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Stoichiometric C═O Bond Oxidative Addition of Benzophenone by a Discrete Radical Intermediate To Form a Cobalt(I) Carbene

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Supporting Information

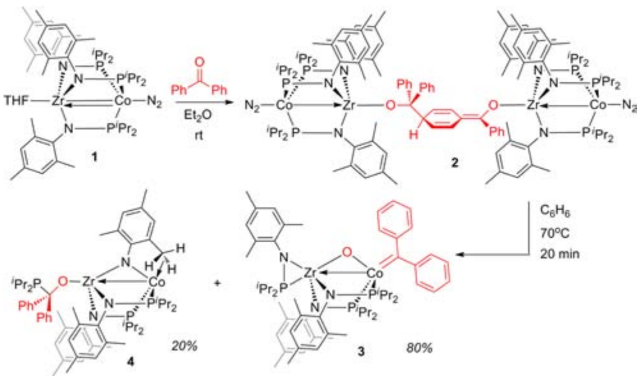
ABSTRACT: Single electron transfer from the $Zr^{III}Co^{0}$ heterobimetallic complex $(THF)Zr(MesNP^{i}Pr_2)_3Co{-}N_2$ (**1**) to benzophenone was previously shown to result in the isobenzopinacol product $[(Ph_2CO)Zr(MesNP^{i}Pr_2)_3Co{-}N_2]_2$ (**2**) via coupling of two ketyl radicals. In this work, thermolysis of **2** in an attempt to favor a monomeric ketyl radical species unexpectedly led to cleavage of the C−O bond to generate a Zr/Co μ-oxo species featuring an unusual terminal $Co{=}CPh_2$ carbene linkage, $(\eta^2\text{-}MesNP^{i}Pr_2)Zr(\mu\text{-}O)(MesNP^{i}Pr_2)_2Co{=}CPh_2$ (**3**). This complex was characterized structurally and spectroscopically, and its electronic structure is discussed in the context of density functional theory calculations. Complex **3** was also shown to be active toward carbene group transfer (cyclopropanation), and silane addition to **3** leads to $PhSiH_2O{-}Zr(MesNP^{i}Pr_2)_3Co{-}N_2$ (**5**) via a proposed Co−alkyl bond homolysis route.

Although implicated as intermediates in a variety of C−C bond-forming reactions such as cyclopropanation, C−H functionalization, and Fischer−Tropsch (FT) synthesis,[1−7] late first-row transition metal terminal carbene complexes without stabilizing heteroatom substituents are rare. First-row transition metal complexes featuring bridging alkylidene ligands are well-known,[8] in contrast to their terminal counterparts. Structurally characterized terminal first-row transition metal carbenes include a nickel diphenylcarbene,[9] copper diphenylcarbenes,[10,11] and several examples of iron carbenes,[12−16] including cycloheptatrienylidene,[17] cyclobutenylidene,[18] and cyclopropenylidene complexes.[19,20] Noticeably absent from this list are cobalt carbenes, for which the only examples are the difluoro- and fluoro(perfluoroalkyl)carbenes recently reported by Baker and co-workers[21] and those in which the carbene carbon is part of a metal-bound cyclopentadienyl ligand.[22,23] Herein we report a rare example of a terminal cobalt carbene complex and its unusual synthesis via reductive C═O bond cleavage.

The cleavage of C−O multiple bonds is a relatively uncommon reaction despite being a proposed step in the FT process. Most proposed FT mechanisms proceed by cleavage of the C≡O bond of carbon monoxide on metal surfaces (typically Fe or Co) followed by hydrogenation to afford metal−carbene intermediates that give rise to long-chain hydrocarbon products.[5−7] Another example from organic synthesis is the McMurry reaction, which involves the reductive cleavage of ketones to olefins by mixtures of $TiCl_3$ and reducing agents, possibly through carbenoid intermediates.[24] Tungsten complexes have been shown to undergo oxidative addition of the C═O bond of ketone substrates to afford W(oxo)(carbene) species,[25,26] and in another example, the C═O bond in a cyclopropenone derivative was added across a Zr−Fe bond, resulting in the formation of an iron carbene.[19] A key step in the reduction of CO_2 to CO is C═O bond cleavage, and our group previously reported the facile cleavage of CO_2 by a Zr/Co heterobimetallic complex, resulting in a $Zr(\mu\text{-}O)Co(CO)$ complex.[27]

In a recent publication on ketone hydrosilylation catalyzed by the heterobimetallic complex $(THF)Zr(MesNP^{i}Pr_2)_3Co{-}N_2$ (**1**) (Mes = 2,4,6-trimethylphenyl),[28] we identified the tetrametallic isobenzopinacol-bridged complex **2** as the product of stoichiometric addition of benzophenone to **1** (Scheme 1).[29] In an attempt to probe for an equilibrium between **2** and a ketyl radical monomer, solutions of **2** were thermolyzed, leading to a C═O bond cleavage event.

Scheme 1



Thermolysis of a benzene solution of **2** at 70 °C for 1 h under N_2 afforded a red-brown solution containing two new paramagnetic complexes in a 4:1 ratio (Scheme 1). Fractional crystallization was used to separate these two compounds, and single-crystal X-ray diffraction determined the connectivity of these structural isomers to be $(\eta^2\text{-}MesNP^{i}Pr_2)Zr(\mu\text{-}O)(MesNP^{i}Pr_2)_2Co{=}CPh_2$ (**3**) and $Ph_2(^{i}Pr_2P)CO{-}Zr(\mu\text{-}NMes)(MesNP^{i}Pr_2)_2Co$ (**4**). The structure of the minor red-orange complex **4** reveals this product to be the result of

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homolysis of one of the amidophosphine ligands (see the Supporting Information).

The major product **3** has a characteristic paramagnetically broadened ^{1}H NMR spectrum with 18 distinct resonances, indicative of a complex with three inequivalent phosphinoamide ligands. Complex **3** was structurally identified as a terminal Co−diphenylcarbene complex featuring a μ-oxo ligand bridging Zr and Co (Figure 1A). This product presumably results from cleavage of **2** into a radical monomer species followed by oxidative addition of the C−O bond. Complex **3** represents a rare structurally characterized non-heteroatom-stabilized cobalt carbene complex. The geometry about the carbene carbon (C46) is planar, consistent with sp^2 hybridization. The Co−C46 distance in **3** [1.906(2) Å] falls in the range of previously reported Fischer-type carbenes on cobalt (based on a 2013 search of the Cambridge Structural Database) but is considerably longer than the M−C distances in diphenylcarbene complexes of most other mid-to-late first-row transition metals (1.77−1.88 Å).[9−11,13,14,30,31] Floriani's calix[4]arene-based Fe=CPh$_2$ systems are the only exceptions, although the long Fe−C distances in that case (~1.95 Å) were attributed to steric constraints.[15] In the case of **3**, we postulate that the long Co−C46 distance might be attributed to the paramagnetic nature of the Co center, which inevitably leads to population of the metal−ligand antibonding orbitals. Indeed, complex **3** has a broad, paramagnetically shifted ^{1}H NMR spectrum and a solution magnetic moment of 3.1μ_B, consistent with an $S = 1$ complex.

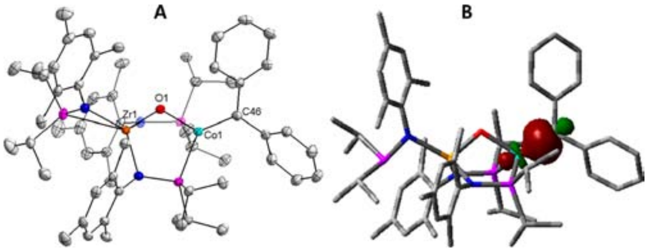


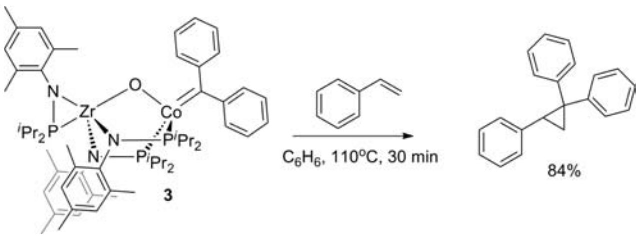
Figure 1. (A) ORTEP drawing of complex **3** with 50% probability ellipsoids. H atoms have been omitted for clarity. Selected bond lengths (Å): Co−C46, 1.906(2); Co−Zr, 3.0667(4); Zr−O1, 1.8459(16); Co−O1, 1.9710(16). (B) Computed NBO depicting the Co−C interaction in complex **3** (BP86/LANL2TZ(f)/6-311+G(d)/D95V).

Several attempts were made to generate **3** via addition of diphenyldiazomethane to coordinatively unsaturated Zr/Co starting materials in an effort to circumvent the formation of byproduct **4**, but none of these routes proved successful. However, we found that **3** was formed exclusively (by ^{1}H NMR spectroscopy) when the labile N$_2$ ligand in **2** was removed in vacuo (generating $[(Ph_2CO)Zr(MesNP^iPr_2)_3Co]_2$ in situ) prior to thermolysis. The isolated yield of **3** was still fairly low because of the solubility of the complex in a wide variety of organic solvents, including hydrocarbons. Conversely, we considered that thermolysis of **2** under higher N$_2$ pressure might result in the exclusive formation of complex **4**. However, heating a benzene solution of **2** under 5 atm N$_2$ at 75 °C for 2 h did not result in any conversion to either **3** or **4**. The results of these reactions imply that N$_2$ dissociation is necessary for the formation of both species. While no mechanistic data are available to suggest how **3** is formed from **2**, the eventual product of ketone C=O bond oxidative addition to **1** is analogous to $(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{Zr}(\mu\text{-O})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}-\text{CO}$, the product of carbon dioxide C=O bond oxidative addition to **1**.[27] This observation permits speculation that a similar CO$_2$-radical-based intermediate may be formed on the CO$_2$ activation reaction pathway.

Despite the absence of heteroatom donors to stabilize the carbene carbon, it was tempting to describe complex **3** as a Zr^{IV}Co^{I} complex featuring a neutral singlet carbene by analogy to $(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{Zr}(\mu\text{-O})(\text{MesNP}^i\text{Pr}_2)_2\text{Co}-\text{CO}$.[27] Further examination of **3** using density functional theory calculations revealed this to be the most accurate description. The geometry of **3** was optimized to a minimum, and the computed structure compared quite well with that determined experimentally using X-ray crystallography (see the Supporting Information). The distribution of the Mulliken spin density of **3** reveals little radical character on the carbene, in contrast to porphyrin-based cobalt carbenes reported in the literature.[32,33] Complex **3** was unable to abstract a hydrogen atom from cyclohexadiene, providing experimental evidence for the lack of radical character on the carbene ligand. Natural bond orbital (NBO) calculations (Figure 1B) revealed a Co−C bond with significantly more carbon character (66.9%) than Co character (33.1%), and the carbene carbon's orbital contribution resembles that of an sp^2-hybridized carbon atom (27.7% s, 72.3% p), suggesting that a dative donation of two electrons from carbon to cobalt is the best way to describe this interaction. Furthermore, the NBO calculations found no significant π interactions between the carbene carbon and cobalt. Consistent with this observation, the Wiberg bond index (WBI) for the Co−C$_{carbene}$ bond was computed to be 0.77, compared with average WBIs of 0.46 and 0.49 for Co−P and Zr−N bonds, respectively, indicating a Co−C bond order between a single and double bond.

Metal carbenes generated via diazoalkane decomposition pathways are often proposed as intermediates in olefin cyclopropanation reactions, and cobalt-based catalysts using porphyrin[32−34] and salen[35] ligand frameworks have been developed. To probe whether heterobimetallic complex **3** reacts with olefins in a similar manner, **3** was treated with styrene. After the reaction mixture was heated at 110 °C for 30 min, (1,2-diphenylcyclopropyl)benzene was observed by GC/MS in 84% yield (Scheme 2). To probe whether this reaction proceeds via carbene extrusion from **3** at elevated temperatures, the thermal stability of **3** was investigated. Upon thermolysis at 110 °C in the absence of styrene, complex **3** decomposed to produce a mixture of tetraphenylethane, tetraphenylethylene, and diphenylmethane, suggesting that the :CPh$_2$ fragment is ejected at elevated temperatures. Moreover, monitoring the disappearance of carbene complex **3** by ^{1}H NMR spectroscopy in the absence or presence of styrene at 90 °C revealed similar rates of reaction. Therefore, it is likely that cyclopropanation

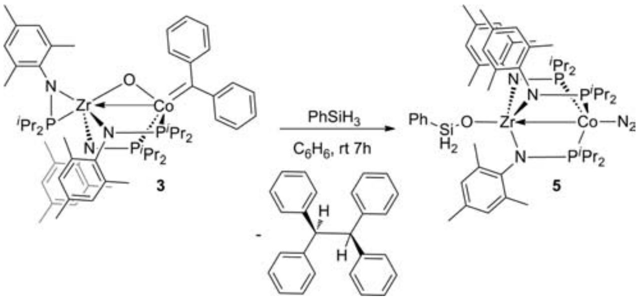
Scheme 2



proceeds via trapping of the extruded free diphenylcarbene fragment by styrene.

To explore the possibility that carbene complex **3** is a possible intermediate in our previously reported hydrosilylation chemistry,[29] the reaction of **3** with a silane was investigated. Allowing a benzene solution of complex **3** to react with phenylsilane at room temperature under N_2 afforded a new $S = {}^{1}/_{2}$ complex identified as $PhSiH_2O{-}Zr(MesNP^iPr_2)_3Co{-}N_2$ (**5**) (Scheme 3). ^1H NMR spectroscopy of **5** revealed nine paramagnetically broadened yet assignable resonances in the −2 to 8 ppm range, and the solution magnetic moment ($\mu_{eff} = 1.8\mu_B$) is consistent with a single unpaired electron. Single-crystal X-ray diffraction (see the Supporting Information) confirmed the structural connectivity and identity of **5** as a zirconium siloxide species analogous to the $PhSiH_2O{-}Zr(MesNP^iPr_2)_3Co(H)(CO)$ complex generated upon addition of $PhSiH_3$ to $(\eta^2\text{-}MesNP^iPr_2)Zr(\mu\text{-}O)(MesNP^iPr_2)_2Co{-}CO$.[27] Analysis of the crude reaction mixture by GC/MS indicated the formation of tetraphenylethane as the carbene-derived by-product of this reaction. We previously reported that the CO_2 activation product $(\eta^2\text{-}MesNP^iPr_2)Zr(\mu\text{-}O)(MesNP^iPr_2)_2Co{-}CO$ reacts readily with $PhSiH_3$ via Si−H addition across the Co−O bond to generate the hydrido/carbonyl complex $PhSiH_2O{-}Zr(MesNP^iPr_2)_3Co(H)(CO)$.[27] By extension, we propose that complex **3** initially reacts with phenylsilane to form a cobalt hydrido/carbene species. Subsequent insertion would afford a diphenylmethylcobalt complex, and homolysis of the Co^I−alkyl bond and dimerization of the resulting benzhydryl radical would form tetraphenylethane. Indeed, homolysis of cobalt−alkyl bonds has been studied extensively[36] and is known to occur in coenzyme B_{12},[37] cobalt-catalyzed polymerization methods,[38] and cross-coupling reactions.[39] From the reaction of carbene complex **3** with phenylsilane, we can conclude that **3** does not play a role in the hydrosilylation of benzophenone, since the C−O bond cleavage appears to be irreversible.

Scheme 3



In summary, we have shown that the highly polar metal−metal multiple bond in the reduced Zr/Co complex **1** facilitates the oxidative addition of the C═O bond in ketones. This particular route to a terminal carbene through a ketyl radical intermediate appears to be unique due to the inability to synthesize **3** via more traditional routes. Further study is required to determine whether this C═O bond cleavage is unique to benzophenone and other diaryl ketones and whether the C═O bond cleavage reaction reported herein is relevant to the mechanism of CO_2 activation. Future studies will also focus on further exploration of the reactivity and properties of carbene complex **3** and potential catalytic applications of this unique ketone activation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, ^1H NMR spectra of **3**−**5**, computational details, X-ray crystallographic data collection and refinement details, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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