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Planar tris-N-heterocyclic carbenes†

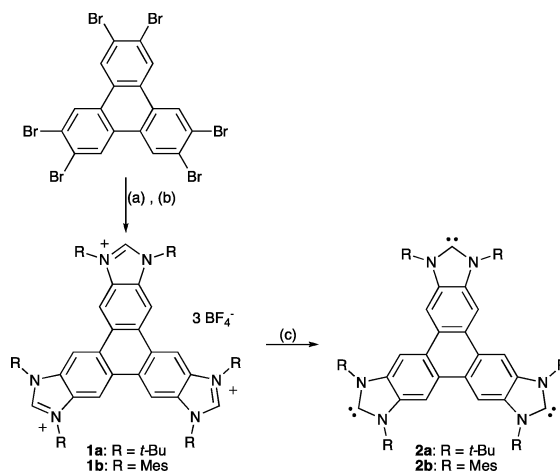Yun-Ting Wang, Meng-Ting Chang, Gene-Hsiang Lee, Shie-Ming Peng and Ching-Wen Chiu*

To further explore the coordination chemistry of poly-carbene complexes, two triphenylene-based planar tridentate N-heterocyclic carbenes and their corresponding tri-gold complexes were synthesized. Molecular structures of the *tert*-butyl substituted tritopic free carbene and the tri-nuclear gold complex were determined experimentally. A silver-dicarbene organometallic polymer was also prepared with the newly synthesized tris-NHC.

Since the isolation of Arduengo's carbene[1] in the early 90s, research on divalent carbon species stabilized within the nitrogen heterocycles has shown tremendous advances in both organic and organometallic catalyses.[2–8] Their superb sigma donating ability in conjunction with imposed steric protection of the bonded elements also led to the discovery of several otherwise unstable low-valent main-group derivatives.[9–11] Not only does the monodentate NHC play an imperative role in recent chemical advances, molecules featuring multiple NHC units have also captivated considerable attention. While the chelating type poly-NHCs facilitate the formation of highly reactive metal catalysts,[12] the bridging type poly-NHCs are utilized in various supramolecules that feature interesting molecular structures, ranging from one-dimensional organic[13–18] and organometallic polymers[19–23] to molecular squares,[24–26] three-dimensional molecular cages[27–29] and organo-metallic polymers.[30] These poly-NHCs containing supramolecules are not only structurally fascinating but also function as active catalysts in heterogeneous catalysis[30–34] and semiconducting materials.[14,18,35,36]

For potential application of poly-NHCs in porous coordination polymers, rigid poly-NHC ligands having angular geometry should be favourable. In fact, the annulated tritopic NHC ligand based on triptycene has been prepared by Bielawski and co-workers.[37] However, the corresponding organometallic polymers have not been reported. Since intermolecular π–π interactions could be extremely helpful in attaining long-range ordered structure, angular poly-NHC ligands in planar aromatic systems could have better chance in realizing crystalline coordination polymers. Therefore, we decided to prepare rigid, planar tridentate NHC ligands and to examine their application in the syntheses of tri-nuclear gold complexes and silver–NHC organometallic polymer. During the reviewing process of this work, Peris' group published the synthesis of compound **1a** and its corresponding tri-gold (**3a**) and tri-palladium complexes. Catalytic activities of both tri-nuclear metal complexes were also evaluated.[38]

As shown in Scheme 1, hexa-amino triphenylenes obtained from Buchwald–Hartwig amination of hexabromo triphenylene with *tert*-butylamine or mesitylamine were subject to formylative cyclization with triethylorthoformate in the presence of HBF₄ to afford compounds [**1a**][BF₄]₃ and [**1b**][BF₄]₃ in good yield. The characteristic ¹H and ¹³C NMR resonances of the [N–*CH*–N]⁺ units of [**1**]³⁺ are typical ([**1a**]³⁺: 9.17 ppm and 142.6 ppm; [**1b**]³⁺: 10.39 ppm and 148.1 ppm).[39] The symmetric nature of [**1a**]³⁺ and [**1b**]³⁺ was evident in the ¹H NMR spectra of both compounds,

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† Electronic supplementary information (ESI) available: Experimental details of all reported compounds. X-ray crystallographic data of **1b**, **2a** and **3a**, ¹³C SSNMR of **2a-Ag**. CCDC 936892–936894. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43278e

Scheme 1 Synthetic procedures for **1** and **2**. Reaction conditions: (a) Pd(OAc)₂, IPr·HCl, NaOᵗBu, RNH₂ (R: *t*-Bu (a); Mes (b)), toluene, 100 °C, 48 h; (b) HC(OEt)₃, HBF₄·OEt₂, r.t. (**1a**: 18 h; **1b**: 72 h); (c) KH, KOᵗBu, THF, 2 h.

in which only one set of proton resonances for the triphenylene backbone ([1a]$^{3+}$: 9.19 ppm; [1b]$^{3+}$: 8.81 ppm) and the azolium units was observed ([1a]$^{3+}$: 2.04 ppm; [1b]$^{3+}$: 7.32, 2.45 (*para*-Me), 2.11 ppm (*ortho*-Me)). Single crystals of [1b][BF$_4$]$_3$ were obtained as dark thin needles by slow diffusion of ether into a dichloromethane solution of [1b][BF$_4$]$_3$ at room temperature. Although the structural connectivity of [1b]$^{3+}$ could be established using single crystal X-ray diffraction analysis, the disordered inclusion solvent molecules in the crystal lattice preclude the precise determination of numerical parameters of [1b]$^{3+}$ (Fig. S1, ESI†).‡ Given the fact that *N,N′*-dimesityl-*ortho*-phenylenediamine is notoriously reluctant to undergo formylative cyclization reaction, the relatively facile synthesis of [1b][BF$_4$]$_3$ at ambient temperature was very surprising.[40,41] An attempt at shortening the reaction time by raising the reaction temperature resulted in a complicated reaction mixture, from which no [1b][BF$_4$]$_3$ was isolated.

With compound [1]$^{3+}$ in hand, we then decided to isolate the corresponding tridentate free carbenes. Generation of tritopic free NHCs (2a and 2b) was accomplished *via* deprotonation of the corresponding azolium salts with potassium hydride in the presence of a catalytic amount of potassium *tert*-butoxide in THF. Upon deprotonation, the characteristic ^{1}H resonance signal of the [N–C*H*–N]$^+$ unit disappeared ([1a]$^{3+}$: 9.17 ppm; [1b]$^{3+}$: 10.39 ppm), and the whole spectrum shifted up-field. The formation of the divalent carbon centers was corroborated by the detection of the distinctive ^{13}C resonance of 2a and 2b at 230.4 ppm and 231.4 ppm, respectively.[39] The bulky *N*-substituents (*tert*-butyl and mesityl) stabilize the active ylidene centres kinetically, and prevent the newly prepared tritopic NHCs from polymerizing through the formation of dibenzotetraazafulvalene.[42,43]

The molecular structure of 2a was further confirmed by single crystal X-ray diffraction analysis. Single crystals of 2a were obtained *via* slow evaporation of a benzene solution of 2a at room temperature in a dry-box. The 2a benzene solvate crystallized as colourless blocks in the monoclinic P2$_1$/m space group. As shown in Fig. 1, compound 2a adopts the C$_{2v}$ symmetry with essentially planar central fused arenes. The distances from each ylidene carbon to the centroid of triphenylene are identical (5.861 Å). The averaged C–N distance of 1.373 Å and the N–C–N angle of 104.4° of the benzimidazol-2-ylidene unit are comparable
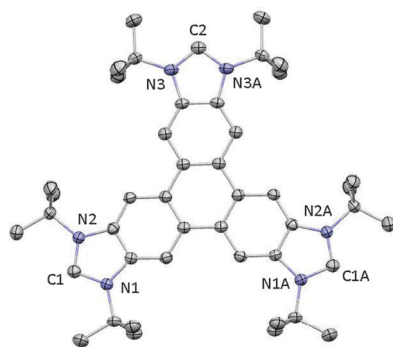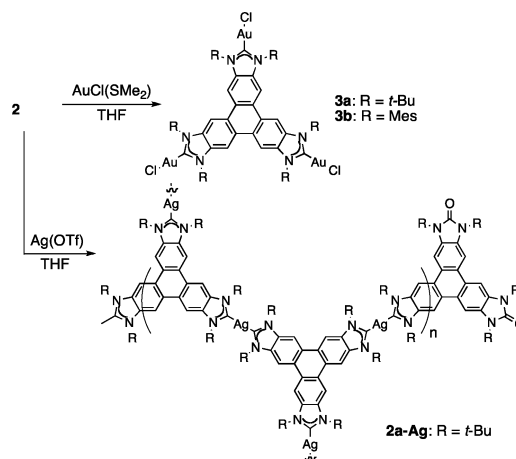
to those observed in the mono-dentate ligand, suggesting that the annulation of three carbene moieties on triphenylene poses negligible electronic constraints on each individual NHC unit.

The lack of electronic constraints is also evident in the reaction of 2 and AuCl(SMe$_2$). 3.5 equivalents of gold complex were introduced to the tritopic free carbene (2) at room temperature (Scheme 2). The resulting mixture was stirred overnight to afford the anticipated tri-gold complexes (3) in good yield (74% for 3a and 68% for 3b). The formation of the carbon–gold bond is verified using ^{13}C NMR spectroscopy, where the C2 carbons of 3a and 3b were respectively detected at 182.3 ppm and 185.2 ppm. The observed ^{13}C resonance values are comparable to those reported for other NHC–AuCl complexes.[39,44] Examination of the crude reaction mixture confirmed the absence of mono- and di-gold complexes, suggesting that the coordination of the first ylidene centre does not impact the reactivity of the rest of the carbene units.

Single crystals of 3a suitable for X-ray diffraction analysis were obtained from diffusion of ether into a CH$_3$CN–CH$_2$Cl$_2$ solution of 3a at room temperature. The molecular structure of 3a shown in Fig. 2 confirms the formation of the desired tri-nuclear gold carbene complex. Interestingly, the central triphenylene back-bone is no longer planar. The ruffled structure of the tri-gold complex could be the result of crystal packing and very weak aurophilic interactions (Fig. S2, ESI†). In each tri-gold complex, two of the gold atoms deviate from the plane of the triphenylene ring and form weak interactions with adjacent tri-gold complexes with Au–Au distances of 3.631 Å and 3.730 Å, which are considerably longer than the typical aurophilic interaction distance of 2.5–3.5 Å.[45]

Encouraged by the isolation of 3 we then decided to investigate whether ligand 2 is capable of forming three-dimensional organo-metallic polymers for potential application in heterogeneous catalysis.[30–33] Since the silver–NHC complex is a common carbene transfer reagent, the silver–NHC coordination polymer could potentially be the starting material for various metal–carbene polymers.[15] Upon mixing the THF solution of 2a and AgOTf, the light brown coordination polymer (2a-Ag) formed and precipitated out of the solution immediately. Formation of the [C$_{(NHC)}$–Ag–C$_{(NHC)}$]$^+$ linkage was corroborated by the detection of a characteristic ^{13}C resonance signal around

Fig. 1 Molecular structure of 2a. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)–C(1) 1.370(2), N(2)–C(1) 1.374(2), N(3)–C(2) 1.374(2), N(1)–C(1)–N(2) 104.33(14), N(3)–C(2)–N(3A) 104.6(2).

Scheme 2 Syntheses of tri-gold NHC complexes (3) and the silver-dicarbene coordination polymer (2a-Ag).
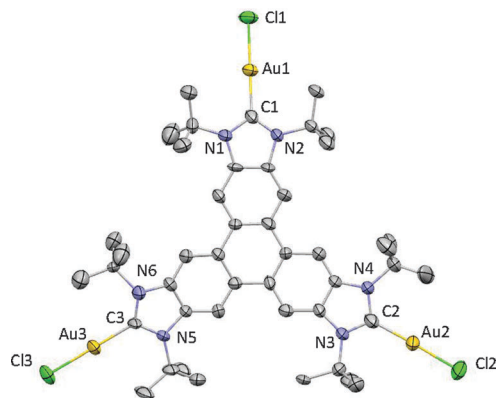
Fig. 2 Molecular structure of **3a**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Au(1) 2.002(16), C(2)–Au(2) 2.002(15), C(3)–Au(3) 1.991(16), Au(1)–Cl(1) 2.304(4), Au(2)–Cl(2) 2.289(5), Au(3)–Cl(3) 2.267(5), N(1)–C(1) 1.347(19), N(2)–C(1) 1.387(18), N(3)–C(2) 1.367(19), N(4)–C(2) 1.342(19), N(5)–C(3) 1.353(19), N(6)–C(3) 1.41(2), N(1)–C(1)–N(2) 108.4(13), N(3)–C(2)–N(4) 108.2(12), N(5)–C(3)–N(6) 107.6(13).

180 ppm in the solid-state NMR spectrum (Fig. S3, ESI†). Interestingly, the ^{13}C resonance signals for the Ag-NHC moiety appear at 179 ppm and 172 ppm, indicating the presence of two types of carbene ligands. The 179 ppm signal is assigned to the internal tris-NHC ligand that bonds to three silver atoms. The 172 ppm signal belongs to the terminal NHC moiety, which is partially oxidized and is linked to only one or two silver metals. The presence of the urea functionality is also confirmed by the detection of a ^{13}C resonance at 161 ppm. Unfortunately, no noticeable diffraction peaks were observed in PXRD, confirming the amorphous nature of the polymer. The lack of crystallinity of the silver–carbene polymer could be a result of the strong metal–carbene bond that leads to the formation of kinetic products exclusively.

In summary, we reported the syntheses of two planar tridentate NHC ligands and their corresponding tri-gold complexes. Structural characterizations of the *tert*-butyl substituted free tris-NHC and the tri-gold complex were achieved. The amorphous organometallic polymer featuring $[C_{(NHC)}$–Ag–$C_{(NHC)}]^{+}$ linkage has also been prepared. Currently, we are focusing on the modification of the electronic properties of the *N*-substituents, and the extension of the tri-metallo-NHC complexes from a discrete molecular structure to an ordered extended polymer network by incorporation of more labile metal-ligand interactions.

Notes and references

‡ Crystal data of **1b** can be found in ESI.†

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