

Biscobaltocenium Ions – Synthesis and Properties

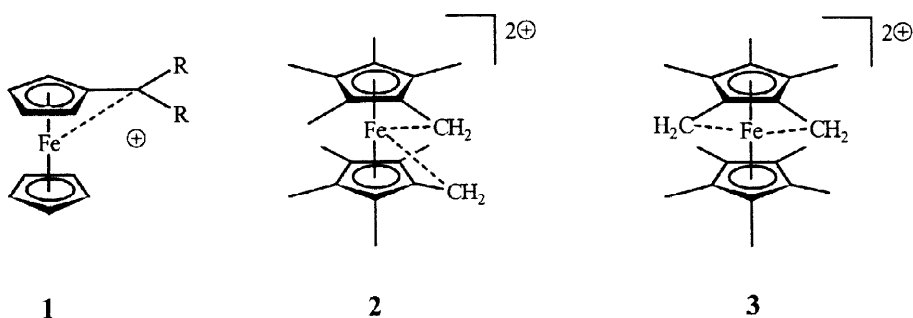
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The synthesis of the first binuclear biscobaltocenium ions in solution and their identification by ^{13}C NMR data is reported. © 1998 Elsevier Science Ltd. All rights reserved.

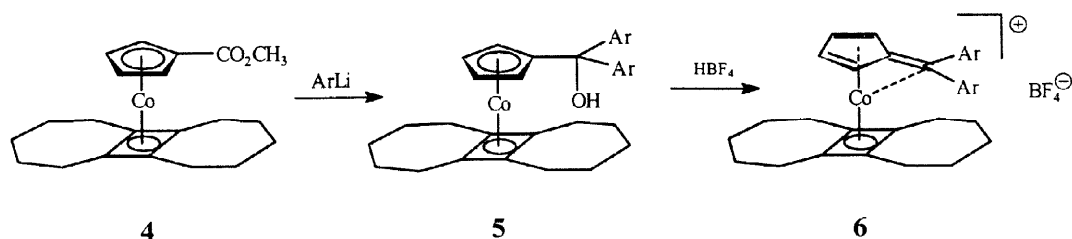
A metal may stabilize an α -carbocationic center. The most prominent case is the ferrocenylcarbocation (**1**) which has been investigated extensively.^{1–4} However, only a few cases are known in which a metal stabilizes two carbocationic centers as in generation of **2** and **3**.⁵ Also, very few cases are known in which two



carbocationic centers are stabilized by two metal centers,⁶ while there are many examples for carbocations.⁷

Our investigations on the ability of an (η^4 -cyclobutadiene)cobalt fragment to stabilize an α -carbocationic center⁸ (Scheme 1) led us to explore ways to generate systems in which two carbocationic centers are stabilized by two metal fragments.

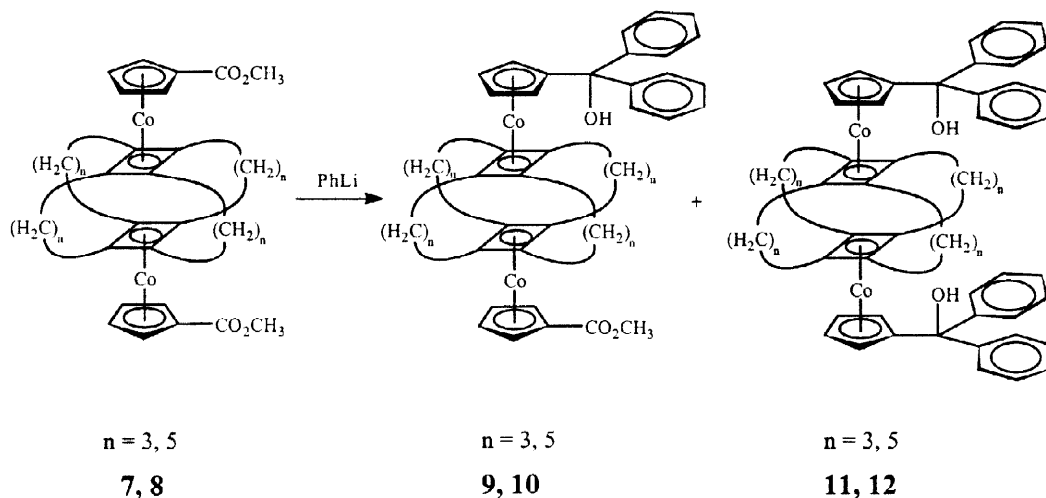
Scheme 1



Ar = C_6H_5 (a), $\text{C}_6\text{H}_4\text{CH}_3$ (b), $\text{C}_6\text{H}_4\text{F}$ (c)

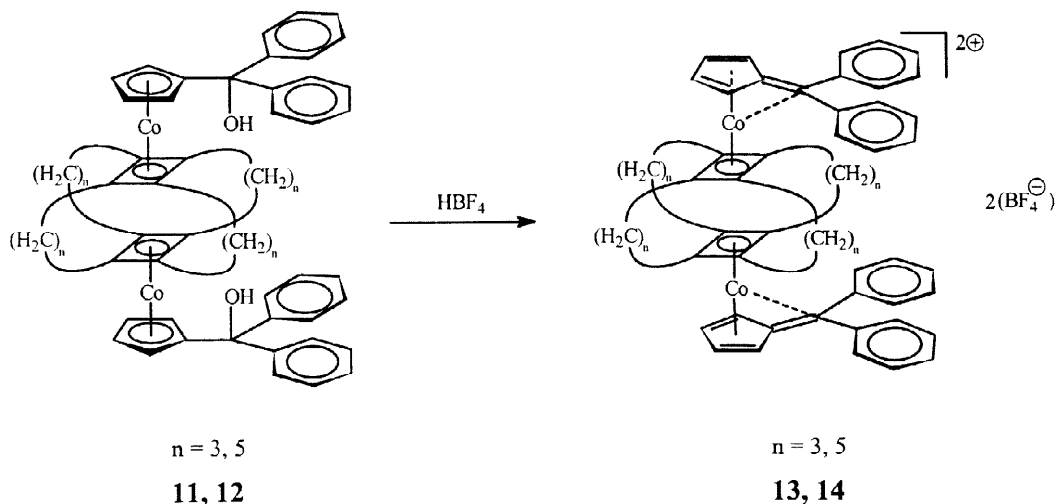
In this paper we demonstrate that the sequence outlined in Scheme 1 can be applied to cyclophanes in which two fragments, related to **6**, are connected in close proximity.

The diesters **7** and **8** were available by reaction of $(\eta^4\text{-cycloocta-1,5-diene})(\eta^5\text{-(methoxycarbonyl-cyclopentadienyl)cobalt}$ with 1,6-cyclodecadiyne or 1,8-cyclotetradecadiyne, respectively.⁹ Treatment of **7** and **8** with an excess of phenyllithium afforded a mixture of the orange colored



monoalcohols (**9, 10**)¹⁰ and dialcohols (**11, 12**)¹¹ (Scheme 2). Both mixtures could be separated by silica gel chromatography ((cyclohexane/ethyl acetate 20:1). Treatment of a saturated solution of either the monoalcohols or the dialcohols in CH_2Cl_2 with HBF_4 at 223 K afforded a deep blue solution. The strong bathochromic shift which was observed is demonstrated in Figure 1 by comparison of the UV/Vis spectra of **11** and **13** in methylene chloride.

Scheme 3



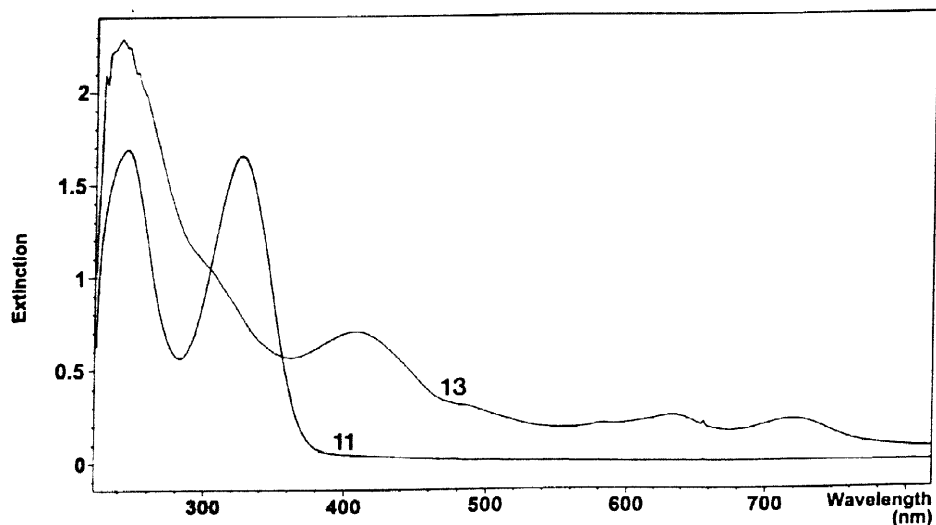


Figure 1. UV/Vis spectra of **11** and **13** in CH_2Cl_2

The relative instability of the dications **13**¹² and **14** did not allow their isolation.¹² However, their spectral properties are similar to those of **6**. The most prominent change is found for the ¹³C signal of the α -carbon atom which was recorded for **11**¹¹ at $\delta = 108.5$ and for **13**¹² at 174.8. The values obtained for **12**¹¹ and **14**¹² are $\delta = 109.6$ and 170.3, respectively. The differences in the ¹³C NMR chemical shifts of the α -carbon atom in going from the alcohol to the carbenium ion stage ($\Delta\delta$ (**11** \rightarrow **13**) = 66.3, $\Delta\delta$ (**12** \rightarrow **14**) = 63.3) are close to those reported for the α -carbon atom of **5a** (108.8) and **6a** (170.6).⁸

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- ¹⁰ **9**: ¹H NMR (300 MHz; CDCl₃): δ = 7.32-7.15 (m, 10 H), 4.99-4.97 (pt, 2H), 4.63-4.62 (pt, 2H), 4.43-4.42 (pt, 2 H), 4.36-4.35 (pt, 2 H), 3.75 (s, 3 H), 3.02 (s, 1 H), 2.20-2.11 (m, 16 H), 1.67-1.59 (m, 8 H). ¹³C NMR (50.3 MHz; CDCl₃): δ = 168.6, 148.1, 127.6, 127.0, 126.6, 107.6, 85.2, 84.0, 83.7, 82.2, 80.7, 79.9, 78.2, 77.3, 51.2, 30.1, 29.8, 27.5. UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 306 nm (4.6).
- 10**: ¹H NMR (200 MHz; CDCl₃): δ = 7.33-7.14 (m, 10 H), 5.01-4.98 (pt, 2 H), 4.63-4.60 (pt, 2 H), 4.47-4.45 (pt, 2 H), 4.38-4.36 (pt, 2 H), 3.75 (s, 3 H), 3.02 (s, 1 H), 2.16 (m, 16 H), 1.25 (m, 24 H). ¹³C NMR (75.4 MHz; CDCl₃): δ = 168.3, 147.8, 127.4, 126.9, 126.4, 107.5, 85.0, 83.9, 83.5, 82.1, 80.6, 79.8, 78.0, 76.6, 51.0, 29.8, 29.7, 29.6, 27.4, 26.4. UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 274 nm (4.59), 302 (3.49).
- ¹¹ **11**: ¹H NMR (200 MHz; CDCl₃): δ = 7.34-7.15 (m, 20 H), 4.42-4.40 (pt, 4 H), 4.36-4.34 (pt, 4 H), 3.02 (s, 2 H), 2.20-2.15 (m, 16 H), 1.67-1.56 (m, 8 H). ¹³C NMR (50.3 MHz; CDCl₃): δ = 148.0, 129.7, 128.8, 128.3, 108.5, 84.5, 81.6, 80.8, 78.1, 30.5, 28.9. UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 246 nm (4.25), 328 (4.25).
- 12**: ¹H NMR (300 MHz; CDCl₃): δ = 7.47-7.15 (m, 20 H), 4.46-4.45 (pt, 4 H), 4.38-4.37 (pt, 4 H), 3.02 (s, 2 H), 2.18-2.04 (m, 16 H), 1.21 (m, 24 H). ¹³C NMR (75.4 MHz; CDCl₃): δ = 148.1, 128.4, 127.3, 126.5, 106.9, 83.4, 80.6, 79.4, 78.4, 29.8, 29.6, 27.3. UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 274 nm (4.70), 300 (3.40).
- ¹² **13**: ¹H NMR (300 MHz; CDCl₃; 223K): The broad signals (> 2 ppm) could not be assigned. ¹³C NMR (75.4 MHz; CDCl₃; 223K): δ = 174.8, 139.6, 133.6, 132.5, 129.3, 110.3, 97.6, 88.2, 84.7, 29.5, 28.1. UV/Vis (CH₂Cl₂): λ_{max} = 242 nm, 306, 408, 486, 632, 718.
- 14**: ¹H NMR (300 MHz; CDCl₃): The broad signals (> 2 ppm) could not be assigned. ¹³C NMR (75.5 MHz; CDCl₃; 223K): δ = 170.3, 139.7, 133.6, 132.5, 129.4, 110.8, 97.9, 88.3, 87.2, 29.6, 29.2, 28.5. UV/Vis could not be recorded at room temperature.