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# A stable Janus bis(*malo*NHC) and its zwitterionic coinage metal complexes<sup>†</sup>

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Daniela Tapu,\*<sup>a</sup> Zachary McCarty<sup>a</sup> and Colin McMillen<sup>b</sup>

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The first stable dianionic Janus-type bis(*malo*NHC) was isolated and characterized. Details on the chemistry of this biscarbene with respect to its ability to support catalytically relevant metal complexes are provided. The molecular structures of two dinuclear gold and silver complexes were determined by X-ray crystallography.

Since the discovery of the first stable nucleophilic carbene by Arduengo over two decades ago,<sup>1</sup> the area of carbene chemistry has emerged as one of the most rapidly investigated and promising fields of study in modern chemistry.<sup>2-5</sup> Due to their functional and synthetic diversity, as well as a high affinity toward a wide range of main group and transition metals, archetypal nucleophilic carbenes, namely N-heterocyclic carbenes (NHCs), have shown remarkable utility as ligands for organometallic catalysts,<sup>6</sup> and as organocatalysts.<sup>7</sup> Moreover, NHCs have found utility in a broad range of medicinal, luminescent, and other functional materials.<sup>8-13</sup> Among NHCs, polyNHCs have attracted great interest because they allow for the preparation of metal complexes with a variety of geometries and reactivities. However, the vast majority of the reported bis-, tris-, and tetra-NHCs were designed to bind in a chelating, pincer or tripodal fashion leading to monometallic complexes.<sup>14-17</sup> Vital to the advancement of NHC-based materials has been the design and synthesis of new rigid multitopic NHCs featuring geometrically isolated carbene moieties.<sup>10,18-40</sup> Among this very restrictive class of NHCs, compounds 1-4 in Scheme 1 are the only known systems containing two linearly opposed NHC moieties (Janus-type coordination). While still in their infancy, these systems have found tremendous utility as building blocks for homo- and heterometallic



complexes,  $^{18-20,26,27,29,37,41-44}$  organic and organometallic polymers,  $^{18-20,38,45-47}$  and supramolecular structures.  $^{10,24,31,34,48}$ 

Having observed the well documented success of these Janus-type NHCs as a new class of bridging ligands, we sought to extend the existing frameworks to a dianionic system of type 5 composed of two linearly opposed NHC moieties connected by a common phenylene fragment. In contrast to carbenes 1-4, all neutral "L2"-type ligands according to the Green formalism, carbene 5 contains two remote anionic functionalities (malonate moieties) within the heterocyclic backbone. This translates into a (-2) overall charge of the ligand. As a consequence, metalation can occur concomitant to the displacement of other anionic ligands (e.g. halides) from various transition metal precursors, thus resulting in neutral bis-zwitterionic species with potentially valuable advantages relative to the classical cationic metal complexes produced by neutral NHCs.49 The idea to incorporate anionic moieties into 5 emerged by noticing the recent success that maloNHCs 650 have had as new topologically distinct ensembles of six-membered NHCs. Investigations into the transition-metal coordination chemistry

<sup>&</sup>lt;sup>a</sup> Department of Chemistry and Biochemistry, Kennesaw State University, 1000 Chastain Road, Kennesaw, GA, 30144, USA. E-mail: dtapu@kennesaw.edu; Fax: +1-770-423-6744; Tel: +1-678-797-2259

<sup>&</sup>lt;sup>b</sup> X-ray Crystallography Laboratory, Department of Chemistry, Clemson University, Clemson, SC, 29634, USA

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Scheme 2 Synthetic procedures for 5 and 7 reaction conditions: (a) N,N'bis(2,6-di-isopropylphenyl)formamidine, dichloromethane, 0 °C, 25 min; (b) Et<sub>3</sub>N, 0 °C, 3 h; (c) KHMDS, THF, 30 min, r.t.

of 6 have led to the synthesis of a series of zwitterionic metal complexes with interesting catalytic properties.<sup>50-54</sup> In addition, it has been shown that by direct reaction of the malonate functionality with an electrophile, the electronic properties of 6 can be finely tuned postcomplexation with various transition metals without disrupting the steric environment created around the metal center.53

As shown in Scheme 2, the zwitterionic precursor 7 was obtained by coupling 1,4-phenylenedimalonyl tetrachloride<sup>55</sup> with N,N'-bis(2,6-di-isopropylphenyl)formamidine<sup>56</sup> in dichloromethane in the presence of excess triethylamine. Compound 7 was found to be neither air nor moisture sensitive. This resistance to moisture advantageously facilitated the removal of the Et<sub>3</sub>N·HCl from the reaction mixture.

The crystallographic analysis for 7 revealed the expected framework (Fig. 1) and confirmed the bis-zwitterionic structure outlined in Scheme 1. The average N-C1 distance (1.311 Å) and the N-C-N angle  $(122.0(6)^{\circ})$  measured were in accord with those previously reported for the NHC·H<sup>+</sup> precursors of mono maloNHC 6.50 The central phenylene moiety is twisted by 31.79° relative to each pyrimidine ring. As expected, the N1-C4 and N2-C2 bonds (1.473(8) and 1.465(8) Å, respectively) are very long for amide functionalities, a result of competitive delocalization of the negative charge over the C4-C3-C2 fragment which reduces the multiple bond character of the amidic C-N bonds.<sup>50,57</sup>

Having isolated 7, subsequent efforts were focused on exploring the synthesis and reactivity of the dianionic carbene 5. The free carbene was generated cleanly and quantitatively by treatment of 7 with 2 equivalents of potassium bis(trimethylsilyl)amide, (KHMDS) at room temperature. Carbene 5 is stable for at least several days and it is only slightly soluble in THF. Despite our best efforts, all attempts to grow X-ray quality crystals of 5 were not successful, at least partly a result of its limited solubility in



Scheme 3 Synthetic procedures for 8 and 9. (a) N,N'-bis(2,6-Di-isopropylphenyl)formamidine, dichloromethane, 0 °C, 25 min; (b) Et<sub>3</sub>N, 0 °C, 3 h; (c) KHMDS, d<sub>8</sub>-THF, 30 min, r.t.

common organic solvents. The <sup>13</sup>C NMR spectrum of 5 exhibited a single diagnostic signal at  $\delta$  249.88 ppm (THF- $d_8$ ) indicative of its formulation as a NHC and also of its highly symmetric structure. For comparative purposes, the anionic monocarbene 9 was also generated (Scheme 3). The <sup>13</sup>C resonance of the carbene nucleus was observed at  $\delta$  249.37 ppm (THF- $d_8$ ). Based on the similarity observed in the spectroscopic data of 5 and 9, we postulated that the reactivity and affinity toward transition metals of each NHC moiety of 5 should be similar to that exhibited by its monotopic analogue 9.

Due to the emergence of numerous catalytic, photophysical and biomedical applications of NHC-coinage metal complexes,<sup>58</sup> homobimetallic complexes of gold and silver were targeted to investigate the nucleophilic behavior of 5. Treatment of the in situ generated carbene 5 with the phosphine-stabilized precursors Ph<sub>3</sub>PAuCl or Ph<sub>3</sub>PAgOTf yields the corresponding complexes 10 and 11 in 76.5% and 91.6% yield, respectively (Scheme 4). As expected, the negative charges of the two zwitterionic metal complexes are delocalized in the remote malonate backbone of the ligand in the outercoordination sphere of the complex. The related monometallic complexes 12 and 13 (Scheme 5) were synthesised in a similar fashion. Complexes 12 and 13 are very soluble in halogenated solvents, whereas complexes 10 and 11 have poor solubilities in almost all common organic solvents. Gold complexes 10 and 12 display their representative carbone carbon resonances as doublets at  $\delta$  = 199.8 ( $J_{P-C}$  = 120.1 Hz) and 201.11 ( $J_{P-C}$  = 119.4 Hz) ppm, respectively. Owing to the limited solubility of complex 11 and





Fig. 1 Solid state molecular structure of 7 with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.



Scheme 5 Monometallic complexes 12 and 13

-PPh<sub>3</sub>



Fig. 2 Solid state molecular structure of **10** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

the expected multiplicity of the resonance arising from coupling with the two silver isotopes and the phosphorus atom, the resonance signal for the carbene carbons in the  ${}^{13}C{}^{1}H{}$  NMR spectrum was not detected. The carbene carbon of **13** appears as two doublets of doublets centered at 200.5 ppm, consistent with splitting by the three 1/2 nuclei:  ${}^{107}$ Ag,  ${}^{109}$ Ag and  ${}^{31}$ P. The  ${}^{13}C{}^{-107,109}$ Ag coupling constants are large (199.5 and 233.2 Hz, respectively). These couplings suggest that **13** does not experience rapid ligand exchange on the NMR time scale. ${}^{59}$ 

To elucidate the solid structures of the two dinuclear complexes 10 and 11, single crystals were obtained by slow evaporation of saturated solutions of 10 or 11 in halogenated solvents (CHCl<sub>3</sub> and 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub>:CHCl<sub>3</sub>, respectively) and subjected to X-ray diffraction analysis. The determinations revealed similar molecular structures for the two complexes as depicted in Fig. 2 and 3. The complexes crystallize in the monoclinic  $P2_1/c$  group and they are heavily solvated. The metal centers possess a classical linear coordination geometry  $(C1-Au1-P1 = 175.6(2)^{\circ} \text{ and } C1-Ag1-P1 = 175.23(17)^{\circ}).$  The N1-C1-N2 angles of 10 and 11 (115.3(6)° and 115.5(6)°, respectively) are smaller than in the corresponding zwitterion 7 (122.0(6) $^{\circ}$ ), as is always observed when comparing structural parameters of NHCs and their protonated precursors. The Au-C1 and Ag-C1 bond distances are 2.027(7) and 2.110(6) Å, respectively which are comparable with those reported for the mono *malo*NHC analogues.<sup>50</sup> The central phenylene rings in **10** and **11** are twisted by 39.12° and 39.7°, respectively, relative to the carbene moieties.

In conclusion, we have prepared and characterized the first dianionic Janus-type ligand combining two facially opposed *malo*NHCs. This dianionic bis-NHC is particularly interesting



Fig. 3 Solid state molecular structure of **11** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

since it gives access to neutral complexes of monocationic metals bearing otherwise neutral ligands, a feature not available with the current arsenal of Janus-type carbenes. The utility of this ligand in the synthesis of new organometallic materials has been demonstrated by its incorporation into two new dinuclear zwitterionic gold and silver complexes. These complexes have been fully characterized by spectroscopic techniques and X-ray crystallography. The similar chemical shifts of the carbonic carbons of 5 and 9, in both free and coordinated forms, suggest that the reactivity and the affinity of each carbene "face" of the Janus ligand 5 toward transition metals do not deviate abnormally from that of their monotopic analogue 9. The facile synthesis of 5 and its unique topological properties renders this new system a promising dianionic scaffold well suited to function as a building block in the synthesis of other functional organic and metal-organic frameworks. Further studies in order to extend the coordination of this ligand to other metals and also afford neutral main-chain zwitterionic organometallic polymers are underway.

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