



Communication

Ring expansion of a Cp moiety upon CO insertion: Synthesis and characterization of $[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9]$

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ABSTRACT

Reaction of $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$, **1** ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with four equivalents of $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}_4(\text{CO})_{12}]$ in hexane at 70°C leads to the isolation of the tetranuclear carbonyl cluster, $[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9]$, **2** in modest yield. The geometry of **2** is similar to that of $[\text{Co}_4(\text{CO})_{12}]$ where all the four Co atoms are arranged in a tetrahedral geometry. The apical cobalt atom in **2** is coordinated to $\text{C}_6\text{H}_5\text{O}$ ring in a η^6 -fashion and the other three cobalt atoms are each coordinated to three carbonyl ligands. Compound **2** has been characterized in solution by IR, ^1H , ^{13}C NMR and mass spectrometry and the structural types were unequivocally established by crystallographic analysis.

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1. Introduction

In metallaborane chemistry, transition metal carbonyl compounds, for example, $[\text{Fe}_2(\text{CO})_9]$ or $[\text{Co}_2(\text{CO})_8]$, has received considerable attention in connection with their potential as versatile reagent in metal cluster building reactions [1–6]. For example, the reaction of $[\text{Fe}_2(\text{CO})_9]$ with $[(\text{Cp}^*\text{Ru})_2\text{B}_6\text{H}_{12}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) results in the formation of $[\text{Fe}_2(\text{CO})_6(\text{Cp}^*\text{RuCO})(\text{Cp}^*\text{Ru})\text{B}_6\text{H}_{10}]$ [4]. In a similar fashion, reaction of $[\text{Co}_2(\text{CO})_8]$ with $[(\text{Cp}^*\text{ReH}_2)_2\text{B}_4\text{H}_4]$ yielded $[(\text{Cp}^*\text{Re})_2(\mu\text{-}\eta^6\text{-}\eta^6\text{-B}_4\text{H}_4\text{Co}_2(\text{CO})_5)]$ [7]. As a part of our interest in synthesizing metallaboranes containing a range of early transition metal atoms, we have recently synthesized a series of low boron content metallaboranes, $[(\text{CpM})_2(\text{B}_2\text{H}_6)_2]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{V}, \text{Nb}$) and $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)_2]$, by the reaction of metal chlorides and monoborane reagent ($\text{LiBH}_4 \cdot \text{THF}$ and $\text{BH}_3 \cdot \text{THF}$) [8]. Consequently, upon availability of $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ **1**, the chemistry is elaborated by the use of cluster expansion reaction with $[\text{Co}_2(\text{CO})_8]$, which led to the isolation of an unusual tetranuclear carbonyl cluster, $[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9]$, **2**. Reported here is the synthesis and structural characterization of the tetranuclear carbonyl cluster **2**.

2. Result and discussion

2.1. Isolation and characterization of $[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9]$, **2**

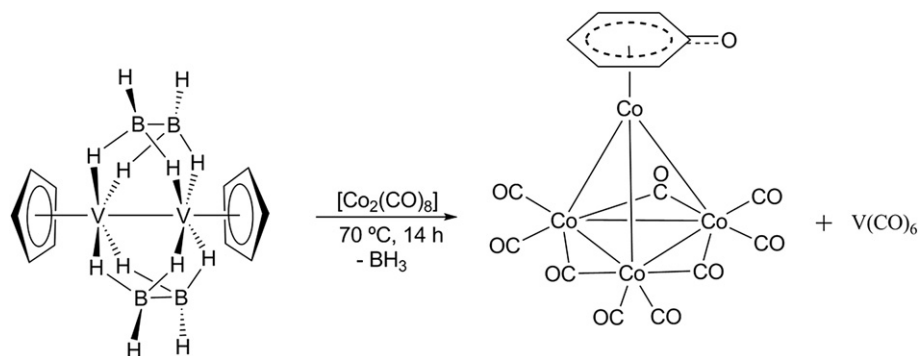
Mild pyrolysis of **1** with four equivalents of $[\text{Co}_2(\text{CO})_8]$ yielded air-stable **2**, isolated by thin-layer chromatography (TLC) in 30% yield

(Scheme 1). Compound **2** can also be generated from $[\text{Co}_4(\text{CO})_{12}]$ under the same reaction conditions. Composition of **2** is defined by the mass, an isotopic distribution pattern characteristics of four cobalt atoms, and fragments corresponding to 9CO losses of the parent atom in the mass spectrum. The infrared spectrum in the $\nu(\text{CO})$ region of **2** is particularly informative with four absorption bands, three corresponding to terminal carbonyl (2081s, 2013w, 2009vs cm^{-1}) and one corresponding to bridging carbonyl (1809s cm^{-1}), which are very similar to those (2074s, 2030vs, 2012w, 1821s cm^{-1}) of $[(\eta^6\text{-benzene})\text{Co}_4(\text{CO})_9]$ in CH_2Cl_2 solution [9]. Furthermore, compound **2** exhibits absorption at 1729 cm^{-1} , characteristics of ketonic carbonyl group. In addition, the ^{13}C NMR of **2** shows the presence of ring carbon resonances at δ 94.6, 93.7 and 93.3 ppm and ketonic carbonyl carbon at δ 167.2 ppm similar to other oxocyclo cobalt complexes [10].

The framework geometry of **2** became clear when a solid state structure was determined. The X-ray structure of **2**, shown in Fig. 1, confirms the presence of terminal, bridging and ketonic carbonyl group. The molecule has four cobalt atoms approximately in regular tetrahedron geometry. The most likely arrangement of CO groups for the molecule is one in which a single cobalt atom is bound to $(\eta^6\text{-C}_6\text{H}_5\text{O})$ group while the other three Co atoms are each coordinated to two terminal CO groups with the three edges between them being spanned by bridging CO groups. Further, the existence of compound **2** permits a spectroscopic data comparison with other related complexes, which are shown in Table 1.

The geometry of **2** is comparable to $[(\eta^6\text{-arene})\text{Co}_4(\text{CO})_9]$ compounds, where the arene is benzene, xylene or [2.2.2]paracyclophane [9,13]. The Co–Co distances in the tetrahedral core of **2**

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Scheme 1. Synthesis of $[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9]$ **2**.

are all essentially the same ($2.477 \pm 0.0001 \text{ \AA}$) except for Co1–Co3 and Co1–Co4 which have a somewhat shorter distance ($2.4486(5) \text{ \AA}$), perhaps as a result of the asymmetric bonding of the $\eta^6\text{-C}_6\text{H}_5\text{O}$ ligand. The average Co–C distance to the bridging CO groups in the basal plane is longer (1.93 \AA) than that of the terminal CO groups (1.78 and 1.80 \AA). The angle between the Co1–Co4–Co3 plane and the plane of the ($\eta^6\text{-C}_6\text{H}_5\text{O}$) ligand is 0° which suggests that the Co2–C distances to the coordinated ($\eta^6\text{-C}_6\text{H}_5\text{O}$) ligand all are same. The average Co–Co bond distances in the base of the cluster **2** is short compared to the sides owing to the contracting action of the bridging CO groups ($2.4486(5)$, $2.4773(5) \text{ \AA}$). Both bridging and equatorial terminal carbonyl ligands point upwards toward the $\text{C}_6\text{H}_5\text{O}$ ligand.

The cobalt nucleus (^{59}Co) provides an interesting probe to investigate tetrahedral clusters in order to get information about their structure [14–19]. The two cobalt environments (apical and basal) in the structure of **2** is similar to that of $[\text{Co}_4(\text{CO})_{12}]$, thus, two resonances are likely to be observed at room temperature ^{59}Co NMR [20]. Indeed, the ^{59}Co NMR spectra recorded at room temperature as well as at low temperature show two very broad resonances at $\delta -2023$ and -2492 ppm, however signals sharpened on going to

the elevated temperature (70°C). The apical:basal signal ratio (1:3) does not match with the observed peak intensities at any temperature. Discrepancies about the relative intensities are partly due to the loss of magnetisation under the effect of transverse relaxation during the receiver dead time [18,21–23].

2.2. Reaction pathway

The migratory CO insertion reaction is well-known in organo-transition-metal chemistry and in organometallic applications in organic synthesis for carbon–carbon bond formation and ring expansion reaction [24–34]. Ring expansion of 2-cyclopropene-1-carbonyl intermediate to η^3 -oxocyclobutenyl complex has been shown to occur intramolecularly involving iron-promoted expansion of a three to four-membered ring (Scheme 2a) [10,25]. As shown in Scheme 2b, a two step mechanism has been suggested to account for the formation of hexmethylbenzene by ring expansion of a Cp* ligand by incorporation of the ‘ $\text{CH}_3\text{C}\equiv$ ’ fragment of the acetyl group of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-COCH}_3)(\text{OCMoCp}(\text{CO})_2)]$ [31]. Messerle and coworkers [32] have shown that a highly distorted η^2 -acyl complex $[(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Ta}(\text{C}(\text{O})\text{CH}_2\text{CMe}_3)\text{Cl}_3]$ ($\text{R} = \text{Me}, \text{Et}$) can be reduced by Mg, Na/Hg, K/Hg, Zn or sodium naphthalenide to arene $\text{C}_6\text{Me}_5(\text{CH}_2\text{CMe}_3)$ (Scheme 2c). Further, surprising carbon–carbon bond activation during certain cobalt-mediated allyl/alkyne cycloadditions reactions, leading to substituted η^5 -cycloheptadienyl products and, in others, to the activation of ancillary cyclopentadienyl ligands have been reported (Scheme 2d) [29c].

As far as the synthetic pathway of this unforeseen reaction is concerned, the formation of **2** may have occurred from an electrocyclic rearrangement, promoted by a metal centre. The substitution of three apical carbonyl ligands in $[\text{Co}_4(\text{CO})_{12}]$ by a η^6 -arene is well precedented [9,13]. Thus, the replacement of two carbonyl ligands from the apical cobalt atom in $[\text{Co}_4(\text{CO})_{12}]$ by η^4 -cyclopentadiene is probable. In the second step, the electrophilic carbonyl carbon atom may react with the electron-rich Cp ring, followed by the scission of Co–C bond, with concomitant formation of the ($\eta^6\text{-C}_6\text{H}_5\text{O}$) ring.

Further, to evaluate any significant role of the metal into this unprecedented CO insertion reaction, analogue reactions were carried out with $[(\text{CpNb})_2(\text{B}_2\text{H}_6)_2]$ and $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)_2]$. Unfortunately, in both the cases no product(s) could be identified except the decomposition of niobaborane or tantalaborane compounds. Attempts were also made to obtain products from the Cp ring exchange of $[(\text{CpV})_2(\text{B}_2\text{H}_6)_2]$ in the presence of the following metal carbonyls/derivatives: $[\text{Fe}_2(\text{CO})_9]$, $[\text{Cr}(\text{CO})_6]$, $[\eta^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3]$, $[\text{M}(\text{CO})_5 \cdot \text{THF}]$ ($\text{M} = \text{Mo}$ and W) and $[\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ($\text{M} = \text{Cr}, \text{Mo}$ and W). None of these reactions provided a tractable product.

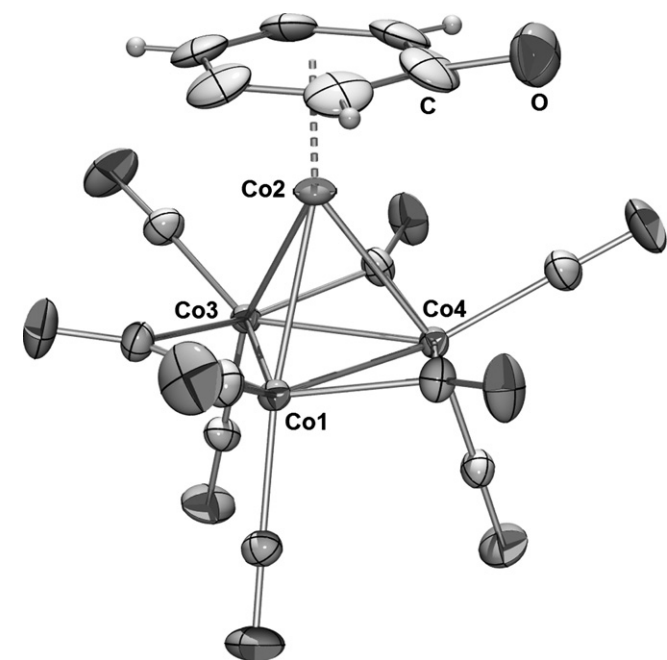
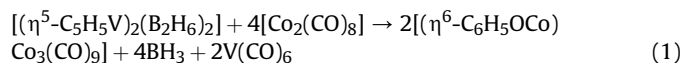


Fig. 1. Molecular structure and labeling diagram for $[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9]$ **2**. The oxygen atom is disordered over three positions in $\text{C}_6\text{H}_5\text{O}$ ring, each with 33.3% occupancy. Relevant bond lengths (\AA) and angles ($^\circ$): Co(1)–Co(2) $2.4773(5)$, Co(1)–Co(3) $2.4486(5)$, C(4)–O(4) $1.257(8)$; Co(3)–Co(1)–Co(2) $60.381(8)$, Co(4)–Co(1)–Co(3) 60.0 , Co(1)–Co(2)–Co(4) $59.237(17)$.

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