Multiple Bonds

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# A Two-Coordinate Cobalt(II) Imido Complex with NHC Ligation: Synthesis, Structure, and Reactivity

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*Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 60th birthday*

***Abstract:*** *The synthesis, structural characterization, and reactivity of the first two-coordinate cobalt complex featuring a metal–element multiple bond [(IPr)Co(NDmp)] (**4**; IPr = 1,3-bis(2′,6′-diisopropylphenyl)imidazole-2-ylidene; Dmp = 2,6-dimesitylphenyl) is reported. Complex **4** was prepared from the reaction of [(IPr)Co($\eta^2$-vtms)$_2$] (vtms = vinyltrimethylsilane) with DmpN$_3$. An X-ray diffraction study revealed its linear C–Co–N core and a short Co–N distance (1.691(6) Å). Spectroscopic characterization and calculation studies indicated the high-spin nature of **4** and the multiple-bond character of the Co–N bond. Complex **4** effected group-transfer reactions to CO and ethylene to form isocyanide and imine, respectively. It also facilitated E–H (E = C, Si) σ-bond activation of terminal alkyne and hydrosilanes to produce the corresponding cobalt(II) alkynyl and cobalt(II) hydride complexes as 1,2-addition products.*

Two-coordinate metal complexes are a unique class of coordinatively unsaturated metal species. These molecules have attracted increasing attention as a result of their novel chemical and physical properties, for example, small-molecule activation and single-molecule-magnetic behavior.[1,2] Transition-metal complexes featuring metal–element bonds have also attracted significant interest.[3] Although such complexes had been mainly known for 4d and 5d metals having low d-electron counts,[3] the report of Hillhouse and Mindiola in 2001 on the $d^8$ nickel(II) imido complex [(dtbpe)Ni(NDipp)] (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane; Dipp = 2,6-diisopropylphenyl) showcased the ability of a low-coordinate late 3d metal center to form a stable metal–element multiple bond.[4] Since then, a series of three-coordinate 3d metal–imido, metal–alkylidene, and metal–silylene complexes with $d^6$–$d^8$ metal centers have been reported.[5] Two-coordinate metal complexes are considered ideal for stabilizing metal–element multiple bonds as coordination unsaturation can lead to metal–ligand π interactions. However, to date only one two-coordinate metal complex bearing a metal–ligand multiple bond has been reported.[6] This nickel(II) complex, prepared by Hillhouse and co-workers, had large, sterically encumbering NHC (N-heterocyclic carbene) and aryl imido ligands [(IPr*)Ni(NDmp)] (IPr* = 1,3-bis(2′,6′-bis(diphenylmethyl)-4′-methylphenyl)imidazole-2-ylidene; Dmp = 2,6-dimesitylphenyl).

Recently, we found that the reaction of [(IMes)Co($\eta^2$:$\eta^2$-dvtms)] (IMes = 1,3-bismesitylimidazole-2-ylidene; dvtms = divinyltetramethyldisiloxane) with 2 equivalents of DippN$_3$ can afford the three-coordinate cobalt(IV) bisimido complex [(IMes)Co(NDipp)$_2$].[7] The formation of this bisimido complex suggests the involvement of a two-coordinate imido intermediate [(IMes)Co(NDipp)]. Noting this and the rarity of two-coordinate metal complexes featuring multiple bonds between a transition metal and an element, we attempted the preparation of two-coordinate cobalt imido complexes from the reactions of low-coordinate cobalt(0) precursors with the bulky organic azide DmpN$_3$. Herein, we report the synthesis and structural characterization of the first two-coordinate cobalt imido complex [(IPr)Co(NDmp)], which is also the first cobalt(II) terminal imido complex. We also report the reactivity of the complex in group-transfer reactions and its employment in E–H (E = C, Si) bond activation.

Initially, we examined the reaction between [(IMes)Co($\eta^2$:$\eta^2$-dvtms)] and DmpN$_3$, which was found to be unsuccessful. Subsequently, the reaction of the cobalt(0) bisalkene complex [(IMes)Co($\eta^2$-vtms)$_2$] (**1**, vtms = vinyltrimethylsilane)[8] with DmpN$_3$ was examined, which, however, afforded the cyclometallated cobalt(II) amide complex [(IMes′)Co(NHDmp)] (**3**; IMes' denotes the bidentate cyclometallated IMes ligand). The structure of **3** was determined by a single-crystal X-ray diffraction study (see Figure S3 in the Supporting Information).[8,9] Complex **3** may be formed from the intramolecular benzylic C–H bond activation of the cobalt(II) imido intermediate [(IMes)Co(NDmp)]. To prevent this, the more bulky NHC-ligand-supported cobalt(0) precursor [(IPr)Co($\eta^2$-vtms)$_2$] (**2**) was used.[8] Treatment **2** with 1 equivalent of DmpN$_3$ in *n*-hexane at room temperature led to a rapid change of color from green to yellow brown along with vigorous N$_2$ release and the concomitant precipitation of a dark-brown crystalline solid (Scheme 1). An X-ray crystallographic study revealed the identity of the solid as the desired two-coordinate cobalt imido complex [(IPr)Co(NDmp)] (**4**). Complex **4** was further characterized by $^1$H NMR, UV/Vis/NIR absorption spectroscopy, solution

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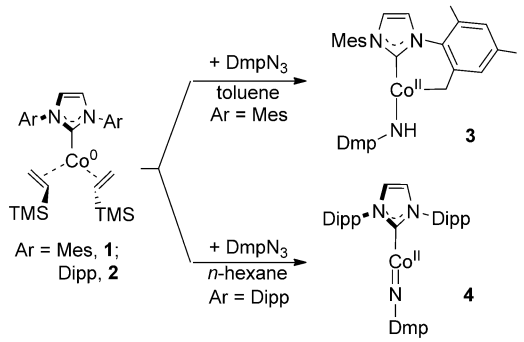



***Scheme 1.*** Reactions of NHC–$Co^0$–alkene complexes with $DmpN_3$.

magnetic susceptibility measurements, and elemental analysis.[8,9]

Figure 1 shows the molecular structure of **4**. The two-coordinate complex has slightly bent C(carbene)-Co-N(imido) (173.0(3)°) and Co-N(imido)-C(aryl) (174.5(5)°) angles. The deviation of these angles from linearity induced

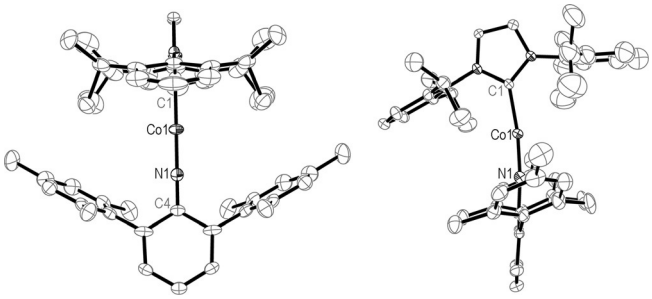



***Figure 1.*** ORTEP drawings of [(IPr)Co(Ndmp)] (**4**) with a partial atom numbering scheme shown. Thermal ellipsoids are set at 30% probability. Left: view of the structure along the imidazoline plane. Right: view along the central arene plane of the Dmp group. Selected distances [Å] and angles [°]: Co1–C1 1.953(6), Co1–N1 1.691(6), N1–C4 1.343(9); C1-Co1-N1 173.0(3), Co1-N1-C4 174.5(5).

the non-perpendicular alignment of the mesityl rings toward the central arene ring of the Dmp moiety, as reflected by the dihedral angle of 73.2°. The core planes in the Dmp group and the IPr ligand are perpendicular to each other, which is different from the small dihedral angle in the nickel imido complex [(IPr*)Ni(NDmp)] (41°).[6] No secondary metal–ligand interaction is evident within the molecule. The Co–N(imido) distance in **4** is 1.691(6) Å, which is much shorter than the Co–N(amido) bonds of the two-coordinate cobalt(II) amido complexes reported by Power (1.84 to 1.91 Å),[1a] but longer than many of the reported cobalt(III) imido complexes (1.61–1.68 Å)[5f,j,10a–e] and the calculated Co–N (nitride) distance of the transient cobalt(IV) nitride complex (1.59 Å) reported by Meyer et al.[10f] The N(imido)–C(aryl) distance in **4** (1.343(9) Å) is comparable to those of the arylimido complexes involving electron delocalization within the arylimido fragments, for example, [(IPr*)Ni(NDmp)] (1.351(4) Å),[6] [(dipyrrin)Fe($NC_6H_4$-*p*-$^t$Bu)Cl] (1.331(2) Å),[11] and [(IMes)Co($NDipp)_2$] (1.357(4) Å).[7] The Co–C(carbene) distance (1.953(6) Å) is close to that of the two-coordinate cobalt–NHC complexes [$(IMes)_2$Co][$BPh_4$] (1.937(2) Å)[2a] and [($IPr_2Me_2$)Co(N($SiMe_3$)($Ar^{\#}$)] (1.962(3) Å; $Ar^{\#} = C_6H_2$-2,6-$(CHPh_2)_2$-4-Me).[2j]

Complex **4** is air-, moisture-, and heat-sensitive. When dissolved in THF, it decomposed completely within hours at room temperature to form intractable paramagnetic species. The instability of **4** is in stark contrast to its nickel analogue [(IPr*)Ni(NDmp)] which is stable at room temperature. In low-polarity solvents, such as benzene and toluene, the decomposition of **4** was slowed down, which enables a study of the properties of the compound in solution. The $^1$H NMR spectrum of **4** in $C_6D_6$ shows broad paramagnetically shifted signals spanning a wide frequency range from $\delta = 137$ to $-150$ ppm. Its solution magnetic moment (4.8(1) μB)[12] is larger than the spin-only value (3.87 μB) for high-spin $d^7$ ions ($S = 3/2$), suggesting the presence of strongly enhanced out-of-state spin–orbit coupling, as detected in Power's two-coordinate cobalt(II) complexes.[1a] The absorption spectrum of **4** measured in $C_6H_6$ features four absorption bands in the UV/Vis region (at $\lambda = 300$, 380, 430, and 500 nm) and three bands in the near-infrared region ($\lambda = 650$, 850, and 1518 nm). These absorptions are tentatively assigned as charge-transfer bands and ligand-field transitions, respectively.

DFT calculations[13] indicated that the two-coordinate imido complex has a high-spin ground state ($S = 3/2$) and the Co–N bond has multiple-bond character. Whereas both the optimized structures at the doublet ($S = 1/2$) and quartet ($S = 3/2$) states have $C_{2v}$ symmetry, the quartet state is lower in energy than the doublet state by 8.5 kcal mol$^{-1}$ and has bond lengths within the {Co(NDmp)} fragment closer in value to the crystal structure data (see Table S1 in the Supporting Information). For the quartet state, two of the unpaired electrons occupy the π*-type orbitals, which are composed of Co $3d_{yz}$ and $3d_{xz}$ orbitals and N $2p_y$ and $2p_x$ orbitals, respectively (Figure 2, MO 209 and MO 208; MO = molecular orbital). The third unpaired electron resides on a nonbonding orbital (MO 207; Figure S8) that is essentially based on the

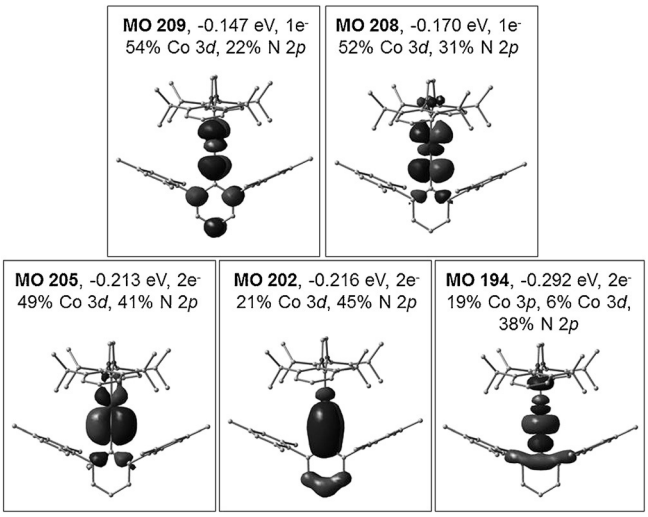
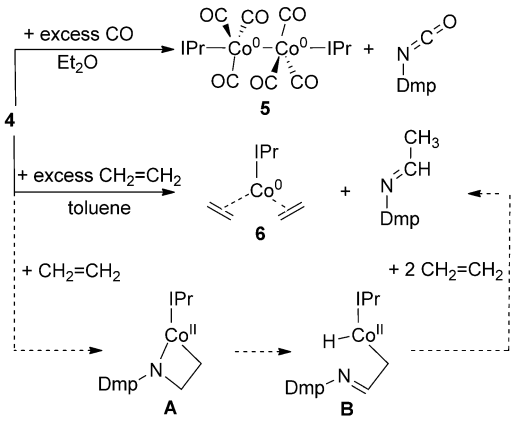



***Figure 2.*** Molecular orbital (MO) plots involving π- and σ-type Co–N interactions for [(IPr)Co(NDmp)] at the $S = 3/2$ state.

3d orbitals of the cobalt center. MO 205 and MO 202 can be viewed as the corresponding π-bonding interactions relative to MOs 208 and 209. In addition to the π interactions, there is also a σ-bonding interaction between Co 3p and N 2p orbitals (Figure 2, MO 194). The sum of these interactions resulted in a Mayer bond order[14] of 1.55 for the Co–N(imido) multiple bond, which differs from that of 0.77 for the Co–C(carbene) bond (Figure S13).

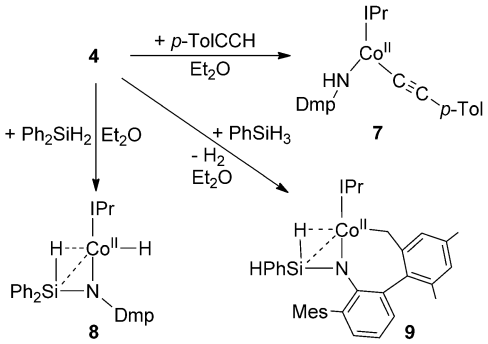
Complex **4** is not only a rare example of a two-coordinate metal complex featuring a metal–element multiple bond, but is also the first reported cobalt(II) terminal imido complex. With this in mind, we next studied the reactivity of the complex. Like other late-transition-metal imido complexes,[3] **4** can transfer its NDmp group to CO to form the isocyanate DmpNCO and the carbonyl complex $[Co_2(IPr)_2(CO)_6]$ (**5**; Scheme 2).[8] Intriguingly, it can also react with ethylene to




***Scheme 2.*** Group-transfer reactivity of **4** and a proposed pathway leading to the formation of the imine.

produce DmpN=CHCH$_3$ and $[(IPr)Co(\eta^2\text{-}CH_2{=}CH_2)_2]$ (**6**; Scheme 2).[8] The structure of DmpN=CHCH$_3$ was unequivocally determined by means of a single-crystal X-ray diffraction study (Figure S5). One plausible mechanism accounting for the formation of the imine is shown in Scheme 2. A [2π + 2π] cycloaddition[15] of ethylene with the Co=N double bond in **4** produces a four-membered metallacycle (Scheme 2, species **A**) that undergoes β-hydride elimination[16] to produce an α-(hydridocobalt)imine species (species **B**). The coordination of ethylene to **B** then leads to reductive elimination to form **6** and the imine. The proposed route is similar to that proposed for the reaction of [(IPr*)Ni(NDmp)] with ethylene by Hillhouse and co-workers, wherein an enamine DmpNHCH=CH$_2$ rather than the imine was formed (Scheme S1).[6] This disparity in reactivity might be related to the different steric properties of the NHC ligands in [(IPr)Co(NDmp)] and [(IPr*)Ni(NDmp)], which affects the outcome of the β-hydride elimination step (Scheme S1). A cobalt-promoted enamine-to-imine isomerization seems less likely because an NMR-scale reaction indicated the immediate formation of the imine without detection of any enamine intermediate (Figure S29,30), and the tautomerization of secondary enamines to the corresponding imines usually occurs under acidic conditions.[17]

In addition to the reactions with the unsaturated substrates, **4** can also promote C–H and Si–H bond activation. The reactions of **4** with *p*-TolC≡CH (p-Tol = *para*-tolyl), $Ph_2SiH_2$, and $PhSiH_3$ produced the corresponding cobalt(II) amide complexes [(IPr)Co(NHDmp)(C≡C–*p*-Tol)] (**7**), [(IPr)CoH{N(SiHPh$_2$)(Dmp)}] (**8**), and [(IPr)Co{N(SiH$_2$Ph)-(Dmp′)}] (**9**; Dmp′ denotes the cyclometallated Dmp fragment) in high yields (Scheme 3).[8,9] The molecular structures




***Scheme 3.*** The activation of C–H and Si–H bonds by complex **4**.

of **7**–**9** were confirmed by single-crystal X-ray diffraction studies (Figure S6–S8). Complex **7** is a pseudo three-coordinate cobalt(II) alkynyl amide complex which features a secondary metal–ligand interaction (Figure S6). The long Co–C(carbene), Co–C(alkynyl), and Co–N(amide) distances (2.0778(15), 1.9585(17), and 1.9181(12) Å, respectively) and large solution magnetic moment (4.5(1) μB) are indicative of its high-spin nature. The square-planar cobalt(II) silylamide complexes **8** and **9** are low spin ($\mu_{eff}$ = 3.0(1) μB), in accordance with the reported square-planar cobalt(II)–NHC complex $[Co(IMes')_2]$[2a] and $[Co(IPr_2Me_2)_2Ph_2]$.[18] In the structure of **8** (Figure S7), the position of the hydrogen atoms coordinated to the silicon and cobalt centers were located using a difference Fourier map and were successfully refined. The Co–Si (2.390(1) Å), Co–H1 (1.67(3) Å), and Si–H1 (1.52(3) Å) distances are indicative of a Si–H···Co β-agostic interaction.[19] The terminal hydride has a Co–H distance of 1.40(4) Å which is comparable to those of the rare low-spin terminal cobalt(II) hydride species, for example, 1.34(8) Å in $[HCo(Pcy_3)_2(BH_4)]$ (Pcy$_3$ = tricyclohexylphosphine)[20] and 1.42 Å in $[HCo(PPh_3)_3(BH_3CN)]$.[21] Ideally, a further reaction involving the cyclometallation of **8**, which might be impeded by steric congestion, would produce $H_2$ and [(IPr)Co{N(SiH$_2$Ph)(Dmp′)}], an analogue of **9**. The fact that cyclometallation product **9** was successfully obtained thus proved indirectly the presence of the terminal Co–H motif in **8**.

The conversions of **4** into **7**–**9** demonstrate the ability of the two-coordinate cobalt(II) imido species to activate sigma E–H (E = C, Si) bonds, and support the aforementioned proposal that [(IMes)Co(NDmp)] could be the intermediate species in the formation of **3**. In spite of the diversity of the E–

H bonds, each of these reactions afforded cobalt(II) complexes with the more electronegative atoms within the E–H moiety bonded to the metal center and the other one bonded to nitrogen. This reactivity pattern is different to the hydrogen atom abstraction reaction of high-valent transition-metal oxo and imido species,[22] and is similar to the 1,2-addition reactions of early-transition-metal imido complexes.[23] Noting this and also the high variation of the bond strengths of the C(alkynyl)–H, C(benzyl)–H, and Si–H bonds (circa 130, 88, and 91 kcal mol$^{-1}$, respectively),[24] one could reason that the E–H activation reactions by **4** might occur by a concerted $[2\sigma + 2\pi]$ addition mechanism,[25] although a radical-type hydrogen atom abstraction mechanism[22] cannot be absolutely ruled out.

In summary, the first two-coordinate cobalt imido complex [(IPr)Co(NDmp)] was prepared by the reaction of a three-coordinate cobalt(0) alkene compound with a bulky organic azide. Characterization data in combination with calculations indicated its high-spin nature and the multiple-bond character of its Co–N bond. The low-coordinate cobalt(II) imido complex undergoes an NDmp group-transfer reaction with ethylene to form an imine. The complex also activates E–H (E = C, Si) bonds to form cobalt(II) alkynyl and hydride complexes as formal 1,2-addition products. The detected reactivities might also be related to the low-coordinate nature and intermediate oxidation state of the cobalt center within the two-coordinate cobalt(II) imido complex.

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