COMMUNICATION

ChemComm
www.rsc.org/chemcomm

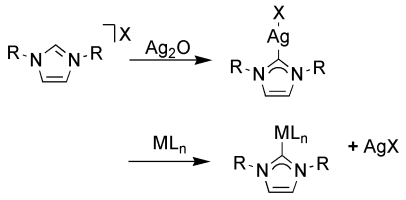
Unexpected oxidative C–C cleavage in the metallation of 2-substituted imidazolium salts to give N-heterocyclic carbene complexes†

Anthony R. Chianese, Brian M. Zeglis and Robert H. Crabtree*
Chemistry Department, Yale University, PO Box 208107, New Haven, Connecticut 06520-8107, USA

Received (in Cambridge, UK) 25th June 2004, Accepted 28th July 2004
First published as an Advance Article on the web 25th August 2004

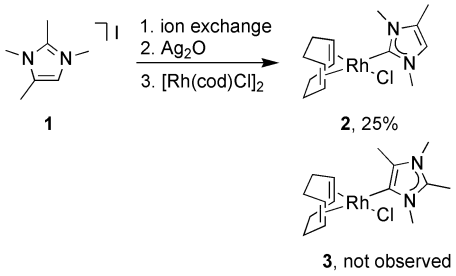
Imidazolium salts blocked at C2 with methyl or benzyl groups unexpectedly react with silver oxide to give N-heterocyclic carbene complexes of silver *via* an oxidative carbon–carbon bond cleavage.

N-Heterocyclic carbenes (NHCs), first isolated by Arduengo,[1] have emerged as an extremely useful class of spectator ligands for homogeneous catalysis.[2] Several methods have now been developed that avoid the free ligand by *in situ* metallation of the imidazolium salts. One such method is the generation of silver–NHC complexes from silver oxide and imidazolium salts [eqn. (1)].[3] The resulting silver complexes are capable of transmetallation to give NHC complexes of Pd, Au, Rh, Ir, and Cu.[4]



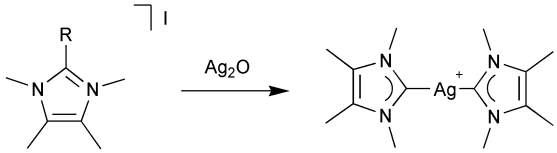
(1)

In contrast to the normal binding mode *via* C2, we[5] and others[6] have shown that abnormal binding of an NHC through C4(5) is also possible. We are studying the factors controlling the mode of binding,[7] and in the electronic properties of abnormal NHCs *versus* normal NHCs.[8] To selectively prepare abnormal NHC complexes, we have blocked the imidazolium ligand precursors by substitution at C2 with alkyl or aryl groups. We previously reported the synthesis of an abnormal NHC–iridium(I) complex, using a 2-phenylimidazolium salt.[8] In attempting to prepare a rhodium(I) complex from the tetramethylimidazolium salt **1** by transmetallation from the silver complex, we were very surprised to isolate by column chromatography the *normal* carbene complex **2** in 25% yield [eqn. (2), cod = 1,5-cyclooctadiene). The formation of **2** requires a C–C bond cleavage. The expected abnormal NHC complex **3** was not isolated but a **1**/Ag_2O mixture showed unidentified compounds (^{1}H NMR) after 4 h.



(2)

To avoid the competitive formation of abnormal silver–NHC complexes, we prepared **4a**,[9] blocked by methyl groups at all positions [eqn. (3)]. The reaction of **4a** with 4 equiv. Ag_2O in CH_2Cl_2 at room temperature gives nearly quantitative formation of the silver–carbene complex **5** in *ca.* 2 d. A redox process is indicated by the formation of a silver mirror on the wall of the reaction vessel. In contrast, a silver mirror is not observed in normal metallation of 2*H*-imidazolium salts under the same conditions. ^{1}H NMR spectroscopy of the reaction mixture from **4a** shows only a 6H singlet at 3.66 ppm for the *N*-methyl groups, and a 6H singlet at 2.14 ppm for the *C*-methyl groups. ES-MS in cation mode shows two peaks of equal intensity at *m*/*z* = 355 and 357 amu, ascribed to $Ag(NHC)_2^+$, arising from ^{107}Ag and ^{109}Ag. A mixture of anions is originally present, but the complex can be isolated in analytically pure form as the PF_6 salt, by washing the crude product with aq. NaOH/KPF_6. The carbene carbon resonates as a singlet at 177.6 ppm in the ^{13}C NMR spectrum. The lack of coupling to ^{107}Ag and ^{109}Ag is indicative of the usual[3] fast exchange of the NHC between silver atoms on the NMR timescale.



(3)

4a, R = Methyl, >90% yield
4b, R = Benzyl, >90% yield
4c, R = Ethyl, <50% yield
4d, R = Isopropyl, No Reaction

The series **4b–d** was prepared with different blocking groups at C2. When treated with Ag_2O, the benzyl-substituted **4b** converted nearly quantitatively to **5** in one day [eqn. (3)]. Ethyl-substituted **4c** reacted incompletely, even with a large excess of silver oxide and prolonged reaction time. Isopropyl-substituted **4d** did not react at all, even at reflux temperature. Our previous results[8] indicate that 2-phenylimidazolium salts do not undergo C–C cleavage to give normal silver–NHC complexes upon reaction with silver oxide under the same conditions. This implies that $PhCH_2$, CH_3, and CH_3CH_2 are cleaved and are therefore ineffective blocking groups, but that iPr and Ph are not cleaved and are therefore effective blocking groups.

The fate of the methyl group (**4a**) and benzyl group (**4b**) gives an important mechanistic clue. With **4b**, the only byproduct observed by ^{1}H NMR is benzoate,[10] in about 84% yield. The analogous byproduct from **4a**, formate, is not observed under the original reaction conditions. However, when the reaction is run with 1 equiv. of NBu_4PF_6, we see *ca.* 54% yield of formate.[10] AgOOCH may precipitate in the absence of the salt.

Carboxylate formation implies the 2-substituent is oxidized, but the reaction goes under Ar in dry, degassed THF; ruling out both air and CH_2Cl_2 as oxidant. The Ag(0) was isolated by washing the solid residue with CH_2Cl_2, then dil. HNO_3 and then aq. NH_3 to remove Ag–NHCs, Ag_2O and Ag salts. Approximately 3.86 equivalents of metallic silver are isolated in a typical reaction, relative to the amount of imidazolium salt used.[11] This is consistent with four electrons being required per imidazolium unit (see below).

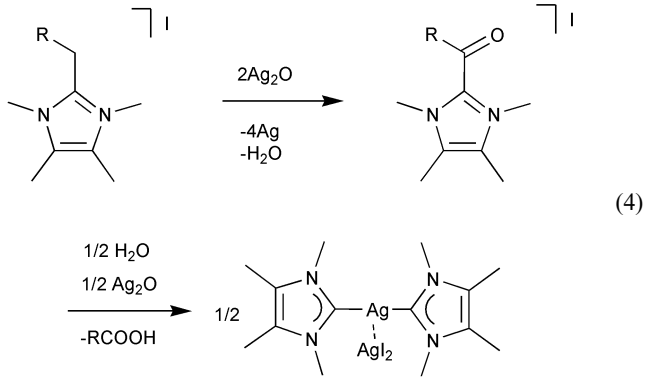
Initial RCHO or RCH_2OH intermediates were not later oxidized to RCOOH by Ag_2O[12] because PhCHO and $PhCH_2OH$ are

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b4/b409672j/

DOI: 10.1039/b409672j

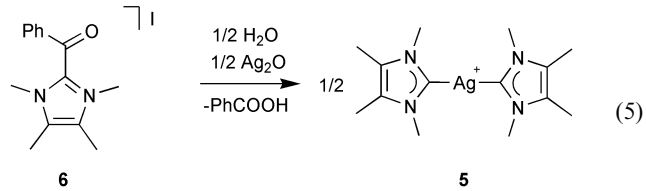
unchanged under our conditions. These observations strongly suggest that in the reaction of **4b** and silver oxide, benzoate is produced directly as a product of C–C cleavage, and not by a subsequent oxidation of benzyl alcohol or benzaldehyde.

The C–C cleavage probably goes *via* an initial four-electron oxidation of the imidazolium 2-substituent to give a 2-formyl (**4a**) or 2-benzoyl (**4b**) imidazolium ion, followed by hydrolytic cleavage to give the NHC, trapped by silver(I), and the carboxylic acid[13] [eqn. (4)]. A variety of oxidants[14–16] can convert 2-alkyl imidazoles to the acyl compounds. The proposed intermediate 2-acylimidazolium salts have previously been shown to hydrolyze to give carboxylic acids and 2*H*-imidazolium salts.[17] This reaction is analogous to other substitutions of RCOX derivatives, such as hydrolysis of an acid chloride or anhydride. In our case, the NHC is the leaving group, and can be intercepted by silver(I). The complete mechanism [eqn. (4)] requires four equivalents of silver for oxidation, and one equivalent for complex formation, consistent with both the measured quantity of silver(0) formed, and the need for a large excess of silver oxide for the reaction to go to completion.



(4)

To investigate the possible intermediacy of 2-acylimidazolium salts, we prepared the 2-benzoylimidazolium salt **6**. During the preparation of **6**, we observed a small amount (4%) of hydrolysis to give the 2*H*-imidazolium salt. When **6** is reacted with silver oxide under the standard conditions [eqn. (5)], quantitative conversion to the silver–NHC complex and benzoate ion is observed by ^{1}H NMR. No metallic silver is produced, as no oxidation is necessary here.



6 **5**

(5)

We[18] and others[19] have demonstrated that 2*H*-imidazolium salts can oxidatively add to palladium(0). Welton has demonstrated the non-innocence of 2*H*-imidazolium-based ionic liquids in chemistry involving Pd(0).[20] The authors also demonstrated that 1,3-dialkyl-2-phenylimidazolium cation could serve as a source of the aryl group for the Suzuki reaction, competing with the aryl halide cosubstrate for coupling with the boronic acid.[20] 1,2,3-Trialkylimidazolium salts, in contrast, did not give Pd–NHC complexes. So the reactivity pattern for C–C cleavage is completely different from the one we find here.

2-Me-, 2-Et-, and 2-PhCH$_2$- can be unreliable blocking groups for imidazolium/Ag$_2$O reactions while 2-iPr- and 2-Ph- resist oxidative C–C cleavage. This is relevant in abnormal NHC synthesis, and in work with imidazolium-based ionic liquids, often blocked by a C2 Me.

We gratefully acknowledge British Petroleum, Johnson Matthey, and the U.S. Department of Energy for funding. We also thank Johnson Matthey for a generous gift of rhodium chloride.

Notes and references

1 A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361–363.
2 (*a*) W. A. Herrmann and C. Kocher, *Angew. Chem., Int. Ed.*, 1997, **36**, 2163–2187; (*b*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309; (*c*) M. C. Perry and K. Burgess, *Tetrahedron: Asymmetry*, 2003, **14**, 951–961.
3 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972–975.
4 (*a*) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White and B. W. Skelton, *J. Organomet. Chem.*, 2001, **617**, 546–560; (*b*) A. R. Chianese, X. W. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663–1667; (*c*) K. S. Coleman, H. T. Chamberlayne, S. Turberville, M. L. H. Green and A. R. Cowley, *Dalton Trans.*, 2003, 2917–2922; (*d*) R. S. Simons, P. Custer, C. A. Tessier and W. J. Youngs, *Organometallics*, 2003, **22**, 1979–1982; (*e*) X. L. Hu, I. Castro-Rodriguez, K. Olsen and K. Meyer, *Organometallics*, 2004, **23**, 755–764.
5 S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274–2275.
6 (*a*) X. Hu, I. Castro-Rodriguez and K. Meyer, *Organometallics*, 2003, **22**, 3016–3018; (*b*) A. A. Danopoulos, N. Tsoureas, J. A. Wright and M. E. Light, *Organometallics*, 2004, **23**, 166–168; (*c*) H. Lebel, M. K. Janes, A. B. Charette and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046–5047.
7 (*a*) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *J. Am. Chem. Soc.*, 2002, **124**, 10473–10481; (*b*) A. Kovacevic, S. Gründemann, J. R. Miecznikowski, E. Clot, O. Eisenstein and T. H. Crabtree, *Chem. Commun.*, 2002, 2580–2581.
8 A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller and R. H. Crabtree, *Organometallics*, 2004, **23**, 2461–2468.
9 N. Kuhn, G. Henkel and J. Kreutzberg, *Z. Naturforsch., B: Chem. Sci.*, 1991, **46**, 1706–1712.
10 Identification of RCO_2^- by NMR (comparison with authentic RCO_2^-) and ES-MS (R = Ph).
11 Average value for two experiments.
12 (*a*) F. Asinger, *Chem. Ber.*, 1942, **75**, 656; (*b*) H. Fiesselmann, *Chem. Ber.*, 1942, **75**, 881.
13 RCO_2Ag, from RCO_2^-/Ag_2O, may precipitate when R = Ph.
14 W. Kuzmierkiewicz, *Acta Pol. Pharm.*, 1986, **43**, 221–226.
15 S. Ram, D. S. Wise and L. B. Townsend, *J. Heterocycl. Chem.*, 1986, **23**, 1109–1113.
16 H. Berner and H. Reinshagen, *Monatsh. Chem.*, 1975, **106**, 1059–1069.
17 S. Ohta, S. Hayakawa, H. Moriwaki, S. Tsuboi and M. Okamoto, *Heterocycles*, 1985, **23**, 1759–1764.
18 S. Gründemann, M. Albrecht, A. Kovacevic, J. W. Faller and R. H. Crabtree, *Dalton Trans.*, 2002, 2163–2167.
19 D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 2001, **123**, 8317–8328.
20 F. McLachlan, C. J. Mathews, P. J. Smith and T. Welton, *Organometallics*, 2003, **22**, 5350–5357.