ORGANOMETALLICS

Note

Formation and Reactivity of a Co_4 - μ -Alkyne Cluster from a Co(I)-Alkene Complex

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Supporting Information

ABSTRACT: Highly reactive Co(I) complex $[CpCo(H_2C=CHSiMe_3)_2]$ (1) easily forms a tetranuclear Co₄ cluster in hydrocarbon solvents under mild conditions, possessing a bridging alkyne ligand stemming from an unusual C-H activation of the H₂C=CHSiMe₃ ligand. The cluster was structurally characterized, and the catalytic reactivity in [2+2+2] cycloaddition, hydroformylation, and hydrogenation reactions investigated. Interesting differences were found and compared to the mononuclear complex 1, which could be relevant for the real catalytically active species.



B esides their rich catalytic chemistry, group 9 transition metal complexes are home to a large number of metal cluster complexes. Among the numerous cluster complexes with many different ancillary ligands, cluster complexes with cyclopentadienyl (Cp) or indenyl ligands exhibit a rich structural chemistry as well as interesting reactivities.¹ Furthermore, the possible formation of cluster complexes from monometallic species can have a profound influence on the catalytic behavior of a certain catalyst system, imaginably causing more than one species to be active. Therefore cluster complexes can act on the borderline of homogeneous and heterogeneous catalysis.²

We are interested in the chemistry of group 9 metal-olefin complexes, especially for application in [2+2+2] cycloaddition reactions.³ During our investigations of highly reactive, lowvalent CpCo(I)-olefin complexes such as [CpCo(H₂C= $CHSiMe_3)_2$] (1) we discovered cleavage of C-Cl bonds in chlorinated solvents even at low temperatures, leading to cobaltocenium compounds such as $[(Cp_2Co)_2(CoCl_4)]^{3a,4}$ Complex 1 requires storage at temperatures below -30 °C, and its application in [2+2+2] cycloaddition reactions demonstrated its uniquely high reactivity as a precatalyst at very low temperatures. Isolated complexes such as the Jonas reagent $[CpCo(H_2C=CH_2)_2]^5$ or CpCo olefin complexes generated in situ are also known to undergo formation of tri- and tetranuclear Co cluster complexes (2 and 3) with complexed alkyne ligands in the presence of cyclic alkenes, as demonstrated by Wadepohl et al. (Scheme 1).⁶ The formation of the cluster complexes comprises unusual reactions such as C-H activation of cyclic olefins in the coordination sphere of this first-row transition metal cluster.^{1,7}

We report here on the formation of a CpCo(I) cluster complex from 1 and a noncyclic olefin under very mild conditions and the investigation of its catalytic reactivity in cycloaddition and other addition reactions in comparison with 1.

RESULTS AND DISCUSSION

Our initial experiments with chlorinated solvents were performed with the cobalt-olefin complexes $[CpCo(H_2C=$ $CHSiMe_{3}_{2}$ (1) and [CpCo(hexadiene)] starting at -78 °C followed by warming to 25 °C, yielding cobaltocenium salt $[(Cp_2Co)_2(CoCl_4)]$. Following these results we treated 1 in halogen-free solvents such as ether, THF, or benzene under the same conditions. To our delight we were able to isolate the tetranuclear cluster complex 4b in 36% yield, containing a bridging trimethylsilylacetylene molecule between two cobalt centers (Scheme 2). The bridging alkyne is the product of a dehydrogenation of one of the trimethylvinylsilane ligands in 1. The required C-H bond activation of the vinylic C-H bonds therefore occurred under remarkably mild conditions, which is relatively rare for this first-row transition metal.⁶ In the reaction hydrogen is formally eliminated, but neither the escape of gas (presumably due to the very small amount if gaseous H₂ is eliminated) nor the product of the reaction with free trimethylvinylsilane as a potential scavenger substrate could be detected.

Interestingly and in contrast to the observations by Wadepohl et al., the corresponding expected trinuclear cluster 4a (compare to Scheme 1) could not be isolated. To gain deeper insight into the formation of the cluster complex 4b, we undertook a time-dependent NMR study of the reaction of 1 in THF- d_8 in the temperature range -78 to 25 °C.^{8,6b} The appearance of several CpCo- and CpCo-hydride resonances was observed at temperatures below -10 °C, but these

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Scheme 1. Formation of Tri- and Tetranuclear Co Cluster Complexes from Jonas Reagent or Cobaltocene with Cyclic Alkenes at Elevated Temperatures



Scheme 2. Formation of the Tetranuclear Co Cluster Complex 4b from 1 under Mild Conditions



disappeared at higher temperatures except one signal at ca. -13ppm of a possibly paramagnetic species, shifting to lower field with increasing temperature. However, the main resonances in this part of the ¹H NMR spectra can be assigned to a trinuclear hydride species such as 4a. The resonances that are found for the two hydrides in 2 at -12 and -29 ppm are also found in our reaction but vanished completely when the mixture is continuously warmed. This observation supports the suggestion that the tetranuclear cluster is built up stepwise via the trinuclear cobalt cluster hydride 4a as an intermediate. We did not find any hint of formation of dinuclear complexes.⁹ It should also be mentioned that the reaction of 1 in THF is more complex than described here, because 4b is not the only Cpcontaining species in this reaction mixture, as seen by different resonances in the Cp region in the NMR, but the sole product that was isolated and characterized unambiguously.¹⁰

The molecular structure of 4b is fully established by X-ray analysis, and the determined structure parameters are similar to those of 3 (Figure 1). The butterfly arrangement of the CpCo fragments can alternatively be described as a one-side-opened tetrahedron that is bridged by the alkyne. While the alkyne moiety coordinates to the cobalt center, the C1-C2 bond is elongated to 1.494(2) Å $[d_{cov}(C \equiv C) = 1.20 \text{ Å}]$,¹¹ which is the same as found for the corresponding C-C bond length in 3 (with n = 5). The loss of the triple bond character in the coordinated alkyne was also observed in the butterfly clusters $[Cp*IrRu_3(CO)_9(RCCR')]$ (e.g. R = SiMe₃, R' = H: 1.454(5) Å).¹² The terminal proton was observed by 1 H NMR spectroscopy with a large downfield shift at 8.96 ppm, again being characteristic for those coordinated alkynes. The compound turned out to be stable in air under ambient conditions.

The structure of 4b and its high stability compared with the cluster complex precursor 1 raises the question of the potential of 4b as a catalyst for cycloaddition and addition reactions. Having the pure 4b in our hands we could now evaluate the reactivity of this cluster in different conversions. This investigation was conducted to obtain more information on the nature of the "real" catalyst, which means finding out if both



Figure 1. ORTEP view of the molecular structure of 4b. The hydrogen atoms of the trimethylsilyl group and Cp ligands are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å]: C1-C2 1.494(2), C1-Co1 1.943(2), C1-Co2 1.935(2), C1-Co4 1.937(2), C2-Co1 1.983(2), C2-Co3 1.922(2), C2-Co4 1.981(2), Co1-Co2 2.3753(3), Co1-Co3 2.3898(3), Co2-Co4 2.3746(3), Co2-Co3 2.3950(3), Co3-Co4 2.3959(3).

1 and 4a/4b or only one of them can act as an active catalyst in the selected reactions. First we wanted to evaluate the activity of 4b in the presence of a diyne and benzonitrile in a [2+2+2] cycloaddition reaction and compare the results with the precursor complex 1 (Table 1).

While precatalyst 1 provided high conversion and essentially quantitative yield at low temperatures as found earlier,^{3a} the application of the same conditions did not lead to the formation of product **5** when **4b** is applied as precatalyst. Raising the temperature to 100 °C gave at least a 26% yield of **5**. Application of irradiation provided **5** in an even lower 15% yield. The large differences in reactivity clearly point toward different reactivities of **1** and **4b** and lead to the conclusion that **4b** is not involved in successful low-temperature cycloaddition reactions as possible with **1**. At higher temperatures (up to 140 °C, sometimes in combination with irradiation) usually applied in CpCo-catalyzed reactions with other catalysts,¹³ however,

 Table 1. Activity of the Cluster Complex 4b in the [2+2+2]

 Cycloaddition Reaction



"In each experiment 5 mol % of catalyst was used. ^b2 equiv of PhCN per equiv of 1,6-heptadiyne was used, and the isolated yield is given referring to the diyne. 'Irradiation in a thermostated Schlenk reactor with two 460 W lamps.

the question still remains whether intermediates like **4a** or **4b** or other cluster complexes with two or more cobalt atoms are capable of providing catalytic activity.

In a previous study of group 9 metal-olefin complexes 1octene (6) was hydrogenated with CpM-olefin complexes (M = Co, Rh, Ir), and it turned out that complex 1 produced *n*octane (7) in 39% yield and the isomerization product 8 in 42% yield (Table 2).^{3b} When pure cluster complex 4b is used under

Table 2. Activity of Cluster Complex 4b in the Hydrogenation of 1-Octene (6)



^{*a*}In each experiment 2 mol % of catalyst was used. ^{*b*}Products were identified by GC analysis and referenced against calibrated pure 6, 7, and 8. ^{*c*}2-Octene (8) is composed of *E*- and *Z*-2-octene, with a ratio of ca. 60:40 (E/Z), measured by GC on a squalane column. ^{*d*}Results refer to experimental data from ref 3b.

the same reaction conditions, the 2-octene (8) is formed quantitatively as a mixture of E/Z-isomers. That led us believe that the 42% observed for 8 in the reaction of 1 is probably a "hidden" reactivity caused by the cluster complex 4b, which is formed during the reaction.

Control experiments with pure 6 and 4b under an argon atmosphere demonstrated that a hydrogen atmosphere is necessary for the isomerization process $6 \rightarrow 8$ to proceed successfully; otherwise no reaction was observed at all. It can be assumed that the formation of cobalt hydride cluster complexes from 4b are responsible for the isomerization reaction. These observations were corroborated by those made by Beller et al. in the isomerization of 1-octene (6) with iron cluster complexes.¹⁴

We have also investigated the corresponding hydroformylation reaction with 1-octene (6, Table 3). Precatalyst 1 gave only small amounts of hydroformylation products octanal (9) and nonanal (10) in a 50:50 ratio. However, the yield of the isomerization product 8 is significantly higher. When starting with isolated cluster complex 4b, the formation of 2-octene (8) was indeed observed, but only in trace amounts. These observations point out that formation of the species acting as the active isomerization catalyst from **4b** under the hydro-formylation conditions is not possible, presumably due to the presence of carbon monoxide, leading to the formation of inactive carbonyl cluster complexes instead of hydride complexes.

Table 3. Activity of the Cluster Complex 4b in theHydroformylation of 1-Octene (6)



^{*a*}In each experiment 0.1 mol % of catalyst was used. ^{*b*}Products were identified by GC analysis and referenced against calibrated pure 6, 8, 9, and 10. ^{*c*}8 is composed of *E*- and *Z*-2-octene (ratio not determined). ^{*d*}Results refer to experimental data from ref 3b.

The amounts of isomerization product observed when using 1 might be explained by the stepwise formation of cluster complexes from the mononuclear complex, giving intermediate cobalt-hydride complexes that can act as isomerization catalysts in accordance with the hydrogenation reaction. Furthermore it can finally be assumed that 1 and 4b in the presence of hydrogen led to the formation of identical cobalt cluster hydride complexes as the active isomerization catalysts.

CONCLUSIONS

Herein we have described the preparation and characterization of a tetranuclear Co_4 - μ -alkyne cluster complex (4b) from $[CpCo(H_2C=CHSiMe_3)_2]$ (1) in hydrocarbon solvents. The cluster complex 4b contains a trimethylsilylacetylene ligand, resulting from the dehydrogenation of a trimethylvinylsilane ligand of 1 via vinylic C-H activation at low temperatures. The cluster was characterized by X-ray crystallography, confirming the butterfly core of the compound. The cluster complex was investigated and compared to 1 in catalytic [2+2+2] cycloaddition reactions, showing the significantly lower reactivity of the cluster as the precatalyst. In the hydrogenation of 1-octene the cluster complex exhibited a selective isomerization reaction to 2-octene as a mixture of E/Z-isomers, presumably as a precatalyst in the formation of cobalt hydride cluster complexes, which act as catalysts in these cases. In the hydroformylation reaction the presence of CO presumably prevents the formation of an active isomerization catalyst due to the formation of inactive carbonyl cluster complexes.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk techniques. All solvents were received from commercial sources and are freshly distilled prior to use.

Synthesis of the Cluster Complex 4b. A solution of 1 (103 mg, 0.32 mmol) in Et_2O (2 mL) was cooled to -78 °C and allowed to

warm to room temperature. After reaching this temperature the slurry was stirred for an additional 30 min. The solvent and volatiles were removed under reduced pressure, and the residue was dried in high vacuum. The residue was taken up in *n*-hexane, and the product isolated in several fractions from crystallization. The product **4b** was isolated as black crystals (17 mg, 0.028 mmol, 36% yield). ¹H NMR ($-20 \,^{\circ}$ C, THF- $d_{8^{\prime}}$ 300 MHz): δ 0.01 (*s*, 9H, SiCH₃), 4.67 (*s*, 10H, C₅H₅), 4.82 (bs, 10H, C₅H₅), 8.96 (s, 1H, CCH) ppm. MS (EI): 594 [MH⁺] (83), 528 [MH⁺ - Cp] (100), 470 [MH⁺ - CpCo] (28), 370 [(CpCo)₃⁺] (21), 189 [Cp₂Co⁺] (73). HRMS (ESI): calcd for [C₂₅H₃₀Co₄Si]⁺ 593.9445, found 593.9446. Anal. Calcd for [C₂₅H₃₀Co₄Si]: C, 50.52; H, 5.09. Found: C, 50.33; H, 4.89. Crystals suitable for X-ray crystal structure analysis were obtained by storing a saturated *n*-hexane/toluene solution of **4b** at -4 °C.

General Procedures for Reactions with Complexes 1 and 4b. General Procedure for the Catalytic [2+2+2] Cycloaddition of 1,6-Heptadiyne with Benzonitrile. 1,6-Heptadiyne (1.0 mmol) and benzonitrile (2.0 mmol) were dissolved in THF (4 mL) and stirred at 0 °C. The cluster complex 4b dissolved in Et₂O (5 mol %, 0.25 mL of Et₂O) was added dropwise, and the solution was stirred for 2 h at 100 °C. Under photochemical conditions the reaction solution was irradiated for 18 h at 25 °C. The product was separated via column chromatography with *n*-hexane/EtOAc (4:1) as eluent, and 5 was isolated as an oil. The product was identified by its NMR and GC-MS data.^{3a}

General Procedure for the Catalytic Hydrogenation of 1-Octene (6). The olefin (6, 1.0 mmol) was added under argon to a solution of the cluster complex 4b (2.0 mol %) in toluene (20 mL). The reaction mixture was transferred into an autoclave, which was then heated to 60 °C. Hydrogen was then introduced and heated for 2 h; then the reaction mixture was heated for 22 h at 80 °C. After the reaction time, the autoclave was allowed to cool to room temperature, and the pressure was released. The reaction mixture was analyzed immediately by GC.

General Procedure for the Catalytic Hydroformylation of 1-Octene (6). The olefin (6, 10.2 mmol) was added under argon to a solution of the cluster complex 4b (0.1 mol %) in toluene (20 mL). The reaction mixture was transferred into an autoclave, which was then heated to 80 °C under introduction of syngas. After 2 h the temperature of the reaction mixture was raised to 120 °C. Following 22 h reaction time, the autoclave was allowed to cool to room temperature, and the pressure was released. The reaction mixture was analyzed immediately by GC.

ASSOCIATED CONTENT

S Supporting Information

Tables of crystallographic data for complex **4b** and temperature-dependent NMR spectra for the formation of **4b** from **1** for the high-field region. 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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