Conversion of Acetylene to a Triple Bridged Ethylidyne Ligand on the Cluster $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$

Charles P. Casey,* Ross A. Widenhoefer, and Susan L. Hallenbeck

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

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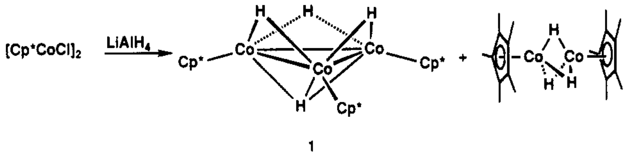
Summary: The paramagnetic tetrahydride cluster, $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (1) reacts with acetylene to ultimately form the bis(ethylidyne) cluster $Cp^*{}_3Co_3(\mu_3\text{-}CCH_3)_2$ (2). Two intermediates were detected during the course of the reaction: the diamagnetic $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3) and the paramagnetic $Cp^*{}_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4). Cluster 3 loses H_2 in refluxing toluene to generate 4, and 4 reacts with H_2 at 80 °C to generate 3. Kinetic analysis indicates 3 and 4 are both formed directly from cluster 1.

In collaboration with Theopold and co-workers, we recently reported the synthesis of the unusual trinuclear tetrahydride cluster $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (1) and the dinuclear trihydride complex $Cp^*{}_2Co_2(\mu\text{-}H)_3$ from the reaction of $[Cp^*CoCl]_2$ with $LiAlH_4$ (Scheme I).[1] Complex 1 is a highly reactive species due to its paramagnetic 46-electron configuration and its lack of bridging ligands other than hydrogen. For example, 1 reacted rapidly with CO at room temperature to form the dicarbonyl dihydride cluster $Cp^*{}_3Co_3(\mu_3\text{-}CO)(\mu_2\text{-}CO)(\mu\text{-}H)_2$.[2] Reaction of 1 with NO occurred instantly to produce the trinuclear cluster $Cp^*{}_3Co_3(\mu_3\text{-}NO)_2$.[3] Here we report that 1 reacts with acetylene to ultimately form $Cp^*{}_3Co_3(\mu_3\text{-}CCH_3)_2$ (2) with preservation of the trinuclear cluster. Two intermediates were detected during the course of the reaction: the diamagnetic mono(ethylidyne) trihydride $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3) and the paramagnetic mono(ethylidyne) monohydride $Cp^*{}_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4).

When a black benzene solution of $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (1) was heated for 2 days at 100 °C with excess acetylene in a sealed tube, the purple bis(μ_3-ethylidyne) complex $Cp^*{}_3Co_3(\mu_3\text{-}CCH_3)_2$ (2) precipitated from the solution and was isolated in 88% yield. Cluster 2 was fully characterized by ^1H NMR, high resolution MS, and single crystal X-ray diffraction.[4] Previously, 2 was reported to be formed in the thermolysis of $Cp^*Co(\eta^2\text{-}CH_2{=}CH_2)_2$ at 110 °C.[5]

Extensive studies on the chemisorption of acetylene on the Pt(111) surface have shown that the stable surface species is a triple bridged ethylidyne.[6] However, the conversion of acetylene to a μ_3-CCH_3 ligand on a homogeneous cluster has been demonstrated in only two instances.[7] Due to the importance of this rearrangement, we searched for intermediates in the reaction of 1 with acetylene.

Scheme I



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Cluster 1 and excess acetylene were heated at 80 °C in benzene-d_6 in a thick-walled NMR tube and monitored periodically by ^1H NMR spectroscopy. After 1 h, the Cp* resonance of 1 (δ 62.4) could no longer be detected and the Cp* resonance of the bis(ethylidyne) cluster 2 (δ 1.57) accounted for only 10% of the Cp* resonances. In addition to cluster 2, two products, $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3) and $Cp^*{}_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4) were observed by ^1H NMR (Scheme II). The major Cp* resonance (55%) at δ 1.67 (45 H) and resonances at δ 5.12 (3 H, μ-CCH_3) and δ −32.26 (3 H, μ-H) were assigned to the diamagnetic mono(ethylidyne) trihydride cluster, $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3). In a preparative experiment, 1 and excess acetylene were heated at 80 °C under H_2 (see below) for 3 h to form 3 in 53% isolated yield as green crystals.[8]

The second Cp* resonance (35%) at δ 53.6 was assigned to the paramagnetic mono(ethylidyne) monohydride cluster, $Cp^*{}_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4). The paramagnetism of 4 is consistent with a 46-electron cluster possessing C_{3v} symmetry.[9] In a preparative experiment, 3 was heated in toluene at 110 °C for 3 days to produce 4 (see below) in 75% isolated yield as a brown microcrystalline solid.[10] The molecular formula of 4 was established by high resolution MS (m/z = 610).

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[4] Redetermination of the originally reported structure[5] gave more precise bond distances for 2: hexagonal, $P6_3/m$, a = 10.716(2) Å, c = 15.485(3) Å, V = 1539.8(7) Å^3, Z = 2; $R(F)$ 2.54%, $R_w(F)$ 4.49%; Co–Co, 2.437(1) Å, Co–(μ-C), 1.873(3) Å. Since 2 prepared in our laboratories is an air-stable compound with sharp ^1H NMR resonances in benzene, while 2 was reported by Pardy[5] to be air-sensitive, to give paramagnetically broadened NMR resonances in benzene, and to have significantly shorter Co–Co bond distances, it is not clear that Pardy's material was in fact 2.

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[8] Acetylene (1.43 mmol) was condensed at 77 K into a 35-mL thick-walled flask which contained 1 (100 mg, 0.17 mmol) in 5 mL of benzene. The flask was sealed under 1 atm of H_2 at 77 K and heated at 80 °C for 3 h to produce a green solution (H_2 pressure at 80 °C is calculated to be ≤4.5 atm). After filtration through Celite, solvent was evaporated and the residue was washed with hexane to give $Cp^*{}_3Co_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3) (51 mg, 53%) as a green microcrystalline solid which was >95% pure by ^1H NMR analysis. 3 was further purified by crystallization from toluene at −20 °C. ^1H NMR (200 MHz, C_6D_6) δ 5.12 (s, 3 H, μ_3-CCH_3), 1.67 (s, 45 H, C_5Me_5), −32.26 (s, 3 H, Co-μ-H). ^{13}C NMR (126 MHz, C_6D_6) δ 92.4 (C_5Me$_5$), 45.7 (μ_3-CCH_3), 11.6 (C$_5$*Me*$_5$), the μ_3-CCH_3 carbon was not observed. HRMS (EI) calc (found) for $C_{32}H_{49}Co_3$ ($M^+ - 2H$): 610.1827 (610.1816). Anal. Calc (found) for $C_{32}H_{51}Co_3$: C, 62.75 (63.03); H, 8.39 (8.09).

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Scheme II

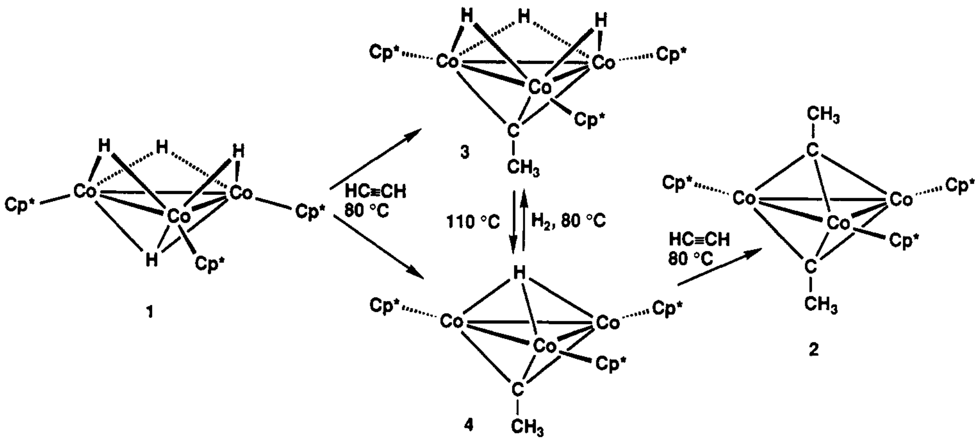
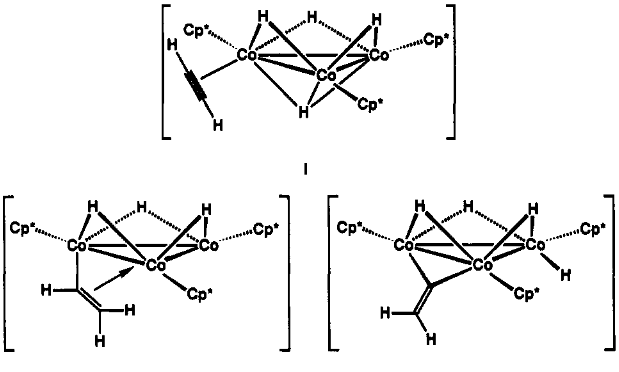


Chart I



Trihydride 3 and monohydride 4 interconvert by reversible loss of H_2, but at a rate much slower than they are formed from 1. When isolated 3 was heated at 110 °C for 18 h in toluene-d_8, 4 was formed nearly quantitatively (92 ± 5% yield by ^1H NMR using C_6Me_6 as an internal standard). When isolated 4 was heated at 80 °C under 1 atm of H_2 in benzene-d_6 for 35 h, 3 was formed quantitatively (99 ± 5% by ^1H NMR). The rate at which 1 reacted with acetylene at 80 °C to produce 3 and 4 is more than 100 times faster than the rate of interconversion of 3 and 4 at 80 °C. This requires that both 3 and 4 be formed directly from 1.

When 4 and excess acetylene were heated at 80 °C for 24 h, clean conversion to 2 was observed. The rate of reaction of 4 with acetylene is about 25 times slower than the reaction of 1 with acetylene.

Several mechanisms are consistent with the formation of both trihydride 3 and monohydride 4 from tetrahydride 1 (Chart I). In one mechanism, initial coordination of acetylene to the 46-electron cluster 1 would produce the 48 electron intermediate acetylene complex I. Hydride addition across the C≡C bond of the coordinated acetylene would produce the μ-η^1,η^2-vinyl intermediate II; metal hydride addition across a coordinated alkyne to form a bridging alkenyl ligand has been observed in Os_3[11] systems. A 1,2-hydrogen shift from the internal to terminal vinyl carbon of II would produce the observed trihydride ethylidyne complex 3. Competitive loss of H_2 from II followed by 1,2 migration would yield monohydride 4. The interconversion of μ-η^1,η^2-alkenyl and μ-alkylidyne complexes via 1,2-hydrogen migration has been observed in Fe_2 cations[12] and in neutral Ru_3[13] and Os_3[14] clusters.

In a second possible mechanism, the acetylene complex I might undergo conversion to the μ_2-vinylidene complex III, possibly via a terminal vinylidene complex. The conversion of a terminal alkyne ligand to a vinylidene ligand has been well documented in mononuclear systems[15] and has also been demonstrated on Pt_3,[16] $RuCo_2$,[17] and Os_6 clusters.[18] Hydride addition to the vinylidene complex would produce the alkylidyne complex 3, and competitive H_2 loss from III followed by hydride addition to the vinylidene ligand would give 4. Several variations of these mechanisms involving interconversion of μ-η^1,η^2-alkenyl and μ-vinylidene complexes are also possible.[11d,14]

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Supplementary Material Available: Textual presentation of experimental procedures for the preparation of compounds 2–4 and analytical and spectroscopic data for compounds 3 and 4 (2 pages). Ordering information is given on any current masthead page.

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(10) A green solution of 3 (130 mg, 0.21 mmol) in 15 mL of toluene was refluxed for 3 days in an open tube under N_2 to produce a brown solution. The solution was filtered through Celite, and the toluene was evaporated under vacuum to give $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4) (97 mg, 75%) which contained 5% 2 by ^1H NMR analysis. Crystallization from toluene at −20 °C afforded pure 4 (41 mg, 32%) as brown crystals. ^1H NMR (200 MHz, C_6D_6): δ 53.6 (br s C_5Me_5). HRMS (EI) calc (found) for $C_{32}H_{49}Co_3$ (M^+): 610.1827 (610.1833). Anal. Calc (found) for $C_{32}H_{49}Co_3$: C, 62.95 (63.01); H, 8.09 (8.22).

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