



Decomposition mechanism of a cobalt-coordinated phosphite–olefin ligand under irradiation



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ABSTRACT

We herein report on the different coordination behavior of phosphite–olefin ligands containing either a terminal olefin moiety or a related compound containing an internal olefin moiety to a CpCo(I)-center. While the former coordinates to the metal center via P atom and olefin moiety upon irradiation, photolysis of the latter led to the subsequent formation of the phosphorus-free [CpCo(η^4 -1,3-butadiene)] complex (**6**). A mechanistic rationale of the decomposition reaction based on an Arbuzov-like rearrangement is suggested.

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Introduction

Over the past decades intensive studies on CpCo(I)-complexes (Cp: η^5 -cyclopentadienyl) as catalysts for [2 + 2 + 2] cycloaddition reactions have been reported [1]. While their catalytic performances under thermal as well as photochemical conditions have been studied extensively, the degradation or reactivity towards cluster formation of only several olefin-ligated CpCo(I)-complexes has been investigated and various respective cluster complexes have been characterized [2]. The reaction of with alkynes can lead to mononuclear [CpCo(η^4 -diene)]-complexes, affording highly stable cyclobutadiene complexes, which can however be subject to oxidative degradation with sterically hindered cyclobutadienes [3]. A number of oligonuclear CpCo-cluster complexes has been investigated by Wadepohl et al. [4]. They demonstrated that the reaction of [CpCo(η^2 -C₂H₄)₂] or in situ generated low-valent complexes starting from cobaltocene/K with various cycloalkenes resulted in the formation of trinuclear CpCo-hydrido cluster complexes. As a result of the dehydrogenation reaction of the cyclic olefin, the corresponding cycloalkyne is coordinated by three CpCo-fragments. The formation of a tetrameric cluster from [CpCo(H₂C=CHSiMe₃)₂], affording a butterfly-type coordination of the derived trimethylsilylacetylene has been

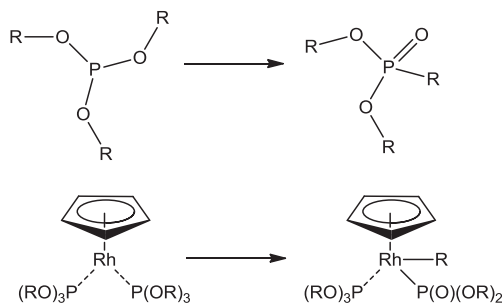
described by our group [2e]. There are only two further reports on this kind of degradation, resulting in tetrameric CpCo-clusters [5].

Reactions of CpCo(I)-sources with phosphine and phosphite ligands leading to oligonuclear Co-complexes have been described occasionally. One example is the report of the reactivity of [CpCo(CO)₂] (**1**) with free phosphines yielding phosphorus-bridged clusters as described by Lal De and Maiti [6]. An interesting example for the decomposition of a phosphorus compound is delivered by the reaction of *tert*-butylphosphaethyne with ω -(*di-tert*-butyl)phosphanyl (ethylcyclopentadienyl)cobalt]-complexes, where the C≡P bond was split completely and a trinuclear μ_3 -carbyne- μ_3 -phosphidotricobalt cluster formed [7].

Therefore, the decomposition of phosphorus ligands poses a serious problem in catalysis [8]. Depending on the ligands of the transition metal complexes various routes of decomposition can be envisioned [9]. Since our group recently focussed on the synthesis of CpCo(I)-bisphosphite as well as CpCo(I)-phosphite–olefin complexes, the decomposition of coordinated phosphite ligands was especially interesting. While phosphites are more stable towards oxidation compared to phosphines, a number of different other reaction pathways is possible including hydrolysis, alcoholysis, *trans*-esterification, O–C and P–O bond cleavage as well as the Arbuzov rearrangement. There are few reports on CpCo(I)- [10] as well as CpRh(I)-complexes [9] with phosphite ligands undergoing an Arbuzov rearrangement leading to phosphite decomposition and an alkylated metal center (Scheme 1).

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Scheme 1. Documented Arbuzov rearrangements in the coordination sphere of a transition metal.

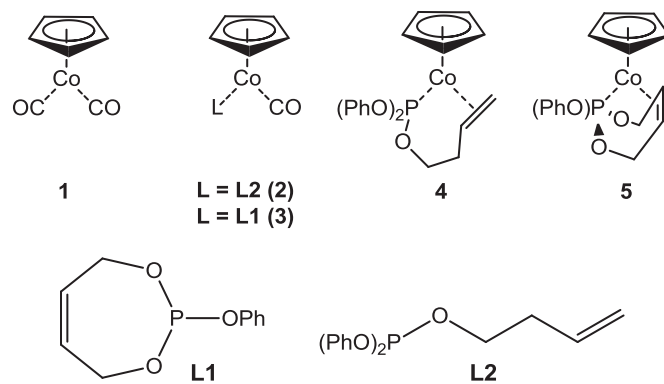
In general aliphatic phosphites are found to be more prone to the Arbuzov rearrangement than arylphosphites. To the best of our knowledge these rearrangement reactions have exclusively been reported for conventional trialkylphosphites and there has not been any account of decomposition of a coordinated phosphorus-olefin ligand. We herein report on the degradation of a cobalt-bound phosphite–olefin ligand under irradiation with light, resulting in the phosphorus-free and purely olefin-ligated [CpCo(η^4 -1,3-butadiene)] (**6**) complex.

Results and discussion

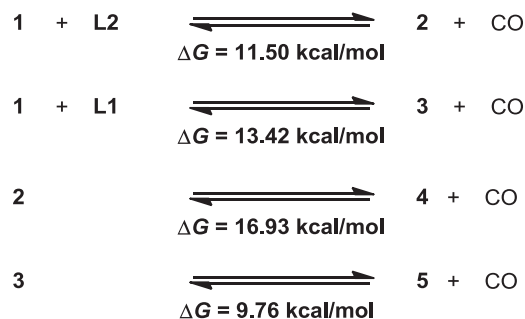
We recently described the synthesis of the first CpCo(I)-complex with a chelating phosphite–olefin ligand [11]. Interestingly in this specific case no stabilizing effect due to the chelation effect was observed. To investigate the influence of the ligands into more detail the application of a different chelating phosphite–olefin ligand seemed to be promising. We chose to compare the cyclic phosphite **L1** and the linear phosphite **L2** (Scheme 2). DFT calculations suggested – after carrying out BP86 density functional theory computations to examine the thermal stability – that the coordination of **L1** and **L2** via the phosphite group leading to the formation of both **4** as well as **5** were endothermic but possible under reaction conditions. Starting from [CpCo(CO)₂] (**1**) as well as the cyclic phosphite **L1** and linear phosphite **L2**, the formation of the corresponding complexes [CpCo(CO)(**L2**)] (**2**) and [CpCo(CO)(**L1**)] (**3**) have been computed to be endergonic by 13.42 and 11.50 kcal/mol, respectively, indicating that the formation of complexes **2** and **3** is thermodynamically not favorable.

Since the formed CO gas molecule can be removed from the reaction mixture to the gas-phase, the chemical potential of the possible equilibrium of the system is changed and the reaction shifted to favor the formation of complexes **2** and **3**. This has indeed been observed since the synthesis of **2** and **3** respectively proceeded smoothly at room temperature. Thus, starting from [CpCo(CO)₂] (**1**) the first carbonyl ligand could easily be replaced by a phosphite at room temperature and the respective complexes with one CO ligand were prepared in very good yields (Scheme 3). Crystals of **3** suitable for X-ray analysis were obtained from a *n*-pentane solution at 4 °C. As shown in Fig. 1 the phosphite–olefin ligand is only coordinated via the phosphorus atom and one CO ligand is still attached to the cobalt center.

Starting from complexes **2** and **3** we further computed the possible intramolecular substitution reaction of the CO ligand with the olefin unit within **L2** and **L1**. As expected, these substitution reactions with the formation of complexes **4** and **5** are also thermodynamically not favorable and endergonic by 16.93 and 9.76 kcal/mol, respectively. Since the same equilibrium shift due to the release of the second CO ligand applies, we were hopeful for the



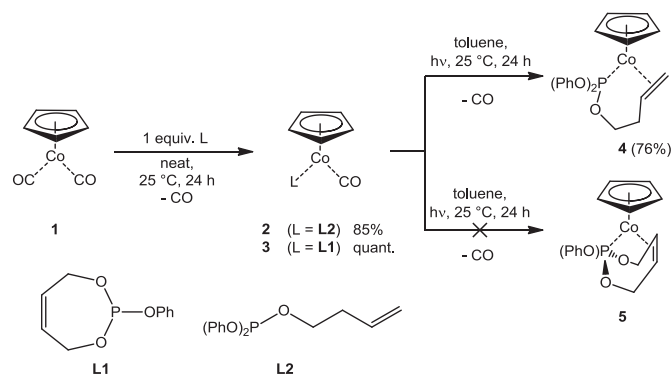
Ligand exchange reaction:



Scheme 2. Calculations on the formation of the new complexes **2–5** from **1–3** at BP86/TZVP.

reaction to yield the chelating complexes **4** and **5** anyway. However, the irradiation with light and the release of the second CO ligand only led to a successful chelation in the case of ligand **L2** and the generation of **4**. Irradiation of **3** led to no chelating compound **5** despite the fact that the formation of complex **5** is less endergonic than that of complex **4**.

If **3** was irradiated with light at 25 °C or even at temperatures as low as –20 °C a black solid precipitated and no ³¹P NMR signal could be detected in the red solution. Filtration of the solution over neutral aluminum oxide and removal of the solvent afforded a red, highly volatile solid in 41% yield. NMR and MS analysis provided evidence for the formation of [CpCo(η^4 -1,3-butadiene)] (**6**). Pruettt and Myers already described **6** as a volatile red solid prepared from **1** and excess 1,3-butadiene at elevated temperatures [12], but only Bergman et al. published a full characterization of **6**, the NMR data being in accordance with our findings [13].



Scheme 3. Synthesis of chelating CpCo(I)-phosphite–olefin complexes.

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