\mathrm{Bu}}$ can be almost quantitatively released by deprotonation with an excess of KO*t*Bu (Scheme 3). TL$^{t\mathrm{Bu}}$ is obtained as an air-stable off-white solid, of which the ^{1}H and ^{13}C NMR resonances (in C_6D_6) for the imidazoline moiety are very similar to those reported for the imine **3**.[9] For instance, the ^{1}H NMR spectrum shows a triplet and a doublet at 7.69 and 7.55 ppm for the bridging pyridine ring together with two singlets at 6.35 and 4.85 ppm for the benzyl CH$_2$ and for the imidazoline CH hydrogen atoms, respectively. The resonance of the *tert*-butyl hydrogen atoms is observed at 1.43 ppm.



Scheme 3 Synthesis of 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)-methyl]pyridine, TL$^{t\mathrm{Bu}}$.

Reactions of TL$^{t\mathrm{Bu}}$ with [Cu(MeCN)$_4$]X (X = PF$_6$, CF$_3$SO$_3$)

The reaction of TL$^{t\mathrm{Bu}}$ with the copper(I) complex [Cu(MeCN)$_4$]PF$_6$ in acetonitrile affords a yellow, extremely air-sensitive solid after evaporation of the solvent. The ^{1}H and ^{13}C NMR spectra of this material in CD$_3$CN or acetone-*d*$_6$ exhibit just one set of resonances for the imidazolin-2-imine moieties, indicating the formation of a symmetric, monomeric structure. Upon coordination of the copper ion, the ^{1}H NMR resonance of the *tert*-butyl hydrogen atoms is shifted to higher field, whereas downfield shifts are observed for all other resonances. Elemental analysis of the yellow solid clearly suggests that a complex of the composition [(TL$^{t\mathrm{Bu}}$)Cu]PF$_6$, [**5**]PF$_6$, without incorporation of acetonitrile, must have formed (Scheme 4). All efforts to obtain single crystals suitable for an X-ray diffraction analysis study proved unsuccessful, and the solid state structure of the cation **5** remains unresolved.

To gain further structural information about the TL$^{t\mathrm{Bu}}$–copper(I) system, we have performed DFT (density functional theory) calculations on the cationic complex **5** and on its acetonitrile adduct. All computations were performed using the hybrid density functional method B3LYP implemented in the *Gaussian 03* program.[22] For all main-group elements (C, H, N, Cl and Br) the all-electron triple-ζ basis set (6-311G**) was used, whereas for the group 11 transition metal Cu the Ahlrichs TZV basis set was employed.[23,24] The calculated structure of **5** reveals a T-shaped geometry with both imino moieties and the pyridine function coordinated to the copper atom (Fig. 1). All Cu–N distances are in the range 2.018–2.039 Å, and a dihedral angle of 9.45° is observed between the CuN$_3$ plane and the pyridine ring.

Calculations on the acetonitrile adduct **5**·NCCH$_3$ afford a trigonal geometry with the pyridine, the acetonitrile and only one imino nitrogen atom attached to the metal centre (Fig. 1). Apparently, the ligand TL$^{t\mathrm{Bu}}$ does not support a four-coordinate

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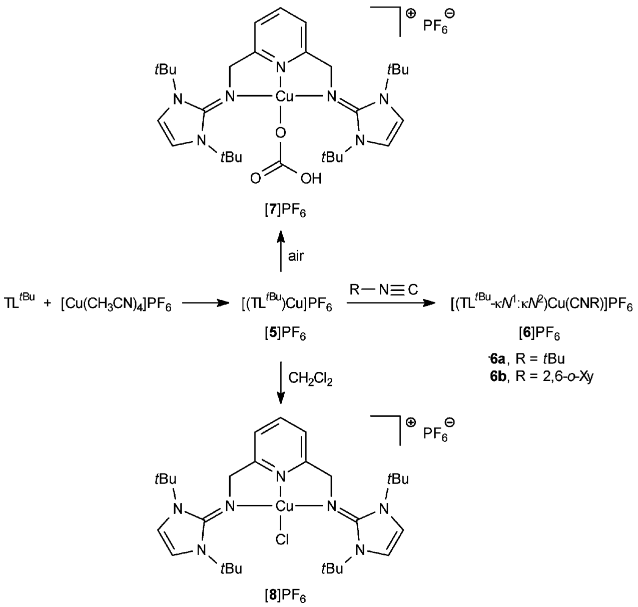

Scheme 4

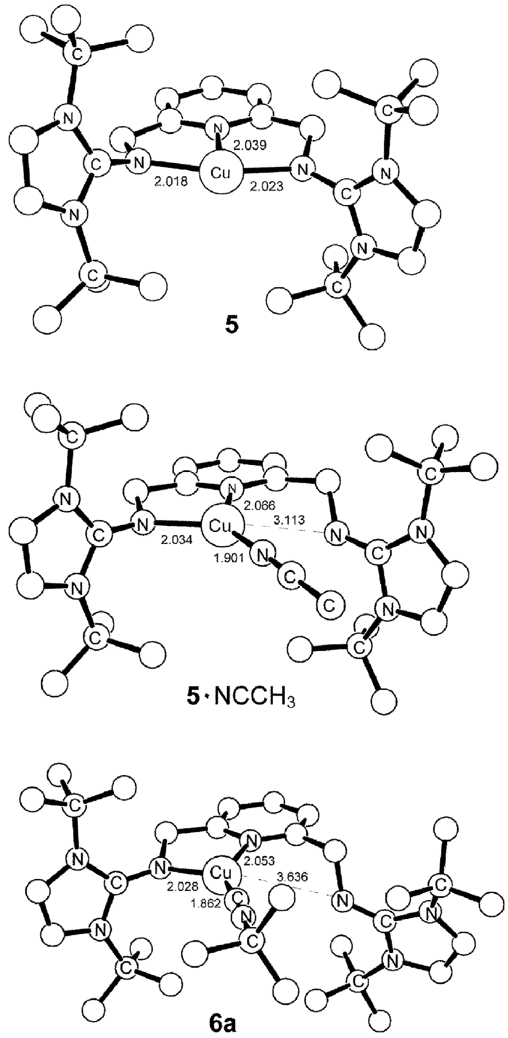

Fig. 1 Calculated geometries for the $[TL^{tBu}Cu]^+$ cation **5**, the acetonitrile adduct **5**·$NCCH_3$ and the *tert*-butyl isocyanide complex **6a**.

copper(I) environment, since a favorable tetrahedral geometry cannot be adopted because of the sterically demanding *tert*-butyl substituents. Accordingly, the reaction enthalpy for the formation of **5**·$NCCH_3$ is found to be slightly exothermic by $\Delta H° = -9.3$ kcal mol^{-1}.[25] It should be noted that similar results have been obtained by DFT calculations on a related Cu(I) system with the pincer ligand 2,6-bis(dimethylaminomethyl)pyridine.[26]

Isocyanide adducts of [5]PF_6

The reactions of [**5**]PF_6 with *tert*-butyl and 2,6-dimethylphenyl isocyanides in THF afforded the isocyanide adducts [**6a**]PF_6 and [**6b**]PF_6 in good yields after precipitation or evaporation of the solvent (Scheme 4). In the ^1H and ^{13}C NMR spectra, coordination of the isocyanides is clearly indicated by the observation of the expected isocyanide resonances together with significantly shifted resonances for the TL^{tBu} ligand in comparison to [**5**]PF_6. In addition, the IR spectra exhibit strong CN stretching vibrations at 2179 [**6a**] and 2140 cm^{-1} [**6b**] which are significantly shifted to higher wave numbers with respect to the free isocyanides [ν_{CN}(*t*BuNC) = 2138 cm^{-1}, ν_{CN}(XyNC) = 2115 cm^{-1}] in agreement with negligible π-back-donation from copper(I) into the isocyanide ligands.[27] Although the ^1H and ^{13}C NMR spectra of [**6a**]PF_6 and [**6b**]PF_6 imply formation of symmetric, four-coordinate copper(I) complexes, low-temperature NMR studies of [**6a**]PF_6 and [**6b**]PF_6 in acetone-d_6 result in broadening of specific signals at −80 °C, suggesting the existence of asymmetric complexes. However, the coalescence temperature appeared to be even lower and could not be reached.

In agreement with the theoretical results obtained for the acetonitrile complex **5**·$NCCH_3$, our DFT calculations on **6a** and **6b** reveal ground-state electronic structures with tricoordinate geometries around the copper atoms. As shown for the calculated structure of the *t*BuNC derivative **6a** in Fig. 1, one ligand arm is clearly bending away with a copper–nitrogen distance of 3.636 Å (3.549 Å in **6b**, see ESI†) indicating full dissociation. Accordingly, [**6a**]PF_6 and [**6b**]PF_6 can be regarded as dynamic $[(TL^{tBu}\text{-}\kappa N^1{:}\kappa N^2)Cu(RNC)]PF_6$ species. Finally, the enthalpies of formation from **5** and the respective isocyanide are found to be $\Delta H° = -21.5$ kcal mol^{-1} for both **6a** and **6b**,[25] which is significantly more exothermic than **5**·$NCCH_3$ and accounts for the higher stability of the isocyanide complexes.

Dioxygen and carbon–halogen bond activation

The interesting results reported for dioxygen activation with related guanidine copper complexes[14a,d] encouraged us to study the reactivity of the cationic copper(I) complex **5** towards dioxygen. Thereby, the bulkiness of the TL^{tBu} ligand might enforce end-on coordination of dioxygen and prevent the formation of dimeric species in a similar fashion as recently described with a sterically congested tetradentate guanidine ligand.[14a,d] However, oxygenation experiments in acetone at −78 °C employing $[(TL^{tBu})Cu]SbF_6$, [**5**]SbF_6, prepared by reaction of TL^{tBu} with $[Cu(CH_3CN)_4]SbF_6$ in acetonitrile, have not been conclusive. The UV/vis profile of the reaction suggested that no stable Cu/O_2 adduct had formed and that decomposition occurs even at −78 °C.[28]

Exposure of an acetone solution of [**5**]PF_6 to the air at room temperature resulted in the formation of a green solution, from

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which deep-green crystals of the acetone solvate [**7**]$PF_6 \cdot C_3H_6O$, suitable for X-ray diffraction analysis, were isolated in high yield (Scheme 4). The asymmetric unit contains two structurally independent moieties, and the molecular structure of one cation **7** is shown in Fig. 2, revealing that a copper(II) complex $[(TL^{tBu})Cu(HCO_3\text{-}\kappa O)]PF_6$ with a monodentate bicarbonate ligand has formed. Presumably, the reaction proceeds *via* formation of an intermediate Cu(II) hydroxo complex $[(TL^{tBu})Cu(OH)]PF_6$, which further reacts with CO_2 from the atmosphere to give the bicarbonate complex [**7**]PF_6. The strong activity of the hydroxo intermediate in CO_2 fixation can be ascribed to the strong electron-donating property of the ligand TL^{tBu}, enhancing the nucleophilicity of the coordinated hydroxide, as previously noted for related systems.[29] Several other examples of CO_2 fixation and activation by Cu(II) complexes have been reported,[30] although the major body of related work deals with Zn(II) complexes, which serve as functional models for carbonic anhydrase, an enzyme that catalyzes hydration of CO_2 and dehydration of HCO_3^-.[31]

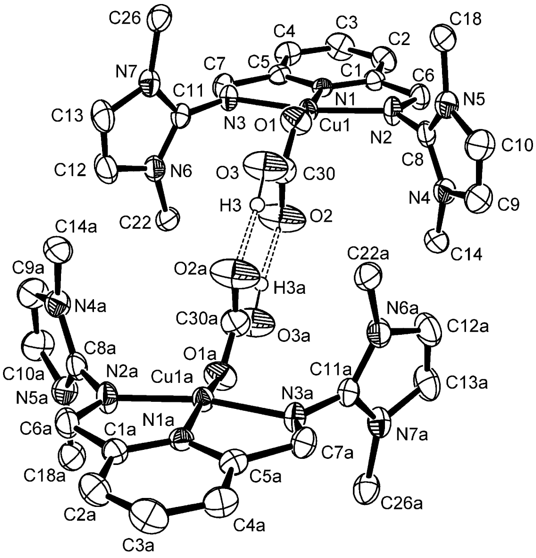

Fig. 2 ORTEP drawing of one of the two independent hydrogen-bridged dimers of the $[(TL^{tBu})Cu(HCO_3\text{-}\kappa O)]^+$ cation **7** in [**7**]$PF_6 \cdot C_3H_6O$ with thermal displacement parameters drawn at 50% probability, methyl groups have been omitted for clarity. The lower half of the molecule is generated by inversion.

Both structurally independent complex cations $[(TL^{tBu})Cu(HCO_3\text{-}\kappa O)]^+$ in [**7**]$PF_6 \cdot C_3H_6O$ display slightly distorted square-planar environments around the copper center, and the sums of the four *cis* angles are 360.2 and 359.3°, respectively. The N–Cu–N angles of about 81° are significantly smaller than the N–Cu–O angles of about 99° (Table 1). Both cations exhibit a slight butterfly-like deformation with the copper atoms showing deviations of 0.06 and 0.05 Å from the planes defined by N1, N2 and N3 and by N8, N9 and N10, respectively, whereas the metal-bound oxygen atoms O1 and O4 of the bicarbonate ligands are significantly more displaced by 0.187 and as much as 0.48 Å, which is presumably a consequence of minimizing the steric interaction with the bulky di-*tert*-butylimidazolin-2-ylidene moieties. Accordingly, the N1–Cu1–O1 and N8–Cu2–O4 angles of 170.81(9)° and 168.67(11)° deviate significantly from linearity. With respect to the copper coordination sphere, each bicarbonate ligand adopts a perpendicular conformation, so that the structure of both cations can be regarded as being essentially C_s-symmetric with each plane containing the respective bicarbonate ligand, the copper atom and the pyridine nitrogen atom.

Table 1 Selected bond lengths (Å) and angles (°) for [**7**]PF_6, [**8**]CF_3SO_3 and [**8**]$CuCl_2$

	[**7**]$PF_6 \cdot C_3H_6O$	[**8**]CF_3SO_3	[**8**]$CuCl_2$
Cu–N1	1.926(2)/1.934(3)	1.951(3)	1.9364(11)
Cu–N2	1.957(2)/1.952(3)	1.968(3)	1.9505(12)
Cu–N3	1.972(2)/1.962(2)	1.987(3)	1.9652(14)
Cu–X	1.906(3)/1.926(3)	2.2207(12)	2.2339(4)
C8–N2	1.343(3)/1.342(4)	1.355(5)	1.3458(17)
C11–N3	1.353(4)/1.348(4)	1.343(5)	1.3479(18)
N1–Cu–N2	81.50(10)/81.32(10)	81.14(13)	81.44(5)
N1–Cu–N3	81.60(9)/81.54(10)	80.76(13)	80.82(5))
N1–Cu–X	170.81(9)/168.67(11)	167.57(9)	176.30(3)
N2–Cu–X	96.77(10)/98.09(10)	101.17(10)	99.12(3)
N3–Cu–X	99.42(9)/99.25(11)	98.56(10)	98.83(3)

Structurally characterized complexes containing monodentate bicarbonate ligands are rare,[32a] and we could only identify five structures of this type containing copper(II),[32] which, except for one Cu–bis(phenanthroline) system with *d*(Cu–O) = 1.998(11) Å, reveal elongated Cu–O distances in the range 2.211 to 2.591 Å because of Jahn–Teller distortion. In comparison, [**7**]PF_6 exhibits significantly shorter distances with Cu1–O1 = 1.906(3) Å and Cu2–O4 = 1.926(3) Å. The angles in the bicarbonate units are close to 120°, and the distances are as follows: C30–O1 = 1.255(4) Å, C30–O2 = 1.233(5) Å, C30–O3 = 1.335(5) Å (cation 1); C60–O4 = 1.259(4) Å, C60–O5 = 1.242(5) Å, C60–O6 = 1.332(5) Å (cation 2). These pronounced differences clearly indicate that the hydrogen atoms of the HCO_3^- units are bound to O3 and O6, respectively, and this could be confirmed by free refinement of these hydrogen positions. Another pertinent feature of this structure is the molecular packing, which involves inversion-symmetric dimers of both independent cations in the asymmetric unit *via* hydrogen bonding of the bicarbonate groups, as observed for some other transition metal bicarbonate complexes (Fig. 2).[33] Short O3–H···O2 [1.63(5) Å] and O6–H···O5 contacts [1.72(7) Å] are observed, and the two hydroxy groups point almost linearly towards the oxygen atoms with O–H···O angles of 176(5) and 172(6)°, which indicates the presence of strong hydrogen bonds.[34]

Another hint of the high reactivity of the cationic copper(I) complex **5** arises from its reactivity in chlorinated solvents. For instance, mixing $[Cu(MeCN)_4]PF_6$ and TL^{tBu} in dichloromethane or chloroform results in an immediate color change from colorless to deep green, and from both solvents the copper(II) complex $[(TL^{tBu})CuCl]PF_6$, [**8**]PF_6, can be isolated almost quantitatively in pure form (Scheme 4). Similar reactivity towards $CHCl_3$ and CH_2Cl_2 has been observed for other copper(I) complexes containing electron-rich *N*-donor ligands.[17b,35] It had been assumed that the dechlorination process is radical in nature;[36] more recently published studies on carbon–halogen bond activation, however, described a reaction mechanism involving (a) an oxidative addition of the copper(I) complex to the C–X bond of a substrate to afford a copper(III) organometallic intermediate, followed by (b) a bimolecular reaction of the intermediate to give the C–C coupled dimer and the copper(II)–halide complex as products.[37] Ligand effects on the redox reactivity of copper(I) complexes are thus

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of great importance, and ligands with stronger electron-donor abilities are more likely to support a high oxidation state proposed for the copper(III) organometallic intermediate, which results in an increased reactivity of the respective copper(I) complexes towards halide substrates. Accordingly, we conclude that this feature also explains the pronounced reactivity of the TL$^{t\mathrm{Bu}}$ copper(I) complexes presented here.

Single crystals of [**8**]PF_6 could be obtained by diffusion of diethyl ether into a CH_2Cl_2 solution, the structure, however, could not be satisfactorily refined because of a severely disordered PF_6^- counterion. Therefore, the corresponding triflate [**8**]CF_3SO_3 was prepared and characterized by X-ray diffraction analysis, and the resulting molecular structure of the cation **8** is shown in Fig. 3. The asymmetric unit consists of a [(TL$^{t\mathrm{Bu}}$)CuCl]$^+$ cation and a $CF_3SO_3^-$ anion. The copper atom is four-coordinate with three nitrogen donor atoms provided by the chelating ligand. The fourth ligand is a chloride ion covalently bound to the Cu(II) center, and this must have been supplied by reductive dechlorination of the CH_2Cl_2 solvent (*vide supra*). The geometry around the copper center can be regarded as slightly distorted square-planar, and the sum of the four *cis* angles is 361.63°, with the N–Cu–N angles of 81.14(13) and 80.76(13)° being significantly smaller than the N–Cu–Cl angles of 101.17 (10) and 98.56(10)°. Compared to the structural parameters determined for the two independent cations in [**7**]PF_6, the cation in [**8**]CF_3SO_3 exhibits a considerably more pronounced butterfly-like deformation with the copper and chlorine atoms showing deviations of 0.19 and 0.88 Å from the plane defined by the nitrogen donor atoms N1, N2 and N3. Accordingly, a comparatively small N1–Cu–Cl angle of 167.57(9)° is observed (Table 1).

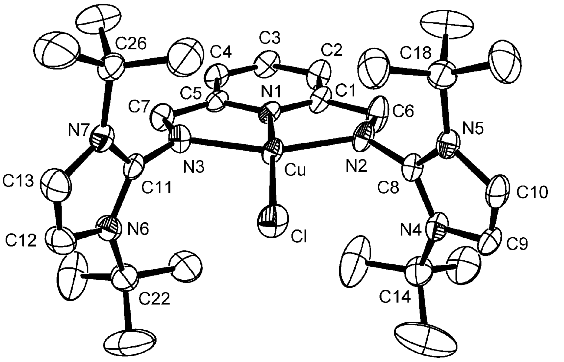

Fig. 3 ORTEP drawing of the [(TL$^{t\mathrm{Bu}}$)CuCl]$^+$ cation **8** in [**8**]PF_6 with thermal displacement parameters drawn at 50% probability.

The copper–nitrogen distances in [**8**]CF_3SO_3 are Cu–N1 = 1.951(3) Å, Cu–N2 = 1.968(3) Å and Cu–N3 = 1.987(3) Å. Whereas the Cu–N1 distance between copper and the pyridine-nitrogen atom falls in the expected range, the Cu–N(imine) bond lengths are appreciably shorter (approximately 0.1 Å) than those observed in analogous copper(II) complexes containing related pyridine-2,6-diimine ligands.[17] This shortening is concomitant with a lengthening of the copper–chlorine distance [Cu–Cl = 2.2207(12) Å] and reflects the strong electron-releasing capability of the TL$^{t\mathrm{Bu}}$ ligand, which has been proposed based on a strong contribution of the ylidic resonance structure **B** shown in Scheme 2. Charge separation in coordinated TL$^{t\mathrm{Bu}}$ can also be clearly deduced from the observation of almost ideally perpendicular imidazole moieties with respect to the square copper coordination plane (dihedral angles = 89.6 and 87.8°). This orientation rules out the possibility of π-interaction between the exocyclic nitrogen atoms and the imidazole rings, leading to elongated C–N distances [N2–C8 = 1.355(5) Å and N3–C11 = 1.343(5) Å], much longer than expected for a N–C(sp^2) double bond (1.28 Å) and almost in the range of a N–C(sp^2) single bond (1.38 Å).[38] In comparison, structurally characterized 2-iminoimidazolines such as the building block 1,3-di-*tert*-butylimidazolin-2-imine (**3**) exhibit much shorter C–N bonds [*d*(C–N) = 1.295(2) Å in **3**].[9] Consequently, the imidazole heterocycles in [**8**]CF_3SO_3 also show consistent differences from the structure of **3**, for which significantly longer internal C–N bonds [1.390(2) and 1.395(2) Å] together with a smaller internal N–C–N angle [105.3(1)°] were observed. This indicates an increase of imidazolium character upon coordination of the imine nitrogen atom, since the structural comparison of imidazolium salts with their corresponding free imidazolin-2-ylidenes reveals the same trend with shortening of the C–N bonds and widening of the N–C–N angles.[39] It should be noted that these considerations are also valid for all other structurally characterized copper complexes discussed in this paper.

Reactions of TL$^{t\mathrm{Bu}}$ with copper(I) halides

Over the past few years, copper(I) halide complexes with nitrogen-based ligands have attracted much attention because of their catalytic use in atom transfer radical polymerization (ATRP).[19,20] Therefore, we decided to study in detail the reactivity of TL$^{t\mathrm{Bu}}$ towards copper(I) bromide and chloride. The reaction of TL$^{t\mathrm{Bu}}$ with copper(I) bromide or with the more reactive dimethylsulfide copper(I) bromide, [(Me_2S)CuBr],[40] in THF afforded a yellow solution, from which a yellow powdery material could be isolated by precipitation with *n*-hexane. Elemental analysis and ^{1}H and ^{13}C NMR spectroscopy pointed to the formation of a symmetric copper(I) complex of the type [(TL$^{t\mathrm{Bu}}$)CuBr] (**9a**). For instance, the resonances for the pyridine ring protons (7.31–7.45 ppm) and for the bridging CH_2 protons (4.94 ppm) in the product are shifted to higher field compared to the signals of the free ligand. However, cooling of an acetone-d_6 solution of **9a** results in broadening of signals, suggesting the formation of a compound with an asymmetric coordination sphere. Since the coalescence temperature could not be reached in acetone-d_6, the low-temperature ^{1}H NMR spectra were additionally recorded in THF-d_8 exhibiting the coalescence temperature at −97 °C and giving the fully resolved spectrum at −112 °C (Fig. 4). It can be seen that the singlet belonging to the bridging methylene protons (d) separates into two peaks (d′). The same behaviour is observed for the singlet from the imidazoline CH hydrogen atoms (c) and the doublet from the pyridine ring protons (b), clearly indicating that one ligand arm remains uncoordinated and that the rapid intramolecular rearrangement can be stopped at low temperature on the NMR timescale. Line-shape analysis was used to estimate the barrier of rearrangement, and it is found to be approximately 8 kcal mol^{-1} (or 33 kJ mol^{-1}).[41]

Further support stems from DFT calculations, which for **9a** confirm the presence of a [(TL$^{t\mathrm{Bu}}$-κN^1:κN^2)CuBr] structure in the gas phase (see ESI† for further details). In addition, the molecular structure of the acetone solvate **9a**·C_3H_6O could be established by means of X-ray diffraction analysis, revealing the presence of

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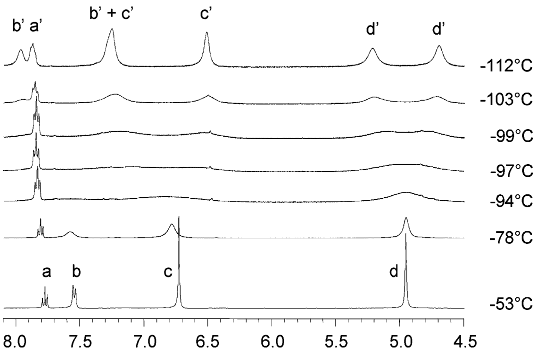


Fig. 4 Variable-temperature ^{1}H NMR study and fluxional behaviour of [(TL^{tBu}-κN^1:κN^2)CuBr] (**9a**) (400 MHz, THF-d_8).

a CuBr unit coordinated in a chelating fashion by the pyridine and the imine nitrogen atom N2 (Fig. 5). As a result, copper attains coordination number 3 and a trigonal-planar geometry with the sum of the angles around the copper atom of 359.91°. The Cu–Br distance of 2.2746(5) Å and the Cu–N distances of Cu–N1 = 2.0855(19) Å and Cu–N2 = 1.9630(19) Å fall in the expected ranges for these types of bonds. The acetone molecule forms a C–H···O1 hydrogen bond to one of the imidazolium moieties with an angle of 162.6° and an O···H distance of 2.37 Å, which is significantly shorter than the sum of the van der Waals radii of 2.72 Å [r_{vdW}(H) = 1.20 Å, r_{vdW}(O) = 1.52 Å].[42] Although tricoordinate copper complexes are well established,[43] only a limited number of such low-coordinate copper halides with *N*-donor ligands have been structurally characterized, and in particular, copper(I) bromide structures showing an N_2CuBr environment as observed in **9a** are exceptionally rare.[44,45] Again, the structure of **9a** is a clear manifestation of the inability of the TL^{tBu} ligand to support a tetrahedral copper(I) environment on steric grounds, as also discussed for the copper(I) isocyanide complexes [**6**]PF$_6$ (*vide supra*).

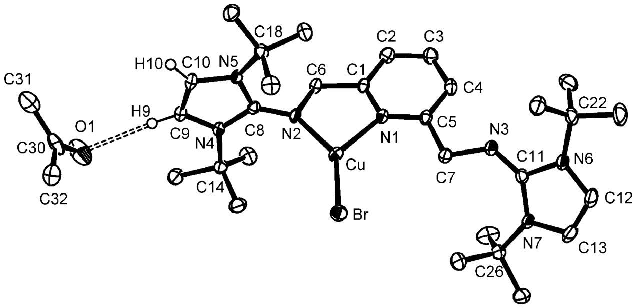
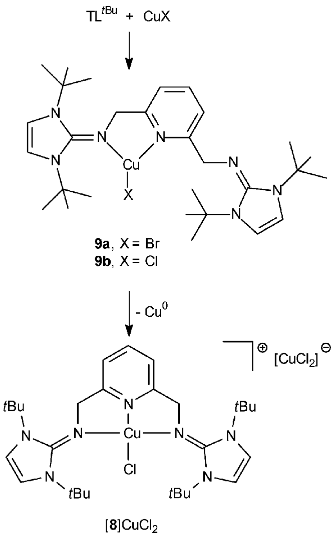


Fig. 5 ORTEP drawing of [(TL^{tBu}-κN^1:κN^2)CuBr]·C_3H_6O (**9a**·C_3H_6O) showing an intermolecular non-covalent contact with thermal displacement parameters drawn at 50% probability. Selected bond distances [Å] and angles [°]: Cu–N1 2.0855(19), Cu–N2 1.9630(19), Cu–Br 2.2746(5), C8–N2 1.336(3), C11–N3 1.289(3), N1–Cu–N2 83.71(8), N1–Cu–Br 134.21(5), N2–Cu–Br 141.99(6).

The reaction of TL^{tBu} with copper(I) chloride in THF at ambient temperature resulted in the initial formation of a yellow solution followed by progressive formation of a deep-green precipitate together with the deposition of copper(0) on the wall of the Schlenk flask (Scheme 5). The deep-green precipitate was isolated by filtration, and the copper(I) complex **9b** was isolated by precipitation from the THF filtrate with *n*-hexane. Formation of **9b** was confirmed by means of ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis, which is in good agreement with the formula [(TL^{tBu}-κN^1:κN^2)CuCl]. As described for the CuBr complex **9a**, low-temperature NMR studies and DFT calculations (see ESI†) also support the presence of a fluxional tricoordinate structure for **9b** in solution with the TL^{tBu} ligand coordinated in a κ^2-fashion.



Scheme 5

Numerous attempts to grow crystals of **9b** suitable for the X-ray diffraction analysis were unsuccessful and led to decomposition and formation of the deep-green precipitate mentioned above. By NMR, this material proved to be paramagnetic, and its elemental analysis is in perfect agreement with the formula [(TL^{tBu})Cu$_2$Cl$_3$], suggesting the presence of a mixed-valence copper system. The result of an X-ray diffraction analysis of crystals grown from dichloromethane solution confirmed this composition and revealed the formation of [(TL^{tBu})CuCl][CuCl$_2$], [**8**]CuCl$_2$, containing the copper(II) cation [(TL^{tBu})CuCl]$^+$ (**8**) and the dichlorocuprate(I) anion (Fig. 6). The cationic part of [**8**]CuCl$_2$ exhibits the same four-coordinate square-planar geometry as described for the cation in [**8**]CF$_3$SO$_3$. Comparison of the two structures reveals that the cation in [**8**]CuCl$_2$ displays a less pronounced butterfly-like deformation with the copper and chlorine atoms showing deviations of 0.08 and 0.31 Å from the

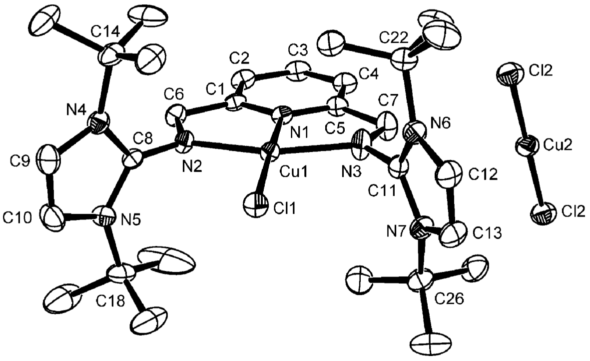


Fig. 6 ORTEP drawing of [(TL^{tBu})CuCl][CuCl$_2$], [**8**]CuCl$_2$, with thermal displacement parameters drawn at 50% probability. Only one of the two independent, inversion-symmetric anions is shown.

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plane defined by the nitrogen donor atoms N1, N2 and N3. Consequently, a larger N1–Cu–Cl angle of 176.30(3)° is observed, and the sum of the four *cis* angles around the copper atom is almost ideal (360.21°). All three copper–nitrogen distances in [**8**]$CuCl_2$ [Cu–N1 = 1.9364(11) Å, Cu–N2 = 1.9505(12) Å, Cu–N3 = 1.9652(14) Å] are shorter than those in [**8**]CF_3SO_3, associated with a slightly elongated copper–chloride bond [Cu–Cl = 2.2339(4) Å] (Table 1).

As described for [**8**]CF_3SO_3, the imidazole rings in [**8**]$CuCl_2$ also adopt an almost perfectly perpendicular arrangement relative to the square-planar copper coordination sphere (dihedral angles = 89.98 and 88.03°) together with significantly elongated N2–C8 and N3–C11 distances of 1.3458(17) and 1.3479(18) Å. The asymmetric unit contains two halves of two independent dichlorocuprate $[CuCl_2]^-$ moieties with the copper atoms located on inversion centres. As a consequence, ideally linear orientations with Cl–Cu–Cl angles of 180° are observed, and the Cu–Cl distances in two independent anions are 2.0954(6) and 2.1027(5) Å, respectively, consistent with previously observed values.[46]

The mixed-valence copper(I/II) complex [**8**]$CuCl_2$ is obviously a product of the partial disproportionation of the initially formed copper(I) complex [(TL^{tBu}-κN^1:κN^2)CuCl] (**9b**). Thus, three equivalents of **9b** lead to the formation of [**8**]$CuCl_2$ and elemental copper in a 1 : 1 ratio, implying that two thirds of the copper(I) atoms disproportionate to give Cu(II) and Cu(0) with the remaining Cu(I) contained in the $CuCl_2^-$ anion. This reaction must be accompanied by release of two equivalents of the free ligand, which has been confirmed by isolation of TL^{tBu} from the hexane mother liquor after complete separation of **9b** and [**8**]$CuCl_2$. Presumably, the instability of **9b** is a consequence of both the electronic and structural properties of TL^{tBu}, which strongly supports the higher oxidation state of copper because of its strong electron-releasing capability and its rigid and planar arrangement of the nitrogen donor atoms. The propensity of copper(I) complexes to undergo disproportionation is well established,[43,47] and is strongly dependant on the auxiliary ligands[35d,48] and solvents.[49] Many examples of mixed-valence copper complexes are known in the literature, but they are mainly obtained either by partial oxidation of copper(I), partial reduction of copper(II) or by using redox active ligand.[50] Few other examples of cationic Cu(II) complexes containing the dichlorocuprate(I) counterion have been described,[51] however, we are not aware of any case where such mixed-valence systems have been accessed by disproportionation as described here.

We propose that the different reactivity of the complexes [(TL^{tBu}-κN^1:κN^2)CuX] (X = Br, **9a**; X = Cl, **9b**) obtained from the reactions of TL^{tBu} with copper(I) bromide or chloride, respectively, could be a consequence of the soft acid behavior of copper(I).[44] Accordingly, the chloride anion is considered to be a weaker ligand for copper(I) than the bromide anion and therefore imposes a stronger driving force towards disproportionation and formation of copper(II) species as observed for **9b**. In contrast, no such reactivity is observed for **9a**.

Conclusions

With this contribution, we have shown that 2-iminoimidazolines such as 1,3-di-*tert*-butylimidazolin-2-imine (**3**) can be conveniently derivatized by *N*-alkylation and are therefore suitable building blocks for the synthesis of multidentate poly(imidazolin-2-imine) ligands with exceptional basic and nucleophilic properties, which should exceed those of related guanidine-type systems.[9] As a result, copper(I) complexes of the pincer ligand 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine, TL^{tBu}, are highly reactive and exhibit a pronounced tendency to form stable, square-planar copper(II) complexes of the type [(TL^{tBu}-κ^3)CuX] allowing effective aerobic CO_2 fixation (X = bicarbonate, HCO_3-κ*O*), C–Cl bond activation and Cu(I) disproportionation (X = Cl). These results point toward the possibility of employing this TL^{tBu}/copper system in oxidation catalysis and in atom transfer radical polymerization (ATRP), and such studies are underway in our laboratories. Thereby, the steric and electronic properties of the poly(imidazolin-2-imine) ligand could be easily tuned by introducing various available 2-iminoimidazolines[9] or by using different bridging moieties.

Experimental

All operations were performed in an atmosphere of dry argon using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on JEOL-GX 400 (400 MHz), JEOL-GX 270 (270 MHz), Bruker AC 200, Bruker DPX 200, Bruker AV 300 and Bruker DPX 400 devices. The chemical shifts are given in ppm relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), sept. (septet) and br. (broad, for unresolved signals). Elemental analysis (C, H, N) by combustion and gas chromatography was carried out with a Vario EL III CHNS, Carlo Erba Mod. 1106 and a Vario Micro Cube. Mass spectrometry was performed with a Finnigan MAT 90 and high-resolution electrospray ionization (ESI) Finnigan MAT 95 XL Trap devices. The IR spectra were recorded on Bruker Vertex 70 and UV-Vis spectra on Varian Cary 50 devices. Copper(I) chloride, copper(I) bromide and 2,6-pyridinedimethanol were obtained from Acros, and $Cu(MeCN)_4PF_6$ was obtained from Strem chemicals and used as received. 2,6-Bis[(tosyloxy)methyl]pyridine[21] and 1,3-di-*tert*-butylimidazolin-2-imine[9] were prepared according to literature procedures.

[(TL^{tBu}H_2)(OTs)$_2$], 4

A solution of the 2,6-bis[(tosyloxy)methyl]pyridine (4.471 g, 10 mmol) in THF (70 mL) was treated dropwise with 1,3-di-*tert*-butylimidazolin-2-imine (**3**) (3.965 g, 20.3 mmol) in THF (30 mL) at ambient temperature, and the resulting reaction mixture was subsequently heated in boiling THF for 24 h. The precipitate was filtered off, washed with THF (2 × 20 mL) and dried in high vacuum. The product was isolated as a pale pink solid (4.7 g, 53%). A subsequent reduction of the volume of the filtrate and further refluxing for 24 h afforded the second portion of the product isolated as described above (cumulative yield: 7.3 g, 87%). Found: C, 61.45; H, 7.23; N, 11.63; S, 7.48. Calc. for $C_{43}H_{63}N_7O_6S_2$: C, 61.62; H, 7.58; N, 11.70; S, 7.65%; δ_H (400 MHz, D_2O; Me_4Si) 7.91 (1 H, t, *p*-Py), 7.64 (4 H, d), 7.49 (2 H, d, *m*-Py), 7.40 (4 H, s, NCH), 7.31 (4 H, d), 4.05 (4 H, s, Py–CH_2), 2.35 (6 H, s), 1.63 (36 H, s, CCH_3); δ_C(100.53 MHz, D_2O; Me_4Si) 156.1, 143.4, 142.5,

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139.9, 139.1, 129.6, 125.8, 121.3, 117.4, 61.5, 53.7, 29.1, 20.4; *m/z* (FAB$^+$) 665 (M$^+$–OTs, 54%), 494.4 (M$^+$–H(OTs)$_2$, 100).

2,6-Bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine, TL^{tBu}

A suspension of **4** (7.25 g, 8.65 mmol) in THF (120 mL) was cooled to 0 °C, and KO*t*Bu (2.329 g, 20.76 mmol) was added. The reaction mixture was stirred at ambient temperature for 2 h, filtered and the solvent was removed *in vacuo.* The product was extracted with a mixture of toluene (50 mL) and *n*-hexane (50 mL) and filtered. Removal of the solvent afforded the product as an off-white solid (4.1 g, 95%). Found: C, 70.56; H, 9.55; N, 19.83. Calc. for $C_{29}H_{47}N_7$: C, 70.55; H, 9.59; N, 19.86; δ_H(400 MHz, C_6D_6; Me_4Si) 8.02 (2 H, d, *m*-Py), 7.72 (1 H, t, *p*-Py), 6.02 (4 H, s, NCH), 5.38 (4 H, s, Py–CH$_2$), 1.43 (36 H, s, CCH$_3$); δ_C (100.53 MHz, C_6D_6; Me_4Si) 164.1 (*o*-C), 146.5 (NCN), 136.2 (*p*-C), 118.7 (*m*-C), 108.4 (N*C*H), 58.1 (C–Py), 54.4 (N*C*Me), 29.5 (*C*CH$_3$); δ_H(400 MHz, acetone-*d*$_6$; Me_4Si) 7.69 (1 H, t, *p*-Py), 7.55 (2 H, d, *m*-Py), 6.35 (4 H, s, NCH), 4.85 (4 H, s, Py–CH$_2$), 1.56 (36 H, s, CCH$_3$); δ_H (400 MHz, CD_3CN, Me_4Si) 7.67 (1 H, t, *p*-Py), 7.48 (2 H, d, *m*-Py), 6.33 (4 H, s, NCH), 4.79 (4 H, s, Py–CH$_2$), 1.53 (36 H, s, CCH$_3$); *m/z* (CI) 493 (M$^+$, 36%), 437 (M$^+$–*t*Bu, 100), 380 (M$^+$–2*t*Bu, 58).

[(TL^{tBu})Cu]PF$_6$, [5]PF$_6$

A solution of TL^{tBu} (198 mg, 0.4 mmol) in CH$_3$CN (5 mL) was added to the solution of Cu(CH$_3$CN)$_4$PF$_6$ (149 mg, 0.4 mmol) in CH$_3$CN (5 mL) at ambient temperature. The reaction mixture turned yellow upon addition of the ligand. After stirring for 45 min at room temperature, the solvent was removed under vacuum to give a yellow solid material (263 mg, 94%). Found: C, 49.49; H, 7.34; N, 13.58. Calc. for $C_{29}H_{47}N_7CuPF_6$: C, 49.60; H, 6.75; N, 13.96; δ_H(400 MHz, acetone-*d*$_6$; Me_4Si) 7.98 (1 H, t, *p*-Py), 7.73 (2 H, d, *m*-Py), 6.56 (4 H, s, NCH), 5.01 (4 H, s, Py–CH$_2$), 1.44 (36 H, s, CCH$_3$); δ_C (100.53 MHz, acetone-*d*$_6$; Me_4Si) 164.2 (*o*-C), 151.2 (NCN), 139.5 (*p*-C), 122.6 (*m*-C), 112.1 (N*C*H), 61.2 (C–Py), 57.6 (N*C*Me), 31.0 (*C*CH3); δ_H(400 MHz, CD_3CN, Me_4Si) 7.82 (1 H, t, *p*-Py), 7.46 (2 H, d, *m*-Py), 6.69 (4 H, s, NCH), 4.77 (4 H, s, Py–CH$_2$), 1.58 (36 H, s, CCH$_3$).

[(TL^{tBu}-κ*N*^{1}:κ*N*^{2})Cu(*t*BuNC)]PF$_6$, [6a]PF$_6$

A solution of TL^{tBu} (198 mg, 0.4 mmol) in THF (5 mL) was added to a solution of Cu(CH$_3$CN)$_4$PF$_6$ (149 mg, 0.4 mmol) in THF (5 mL) at ambient temperature. Some minutes later *t*BuNC (47 µL, 0.41 mmol) was added and the mixture was stirred for 1 h. Evaporation of the solvent and washing with *n*-hexane (2 × 5 mL) afforded the product, which was isolated as a pale yellow solid (286 mg, 91%). Found: C, 51.56; H, 7.00; N, 13.94. Calc. for $C_{34}H_{56}N_8CuPF_6$: C, 52.00; H, 7.19; N, 14.27; δ_H (400 MHz, acetone-*d*$_6$; Me_4Si) 7.96 (1 H, t, *p*-Py), 7.59 (2 H, d, *m*-Py), 6.85 (4 H, s, NCH), 4.91 (4 H, s, Py–CH$_2$), 1.65 (36 H, s, CCH$_3$), 1.48 (9 H, s, *t*BuNC); δ_C (100.53 MHz, acetone-*d*$_6$; Me_4Si) 164.1 (*o*-C), 152.8 (NCN), 140.4 (*p*-C), 137.0 (*C*NC*t*Bu), 122.1 (*m*-C), 113.2 (N*C*H), 61.5 (C-Py), 59.1 (CN*Ct*Bu), 58.8 (N*C*Me), 31.27 (CNC*tBu*), 31.23 (*C*CH3) ppm, ν_{max}(KBr)/cm^{-1} 2179 (C≡N); *m/z* (FAB$^+$) 639.8 (M$^+$–PF$_6$, 3%), 556.8 (M$^+$–*t*BuNC–PF$_6$, 3), 493.9 (TL^{tBu+}, 10).

[(TL^{tBu}-κ*N*^{1}:κ*N*^{2})Cu(2,6-*o*-XyNC)]PF$_6$, [6b]PF$_6$

A solution of TL^{tBu} (198 mg, 0.4 mmol) in THF (5 mL) was added to a solution of Cu(CH$_3$CN)$_4$PF$_6$ (149 mg, 0.4 mmol) in THF (5 mL) at ambient temperature. Some minutes later 2,6-dimethylphenyl isocyanide (52.5 mg, 0.40 mmol) was added and the mixture was stirred for 1 h. Evaporation of the solvent and washing with *n*-hexane (2 × 5 mL) afforded the product, which was isolated as a pale yellow solid (297 mg, 89%). Found: C, 54.85; H, 6.52; N, 13.10. Calc. for $C_{38}H_{56}N_8CuPF_6$: C, 54.76; H, 6.77; N, 13.44; δ_H (400 MHz, acetone-*d*$_6$; Me_4Si) 8.01 (1 H, t, *p*-Py), 7.64 (2 H, d, *m*-Py), 7.41-7.24 (3 H, m, Xy–H), 6.85 (4 H, s, NCH), 5.01 (4 H, s, Py–CH$_2$), 2.36 (6 H, s, Ar–CH$_3$), 1.65 (36 H, s, CCH$_3$); δ_C (100.61 MHz, acetone-*d*$_6$; Me_4Si) 164.0 (*o*-C), 152.9 (NCN), 140.6 (*p*-C), 136.7, (Xy-*o*-*C*) 131.6 (Xy-*p*-*C*), 130.1 (Xy-*m*-*C*), 122.2 (*m*-C), 111.3 (N*C*H), 61.6 (C-Py), 58.9 (N*C*Me), 31.2 (CNC*tBu*), 19.7 (Xyl-*Me*); ν_{max}(KBr)/cm^{-1} 2140 (C≡N).

[(TL^{tBu})Cu(HCO$_3$-κ*O*)]PF$_6$, [7]PF$_6$

A solution of [5]PF$_6$ (50 mg, 0.0712 mmol) in acetone (3 mL) was exposed to the air at room temperature and immediately changed color from light yellow to deep-green. Slow evaporation of the solvent over a period of two days afforded deep-green crystals, which were isolated, washed with diethyl ether (2 × 5 mL) and dried *in vacuo* (46 mg, 85%). Found: C, 47.49; H, 6.03; N, 12.87. Calc. for $C_{30}H_{48}N_7CuPF_6O_3$: C, 47.21; H, 6.34; N, 12.85; λ_{max}(acetone)/nm 371 (ε/dm^3 mol^{-1} cm^{-1} 1764) and 622 (286); ν_{max}(KBr)/cm^{-1} 3209, 2983, 1618, 1580, 1488, 1448, 1425, 1371, 1340, 1299, 1234, 1195, 1107, 1084, 1052, 965, 835, 786, 703 cm^{-1}.

[(TL^{tBu})CuCl]PF$_6$, [8]PF$_6$

A solution of TL^{tBu} (278 mg, 0.563 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise to a solution of Cu(CH$_3$CN)$_4$PF$_6$ (200 mg, 0.537 mmol) in CH$_2$Cl$_2$ (10 mL) at ambient temperature, the reaction mixture turned deep green. After 3 h stirring, solvent volume was reduced to 5 mL and the product was precipitated with addition of *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying *in vacuo* afforded the product as a deep-green solid (370 mg, 94%). Found: C, 47.01; H, 6.36; N, 13.16. Calc. for $C_{29}H_{47}N_7CuClPF_6$: C, 47.22; H, 6.42; N, 13.29; λ_{max}(acetone)/nm 371 (ε/dm^3 mol^{-1} cm^{-1} 1815) and 627 (271); *m/z* (FAB$^+$) 592.7 (M$^+$–PF$_6$, 82%), 493.9 (TL^{tBu+}, 6).

[(TL^{tBu}-κ*N*^{1}:κ*N*^{2})CuBr], 9a

A solution of TL^{tBu} (262 mg, 0.53 mmol) in THF (10 mL) was added dropwise to a suspension of [(Me$_2$S)CuBr] (103 mg, 0.50 mmol) in THF (5 mL) at 0 °C. During the addition of the ligand the reaction mixture turned yellow and the starting material dissolved. The solution was allowed to warm to room temperature over 15 min, the volume of THF was reduced to 5 mL and the product was precipitated with *n*-hexane (40 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying *in vacuo* afforded the product as a yellow solid (286 mg, 90%). Found: C, 54.79; H, 7.61; N, 14.72. Calc. for $C_{29}H_{47}N_7CuBr$: C, 54.66; H, 7.43; N, 15.39; δ_H (200.13 MHz, C_6D_6; Me_4Si) 7.45-7.31 (3 H, m), 6.25 (4 H, s, NCH), 4.94 (4 H, s, Py–CH$_2$), 1.43 (36 H, s, CCH$_3$); δ_C (50.32 MHz, C_6D_6; Me_4Si) 162.8 (*o*-C), 150.7 (NCN), 136.8

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Table 2 Crystallographic data for [**7**]PF_6, [**8**]CF_3SO_3, [**8**]$CuCl_2$ and **9a**

	[**7**]$PF_6 \cdot C_3H_6O$	[**8**]CF_3SO_3	[**8**]$CuCl_2$	**9a**$\cdot C_3H_6O$
Empirical formula	$C_{33}H_{54}CuN_7O_4F_6P$	$C_{30}H_{47}ClCuF_3N_7O_3S$	$C_{29}H_{47}Cl_3Cu_2N_7$	$C_{32}H_{53}BrCuN_7O$
FW	821.35	741.82	727.19	695.26
a/Å	9.3457(1)	17.8950(4)	14.9281(12)	10.3778(14)
b/Å	16.0642(1)	8.7368(2)	10.1533(8)	10.8771(14)
c/Å	28.0336(2)	24.0711(6)	22.6904(16)	15.850(2)
α/°	89.1268(3)	90	90	78.792(3)
β/°	81.5051(3)	105.9805(9)	98.363(3)	76.017(3)
γ/°	74.4997(5)	90	90	87.240(3)
V/Å^3	4009.85(6)	3617.96(15)	3402.6(5)	1703.0(4)
T/K	173	173	133	133
ρ_{calc}/g cm^{-1}	1.361	1.362	1.419	1.356
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P(-1)$	Cc	$P2_1/n$	$P(-1)$
Z	4	4	4	2
μ/mm^{-1}	0.656	0.791	1.516	1.850
2θ range/°	2.94–50.76	3.52–50.72	3.08–61.08	2.70–61.02
Total reflections	62895	9718	66907	37076
Unique data	14679	6063	10401	10339
'Observed' data $\{I > 2\sigma(I)\}$	12242	5530	8936	6676
R_{int}	0.040	0.045	0.022	0.053
$R1$ ('observed' data)	0.0509	0.0479	0.0365	0.0404
$wR2$ (all data)	0.1281	0.0957	0.0781	0.0930
GoF	1.04	1.026	1.046	1.011
No. of parameters	987	428	407	393
Res. electr. dens./e Å^{-3}	−0.59/0.69	−0.346/0.609	−0.327/0.66	−0.395/0.548

$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, and a and b are constants set by the program.

(*p*-C), 119.8 (*m*-C), 110.6 (N*C*H), 59.0 (C-Py), 56.6 (N*C*Me), 29.9 (C*C*H3).

[(TL^{tBu}-κN^1:κN^2)CuCl], 9b and [(TL^{tBu})CuCl][CuCl$_2$], [8]CuCl$_2$

A solution of TL^{tBu} (262 mg, 0.53 mmol) in THF (10 mL) was added dropwise to a suspension of CuCl (50 mg, 0.50 mmol) in THF (10 mL) at ambient temperature. During the addition of the ligand the reaction mixture turned yellow and the starting material dissolved. The mixture was stirred for 20 h at ambient temperature, during which time a formation of a green precipitate, accompanied by a mirror of elemental copper on the flask wall, was observed. Filtration, washing of the precipitate with THF (2 × 5 mL) and drying *in vacuo* afforded the compound [**8**]$CuCl_2$ as a deep green solid. The volume of the pale yellow filtrate was reduced to 5 mL and the compound **9b** was precipitated with addition of *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying *in vacuo* afforded the compound **9b** as a pale yellow solid.

[(TL^{tBu}-κN^1:κN^2)CuCl], 9b

(115 mg, 39%). Found: C, 58.41; H, 8.03; N, 16.08. Calc. for $C_{29}H_{47}N_7CuCl$: C, 58.76; H, 7.99; N, 16.54; δ_H(200.13 MHz, C_6D_6; Me_4Si) 7.51 (1 H, t, *p*-Py), 7.30 (2 H, d, *m*-Py), 6.09 (4 H, s, NCH), 5.19 (4 H, s, Py–CH_2), 1.48 (36 H, s, CCH_3); δ_C (50.32 MHz, C_6D_6; Me_4Si) 162.7 (*o*-C), 150.5 (NCN), 136.8 (*p*-C), 119.6 (*m*-C), 110.6 (N*C*H), 58.6 (C-Py), 56.5 (N*C*Me), 31.2 (C*C*H$_3$).

[(TL^{tBu})CuCl][CuCl$_2$], [8]CuCl$_2$

(65 mg, 36%, based on Cu). Found: C, 47.80; H, 6.51; N, 13.48. Calc. for $C_{29}H_{47}N_7Cu_2Cl_3$: C, 47.80; H, 6.52; N, 13.30; *m*/*z* (ESI) 593.5 (M^+–$CuCl_2$, 91%).

Single crystal X-ray structure determination of compounds [7]PF$_6$, [8]CF$_3$SO$_3$, [8]CuCl$_2$ and 9a

Crystal data and details of the structure determinations are presented in Table 2. Crystals of the compounds [**7**]PF_6 and [**8**]CF_3SO_3 were transferred to a Lindemann capillary. Measurements were carried out at 143 K (Oxford Cryosystems) on an area detector system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Raw data were corrected for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. The structures were refined on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included using a riding model or with rigid methyl groups allowed to rotate but not tip, exceptions were the freely refined hydrogens of hydrogencarbonate in compound [**7**]PF_6 or disordered methyls (see below). *Exceptions/special features*: For [**7**]PF_6, the *tert*-butyl methyl groups at the atoms C18 and C48 were disordered over two positions, which were refined ideally staggered with 49.9/50.1% occupancy and 83.9/16.1% occupancy, respectively, and appropriate similarity restraints. For [**8**]CF_3SO_3, the structure was refined as a racemic twin with a scale factor of 0.465(12).

Crystals of the compounds [**8**]$CuCl_2$ and **9a** were mounted on glass fibers and measured on a Bruker SMART 1000 CCD diffractometer at 133 K (Mo-Kα radiation, $\lambda = 0.71073$ Å). Absorption corrections were performed using multi-scans (program SADABS). Hydrogen atoms were included using rigid methyl groups allowed to rotate but not tip, or a riding model. *Exceptions/special features*: For [**8**]$CuCl_2$, the *tert*-butyl methyl

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groups at the atoms C22 and C26 were disordered over two positions, which were refined ideally staggered with 75.8/24.2% occupancy and 74.4/25.6% occupancy, respectively. One improbably short intramolecular H · · · H contact for the minor component at C26 may be attributable to a non-ideally staggered geometry; dimensions of disordered groups should in any case be interpreted with caution. For the disordered structures, a series of similarity restraints were used to improve stability of refinement. For the same reason, **[8]**CF_3SO_3 was additionally subjected to restraints of displacement parameters.

CCDC reference numbers 638693–638696.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703183a

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG Ta 189-6/1). D. P. thanks the Bavarian Science Foundation (Bayerische Forschungsstiftung) for a scholarship (2003–2006). We would like to thank Prof. Dr William B. Tolman and his group for helpful discussions.

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