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## Homoleptic and heteroleptic bis-NHC-Cu(I) complexes as carbene transfer reagents

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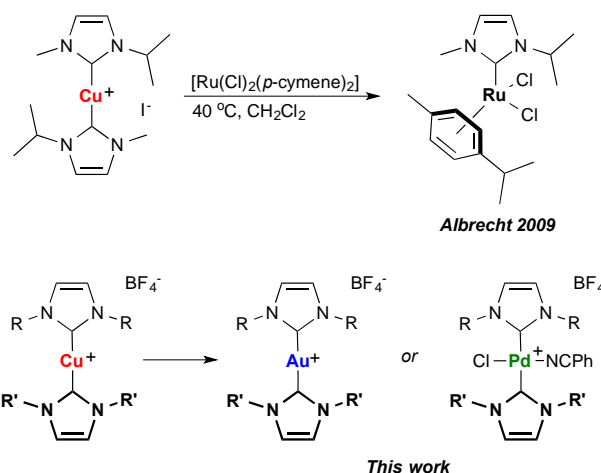
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**Homo- and heteroleptic bis-NHC copper(I) complexes have been efficiently used as carbene transfer reagents to Au and Pd. The simple and straightforward procedure allows for the synthesis of well-known gold complexes as well as novel cationic bis-NHC-Pd(II) species.**

The synthesis of transition metal complexes bearing *N*-heterocyclic carbene (NHC) ligands by carbene transfer from another metal represents a useful alternative to the synthetic methods involving highly unstable free carbenes. Commonly, Ag(I)- and Au(I)- based complexes are efficiently used as transmetallating agents.<sup>1,2</sup> Nevertheless, the use of expensive metals and the requirement of PPh<sub>3</sub> and/or light-free conditions are significant drawbacks associated with these protocols. Recently, inexpensive and air/moisture stable NHC-Cu(I) complexes have been proposed as alternative carbene transfer reagents to other transition metals.<sup>3,4</sup> In 2010, we developed a protocol permitting the synthesis of the most commonly used [Au(Cl)(NHC)] and [Pd( $\mu$ -Cl)Cl(NHC)]<sub>2</sub> *via* transmetallation from [Cu(Cl)(NHC)] precursors.<sup>3</sup> This study showed that sterically demanding NHCs require longer reaction times to be transferred. Recently, the synthesis of the novel [Cu(Cl)(BAC)] complex (BAC = bis-(di-*iso*-propylamino)cyclopropenyldiene) and its role as carbene transfer reagent to Au, Pd, Rh and Ir has been disclosed.<sup>4</sup> The reaction reaches full completion at room temperature within 1 *minute* for gold, rhodium and iridium while the synthesis of the analogous dimeric palladium complex requires 4 h and a temperature of 40 °C. Aside from neutral species, cationic copper(I) complexes bearing two NHC moieties have also been reported. Indeed, these have shown interesting catalytic activity in the hydrosilylation of carbonyl compounds and in the [3+2] cycloaddition of alkynes and azides.<sup>5</sup> Concerning their application in synthesis, Albrecht and co-workers isolated

in 2009 a Ru(II) complex by transmetallation from a homoleptic bis-NHC copper(I) compound (Scheme 1).<sup>6</sup> To the best of our knowledge, this is the sole example of carbene transfer from a cationic bis NHC-Cu complex to another transition metal. In addition, the reaction involving their heteroleptic analogues has never been investigated.



**Scheme 1** Cationic bis-NHC-Cu complexes as carbene transfer reagents

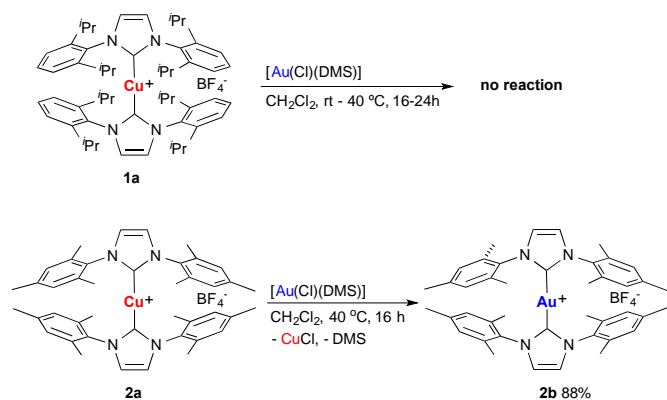
Recently, bis-NHC gold(I)- and palladium(II) complexes have been the subject of synthetic and biomedical applications.<sup>7,8</sup> Gold species have exhibited interesting activity not only as catalysts but also as antimicrobial and anticancer agents.<sup>1c,7a</sup> Concerning the palladium analogues, these have shown to be efficient catalysts in direct arylation reactions,<sup>8a</sup> Suzuki-Miyaura coupling<sup>8b</sup> and alkene oxidation.<sup>8c</sup> As the common synthetic routes towards bis NHC-gold complexes require the isolation of a gold hydroxide synthon<sup>7d</sup> or the use of a microwave reactor,<sup>7e</sup> their synthesis by transmetalation from inexpensive and commercially available copper precursors would be highly desirable. In addition, this strategy would represent an improvement of the well-known synthetic protocols for bis NHC palladium(II) complexes requiring the use of light-sensitive silver(I) species.<sup>8a,b</sup> Herein, we report the

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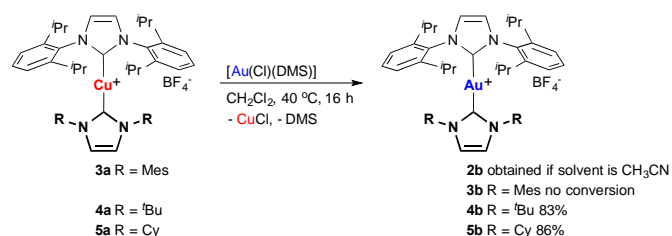
first synthesis of cationic bis NHC gold(I) and Pd(II) complexes by transmetallation from Cu(I) precursors.

In the first instance, the synthesis of homoleptic gold(I) complexes was undertaken and the reaction involving the commercially available  $[\text{Cu}(\text{IPr})_2][\text{BF}_4]$  (**1a**) (IPr = *N,N'*-bis(2,6-(*di-iso*-propyl)phenyl)imidazol-2-ylidene) as carbene source was investigated (Scheme 2). Based on the successful results achieved in the previously reported transmetallation procedures,<sup>3,4</sup>  $[\text{Au}(\text{Cl})(\text{DMS})]$  (DMS = dimethyl sulfide) was chosen as the gold precursor while dichloromethane was selected as solvent. This choice seemed reasonable as both the starting materials and the organometallic product present high solubility in this solvent. In addition, the formation of insoluble CuCl should drive the reaction to completion.<sup>3</sup> Unfortunately, the carbene transfer was unsuccessful both at room temperature and at 40 °C. This can be rationalised by the high steric demand of the NHC.<sup>3</sup> Attempts to promote the reaction by increasing the temperature and/or by using different solvents (acetonitrile, isopropanol) resulted in the decomposition of the organometallic compound.<sup>9</sup>



Scheme 2 Transmetallation from homoleptic bis-NHC-Cu complexes to Au(I)

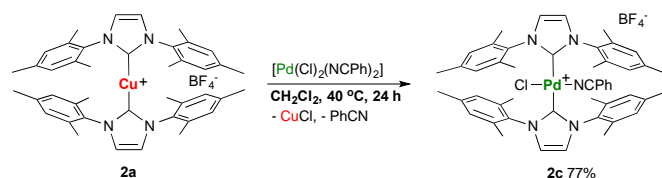
Therefore, the reaction of complex **2a** bearing a smaller NHC (IMes = *N,N'*-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene) was investigated. To our delight, the corresponding  $[\text{Au}(\text{IMes})_2][\text{BF}_4]$  (**2b**)<sup>7e</sup> was isolated in 88% yield after 16 h in  $\text{CH}_2\text{Cl}_2$  at 40 °C (Scheme 2). It has to be noted that the transmetallation can be performed at room temperature but requires a longer reaction time.<sup>9</sup> With these conditions in hand, the synthesis of heteroleptic complexes was addressed (Scheme 3).



Scheme 3 Transmetallation from heteroleptic bis-NHC-Cu complexes to Au(I)

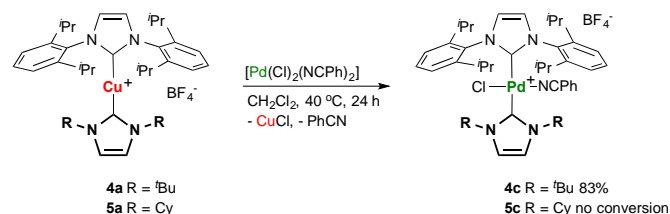
The first species investigated was  $[\text{Cu}(\text{IMes})(\text{IPr})][\text{BF}_4]$  (**3a**). Under the standard conditions ( $\text{CH}_2\text{Cl}_2$ , 40 °C, 24 h), only

starting material and traces of decomposition were observed.<sup>9</sup> By conducting the reaction at room temperature, the decomposition of the copper complex was avoided, but the transfer process was still unsuccessful even after 24 h.<sup>9</sup> Interestingly, by using acetonitrile instead of dichloromethane, the formation of the homoleptic species  $[\text{Au}(\text{IMes})_2][\text{BF}_4]$  **2b** was observed.<sup>9</sup> This result is interesting as such a complex arises from the transfer of the smallest NHC featured in  $[\text{Cu}(\text{IMes})(\text{IPr})][\text{BF}_4]$  (**3a**). These findings provided further evidence supporting the critical influence of the sterics of the ligand on the transfer process.<sup>3</sup> Heteroleptic complexes featuring the IPr moiety and NHCs with alkyl *N*-substituents were next considered. Complexes **4a** and **5a**, bearing <sup>t</sup>Bu (*N,N'*-(*di-tert*-butyl)imidazol-2-ylidene) and ICy (*N,N'*-(dicyclohexyl)imidazol-2-ylidene) respectively, were selectively converted into the corresponding heteroleptic gold(I) complexes. Neither homoleptic species nor decomposition products were observed under the standard conditions, and high isolated yields of the targeted complexes were obtained. Transmetallation to Pd(II) was next investigated. Based on the successful results achieved in the reaction with gold,  $[\text{Cu}(\text{IMes})_2][\text{BF}_4]$  **2a** was considered as carbene transfer reagent for palladium using  $[\text{Pd}(\text{Cl})_2(\text{NCPH})_2]$  as the palladium source. Under the standard conditions ( $\text{CH}_2\text{Cl}_2$ , 40 °C, 16 h), 80% conversion of the starting complex towards an unknown compound was observed by <sup>1</sup>H NMR spectroscopy. In order to improve the conversion to this compound, the reaction time was extended to 24 hours. Full conversion of **2a** was achieved and the new complex  $[\text{Pd}(\text{Cl})(\text{NCPH})(\text{IMes})_2][\text{BF}_4]$  **2c** was obtained microanalytically pure in 77% yield as a yellow powder.

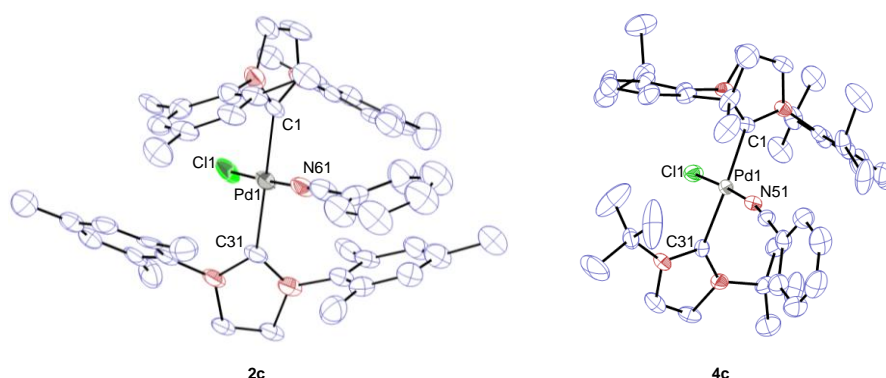


Scheme 4 Synthesis of the homoleptic bis-NHC palladium(II) complex **2c**.

Based on these promising results, attempts to synthesise heteroleptic bis-NHC palladium species were undertaken. To our delight, the reaction involving  $[\text{Cu}(\text{IPr})(<sup>t</sup>\text{Bu})][\text{BF}_4]$  led to the isolation of the novel  $[\text{Pd}(\text{Cl})(\text{NCPH})(\text{IPr})(<sup>t</sup>\text{Bu})][\text{BF}_4]$  (**4c**) complex in 83% yield.



Scheme 5 Synthesis of heteroleptic bis-NHC palladium(II) complexes



**Fig. 1** Molecular structures of  $[\text{Pd}(\text{Cl})(\text{NCPH})(\text{IMes})_2]\text{BF}_4$  **2c** and  $[\text{Pd}(\text{Cl})(\text{NCPH})(\text{IPr})(t\text{Bu})]\text{BF}_4$  **4c**. Ellipsoids are represented at the 50% probability level. Hydrogen atoms and anion are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) (esd): **2c** Pd(1)–C(1) 2.03(2), Pd(1)–C(31) 2.06(2), Pd(1)–Cl(1) 2.261(5), Pd(1)–N(61) 1.958(16), C(1)–Pd(1)–C(31) 178.5(9), Cl(1)–Pd(1)–N(61) 176.1(7), N(61)–Pd(1)–C(1) 88.4(9), Cl(1)–Pd(1)–C(31) 88.6(7),  $\Theta_{\text{NHC-NHC}}$  (torsion angle between the NHCs) 55.0. **4c** Pd(1)–C(1) 2.047(7), Pd(1)–C(31) 2.049(8), Pd(1)–Cl(1) 2.3007(18), Pd(1)–N(51) 2.026(6), C(1)–Pd(1)–C(31) 173.8(3), Cl(1)–Pd(1)–N(51) 176.50(19), N(51)–Pd(1)–C(1) 96.5(3), Cl(1)–Pd(1)–C(31) 86.9(2),  $\Theta_{\text{NHC-NHC}}$  4.0.

Unfortunately, the outcome of the reaction of  $[\text{Cu}(\text{ICy})(\text{IPr})][\text{BF}_4]$  **5a** with the Pd precursor is in contrast with the results obtained with gold. Indeed, under the standard conditions, a complex mixture of products was obtained. After recrystallisation, the main compound was characterised as the dimeric  $[\text{Pd}(\mu\text{-Cl})\text{Cl}(\text{IPr})]_2$ .<sup>3</sup> Nevertheless, the successful synthesis of complexes **2c** and **4c** is remarkable as cationic bis NHC palladium(II) species bearing two different co-ligands (Cl and PhCN) and a tetrafluoroborate unit as counterion have never been reported to date. In addition, complex **4c** represents, to the best of our knowledge, the first example of heteroleptic bis NHC palladium(II) species. In order to unambiguously assess the nature of the two new species, crystals were obtained from a saturated solution of **2c** and **4c** in chloroform and analysed by X-ray diffraction (Figure 1).<sup>10</sup> Both complexes present a square-planar geometry with Pd–C<sub>carbene</sub> and Pd–Cl distances in agreement with the ones found in the corresponding  $[\text{Pd}(\text{Cl})_2(\text{NHC})_2]$  complexes.<sup>8</sup> Interestingly, the torsion angle between the two NHC fragments is wider in **2c** than in **4c** (55.0 and 4.0° respectively). Although this is in contrast with the steric properties of the ligands involved, the narrow angle in **4c** can be justified considering the high flexibility of the *tert*-butyl substituents. In addition, the twist between the two IMes fragments in **2c** explains the *non*-equivalence of the three methyl groups in the mesityl units observed by both <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H} NMR spectroscopy.<sup>9</sup>

## Conclusions

The carbene transfer from homoleptic and heteroleptic bis-NHC-Cu complexes to gold(I) and palladium(II) was investigated. This synthesis protocol employs commercially

available starting materials and allows for the synthesis of the most common homo- and heteroleptic bis NHC gold(I) species under mild conditions avoiding the isolation of  $[\text{Au}(\text{OH})(\text{NHC})]$  synthons and/or the use of a microwave reactor. In addition, by means of this procedure, two novel cationic bis-NHC palladium(II) complexes have been isolated and fully characterised. Scope and limitations, as well as the mechanism of this transformation are still under investigation in our laboratory.

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- 9 See ESI for further information
- 10 CCDC-1435102 (**2c**) and CCDC-1435103 (**4c**) contain the supplementary crystallographic data for this contribution.