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Iron and Cobalt Metallotropism in Remote-Substituted NHC Ligands, Metallation to Abnormal NHC Complexes or NHC Ring Opening

Andreas A. Danopoulos,*^{[a],[b]} Alexandre Massard,^[a] Gilles Frison,^[c] and Pierre Braunstein*^[a]

Dedicated to Prof. Richard J. Puddephatt on the occasion of his 75th birthday, with our warmest congratulations and best wishes.

Abstract: Metallotropism of the M[N(SiMe₃)₂]₂ metal fragment in the tautomeric system $IA^{R} \rightleftharpoons AC^{R}$ involving imidazolium salts / N-heterocyclic carbenes with remote amine / aminide substituents, respectively, is manifested by its C_{NHC} carbophilicity (R = tBu, M = Co, Fe) or NR_{aminido} nitrogenophilicity (R = Cy, M = Co, Fe; R = Mes, M = Fe) and has been rationalized on the basis of steric and electronic effects. The thermolysis products of the [M{N(SiMe₃)₂}₂] / $IA^{R} \rightleftharpoons AC^{R}$ system are also substituent-dependent, leading to a rearranged aminide-functionalized aNHC Co₂ complex of an unprecedented type or to ring-opened metallaketenimines; they are postulated to originate from different metalloisomers. The results are interpreted on the basis of the X-ray diffraction analysis of 11 new compounds.

Molecular complexity in metal-centered chemistry heavily relies on ligands, and their own versatility is enhanced by their functionalization. If simple N-heterocyclic carbene (NHC) ligands have already led to impressive achievements in numerous areas of chemistry, functionalized NHC often bring about additional properties of considerable impact in structural chemistry, catalysis, material science, medicine, etc.. N-heterocyclic 'remote'substituted imidazol-2-ylidenes r(NHCs) with heteroatom substituents at the 4- and / or 5-positions of the heterocycle (denoted as r(substituent)) have been studied apropos of modulating the nucleophilicity and donor properties of the NHC functionality by means of the inductive and mesomeric effects of the r(substituent). Diverse substituent types have been described, resulting in NHC ligands that are charge-neutral, cationic or anionic (e.g. r(NexoR2), r(NexoHR), r(PPh2), r(RS), r(SiMe3), $r(SiPh_3)$,^[1] or $r(PPh_3^+)$ and $r(N_{exo}H_3^+)$ ^[2] or $r[B(Ar^F_3)^-]$, $r(O^-)$ and $r(N_{exo}R^{-})$, respectively).^[1f,1g,3] Neutral and anionic r(substituents)can render the rNHCs ambident, occasionally acting as bridging ligands.^[4] Competition between the C_{NHC} and r(substituent) sites for metal coordination is sterically and electronically tunable.^[3a]

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Tautomeric equilibria involving the C_{NHC} basic site and the r(substituent), altering the nature and electronic characteristics of the donors, can lead to increased bonding diversity (*cf.* equilibria involving Nitron, recently extended to its alkyl analogues^[5] and other mesomeric betaines^[6]). With 1,3-bis-(DiPP)imidazolium systems (DiPP = di/sopropylphenyl), the tautomerism between the *I*midazolium Aminide (*IA*) (with anionic $r(N_{exo}R)$) and the Amino Carbene (*AC*) (with neutral r(NHR)) depends on the nature of R: aromatic and *f*Bu substituents favor the *IA* and *AC* forms, respectively (Scheme 1).^[7] When R = *t*Bu, both tautomers could be isolated from the equilibrium mixture $IA^{tBu} \rightleftharpoons AC^{tBu}$ and crystallographically characterized: the IA^{tBu} [7] by cooling at -40 °C and the *ACt^{Bu}* by slow solvent evaporation at room temp. (Supporting Information and Figure S2.1).



Scheme 1.

Whereas efforts are directed towards the use of well-defined earth-abundant NHC metal complexes in homogeneous catalysis, competent Fe and Co complexes are often generated *in-situ*, unexpected transformations being possibly overlooked.^[8] Herein, we describe fully characterized complexes obtained in the course of a study on metallotropism in *IA* and *AC* associated with $[M{N(SiMe_3)_2}_2]_2$ (M = Co, Fe) as a function of R in $r(N_{exo}R)$ and $r(N_{exo}HR)$. Two types of unexpected and unprecedented products were obtained from thermolysis of the system $IA^R \Rightarrow AC^R$ (R = *t*Bu, Mes) and $[M{N(SiMe_3)_2}_2]_2$, the different nature of which can be traced to metallotropism. All the reactions and manipulations were carried out under inert atmosphere (glove-box, N₂-sealed ampoules) and all described complexes are (very) sensitive in solution and solid-state to air/moisture (see SI).

The equilibrium mixture $IA^{tBu} \rightleftharpoons AC^{tBu}$ (K_{eq} at rt *ca.* 0.5) reacted with 0.5 equiv. [M{N(SiMe_3)_2}_2] (M = Co, Fe) in toluene to give selectively **1a** and **1b** as green and orange crystals, respectively (Scheme 2). Despite their paramagnetism, **1a** and **1b** exhibit diagnostic ¹H-NMR spectra in the region δ 100 to -50 ppm

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(see SI); no other paramagnetic product could be detected in solution by NMR spectroscopy. The molecular structure of **1b** (Figure 1) reveals trigonal planar geometry with C_{NHC} -coordinated AC^{tBu} and two bis(trimethylsilyl)amide ligands; the metrical data are very similar to the archetypical [Fe(IPr){N(SiMe_3)_2}_2] with identical sterics (*cf.* Fe-C_{NHC} = 2.182(2) - 2.184(2) Å *vs.* 2.192(3) in **1b**); the NHC plane makes an angle of *ca.* 42° with the metal coordination plane.^[9] The data set from the weakly diffracting crystals of **1a** established identical atom connectivity to **1b** (Figure S2.3). Interestingly, preliminary reactions of $IA^{tBu} \rightleftharpoons AC^{tBu}$ with the sterically exposed anhydrous CoCl₂ led to the C_{NHC}-metallated halide-bridged complex [Co(AC^{tBu})Cl(μ -Cl)]₂ (Figure S2.5), further underlining the preferred coordination site of the AC^{tBu} tautomer. Insight into the apparent metal carbophilicity when R = *t*Bu resulted from computational studies (see below).



Scheme 2.



Figure 1. Molecular structure of 1b; DiPP methyls are omitted (metrical data in SI).

In contrast to the above where R = tBu, the reaction of $IA^{Cy} \rightleftharpoons AC^{Cy}$ (K_{eq} at rt *ca.* 3.2) with $[M\{N(SiMe_3)_2\}_2]_2$ (M = Co, Fe) led to the isostructural **2a** and **2b** in good yields, as green and

light yellow paramagnetic solids (Figures 2 and S2.7, respectively). The metals in **2a/2b** are in a trigonal planar environment, with a N_{exo}-coordinated *IA^{Cy}*. In **2a** there are two types of Co-N bonds, Co-N_{exo} (1.993(2) Å) being longer than Co-N_{N(SiMe3)2} (1.943(2) and 1.956(2) Å). A analogous metrical trend was found in [Co{N(SiMe₃)₂}(pyridine)], with Co-N_{pyridine} and Co-N_{N(SiMe3)2} at 2.055(5) Å, 1.904(3) Å, respectively;^[10] this comparison places the Co-N_{exo} bond distances in the region of Co-N_{imine} bonds. The conjugated mesomeric betaine *IA^{Cy}* can be classified as an imidazolin-4-imine and expands the class of regioisomeric imidazolin-2-imines recently described.^[11] Similar considerations apply to the structure of **2b**.



Figure 2. Molecular structure of 2a (metrical data in SI).

DFT calculations have been performed at the (U)M06-2X level for AC^R and IA^R tautomers and their metal complexes for R = tBu, Cy and Mes. The case R = H has been also studied to serve as a reference (see the SI for the computational methods and detailed discussion). Each tautomer IAR and ACR can exist in two isomeric forms, with the R substituent at the Nexo site being proximal or distal to the neighboring DiPP. Owing to the steric hindrance of the latter, distal isomers are more stable than proximal ones for $R \neq H$, in particular for R = tBu. Similarly, the presence of the DiPP substituent renders the coordination of a large metal fragment such as M[N(SiMe₃)₂]₂ to the N_{exo} atom of IAR_{distal} computationally impossible, in contrast to Nexo coordination of IAR prox; these results are in agreement with the experimental structures 2a/b and 3b. Consequently, coordination of M[N(SiMe₃)₂]₂ fragments has been further analyzed only for AC^{R}_{distal} and IA^{R}_{prox} isomers (R = H, Cy, tBu, Mes) (Figure 3), the latter ligand being less stable than the former $(G(IA^{R}_{prox}) G(AC^{R}_{distal}) = 26.2, 56.2 \text{ and } 10.4 \text{ kJ} \cdot \text{mol}^{-1}$ for R = Cy, tBu and Mes, respectively), except for R = H (-2.2 kJ mol⁻¹) (Table S4.1).

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Figure 3. Coordination of *ACR_{distal}* and *IAR_{prox}* isomers (R = H, Cy, *t*Bu, Mes) to M[N(SiMe₃)₂]₂ fragments. Bond lengths (in Å) and relative free energies (in kJ·mol⁻¹) computed at the UM06-2X/def2-TZVPP//UM06-2X/def2-SVP level for M = Fe (blue) and Co (red). The structures corresponding to those obtained experimentally have been framed.

The relative free energies of the metal complexes, depending on the AC^{R}_{distal} vs. IA^{R}_{prox} ligand nature, are in excellent agreement with the experimental results: only the most stable complexes have been observed experimentally. Calculations of the Percent Buried Volume ($\%V_{bur}$) of ligands (N{SiMe₃}₂)₂, AC^{R}_{distal} and IA^{R}_{prox} reveal severe steric congestion around the metal center and the larger steric demand of ligand AC^{R}_{distal} relative to IA^{R}_{prox} for R = Cy and Mes, whereas the opposite is found for R = tBu.

Even for R = H, there is steric hindrance between DiPP and N(SiMe₃)₂ ligands and IA^{H}_{prox} complexes are significantly more stable than AC^{H}_{distal} (-53.0 and -34.2 kJ·mol⁻¹ for M = Fe and Co, respectively). The coordination of the IA^{R}_{prox} ligand to [M{N(SiMe₃)₂}₂]₂ remains preferred to that of AC^{R}_{distal} for R = Cy and Mes because the steric repulsion between R and DiPP groups in IA^{R}_{prox} induces only a relatively small destabilization and the steric bulk of IA^{R}_{prox} remains smaller than that of AC^{R}_{distal} . In contrast, IA^{tBu}_{prox} is strongly destabilized relative to AC^{tBu}_{distal} due to steric hindrance between the DiPP and tBu groups. Furthermore, IA^{tBu}_{prox} is bulkier than AC^{tBu}_{distal} . These combined steric effects induce the preferred formation of 1a / 1b with AC^{tBu}_{distal} .

The mixture IA^{Mes} ⇒ AC^{Mes} reacted with [Fe{N(SiMe₃)₂}₂]₂ only under forcing conditions (toluene, 110 °C, 3 d) and in the presence of excess [Fe{N(SiMe₃₎₂}₂]₂ (2:1 on metal basis) giving complex 3b (isolated in two different isomorphs, Scheme 2, SI and Figures S2.8 and S2.9). In stark contrast, heating of *IA^{Mes}*⇒*AC^{Mes}* with [Co{N(SiMe₃)₂}₂] (1:1 ratio on metal basis) at 90 °C in toluene for ca. 16 h gave brown crystals of the paramagnetic 4a (Scheme 3 and Figure 4). Plausible reaction steps leading to 4a are presented in the SI (Scheme S3.3). In contrast, [Fe{N(SiMe₃)₂}₂] was unreactive under these conditions and only the starting materials were recovered. The structure of 4a unveiled a unique binuclear mixed-valence complex featuring metalation of the heterocyclic ring ortho to the Nexo substituent. In 4a, both Co centres (Co1 and Co2 in Figure 5) adopt distorted planar T-shaped geometries (assuming one coordination site along the Co-Co vector). The Co1-Co2 distance (2.5628(3) Å) is comparable to that in [Co2(CO)8] (2.52 Å).[12] All Co-N distances (Co1-N3, Co1-N4, Co2-N5) fall into the narrow range characteristic of aminide ligands, with a typical Co-C_{NHC} bond distance (1.951(1) Å).^[13]Thus, a plausible description of the ligand system in **4a** emerging from the metrical data is an aminide-functionalized mesoionic aNHC, leading to consider Co1 and Co2 as Co^{II} as Co^I, respectively. Alternative resonance formulations can be found in the SI (Scheme S3.2). Interestingly, **4a** is the only dinuclear complex with two Co{N(SiMe₃)₂} moieties and nonbridging N(SiMe₃)₂ groups and represents a rare example of heteroatom-functionalized aNHC.



Figure 4. Molecular structure of 4a; DiPP methyls are omitted (metrical data in SI).



Scheme 3. Thermal rearrangement products of $IA^{Mes} \Rightarrow AC^{Mes}$ with $[Co\{N(SiMe_3)_2\}_2]_2$ (4a) and of $IA^{IBu} \Rightarrow AC^{IBu}$ with $[M\{N(SiMe_3)_2\}_2]_2$ (M = Co (5a), Fe (5b); description by alternative resonance forms is given in the SI.

In contrast to 1a/1b, complexes 5a and 5b were obtained from the reaction of the tautomeric mixture $IA^{tBu} \Rightarrow AC^{tBu}$ with

 $[M{N(SiMe_3)_2}_2]_2$ (M = Co, Fe) in toluene at room temperature for 3 d or heating at 90 °C for 1 h (Scheme 3 and Figures 5 and 6). They were isolated in good yields as purple and red solids that were crystallized from ether or pentane, respectively.

The crystal structures of **5a** and **5b** established the atom connectivity of a ring-opened, rearranged ligand system, and the metrical data proved crucial in extracting the bond orders between the constituent atoms.



Figure 5. Molecular structure of complex 5a (metrical data in SI).



Figure 6. Molecular structure of complex 5b (metrical data in SI).

Although the metals in **5a** and **5b** adopt pseudo-tetrahedral and trigonal planar coordination geometries, respectively, due to coordination of an ether molecule in **5a**, the skeleton of the ligand and the associated $\kappa N, \kappa C$ -coordination are identical in both cases. The metrical data (see SI) support the depicted resonance forms showing the metallated ketenimine structures (Schemes 3 and S3.3). When complexes **1a** and **1b** were heated in C₆D₆ at 90 °C for 1 h, they fully converted to **5a** and **5b**, respectively, which strongly indicates their intermediacy in the formation of the latter, although possible lability of the M{N(SiMe₃)₂}₂ fragment in **1a**/**1b**, may point to an alternative rearrangement mechanism (SI).

Skeletal rearrangements of coordinated imidazol(in)-2ylidenes are rare but not unprecedented. Heterocycle ring opening reactions may be preceded by migratory insertion of alkyl co-ligands to the C_{NHC} (Ni),^[14] (Hf),^[15] or not;^[16] imidazol(in)-2ylidene ring expansion to 6-membered metallacycles can take place *via* metal insertion into the C-N bond (Ni,^[17] Ru).^[18] Ring expansions involving insertion of heteroelements have been described and recently reviewed;^[19] remote lithiation preceding SIMes ring opening has recently been reported.^[20] Furthermore, hydrolytic cleavage of expanded NHC coordinated to Cu has been described.^[21] However, the transformation of **1** to **5** constitutes the first example of *r*NHC skeletal rearrangement and the formation of metalla-ketenimines, which may be initiated by remote coordination of the *r*NHCs species.

In conclusion, we have demonstrated experimentally and theoretically that the tautomers involved in the equilibrium $IA^{R} \rightleftharpoons AC^{R}$ adopt diverse coordination modes with the fragment $M[{N(SiMe_3)_2}_2]$ (M = Co, Fe), depending on the nature of the R substituent of the Nexo atom. The preference towards KC or KN coordination as a function of R correlates with the nature of the most abundant tautomer in the $IA^R \Rightarrow AC^R$ equilibrium. Owing to the bulk of the metal fragment, its coordination to the IAR forms (R = Cy, Mes) is accompanied by reorientation of the NexoR group from dist to prox; in the ACtBu case, reorientation is irrelevant, since the metal fragment is coordinated to the C_{NHC} . However, the reactivity of the IA^{tBu} ⇒AC^{tBu} / [M{N(SiMe₃)₂}₂]₂ system at elevated temperature features ring opening of the heterocyclic ring moiety and rearrangement to metallacycles comprising metallated ketenimines. In contrast, with IA^{Mes} ⇒ AC^{Mes}, formation of a dinuclear mixed valence complex with functionalized aNHC occurred for M = Co only. Based on the computed stability of the r(NHC) metal silylamide adducts, it may be plausible to associate the divergent rearrangement patterns with the metallotropism, i.e. coordination of the C_{NHC} or N_{exo} sites. This contention is based on coordination modes established by X-ray diffraction on welldefined complexes, but in-situ mechanistic investigations were hampered by paramagnetism. Predissociation of M[N(SiMe₃)₂]₂ governed by temperature or electronic and steric effects of the substituent cannot be ruled out. At present, studies of the catalytic chemistry with rNHC complexes, in particular of 3d metals, are very sparse, and the results described herein point to a complex coordination chemistry, which may have considerable repercussions in future catalytic applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt • dinuclear complex • N-heterocyclic carbenes • iron • metallotropism

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- [22] CCDC 1854989 (*AC^{tBu}*), 1854990 (*IA^{Mes}*), 1854987 (1b), 1854995 (2a), 1854988 (2b), 1854992 ([Co(*AC^{tBu}*)Cl(µ-Cl)]₂·2(C₇H₈)), 1854991 (3b, isom. A), 1854993 (3b, isom. B), 1854996 (4a), 1854994 (5a), and 1854986 (5b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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