Structure and reactivity of a new anionic *N*-heterocyclic carbene silver(I) complex†

Claude Y. Legault, Christopher Kendall and André B. Charette*

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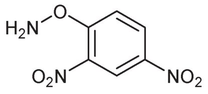
The efficient synthesis of a *N*-benzoyliminoimidazolium ylide provides access to a new type of *N*-heterocyclic anionic carbene, from which air stable Ag(I) and Cu(II) complexes and a catalytically active Rh(I) complex were formed.

The synthesis and isolation of the first stable free carbene by Arduengo *et al.* in 1991 has greatly impacted the field of organic chemistry.[1] *N*-Heterocyclic carbenes (NHCs) are now used as ligands in numerous applications, notably Suzuki, Heck and related cross-couplings,[2] and olefin metathesis.[3] Since they are strong σ-donors, NHCs serve as phosphine surrogates and, in many cases, the carbene metal complexes are more stable to air, water and heat than their phosphine counterparts.[4]

We recently published an efficient preparation of *O*-(2,4-dinitrophenyl)hydroxylamine **1**, an electrophilic aminating reagent that was used for the direct *N*-amination–benzoylation of various aromatic heterocycles, affording ylides **2**.[5,6] We have now applied this methodology of *N*-amination–benzoylation to an imidazole and wish to report a new type of anionic *N*-heterocyclic carbene, derived from the resulting imidazolium ylide.



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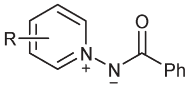

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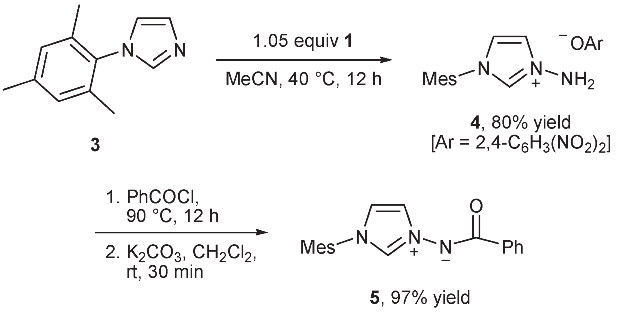
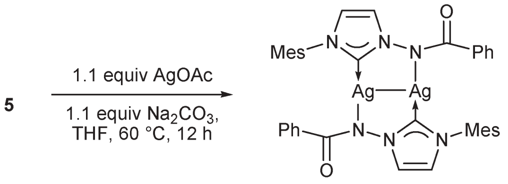
Anionic carbene ligands (that is bidentate ligands with a carbene carbon and an anionic site forming an [L,X]-type chelate) are starting to be widely studied as ligands for transition-metal catalyzed reactions.[7] Three asymmetric variants of these types of ligands have recently been reported, for Cu-catalyzed conjugate addition[7f,r] and allylic alkylation[7l] using dialkylzinc reagents.

We applied our *N*-amination methodology to *N*-mesityl imidazole (**3**),[8] and were able to obtain the corresponding *N*-aminoimidazolium salt **4** in high yield. Treatment of imidazolium **4** with benzoyl chloride then deprotonation of the resulting salt with K_2CO_3 afforded the desired *N*-benzoyliminoimidazolium ylide **5** in 97% yield (Scheme 1).‡ Deprotonation of this ylide should afford a bidentate NHC. Due to the delocalized nature of the anionic tether, we envision that the electronic properties of the resulting ligand could be easily tuned by modifying the nature of the acyl chloride used in the second step, whereas its steric properties could be modified based on the starting imidazole.



Scheme 1 Synthesis of *N*-benzoyliminoimidazolium ylide **5**.

At this point, we decided to prepare a Ag(I) complex with **5**, based on precedent for the facile exchange between Ag(I) carbene complexes and other metals.[9] Readily available silver acetate was selected as our Ag(I) source and, when used in combination with a slight excess of sodium carbonate,† we were able to obtain the desired normally bound NHC–Ag(I) complex, isolated in near quantitative yield (eqn. (1)).[10]



(1)

6, 95% yield

The complex obtained is an off-white crystalline solid that is extremely stable, as we were able to observe the parent ion under harsh APCI mass spectroscopy conditions.‡ As can be seen from its X-ray crystal structure, **6** exists in a dimeric form (Fig. 1).§ We were surprised to observe that instead of an internal *O*-chelate, the complex exists with a co-operative intermolecular *N*-tether, possibly due to the long Ag–C1 bond making an *O*-chelate too geometrically distorted. The Ag–C1 bond length of 2.081(4) Å shows the absence of a π-interaction in this bond, which is not surprising due to the enhanced electron density on Ag(I) caused by *N*-complexation of the amide. The Ag–Ag′ distance of 2.782(5) Å means a significant Ag–Ag bonding interaction.[11]

Though the Ag(I) complex **6** is a very air- and moisture-stable solid,[12] it is also a very reactive carbene transfer reagent. To test the carbene transferability of **6**, it was treated with $CuCl_2·2H_2O$, in THF at room temperature (eqn. (2)). The reaction was very rapid, with almost instantaneous precipitation of AgCl. To ensure the

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Département de Chimie, Université de Montréal, P.O. Box 6128, Station Downtown, Montréal, QC, Canada H3C 3J7.
E-mail: andre.charette@umontreal.ca; Fax: +1 514 343 5900;
Tel: +1 514 343 6283

† Electronic supplementary information (ESI) available: full synthetic and structural details. See http://dx.doi.org/10.1039/b506232b

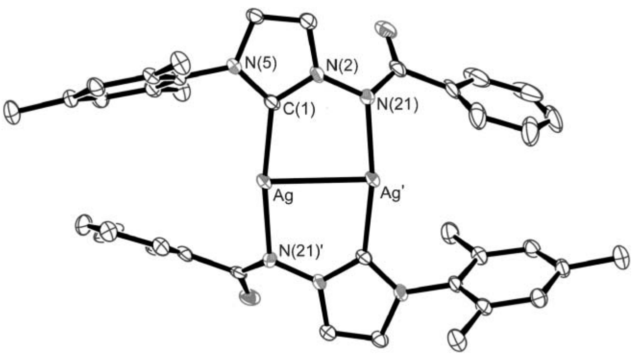
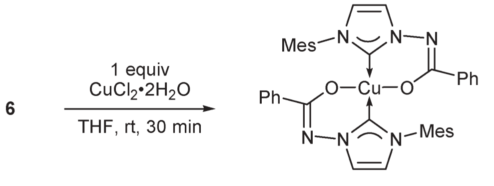


Fig. 1 Thermal ellipsoid drawing of the molecular structure of **6**. Hydrogens are omitted for clarity and ellipsoids are plotted at 50% probability. Selected distances (Å) and angles (°): C(1)–Ag 2.081(4), Ag–Ag′ 2.782(5), Ag′–N(21) 2.130(3), N(21)–N(2) 1.416(4), N(2)–C(1) 1.361(5), C(1)–Ag–Ag′ 83.17(11), C(1)–Ag–N(21)′ 169.46(14), N(5)–C(1)–N(2) 104.3(3). Symmetry codes for Ag′ and N(21)′: −*x*, *y*, ½ − *z*.

complete conversion of **6** to a Cu complex, the reaction was left to stir for 30 mins, which afforded **7** in 84% yield as a green, air-stable solid. The complex **7** is also very stable, again demonstrated by observation of the parent ion by APCI MS.‡



(2)

7, 84% yield

A single crystal X-ray structure was obtained of **7**, which showed in this case a monomeric structure, where the internal *O*-chelation mode was preferred (Fig. 2).¶ Carbon-bound organometallic Cu(II) complexes are very rare and to the best of our knowledge such complexes have been crystallographically characterized only three other times.[7f,l,13] The Cu–C(11) bond length observed of 1.945(4) Å is well within the bond lengths observed in the other known examples. The Cu center has a distorted square planar geometry, while the C122–N121 bond length of 1.316(6) Å and C122–O122 of 1.259(5) Å shows a noticeable delocalization of the π-system throughout the imidate. The Cu–O122 bond length of 1.950(3) Å can be considered a normal single bond.[7f,l]

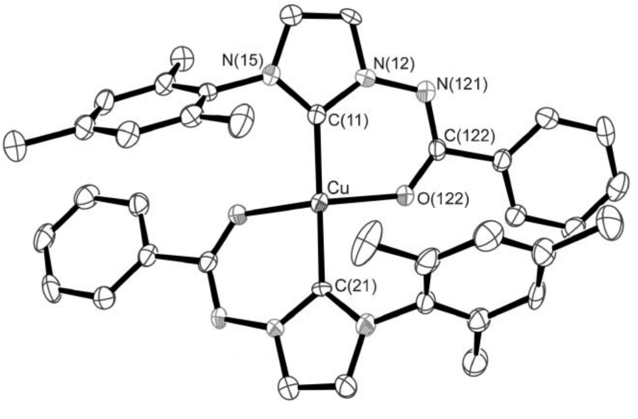
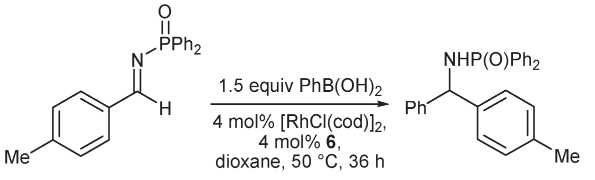


Fig. 2 Thermal ellipsoid drawing of the molecular structure of **7**. Hydrogens are omitted for clarity and ellipsoids are plotted at 50% probability. Selected distances (Å) and angles (°): C(11)–Cu 1.945(4), Cu–O(122) 1.950(3), O(122)–C(122) 1.259(5), C(122)–N(121) 1.316(6), N(121)–N(12) 1.403(5), N(12)–C(11) 1.362(6), C(11)–Cu–O(122) 88.42(16), C(11)–Cu–C(21) 157.9(2), N(15)–C(11)–N(12) 103.8(4).

A Rh(I) complex of **5** has also been prepared. As with the transfer reaction to Cu(II), the reaction between dioxane solutions of **6** and [RhCl(cod)]$_2$ resulted in almost instantaneous precipitation. This Rh(I)·**5** complex was shown to be catalytically active in the arylation of aldimines with arylboronic acids (eqn. (3)).[14] Treatment of imine **8**[15] with PhB(OH)$_2$ and a mixture of 4 mol% of [RhCl(cod)]$_2$ and 4 mol% of **6** in dioxane at 50 °C gave a complete conversion to diarylmethylamide **9**, isolated in 77% yield. Omitting **6** resulted in a very sluggish reaction, with only 54% conversion after 48 h at 75 °C, and significant decomposition.



(3)

8

9, 77% yield

In conclusion, a new type of anionic *N*-heterocyclic carbene ligand has been described. The proligand was reacted with AgOAc to afford an Ag(I) complex, and this complex was then used successfully as a carbene transfer agent to CuCl$_2$·2H$_2$O, to afford a rare carbon-bound organometallic Cu(II) complex, and to [RhCl(cod)]$_2$, to afford a catalytically active Rh(I) complex. The steric and electronic properties of this new ligand could easily be tuned by modifying either the imidazole or the acyl chloride used in its preparation. Synthetic applications of an asymmetric variant of this ligand will be reported in due course.

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Notes and references

‡ **5**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.82 (s, 1H), 8.20–8.15 (m, 2H), 7.75 (t, 1H, J = 1.6 Hz), 7.44–7.41 (m, 3H), 7.03 (s, 2H), 6.98 (t, 1H, J = 1.8 Hz), 2.37 (s, 3H), 2.11 (s, 6H).**6**: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.94 (s, 2H), 7.67 (d, 4H, J = 7.2 Hz), 7.35 (t, 2H, J = 7.2 Hz), 7.09 (t, 4H, J = 7.6 Hz), 7.00 (s, 4H), 6.83 (s, 2H), 2.48 (s, 6H), 1.88 (s, 12H); APCI MS (+ve, 120 eV) 825 ([M + H]$^+$, 12), 306 (18), 187 (100); Anal. calcd. (found) for $C_{38}H_{36}Ag_2N_6O_2$: C 55.36 (55.96), H 4.40 (4.46), N 10.19 (9.95).**7**: APCI MS (+ve, 120 eV) 673 ([M + H]$^+$, 32), 306 (100), 187 (21); Anal. calcd. (found) for $C_{38}H_{36}CuN_6O_2$: C 67.89 (68.11), H 5.40 (5.52), N 12.50 (11.95).

§ Crystal data for **6**: $C_{38}H_{36}Ag_2N_6O_2 \cdot C_4H_{10}O$. M = 898.59, monoclinic, space group $C2/c$, a = 19.3478(3) Å, b = 12.5755(2) Å, c = 16.6032(2) Å, β = 107.2320(10)°, V = 3858.37(10) Å^3, Z = 4, μ = 8.517 mm^{-1}, T = 100 K. 20757 measured, 3829 independent reflections (R_{int} = 0.041). The final $wR(F^2)$ was 0.1042 and R = 0.0415 [$F^2 > 2\sigma(F^2)$]. CCDC 267321. See http://dx.doi.org/10.1039/b506232b for crystallographic data in CIF or other electronic format.

¶ Crystal data for **7**: $C_{38}H_{36}CuN_6O_2$. M = 672.27, monoclinic, space group $P2_1/c$, a = 10.6331(2) Å, b = 13.8447(2) Å, c = 21.9638(4) Å, β = 91.2230(10)°, V = 3232.60(10) Å^3, Z = 4, μ = 1.306 mm^{-1}, T = 100 K. 26148 measured, 6213 independent reflections (R_{int} = 0.039). The final $wR(F^2)$ was 0.2260 and R = 0.0820 [$F^2 > 2\sigma(F^2)$]. CCDC 267322. See http://dx.doi.org/10.1039/b506232b for crystallographic data in CIF or other electronic format.

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