

## Homogeneous Catalysis

## C–H Bond Activation by an Imido Cobalt(III) and the Resulting Amido Cobalt(II) Complex

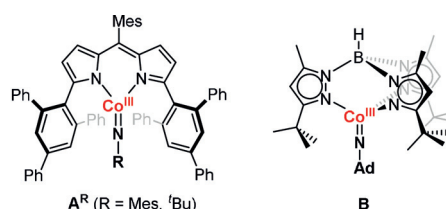
Alexander Reckziegel, Clemens Pietzonka, Florian Kraus, and C. Gunnar Werncke\*

**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 a bond dissociation energy of up to 92 kcal mol<sup>-1</sup> in an intermolecular fashion, unprecedented for imido cobalt complexes. This resulted in the amido cobalt(II) complex [Co(hmds)<sub>2</sub>(NH<sup>t</sup>Bu)]<sup>-</sup>. 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 fundamental 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.<sup>[1]</sup> An important factor that determines their reactivity is the electronic situation of the imido-bound metal ion, which is influenced by its coordination number, electronic spin, and oxidation state. Whereas imido iron complexes have been studied in detail,<sup>[2,3]</sup> less 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 due among other things to a higher d-electron count and reduced ligand-to-metal back-bonding.<sup>[4]</sup> This is reminiscent of observations in metal–oxido chemistry, where terminal late transition metal oxido complexes are inherently labile for the same reasons. Therefore, isolable imido complexes of copper,<sup>[5]</sup> nickel,<sup>[6]</sup> and cobalt<sup>[3,7–19]</sup> are scarce and knowledge on the structure, electronic situation and their reactivity is limited.

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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.<sup>[3,7–20]</sup> 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 the 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).<sup>[9,13]</sup> To acquire an imido metal complex in a higher spin state the use of weak-field ancillary ligands, which support the metal–nitrogen multiple bond, is thought to be beneficial. This was showcased by King et al. using a bidentate pyrromethane ligand (Scheme 1, left).<sup>[9]</sup> 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.<sup>[21]</sup> However, no intermolecular C–H bond activation by imido cobalt complexes has been observed so far. Further, the knowledge on the behavior 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 (catalytic) nitrene transfer.



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

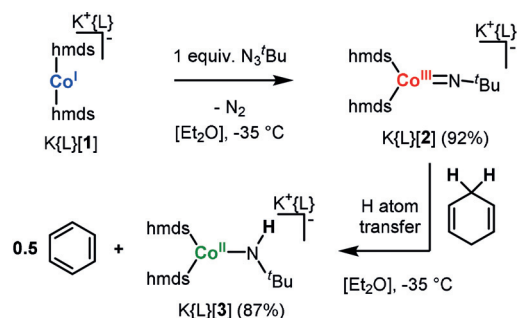
We recently reported on the synthesis of two-coordinate metal(I) complexes such as [Co<sup>I</sup>(hmds)<sub>2</sub>]<sup>-</sup>, [1]<sup>-</sup>, (hmds = -N(SiMe<sub>3</sub>)<sub>2</sub>), which exhibit a very weak ligand field.<sup>[22]</sup> Given the lack of chelating and highly encumbering ligands that enforce a given coordination sphere we hypothesized the use of [1]<sup>-</sup> 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 the resulting cobalt(II) amide towards C–H bonds.

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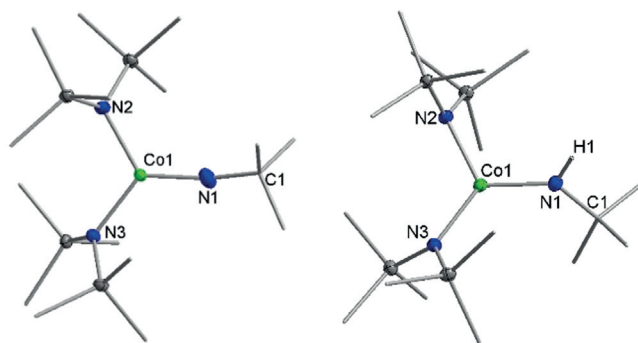
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Reaction of  $K\{L\}[1]$  ( $L = \text{crypt.222}$ ) with *tert*-butyl azide (Scheme 2) led to the formation of the imido cobalt complex  $K\{L\}[2]$  (Figure 1). In the crystal structure the complex anion  $[2]^-$  exhibits a cobalt ion surrounded by two hm<sub>ds</sub> ligands and the *N*<sup>t</sup>Bu unit in a distorted trigonal-planar fashion. The Co–N<sub>imido</sub> bond length is 1.7067(12) Å, which is slightly longer than those for other reported imido cobalt complexes (1.60–1.69 Å). In the case of  $[2]^-$  this is attributed to the anionic charge and the higher spin state of the complex.<sup>[3,7–19]</sup> The Co–N–C<sub>tBu</sub> angle is slightly bent (160.78(12)°).



**Scheme 2.** Synthesis of  $K\{L\}[2]$  ( $L = \text{crypt.222}$ ;  $\text{hm}_{\text{ds}} = \text{N}(\text{SiMe}_3)_2$ ) and its H atom abstraction ability, which leads to  $K\{L\}[3]$  (shown for 1,4-cyclohexadiene).



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

<sup>1</sup>H NMR spectroscopic examination in  $[D_8]\text{THF}$  showed two paramagnetically shifted signals at  $-2.68$  and  $32.8$  ppm for the hm<sub>ds</sub> and the <sup>t</sup>Bu group, respectively. The paramagnetic nature of  $K\{L\}[2]$  was confirmed in solution ( $\mu_{\text{eff}} = 3.75 \mu_{\text{B}}$ , Evans method) as well as in solid state by VT-dc susceptibility measurements ( $\mu_{\text{eff}} = 3.52 \mu_{\text{B}}$  at 300 K), which suggested a triplet configuration ( $S = 1$ ) as the electronic ground state. These values are similar to those for the imido cobalt(III) complex **A**<sup>Mes</sup> ( $\mu_{\text{eff}} = 3.68 \mu_{\text{B}}$ , Scheme 1)<sup>[9]</sup> for which a triplet ground state was proposed, too, and slightly above values found for other low-coordinate cobalt(III) complexes (e.g.  $[\text{Co}^{\text{III}}(\text{SAr})_4]^{-[23]}$ ). X-Band perpendicular-mode EPR measurements at 12 K gave no useful signal, expected for an integer spin system.

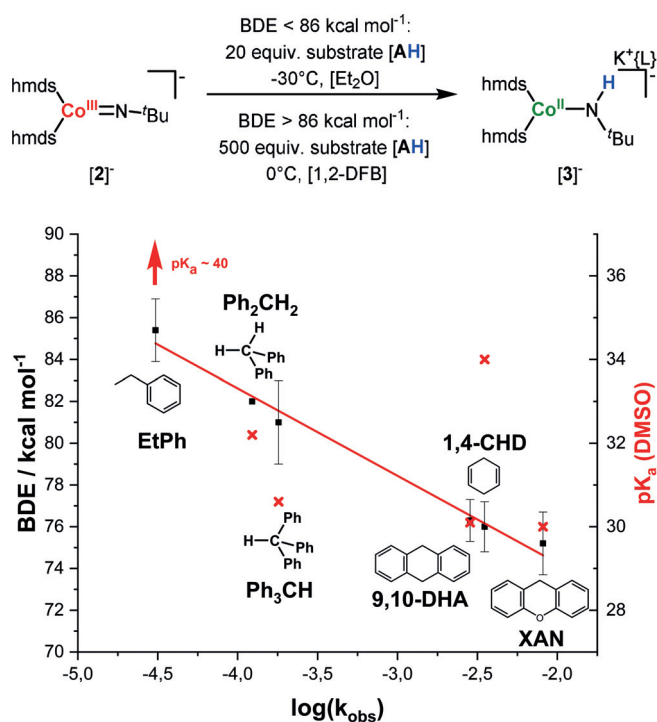
Surprisingly,  $K\{L\}[2]$  showed no reactivity in nitrene transfer reactions (e.g. to phosphines or alkenes), contrasting the behavior of most imido cobalt complexes. We then

analyzed the reactivity of  $K\{L\}[2]$  in H atom abstraction (HAA) (Scheme 2). When  $K\{L\}[2]$  was treated with 1,4-cyclohexadiene (1,4-CHD) in  $[D_8]\text{THF}$ , <sup>1</sup>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  $K\{L\}-[\text{Co}(\text{hm}_{\text{ds}})_2(\text{HN}^t\text{Bu})]$ ,  $K\{L\}[3]$ , 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.<sup>[24]</sup> The Co–N<sub>hm<sub>ds</sub></sub> bonds in complex  $[3]^-$  are elongated by about 0.05 Å in comparison with those in complex  $[2]^-$ , indicative of a lower oxidation state of the metal ion in complex  $[3]^-$ . The magnetic moment of complex  $[3]^-$  in solution is  $\mu_{\text{eff}} = 4.58 \mu_{\text{B}}$ , in the range expected for a high-spin cobalt(II) complex (4.3–5.3  $\mu_{\text{B}}$ ).

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),  $\text{Ph}_2\text{CH}_2$ ,  $\text{Ph}_3\text{CH}$ , and ethylbenzene (EtPh); bond dissociation energies  $\text{BDE} < 85 \text{ kcal mol}^{-1}$ )<sup>[25]</sup> at ambient conditions in  $[D_8]\text{THF}$ , 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  $[D_8]\text{THF}$ , respective substrate transformations (including used solvents) were performed either under neat conditions or in 1,2-DFB ( $t_{1/2(\text{DFB})} = 2.5$  h) and subsequently analyzed by <sup>1</sup>H NMR spectroscopy.  $K\{L\}[2]$  reacted at room temperature rapidly with pure THF ( $92.1 \pm 1.6 \text{ kcal mol}^{-1}$ )<sup>[25]</sup> and  $\text{Et}_2\text{O}$  ( $91.7 \text{ kcal mol}^{-1}$ )<sup>[26]</sup> giving  $K\{L\}[3]$  as the main product. For toluene ( $88.0 \pm 1 \text{ kcal mol}^{-1}$ )<sup>[25]</sup> and ethylbenzene ( $85.4 \text{ kcal mol}^{-1}$ )<sup>[25]</sup> the selective formation of  $K\{L\}[3]$  was observed over the course of 12 h. Kinetic studies on these reactions by UV/Vis spectroscopy showed substrate conversion with pseudo first-order kinetics with respect to the imido cobalt complex  $[2]^-$ .

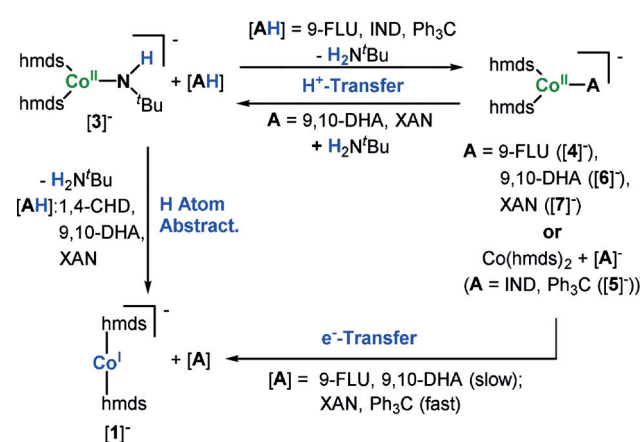
The observed reaction rates correlated well with the BDE of the involved C–H bond(s) (Figure 2 and S27) but not their acidity. The use of partially deuterated  $[D_4]9,10\text{-DHA}$  revealed a kinetic isotope effect of  $\text{KIE}_{\text{H/D}} = 6.5(2)$ . This is lower than the semi-classical limit at that temperature ( $\approx 13$ ), 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 the range of  $-70^\circ\text{C}$  to  $-30^\circ\text{C}$  gave a rather small activation enthalpy ( $\Delta H^\ddagger = 19(3) \text{ kJ mol}^{-1}$ ). 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.<sup>[27]</sup> 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.

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 by <sup>1</sup>H NMR spectroscopy and X-ray diffraction analysis of the reaction products. For fluorene and indene simple deprotonation of the substrate by the amide  $[3]^-$  occurred

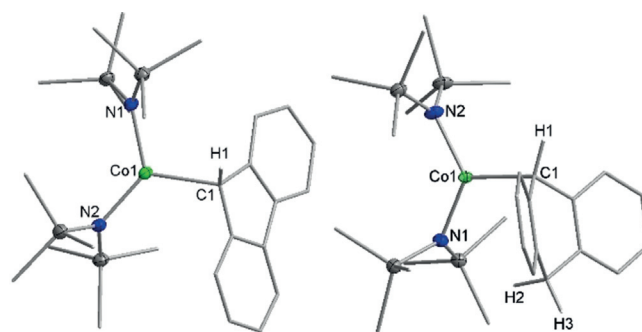


**Figure 2.** Correlation between the reaction constants  $k_{\text{obs}}$  and the C–H BDE (■) (and their acidity (red x)) for different substrates (shown for BDE < 85 kcal mol<sup>-1</sup>) for their reaction with [2]<sup>-</sup>.

(Scheme 3). This gave either the cobalt(II) fluorenyl compound K{L}[Co(hmnds)<sub>2</sub>(9-FLU)], K{L}[4] (Figure 3, left), or a mixture of the indenyl anion and Co(hmnds)<sub>2</sub>. The organo cobalt complex [4]<sup>-</sup> is rather stable. Only upon heating (60°C, 1 h) were marginal amounts of complex [1]<sup>-</sup>, the result of a formal homolytic Co–C cleavage, detected. For the reaction of triphenyl methane with [3]<sup>-</sup> in 1,2-DFB, immediate formation of [1]<sup>-</sup> and 'BuNH<sub>2</sub> was observed. Intriguingly, the same reaction in THF led to the formation of mainly Co(hmnds)<sub>2</sub> and the precipitation of K{L}[CPh<sub>3</sub>], K{L}[5], due to its low solubility in this solvent. When Co(hmnds)<sub>2</sub> was then subjected to the methanide anion in 1,2-DFB, the rapid formation of [1]<sup>-</sup> and the Gomberg dimer was observed,



**Scheme 3.** H atom transfer reactivity of [3]<sup>-</sup> as well as the behavior of resulting Co(hmnds)<sub>2</sub>/substrate anion complexes.



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

which overall implied a stepwise proton/electron transfer for Ph<sub>3</sub>CH in its reaction with the cobalt amide. Remarkably, the reaction of Ph<sub>3</sub>CH with [3]<sup>-</sup> proceeded significantly faster than the analogous reaction with the imide [2]<sup>-</sup>. For 9,10-DHA, and slower for 1,4-CHD and xanthene, the reaction with complex [3]<sup>-</sup> led to the formation of the starting cobalt(I) complex [1]<sup>-</sup>, *tert*-butyl amine, and the respective dehydrogenation product. Thereby these reactions were slower than the analogous ones with the imide [2]<sup>-</sup>. 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(hmnds)<sub>2</sub>(thf) was treated with crypt.222 and K(9,10-DHA) or K(XAN), which gave the organometallic complexes (K{L}[Co(hmnds)<sub>2</sub>(9,10-DHA)], K{L}[6] (Figure 3, right) and (K{L}[Co(hmnds)<sub>2</sub>(XAN)], K{L}[7] (Figure S43, see the Supporting Information). These complexes underwent only moderate homolytic Co–C bond cleavage and complex [1]<sup>-</sup> formation. When [6]<sup>-</sup> and [7]<sup>-</sup> were subjected to 'BuNH<sub>2</sub>, the immediate deprotonation of the amine under formation of [3]<sup>-</sup> and 9,10-DHA or xanthene occurred. Thereby, the deprotonation of the amine was not fully achieved in the case of [7]<sup>-</sup>. 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]<sup>-</sup> with the reaction of the amide [3]<sup>-</sup> 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]<sup>-</sup> was much quicker than the formation of [1]<sup>-</sup> from complex [6]<sup>-</sup>. Therefore, a direct H atom transfer is hypothesized for this substrate. Such a mechanism is also likely for the reaction of the amide [3]<sup>-</sup> with 1,4-CHD ( $pK_a \approx 34$ ).

These C–H atom abstraction reactions by [3]<sup>-</sup> are, besides being unprecedented for external substrates in the case of an *amido* cobalt complex, striking for several reasons: a) The amide [3]<sup>-</sup> can deprotonate substrates bearing slightly acidic C–H bonds which potentially poses an unproductive pathway for catalytic nitrene transfer into C–H bonds. 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 a synchronous fashion. This behavior resembles

the H atom abstraction behavior of a copper or a rhodium aminyl radical complex.<sup>[28]</sup> 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  $pK_a$  value ( $<22$ ) of the C–H bond leads to simple protonation, whereas a moderate  $pK_a$  value and a higher C–H BDE lead to a stepwise PT/ET. In contrast, for a 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.<sup>[29]</sup> Next, we wanted to assess the N–H bond strength of the amide  $[3]^-$ . In view of the rather slow reaction of  $[2]^-$  with  $PH_3C-H$ ,  $[3]^-$  was treated with a fivefold excess of the trityl radical (Gomberg dimer). This led to the detection of small amounts of  $PH_3C-H$ ; which, however, could not be quantified due to subsequent reactions. Together with the results of the substrate scope of  $[2]^-$ , this implies a N–H bond strength range of approximately 85–90 kcal mol<sup>-1</sup> 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 also gave unidentified side products, possibly resulting from C–N bond formation processes. In the case of liquid 1,4-CHD and indene, the catalysis could also be performed under neat conditions.

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

$${}^tBuN_3 + 2 [AH] \xrightarrow[ - N_2 ]{ 5 \text{ mol\% } K[L][1] } {}^tBuNH_2 + 2 [A]$$

Substrate [AH]	Solvent	t [h]	Conversion [%] (azide)	Yield [%] (amine)
9,10-DHA	[D <sub>8</sub> ]THF	24	49	49
1,4-CHD	/	36	99	99
XAN	[D <sub>8</sub> ]THF	36	61	31
IND	/	36	72	72

In conclusion, we have presented the synthesis, isolation and characterization of a rare paramagnetic imido cobalt(III) complex by reaction of a two-coordinate cobalt(I) complex with *tert*-butyl azide. The complex exhibits a rather long Co–N<sub>imido</sub> bond and facilitates the rapid intermolecular H atom abstraction from C–H bonds with a BDE of up to 92 kcal mol<sup>-1</sup> 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:** amido cobalt complex · catalysis · C–H activation · H atom transfer · imido cobalt complex

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