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Synthesis and fluxionality of the mixed metal *syn*-(μ -cycloheptatriene) complex [CpCo(C₇H₈)RhCp]

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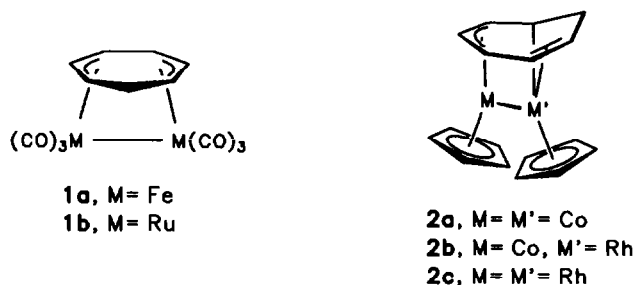
Abstract

The mixed metal μ -cycloheptatriene complex [CpCo(μ -(η^3 : σ^1 , η^2 -C₇H₈))RhCp] (**2b**) has been made from [CpRh(η^4 -C₇H₈)] (**4b**) and [CpCo(C₂H₄)₂] (**5a**). In solution **2b** has a dynamic structure with a *syn*- μ -[η^3 (Co): σ^1 , η^2 (Rh)] coordinated cycloheptatriene bridge.

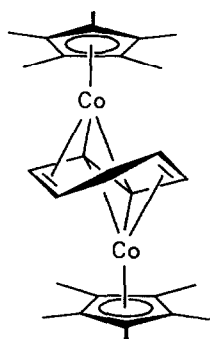
In dinuclear transition metal complexes cycloheptatriene can adopt a variety of coordination modes [1]. The symmetrical *syn*- μ -(1-3- η :4-6- η) bis-enyl type coordination was established for [((CO)₃Fe)₂(μ -C₇H₈)] (**1a**) [2] in the solid state by a X-ray crystal structure analysis [3]. From the temperature independent ¹H and ¹³C NMR spectra it was shown that the rigid *syn*- μ -(η^3 : η^3) coordination is retained in solution [3,4]. The same structure was assumed for the ruthenium analog [((CO)₃Ru)₂(μ -C₇H₈)] (**1b**) [5]. In contrast, the cycloheptatriene bridge in [(CpRh)₂(μ -C₇H₈)] (**2c**) is highly flexible in solution [6]. By variable temperature NMR spectroscopy the dynamic process was identified as involving the interconversion of the two enantiomers with a *syn*- μ -(η^3 : σ^1 , η^2)-coordinated cycloheptatriene. Recently we reported the syntheses and structures of the dicobalt complexes [(C₅R₅Co)₂(μ -C₇H₈)] (**2a**, R = H; **3**, R = Me) [7]. The pentamethylcyclopentadienyl derivative **3** has the very unusual *anti*- μ -(η^4 : η^4) coordination geometry for the cycloheptatriene, both in solution and in the solid state. The NMR spectra of **2a** are consistent with a fluxional *syn*- μ -(η^3 : σ^1 , η^2) cycloheptatriene bridge, as in **2c**. A second, higher energy dynamic process involves interconversion of the two CpCo groups in **2a**. This can be attributed to an almost free rotation of the cycloheptatriene on top of the (CpCo)₂ backbone.

We were interested in preparing unsymmetrical derivatives [(ML_n)(M'L'_n)(μ -C₇H₈)] (M ≠ M' or L_n ≠ L'_n). Unfortunately no dinuclear complexes with both a CpCo and a Cp*Co group in the molecule could be obtained [7]. In order to synthesize the mixed metal CoRh complexes the mononuclear cycloheptatriene complex [CpRh(η^4 -C₇H₈)] (**4b**) was treated with sources of CpCo and Cp*Co fragments. From the reaction with the Jonas reagent [CpCo(C₂H₄)₂] (**5a**) the heterobimetallic complex [CpCo(μ -(η^3 : σ^1 , η^2 -C₇H₈))RhCp] (**2b**) was obtained in ca. 30% yield. With [Cp*Co(C₂H₄)₂] (**5b**) the main reaction pathway involved exchange of the cycloheptatriene ligand, leading mainly to [Cp*Co(η^4 -C₇H₈)], with concurrent decomposition of the rhodium complex.

At room temperature, only three signals are observed for the olefinic CH groups of the cyclohepta-

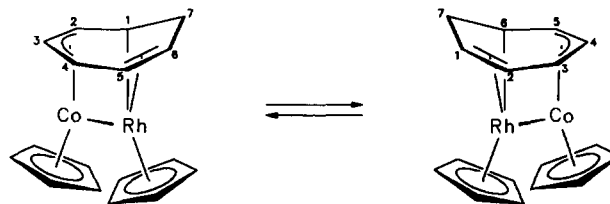


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triene in both the ^1H and ^{13}C NMR spectra of **2b**, indicating the presence of an effective plane of symmetry in the cycloheptatriene ligand. As in **2a** and **2c**, the ^{13}C resonances of the cycloheptatriene carbon atoms C-1 and C-6 (*i.e.* the carbon atoms in the α -positions to the methylene group) are at rather high field (δ 1.2, compared with δ 2.6 in **2a** [7] and δ 2.0 in **2c** [6]) and show a large (11 Hz) coupling to the ^{103}Rh nucleus. This can be taken as an indication of a dynamic *syn*- μ - $[\eta^3(\text{Co}):\sigma^1,\eta^2(\text{Rh})]$ coordination of the bridging ligand. The dynamic process involves interchanges of the carbon atoms C-1 with C-6, C-2 with C-5 and C-3 with C-4, along with the hydrogen atoms bonded to them (Scheme 1). The average ^{103}Rh - ^{13}C coupling constant indicates that the cycloheptatriene is σ^1,η^2 -bonded to the CpRh rather than to the CpCo group, as expected from the greater strength of the C-Rh σ -bond.

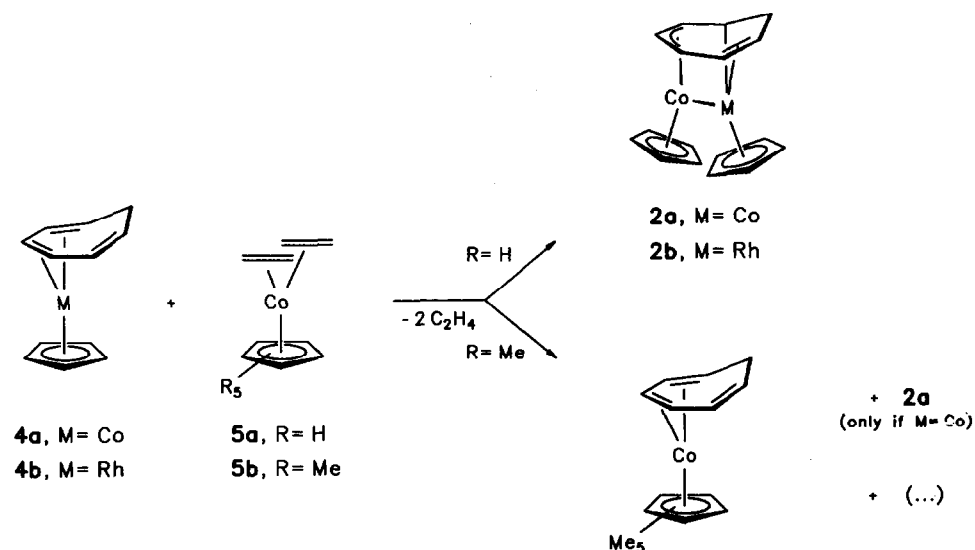


Scheme 1.

The ^1H NMR spectrum of **2b** is virtually independent of temperature in the range $200\text{ K} \leq T \leq 390\text{ K}$. In the ^{13}C NMR spectrum at 200 K the resonances at δ 60.1 and 55.5 are slightly, the signal at δ 1.5 is substantially broadened, indicating that the enantiomerisation is beginning to slow down on the NMR time scale. Assuming similar chemical shift differences between the individual carbon atoms of the cycloheptatriene ligands a comparison can be made with **2a** (no broadening of the four ^{13}C NMR signals of the cycloheptatriene ring) and **2c** (a close-to-limiting ^{13}C NMR spectrum with seven resonances for the cycloheptatriene at 200 K). Hence it can be assumed that the activation barrier for the low energy dynamic process (*i.e.* the enantiomerisation of the *syn*- μ - $(\eta^3:\sigma^1,\eta^2)$ structure) increases in the series **2a** \rightarrow **2b** \rightarrow **2c**. The high energy process (which can be attributed to the full 'rotation' of the cycloheptatriene) is thermally accessible only in the case of the dicobalt complex **2a**.

1. Experimental details

All reactions were carried out under prepurified nitrogen by use of Schlenk techniques. Solvents were



dried by conventional methods and stored under nitrogen. Complexes [CpCo(C₂H₄)₂] (**5a**) [8] and [Cp⁺Co(C₂H₄)₂] (**5b**) [9] were prepared by published methods. NMR spectra were recorded on a Bruker AC-200 instrument (200.1 for ¹H, 50.3 MHz for ¹³C). Electron impact mass spectra were obtained using a Finnigan 8230 instrument operating at 70 eV. Microanalyses were performed by the Microanalytisches Labor Beller, Göttingen.

1.1. Improved synthesis of [CpRh(η⁴-C₇H₈)] (**4b**)

The complex [CpRh(C₂H₄)₂] [10] (620 mg, 2.76 mmol) was refluxed with *ca.* 10 ml of cycloheptatriene for 3.5 h. All volatiles were then removed *in vacuo*, and the yellowish-orange oily residue was dissolved in light petroleum (*ca.* 20 ml). Complex **5a** crystallized out from this solution as orange microcrystals (420 mg, 58%) at -20°C. ¹H NMR (C₆D₆): δ 5.9 (tq, 1H, C₇H₈); 5.2 (m, 1H, C₇H₈); 5.10 (d, *J*(RhH) = 1.0 Hz, 5H, Cp); 4.8 (m, 1H, C₇H₈); 4.6 (m, 1H, C₇H₈); 3.7 (m, 1H, C₇H₈); 3.6 (m, 1H, C₇H₈); 2.0 (m, 1H, C₇H₈); 1.1 (m, 1H, C₇H₈). ¹³C{¹H} NMR (C₆D₆): δ 129.0 (d, *J*(RhC) = 0.04 Hz, CH); 125.7 (d, *J*(RhC) = 0.04 Hz, CH); 84.7 (d, *J*(RhC) = 6.0 Hz, CH); 83.6 (d, *J*(RhC) = 5.0 Hz, Cp); 78.8 (d, *J*(RhC) = 6.0 Hz), 51.2 (d, *J*(RhC) = 18.0 Hz, CH); 47.4 (d, *J*(RhC) = 16.0 Hz, CH); 32.1 (d, *J*(RhC) = 15.0 Hz, CH₂).

1.2. Synthesis of [syn-CpCo{μ-(η³:σ¹,η²-C₇H₈)RhCp}] (**2b**)

A mixture of 340 mg of (1.31 mmol) [CpRh(η⁴-C₇H₈)] (**4b**) and 236 mg (1.31 mmol) of [CpCo(C₂H₄)₂] (**5a**) in *ca.* 40 ml of light petroleum was heated at 40–60°C for 1 h. The solvent was then removed *in vacuo* and the residue redissolved in toluene (10 ml). An equal volume of light petroleum was added, and the solution cooled to -20°C to give a brown solid precipitate, which was collected and recrystallised from a small volume of toluene to give 140 mg (28%) of **2b** as brown microcrystals. Mp. 190°C (dec.). Anal. Found: C, 52.95; H, 4.92. C₁₇H₁₈CoRh (384.168) calc.: C, 53.12; H, 4.68%. ¹H NMR (C₆D₆): δ 5.22 (d, *J*(RhH)

= 0.7 Hz, 5H, Cp); 4.74 (s, 5H, Cp); 4.2 (m, 2H, C₇H₈); 3.9 (m, 2H, C₇H₈); 2.4–2.0 (3 m, 4H, C₇H₈, CH₂). ¹³C{¹H} NMR in C₆D₆, 298 K: δ 88.0 (d, *J*(RhC) = 3.5 Hz, CpRh); 79.7 (CpCo); 59.7 (C-3, C-4); 55.4 (d, *J*(RhC) = 3.5 Hz, C-2, C-5); 39.1 (d, *J*(RhC) = 5.0 Hz, CH₂); 1.2 (d, *J*(RhC) = 11.0 Hz, C-1, C-6); in THF-*d*₈, 200 K: δ 88.2 (d, *J*(RhC) = 4 Hz, CpRh); 80.1 (CpCo); 60.1 (br, C-3, C-4); 55.5 (d, br, *J*(RhC) = 4 Hz, C-2, C-5); 39.3 (d, *J*(RhC) = 5 Hz, CH₂); 1.5 (br, C-1, C-6). MS: *m/z* 384 (100% rel. int., M⁺), 318 (97, [M - CpH]⁺), 259 (28, [CpRh(C₇H₇)]⁺), 240 (37), 233 (58, [Cp₂Rh]⁺), 189 (18, [Cp₂Co]⁺), 181 (25), 168 (27, [CpRh]⁺), 124 (6, [CpCo]⁺), 103 (7, Rh⁺), 91 (8, [C₇H₇]⁺), 59 (5, Co⁺).

Acknowledgements

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