

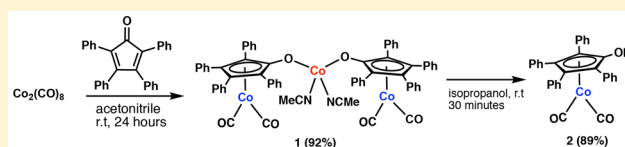
Synthesis, Characterization, and Reactivity of Hydroxycyclopentadienyl Cobalt Complexes

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Supporting Information

ABSTRACT: The reaction of tetraphenylcyclopentadienone with $\text{Co}_2(\text{CO})_8$ generates the mixed-valence tricobalt complex $[\text{Ph}_4\text{C}_4\text{CO}]\text{Co}(\text{CO})_2$ $[\mu\text{-Co}(\text{MeCN})_2]$. In contrast to the conventional Pauson–Khand reaction to generate cyclopentadienone-ligated cobalt complexes, this method benefits from both mild reaction conditions and high yields. Treatment



of this tricobalt complex with proton sources such as water or alcohols yields the monomeric hydroxycyclopentadienyl cobalt complex $[\text{Ph}_4\text{CpOH}]\text{Co}(\text{CO})_2$. Phosphite substituted monomeric cobalt complexes $[\text{Ph}_4\text{CpOH}]\text{Co}(\text{CO})[\text{P}(\text{OR})_3]$ were also synthesized, and protonation of these complexes transiently formed cobalt hydride species.

INTRODUCTION

Redox-active ligands can exhibit synergistic behavior with transition metals to enhance and modulate the stoichiometric and catalytic behavior of coordination compounds.^{1–4} The tetraphenylcyclopentadienone ligand on the Ru Shvo catalyst^{5–7} acts as both a redox and proton-donor/acceptor ligand which facilitates hydrogenation and transfer hydrogenation reactions (Scheme 1).

The addition of H_2 to the Ru(0) tetraphenylcyclopentadienyl carbonyl complex is accompanied by the conversion of a formally neutral cyclopentadienone ligand to a formally anionic hydroxycyclopentadienyl ligand. This is an unusual situation in which Ru(II), the species with a higher formal oxidation state, is the reducing agent and the formal Ru(0) species is the oxidizing agent.

The broad synthetic utility of the Shvo complex in catalytic oxidation and reduction reactions^{6,8} has stimulated efforts to generate analogous complexes, including those based on ruthenium^{9–13} as well as other metal complexes (Os, Fe, Rh, Ir, Re, Co, Ni).^{14–21} We sought to develop expedient synthetic routes to hydroxycyclopentadienyl Co complexes^{22,23} analogous to the Ru Shvo complex as there was some precedent for the synthesis of cyclopentadienone Co complexes^{22,24–28} and the related cyclopentadienyl Co complexes are known to exhibit a broad range of stoichiometric and catalytic activity.^{29–39}

Herein, we report new synthetic strategies to generate cyclopentadienone and hydroxycyclopentadienyl complexes of Co and some initial investigations on their reactivity. These studies include the synthesis and characterization of a tetraphenylcyclopentadienone-ligated tricobalt mixed-valence complex **1**, the monomeric hydroxycyclopentadienyl cobalt dicarbonyl complex **2**, the monophosphite analogues **3**, **4**, **5**, **6**, and the protonation of the latter compounds to generate cobalt hydride intermediates.

RESULTS AND DISCUSSION

In the course of exploring synthetic routes to ligate tetraphenylcyclopentadienone (tetracyclone) to cobalt, we discovered that the reaction of $\text{Co}_2(\text{CO})_8$ and tetracyclone in acetonitrile at room temperature resulted in a black tar, from which dark red crystals could be crystallized in 92% isolated yield (with respect to tetracyclone) from benzene (Scheme 2). This air-sensitive paramagnetic compound was characterized as the tricobalt complex $\{[\text{Ph}_4\text{C}_4\text{CO}]\text{Co}(\text{CO})_2\}_2[\mu\text{-Co}(\text{MeCN})_2]$ **1** by single crystal X-ray crystallography, where two tetracyclone-ligated cobalt dicarbonyls are bridged by a central cobalt atom (Figure 1).

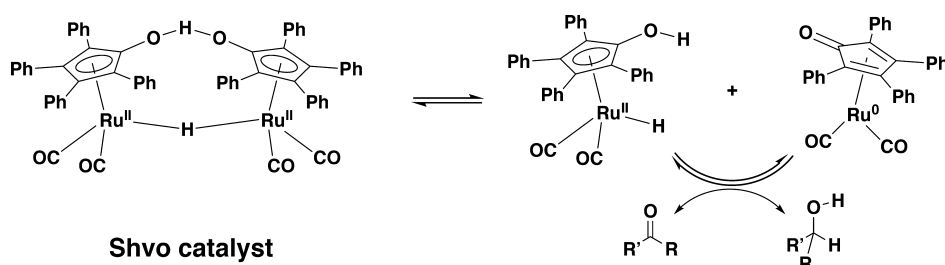
As the disproportionation of $\text{Co}_2(\text{CO})_8$ in acetonitrile is known to yield a 2:1 mixture of anionic tetracarbonylcobaltate $[\text{Co}(\text{CO})_4]^-$ and dicationic $[\text{Co}(\text{MeCN})_X]^{2+}$,⁴⁰ we propose that tetraphenylcyclopentadienone reacts with the $[\text{Co}(\text{CO})_4]^-$ generated in the disproportionation reaction to give the Co tetraphenylcyclopentadienolate which subsequently associates with the cationic $\text{Co}(\text{CH}_3\text{CN})^{2+}$ to generate **1**. The syntheses of $(\eta^3\text{-cyclopropenyl})$ and $(\eta^3\text{-cyclobutenyl})$ cobalt complexes from $[\text{Co}(\text{CO})_4]^-$ are known.^{40,41} The syntheses of cyclopentadienone Co complexes^{22,24–28} are typically carried out by reactions of $\text{Co}_2(\text{CO})_8$ and substituted alkynes (e.g., Pauson–Khand cycloaddition) at high pressure and temperature to afford a mixture of products with modest yields;^{22,25} the alternative approach reported herein has the advantages of both high yields and mild reaction conditions.

The solid-state structure of **1**, shown in Figure 1, reveals two different coordination geometries for Co: a central Co in a tetrahedral geometry bound by two acetonitrile ligands and two tetraphenylcyclopentadienolate ligands each ligated with flanking Co in geometries typical of $\text{CpCo}(\text{CO})_2$ ⁴² and other cyclopentadienyl group 9 metal complexes.^{43,44}

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Scheme 1. Thermolysis of Ru Shvo Dimer Generates (Hydroxytetraphenylcyclopentadienyl) Ru-H and Tetraphenylcyclopentadienone Ru Complexes



Scheme 2. Synthesis and Proposed Mechanism for Formation of 1

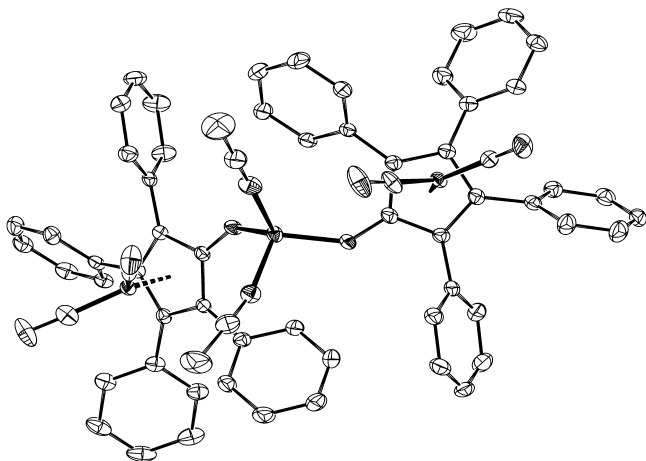
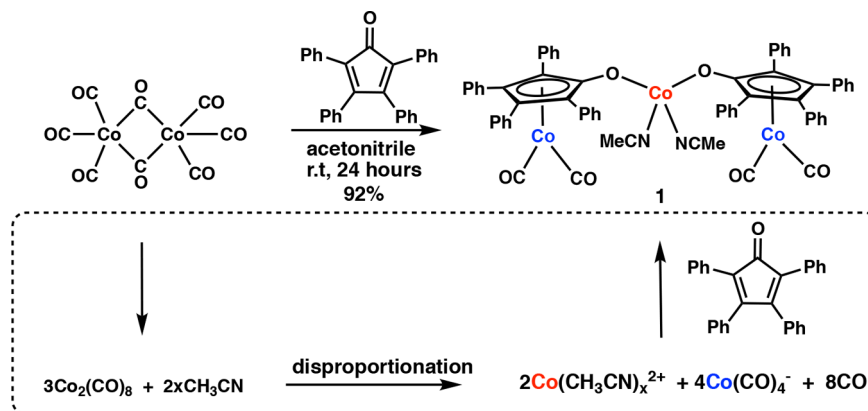


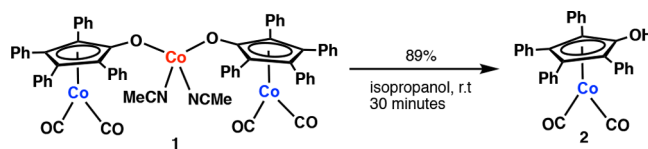
Figure 1. Molecular structure of **1** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Bond lengths and angles can be found in the [Supporting Information](#).

The oxidation state of each Co in compound **1** could not be unambiguously assigned based solely on the X-ray structure, but coordination geometries and bond lengths are suggestive of a mixed-valence Co(I)-Co(II)-Co(I) complex. The bond distances and coordination geometries for the terminal cobalts in compound **1** are most consistent with the formulation of Co(I) centers bound to a cyclopentadienolate. The C–C bond lengths within the cyclopentadienolate ring are nearly equivalent (C=C, 142 pm; C–C, 143–146 pm), and the carbonyl carbon to cobalt center Co–C(O) distances (217, 218 pm; see the [Supporting Information](#)) are only slightly longer than the other Co–C distances (206–212 pm), which are comparable to distances observed for hydroxycyclopentadienyl Co complexes.²² In contrast, Co cyclopentadienone

complexes^{22,27} exhibit alternating shorter and longer C–C bonds in the five-membered ring and Co–C(O) bond lengths that are longer than the other four Co–C lengths. These bonding parameters for **1** resemble those reported for the dimeric form of the ruthenium Shvo catalyst with similar C–C bond lengths among the cyclopentadienone ring and Ru–C distances.⁶

Treatment of **1** under nitrogen with proton sources such as water or alcohols at room temperature provides an efficient and high yielding synthesis of hydroxycyclopentadienyl cobalt complex **2** (89% yield) ([Scheme 3](#)). The related Co

Scheme 3. Synthesis of Compound 2 from 1



hydroxycyclopentadienyl complexes [H₂Ph₂CpOH]Co(CO)₂²³ and [n-Pr₂(PhMe₂Si)₂C₅OH]Co(CO)₂²² were reported previously by alternative routes in lower yields (15% and 21%, respectively).

X-ray crystallography of orange crystals obtained from benzene confirmed the structure as [Ph₄CpOH]Co(CO)₂, **2** ([Figure 2](#)), although the elemental analysis deviated from expected values. This structure is also supported by sharp resonances in the ¹H NMR spectrum which showed a 20:1 ratio between the aromatic protons and the hydroxyl proton. Compound **2** is stable at room temperature under a nitrogen atmosphere, but it slowly decomposes under nitrogen above 50 °C.

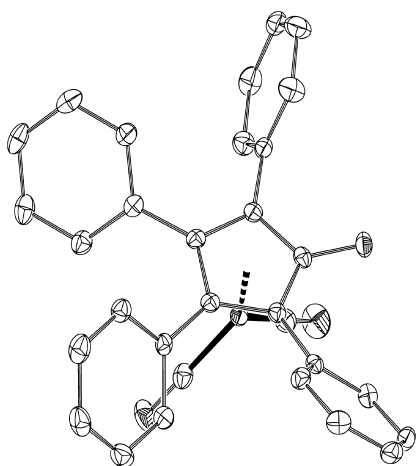
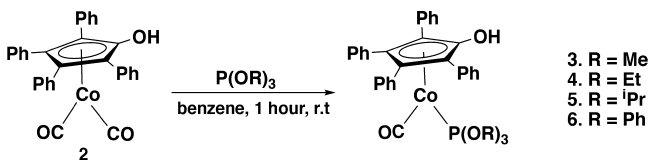


Figure 2. Molecular structure of **2** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Bond lengths and angles can be found in the [Supporting Information](#).

The infrared spectra reveal carbonyl bands $\nu(\text{CO})$ at 1918, and 1991 cm^{-1} for compound **1** and 1951 and 2010 cm^{-1} for compound **2** (KBr), comparable to those of similar complexes ($\text{CpCo}(\text{CO})_2$: 2033, 1972 cm^{-1} ; $\text{Cp}^*\text{Co}(\text{CO})_2$: 2011, 1949 cm^{-1} ; $[\text{H}_2\text{Ph}_2\text{C}_5\text{OH}]\text{Co}(\text{CO})_2$: 1997, 1942 cm^{-1}).²² The lower $\nu(\text{CO})$ stretching frequencies observed for **1** relative to **2** is indicative of less back-bonding from the cobalt center in **1**, consistent with the formulation of a Co(I) oxidation state for each of the $[\text{Ph}_4\text{C}_4\text{CO}]\text{Co}(\text{CO})_2$ fragments of **1**.

While cyclopentadienyl cobalt biscarbonyl complexes, $\text{Cp}'\text{Co}(\text{CO})_2$, are known to undergo ligand exchange reactions with phosphine and phosphite ligands to form mono- and bis-substituted complexes,^{29,31,45} attempts to replace one or both of the carbonyl ligands of **2** with various mono- and bidentate phosphine ligands were unsuccessful (see the [Supporting Information](#)). However, compound **2** reacts cleanly with tertiary phosphites at room temperature to yield monophosphite substituted complexes $[\text{Ph}_4\text{CpOH}]\text{Co}[\text{P}(\text{OR})_3](\text{CO})$ **3**, $[\text{Ph}_4\text{CpOH}]\text{Co}[\text{P}(\text{OEt})_3](\text{CO})$ **4**, $[\text{Ph}_4\text{CpOH}]\text{Co}[\text{P}(\text{OiPr})_3](\text{CO})$ **5**, and $[\text{Ph}_4\text{CpOH}]\text{Co}[\text{P}(\text{OPh})_3](\text{CO})$ **6** in quantitative yields ([Scheme 4](#)).

Scheme 4. Synthesis of Compounds **3–6** from **2**

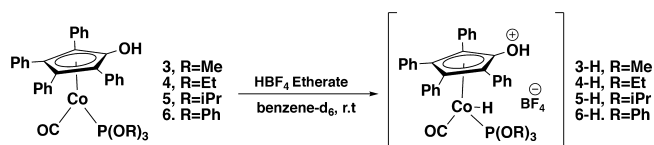


Compounds **3–6** were characterized by ^1H , ^{31}P , ^{13}C NMR and elemental analysis. The trends in the carbonyl stretching frequencies ($\nu(\text{CO})$: **2**, 1951 cm^{-1} > **6**, 1940 cm^{-1} > **3**, 1930 cm^{-1} > **4**, 1929 cm^{-1} > **5**, 1920 cm^{-1}) are also in the order of electron donating ability of the substituted ligand according to Tolman's Electronic Parameter⁴⁶ ($\text{CO} < \text{P}(\text{OPh})_3 < \text{P}(\text{OMe})_3 < \text{P}(\text{OEt})_3 < \text{P}(\text{OiPr})_3$).

Co complexes **2–6** were subjected to protonation by different acids under various conditions (see the [Supporting Information](#)). While several attempts were made to protonate compound **2**, ^1H NMR revealed the formation of the trans-hydrogenated tetracyclone ligand, 2,3,4,5-tetraphenyl-

cyclopent-2-en-1-one,⁴⁷ and unidentified paramagnetic products. In contrast, treatment of compound **3** with tetrafluoroboric acid exhibited a transient formation of an intermediate characterized as the cationic **3-H** by ^1H NMR with clear $^2J_{\text{HP}}$ coupling (72.8 Hz). *In situ* high resolution mass spectroscopy of this reaction mixture revealed an ion at m/z 597.1249, consistent with the Co-H complex $[(\text{C}_5\text{Ph}_4\text{OH})\text{Co}(\text{H})(\text{CO})\text{P}(\text{OMe})_3]^+$ ([Scheme 5](#)). Analogous reactivity was

Scheme 5. Protonation of Compounds **3–6** and Formation of Cobalt Hydrides



observed for compounds **4**, **5**, and **6**. Unfortunately, further characterization or isolation of these species was not possible due to their instability at room temperature. *In situ* treatment of **3-H** with a stoichiometric amount of acetone did not result in any conversion of acetone or the generation of isopropanol after 2 h, but signals due to the Co-H slowly diminished over the course of the experiment. Further evaluation of the reactivity of **3-H** was compromised by the limited solution stability of this compound. Koelle et al. have shown that cyclopentadienyl cobalt phosphine- and phosphite-ligated complexes are basic enough to be protonated by mild acids in organic solvents to form cobalt hydride species that exhibit sufficient chemical stability to persist in dilute solutions.^{31,48} The lower stabilities of the cobalt hydride species derived from **3–6** can be attributed to the π -acidic nature of tetracyclone and carbonyl ligands compared with the relatively electron rich Cp ligand.

CONCLUSION

In conclusion, a rare mixed-valence cyclopentadienone ligated tricobalt complex **1** was directly synthesized in good yields by a simple reaction starting from the commercially available tetraphenylcyclopentadienone ligand and $\text{Co}_2(\text{CO})_8$. The mixed-valence nature of **1** can potentially provide a wide range of applications,^{26–28,49,50} and it serves as a good intermediate toward the synthesis of hydroxytetraphenylcyclopentadienyl cobalt complexes. Hydrogenative cleavage of **1** results in clean formation of monomeric hydroxytetraphenylcyclopentadienyl cobalt complex **2**. Phosphite substituted monomeric cobalt complexes **3–6**, $[\text{Ph}_4\text{CpOH}]\text{Co}(\text{CO})[\text{P}(\text{OR})_3]$, were also synthesized, and protonation of these complexes yielded *in situ* cobalt hydride species. We are currently exploring the detailed characteristics of these complexes and their potential use as catalysts and electrocatalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.organomet.8b00486](https://doi.org/10.1021/acs.organomet.8b00486).

Experimental procedures, characterization data, and spectra ([PDF](#))

Accession Codes

CCDC 1855076 and 1855077 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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