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## COMMUNICATION

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## One Electron Reduction Transforms High-Valent Low-Spin Cobalt Alkylidene into High-Spin Cobalt(II) Carbene Radical

Amanda Grass,<sup>a</sup> James A. Bellow,<sup>a</sup> Gregory Morrison,<sup>b</sup> Hans-Conrad zur Loye,<sup>b</sup> Richard L. Lord,<sup>c\*</sup> Stanislav Groysman<sup>a\*</sup>

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**One electron reduction of formally  $\text{Co}^{\text{IV}}(\text{OR})_2(\text{CPh}_2)$  forms  $[\text{Co}^{\text{II}}(\text{OR})_2(\text{CPh}_2)]^-$  anion. Whereas low-spin  $\text{Co}(\text{OR})_2(=\text{CPh}_2)$  demonstrated significant alkylidene character, high-spin  $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$  anion features a rare Co(II)-carbene radical. Treatment of  $[\text{Co}(\text{OR})_2(\text{CPh}_2)][\text{CoCp}^*_2]$  with xylyl isocyanide triggers formation of two new C-C bonds, and is likely mediated by nucleophilic attack of deprotonated “ $\text{CoCp}^*_2$ ” on a transient ketenimine.**

Transition metal carbene complexes are among the most important organometallic functionalities, catalyzing formation of new C-C, C-N, and C-O bonds.<sup>1</sup> The reactivity exhibited by transition metal carbenes is strongly correlated with their electronic structure.<sup>2</sup> While metal-carbenes can exhibit a broad spectrum of electronic structures, Fischer and Schrock carbenes (alkylidenes) clearly define the electrophilic and nucleophilic ends of the spectrum.<sup>1,2</sup> Fischer carbenes are typically composed of middle or late low-valent transition metals surrounded by soft, strong-field ligands.<sup>3</sup> Fischer carbenes demonstrate longer M=C bonds, nucleophilic metal centers, and electrophilic carbene carbons. In contrast, alkylidenes contain early, high-valent metal centers and often feature hard, weak-field ancillary ligation.<sup>4,5</sup> Alkylidenes demonstrate shorter M=C bonds, electrophilic metals, and nucleophilic carbene carbons. More recently, metal carbene complexes featuring radical character on the carbene carbon received growing attention,<sup>6-8</sup> in particular due to their pronounced ability to promote C-H bond activation and C-C bond formation.<sup>9-12</sup> Various types of metal carbenes require different types of metals/ligands that specifically stabilize a

particular type of carbene complex. In this manuscript, we demonstrate that the carbene nature within a single metal/ligand system can be changed via a simple reduction.

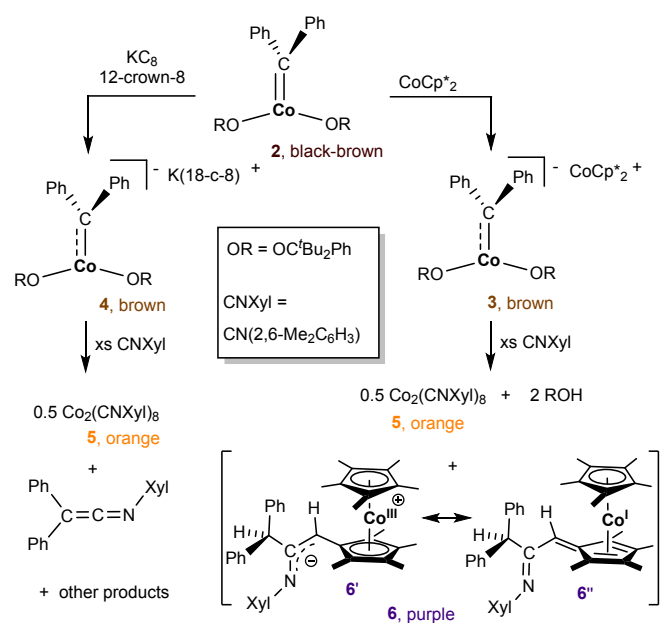
Isolable cobalt carbene complexes typically contain low-valent Co(0)/Co(I) metal centers ligated by Fischer-type carbenes.<sup>13-27</sup> In contrast, Co(III)-carbene radicals have been proposed to mediate various C-C bond formation reactions. While the reactivity and electronic structures of these species have been thoroughly studied during the last decade, they are generally highly reactive and therefore elusive to isolation.<sup>28-31</sup> As part of our studies targeting high-valent late transition metal complexes in weak-field ligand environments,<sup>32,33</sup> we have reported the synthesis of  $\text{Co}(\text{OR})_2(=\text{CPh}_2)$  (**2**, Scheme 1).<sup>34</sup> **2** was obtained by the reaction of diphenyldiazomethane with a cobalt(II) bis(alkoxide) precursor,  $\text{Co}(\text{OR})_2(\text{THF})_2$  (**1**, OR = OC<sup>t</sup>Bu<sub>2</sub>Ph).<sup>35, 36</sup> **2** demonstrated a short Co-C bond of 1.773(3) Å (**Fig. 1**), and Co-O bonds significantly shorter than in **1**. Spectroscopic, magnetic, and computational studies suggested a low-spin ( $S=1/2$ ) high-valent cobalt structure intermediate between cobalt(III) antiferromagnetically coupled with a carbene radical and a genuine cobalt(IV) alkylidene.<sup>34</sup> The reaction of **2** with isocyanides, which proceeded via the initial isocyanide coordination to the metal, provided further evidence for its electrophilic alkylidene-like nature.<sup>37,38</sup> **2** exhibited several electrochemical events by CV, with the first two (-1.2 V and -2.5 V) exhibiting quasi-reversible behavior. The accessibility of these reductions, particularly the first one, prompted us to investigate chemical reduction of **2**. Herein we demonstrate that one-electron reduction of  $\text{Co}(\text{OR})_2(=\text{CPh}_2)$  retains the overall structure of the complex, while transforming the original low-spin high-valent “alkylidene” into a high-spin low-valent Co(II)-carbene with pronounced radical character at the carbene carbon. We also show that while the parent complex (**2**) exhibited efficient coupling of carbenes with isocyanides to form ketenimines as final products, the formation of ketenimines by  $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$  can be followed by subsequent transformations, likely triggered by the anionic nature of the complex.

<sup>a</sup> Department of Chemistry, Wayne State University, 5101 Cass Ave. Detroit MI 48202. E-mail: groysman@chem.wayne.edu

<sup>b</sup> Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

<sup>c</sup> Department of Chemistry, Grand Valley State University, 1 Campus Dr., Allendale, MI 49401. E-mail: lordri@gvsu.edu

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Scheme 1. Synthesis and reactions of the reduced carbene complexes **3** and **4**.

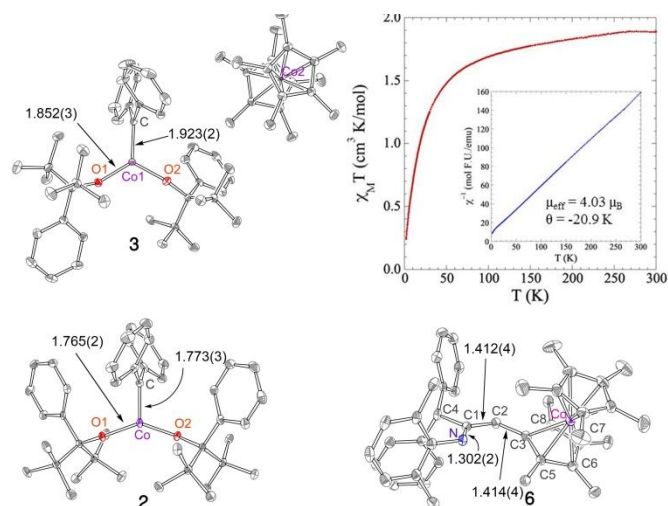


Fig. 1 Top: X-ray structure (50% probability ellipsoids) of **3** and its variable-temperature susceptibility data (measured at 1000 Oe). Bottom left: X-ray structure of **2**,<sup>32</sup> 50% probability. Bottom right: X-ray structure of **6**, 50% probability ellipsoids. Selected bond lengths (Å) are presented above.

Treatment of the cold, dark brown solution of **2** in ether with decamethylcobaltocene (CoCp\*<sub>2</sub>) resulted in a color change to lighter brown within minutes. Work-up and recrystallization from an ether/THF mixture led to the formation of brown X-ray quality crystals of [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)] [CoCp\*<sub>2</sub>] (**3**). The composition of **3** was confirmed by X-ray structure determination and elemental analysis. The structure of **3** is given in Fig. 1. **3** consists of [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)]<sup>-</sup> anion and [CoCp\*<sub>2</sub>]<sup>+</sup> cation in the asymmetric unit. The structure of the [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)]<sup>-</sup> anion demonstrates a similar trigonal planar geometry to **2** comprised of two alkoxide and one carbene ligands. However, [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)]<sup>-</sup> also exhibits notable differences from **2**. The most significant difference between [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)]<sup>-</sup> in **3** and the structure of **2**

is in the longer Co-C bond, 1.923(2) Å for **3** vs. 1.773(3) Å for **2**. Co-O bonds are also considerably longer (1.852(3) Å in **3**, 1.765(2) in **2**), and are close to Co-O bonds in **1** (1.849(1) Å), suggesting similar oxidation state of Co(II).<sup>36</sup> Close examination of the brown crystals of [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)] [CoCp\*<sub>2</sub>] revealed the presence of a second (polymorphic) structure (**3a**, see ESI). While **3** crystallized in a triclinic cell, **3a** crystallizes in a monoclinic base-centered setting C<sub>2</sub>/c; both anion and cation feature crystallographic C<sub>2</sub> symmetry. Anions in **3** and **3a** are rotamers, differing by the alkoxide conformation (see Figure S1 for the structure of **3a**). However, metric parameters obtained from the structure of **3a** are virtually identical to **3** (Co-C bond of 1.91(1) Å, Co-O bond of 1.861(5) Å), further supporting significant elongation of cobalt-ligand bonds as a result of one-electron reduction. Close inspection of the carbene aryl C-C bonds reveals slight bond distance alternation for both **3** and **2**, consistent with the radical nature of the carbene (see Figure S21).

In addition to X-ray crystallography, **3** was also investigated by <sup>1</sup>H NMR, UV-vis, and IR spectroscopy, and magnetic measurements. The <sup>1</sup>H NMR spectrum of **3** in THF-d<sub>8</sub> spans a wide range of 152 ppm (108 ppm to -44 ppm), consistent with its paramagnetic nature. The UV-vis spectrum of **3** exhibits peaks at 500, 648, and 712 nm. Magnetic measurements on **3** were conducted both in solution (Evans' method) and in solid state (magnetic susceptibility measurements, SQUID). Notably, the solution magnetic moment of 4.2(3) μ<sub>B</sub> suggests a high-spin cobalt carbene, in contrast to the low-spin cobalt carbene **2** (2.0 μ<sub>B</sub> ± 0.2 μ<sub>B</sub>).<sup>34</sup> These observations were further supported by magnetic susceptibility measurements. Measurements were performed in the temperature range of 2 K to 300 K at 0.1 T. Both **2** and **3** follow Curie-Weiss behavior, as evidenced by the linear relationship between χ<sup>-1</sup> vs. T. Fitting the susceptibility data gave effective magnetic moments of 2.19 μ<sub>B</sub> for **2** and 4.03 μ<sub>B</sub> for **3**, consistent with the solution magnetic data described above (Fig. 1, S18, and S19).

The electronic structure of the anionic fragment of **3** (denoted **3'** for simplicity) was investigated by DFT calculations at the B3LYP/6-31G(d) level of theory,<sup>39-42</sup> based on our earlier study on **2**.<sup>34</sup> Singlet and triplet states corresponding to anti- and ferromagnetically coupled low-spin Co(II) and carbene radical were found to be higher (+15-16 kcal/mol) in free energy than the triplet and quintet states corresponding to anti- and ferromagnetically coupled high-spin Co(II) and carbene radical. These latter two states are only separated by 1 kcal/mol in free energy. DFT predicts the triplet state to be lowest in electronic and free energy, so our analysis focuses on that state. Mulliken spin analysis of the [Co(OR)<sub>2</sub>] and [CPh<sub>2</sub>] fragments shows spins of 2.87 and -0.87, in contrast to 1.89 and -0.89 for **2**.<sup>34</sup> This suggests reduction occurs primarily at the Co center of **2**. Corresponding orbitals are shown in Fig. 2. Based on these data, and similar analyses for the quintet (see ESI), we interpret **3'** to be a high-spin cobalt(II) ion antiferromagnetically coupled to a carbene radical anion with thermal population of the corresponding ferromagnetic state. This interpretation is consistent with the magnetic data, where a fit of χT results in a small, negative coupling constant

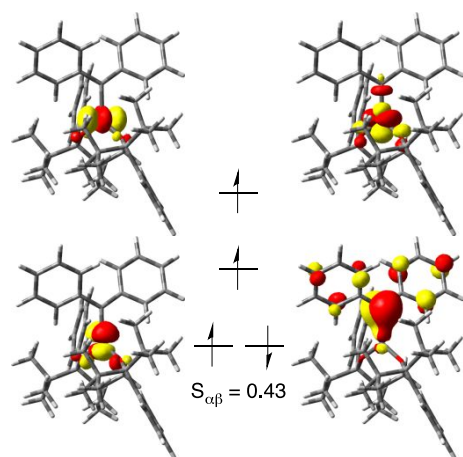
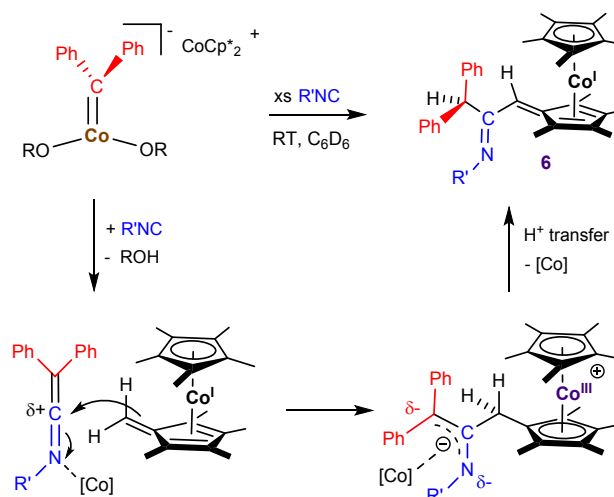


Fig. 2 Corresponding orbital diagram (iso = 0.05 au) of **3'**.

between the high-spin Co(II) and carbene radical,  $J/k_B < -10$  K (see ESI).

**2** demonstrated facile carbene-transfer reactivity with isocyanides (including xylyl and adamantyl isocyanide).<sup>37</sup> To understand reactivity differences between **2** and **3**, the reactivity of **3** with xylyl isocyanide was also investigated. Addition of excess xylyl isocyanide (CNXyl) to **3** manifested a color change to dark purple. Recrystallization of the crude reaction mixture from ether produced two different types of crystals: larger orange and smaller purple. As the orange and the purple products exhibited similar solubility and crystallized together, the only route to separate these products was via mechanical separation. X-ray diffraction studies carried out on the orange crystals revealed previously reported structure of  $\text{Co}_2(\text{CNXyl})_8$  (**5**, Scheme 1).<sup>43</sup>  $^1\text{H}$  NMR spectrum of the isolated orange product was also consistent with  $\text{Co}_2(\text{CNXyl})_8$ . Structural determination of the purple crystals revealed the intriguing product **6**. **6** can be approximated by two resonance structures: zwitterionic form **6'**  $\text{Ph}_2\text{C}(\text{H})\text{C}(\text{NXyl})\text{C}(\text{H})[\text{Cp}(\text{Me})_4\text{Co}^{\text{III}}\text{Cp}^*]$  that contains decamethylcobaltocenium covalently linked to enamide with delocalized negative charge, and form **6''**, that contains  $\text{Cp}^*\text{-Co}(\text{I})\text{-tetramethylfulvene}$  further conjugated to the (C1=N) imine. The X-ray structure of **6** (Fig. 1) is in agreement with **6''**. The bond distances within the NC1C2C3 fragment and relatively narrow dihedral angle between the [NC1C2] plane and tetramethylfulvene ( $\sim 18^\circ$ ) are consistent with the delocalized conjugated system. The formulation of the metal fragment as tetramethylfulvene-Co(I) is further supported by a significantly longer Co-C3 bond (2.216(3) compared with bonds to other carbons (Co-C5/C6/C7/C8, 2.011-2.064 Å).  $^1\text{H}$  NMR spectrum of isolated **6** ( $\text{C}_6\text{D}_6$ ) is consistent with the solid-state structure, containing a singlet for the allylic  $\text{Ph}_2\text{C}(\text{H})\text{C}$  proton at 3.82 ppm and a singlet for the vinylic proton at 5.34 ppm (see ESI). **6** likely originates from the activation of decamethylcobaltocene by transient ketenimine  $\text{Ph}_2\text{C}=\text{C}=\text{N}(\text{Xyl})$ . Observation of the previously reported  $\text{Ph}_2\text{C}=\text{C}=\text{N}(\text{Ad})$ <sup>37</sup> in the reaction of **3** with adamantyl isocyanide lends further support for the postulated  $\text{Ph}_2\text{C}=\text{C}=\text{N}(\text{Xyl})$  intermediate.



Scheme 2. Possible mechanism for the formation of **6**.  $\text{R}' = \text{xylyl}$ .

What is the mechanism behind the formation of **6**? Decamethylcobaltocenium (and related species) has been previously demonstrated to undergo deprotonation to form the tetramethylfulvene complex (resonance form of deprotonated  $\text{CoCp}^*_2$ ).<sup>44-47</sup> It is feasible that the initial deprotonation of decamethylcobaltocenium by  $\text{RO}^-$  is followed by a nucleophilic attack on  $\text{Ph}_2\text{C}=\text{C}=\text{N}(\text{Xyl})$ .<sup>48</sup> In support of this mechanism, ROH was observed in the reaction mixture. No ligand decomposition products consistent with alkoxide radicals were observed by NMR.<sup>36</sup> The reaction is completed by proton transfer from the ( $\text{Cp}^*$ ) methylene position to the benzylic position and formal reduction of the metal, to form the fully conjugated product (Scheme 2). However, we cannot rule out that the formation of **6** is initiated via radical H-atom abstraction from the  $\text{Cp}^*\text{-methyl}$  group, as H-atom abstraction has been also previously demonstrated for the decamethylcobaltocenium ion,<sup>49</sup> and ketenimines have been shown to exhibit radical reactivity in the presence of radical initiators.<sup>50</sup>

To obtain further insight into the reaction, we have also prepared the potassium salt of the reduced carbene,  $[\text{Co}(\text{OR})_2(\text{CPh}_2)][\text{K}(18\text{-crown-6})]$  (**4**). **4** was obtained by the reduction of **2** with potassium graphite ( $\text{KC}_8$ ), followed by the addition of 18-crown-6 (Scheme 1). The complex was characterized by UV-vis, IR, and elemental analysis. The UV-vis spectrum of **4** (peaks at 503, 651, and 712 nm) closely resembles the spectrum of **3** (500, 648, and 712 nm). We also note that treatment of **2** with two equivalents of  $\text{CoCp}^*_2$  or  $\text{KC}_8$  did not result in a doubly reduced species, forming again complexes **3** and **4**, respectively. The reaction of cobaltocenium-free **4** with xylyl isocyanide leads to the observation of stable ketenimine<sup>37</sup> (in addition to **5**), consistent with the absence of relatively acidic  $\text{CoCp}^*_2$ , and providing further support for the mechanism depicted in Scheme 2.

In summary, we demonstrated that one-electron reduction of the high-valent alkylidene-like formally  $\text{Co}^{\text{IV}}(\text{OR})_2(\text{CPh}_2)$  (**2**) produced low-valent carbene-like  $[\text{Co}^{\text{II}}(\text{OR})_2(\text{CPh}_2)]^-$  product, which was isolated as  $[\text{Co}(\text{OR})_2(\text{CPh}_2)][\text{CoCp}^*_2]$  (**3**) or

[Co(OR)<sub>2</sub>(CPh<sub>2</sub>)]<sub>2</sub>[K(18-crown-6)] (4). Treatment of [Co(OR)<sub>2</sub>(CPh<sub>2</sub>)]<sub>2</sub>[CoCp\*<sub>2</sub>] with xylyl isocyanide led to the formation of compound 6 and Co<sub>2</sub>(CNXyl)<sub>8</sub> (5). The formation of the intriguing conjugated product 6 likely proceeded via nucleophilic attack of deprotonated decamethylcobaltocenium on pre-formed ketenimine. Consistently, substitution of the decamethylcobaltocenium counterion by potassium counterion led to the observation of the corresponding ketenimine and Co<sub>2</sub>(CNXyl)<sub>8</sub>. Our future studies will focus on the design of new cobalt-carbene species featuring related, yet more stable alkoxide ligand environments and the investigation of their reactivity.

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### Conflicts of interest

There are no conflicts to declare.

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**TOC entry**

Synthesis, electronic structure, and reactivity of a novel Co(II) carbene radical in the bis(alkoxide) ligand environment are reported.

