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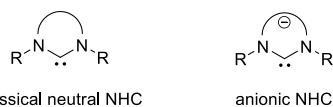
A Stable Anionic N-Heterocyclic Carbene and its Zwitterionic Complexes

Vincent César,* Noël Lugan and Guy Lavigne*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France.

RECEIVED DATE () Vincent.Cesar@lcc-toulouse.fr; Guy.Lavigne@lcc-toulouse.fr

With very few exceptions, N-Heterocyclic Carbenes (NHCs)¹ are traditionally neutral “L” type ligands according to the Green formalism. Though their functionalization by anionic non-coordinating substituents has been achieved,² the present account is focusing on the design of stable monodentate ligands whose main characteristic will be the presence of a remote anionic functional group within the heterocyclic backbone.

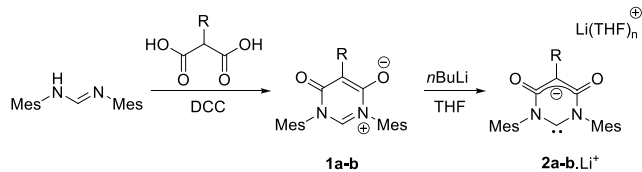


The anticipated benefit of such ligands in coordination chemistry is that the anionic moiety pointing toward the outer coordination sphere will not interfere with the metal's cavity shape, controlled exclusively by the size of the ring and the nature of the nitrogen substituents. Roesler and co-workers recently reported the unique archetype of such a family, consisting of a six- π -electron $B_2N_2C_2$ framework, but the coordination chemistry of such a derivative remains unexplored.³

Direct reaction of monodentate anionic NHCs with transition metal complexes is prone to produce neutral zwitterionic species exhibiting valuable advantages relative to classical cationic complexes.⁴ This concept was previously applied to N, P and S ligands containing tetraorganoborate, indenyl, or substituted-boratabenzene anions.^{5,6}

While thinking of malonate as an alternate anionic function to be installed within the heterocyclic framework, we reasoned that pyrimidinium betaines (**1**) might constitute convenient precursors for the intended anionic carbene since they can be prepared in high yield with various substituents by a classical double peptide-type coupling between a formamidine and a mono-substituted malonic acid (Scheme 1, first equation).⁷

Scheme 1



a: R = Me; b: R = *t*Bu

The new anionic, 6-membered carbene **2** (abbreviated as *malo*NHC) was generated cleanly and quantitatively by treatment of **1** with *n*BuLi (or KHMDS) (Scheme 1, second equation). The appearance of a highly deshielded ¹³C NMR (THF-*d*₈) signal at δ 243.7 ppm for **2a.Li⁺** was consistent with its formulation as a NHC.^{8,9} An X-ray structure analysis of **2a.Li⁺**(THF)₂ (Figure 1) revealed the occurrence of a trimeric annular association where

three cationic Li(THF)₂⁺ units serve as linkers between neighbouring anionic carbenic units through the formation of O-Li-O bridges. The carbenic heterocycle is almost planar (dihedral angles: C11-N21-C41-C31: 2.5°; C41-C31-C21-N11: 0.6°) and the averaged angle NCN in the carbene **2a.Li⁺** (112.7°) is more acute than in the corresponding betaine **1a** (122.1°) as always observed when comparing geometrical parameters of NHCs and their NHC.H⁺ precursors.

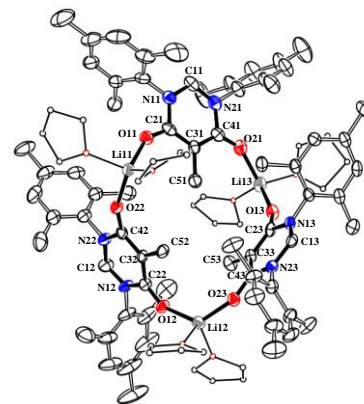
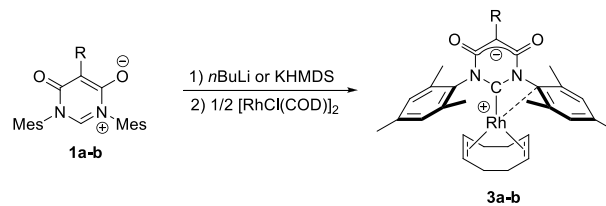


Figure 1: Molecular structure of the lithium salt of the carbene **2a.Li⁺**(THF)₂ revealing a trimeric annular association (ellipsoids drawn at 30% probability level).

In a first attempt to obtain a Rh(I) complex prototype, the carbene **2** was generated *in situ* and reacted with half an equivalent of [RhCl(1,5-COD)]₂ (Scheme 2). This readily produced the neutral 14e⁻ complex Rh(*malo*NHC)(COD) (**3**), which was isolated (**3a**: 73% yield; **3b**: 77% yield) and fully characterized both in solution and in the solid state. Clearly, the anionic carbene **2** behaves as a halide scavenger, and the negative charge of the resulting zwitterionic Rh(I) species **3** is delocalized on the remote malonate-type ligand backbone,¹⁰ in the outer-coordination sphere of the complex.

Scheme 2



Interestingly, coordinative unsaturation at the metal is relieved in the solid state by an uncommon labile bonding interaction between the *Cipso* of one of the mesityl arms and the Rh center,

albeit with no observable structural change of metrical values within the mesityl group. This must be a dynamic process in solution, given that ^1H NMR data revealed the occurrence of a symmetrical structure, even at -80°C . A closely related structural pattern was previously identified in the case of the cationic NHC Rh(I) complex $[\text{Rh}(\text{NHC})(\text{COD})]^+\text{PF}_6^-$ involving the neutral NHC ligand 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene.¹¹

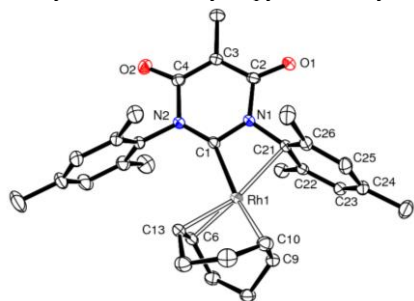
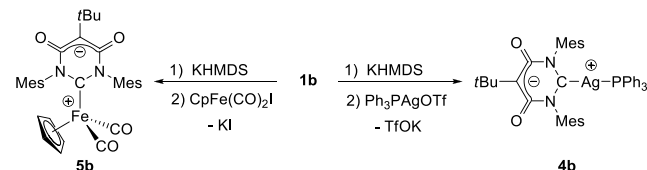


Figure 2: Molecular structure of the zwitterionic complex **3a** (ellipsoids drawn at 50% probability level) revealing an uncommon Rh-C(ipso) interaction. Selected bond distances (Å) and angles ($^\circ$): Rh1-C1 2.036(2), Rh1-C21 2.346(2), Rh1-C6 2.091(2), Rh1-C13 2.130(2), Rh1-C9 2.248(2), Rh1-C10 2.230(2), C1-Rh1-C21 62.78(6), N1-C1-N2 115.5 (1).

In line with these observations, we were logically prompted to validate the generality of the present approach by reacting **2** with a series of simple basic transition metal complexes.

Beginning with silver, we found that **2b.K⁺** reacts cleanly with the phosphine-stabilized precursor PPh_3AgOTf (Scheme 3) to produce the zwitterionic complex (*malo*NHC)Ag(PPh_3) **4b** (84% yield), characterized by an X-Ray structure analysis (see ESI).

Scheme 3



In further work aimed at estimating the donor properties of **2** as compared with those of a “normal” NHC by using CO stretching frequencies as a probe,¹² we were led to prepare a simple carbonyl *malo*NHC complex having a known cationic NHC-complex equivalent. As a standard reference, we chose the known cationic species $[\text{CpFe}(\text{NHC})(\text{CO})_2]^+\text{I}^-$ previously prepared both with NHC = IMes ($\nu(\text{CO})$: 2050, 2006 cm^{-1}) and SIMes ($\nu(\text{CO})$: 2049, 2005 cm^{-1}).^{13,14} Our parallel reaction of $\text{CpFe}(\text{CO})_2\text{I}$ with **2b.K⁺** generated *in situ* produced the zwitterionic equivalent $\text{CpFe}(\text{maloNHC})(\text{CO})_2$ (**5b**) (Scheme 3, left reaction) which was fully characterized (Figure 3). The observation of $\nu(\text{CO})$ bands at 2038 and 1993 cm^{-1} for **5b** tends to indicate that the anionic *malo*NHC **2b** is a better donor than IMes or SIMes.

In view of the general synthetic approach disclosed here, it can be reasonably anticipated that a much broader range of zwitterionic complexes will now become accessible from our new ligand and its congeners. Taking advantage of the modularity of the present synthesis, we will now concentrate our efforts on the evaluation of their scope in homogeneous catalysis.

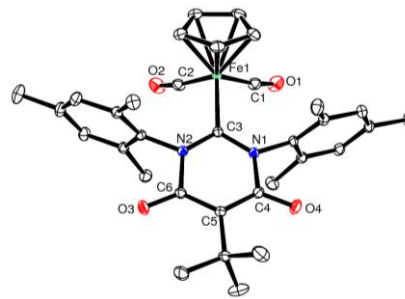


Figure 3: Molecular structure of complex **5b** (ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles ($^\circ$): Fe1-C1 1.786 (1), Fe1-C2 1.779(1), Fe1-C3 2.041(1), N1-C3-N2 113.42(8), Fe1-C1-O1 169.89(10), Fe1-C2-O2 170.13(10).

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SUPPORTING INFORMATION AVAILABLE: Experimental details for the preparation of the reported compounds and crystallographic data (CIF files) for **1a**, **2a**.Li(THF)₂⁺, **3a**, **4b** and **5b**. This material is available free of charge via the internet at <http://pubs.acs.org/>

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