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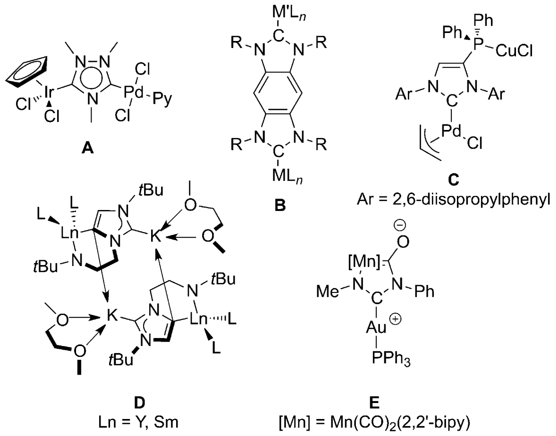
An Ambidentate Janus-Type Ligand System Based on Fused Carbene and Imidato Functionalities

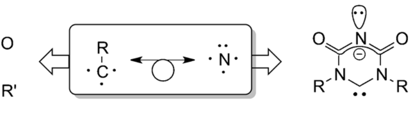
Nadia Vujkovic, Vincent César,* Noël Lugan, and Guy Lavigne*[a]

Thanks to the extensive development of rational synthetic routes to N-heterocyclic carbenes and related species,[1] a growing diversity of exciting new archetypes of persistent carbenes are now becoming accessible. Of particular interest are "functional" carbenes with their backbone being decorated by chemically or electrochemically responsive entities enabling a suitable control of the electronic donor properties of the carbene center, with observable consequences on catalytic performances and/or product selectivity.[2,3] Whereas most of these carbenes are designed to bind only one metal center, several original ideas to devise ditopic NHC-based ligands for organometallic polymer synthesis, or for the design of multifunctional tandem catalysts, have recently appeared (Scheme 1). These are illustrated, for example, by heterobimetallic complexes of 1,2,4-triazolyl-3,5-diylidenes (**A**),[4] benzobis(imidazolylidene)s (**B**),[5] 4-phosphinoimidazol-2-ylidenes (**C**)[6] and 1,3-imidazol-2,4-ylidenes (**D**)[7] as well by the gold(I) complex **E** supported by a Fischer carbene-containing NHC (Scheme 1).[8]



Scheme 1. Representative examples of ambidentate bimetallic complexes incorporating a ditopic NHC-based ligand.

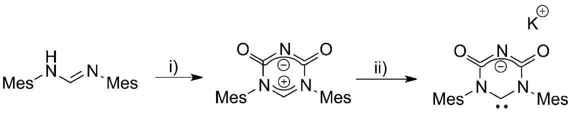
In a logical continuation of our original work on the construction of modular anionic and neutral NHCs incorporating a malonate backbone,[3f,9] which are receiving growing attention,[10] we reasoned that, based on the isolobal analogy between "C–R" group and "N" atom, it would be of interest to synthesize the N-heterocyclic carbene *imid*NHC (Scheme 2) incorporating an imidato backbone (a biologically relevant functionality)[11] susceptible to act as a labile donor group toward various transition metals.[12]



Scheme 2. Relationship between *malo*NHC and *imid*NHC.

The mesoionic precursor 1,3-dimesityl-*s*-triazine-4,6-dione **2**·H was prepared in high yield through decisive modifications of a procedure which had been previously found to give only poor yields of analytically impure samples of the compound.[13] In our hands, treatment of 1,3-dimesitylformamidine with *n*-butyl lithium, followed by stepwise addition of Me_3SiCl and N-phenoxycarbonyl isocyanate afforded compound **2**·H in 86 % yield (Scheme 3).

The crucial role of Me_3SiCl is to scavenge the released phenoxide, which otherwise would add to the N-phenoxycarbonyl isocyanate substrate, thereby reducing the yield in final product. The compound was fully characterized by various spectroscopic techniques,[14a] and its molecular structure was elucidated by X-ray crystallography (Figure 1).[14b] Compound **2**·H can be described as a four π-electron formamidi-



Scheme 3. Synthesis of the precursor **2**·H and of anionic NHC **2**·K: i) 1) *n*BuLi, THF, 25 °C, 20 min; 2) Me_3SiCl, 0 °C, 2 min; 3) N-phenoxycarbonyl isocyanate, 0 to 25 °C, overnight. ii) KHMDS, THF, 0 °C, 20 min. Mes = 2,4,6-trimethylphenyl.

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[a] Dr. N. Vujkovic, Dr. V. César, Dr. N. Lugan, Dr. G. Lavigne
CNRS, LCC (laboratoire de chimie de coordination)
205 route de Narbonne, 31077 Toulouse Cedex 4 (France) and
Université de Toulouse, UPS, INPT
31077 Toulouse (France)
E-mail: vincent.cesar@lcc-toulouse.fr
guy.lavigne@lcc-toulouse.fr

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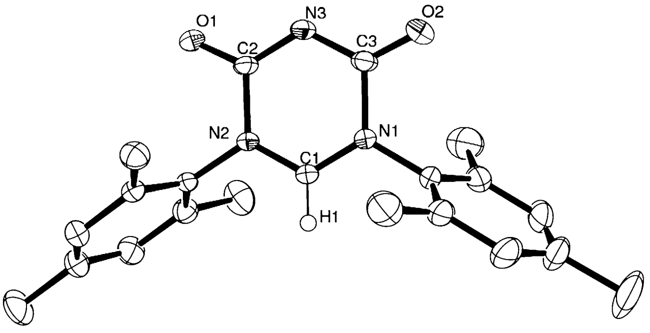
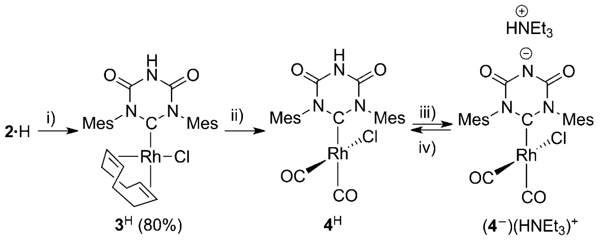


Figure 1. Molecular structure of **2**·H (ellipsoids drawn at 30 % probability level). Hydrogen atoms on the mesityl groups were omitted for clarity. Selected bond lengths [Å]: C1–N1 1.3142(13), C1–N2 1.3210(14), N1–C3 1.4651(14), N2–C2 1.4538(14), C2–N3 1.3367(13), C3–N3 1.3420(15), C2–01 1.2178(15), C3–O2 1.2139(13).

nium unit linked to a six π-electron imidate unit with only negligible interactions between the two systems, as indicated by the magnitude of the bond lengths N1–C3 (1.4651(14) Å) and N2–C2 (1.4538(14) Å) falling within the range of single N–C_{sp^2} bonds.[15]

Treatment of **2**·H with potassium bis(trimethylsilyl)amide (KHMDS) in THF cleanly afforded the potassium salt of the anionic NHC **2**⁻. The ^{13}C NMR resonance of the carbene nucleus was observed at δ 258.9 ppm, a value appearing downfield relative to that found in the corresponding *malo*NHC carbene (δ 243.7 ppm), thus reflecting a reduced donicity of the carbene, with the imidate nitrogen atom being more electronegative than the malonic carbon atom of the *malo*NHC derivative.[9a] Such differences were also substantiated in terms of chemical reactivity (Scheme 4).



Scheme 4. Generation of Rh complexes $\mathbf{3}^{H}$, $\mathbf{4}^{H}$ and $\mathbf{4}^{-}$. i) 1) KHMDS, THF, 0 °C, 20 min; 2) $[RhCl(cod)]_2$, 25 °C, 30 min; 3) SiO_2, CH_2Cl_2. ii) CO, CH_2Cl_2, 15 min. iii) NEt_3, CH_2Cl_2, 25 °C. iv) HCl in Et_2O, CH_2Cl_2, 25 °C.

Indeed, in situ generation of **2**⁻ in THF followed by addition of 0.5 equiv of $[RhCl(1,5\text{-cod})]_2$ led to abundant precipitation of a red species, which was readily and cleanly protonated by simple treatment with silicagel in dichloromethane. Further purification by flash chromatography afforded the bright orange complex $[RhCl(\mathbf{2}^{H})(1,5\text{-cod})]$ ($\mathbf{3}^{H}$), which was fully characterized (Figure 2).[14b]

Very characteristically, its spectral and geometrical characteristics appeared to be comparable with those previously ascribed to a *diamido*carbene complex, due to i) the presence of a highly deshielded ^{13}C NMR resonance of the carbene (δ = 240.6 ppm),[9b,16] ii) the occurrence of relatively short N1–C2 and N2–C3 bonds (N1–C2: 1.405(3) Å, N2–C3: 1.389(3) Å), reflecting electron delocalization along the lateral amido groups NCO, and, iii) a very short Rh–$C_{carbene}$ bond length 1.998(3) Å (the shortest reported so far within such a ligand family) typical of those found in diamidocarbene-Rhodium complexes.[9b,16] The electronic nature of $\mathbf{2}^{H}$ was inferred from the IR spectra of the carbonyl-derivative $[RhCl(\mathbf{2}^{H})(CO)_2]$ ($\mathbf{4}^{H}$), obtained by simple carbonylation of $\mathbf{3}^{H}$ under ambient conditions. Its average ν_{CO}^{av} frequency of 2046 cm^{-1} is comparable to the value recorded for the *malo*NHC-type diamidocarbene analogue (ν_{CO}^{av} = 2045 cm^{-1}).[9b] Complex $\mathbf{4}^{H}$ could be readily deprotonated with triethylamine to yield $(\mathbf{4}^{-})(HNEt_3)^{+}$. Further addition of HCl led to clean regeneration of $\mathbf{4}^{H}$, demonstrating that the present metal/ligand system is switchable.[17] Infrared data collected from $\mathbf{4}^{-}$ (ν_{CO}^{av} = 2036 cm^{-1}) indicate that the relevant anionic ligand **2**⁻ is much more electron-donating than $\mathbf{2}^{H}$, but less than the anionic *malo*NHC analogues (ν_{CO}^{av} = 2028 cm^{-1}).[3f]

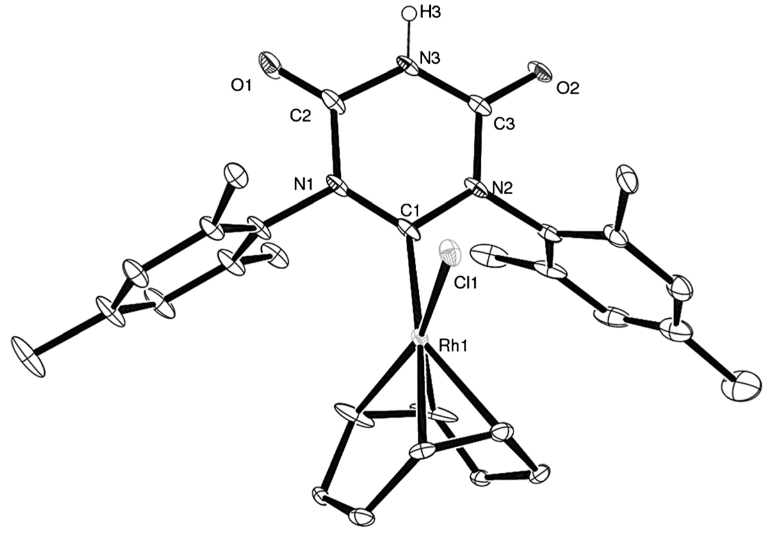
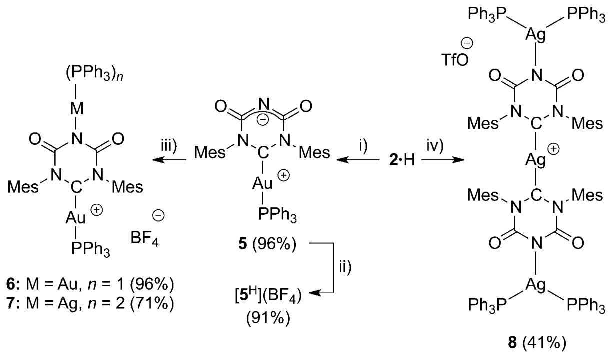


Figure 2. Molecular structure of $\mathbf{3}^{H}$ (ellipsoids drawn at 30 % probability level). Hydrogen atoms on mesityl and cyclooctadiene have been omitted for clarity. Selected bond lengths[Å]: Rh1–C1 1.998(3), C1–N1 1.365(4), C1–N2 1.382(3), N1–C2 1.405(3), N2–C3 1.389(3), C2–N3 1.380(3), C3–N3 1.366(3), C2–01 1.198(3), C3–O2 1.215(3). Selected bond angles [°]: C1-Rh1-Cl1 83.86(7), N1-C1-Rh1-Cl1 85.32.

The ambidentate nature of **2**⁻ was further established through the directed formation of polymetallic silver and gold complexes. Due to the availability of two potentially coordinating sites in the NHC, two strategies could be envisioned, starting either from **2**$^{-}$ or **2**·H, and thus determining the order in which the donor groups were to be connected to a metal center. Various tries led us to adopt the more convenient procedure, where the ligand **2**$^{-}$ is first selectively bound to a first transition metal through the carbene center, thus giving a starting complex that is subsequently used as an "imidato" ligand for a second metal center. As shown in Scheme 5, treatment of **2**·H with one equivalent of KHMDS followed by addition of AuCl(tht) and triphenylphosphine selectively gave the zwitterionic heteroleptic complex [Au(**2**)(PPh$_3$)] (**5**) in excellent yields (96 % yield).[18]



Scheme 5. Formation of polymetallic complexes **6**–**8**. i) 1) KHMDS, THF, 0 °C, 20 min; 2) AuCl(tht), PPh$_3$, RT, 6 h; ii) HBF$_4$·OEt$_2$, CH$_2$Cl$_2$, 0 °C, 10 min; iii) for **6**: [(PPh$_3$)Au(CH$_3$CN)](BF$_4$), for **7**: AgBF$_4$, PPh$_3$, CH$_2$Cl$_2$, RT, 1 h. iv) 1) KHMDS, THF, 0 °C, 15 min; 2) AgOTf (0.5 equiv), RT, 1.5 h; 3) PPh$_3$ (2 equiv), AgOTf (1 equiv), RT, 3 h. tht = tetrahydrothiofurane.

Its subsequent treatment with a second cationic metallic fragment gave in good yields the stacked bimetallic complexes [L$_n$M(**5**)]$^{+}$(BF$_4$)$^{-}$ (**6**: ML$_n$ = Au(PPh$_3$); **7**: ML$_n$ = Ag(PPh$_3$)$_2$, which were both fully characterized. The playful possibility to construct even more elaborated polymetallic complexes in a one-pot reaction is nicely illustrated here by the preparation of the trimetallic silver complex **8** (Scheme 5, reaction iv).

Here, the central unit [Ag(**2**)$_2$]$^{-}$ where the cationic silver atom is encapsulated between two molecules of the anionic carbene ligand **2**$^{-}$ both coordinated through their carbene center, was selectively obtained by simply adjusting the required metal/ligand stoichiometry, whereas the remote silver centers were further introduced to obtain a closed-shell species. The syntheses of these complexes nicely illustrate some of the multiple possibilities of this new ligand in coordination chemistry.

Interestingly, a close examination of the molecular structures of complexes **5** (Figure 3)[14b] and **8** (Figure 4)[14b] reveals that the electronic distribution within the carbenic heterocycle **2** is subject to a redistribution apparently governed by the substitution patterns. Very characteristically, in the zwitterionic gold(I) complex **5**, there is no apparent communication between the anionic six π-electron imidate unit and the four π-electron diaminocarbene unit of the ligand **2**$^{-}$. This is reflected in the bond lengths N1–C2 (1.460(4) Å) and N2–C3 (1.466(5) Å) falling within the range of single N–C bonds. By contrast, as soon as ligand **2** is bridging two metal centers such as in the trimetallic silver(I) complex **8**, the same bonds slightly shorten (N1–C3: 1.430(3) Å, N2–C2: 1.424(3) Å, N4–C5: 1.430(3) Å, N5–C6: 1.430(3) Å), reflecting an electronic situation intermediate between that of an anionic *diamino*carbene and a *diamido*carbene.[3f,9b,10] Such a behavior is also clearly illustrated by the low-field drift of the ^{13}C NMR resonance of the carbenic carbon in the gold complexes series ($\delta = 210.3$ ppm in **5**, $\delta = 215.6$ ppm in **6** and $\delta = 218.2$ ppm in **5**$^{\mathrm{H}}$).

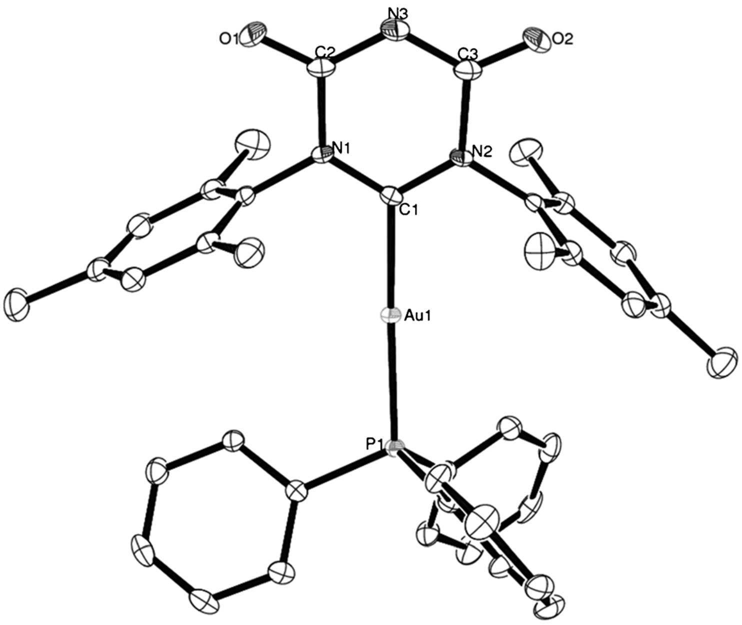


Figure 3. Molecular structure of the zwitterionic complex **5** (ellipsoids drawn at 30 % probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Au1–C1 2.049(3), Au1–P1 2.2811(7), C1–N1 1.332(4), C1–N2 1.324(4), N1–C2 1.460(4), N2–C3 1.466(5), C2–N3 1.343(5), C3–N3 1.348(6), C2–01 1.215(4), C3–O2 1.208(5). Selected bond angle [°]: C1-Au1-P1 173.29(8).

In conclusion, we have disclosed here a new type of ambidentate Janus-type ligand combining two different donor functionalities—a carbene and an anionic imidate—within the *same* heterocyclic framework. This anionic carbene, representing a synthetic challenge, is yet available in high yield through a simple and highly efficient original method. It appears to be suitable for the directed construction of a variety of homo-and/or hetero-polymetallic complexes in a stepwise approach. The present work also reveals that, as a polyfunctional carbene is engaged in bonding with several metal atoms, its electronic structure is no longer a *purely intrinsic* ligand property, but is becoming subject to the influence of the metal atoms, these tending to shepherd mobile electrons between the two parts of the heterocycle. Further synthetic possibilities and applications of this fascinating new carbenic

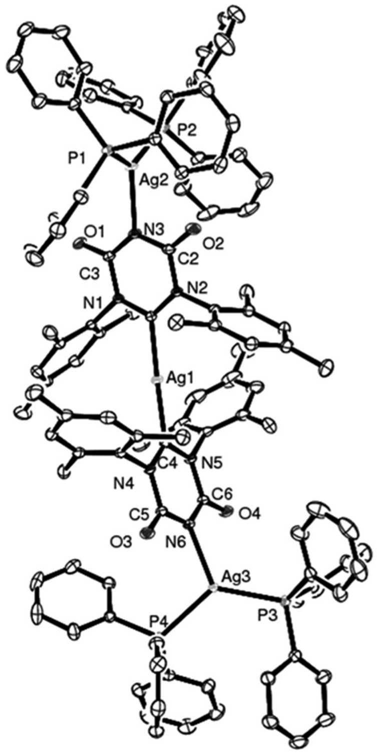


Figure 4. Molecular structure of the cationic part of the trimetallic complex **8** (ellipsoids drawn at 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Ag1−C1 2.091(3), Ag1−C4 2.091(3), C1−N1 1.333(4), C1−N2 1.338(4), N1−C3 1.430(3), N2−C2 1.424(3), C2−N3 1.340(4), C3−N3 1.343(4), C2−-02 1.215(4), C3−O1 1.208(4). Selected angles [°]: C1-Ag1-C4 175.63(11), Ag2-Ag1-Ag3 165.25.

structure in materials science as well as in homogeneous catalysis are currently under investigation in our laboratory.

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Keywords: ambident compounds · carbenes · gold · organometallic compounds · polymetallic compounds

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