Synthesis and Characterization of a Stable High-Valent Cobalt Carbene Complex

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S *Supporting Information*

ABSTRACT: The formally Co^{IV} carbene $Co(OR)_2(=CPh_2)$ is formed upon the reaction of diphenyldiazomethane with the cobalt bis(alkoxide) precursor $Co(OR)_2(THF)_2$. Structural, spectroscopic, and theoretical studies demonstrate that $Co(OR)_2(=CPh_2)$ has significant high-valent $Co^{IV}=CPh_2$ character with non-negligible spin density on the carbene moiety.

High-valent cobalt carbene species are often postulated intermediates in the catalytic cyclopropanation of olefins.[1] These intermediates are generally elusive to isolation and are often studied using spectroscopic and computational methods.[2] While several stable high-valent, formal cobalt(IV) and cobalt(V) complexes have been isolated and structurally characterized,[3] none reported contain terminal carbene ligands. Isolated and structurally characterized cobalt carbene complexes are, in contrast, generally formulated as low-valent Co^I species containing Fischer carbenes.[4] Herein we describe the first example of a structurally characterized high-valent cobalt carbene complex and provide insight into its intriguing electronic structure.

Recently we have reported the synthesis of reactive bis(alkoxide) complexes containing the bulky alkoxide ligand OR^- ($R = C^tBu_2Ph$).[5] Specifically, the iron bis(alkoxide) complex $Fe(OR)_2(THF)_2$ (**1**) reductively couples adamantyl azide, leading to the formation of the Fe^{III} hexazene-ligated dimer, $(RO)_2Fe(\mu\text{-}\kappa^2:\kappa^2\text{-}AdN_6Ad)Fe(OR)_2$.[5a] In contrast, reaction with aryl azides leads to catalytic nitrene coupling to form azoarenes (ArNNAr) via a putative iron(III) imido radical intermediate.[5b] Due to the generation of reactive nitrene species from azides, we next turned to study the reactivity of our bis(alkoxide) complexes with diazoalkanes (R_2CN_2) to form reactive carbene species in a similar manner.

For our preliminary investigation, we decided to focus on diphenyldiazomethane as a carbene source. Diphenylcarbene was previously found to form stable carbene complexes with other first-row transition metals.[4e,6] The presence of two phenyl groups provides electronic stabilization, via charge delocalization on the carbene carbon, as well as through steric protection. The 1:1 addition of diphenyldiazomethane to a stirred solution of **1** in hexanes led to an instantaneous color change to red. Reaction workup afforded colorless crystals as the major
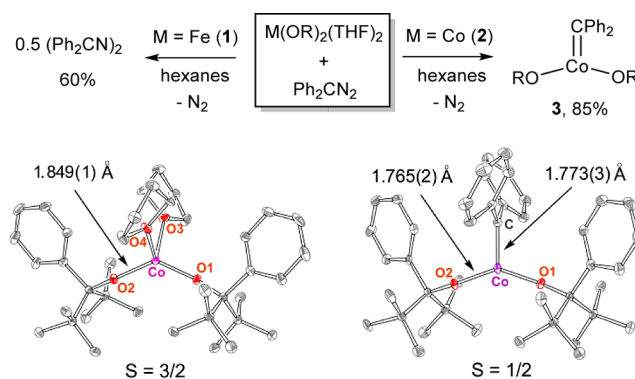

Figure 1. (Top) Reaction of iron (**1**) and cobalt (**2**) bis(alkoxide) complexes with diphenyldiazomethane. (Bottom) Molecular structures of $Co(OR)_2(THF)_2$ (left, **2**) and $Co(OR)_2(=CPh_2)$ (right, **3**) (40% probability ellipsoids), demonstrating selected bond distances. H atoms are omitted for clarity.

product, confirmed to be benzophenone azine, $(Ph_2CN)_2$ (Figure 1, 60%). Attempts to isolate or characterize the inorganic byproducts were unsuccessful. Presumably an iron carbene complex is generated in this reaction, but it rapidly reacts with additional diazoalkane present in solution to yield the azine. Formation of benzophenone azine from the decomposition of diphenyldiazoalkane has been previously reported in the literature for both the reaction of diphenyldiazomethane with transition metal compounds[7] and the thermal decomposition of diphenyldiazomethane.[8]

An analogous reaction performed with the cobalt bis(alkoxide) complex $Co(OR)_2(THF)_2$ (**2**) gave markedly different results (Figure 1). Upon diphenyldiazomethane addition, the solution color gradually changed to red-brown over the course of a few minutes. Workup and crystallization led to the isolation of brown crystals in high yield (85%), confirmed by X-ray crystallography to be the novel cobalt carbene complex $Co(OR)_2(=CPh_2)$ (**3**). To the best of our knowledge, complex **3** is the first example of an isolable, structurally characterized cobalt carbene complex in a weak-field ligand environment. Carbene complexes of the later first-row transition metals that possess high-valent metal centers or

that are stabilized by weak-field ligands are largely nonexistent, although a few cases for iron have been reported.[9] The first spectroscopically[10a] and structurally[10b] characterized dirhodium carbenes were also recently reported. Intriguingly, complex **3** is stable at room temperature under an inert atmosphere, and crystals of it can be stored for weeks at −35 °C without any evidence of degradation.

The crystal structure of **3** is shown in Figure 1. The structure depicts a Co=C bond length of 1.773(3) Å, which, of the 11 reported terminal cobalt−carbene (non-NHC) structures, is among the shortest, with the shortest Co=C bond length being 1.740(1) Å for the cobalt fluorocarbene complex $Co(Cp)(PPh_3)(=CF_2)$.[4d] This short carbene bond suggests increased metal−carbon π-bonding and directly contrasts with the longer (1.9−2.0 Å) bond lengths reported for cobalt(I) terminal carbenes. Additionally, the Co-alkoxide bond lengths are 1.765(2) and 1.773(3) Å, significantly shorter than those of the bis(alkoxide) precursor (complex **2**; see Figure 1). This suggests that the oxidation state of cobalt in the complex is likely higher than 2+ and that the carbene here is not behaving as a Fischer carbene. Solution magnetic measurements and cyclic voltammetry further corroborate this possibility. Compound **3** demonstrates a magnetic moment of 2.0 ± 0.1 μ_B, consistent with the overall low spin (S = 1/2). In contrast, compound **2** is high spin (S = 3/2), which is typical of low-coordinate M^{II} species in weak-field ligand environments.[7f,11] The cyclic voltammogram (Figure S7) demonstrates several reduction events, at −1.17 V, −2.46 V, and −3.16 V, with the first two being quasi-reversible. No complex oxidation was observed in the accessible solvent window. This finding supports the presence of a highly oxidized metal center in complex **3**.

The EPR spectra recorded for **3** (Figures 2 and S12) support an S = 1/2 ground spin state. Resonance fields in the 50−400 GHz spectra exhibit a linear dependence on the microwave frequency (Figure S13), demonstrating that the spin ground state of **3** is an isolated Kramers doublet (S = 1/2 spin state). Simulations of the individual spectra, as well as the linear fit of the field vs frequency dependence of the resonant field values, yield a rhombic g tensor such that $g_x = 3.04(1)$, $g_y = 2.17(1)$, and $g_z = 1.91(1)$. The X-band spectra exhibit well-defined, eight-line hyperfine splitting patterns for which the individual features become progressively broader as their effective g-value increases. These eight-line patterns establish that the observed hyperfine structure is dominated by coupling to the I = 7/2 spin of the ^{59}Co ion. Analysis of the spin functions in our coupled system shows that the $|S = 1/2, M_S = \pm 1/2\rangle$ states should exhibit effective g values according to $g_{eff} = (4g_{Co} - g_{radical})/3$. Reasonable cobalt g components $g_{x,Co}$, $g_{y,Co}$, and $g_{z,Co}$ of 2.78, 2.12, and 1.93, respectively, can thus be extracted from the experimental values (see Supporting Information (SI) for more details). Interestingly, the spectra observed for **3** are dramatically different from those associated with the Co-(porphyrin)-supported bridging and terminal carbene species described by Dzik and co-workers.[2a] In particular the terminal carbene, the only Co(porphyrin)-based species that exhibits unpaired spin density delocalized over the carbene moiety, is characterized by g ≈ 2 and small ^{59}Co hyperfine coupling constants. This behavior demonstrates the presence of an S = 0 cobalt(III) ion and that the unpaired spin density is found nearly exclusively on the carbene. In contrast, the parameters observed for **3** prove that this species contains a paramagnetic
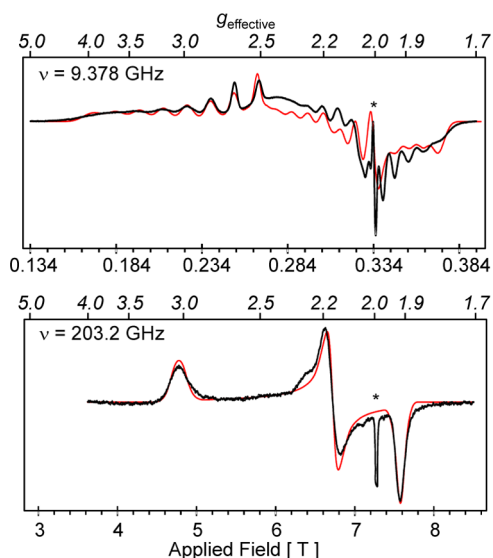

Figure 2. Continuous-wave, variable-frequency EPR spectra recorded at 9.38 GHz, 20 K (top) and 203.20 GHz, 10 K (bottom) for frozen toluene solutions of **3**. Solid red lines are simulations obtained using a S = 1/2 spin-Hamiltonian ($g_x = 3.04(4)$, $g_y = 2.17(5)$, $g_z = 1.91(3)$, $\sigma(g_x) = 0.03(2)$, $\sigma(g_y) = 0.01(1)$, $\sigma(g_z) = 0.01(1)$, $A_x = 585$ MHz, $A_y = 280$ MHz, $A_z = 230$ MHz, $\sigma(A_x) = 25$ MHz, $\sigma(A_y) = 10$ MHz, $\sigma(A_z) = 5$ MHz) that includes hyperfine coupling to an I = 7/2, ^{59}Co nucleus. The feature marked by (*) appears at g = 2.0023 and originates from a minor, radical-based impurity.

Co ion. To better understand the electronic structure of **3**, we turned to DFT calculations.

Calculations were performed at the B3LYP/6-31G(d) level of theory.[12] Despite the tendency of B3LYP to favor high-spin configurations,[13] the doublet species was calculated to be lower in energy than the quartet and sextet states (Table S8), consistent with the EPR and magnetic data. This doublet, with a Co−C bond length of 1.818 Å, was obtained from two distinct starting geometric and electronic structures: (i) a Co−C distance of 1.6 Å and S = 1/2 localized at Co to test for $Co^{IV}=C$ and (ii) a Co−C distance of 2.0 Å and a S = 1 Co^{III} center antiferromagnetically coupled to a carbene radical.[14] The quartet state, which features Co^{III} ferromagnetically coupled to a carbene radical, shows significant elongation of Co−C to 1.930 Å.

The spin density for **3** is shown in Figure 3 with the α spin at Co and β spin on the carbene. Significant spin on Co is consistent with the g tensor deviating from 2 and in contrast to the Co-porphyrin system whose spin density was entirely localized on the carbene.[2] Mulliken spin densities of 1.77 on Co
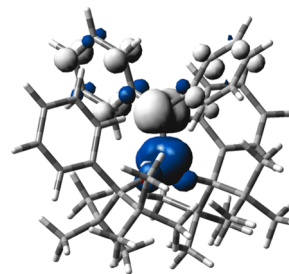

Figure 3. Spin density isosurface plot (iso = 0.005 au) with α spin represented by blue and β spin represented by white.

and −0.68 on the carbene C suggest two α electrons on Co and one β electron on the carbene. A corresponding orbital analysis[15] (Figure 4) partially supports this assignment, but the
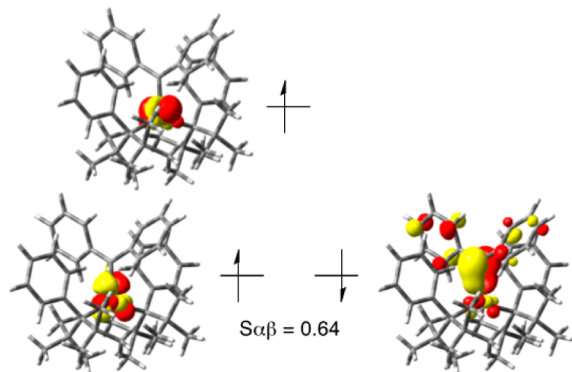

Figure 4. Corresponding orbital diagram (iso = 0.05 au) for **3**.

large overlap of 0.64 between the Co d orbital and the carbene p orbital indicates significant π bonding. Calculation of the quartet at the doublet geometry produces an electronic structure that is qualitatively different than the doublet (Mulliken spins of 2.51 and 0.09 on Co and C) and is best described as a genuine high-spin Co^{IV} complex. Thus, while we were unable to calculate the energy of the ferromagnetically coupled Co^{III}−C$^{\bullet}$ state, the ^{HS}Co^{IV} state obtained places a lower bound on J = 4135 cm^{-1}. This large coupling constant, combined with elongation of Co−C by 0.11 Å from the doublet to quartet state, suggests that **3** is an intermediate-spin Co^{III} (S = 1) *strongly* coupled to a CR$_2^-$ radical. Moreover, re-evaluation of this wave function with OPBE[16] (see Table S4) predicts less spin density on C (suggesting more Co^{IV}=C character), with values approaching those predicted for an analogous, hypothetical Rh complex that should be Rh^{IV}=C. Thus, DFT predicts that **3** falls on the spectrum between Co^{III} and Co^{IV}, but with significant Co^{IV}−alkylidene character. A HYSCORE experiment (Figure S17) confirms the presence of unpaired spin density on the diphenylcarbene moiety.

The porphyrin-ligated Co^{III}-carbene radical is a proposed intermediate in olefin cyclopropanation.[2] Consequently, we tested compound **3** for carbene-transfer reactivity. Two olefins were chosen for the preliminary investigation: styrene and methyl acrylate. The previously reported cobalt porphyrin complexes proved to be excellent catalysts for the efficient and selective cyclopropanation with both of these substrates, albeit with different carbenes (primarily derived from diazoesters).[1f,i] We also note that while transfer of the [CPh$_2$] carbene moiety to olefins has been reported, it is not common with Co.[4e,17,18] Reaction of a stoichiometric amount of **3** with styrene at 60 or 90 °C led to about 15% conversion to 1,1,2-triphenylcyclopropane after 1 h;[17] no further conversion occurred with additional heating. Similarly, under catalytic conditions (10 mol % of **3** at 60 °C) the formation of about 1 equiv of the cyclopropane was observed after 1 h, as demonstrated by ^{1}H NMR (see SI). Conversely, no cyclopropane formation was observed for a stoichiometric reaction of **3** with methyl acrylate at 60 °C. Thus, our preliminary studies indicate that our Co-carbene, which features a different electronic structure and a relatively bulky carbene, shows diminished reactivity. Our future studies in this project will focus on the stoichiometric and catalytic reactivity of compound **2** in cyclopropanations

involving less sterically bulky carbenes that are commonly used in cyclopropanation reactions. We will also explore the reactivity of our cobalt carbenes in [2 + 2] reactions which are more typical of "alkylidenes".

In summary, we reported and structurally characterized a unique cobalt−carbene complex featuring an unusual high-valent cobalt−carbene functionality in a weak-field ligand environment. EPR spectra show Co-centered spin density, which is consistent with a species with significant Co^{IV}−alkylidene character based on DFT calculations. Further spectroscopic and reactivity studies are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02747.

> X-ray crystallographic details for **3** (CIF)
>
> Synthetic procedures, CV data, NMR spectra, IR spectra, UV−vis spectra, Evans data, EPR data, and computational data (PDF)

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Notes
The authors declare no competing financial interest.

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