

Preparation of Dimeric $[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{CoBr}]_2$ and Convenient Synthesis of the Homodinuclear Cobalt Complex $[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{Co}]_2\text{H}_3$ therefrom.

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Homonuclear Cobalt Hydride Cluster

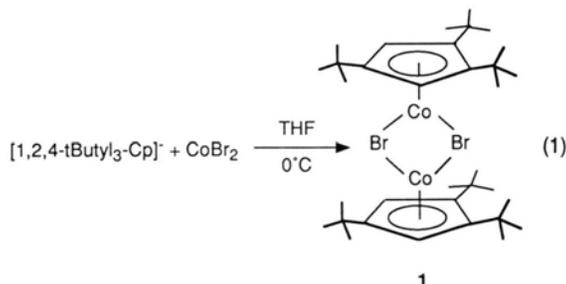
The title compound $[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{CoBr}]_2$ **1** is prepared in a one pot reaction starting from 1,2,4-*t*Bu₃cyclopentadiene followed by metallation and by reaction of the resulting *t*Bu₃Cp[−]K⁺ anion salt with anhydrous CoBr₂ in THF. **1** was isolated from this reaction in 78% yield as black crystals. **1** reacts with LiAlH₄ in THF at 0 °C. Subsequent alcoholysis of the crude reaction mixture with ethanol at −78 °C gives the novel trihydride cluster $[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{Co}]_2\text{H}_3$ **2** in 58% isolated yield as black crystals. **2** has been characterized by ¹H NMR, ESR, MS, and IR spectroscopy, as well as by elemental analysis.

The use of sterically demanding Cp ring ligands has an enormous impact on the synthesis of unusual organometallic compounds [1]. Bulky ring substituents can stabilize such metal complexes either kinetically or electronically. A prominent example is the pentamethylcyclopentadienyl ring ligand Cp* from which a great number of organometallic complexes have been prepared. Therein the methyl substituents shield the metal atoms and stabilize the ring to metal bond *via* their electron donating capability. In contrast to this the *t*Bu₃Cp ligand has not found much attention in organometallic chemistry in recent years.

This is due to the laborious synthesis route for this ligand [2]. There is only a limited number of reports which deal with metal complexes of this ligand and the potential of the *t*Bu₃Cp ligand with respect to the synthesis of new transition metal complexes is still high and virtually unexplored [3].

Recently we have learned that this extremely bulky ligand can offer some advantage over the Cp* ring ligand with respect to product selectivity. For example the Cp* derivative of the title compound **2**, the cobalt cluster $[(\eta^5\text{-Cp}^*)\text{Co}]_2\text{H}_3$ **3**, can only be prepared in a mixture, together with other products, whether one uses our metal vapor approach [4] or a classical wet chemical synthesis route [5] for its synthesis. Subsequent purification of **3** is not easy, and our further studies of the reaction chemistry of **3** were mainly hampered by a tedious chromatography and crystallization procedure to obtain **3** in a pure form in good yields. Moreover, an alternative purification procedure for **3** using sublimation and crystallization procedures as reported [5] does not work in our hands. These problems can be overcome when using the *t*Bu₃Cp ring ligand instead of the Cp* system for the synthesis of this dinuclear type of cobalt complex.

The necessary starting compound for the synthesis of **2**, the bridged dibromide **1** is obtained in about 80% yield in a straightforward manner by the reaction of the potassium salt *t*Bu₃Cp[−]K⁺ with anhydrous CoBr₂ in THF at 0 °C (eq. (1)).



1 is paramagnetic according to its ¹H NMR data. This and all other analytical data (see experimental section) identify **1** as a member of the series $[(\eta^5\text{-Cp}^R)\text{CoX}]_2$ (R = Me, Me₄Et; X = Cl, Br) which has already proven to have a rich chemistry [6]. We assume a butterfly arrangement of the ligands in **1** similar to the solid state structures we have already obtained for the Cp* and the Me₄EtCp derivatives of **1** [6, 7].

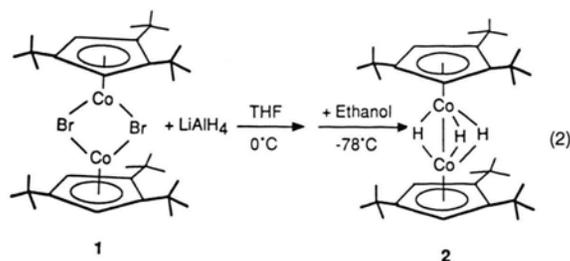
When **1** is reacted with LiAlH₄ at 0 °C in THF followed by ethanolysis of the crude reaction mixture at −78 °C a black colored solution results (eq. (2)).

The crude oily reaction product which results after THF solvent removal can be crystallized from ether/acetonitrile by slow cooling to yield black crystals of the dinuclear Co-hydride complex

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$[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{Co}]_2\text{H}_3$ **2**. **2** is paramagnetic and has been characterized by its ^1H NMR, ESR, MS and IR spectra, as well as by elemental analysis. Here, in sharp contrast to the synthesis of the Cp* derivative **3** which is obtained by a similar reduction of the bridged dichloro compound $[(\eta^5\text{-Cp}^*)\text{CoCl}]_2$ with LiAlH_4 [5], only one product, **2**, was isolated in good yields. This result is certainly due to the steric requirements of the bulky $t\text{Bu}_3\text{Cp}$ ring ligand with which no formation of other products, especially higher nuclearity clusters as observed in the synthesis of **3**, is possible.

By using the $t\text{Bu}_3\text{Cp}$ ligand the cobalt hydride complex **2** is now available in g-amounts by a convenient synthesis in pure form simply by recrystallization. Furthermore no chromatographic or sublimation purification procedure as for the Cp* derivative **3** is necessary. It should be mentioned that **2** as well as the $t\text{Bu}_2\text{Cp}$ derivative $[(\eta^5\text{-}t\text{Bu}_2\text{Cp})\text{Co}]_2\text{H}_3$ **4** are also available by a direct metal vapor route using cobalt atoms and the appropriate $t\text{Bu}_{2,3}\text{Cp}$ ligands [7]. We are currently exploring this synthesis route as well as the solid state structures, the electrochemical behaviour and the reaction chemistry of **2**, **3** and **4**, and will report on our results with respect to this regards in the future.

Experimental

$[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{CoBr}]_2$ **1**: 15.0 g (0.062 mol) 1,2,4- $t\text{Bu}_3$ -cyclopentadiene prepared by butylation of freshly cracked monomeric cyclopentadiene as reported by Riemschneider [2a–c] are dissolved in 500 ml of THF and cooled to 0°C . To this solution 2.47 g (0.062 mol) of dry KH are added in one batch. After an induction period of approx. 10 min a creamy white precipitate begins to form. The mixture is allowed to warm to room temperature overnight with stirring until gas evolution completely ceases. After cooling to 0°C 13.48 g (0.062 mol) of anhydrous CoBr_2 is added resulting in an

immediate formation of a brown, in later stages of the reaction black mixture. After stirring overnight at r.t. all volatiles were stripped off in a vacuum and the black oily residue is extracted 5 times with 100 ml portions of pentane and then filtered to remove solid KBr. Cooling of the combined pentane extracts gives 18.0 g (0.024 mol, 78%) of cube shaped black crystals of **1** which lose their habitus when dried for an extended time in a vacuum indicating some loss of incorporated solvent during the drying process of the crystals. – MS (70 eV): m/z (%) = 744 (1) $[\text{M}^+]$, 585 (3), 527 (15), 475 (17), 371 (11) $[\text{M}^+/2]$, 203 (28), 121 (17), 57 (100). – ^1H NMR (200 MHz, $[\text{D}_6]$ benzene, 27°C) δ = 6.2 (36 s, br (95 Hz), $t\text{Bu}$), 9.55 (18 s, br (130 Hz), $t\text{Bu}$). – IR (KBr) ν = 2970 (s), 2920 (s), 2880 (s), 1480 (s), 1460 (s), 1390 (s), 1360 (s), 1240 (s).

$\text{C}_{34}\text{H}_{58}\text{Br}_2\text{Co}_2$ (744.55)

Calcd C 54.85 H 7.85 Br 21.47 Co 15.83%,
Found C 55.30 H 8.15 Br 21.06 Co 15.41%.

$[(\eta^5\text{-}t\text{Bu}_3\text{Cp})\text{Co}]_2\text{H}_3$ **2**: 11.3 g (15.18 mmol) of **1** are dissolved in 150 ml of THF and cooled to 0°C . 0.58 g (15.18 mmol) of LiAlH_4 are added to this solution in small batches with stirring. Every addition resulted in a vigorous reaction with gas evolution. After all LiAlH_4 was added the reaction mixture was stirred at 0°C for 3 h and then cooled to -78°C , and 30 ml of dry ethanol was added dropwise, then in 5 ml portions. The resulting mixture was stirred for 2 h while warming slowly to room temperature. Then all volatiles were removed in a vacuum. Exhaustive extraction of the residue with pentane and filtration of the resulting purple solution, followed again by complete removal of the solvent in a vacuum gives a semicrystalline black residue. This material was dissolved in 100 ml of diethylether to which 40 ml CH_3CN is added. Cooling, first to 0°C , then to -30°C afforded 5.2 g (8.85 mmol, 58.3%) of **2** as black crystals. – MS (70 eV): m/z (%) = 587 (100) $[\text{M}^+]$, 523 (15), 469 (17), 455 (24), 57 (42). – ^1H NMR (200 MHz, $[\text{D}_6]$ benzene, 27°C) δ = 3.45 (54 s, br (20 Hz), $t\text{Bu}$). – ESR (toluene, -120°C , standard TMPO) single isotropic signal, g_{iso} = 1.9841. – IR (KBr) ν = 2960 (s), 2910 (s), 2880 (s), 1460 (s), 1480 (s), 1360 (s), 1245 (s).

$\text{C}_{34}\text{H}_{61}\text{Co}_2$ (587.73)

Calcd C 69.48 H 10.46 Co 20.09%,
Found C 69.82 H 10.15 Co 20.01%.

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