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Janus-type homo-, hetero- and mixed valence-bimetallic complexes with one metal encapsulated in a cyclodextrin

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Bis-azolium salts with one azolium capping a perbenzylated α -cyclodextrin have been designed to generate Janus-type bimetallic complexes with various combinations of copper, silver, gold or palladium salts. Encapsulation of one metal center inside the cavity allowed to control (trans)metalation and oxidation reactions at selected positions. In particular, it was possible to oxidize Au^I into Au^{III} selectively on the position outside the cavity of the cyclodextrin on the bis-Au^I Janus complex.

Janus-type bimetallic complexes are metal complexes in which the two metal centers are placed in opposite directions through a single-molecule ditopic ligand, with no direct metallophilic interactions. *N*-heterocyclic carbene (NHC)-based bimetallic complexes have been reported with ditopic NHC ligands (Figure 1).^{1,2,3,4,5,6,7,8} Such structures, which involve two identical or two different metal centers (homo- or heterobimetallic) are particularly interesting for applications in tandem catalysis,^{9,10,11,12} organometallic polymers,^{13,14,15,16} or single molecular electronics.^{17,18,19,20,21,22} NHC-based Janus-type *heterobimetallic* complexes have been reported with different metal combinations (Ir^{III}/Pd^{II}, Pt^{II}, Ru^{II}, Rh^{III}, Au^I; Rh^{III}/Au^I, Ag^I, Pd^{II}, Ru^{II}; Rh^I/Pd^{II}, Au^I, Ir^I, Ru^{II}; Ru^{II}/Pd^{II}; Mn^I/Fe^{II}; or Au^I/Ag^I).¹ Some of these complexes displayed enhanced activity and selectivity in catalysis by comparison with the joint activity of the two corresponding monometallic complexes or homobimetallic complexes.^{7,8,9,10} The synthesis of NHC-based heterobimetallic complexes from (bis)azolium salts precursors is challenging due to the identical or very close properties of the reactive centers in these precursors. The most common Janus-type bis-NHC precursors are symmetrical.^{7,8} In this case, site selective and sequential metalation strategies have been developed to give heterobimetallic complexes such as ditriazolylidene(ditz)-based or phenylene-bridged bis-NHC-based complexes (**A**) and (**B**) (Scheme 1).^{23,24,25,26} Another strategy lies in the design of non-symmetrical precursors to control the sequential introduction of the two different metallic centers.^{27,28,29,30,31} For instance, benzimidazolylidene-imidazolylidene-based heterobimetallic complexes (**C**) have been efficiently prepared from the corresponding bis-azolium salts through selective deprotonation, metalation,²⁷ and orthometalation reactions.²⁸ Alternatively, oxidative addition/metalation sequences were reported as efficient tools for preparing bis-NHC heterobimetallic complexes from azolium-2-halogenoazolium salts.^{30,31}

We previously described a family of NHC-capped cyclodextrins (CDs) and the corresponding encapsulated complexes with coinage metals (Cu^I, Ag^I, Au^I)^{32,33}, and Pd^{II}.³⁴ We showed that the CD, which acts as first and second coordination sphere for the encapsulated metal reactive center,^{33,35,36,37} induced impressive cavity-dependent regio-,^{38,39,40} stereo-,^{32,33,40,41} and chemoselectivity^{32,33,42} in catalytic reactions.⁴³ We could also change the course of a given reaction with the size of the cavity^{32,33} or the size of an incoming nucleophile.⁴¹ More recently, we also showed that the structure/shape of the CD cavity affected the coordination modes of encapsulated metal complexes.³⁴

We show here that encapsulation of one metal center in complexes **D**, based on a symmetrical ditopic NHC core, gave a unique opportunity to generate Janus-type homo-, hetero- and heterovalent bimetallic complexes with various combinations of metal centers.

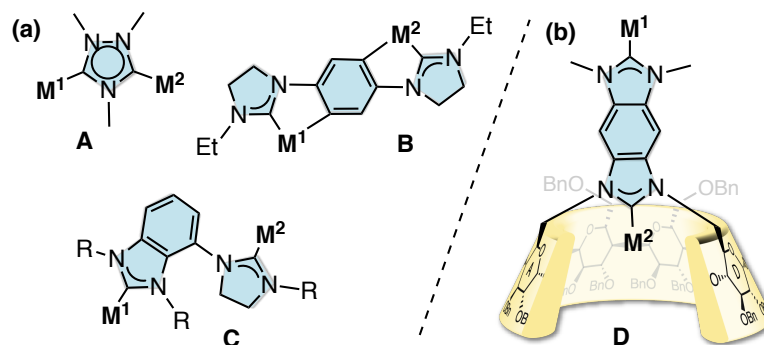


Figure 1. (a) Examples of bimetallic complexes with ditopic NHC ligands. $M^1=M^2$: homobimetallic complexes. $M^1\neq M^2$: heterobimetallic complexes; (b) CD-bis(NHC)-based bimetallic complexes developed in this work.

Bimetallic complexes **D** were obtained from the bis(azolium) precursor **1** which was prepared from the previously reported bis-mesylate **2** derived from α -CD.^{32,44} Substitution with iodide ions gave the bis(iodo) derivative **3**. This transformation was found to favor subsequent capping of the CD in the presence of an excess of benzo-bis(imidazole) (BBI),⁴⁵ leading to the monoazolium iodide **4** in 51% yield over two steps (Figure 2). A controlled mono-methylation/dimethylation sequence was applied to obtain the expected benzo-bis(imidazolium) bis-chloride **1** in 57% yield after halogen exchange with a chloride resin.

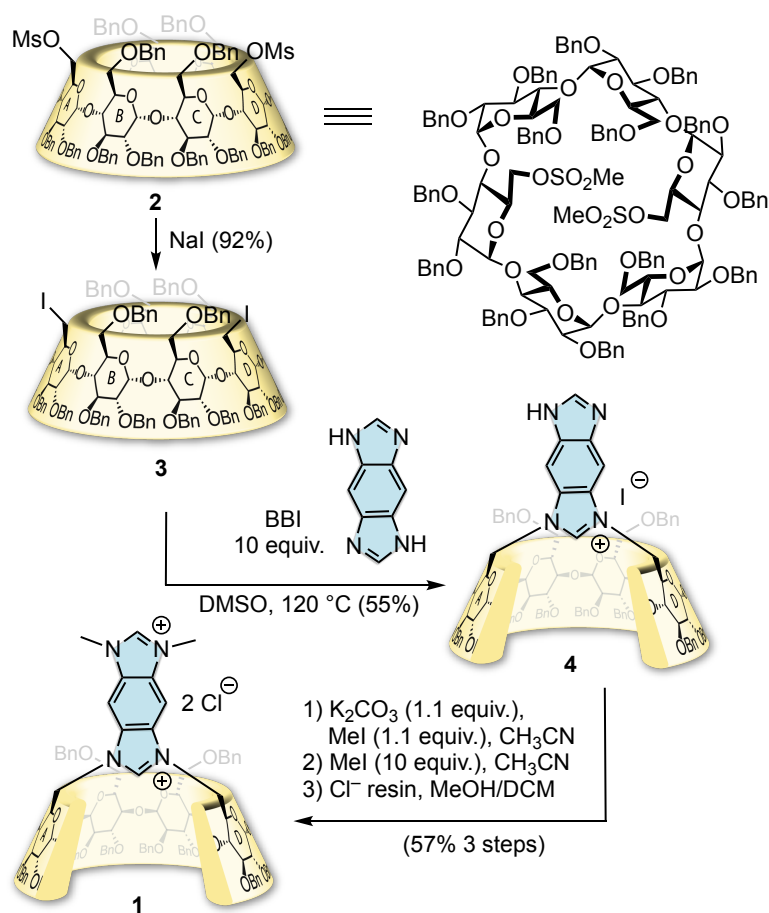


Figure 2. Synthesis of the cyclodextrin(CD) bis-azolium precursor **1**.

From the bis(azolium) precursor **1**, various reactions were tested to get mono-, homobi- and heterobimetallic complexes (Figure 3). The bis-silver complex **5** was easily obtained in 98% yield after reaction of **1** with an excess (10 equiv.) of Ag_2O at 40 °C (eq. (i)).⁴⁶ The formation of the bis-gold complex **6** was found more difficult. Direct metalation of **1** with $AuCl_3 \cdot SMe_2$ and K_2CO_3 gave complex **6** in only 8% yield (eq. (ii)). Here, the major

complex (40%) is the mono-gold complex **7** with a gold chloride unit outside the cavity. A side product of the reaction is the formation of the corresponding urea. Similarly, reaction of the bis-silver complex **5** with an excess of AuCl.SMe₂ gave exclusively the heterobimetallic Au^I/Ag^I complex **8** in 59% yield, with no exchange of silver inside the cavity (eq. (iii)). These results suggested that the constraint imposed by the α -CD cavity made difficult the introduction of gold inside the cavity through metalation or transmetalation reactions using AuCl.SMe₂ complex, while it is possible when using AuCl itself.³² Hence, transmetalation from silver to copper using CuCl was found to be possible inside the CD cavity. The reaction of the bimetallic Au^I/Ag^I complex **8** with CuCl gave the hetero-bimetallic Au^I/Cu^I complex **9** with an encapsulated copper center in 78% yield (eq. (iv)). Unexpectedly, the introduction of gold inside the cavity and the preparation of the bis-gold complex **6** in reasonable yields could be achieved through a Pd to Au NHC ligand exchange, as detailed next.

In previous studies, we demonstrated that square planar coordination was not allowed in the cavity of α -CD.³⁴ Therefore, reaction of the bis(azolium) **1** with Pd(allyl)Cl dimer and K₂CO₃ led to the exclusive formation of the Pd complex **10** (72%) with the metal outside the cavity (eq. (v)). Surprisingly, when **10** was reacted with AuCl.SMe₂/K₂CO₃ to introduce AuCl inside the cavity, the bis(gold) complex **6** was obtained in 31% yield instead of the expected Pd/Au complex (eq. (vi)). To get complex **6**, a Pd to Au exchange must take place on the NHC unit outside the cavity. The reverse transfer of NHC from (NHC)AuCl to [(PhCN)₂PdCl₂] was reported,⁴⁷ but to the best of our knowledge, Pd to Au NHC transfer is unprecedented. Mechanisms involving species with Pd–Au interactions have been proposed for Au to Pd transmetalation processes in catalytic reactions.^{48,49} In the present case, such interactions, and the presence of an excess of AuCl, could favor a reverse Pd to Au NHC transfer. Next, the introduction of a silver center inside the cavity from the Pd complex **10** was achieved by reaction with an excess of Ag₂O. The corresponding Pd^{II}/Ag^I heterobimetallic complex **11** was isolated in 45% yield (eq. (vii)). Finally, protection of the Au^I center inside the CD cavity from oxidation was explored.³⁴ Treatment of the Au^I/Au^I complex **6** with a large excess of dichloro(iodobenzene) (PhICl₂) was found to give exclusively the mixed-valence Au^{III}/Au^I complex **12** in 90% yield through selective oxidation of the Au^I center outside the cavity (eq. (viii)). Tetra(NHC) mixed-valence Au^{III}/Au^I complexes have been reported with chelating bis(NHC) ligands,^{50,51,52} but to the best of our knowledge, not with Janus-type bis(NHC). Tetra(NHC) Au^{III}/Au^I complexes were first observed as by-products due to bromine reductive elimination from an Au^{III}/Au^{III} complex,⁵⁰ or to formal disproportionation of an Au^{II}/Au^{II} complex.⁵¹ More recently, bis-cationic tetra(NHC) Au^{III}/Au^I complexes stabilized by Au^{III}–Cl...Au^{I+} interactions have been prepared in high yields by Br₂ or SOCl₂ oxidation of Au^I/Au^I complexes.⁵² In our case, stable Au^{III}/Au^I complexes **12** are isolated with no aurophilic or halogen-gold interactions. Under similar conditions, oxidation of Au^I/Ag^I and Au^I/Cu^I complexes **8** and **9** gave the Au^{III}/Ag^I and Au^{III}/Cu^I heterobimetallic complexes **13** and **14** in 94 and 93% yields, respectively (eq. (ix) and (x)). Therefore, Au^I, Ag^I and Cu^I centers inside the α -CD cavity are highly protected from chemical oxidation under the conditions used.

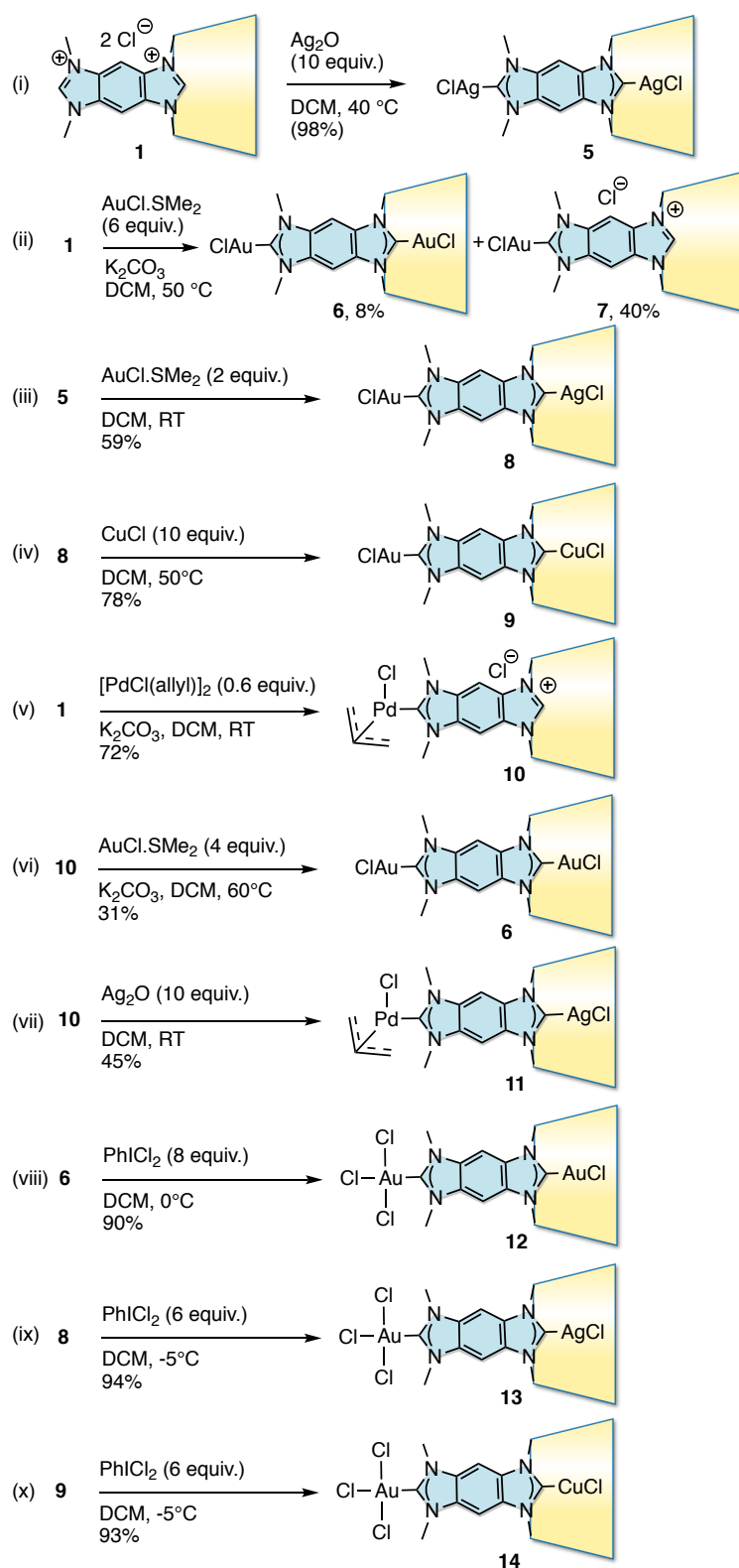


Figure 3. CD-bis(NHC)-based homo-, hetero- and mixed-valence bimetallic complexes.

All these transformations led to a series of eight different bimetallic complexes, with one encapsulated metal center, which have all been fully characterized by ^1H and ^{13}C NMR. Of particular interest are the ^{13}C chemical shifts of the carbene carbons which reflect, to a certain extent, the s -character of the NHC σ orbital and the

strength of the C–metal bond.⁵³ For the homobimetallic complex **6**, the two ¹³C chemical shifts are not identical, reflecting the different environments of the two Au^I centers (Table 1). Although the ditopic NHC core is identical for both metal centers, the carbene carbon inside the cavity is more shielded by 0.7 ppm suggesting that the C–Au bond is slightly stronger. For comparison, a single δ_{carbene} of 181.9 ppm was reported for the symmetrical bimetallic complex BBI(AuCl)₂.⁵⁴ Next, careful examination of ¹³C carbene NMR values of bimetallic complexes with an Au^I or an Au^{III} center outside the cavity and the same or another coinage metal (Au, Ag, or Cu) inside the cavity was performed to investigate the potential communication between the two carbene centers in the complexes (Table 1).

Entry	Complex	[M]out	δ_{out} (ppm)	[M]in	δ_{in} (ppm)
1	6	AuCl	182.54	AuCl	181.84
2	12	AuCl ₃	155.62	AuCl	183.86
3	8	AuCl	183.15	AgCl	189.93
4	13	AuCl ₃	155.86	AgCl	192.05
5	9	AuCl	182.74	CuCl	185.66
6	14	AuCl ₃	155.28	CuCl	187.48

Table 1. ¹³C carbene NMR values of selected CD-bis(NHC) metal complexes (CDCl₃, 150 MHz).

Comparison of δ_{out} values first showed that changing the metal inside the cavity only slightly affected the ¹³C chemical shift of the carbene outside the cavity with a $\Delta\delta_{\text{out}}$ of ca. 0.6 ppm. Values ranging from 182.54 to 183.15 ppm were observed for C–AuCl outside (δ_{out} of complexes **6**, **8**, **9**) and from 155.28 to 155.86 for C–AuCl₃ outside (δ_{out} of complexes **12–14**).⁵⁵ More significantly, changing the oxidation state of the metal outside from Au^I to Au^{III} induces a downfield shift of the carbene inside for which a deshielding of ca. 2 ppm was observed in the three cases (compare δ_{in} of **6/12**, **8/13**, and **9/14**). Therefore, Au^I-to-Au^{III} oxidation outside the cavity affects the electronic properties of the carbene inside the cavity, that behaves as a weaker σ -donor. The effect observed could be related to an increase of the s-character of the carbene σ orbital inside the cavity and to an elongation of the corresponding C–M bond. Cyclic voltammetry can be used to quantify metal-to-metal interactions in homobimetallic complexes with ditopic NHC ligands,^{56,57,58,59} but is difficult to apply to bis-gold complexes.^{5,6} In a preliminary cyclic voltammetry (CV) study of the BBI-based bis-gold(I) homobimetallic complex **6**, we observed that none of the Au^I centers (inside or outside the CD cavity) were oxidized under the conditions used, although the outside Au^I center could be chemically oxidized to give complex **12**. Additional CV experiments starting from the Au^{III} complexes **12–14** suggested that the nature of the encapsulated metal in the cavity (Au^I, Ag^I or Cu^I) had no significant influence on the Au^{III}/Au^I reduction potential of the gold center outside the cavity (See SI), a similar trend to that observed by NMR for the C_{carbene} chemical shifts.

In conclusion, we showed here that capping one side of a symmetrical BBI-based ditopic NHC precursor by a modified α -CD enables selective metalation, transmetalation and oxidation reactions to take place to form a series of homo-, hetero-, and mixed-valence bimetallic complexes. Due to the constraint induced by the cavity, the metal center inside the CD is protected from oxidation, and is also more difficult to introduce and exchange. Au^I-to-Au^{III} oxidation outside the cavity was shown by ¹³C NMR to slightly affect the electronic properties of the carbene inside the cavity. Studies are ongoing to further investigate metal-to-metal connection in these systems and the effect of the CD cavity.

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