ELSEVIER

Note

Protonation of *N*-heterocyclic carbene ligand coordinated to copper(I): Coordination mode of imidazolium cation as a function of counterion as determined by solid-state structures

Elizabeth D. Blue [a], T. Brent Gunnoe [a,*], Jeffrey L. Petersen [b], Paul D. Boyle [a]

[a] *Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA*
[b] *C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045, USA*

Abstract

Reactions of (IPr)Cu(X) (X = Cl or trifluoromethanesulfonate, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complexes with the strong acids HOTf or HCl result in protonation of the C2 carbon of the IPr ligand to form imidazolium cations. Coordination of the imidazolium to the resulting Cu^I system depends upon the identity of the two counterions (chloride or triflate). The copper complexes [(IPrH)Cu(OTf)(μ-OTf)]$_2$ and [IPrH][CuCl$_2$] as well as the imidazolium salt [IPrH][OTf] have been characterized by NMR spectroscopy and single crystal X-ray diffraction studies.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Copper; *N*-Heterocyclic carbene; Imidazolium

1. Introduction

N-Heterocyclic carbenes (NHC) (Chart 1), first isolated as free carbene species by Arduengo and coworkers [1,2], have received substantial attention as relatively robust ligands to support homogeneous catalysts as well as to access a variety of new organometallic complexes [3,4]. These ligands are attractive due to their tunable steric and electronic properties and their propensity to form strong bonds with transition metals [3,5,6]. In fact, this class of ligand has proved useful in many types of catalysis, including prominent examples such as olefin metathesis and Heck type reactions [7–10].

The protonation of unsaturated NHCs forms imidazolium cations, which are infrequently observed coordinated to or interacting with transition metals due to the absence of a basic site. With increasing interest focused on the utilization of ionic liquids as solvents for catalysis, many of which are comprised of imidazolium salts [11,12], studies centered on the interaction between imidazolium cations and transition metals are of interest. Potentially relevant complexes include a pentachloride Hf anion with a single NHC ligand and imidazolium counterion and Cu^{II} oxalato systems with imidazolium counterions [13,14]. The solid-state structures of these systems indicate no direct interaction between the imidazolium cation and the transition metal.

Recently, efforts to explore NHC coordination have been extended to group 11 metals [15–19]. (NHC)Ag^I complexes have been synthesized and used primarily for metallation reactions in the synthesis of other (NHC)M complexes [20,18]. NHC complexes of Au^I are active for cycloisomerization of enynes and alkane C–H bond functionalization [17,20,21], and NHC ligands have allowed the isolation of well-defined species such as copper(I) amido, hydride, alkoxide and aryloxide complexes as well as a Au(I) fluoride complex [15,16,22,23]. In addition, recent reports have shown that (NHC)Cu^I complexes are active catalysts for hydroamination and hydroalkoxylation
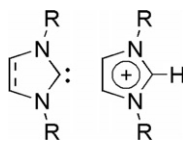
Chart 1. Generic depiction of *N*-heterocyclic carbene ligand and imidazolium cation.

of electron-deficient olefins, reduction of carbon dioxide and alkane C–H bond functionalization [17,24,25].

NHCs are typically quite stable ligands, although they have been observed to undergo reactivity. For example, NHC ligands have been reported to undergo reductive elimination, C–H activation at pendant aryl groups, partial hydrogenation of the imidazolylidene ring, dihydroxylation of the backbone of a coordinated NHC by OsO_4 as well as displacement by other ligands [26–28]. Herein, we report three examples of protonation of IPr coordinated to Cu^I and the impact of anion identity on the coordination mode, or lack of coordination, of the resulting imidazolium cations.

2. Results and discussion

The reaction of previously reported (IPr)Cu(OTf) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, OTf = trifluoromethanesulfonate) [24] with HOTf forms the dimer [(IPrH)Cu(OTf)(μ-OTf)]₂ (1) (Eq. (1)). For complex 1, a broad singlet is observed by ¹H NMR spectroscopy (CDCl₃) at 8.87 ppm, which is consistent with the chemical shift (C2–H) of an imidazolium cation. The chemical shift of the C2 proton and the chemical shifts of other resonances are slightly shifted from those of the independently prepared imidazolium salt [IPrH][OTf] (see Section 4 for details). For example, the C2–H resonance of [IPrH][OTf] appears at 9.11 ppm in CDCl₃. Thus, we assumed that the protonated IPr-H remains coordinated to Cu, which is confirmed by the solid-state structure of 1 (see below). Consistent with a weakly coordinated imidazolium

ligand for complex 1, a 1:1 molar ratio of "free" [IPrH][OTf] and complex 1 in CDCl₃ reveals the resonance due to the C2–H at 9.02 ppm, which is the approximate time average between 8.87 ppm (for 1) and 9.11 ppm (for [IPrH][OTf]). At room temperature, the ¹H NMR spectrum of complex 1 reveals a symmetric imidazolium fragment even though the η²-coordination revealed by the solid-state structure (see below) results in an asymmetric structure. This is consistent with the rapid exchange between coordinated and free [IPrH]⁺ on the NMR time scale. Cooling the CDCl₃ solution of 1 and [IPrH][OTf] to −55 °C results in line broadening; however, decoalescence of the resonances is not observed at this temperature. Similarly, cooling a solution of 1 in CDCl₃ to −55 °C does not result in the observation of new resonances. In addition, ¹⁹F NMR spectroscopy between room temperature and −55 °C reveals a single resonance due to triflate at −75 ppm, which indicates that the bridging and terminal triflate ligands are likely undergoing rapid exchange relative to the NMR time scale.
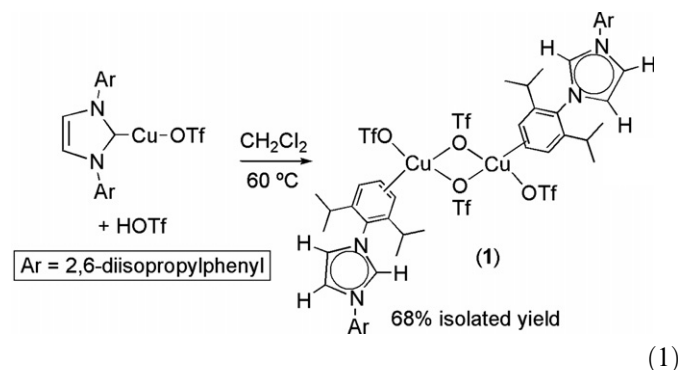
A single crystal of [(IPrH)Cu(OTf)(μ-OTf)]₂ (1) was grown, and analysis by X-ray crystallography revealed a binuclear copper system bridged by two triflate ligands (Fig. 1). Table 1 provides representative crystallographic data and collection parameters. For each copper center, there are two triflate ligands, one terminal and one bridg-
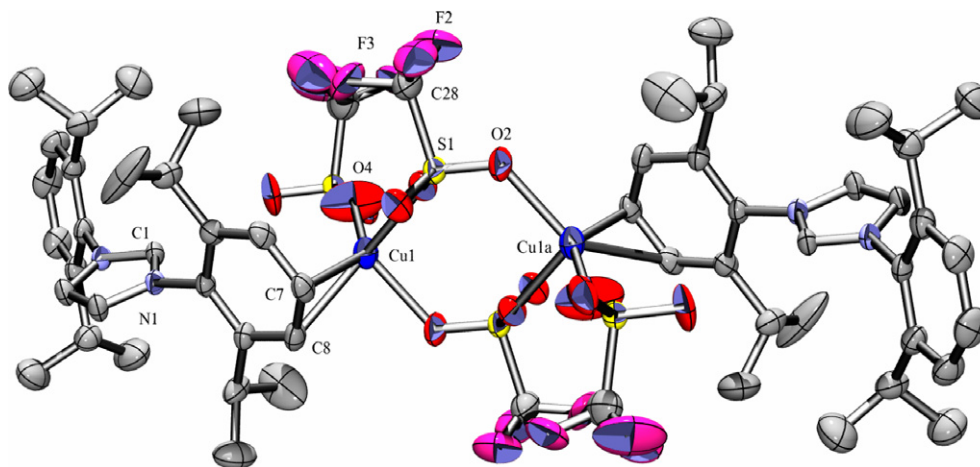
$$(1)$$

Fig. 1. Perspective view of the molecular structure of the [(IPrH)Cu(OTf)(μ-OTf)]₂ (1) dimer with the atom numbering scheme. Thermal ellipsoids are scaled to 30% probability. Selected bond distances (Å): Cu1–O4, 1.933(5); Cu1–O1, 2.126(2); Cu1–C7, 2.094(2); Cu1–C8, 2.354(2). Selected bond angles (°): O4–Cu1–O1, 97.3(1); C7–Cu1–O1, 104.8(1); O4–Cu1–C7, 130.5(1); O4–Cu1–C8, 118.8(1); C7–Cu1–C8, 35.5(1); O1–Cu1–C8, 138.0(1).

Table 1
Selected crystallographic data and collection parameters for [(IPrH)Cu(OTf)(μ-OTf)]$_2$ (**1**), [IPrH][CuCl$_2$] (**2**) and [IPrH][OTf]

	Complex **1**-CH$_2$Cl$_2$	Complex **2**-CH$_2$Cl$_2$	[IPrH][OTf]
Empirical formula	C$_{30}$H$_{39}$Cl$_2$CuF$_6$N$_2$O$_6$S$_2$	C$_{28}$H$_{39}$N$_2$CuCl$_4$	C$_{34}$H$_{43}$F$_3$N$_2$O$_3$S
Formula weight	836.19	608.95	616.76
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	10.3339(7)	9.3323(5)	18.480(1)
b (Å)	10.8422(7)	22.176(1)	9.7430(8)
c (Å)	18.103 (1)	15.372(1)	21.008(2)
α (°)	101.520(1)	90	90
β (°)	92.768(1)	93.397(1)	115.130(4)
γ (°)	100.828(1)	90	90
V (Å^3)	1944.3(2)	3175.7(3)	3424.5(5)
Z	2	4	4
D_{calcd} (g cm^{-3})	1.428	1.274	1.196
Crystal size (mm)	$0.20 \times 0.22 \times 0.32$	$0.24 \times 0.28 \times 0.48$	$0.28 \times 0.18 \times 0.06$
R_1, wR_2 {$I > 2\sigma(I)$}	0.0650, 0.1617	0.0647, 0.1653	0.0879, 0.2357
GOF	0.990	0.929	1.098

ing, with the Cu–O bond distance to the terminal triflate ligand {1.933(5) Å} shorter than the bond to the bridging triflate ligand {2.126(2) Å}. The imidazolium ligands are coordinated η^2 through the carbons that are *ortho* and *meta* to the isopropyl group. The distances between Cu and the coordinated C7 and C8 carbons are 2.094(2) Å and 2.354(2) Å, respectively. Thus, the aromatic carbons are asymmetrically bound with the more sterically encumbered carbon (C8, *ortho* to ^{i}Pr substituent) exhibiting a longer Cu–C bond than C7, which is *meta* to the ^{i}Pr substituent. A search of the Cambridge Structural Database (CSD) reveals several examples of Cu(I) complexes with η^2-coordinated arene ligands with the Cu–C bond distances of the coordinated arene carbons varied from 2.072 to 2.455 Å with an average distance of 2.17 Å [29–39]. The imidazolium cation is oriented to hydrogen-bond with an uncoordinated oxygen of the terminal triflate ligand with the distance between the imidazolium proton (between N1 and N2) and triflate oxygen of 2.22 Å.

In order to probe the impact of replacing triflate with chloride, (IPr)CuCl was reacted with HCl. Monitoring this reaction by ^{1}H NMR spectroscopy (CDCl$_3$) reveals the quantitative formation of [IPrH][CuCl$_2$] (**2**) after 48 h at room temperature (Eq. (2)). Alternatively, **2** can be prepared upon combination of the free imidazolium salt [IPrH][Cl] and CuCl in 79% isolated yield in a reaction that is complete in less than 1 h in CHCl$_3$ (Eq. (3)). Complex **2** is not air sensitive in CDCl$_3$ as exposure to air for 24 h causes no changes in the ^{1}H NMR spectrum, except for appearance of a resonance due to water. The ^{1}H NMR spectrum of **2** (CDCl$_3$) reveals a diagnostic downfield resonance at 9.28 ppm due to the C2–H of the imidazolium. The ^{1}H NMR spectrum of [IPrH][Cl] in CDCl$_3$ reveals the resonance due to the C2–H at 10.1 ppm. Thus, exchange of chloride anion with CuCl$_2$-anion results in an upfield shift of the C2–H resonance, which is likely due to the influence of hydrogen-bonding between the C2–H proton and the anion.
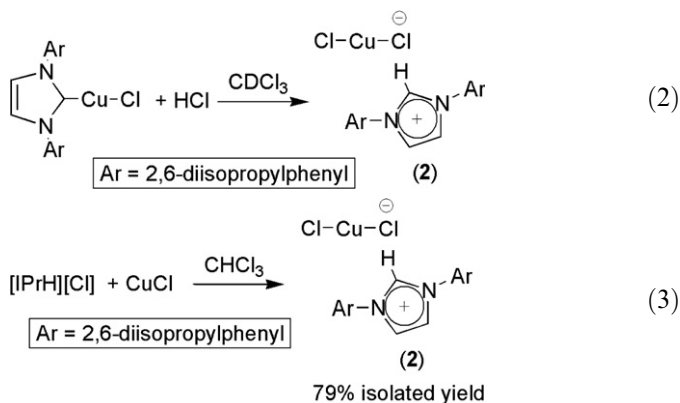
The impact of replacement of OTf with chloride is revealed by the solid-state structure of complex **2**. X-ray quality crystals were grown by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of **2**. The ORTEP of **2** is shown in Fig. 2. In the solid state, **2** is composed of nearly linear CuCl$_2$ anions with a Cl–Cu–Cl bond angle of 171.4°. In contrast to **1**, which possesses binuclear Cu systems bridged by OTf ligands, the chloride anions do not bridge Cu atoms in **2**. The nearest distances between Cu and the aryl group of the imidazolium moieties are 3.89 and 3.82 Å, which indicate no bonding between Cu and the arene unit. *Thus, the substitution of the more basic chloride for triflate decreases the predisposition toward coordination of the imidazolium cation in the solid state.* The distance between the H1 hydrogen of the imidazolium cation and Cl2 of 2.52 Å indicates a hydrogen-bonding interaction, and is similar to the average H–Cl hydrogen-bonding distances for related structures {2.54(2) Å} [38].

When (IPr)CuCl is reacted with triflic acid at 60 °C, a precipitate forms and the ^{1}H NMR spectrum reveals a resonance for the imidazolium C2 proton at 9.11 ppm, which is identical to that of [IPrH][OTf] in CDCl$_3$. The precipitate that is formed during the reaction is likely CuCl. Indeed, recrystallization from the filtered reaction solution and a solid-state X-ray diffraction study of the resulting material
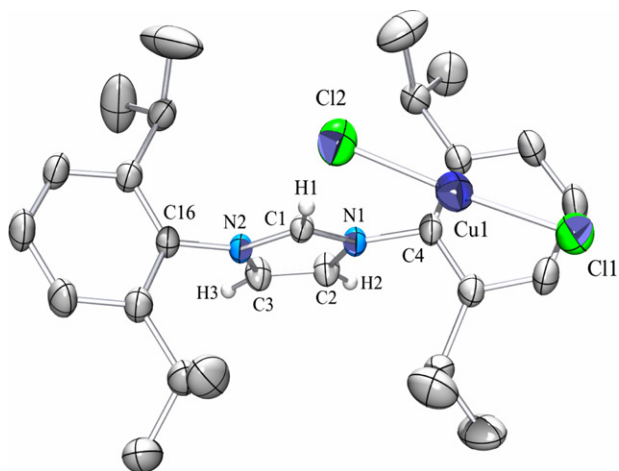
Fig. 2. ORTEP of [IPrH][CuCl₂] (**2**) at 30% probability (aryl hydrogen atoms omitted). Selected bond distances (Å): Cu1–Cl1, 2.100(1); Cu1–Cl2, 2.101(1); N1–C1, 1.318(3); N1–C2, 1.386(3); N2–C1, 1.338(3); N2–C3, 1.380(3). Selected bond angles (°): Cl1–Cu1–Cl2, 171.43(3); C1–N1–C2, 108.3(2); C1–N2–C3, 107.8(2); N1–C1–N2, 109.1(2); C3–C2–N1, 107.3(2); C2–C3–N2, 107.5(2).

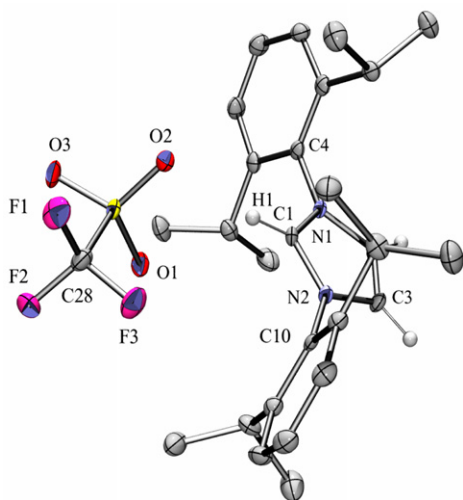Fig. 3. ORTEP of [IPrH][OTf] at 30% probability (all hydrogen atoms except those of the NHC ring and benzene solvent omitted). Selected bond distances (Å): C1–N1, 1.324(4); C1–N2, 1.333(4); O1–H1, 2.51 Å; O2–H1, 2.11 Å. Selected bond angles (°): N1–C1–N2, 109.1(3).

revealed the structure of [IPrH][OTf] with no identification of CuCl (Fig. 3).

3. Conclusions

IPr ligands coordinated to Cu(I) are subject to protonation by the strong acids HOTf and HCl. The interaction, or lack thereof, of the imidazolium cation with the resulting Cu^I fragment depends on the identity of the anions (chloride or triflate). For bis-triflate systems, [IPrH]$^+$ coordinates η^2 through the aryl group. For the bis-chloride system, the interaction of the imidazolium cation with Cu^I is apparently weaker and in the solid-state the only observed

interaction between the ions is hydrogen-bonding between the C2–H and chloride of the CuCl₂-anion. For the mixed chloride/triflate, CuCl precipitates and leaves [IPrH][OTf] in solution.

4. Experimental

4.1. General methods

All reactions and procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and monitored by an oxygen analyzer. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury 300 or 400 MHz (operating frequencies for ^{13}C NMR spectra were 100 and 75 MHz, respectively). All ^{1}H and ^{13}C NMR spectra were referenced against tetramethylsilane using residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). ^{19}F NMR spectra were obtained on a Varian Mercury 300 or 400 MHz and referenced against the external standard C_6F_6 (−163 ppm). Variable-temperature NMR experiments were performed on a Varian Mercury 300 or 400 MHz spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc.

Hexanes and CH_2Cl_2 were purified by passage through a column of activated alumina. $CHCl_3$ was distilled from P_2O_5. THF was dried by distillation over sodium/benzophenone. Pentane was distilled over sodium. $CDCl_3$ was degassed via three freeze–pump–thaw cycles and stored over 4 Å molecular sieves. [IPrH][Cl], IPr [8,39], (IPr)CuCl [40] and (IPr)Cu(OTf) [24] were prepared according to published procedures. All other reagents were used as purchased from commercial sources.

4.2. [(IPrH)Cu(OTf)(μ-OTf)]₂ (**1**)

In a pressure tube, (IPr)Cu(OTf) (0.111 g, 0.19 mmol) was dissolved in CH_2Cl_2 (20 mL). HOTf (33 μL, 0.37 mmol) was added to the reaction solution, the pressure tube was sealed and the mixture was heated to 60 °C for 2 h. During the heating, a pale pink precipitate formed at the bottom of the tube. The solution was filtered, and the volatiles were removed from the filtrate *in vacuo*. The resulting off-white solid was dissolved in approximately 5 mL of THF, and a white precipitate formed after addition of hexanes (10 mL). The precipitate was collected by vacuum filtration and dried (0.095 g, 68% yield). X-ray quality crystals were grown from a solution of 1 in CH_2Cl_2 layered with pentane. ^{1}H NMR (CDCl₃, δ): 8.87 (bs, 1H, N(CH)N), 7.75 (s, 2H, IPrH C=C), 7.63 (t, $^3J_{HH}$ = 8 Hz, 2H, *para* aryl), 7.40 (d, $^3J_{HH}$ = 8 Hz, 4H, *meta* aryl), 2.41 (sept, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Pr methine), 1.31 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Pr methyl), 1.24 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Pr methyl). ^{13}C NMR (CDCl₃, δ): 145.1 (NCHN), 137.8, 132.2, 129.7, 126.4 (aryl), 124.9 (NCHCHN), 29.5 (CH(CH₃)₂), 24.7, 24.1 (CH(CH₃)₂). ^{19}F NMR (CDCl₃, δ): −75.0.

Despite pure samples (by NMR spectroscopy), we were unable to obtain satisfactory elemental analysis. The ^{1}H NMR spectrum of **1** has been submitted in Supporting information.

4.3. [IPrH][CuCl$_2$] (2)

Method A: In a round bottom flask, [IPrH][Cl] (0.607 g, 1.4 mmol) and CuCl (0.144 g, 1.5 mmol) were combined in CHCl$_3$ (20 mL). The pale brown solution was stirred for 2 h and vacuum filtered. The volatiles were removed from the filtrate *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ (5 mL), and the addition of pentane resulted in the formation of a white precipitate. The white solid was isolated by vacuum filtration and dried *in vacuo* (0.591 g, 79%). X-ray quality crystals were grown from a solution of **2** in CH$_2$Cl$_2$ layered with pentane. *Method B* (NMR scale): (IPr)CuCl (0.014 g, 0.029) was dissolved in CDCl$_3$ (~0.7 mL), and the NMR tube was capped with a septum. HCl (4 M in Et$_2$O, 36 µL, 0.14 mmol) was added to the NMR tube via syringe. The reaction was monitored by ^{1}H NMR spectroscopy until the reaction was complete, which took approximately 48 h. ^{1}H NMR (CDCl$_3$, δ): 9.28 (bs, 1H, N(C*H*)N), 7.86 (bs, 2H, IPrH C=C), 7.63 (t, $^3J_{HH}$ = 8 Hz, 2H, *para* aryl), 7.40 (d, $^3J_{HH}$ = 8 Hz, 4H, *meta* aryl), 2.43 (sept, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Pr methine), 1.32 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Pr methyl), 1.25 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Pr methyl). ^{13}C NMR (CDCl$_3$, δ): 144.7 (N*C*HN), 137.6, 132.5, 129.3, 126.0 (aryl), 124.9 (N*C*H*C*HN), 29.3 (*C*H(CH$_3$)$_2$), 24.8, 24.0 (CH(*C*H$_3$)$_2$). Anal. Calc. for C$_{27}$H$_{37}$Cu$_1$Cl$_2$N$_2$: C, 61.88: H, 7.12: N, 5.35. Found: C, 62.05 H, 7.05; N, 5.43%.

4.4. [IPrH][OTf]

[IPrH][Cl] (0.325 g, 0.76 mmol) and AgOTf (0.197 g, 0.78 mmol) were combined in THF (20 mL). The white slurry was stirred for 2 h and vacuum filtered with a fine-porosity frit. The colorless filtrate was concentrated *in vacuo* to 5 mL, and hexanes were added to precipitate a white solid (0.383 g, 88% yield). ^{1}H NMR (CDCl$_3$, δ): 9.11 (bs, 1H, N(C*H*)N), 7.82 (bs, 2H, IPrH C=C), 7.59 (t, $^3J_{HH}$ = 8 Hz, 2H, *para* aryl), 7.36 (d, $^3J_{HH}$ = 8 Hz, 4H, *meta* aryl), 2.43 (sept, $^3J_{HH}$ = 7 Hz, 4H, ^{i}Pr methine), 1.30 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Pr methyl), 1.24 (d, $^3J_{HH}$ = 7 Hz, 12H, ^{i}Pr methyl). ^{13}C NMR (CDCl$_3$, δ): 144.9 (N*C*HN), 138.0, 132.3, 129.7, 126.4 (aryl), 124.8 (N*C*H*C*HN), 29.5 (*C*H(CH$_3$)$_2$), 24.8, 24.2 (CH(*C*H$_3$)$_2$). ^{19}F NMR (CDCl$_3$, δ): −78.0. Anal. Calc. for [IPrH][OTf]: C$_{56}$H$_{74}$F$_6$N$_4$O$_6$S$_2$: C, 62.43: H, 6.92: N, 5.20. Found: C, 62.13H, 6.86; N, 5.11%.

4.5. Reaction of (IPr)CuCl with HOTf

In a pressure tube, (IPr)CuCl (0.171 g, 0.35 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL). HOTf (31 µL, 0.35 mmol) was added, the pressure tube was sealed and the reaction

mixture was heated to 60 °C for 2 h. After the heating period, the solution was colorless with a white precipitate at the bottom. The solution was filtered, and the volatiles were removed *in vacuo* from the filtrate. The off-white solid was dissolved in approximately 5 mL of THF and a white precipitate formed upon addition of hexanes (10 mL). The white solid was collected by vacuum filtration and dried (0.153 g, 68% yield). The material was identical to [IPrH][OTf] by ^{1}H NMR spectroscopy. X-ray quality crystals were grown layering a solution of the product in benzene with pentane.

4.6. Exchange of [IPrH][OTf] and [(IPrH)Cu(OTf)(µ-OTf)]$_2$ (1)

[IPrH][OTf] (0.016 g, 0.028 mmol) was dissolved in CDCl$_3$ (approx. 0.7 mL). An initial ^{1}H NMR spectrum was acquired with the imidazolium C2–H resonance observed at 9.11 ppm. Complex **1** (0.021 g, 0.027 mmol) was added, and a ^{1}H NMR spectrum was acquired. The imidazolium C2–H proton resonance shifted to 9.02 ppm. The solution was cooled to −55 °C and monitored by ^{1}H NMR spectroscopy with only slight line broadening observed.

Appendix A. Supplementary data

CCDC 620850, 620849 and 620848 contain the supplementary crystallographic data for [(IPrH)Cu(OTf)(µ-OTf)]$_2$ (**1**), [IPrH][CuCl$_2$] (**2**) and [IPrH][OTf]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.051.

References

[1] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
[2] A.J. Arduengo, R. Krafczyk, R. Schmutzler, H.A. Craig, J.R. Goerlich, W.J. Marshall, M. Unverzagt, Tetrahedron 55 (1999) 14523.
[3] W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1290.

[4] F.E. Hahn, Angew. Chem., Int. Ed. Engl. 45 (2006) 1348.
[5] J. Huang, H.J. Schanz, E.D. Stevens, S.P. Nolan, Organometallics 18 (1999) 2370.
[6] A.C. Hillier, W.J. Sommer, B.S. Yong, J.L. Petersen, L. Cavallo, S.P. Nolan, Organometallics 22 (2003) 4322.
[7] M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953.
[8] L. Jafarpour, E.D. Stevens, S.P. Nolan, J. Organomet. Chem. 606 (2000) 49.
[9] G.D. Frey, J. Schutz, E. Herdtweck, W.A. Herrmann, Organometallics 24 (2005) 4416.
[10] H. Lebel, M.K. Janes, A.B. Charette, S.P. Nolan, J. Am. Chem. Soc. 126 (2004) 5046.
[11] Z. Fei, T.J. Geldbach, D. Zhao, P.J. Dyson, Chem. Eur. J. 12 (2006) 2122.
[12] T. Welton, Chem. Rev. 99 (1999) 2071.
[13] M. Niehues, G. Kehr, R.E. Fröhlich, G. Erker, Z. Naturforsch. B Chem. Sci. 58 (2003) 1005.
[14] S.K. Chattopadhyay, T.C.W. Mak, B.-S. Luo, L.K. Thompson, A. Rana, S. Ghosh, Polyhedron 14 (1995) 3661.
[15] N.P. Mankad, D.S. Laitar, J.P. Sadighi, Organometallics 23 (2004) 3369.
[16] N.P. Mankad, T.G. Gray, D.S. Laitar, J.P. Sadighi, Organometallics 23 (2004) 1191.
[17] M.R. Fructos, P. de Fremont, S.P. Nolan, M.M. Diaz-Requejo, P.J. Pérez, Organometallics 25 (2006) 2237.
[18] J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978.
[19] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, Organometallics 23 (2004) 755.
[20] P. de Fremont, N.M. Scott, E.D. Stevens, S.P. Nolan, Organometallics 24 (2005) 2411.
[21] N. Marion, P. de Fremont, G. Lemiere, E.D. Stevens, L. Fensterbank, M. Malacria, S.P. Nolan, Chem. Commun. (2006) 2048.
[22] L.A. Goj, E.D. Blue, C. Munro-Leighton, T.B. Gunnoe, J.L. Petersen, Inorg. Chem. 44 (2005) 8647.
[23] D.S. Laitar, P. Muller, T.G. Gray, J.P. Sadighi, Organometallics 24 (2005) 4503.
[24] C. Munro-Leighton, E.D. Blue, T.B. Gunnoe, J. Am. Chem. Soc. 128 (2006) 1446.
[25] D.S. Laitar, P. Muller, J.P. Sadighi, J. Am. Chem. Soc. 127 (2005) 17196.
[26] C.M. Crudden, D.P. Allen, Coord. Chem. Rev. 248 (2004) 2247.
[27] S. Grundemann, A. Kovacevic, M. Albrecht, J.W. Faller, R.H. Crabtree, J. Am. Chem. Soc. 124 (2002) 10473.
[28] W.A. Herrmann, P.W. Roesky, M. Elison, G. Artus, K. Oefele, Organometallics 14 (1995) 1085.
[29] D.S. Laitar, C.J.N. Mathison, W.M. Davis, J.P. Sadighi, Inorg. Chem. 42 (2003) 7354.
[30] A. Sundararaman, R.A. Lalancette, L.N. Zakharov, A.L. Rheingold, F. Jakle, Organometallics 22 (2003) 3526.
[31] L.D. Amisial, X. Dai, R.A. Kinney, A. Krishnaswamy, T.H. Warren, Inorg. Chem. 43 (2004) 6537.
[32] A.M. Dattelbaum, J.D. Martin, Polyhedron 25 (2006) 349.
[33] C.W. Hamilton, D.S. Laitar, J.P. Sadighi, Chem. Commun. (2004) 1628.
[34] S.Y. Lee, S.J. Na, H.Y. Kwon, B.Y. Lee, S.O. Kang, Organometallics 23 (2004) 5382.
[35] R.W. Turner, E.L. Amma, J. Am. Chem. Soc. 88 (1966) 1877.
[36] S.M. Hubig, S.V. Lindeman, J.K. Kochi, Coord. Chem. Rev. 200-202 (2000) 831.
[37] H. Schmidbaur, W. Bublak, B. Huber, G. Reber, G. Muller, Angew. Chem., Int. Ed. Engl. 25 (1986).
[38] T. Steiner, Acta Crystallogr., Sect. B 54 (1998) 456.
[39] V.P.W. Böhm, T. Weskamp, C.W.K. Gstöttmayr, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 39 (2000) 1602.
[40] V. Jurkauskas, J.P. Sadighi, S.L. Buchwald, Org. Lett. 5 (2003) 2417.