

Evidence for Transmetalation of Zirconacyclopentadiene to Cobalt Complex

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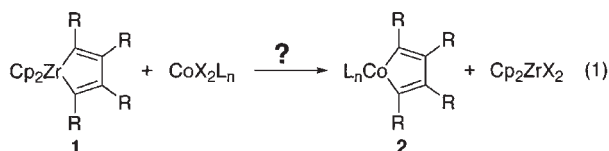
Transmetalation reaction of zirconacyclopentadienes with cobalt(III) complex, $\text{CpCo}(\text{PPh}_3)_2$, proceeded to afford (cyclobutadiene)cobalt(I) complexes, $\text{CpCo}(\text{C}_4\text{R}_4)$. The structure of one of the cobalt complexes was verified by X-ray structure analysis.

Transmetalation of zirconacycles to other metal species is of increasing importance in organic synthesis. Since we have reported the first example of transmetalation from zirconacyclopentadienes to Cu,¹ Ni,² Li,³ and Zn,⁴ both stoichiometric and catalytic reactions have been rapidly developed illustrating their growing importance in organic synthesis.⁵

In order to study the scope of such transmetalation reactions of zirconacyclopentadienes with respect to other transition metal salts, we decided to investigate their reactions with cobalt compounds.

We envisioned that this approach could grant us a new access to cobaltacyclopentadienes that are useful intermediates in organic synthesis for the preparation of arenes and heteroarenes derivatives.⁶ Herein, we would like to report our results and the evidence for transmetalation of zirconacyclopentadienes (**1**) to a cobalt complex.

We assumed that the reaction of **1** with cobalt complexes would proceed in a similar manner to previously observed reactions, e.g. Ni, as shown in eq 1 and will give rise to cobaltacyclopentadiene (**2**).



Initially, we carried out reactions of tetraarylzirconacyclopentadienes. The results are shown in eq 2. A typical procedure is as follows: to a toluene solution of tetraphenylzirconacyclopentadiene (**1a**), which was prepared in situ by the reaction of Cp_2ZrCl_2 (1.0 mmol) and 2 eq of *n*-BuLi (Negishi reagent) with 2 eq of diphenylacetylene (2.0 mmol),⁷ was added $\text{CpCo}(\text{PPh}_3)_2$ (1 mmol) at room temperature. The mixture was stirred at 110 °C for 3 days under nitrogen atmosphere. After cooling, the solvent was removed under reduced pressure and the crude product was separated by column chromatography on silica gel (10/1 hexane/ether). However, instead of **2**, (cyclobutadiene)cobalt(I) complex, $\text{CpCo}(\text{C}_4\text{Ph}_4) \cdot \text{C}_6\text{H}_6$ (**3a**) was obtained in 24% yield after recrystallization from a mixture of benzene/hexane. The ¹³C NMR spectrum in C_6D_6 of **3a** showed signals which were consistent with previously reported data.^{9,10} Furthermore, the structure of **3a** was confirmed by X-ray structure analysis, as shown in Figure 1.¹¹ However, our data were obtained

as monoclinic crystals, whereas the published ones were as triclinic crystals.¹²

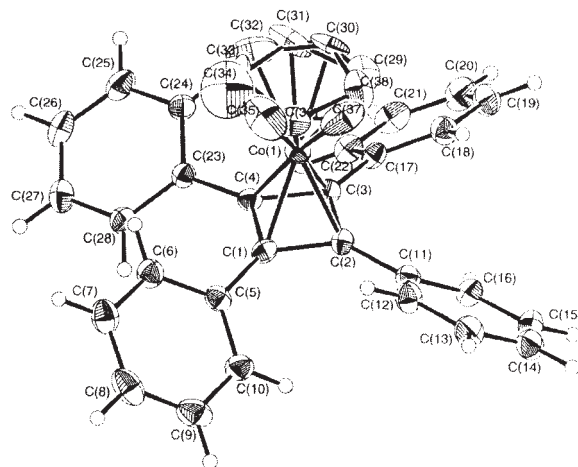
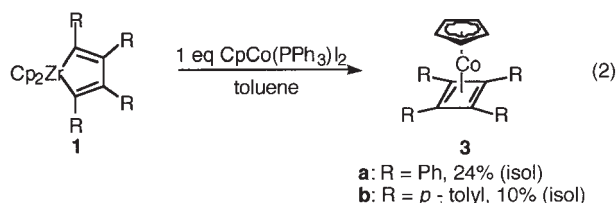


Figure 1. ORTEP drawing of **3a**. Benzene molecule was omitted. Some selected interatomic distances (Å) and angles (deg): Co–C(1) 1.978(3), Co–C(2) 1.972(3), Co–C(3) 1.978(3), Co–C(4) 1.963(3), C(1)–C(2) 1.463(3), C(2)–C(3) 1.455(4), C(3)–C(4) 1.458(3), C(1)–C(4) 1.463(4), C(1)–C(2)–C(3) 90.8(2), C(2)–C(3)–C(4) 89.6(2), C(1)–C(4)–C(3) 90.6(2), C(2)–C(1)–C(4) 89.1(2).

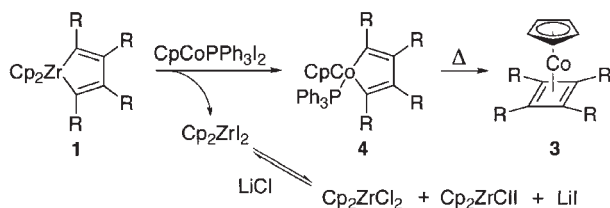
Complex **3b** with tolyl groups was prepared by using the same strategy and its ¹³C NMR spectrum in C_6D_6 showed characteristic signals at 74.50 and 83.02 ppm of a cyclopentadienyl ligand and a cyclobutadiene moiety, respectively.¹³

In order to understand the process during the transmetalation of zirconacyclopentadiene with cobalt(III) complex, the reaction mixture was monitored by NMR and the change of shifts for cyclopentadienyl signals of organozirconium compound was followed. The NMR analysis of aliquots of the reaction mixture revealed only signals of starting materials and that of product **3a**. Moreover, Cp signals belonging to zirconium species were observed at 114.63, 115.34 and 115.69 ppm which can be assignable to Cp_2ZrI_2 , Cp_2ZrClI and Cp_2ZrCl_2 . Its presence indicates a transfer of iodine from cobalt to zirconium and hence the transmetalation of the Zr–C bond to the Co–C bonds.

The formation of cobalt complexes **3** from zirconacyclopent-

tadienes can be explained as shown in Scheme 1. Zirconacyclopentadiene **1** reacts with $\text{CpCo}(\text{PPh}_3)_2\text{I}_2$ at 110°C to give **4** with concomitant formation of Cp_2ZrI_2 . High reaction temperature induces rapid rearrangement of **4** into **3**. Such a type of the rearrangement has been observed by Yamazaki and Hagihara.¹⁴ Due to the presence of 2 eq of LiCl in the reaction mixture, Cp_2ZrCl_2 and Cp_2ZrClI were formed by halogen exchange process from Cp_2ZrI_2 . In fact, addition of LiCl to Cp_2ZrI_2 in afforded Cp_2ZrCl_2 and Cp_2ZrClI .

Although, the phosphorus signal of the intermediate **4** was not observed during monitoring of the reaction mixture, **4** is the most likely intermediate with respect to the above-obtained results. In addition, the rate-determining step is the transmetalation, which is considerably slower than the metalacyclopentadiene-cyclobutadiene complex rearrangement.



In addition, we also carried out the reaction of tetraethylzirconacyclopentadiene with $\text{CpCo}(\text{PPh}_3)_2\text{I}_2$ in THF at 75°C . The reaction mixture was again monitored by NMR, and we observed disappearance of signals at 110.10 and 86.92 ppm, which account for signals of Cp rings of tetra-ethylzirconacyclopentadiene and $\text{CpCo}(\text{PPh}_3)_2\text{I}_2$, respectively, and appearance of new peaks at 85.88 and 81.72 ppm, which should belong to unsaturated systems attached to Co(I) metal center. Unfortunately, we were not able to isolate the products to unequivocally characterize them.

In conclusion, we demonstrated here the evidence for transmetalation of zirconacyclopentadienes to cobalt complexes.

References and Notes

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- 11 Crystal data for **3a**: $\text{C}_{39}\text{H}_{31}\text{Co}$, $M = 558.61$, monoclinic, space group $P2_1$; $a = 11.4741(9)$, $b = 11.427(1)$, $c = 11.503(1)$ Å; $\beta = 106.580(3)^\circ$; $V = 1445.4(2)$ Å³; $Z = 2$; $D_c = 1.283$ g cm⁻³; No. of reflections measured = 6153; No. of reflections with $I > 2.0\sigma(I) = 5203$; $R = 0.044$, $R_w = 0.054$. A cyclopentadienyl ring was found to be disordered, and this was resolved into two half-occupancy orientations. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-183109. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Instruction for depositing the crystallographic data is available on the Web at <http://www.ccdc.cam.ac.uk/conts/depositing.html>.
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