Reactivity of an Arene Cobalt Triple Decker Complex Towards Various Ligands. Facile Arene Displacement in \([\text{Bis}(\eta^5\text{-pentamethylcyclopentadienyl})\text{cobalt}]\)-\(\mu\)\(-\eta^4;\eta^4\)\(-\text{toluene})\)

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Introduction

At present several examples of organometallic triple decker complexes are known [1]. However, the number of those complexes with bridging arene ligands is still small. In complexes of this kind the arenes usually bind the terminal metal ligand fragments either in \(\mu\)-\(\eta^1;\eta^2\), \(\mu\)-\(\eta^3;\eta^3\), or \(\mu\)-\(\eta^4;\eta^4\) bonding modes [2]. Very recently we described the synthesis of a new type of organometallic triple decker complex \(1\) [3]. \(1\) is accessible in a reductive ligand degradation from \([\eta^5\text{-Cp}^*]\text{Co}(\text{O,O}'\text{-acac})\) [4] by potassium metal in various arenes. The arene ligands in \(1\) are bonded in a \(\mu\)-\(\eta^4;\eta^4\) fashion to the metal ligand fragments (Fig. 1) [3]. In the solid state the isopropylbenzene ligand in the derivative \(1f\) is folded to a remarkable extent as found by X-ray crystallography [3]. When it comes to the reactivity, very little is known about such bridging aromatic ring ligands in carbacyclic triple decker complexes. In \([\eta^5\text{-Cp}^*]\text{V}_{2}\)-\(\mu\)-\(\eta^4;\eta^4\)\(-\text{benzene})\) \(2\) [2c] the aromatic “middle deck” can be substituted by other arenes like toluene and mesitylene with retention of the triple decker structure, albeit only at temperatures above 100 °C. Aside from these results no such reactivity of a triple decker complex has been reported. However, very recently we found that the toluene ligand in \(1b\) can be easily substituted at room temperature by \(\text{D}_2\)\(-\text{benzene}, \text{cycloheptatriene or cot}) to produce the triple decker complexes \([\eta^5\text{-Cp}^*]\text{Co}_{2}\)-\(\mu\)-\(\eta^4;\eta^4\)-\(\text{D}_2\)\(-\text{benzene})\) \(3\) \([3, \text{[(}\eta^5\text{-Cp}^*\text{)Co}]_{2}\)-\(\mu\)-\(\eta^4;\eta^4\)-\(\text{cycloheptatriene})\) \(3\) \([5\text{ and [Bis(}\eta^5\text{-Cp}^*\text{)Co}]_{2}\)-\(\mu\)-\(\eta^4;\eta^4\)-\(\text{cot})\)]\) \(6\) \(4\), respectively.

As an extension of these studies we describe herein the reaction of \(1b\) with a variety of organic, inorganic and organometallic ligands. This investiga-
gation was undertaken in order to study the unusual reaction behaviour of this triple decker in further detail especially with respect to a) the possibility of the arene exchange of the aromatic “middle deck” and b) to test the scope of the arene exchange reaction with respect to a variety of different ligands.

Results and Discussion

In Scheme 1 the reaction products of 1b with a variety of ligands are shown. The products 5–15 obtained in these reactions are mainly mononuclear organocobalt complexes. Although complexes 5–7, 9 and 11 are already known, the ease of their formation and the good yields of products are most remarkable. Except from the ring ligand transfer reaction g and the synthesis of the fluorinated sandwich 8, all other reactions can be run at ambient temperature within 1 h. These findings in connection with the results already obtained on the reactivity of 1b [3], show that this triple decker can be regarded as an excellent source of the \( (\eta^5\text{-Cp}^\ast)\text{Co} \) fragment.

When 1b is reacted with anthracene in a 1:1 stoichiometric ratio, the formation of mononuclear 13 and dinuclear 14 is observed. For the latter we assign a slipped triple decker structure \( \{(\eta^5\text{-Cp}^\ast)\text{Co}\}_{2-\mu-}\{(\eta^4\text{-anthracene})\} \) in analogy to complexes 1a–f, with a bridging anthracene ligand according to the \( ^1\text{H NMR} \) and MS data. However, 13 and 14 are formed as a mixture (see \( ^1\text{H NMR} \) spectrum, Fig. 2) which could not be separated, neither by crystallization or by sublimation. According to the \( ^1\text{H NMR} \) spectrum 13 and 14 are formed in the ratio 4:1. In the mass spectrum, at a temperature of 110 °C/10^{-3} Torr, 13 ([M\(^+\): m/z 372) could be detected by fractional sublimation from the crude reaction product. Gradually rising the temperature of the sample gave the molecular peak of 14 ([M\(^+\): m/z 556] at 150 °C/10^{-3} Torr. Unsubstituted 13 (Cp analogue) can be obtained by a similar reaction when \( (\eta^5\text{-Cp})(\eta^2\text{-ethen})\text{Co} \) is reacted with anthracene [11]. However, no dimeric complex like 14 could be detected when using \( (\eta^5\text{-Cp})(\eta^2\text{-ethen})\text{Co} \) as the source of the Cp–Co fragment [11]. This different behaviour of 1b compared to \( (\eta^5\text{-Cp})(\eta^2\text{-ethen})\text{Co} \) as the source of the Cp–Co fragment [11].
Fig. 2. $^1$H NMR spectrum of the crude reaction product mixture containing 13 and 14 (ratio: 4:1) as obtained from reaction i. Peaks without notation are due to impurities present in the crude reaction mixture.

(ethen)$_2$Co] in the reaction with anthracene is obviously due to the monomeric nature of [(η$^5$-Cp)(η$^2$-ethen)$_2$Co] with which no simultaneous complexation of both terminal arene units of the anthracene ligand seems possibly. In contrast to this with 1b twofold complexation of the anthracene ligand can be achieved even under mild conditions.

In contrast to the reaction with anthracene, the formation of a similar dinuclear complex in the reaction of 1b with naphthalene, was detected by mass spectrometry. However, only the mononuclear complex 15 (Scheme 1) could be isolated and characterized by MS, $^1$H NMR, and IR spectroscopy from this reaction.

Reaction of a red-brown solution of 1b in ether with NO (1 atm) results in the immediate precipitation of a brown powder. Therefrom a brown microcrystalline paramagnetic solid (according to $^1$H NMR studies) could be obtained by crystallization from THF. By mass spectrometry a molecular composition corresponding to the formula [(η$^5$-Cp)*CoNO]$_2$ ([M$^+$]: m/z 448 (52)) can be deduced. With one equivalent elemental sulfur, 1b reacts to form mainly [(η$^5$-Cp)*CoS]$_4$ as a black microcrystalline powder after work up by chromatography and crystallization from THF/ether. By mass spectrometry trace amounts of [(η$^5$-Cp)*CoS]$_3$ could be detected. No formation of [(η$^5$-Cp)*Co]$_3$S$_2$ was observed by MS analysis. Synthesis and structural characterization of [(η$^5$-CpMe)Co]$_3$S$_2$ [12] have already been reported.

Dinuclear reaction products of the analytical composition [[(η$^5$-Cp*)(R$_{1,2}$=t-Bu$_2$)]Co$_2$] 16 (R$_{1,2}$ = t-Bu$_2$) and [[(η$^5$-Cp*)(R=R=N)Co]$_2$] 17 (R = 1,1’,3,3’-tetramethylecyclohexyl residue) were obtained when 1b was reacted with di-t-butyl-diazo methane (C$_4$H$_9$(t-Bu)$_2$C=N=N and 2-diazo-1,1’,3,3’-tetramethylecyclohexane (eq. (1)). In the course of both reactions no evolution of N$_2$ was detected. This is in contrast to the reaction of 1b with diphenyldiazo methane from which N$_2$ is evolved immediately after mixing of the components at 0 °C. On the basis of the spectroscopic data we propose the bridged R-methylene-N,N-hydrazido structures 16 and 17 for the products. Furthermore MS data (16, [M$^+$]: m/z 696 (2%); 17, m/z 554 (12) [M$^+$−166 (= −2-diazo-1,1’,3,3’-tetramethylecyclohexane) as well as elemental analysis confirm the composition of 16 and 17. For 17 a weak to medium intensity band of the N=C=N absorption could be observed at 1515 cm$^{-1}$. There is precedent in the literature which of a Co$_3$ cluster with an analogous hydrazido type ligand [13].

The compounds 16 and 17 are formulated with a Co-Co double bond, in accord with the 18VE rule and the observed diamagnetism. In this respect the compounds are structural analo-
gies of the well known dinuclear complex $[(\eta^5-Cp^*)CoCo]_2$ [8]. For 16 two sets of $t$-butyl protons were observed at 1.89 and 2.38 ppm, respectively. The protons of the Cp* rings resonate at 3.51 ppm. In 17 two different sets of methyl groups for the diazoalkane at 1.10 and 2.0 ppm were observed. In 17 the Cp* protons resonate at 2.30 ppm. For all the aforementioned resonances of 16 and 17 this reflects an unusual high shift upon coordination to Co.

**Conclusions**

The results on the reactivity of 1b presented here show that 1b is a valuable source of either one or two $[(\eta^5-Cp^*)Co]$ fragments and can be used as a transfer agent for these M–L fragments. With 1b those fragments can be easily transferred to a number of ligands under mild reaction conditions offering a new access to a variety of monomeric and dinuclear organocobalt complexes. 1b is the first triple decker arené complex with exhibits such a high reactivity. Therefore 1b is a real alternative to the use of $[(\eta^5-Cp^*)(\eta^2$-ethene)$_2Co]$ in $[(\eta^5-Cp^*)Co]$ transfer reactions, which usually need much higher reaction temperatures.

**Experimental**

All reactions were carried out under argon using Schlenck type glassware and techniques. Solvents were dried appropriately and distilled under argon prior to use. CO and C$_2$H$_4$ were used from storage cylinders without further purification or drying. All other reagents were dried by stirring with molecular sieves (3.5 Å) followed by vacuum condensation. $[(\eta^5-Cp)NiP(C_2H_4)_3]$ [14], di-$t$-butyl-diazomethane [15] and 2-diazo-1,1’3,3’-tetramethylcyclohexane [16] were prepared according to the literature. Activated Al$_2$O$_3$ was prepared by heating it for several days at 160 °C/10$^{-3}$ Torr and was stored under argon prior to use. Elemental analyses were performed by Dornis & Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

**Preparation of compounds**

5: synthesized from 0.26 mmol 1b [3] in diethyl ether by passing C$_2$H$_4$ into this solution at ambient temperature, yield: 0.28 mmol 5 (54%) as red crystals from pentane (−78 °C).

$C_{14}H_{27}$Co (250.27)

Calcd C 67.19 H 9.26 Co 23.55%

Found C 67.14 H 9.33 Co 23.43%

6: synthesized from 0.18 mmol 1b in ether by passing CO through this solution at ambient temperature, yield: 0.12 mmol 6 (33%) as green microcrystals from pentane (−78 °C).

IR (KBr) $v = 1745$ (vs, br, μ-CO), 1880 (vs, br, μ-CO).

$C_{22}H_{30}$O$_2$Co (444.34)

Calcd C 59.47 H 6.81 Co 26.52%

Found C 58.44 H 6.95 Co 27.25%

7: 0.82 mmol 1b was dissolved in 30 ml diethyl ether, 0.82 mmol butadiene was added, and the resulting red-brown solution stirred for 30 min to form a red solution. Evaporation of all volatiles and crystallization from ether (−78 °C) gave 0.6 mmol red crystals of 7 (37%).

MS (EI, 70 eV); $m/z = 248$ (100) [M$^+$], 194 (45), 133 (25).

− IR (KBr): in addition to peaks for complexed Cp*: $v = 3040, 1190, 940, 890, 860, 670$ (s, butadiene).

− $^1$H NMR (400 MHz, [D$_2$]THF, 27 °C): $\delta = 4.18$ (m, butadiene), 1.73 (s, 15 H, Cp*), 0.95 (m, butadiene), −0.55 (m, butadiene).

8: 1b did not react with C$_6$F$_6$ at room temperature within several hours, therefore 0.7 mmol 1b was dissolved in 20 ml C$_6$F$_6$ in a glass ampule sealed under argon and stirred with a teflon stir bar at 50 °C for 24 h. After removal of excess C$_6$F$_6$ and toluene 0.6 mmol crystalline 8 (43%) remained.

MS (EI, 70 eV); $m/z = 380$ (33) [M$^+$], 194 (100), 133 (67), 59 (13).

− IR (KBr): $v = 380$ (33) [M$^+$], 194 (45), 133 (67), 59 (13).

− IR (KBr): in addition to peaks for complexed Cp*: 1750, 1680, 1530, 1320, 1235, 1202, 1168, 1045, 990, 940, 890, 860, 670 (s, butadiene).

− $^1$H NMR (200 MHz, [D$_2$]THF, 27 °C): $\delta = 3.38$ (m, butadiene), 1.73 (s, 15 H, Cp*), 0.95 (m, butadiene), −0.55 (m, butadiene).

9: 0.49 mmol 1b and 0.49 mmol 1.5 cod were dissolved in 30 ml diethyl ether and stirred for 1 h which gave a red solution. Removal of all volatiles resulted in a semicrystalline residue which can be recrystallized to yield 0.3 mmol 9 (31%).

MS (EI, 70 eV); $m/z = 302$ (100) [M$^+$], 285 (92), 273 (75), 192 (64), 133 (52), 59 (12).

− IR (KBr): in addition to the peaks for complexed Cp*: 1750, 1680, 1250, 1168, 1045, 990, 940, 890, 850, 810 (s, all Cod).

− $^1$H NMR (200 MHz, [D$_2$]THF, 27 °C): $\delta = 3.33$ (s, Cod), 2.2 (m, Cod), 1.54 (m, Cod), 1.52 (m, Cod), 1.48 (s, Cp*), all signals significantly broadened.

10: 0.4 mmol 1b was dissolved in 50 ml of diethyl ether and during 30 min a slow stream of H$_2$
gas was bubbled through this solution, resulting in a color change to deep red. Concentration of the solution, filtration and cooling to −30 °C resulted in the formation of 0.3 mmol 10 (38%). 10 can also be prepared from 1b in 60% yield by filtration of a pentane solution of 1b over a column (2 cm diam., 1 = 15 cm) filled with activated Al₂O₃.

**C₁7H₅Co (288.03)**
- **Caled** C 70.82 H 8.74 Co 20.44%.
- **Found** C 70.95 H 8.57 Co 20.35%.

**MS** (70 eV, El): m/z = 288 (52) [M⁺], 286 (100), 194 (34), 133 (17), 59 (5). — **IR (KBr):** ν = 3010 (HC≡C), 2820–2880 (Cp*), 1320, 1410, 1375 (m, Cp*), 1105 (m, Cp), 1070 (m, Cp*), 1430, 1370, 1015, 1030 (all Cp*). — **1H NMR** (400 MHz, CDCl₃): δ = 5.84 (s, 2H, phen), 5.68 (m, 1H), 2.15 (m, 1H), 1.97 (m, 1H), 1.82 (s, 15 H), 1.79 (s, 3 H), 1.38 (s, 2H, br), 0.73 (q, 2H). — **13C NMR** (100 MHz, CDCl₃): δ = 9.0, 18.2, 23.7, 23.8, 35.5, 56.2, 77.2, 87.8, 88.8.

**11**: 0.4 mmol 1b and 0.44 mmol [(η⁵-Cp)NiP(C₂H₅)₃]: were dissolved in 100 ml diethylether and stirred for 2 h at 40 °C. After removal of all volatiles the remaining residue was extracted with pentane, filtered and cooled to −30 °C which gave 0.2 mmol of 11 (25%).

**MS** (70 eV, El): m/z = 259 (100) [M⁺]. — **IR (KBr):** ν = 3100 (s, Cp), 2840–2960 (s, br, Cp*), 1410, 1375 (m, Cp*), 1105 (m, Cp), 1070 (m, Cp*), 1025 (s, Cp), 1000 (s, Cp), 780 (vs, Cp).

**12**: 0.8 mmol 1b was dissolved in 20 ml 2-butyn and stirred for 30 min at 0 °C. Stripping of excess 2-butyn under vacuum affords a brown crystalline residue which is characterized as 12 (31%) (0.5 mmol). Only trace amounts of hexamethylbenzene were formed in this reaction.

**MS** (70 eV, El): m/z = 356 (100) [M⁺], 211 (20), 178 (17).

**C₂₂H₃₅Co (356.43)**
- **Caled** C 74.14 H 9.33%.
- **Found** C 73.94 H 9.88%.

**13, 14**: 0.7 mmol 1b was dissolved in 30 ml diethyl ether and 0.7 mmol anthracene was added. Stirring for 1 h resulted in a red solution. All volatiles were removed under vacuum and the residue analyzed spectroscopically. Yield of the crude mixture of 13 and 14 was 55%.

**13**: **MS** (70 eV, 130 °C, EI): m/z = 372 (100) [M⁺], 192 (14), 178 (22), 133 (11). — **1H NMR** (400 MHz, CDCl₃): δ = 7.45 (m, 2H, phen), 7.2 (m, 2H, phen), 6.76 (s, 2H, phen), 5.68 (m, 2H, phen), 2.52 (m, 2H, phen), 1.51 (s, 15 H, Cp*).

**14**: **MS** (70 eV, 130 °C, EI): m/z = 566 (100) [M⁺], 386 (27), 372 (31), 329 (10), 133 (28). — **1H NMR** (400 MHz, CDCl₃): δ = 5.93 (m, 4H, phen), 5.84 (s, 2H, phen), 2.08 (m, 4H, phen), 1.79 (s, 30 H, Cp*).

**15**: 0.52 mmol 1b and 0.52 mmol naphthalene were dissolved in diethyl ether and stirred for 1 h at r.t. After removal of all volatiles a red oil remains. This can be crystallized from ether (−78 °C, several weeks) to yield 0.3 mmol 15 (29%).

**MS** (70 eV, 130 °C, EI): m/z = 516 (1) [M⁺] + Cp*Co, 322 (100) [M⁺], 192 (52), 161 (18), 128 (11), 59 (11). — **1H NMR** (400 MHz, CDCl₃): δ = 6.1 (d, br, 4H, napht.), 5.7 (s, br, 2H, naph.), 1.98 (s, 2H, napht.), 1.33 (s, 15 H, Cp*).

**[(η⁵-Cp*NO)₂]:** 0.37 mmol 1b was dissolved in 50 ml ether and NO was passed through the solution at ambient temperature. Almost immediately a brown residue was formed. NO bubbling was continued for 30 min resulting in a nearly colorless ether solution. Decantation of the solvent and recrystallization of the residue from THF affords a brown microcrystalline material.

**MS** (70 eV, El): m/z = 448 (52) [M⁺], 329 (18), 224 (19), 134 (74), 119 (100), 91 (29), 30 (81). — **IR (KBr)** in addition to peaks for complexed Cp*: ν = 1550, 1525, 1305, 812.

**[(η⁵-Cp*)Co:S₄]₄:** 0.9 mmol 1b was dissolved in 80 ml diethylether and 0.9 mmol yellow sulfur were added. After stirring for 12 h at r.t. the reaction mixture was brought to dryness and chromatographed on Al₂O₃. With ether a small amount of brown material could be eluated which was discarded. The main product was eluated as a single black zone with THF. Evaporation of the solvent yielded 0.2 mmol [[(η⁵-Cp*)Co:S₄]₄] (44%) as a black powder.

**MS** (70 eV, El): m/z = 904 (100) [M⁺], 770 (63), 601 (61), 452 (25), 16 (25), 119 (66).

**17**: 0.43 mmol 1b was dissolved in 30 ml diethyl ether and 1.28 mmol di-t-butyl-diazomethane was added in one batch at 0 °C. After the addition a color change from brown to green was observed. No gas evolution could be detected. Stirring was continued for 1 h at ambient temperature after which all volatiles were removed in vacuum. The semicrystalline, oily residue was dissolved in a minimum amount of ether and filtered. The same amount of CH₃CN was added and the solution cooled to −10 °C giving 0.31 mmol brown crystals of 17 (72.1%).

**MS** (70 eV, El): m/z = 696 (100) [M⁺], 542 (32), 402 (63), 386 (100), 329 (15), 57 (73). — **IR (KBr):** in addition to peaks for complexed Cp*: ν = 1380,
ether, filtered and cooled to 0 °C, giving 0.4 mmol \textbf{18} (69%) as brown rod-shaped crystals.

**MS** (70 eV, EI): \( m/z = 554 \ (12) \ [\text{M}^+-166]. \) 386 (19), 125 (100), 69 (43), 28 (98). – IR (KBr): in addition to peaks for complexed \( \text{Cp}^+ \): \( \nu = 1515 \ (w), \) 1220 (s). – \(^1\text{H} NMR\) (400 MHz, \([\text{D}_6]\)benzene, 27 °C): \( \delta = 111.06, \) 46.28, 45.73, 39.09, 34.71, 3.10.

\[ C_{38}H_{66}N_4\text{Co}_2 \ (696,84) \]
Calcld C 65.50 H 9.55%.

Found C 62.20 H 9.51%.

\textbf{18}: 0.58 mmol \textbf{1b} was dissolved in 30 ml diethyl-ether and 1.37 mmol 2-diazo-1,1',3,3'-tetramethylcyclohexane was added at 0 °C in one batch. Immediately after the addition a color change from brown to green was observed. No gas evolution was detected. Stirring was continued for an additional hour at ambient temperature after which all volatiles were removed in vacuum. The crystalline residue was dissolved in a minimum amount of

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