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C−H bond activation by an Imido Cobalt(III) and the Resulting Amido Cobalt(II) Complex

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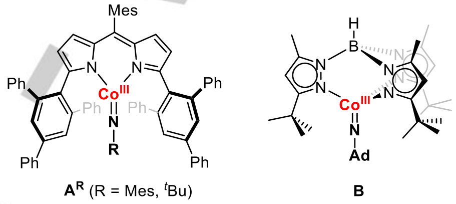
Abstract: The 3d-metal mediated nitrene transfer is under intense scrutiny due to its potential as an atom economic and ecologically benign way for the directed amination of (un)functionalised C−H bonds. Here we present the isolation and characterisation of a rare, trigonal imido cobalt(III) complex, which bears a rather long cobalt-imido bond. It can cleanly cleave strong C−H bonds with an bond dissociation energy of up to 92 kcal/mol in an intermolecular fashion, unprecedented for imido cobalt complexes. This resulted in the amido cobalt(II) complex $[Co(hmds)_2(NH^tBu)]^-$. Kinetic studies on this reaction revealed an H atom transfer mechanism. Remarkably, the cobalt(II) amide itself is capable of mediating H atom abstraction or stepwise proton/electron transfer depending on the substrate. A cobalt mediated catalytic application for substrate dehydrogenation using an organo azide is presented.

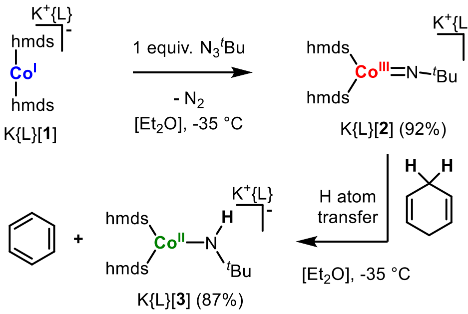
Imido metal complexes of the late 3d-transition metals are of principal interest as they feature a multiply bonded [N−R] functionality that can be potentially transferred to unreactive substrates. As such they are key intermediates in the metal catalyzed aziridation of olefins and amination of substrates bearing (un-)functionalized C−H bonds.[1] An important factor that determines their reactivity is the electronic situation of the imido bound metal ion, which is impacted by coordination number and electronic spin as well as oxidation state. Whereas imido iron complexes have been under intense scrutiny[2,3] lesser is known about isolable heavier 3d-metal imido complexes of cobalt to copper. This can be rationalized by a weaker, more reactive metal nitrogen double bond of late 3d-transition metals which is *inter alia* due to a higher *d*-electron count and reduced ligand-to-metal back-bonding.[4] This is reminiscent of observations in the metal oxido chemistry, where terminal late transition metal oxido complexes are inherently labile for the same reasons. Therefore, isolable imido complexes of copper,[5] nickel,[6] and cobalt[3,7–19] are scarce and knowledge on the structure, electronic situation as well as their reactivity is still largely lacking.

For example, isolable imido cobalt complexes showed a variety of observable oxidation states (+II to +V), however no clear correlation with respect to their reactivity, such as H-atom transfer, has emerged.[3,7–20] High-spin complexes are generally ascribed a higher reactivity, whereas low-spin complexes are found to be more stable. This can be reasoned by reduced back bonding into the partially filled *d*-orbitals in case of high-spin complexes. Indeed, nearly all isolable cobalt complexes are found in a low-spin state. Only two imido cobalt systems with higher spin states at room or near room-temperature are known (Scheme 1).[9,13] To acquire a imido metal complex in a higher spin state the use of weak-field ancillary ligands, that support the metal nitrogen multiple bond, is thought to be beneficial. This was show-cased by King et al. using a bidentate pyrromethane ligand (Scheme 1, left).[9] Respective imido cobalt complexes could perform the intramolecular C−H activation and amination of the ancillary or imido ligand (e. g. benzylic positions), the latter even on a catalytic scale when using an appropriate organo azide.[21] However, no intermolecular C−H bond activation by imido cobalt complexes has been observed so far. Further, the knowledge on the behaviour of the cobalt amides, which inevitably result from the initial H atom abstraction, towards these substrates beyond deprotonation is absent in the literature. However, knowledge thereof is crucial to fully understand the (catalytic) nitrene transfer .



Scheme 1. Paramagnetic imido cobalt(III) complexes (Ad = adamantyl).

We recently reported on the synthesis of two-coordinate metal(I) complexes such as $[Co^{I}(hmds)_2]^-$, $[\mathbf{1}]^-$, (hmds = $-N(SiMe_3)_2$), which exhibit a very weak ligand field.[22] Given the lack of chelating and highly encumbering ligands that enforce a given coordination sphere we hypothesized the use of $[\mathbf{1}]^-$ as an entry into reactive yet isolable imido higher spin cobalt complexes. In this study we present the isolation of a paramagnetic cobalt(III) imide bearing a rather long Co−N imide bond, its unprecedentedly potent intermolecular H atom abstraction capability as well as the multifaceted reactivity of resulting cobalt(II) amide towards C−H bonds.



Scheme 2. Synthesis of K{L}[**2**] (L = crypt.222; hmds = $-N(SiMe_3)_2$) and its H atom abstraction ability leading to K{L}[**3**] (shown for 1,4-cycloexadiene).

Reaction of K{L}[**1**] (L = crypt.222) with *tert*-butyl azide (Scheme 2) lead to the formation the imido cobalt complex K{L}[**2**] (Figure 1). In the crystal structure the complex anion $[\mathbf{2}]^-$ exhibits a cobalt

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ion surrounded by two hmds ligands and the N^{t}Bu unit in a distorted trigonal planar fashion. The Co−N$_{imido}$ bond length amounts to 1.7067(12) Å which is slightly longer than of other reported imido cobalt complex (1.60 − 1.69 Å) which can be connected to the anionic charge and the higher spin state of the complex.[3,7–19] The Co−N−C$_{tBu}$ angle is with 160.78(12)° slightly bent.

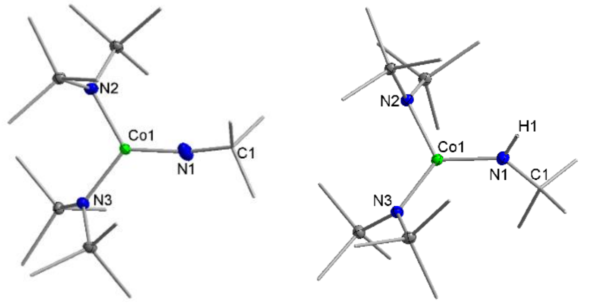
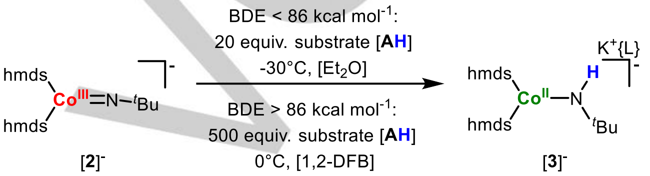


Figure 1. Sections of the crystal structures of KL}[**2**] (left) and K{L}[**3**] (right). Cations and unnecessary H atoms are omitted for clarity.

^{1}H-NMR spectroscopic examination in [D8]THF showed two paramagnetically shifted signals at −2.68 and 32.8 ppm for the hmds as well as the ^{t}Bu group. The paramagnetic nature of K{L}[**2**] was confirmed in solution (μ_{eff} = 3.75 μ_B, Evans method) as well as in solid state via VT-dc susceptibility measurements (μ_{eff} = 3.52 μ_B at 300 K), which suggested a triplet configuration (S = 1) as the electronic ground state. These values are similar to the cobalt (III) imido complex **A^{Mes}** (μ_{eff} = 3.68 μ_B, Scheme 1)[9] for which a triplet ground state was proposed, too, and slightly above values found for other low-coordinate cobalt(III) complexes (e.g. [Co^{III}(SAr)$_4$]$^{-}$[23]). X-Band perpendicular-mode EPR-measurements at 12 K gave no useful signal, expected for an integer spin system.

K{L}[**2**] is surpisingly incompetent in nitrene transfer reactions (e.g. to phosphines or alkenes), contrasting the behavior of most imido cobalt complexes. We then analysed the reactivity of K{L}[**2**] concerning H atom abstraction (HAA) (Scheme 2). When K{L}[**2**] was treated with 1,4-cyclohexadiene (1,4-CHD) in [D8]THF ^{1}H-NMR spectroscopic examination revealed the full conversion of K{L}[**2**], formation of benzene and new paramagnetic signals at 76.2 and −15.5 ppm. Layering the reaction mixture with pentane gave the formal H atom abstraction (HAA) product K{L}[Co(hmds)$_2$(HN^{t}Bu)], K{L}[**3**], which in the crystal structure exhibits a three coordinate cobalt ion with a clearly bent *tert*-butyl amide unit (134.79(10)°). The Co−N1 bond length of 1.8832(12) Å is in line with a cobalt amide single bond.[24] The Co−N$_{hmds}$ bonds in complex [**3**]$^-$ are elongated by about 0.05 Å in comparison with complex [**2**]$^-$, indicative of a lower oxidation state of the metal ion in complex [**3**]$^-$. Its magnetic moment in solution amounts to μ_{eff} = 4.58 μ_B, expected for a high spin cobalt(II) complex (4.3 – 5.3 μ_B).

Given the unprecedented intermolecular HAA by an isolable imido cobalt complex, we were interested in the HAA potential of K{L}[**2**]. K{L}[**2**] reacted rapidly with stoichiometric amounts of substrates bearing rather weak C−H bonds (9,10-dihydroanthracene (9,10-DHA), xanthene (XAN), indene (IND), 9-fluorene (9-FLU), Ph$_2$CH$_2$, Ph$_3$CH and ethylbenzene (EtPh); bond dissociation energies BDE <85 kcal mol^{-1}l)[25] at ambient conditions in [D8]THF, leading to the formation of K{L}[**3**]. As in-situ analysis of reactions with substrates bearing stronger C−H bonds was limited by the concurrent reaction of the imide with [D8]THF, respective substrate transformations (including used solvents) were performed either under neat conditions or in 1,2-DFB ($t_{1/2(DFB)}$ = 2.5 h) and subsequently analysed by ^{1}H NMR spectroscopy. K{L}[**2**] reacted at room temperature rapidly with pure THF (92.1±1.6 kcal mol^{-1})[25] and Et$_2$O (91.7 kcal mol^{-1}),[26] giving K{L}[**3**] as the main product. For toluene (88.0±1 kcal/mol)[25] and ethylbenzene (85.4 kcal/mol)[25] the selective formation of K{L}[**3**] was observed over the course of 12 h. Kinetic studies on these reactions via UV/Vis spectroscopy showed substrate conversion with pseudo first-order kinetics with respect to the imido cobalt complex [**2**]$^-$.



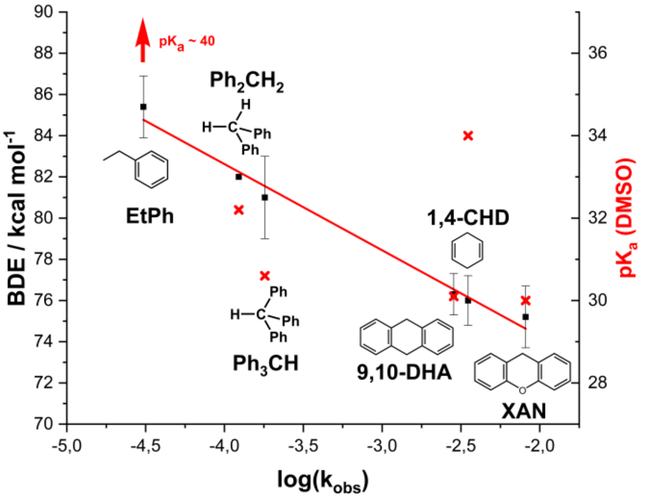
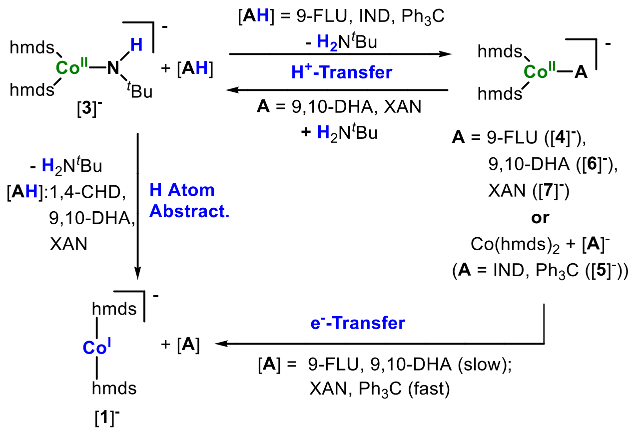


Figure 2. Correlation between the reaction constants k_{obs} and the C−H BDE (■) (and their acidity (×)) for different substrates (shown for BDE < 85 kcal mol^{-1}) for their reaction with [**2**]$^-$.

The observed reaction rates correlated well with the BDE of the involved C−H bond(s) (Figure 2 and S27) but not their acidity. The use of partially deuterated [D4]9,10-DHA revealed a kinetic isotope effect of KIE$_{H/D}$ = 6.5(2). This is lower than the semi classical limit at that temperature (≈13), pointing to a non-linear C··H··N trajectory. An Eyring analysis of the temperature dependence of the rate constants of the reaction of complex [**2**]$^-$ with 1,4-CHD in a range of −70 °C to −30 °C gave a rather small activation enthalpy ($\Delta H^\ddagger$ = 19(3) kJ mol^{-1}). The $\Delta H^\ddagger$ value is similar to the one for H atom abstraction of C−H or O−H bonds by metal oxido or hydroxido complexes.[27] Overall, these findings clearly indicate the partition of the C−H bond cleavage in the rate determining step and suggest an H atom transfer mechanism.



Scheme 3. H atom transfer reactivity of [**3**]$^-$ as well as the behaviour of resulting Co(hmds)$_2$/substrate anion complexes.

As during the reaction of substrates with K{L}[**2**] follow-up reactions could be observed, the reaction of the resulting cobalt amide complex **[3]**$^-$ was examined more closely via ^{1}H NMR spectroscopy and X-ray diffraction analysis of reaction products. For fluorene and indene simple deprotonation of the substrate by the amide [**3**]$^-$ occurred (Scheme 3). This gave either the cobalt(II) fluorenyl compound K{L}[Co(hmds)$_2$(9-FLU)], K{L}[**4**] (Figure 3, left), or a mixture of the indenyl anion and Co(hmds)$_2$. The organo cobalt complex [**4**]$^-$ is rather stable and as only upon heating (60 °C, 1 h) marginal amounts of complex [**1**]$^-$, the result of a formal homolytic Co−C cleavage, were detected. For the reaction of triphenyl methane with [**3**]$^-$ in 1,2-DFB immediate formation of [**1**]$^-$ and ^{t}BuNH$_2$ is observed. Intriguingly, the same reaction in THF led to the formation of mainly Co(hmds)$_2$ and the precipitation of K{L}[CPh$_3$], K{L}[**5**], due to its low solubility of the latter in this solvent. When Co(hmds)$_2$ was then subjected to the methanide anion in 1,2-DFB, the rapid formation of [**1**]$^-$ and the Gomberg dimer was observed, which overall implied a stepwise proton/electron transfer for Ph$_3$CH in its reaction with the cobalt amide. Remarkably, the reaction of Ph$_3$CH with [**3**]$^-$ proceeded significantly faster than the analogous reaction with the imide [**2**]$^-$. For 9,10-DHA, and slower for 1,4-CHD and xanthene, the reaction with complex [**3**]$^-$ lead to the formation of the starting cobalt(I) complex [**1**]$^-$, *tert*-butyl amine and the respective dehydrogenation product. Thereby these reactions were slower than the analogous ones with the imide [**2**]$^-$. For xanthene an additional set of paramagnetic signals was observed, pointing to parallel substrate deprotonation. To elucidate a possible stepwise PT/ET process for these substrates, Co(hmds)$_2$(thf) was reacted with crypt.222 and K(9,10-DHA) or K(XAN), which gave the organometallic complexes (K{L}[Co(hmds)$_2$(9,10-DHA)], K{L}[**6**] (Figure 3, right) and (K{L}[Co(hmds)$_2$(XAN)], K{L}[**7**] (Figure S43, ESI). These complexes underwent only moderate homolytic bond Co−C bond cleavage and complex [**1**]$^-$ formation. When [**6**]$^-$ and [**7**]$^-$ were subjected to ^{t}BuNH$_2$, the immediate deprotonation of the amine under formation of [**3**]$^-$ and 9,10-DHA or xanthene occurred. Thereby the deprotonation of the amine was not fully achieved in case of [**7**]$^-$. This pointed to a readily adjusted equilibrium between the cobalt amide and the cobalt substrate complexes. In view of this equilibrium and the comparison of the speed of homolytic Co-C cleavage by [**7**]$^-$ with the reaction of the amide [**3**]$^-$ with xanthene, a stepwise PT/ET mechanism can be assumed for this substrate. In contrast, for 9,10-DHA such a pathway is not plausible, as the substrate conversion by the cobalt amide [**3**]$^-$ exceeded dramatically the formation of [**1**]$^-$ from complex [**6**]$^-$. Therefore, a direct H atom transfer is hypothesized for this substrate. Such a mechanism is also likely for the reaction of the amide [**3**]$^-$ with 1,4-CHD (pka ≈ 34).

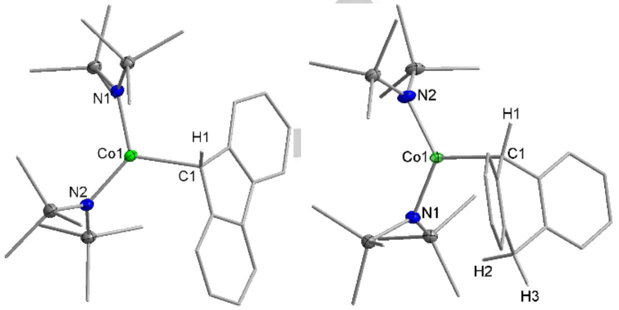


Figure 3. Sections of the crystal structure of K{L}[**4**] (left) and K{L}[**6**] (right). Cations and unnecessary H atoms are omitted.

These C−H atom abstraction reactions by [**3**]$^-$ are, besides being so far unreported for exogeneous substrates in case of an *amido* cobalt complex, striking for several reasons: (a) The amide [**3**]$^-$ can deprotonate substrates bearing little acidic C−H bonds which potentially poses an unproductive pathway for catalytic nitrene transfer into C−H bonds. (b) This can be followed by reduction of the cobalt(II) complex by the formed substrate anion, which overall constitutes a stepwise proton/electron transfer. c) The formal H atom transfer can also occur in an synchronous fashion. This behaviour resembles the H atom abstraction behavior of a copper or a rhodium aminyl radical complex.[28] The reaction trichotomy can be loosely correlated to an interplay between the BDE and pK$_A$ values of the C−H bond of the substrate. Thereby a very low pka value (<22) of the C−H bond lead to simple protonation, whereas a moderate pkA value and a higher C−H BDE lead to a stepwise PT/ET. In contrast, for higher C−H pK$_A$ and moderate BDE values of the substrate a direct HAT pathway is seemingly preferred. The divergent behavior of amide [**3**]$^-$ is reminiscent of related terminal metal hydroxido complexes, which – besides deprotonation – can also facilitate H atom abstraction of C−H bonds.[29] Next, we wanted to assess the N−H bond strength of the amide [**3**]$^-$. In view of the rather slow reaction of [**2**]$^-$ with PH$_3$C−H, [**3**]$^-$ was reacted with a fivefold excess of the trityl radical (Gomberg dimer). This lead to the detection of small amounts of PH$_3$C−H; which however could not be quantified due to subsequent reactions. Together with the results of the substrate scope of [**2**]$^-$, this implicates a N−H bond strength range of approximately 85−90 kcal/mol for [**3**]$^-$.

Lastly, we probed selected transformations in a catalytic setting. With 5 mol% of K{L}[**2**], H atom transfer from 9,10-DHA to *tert*-butyl azide is observed (49% conversion, 24 h, 25 °C; Table 1). However, examination of the reaction mixture showed decomposition of the employed cobalt complex although the system remained partially catalytically active. For xanthene, catalytic dehydrogenation was possible but gave also unidentified side products, possibly result of C-N bond formation processes. In case of liquid 1,4-CHD and indene the catalysis could also be performed under neat conditions.

$${}^{t}\mathrm{BuN_3} + 2\,[\mathbf{AH}] \xrightarrow[-\,\mathrm{N_2}]{5\text{ mol\%}\ \mathrm{K\{L\}}[\mathbf{1}]} {}^{t}\mathrm{BuNH_2} + 2\,[\mathbf{A}]$$

Table 1. Catalytic dehydrogenation of substrates by K{L}[**1**] using *tert*-butyl azide.

Substrate [**AH**]	Solvent	Time /h	Conversion (azide)*	Yield (amine)*
9,10-DHA	[D8]THF	24	49%	49%
1,4-CHD	/	36	99%	99%
XAN	[D8]THF	36	61%	31%**
IND	/	36	72%	72 %

In conclusion, we presented the synthesis, isolation and characterization of a rare paramagnetic cobalt(III) imido complex via reaction of a two-coordinate cobalt(I) complex with *tert*-butyl azide. It exhibits a rather long $\mathrm{Co{-}N_{imido}}$ bond and facilitated the rapid intermolecular H atom abstraction from C−H bonds with a BDE of up to 92 kcal/mol under formation of a cobalt(II) amido complex. Kinetic and mechanistic studies implicated an H atom transfer mechanism. Remarkably, the formed cobalt(II) amide could also abstract an H atom from the substrate, which gave free *tert*-butyl amine and regenerated the cobalt(I) complex [**1**]$^{-}$. Depending on the substrate, the formal H atom abstraction occurred via a concerted or a stepwise proton/electron transfer mechanism. A first catalytic study showed the possibility of employing complex [**1**]$^{-}$ as a precatalyst for substrate dehydrogenation using *tert*-butyl azide as the H atom acceptor.

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Keywords: Imido cobalt complex • H atom transfer • C−H activation • Amido cobalt complex • Catalysis

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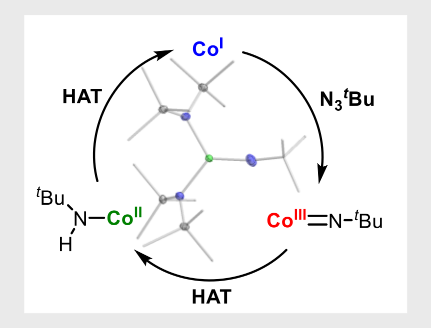
A trigonal planar imido cobalt(III) complex, obtained from reaction of a quasi-linear cobalt(I) complex with an organo azide, is capable of intermolecular H atom abstraction of C-H bonds. The resulting cobalt(II) amide itself can either deprotonate the substrate, facility an H atom abstraction or mediate a stepwise proton/electron transfer. As the latter regenerates the starting cobalt(I) complex, a first catalytic application is presented.



*A. Reckziegel, C. Pietzonka, F. Kraus, C. G. Werncke**

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A Trigonal Imido Cobalt(III) Complex: Synthesis and H Atom Abstraction Reactivity

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