Comparison between a Diarylferrocenylmethylium Ion and Its Isolobal Cobalt Species: Similarities and Differences

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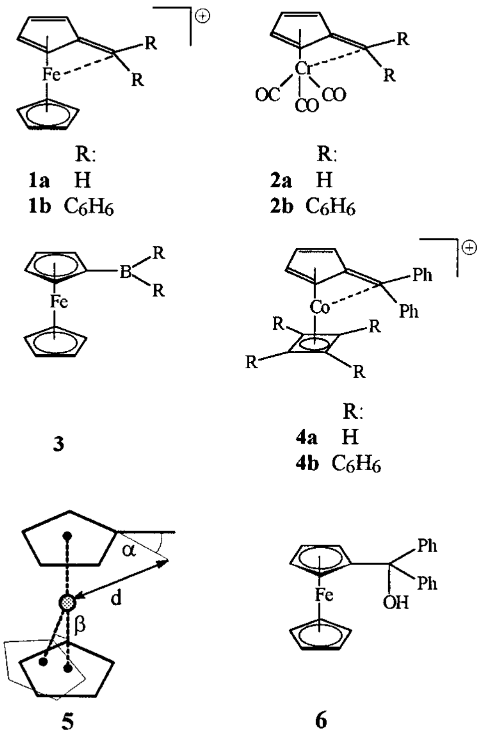
Reaction of {(1,2,8,9-η)-tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene}{η^5-(methoxycarbonyl)-cyclopentadienyl}cobalt (**9**) with either 2 mol of arylmagnesium bromide or aryllithium and subsequent hydrolysis yields the alcohols {(1,2,8,9-η)tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene}-{η^5-(diarylhydroxymethyl)cyclopentadienyl}cobalt (**13a**−**c**). The treatment of the yellow colored alcohols **13a**−**c** with HBF_4 in ether affords the tetrafluoroborates of the violet colored carbocations **14a**−**c**. Investigations of single crystals of **14b** by means of the X-ray technique show a displacement of the C_1-C_{exo} bond by $\alpha = 10.8°$ toward the metal and a pronounced bond alternation in the fulvene moiety. The bending of C_1-C_{exo} is considerably larger than in the corresponding alcohol **13b** ($\alpha = 2.5°$). The interaction between the exo-carbon and the metal in **14b** is further substantiated by comparison of the ^{13}C-NMR chemical shift of **14b** with **13b** ($\Delta\delta = -65$ ppm). The comparison of the data obtained for **14b** with those of diphenylferrocenylcarbenium ion **1b** suggests a stronger bonding between metal and fulvene moiety in **1b** as compared to **14b**. These results are substantiated by the results of ab initio calculations on **1b** and **4a** which show a smaller positive charge at the exo-carbon in **4a** than in **1b** and a stronger bond index between the exo-carbon and the metal in **1b** as compared to **4a**.

Introduction

The remarkable stability of ferrocenylcarbocations (**1**) (Chart 1) has been demonstrated extensively by a number of structural studies[1−3] and physicochemical measurements.[4,5] It has been agreed that the stability of **1** is due to a sizable interaction of the exo-carbon of the fulvene moiety and the metal. This could be traced back to the interaction of the LUMO of the fulvene moiety with the $3d_{z^2}$ orbital of the metal.[6]

There are many studies of systems like **1**[1] and some studies of the isolobal neutral systems **2**[7,8] and **3**,[9] but only one investigation is known to us of a substituted (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt carbocation system. Seyferth and Merola have prepared **4b**,[10] whose ^{13}C NMR spectrum indicates an interaction between the exo carbon and the metal. In this paper we present solid evidence for an interaction between cobalt and the cationic center and discuss the isolobal relation between the $CpFe^+$ and the $CbCo^+$ fragments (Cp = η^5-cyclopentadienyl, Cb = η^4-cyclobutadienyl).

Chart 1



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Scheme 1

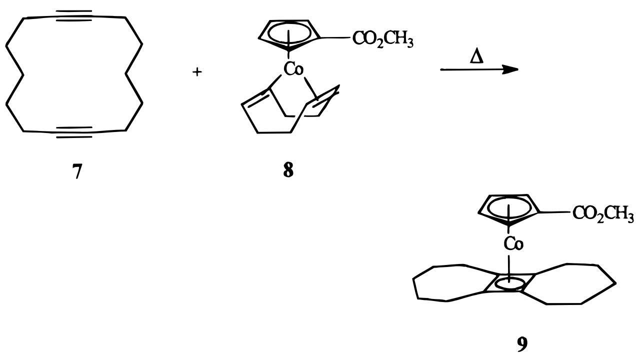

Table 1. Conditions for the Formation and Solubilities of the Cationic Compounds 14a–c

compd	HBF$_4$ in ether	CF$_3$COOH	HPF$_6$ in water	HClO$_4$ in water
14a (R = H)	precipitate	solution	solution	decomposn
14b (R = CH$_3$)	precipitate	solution	solution	solution
14c (R = F)	solution	solution	decomposn	decomposn

Results and Discussion

{(1,2,8,9-η)-Tricyclo([7.5.0.0^{1,7}]tetradeca-1,8-diene}-{η^5-(diarylhydroxymethyl)cyclopentadienyl}-cobalt. The reason for the lack of investigations on the cobalt systems might be the comparatively difficult access to systems such as **4**. Our recent work on the reaction between cyclic diynes and CpCoL$_2$ species has resulted in easy access to {(1,2,8,9-η)-tricyclo[7.5.0.0^{1,7}]-tetradeca-1,8-diene}{η^5-(methoxycarbonyl)cyclopentadienyl}cobalt (**9**) as a suitable precursor for cationic cobalt species as shown in Scheme 1.[11] The synthesis of this carboxylic ester commenced with an intramolecular [2 + 2] cycloaddition of the two triple bonds in cyclotetradeca-1,8-diyne (**7**),[12] mediated by the cobalt of **8,** to afford **9** in 21% yield. To synthesize the unsubstituted cobaltocenium compound **11**, **9** can easily be converted into the primary alcohol {(1,2,8,9-η)-tricyclo-[7.5.0.0$^{1.7}$]tetradeca-1,8-diene}{η^5-(diarylhydroxymethyl)-cyclopentadienyl}cobalt (**10**) via reduction with LiAlH$_4$ in 96% yield, followed by hydrolysis, as shown in Scheme 2. After treatment with acid only pentafulvene **12** could be isolated as a resulting product of the decomposition of **11**. We solved the problem of the obvious instability of **11** by using para-substituted benzene rings to stabilize the carbocationic center. The reaction of the latter with aryllithium or Grignard reagents resulted in the formation of the tertiary alcohols with R = hydrogen, methyl, and fluorine (**13a–c)** in 57–87% yield after hydrolysis. We also tried the syntheses of the methoxy-, thiomethyl-, trifluoromethyl-, and *N,N*-dimethyl-substituted compounds but observed only the correspondig fulvenes or decomposition of the starting material.

{(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene}-{η^5-(diarylhydroxymethylium)cyclopentadienyl}cobalt Salts. Treatment of the yellow colored alcohols, dissolved in ether, with different acids led to an immediate change to a deep blue-violet colored solution. As shown in Table 1, the formation of the {(1,2,8,9-η)-tricyclo[7.5.0.0$^{1.7}$]tetradeca-1,8-diene}{η^5-(diarylmethylium)cyclopentadienyl}cobalt compounds **14a–c** could be observed, but only in case of the tetrafluoroborates **14a**,**b** was a dark violet solid precipitated that could be filtered and recrystallized. In Figure 1 the electron absorption spectrum of **14b** is compared with that of **13b**, demonstrating a considerable bathochromic shift of the long wavelength absorption band. The shift is due to the more extended π-system in **14,** compared to **13**. As expected for carbocationic compounds, **14a**,**b** could be easily reduced by means of cyclovoltammetry. Figure 2 shows the potentials, which could be interpretated as reversible one-electron oxidations.

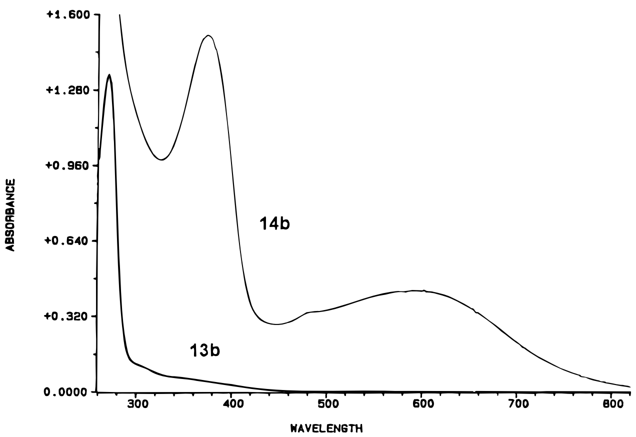

Figure 1. Comparison between the electron absorption spectra of **13b** and **14b** in CH$_2$Cl$_2$.

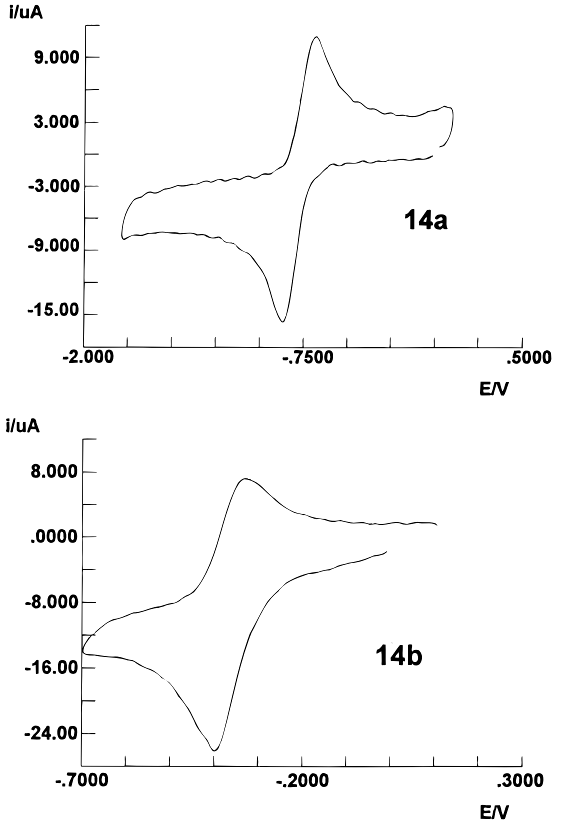

Figure 2. Cyclovoltammograms of **14a** (top) and **14b** (bottom) in CH$_2$Cl$_2$ vs SCE, at 272 K, scan rate 200 mV (s, *E* = −785 mV (**14a**) and −368 mV (**14b**)).

To elucidate the structural parameters of the cationic compounds, single crystals of **14b** were grown and investigated by means of X-ray crystallography. The

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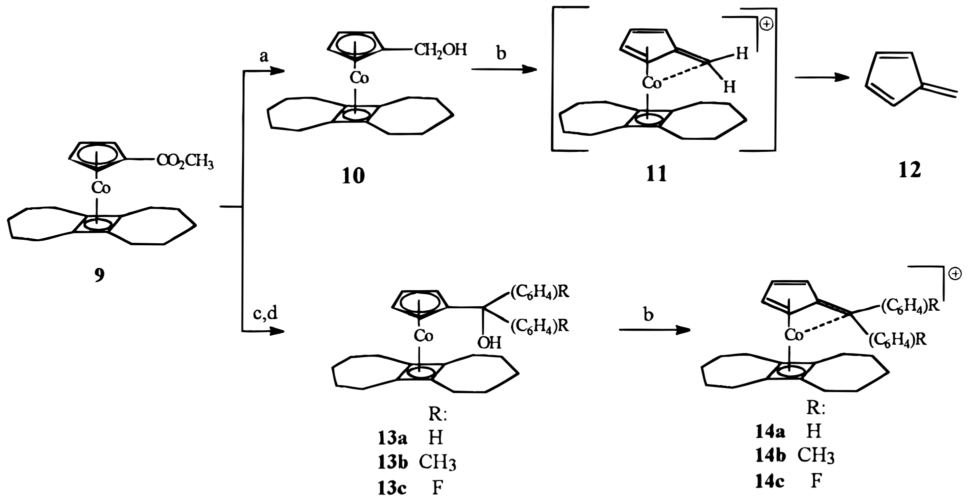
Scheme 2[a]



[a] Key: (a) $LiAlH_4$/THF, H_2O; (b) HBF_4/ether; (c) PhMgBr, H_2O; (d) $Li(C_6H_4)R$, H_2O.

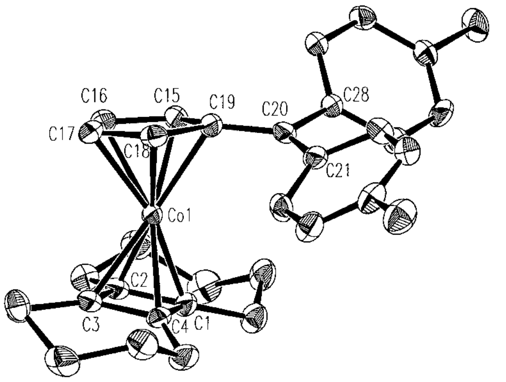


Figure 3. ORTEP drawing of **14b**. The core atoms are labeled. Ellipsoids are at the 50% probability level, and hydrogens atoms have been omitted for the sake of clarity.

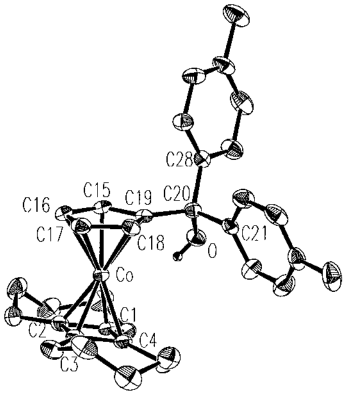


Figure 4. ORTEP drawing of **13b**. The core atoms are labeled. Ellipsoids are at the 50% probability level, and hydrogens atoms have been omitted for the sake of clarity.

resulting structure is shown in Figure 3. The most striking features of **14b** are a displacement of the C_1-C_{exo} bond by α = 10.8° (as defined in **5**[6]) toward the metal and pronounced bond alternation in the fulvene moiety. The bending in **14b** is considerably larger than in alcohol **13b** (α = 2.3°), from which we have also grown single crystals. Figure 4 shows the structure of the alcohol **13b**. The most relevant X-ray crystallographic data obtained are given in Tables 2 and 3, containing also the data of the second independent molecule **14b′** found in the elementary cell. In Table 4 we have compared the parameters α, *β*, and *d* (defined in **5**[6]) in **1b**, **2b, 14b**, and **14b′**. In all three cases there is clearly an interaction between the exo-carbon and the metal. This interaction is also indicated by comparison of the difference in the ^{13}C-NMR chemical shift of the exo-methylene carbon between the alcohols **6** and **13b** and the corresponding carbenium ions **1b** and **14b**, respectively: Δ*δ*(**6** − **1b**) = −71 ppm, Δ*δ*(**13b** − **14b**) = −65 ppm. The structural parameters in Table 4 point to a decreased metal−carbon interaction in **14b,** as compared to **2b** and **1b**. This might be at least in part due to steric interactions between the exo $C(C_7H_7)_2$ group and the pentamethylene chains in **14b**.

Table 2. Crystal Data and Data Collection Parameters of 13b and 14b

	13b	14b
mol formula	$C_{34}H_{39}CoO$	$C_{34}H_{38}BCoF_4$
fw	522.58	592.42
cryst syst	monoclinic	triclinic
space group	*P*2$_1$/*n* (No. 14)	*P*$\bar{1}$ (No. 2)
cell dimens		
a, Å	9.786	13.774
b, Å	19.991	14.057
c, Å	13.983	15.401
α, deg	90.00	92.05
β, deg	98.72	94.31
γ, deg	90.00	100.07
V, Å^3	2703.9	2924.10
Z	4	4
d_{calc}, g·cm^{-3}	1.284	1.355
abs coeff, mm^{-1}	0.659	0.635
F(000)	1112	1248
T, K	200	200
radiation, Å	*λ*(Mo Kα)	*λ*(Mo Kα)
scan type	*ω*	*ω*
reflns measd	*h*, 0 to 10; *k*, −21 to 0; *l*, −15 to 15	*h*, −8 to 17; *k*, −17 to 17; *l*, 19 to 19
2*θ* range, deg	3.679−46.00	2.7−54.00
no. of reflns measd	4015	13 303
no. of params	481	746
R(*F*)	0.0431	0.0854
$R_w(F^2)$	0.116	0.247
GOF on F^2	0.996	1.041

In order to compare the interaction between the 6,6′-diphenylfulvene ligand—especially the interaction between the exo-methylene carbon—and M (M = Fe (**1b**); M = Co (**14b**)), we have carried out restricted Hartree−Fock ab initio calculations on **1b** and **4a**, as well as on their fragments $CpFe^+$ and $CbCo^+$. **4a** is a model

Table 3. Selected Interatomic Distances (Å) for 13b and 14b

Compound **13b**

Co−C1	2.003(4)	Co−C19	2.086(4)
Co−C2	1.977(4)	C19−C20	1.522(5)
Co−C3	1.989(4)	C15−C16	1.420(6)
Co−C4	2.012(4)	C16−C17	1.405(6)
Co−C15	2.077(4)	C17−C18	1.434(6)
Co−C16	2.077(4)	C18−C19	1.422(5)
Co−C17	2.079(4)	C15−C19	1.431(5)
Co−C18	2.083(4)		

Compound **14b**

Co1−C1	1.996(6)	Co1−C19	2.085(6)
Co1−C2	2.010(7)	C19−C20	1.411(9)
Co1−C3	2.003(6)	C15−C16	1.396(9)
Co1−C4	2.002(6)	C16−C17	1.425(10)
Co1−C15	2.086(6)	C17−C18	1.377(9)
Co1−C16	2.104(6)	C18−C19	1.479(9)
Co1−C17	2.108(6)	C15−C19	1.441(9)
Co1−C18	2.077(7)		

Table 4. Selected Geometrical Parameters for 1b and the Isolobal Species 2b, 14b, and 14b

compd	α (deg)	β (deg)	*d* (Å)	ref (Å)
2b	31.0	2.55	9	
1b	20.7	8.1	2.72	3
14b	10.8	12.4	2.95	this work
14b′	6.4	13.4	3.03	this work

Table 5. Natural Charges and Wiberg Bond Indices of Selected Atoms and Fragments in 1b and 4a

Natural Charges

atom	CpFe$^+$	**1b**	CbCo$^+$	**4a**
Fe	+1.24	+0.54		
Co			+0.92	+0.68
C$_{exo}$		+0.31		+0.28

Wiberg Bond Indices

bond	CpFe$^+$	**1b**	CbCo$^+$	**4a**
Fe−C$_{exo}$		0.061		
Co−C$_{exo}$				0.016

compound for **14b**, in which the tricyclo[7.5.0.0^{1,7}]-tetradeca-1,8-diene ligand is replaced by a simple cyclobutadiene (Cb) ligand. Our results refer to the singlet state of the Hartree−Fock wave functions of **4a**, **14b**, CpFe$^+$, and CbCo$^+$.

Pseudopotentials were employed for inner shell electrons of Fe and Co, which have been developped by Hay and Wadt.[13] The valence orbitals, and the outermost core orbitals, were treated as a Gaussian orbital basis set (3s, 4s, 3p, 4p, 3d). The valence orbitals are contracted to a double-ξ basis. Respective basis sets of (10s, 5p) and (4s) were used for carbon and hydrogen and contracted to a split-valence. The geometrical parameters adopted for the calculations were those determined by the X-ray investigations of **1b**[7] and **14b**.

The natural charges at the metal center and at the exo-methylene carbon atom in **1b** and **4a** and at the metal centers in the isolobal CpFe$^+$ and CbCo$^+$ fragments are compared in Table 5. Consider first the CpFe$^+$ and the CbCo$^+$ fragments. In these fragments the charges at the metal centers are computed to be +1.24 (Fe) and +0.92 (Co), respectively. This indicates that the positive charge of the CbCo$^+$ fragment is more distributed over the Cb ring, while the positive charge of the CpFe$^+$ fragment remains at the iron atom. This is in good agreement with the ^{13}C-NMR spectra. The calculated Wiberg bond indices (wbi) between the iron atom and the carbon atoms in the Cp ring of CpFe$^+$ are 0.28 and are considerably smaller than the corresponding Wiberg bond indices between the cobalt atom and the carbon centers (wbi = 0.42) in the Cb ring of CbCo$^+$. Both results point to a stronger bonding of the cobalt atom with the Cb moiety in the CbCo$^+$ fragment as compared to the iron atom with the Cp ligand in the CpFe$^+$ fragment.

If we compare now the natural charges at the metal centers of **1b** and **4a**, we find a smaller charge at the iron species (+0.54) as compared to the cobalt compound (+0.68). Thus more electron density is transferred from the diphenylfulvene ligand in **1b** to the CpFe$^+$ fragment (0.70 e) than to the CbCo$^+$ fragment (0.24 e) in **4a**. The calculations on **1b** predict 85% of the positive charge to be at iron and the exo-methylene carbon; in the case of **4a** 96% of the positive charge is found on cobalt and the exo-methylene carbon. The positive charge at the exo-methylene carbon is smaller in **4a** (+0.28) than in **1b** (+0.31). The Wiberg bond index between the metal and exo-methylene carbon center of the 6,6′-diphenylfulvene ligand is smaller in the case of **4a** (wbi = 0.016) compared to **1b** (wbi = 0.061). These findings are in a good agreement with the shorter Fe−C(exo) distance and the larger bond angle (α) (Table 4) in **1b** as compared to the corresponding values for **14b**. Thus the stronger metal−fulvene interaction in **1b** as compared to **4a** is due to a higher stability of the CbCo$^+$ moiety with respect to the CpFe$^+$ fragment. This difference in the stability can be traced back to the stronger bonding of the cobalt atom with the Cb ligand and a better distribution of the positive charge in the CbCo$^+$ fragment over the Cb ring as compared to the CpFe$^+$ fragment.

Conclusion

Although **1b** and **14b** are isolobal species, there is a considerable difference between them. We ascribe this difference to the stronger interactions between fulvene and the CpFe$^+$ fragment compared to the CbCo$^+$ fragment, due to a higher stability of the CbCo$^+$ fragment.

Experimental Section

Equipment. All melting points are uncorrected. The NMR spectra are measured with a Bruker AS200 or AS300 (^{1}H-NMR at 200 or 300 MHz and ^{13}C-NMR at 50.32 or 75.45 MHz) using the solvent as internal standard (δ; *J* (Hz)). IR spectra were recorded with an Perkin-Elmer 580 B. UV light absorption data were recorded using a Hewlett Packard 8452A spectrometer. Cyclovoltammograms were collected on a HEKA PG 28 potentiostat vs SCE in a 0.1 M solution of (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$. The potential of the ferrocene/ferrocenyl system was recorded at 487 mV vs SCE. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Heidelberg. All reactions were carried out in argon atmosphere using dried oxygen-free solvents.

{(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene}{η^5-(hydroxymethyl)cyclopentadienyl}cobalt (10). To a suspension of 379 mg (10 mmol) of LiAlH$_4$ in 500 mL of tetrahydrofuran was added dropwise 1.85 g (5 mmol) of **9** dissolved in 28 mL of tetrahydrofuran. After the mixture was stirred for 4 h, 250 mL of a saturated NaCl solution in water

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(13) a. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

was added, the layers were separated, and the aqueous layer was extracted with ether. The combined organic layers and extracts were dried with MgSO$_4$, concentrated in vacuo, and absorbed on Celite. The product was purified by column chromatography (alumina, 6% water/2:3 ether−*n*-pentane) and yielded 1.63 g (96%) of **10a** as a yellow solid. **10a**: Mp 129 °C; ^{1}H-NMR (300 MHz, CDCl$_3$) δ = 4.95−4.93 (m; J = 2.0 Hz; 2H), 4.69−4.67 (m; J = 2.0 Hz; 2H), 4.30−4.28 (d; J = 5.6 Hz; 2H), 2.00−1.92 (m; 10H), 1.69 (m; 8H); 1.27−1.23 (t; J = 5.6 Hz; 1H), 0.95−0.87 (m, 2H); ^{13}C-NMR (75.4 MHz, CD$_2$Cl$_2$) δ = 97.0 (C), 79.9 (CH), 79.6 (CH), 79.0 (C), 60.0 (CH$_2$), 30.6 (CH$_2$), 30.4 (CH$_2$), 27.8 (CH$_2$); UV (*n*-pentane) λ_{max} [nm (log ϵ)] = 212 (4.13), 266 (4.21), 348 (2.54); IR (KBr) 2916, 2840, 2810, 1440, 1325, 1036; HRMS (EI, 70 eV) calcd for $C_{20}H_{27}CoO$ *m/z* 342.1394, found *m/z* 342.1382.

{**(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene**}{**η^5-(diphenylhydroxymethyl)cyclopentadienyl**}**cobalt (13a).** To a solution of 1.5 g (4.05 mmol) of **9** in 100 mL of tetrahydrofuran, cooled to −78 °C, was added 6.1 mL of a 2 M phenyllithium solution in *n*-hexane. The reaction was quenched after 60 min by adding 20 mL of water. After the reaction mixture was poured onto 80 mL of water, the layers were separated and the aqueous layer was extracted with ether. The combined organic layers and extracts were washed with saturated NaHCO$_3$ solution, dried over MgSO$_4$, concentrated in vacuo, and absorbed on Celite. The product was purified by column chromatography (alumina, 6% water/1:20 ether−*n*-pentane) and yielded 1.74 g (87%) of **13a** as a yellow solid. **13a**: Mp 178 °C; ^{1}H-NMR (300 MHz, CDCl$_3$) δ = 7.37−7.16 (m; 10H), 4.88−4.86 (m; J = 2.1 Hz; 2H), 4.61−4.59 (m; J = 2.1Hz; 2H), 2.83 (s; 1H), 2.01−1.79 (m; 10H), 1.66−1.52 (m; 4H), 1.23−1.15 (m;4H), 0.92−0.73 (m; 2H); ^{13}C-NMR (75.4 MHz, CD$_2$Cl$_2$) δ = 148.1 (C), 127.7 (CH), 127.2 (CH), 126.7 (CH), 108.8 (C), 80.9 (CH), 80.8 (C), 79.8 (CH), 77.3 (C), 31.1 (CH$_2$), 30.5 (CH$_2$), 28.3 (CH$_2$); UV (*n*-pentane) λ_{max} [nm (log ϵ)] = 376 (2.85), 298 (3.25), 268 (4.43), 220 (4.46), 206 (4.64), 192 (4.87); IR (KBr) 3481, 2915, 2843, 1441, 1325, 810, 756, 701. Anal. Calcd for $C_{32}H_{35}CoO$ (494.20): C, 77.70; H, 7.14. Found: C, 77.66; H, 7.16.

{**(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene**}{**η^5-(bis(*p*-methylphenyl)hydroxymethyl)cyclopentadienyl**}**cobalt (13b).** To a dispersion of 34 mg (4.8 mmol) of lithium in 15 mL of ether was added 831 mg (0.54 mmol) of *p*-bromotoluene at −15 °C. After the reaction mixture was stirred for 30 min, 200 mg (0.54 mmol) of **9**, dissolved in 5 mL of ether, was added dropwise at −15 °C. After being warmed to 0 °C and stirred for an additional 2 h, the reaction mixture was poured in 50 mL of ice cold water. The working up procedure was carried out as decribed for **13a** yielding 80 mg (0.15 mmol) (57%) of **13b** as an orange-red solid. **13b**: Mp 173−175 °C (dec); ^{1}H-NMR (300 MHz, CDCl$_3$) δ = 7.25−7.20 (m; 4H), 7.05−7.02 (m; 4H), 4.86 (m; J = 2.1 Hz; 2H), 4.58 (m; J = 2.1; 2H), 2.76 (s; 1H), 2.28 (s; 6H), 2.00−1.80 (m; 12H), 1.64−1.50 (m; 2H), 1.26−1.19 (m; 4H), 0.88−0.75 (m; 2H); ^{13}C-NMR (75,4 MHz, CD$_2$Cl$_2$) δ = 144.9 (C), 135.7 (C), 128.0 (CH), 126.7 (CH), 108.7 (C), 80.3 (C), 80.2 (CH), 79.4 (CH), 77.1 (C), 30.7 (CH$_2$), 30.1(CH$_2$); 27.9 (CH$_2$), 20.9(CH$_3$); UV (CHCl$_3$) λ_{max} [nm (log ϵ)] = 244 (4.08), 270 (4.40), 298 (3.36), 350 (2.99); IR (KBr) 3496, 2919, 2846, 2816, 1509, 1442, 810, 784, 519, 585, 435. Anal. Calcd for $C_{34}H_{39}CoO$ (522.23): C, 78.13; H, 7.53. Found: C, 78.20; H, 7.51.

{**(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene**}{**η^5-(bis(*p*-fluorophenyl)hydroxymethyl)cyclopentadienyl**}**cobalt (13c).** To a dispersion of 34 mg (4.8 mmol) of lithium in 15 mL of ether was added 840 mg (0.54 mmol) of *p*-bromoflourobenzene at −30 °C. After the reaction mixture was stirred for 30 min, 200 mg (0.54 mmol) of **9**, dissolved in 5 mL of ether, was added dropwise at −30 °C. After being warmed to 0 °C and stirred for an additional 2 h, the reaction mixture was poured in 50 mL of ice cold water. The working up procedure was carried out as described for **13a** yielding 232 mg (0.15mmol) (81%) of **13c** as a yellow solid. **13c**: Mp 133 °C (dec); ^{1}H-NMR (300 MHz, CDCl$_3$) δ = 7.32−7.25 (m; 4H), 6.95−6.89 (m, 4H), 4.83−4.82 (m; J = 2.1; 2H), 4.61−4.60 (m; J = 2.1; 2H), 2.84 (s; 1H), 1.98−1.83 (m, 12H), 1.66−1.56 (m; 2H), 1.26−1.13 (m;4H); 0.88−0.80 (m, 2H); ^{13}C-NMR (75,4 MHz, CD$_2$Cl$_2$) δ = 163.5 (C), 160.3 (C), 143.9 (C), 128.9 (CH), 128.8 (CH), 114.5 (CH), 114.2 (CH), 108,6 (C), 81.2 (C), 81.1 (CH), 79.7 (CH), 76.7 (C), 31.1 (CH$_2$), 30.5 (CH$_2$), 28.2 (CH$_2$); UV (CHCl$_3$) λ_{max} [nm (log ϵ)] = 246 (4.04), 268 (4.32), 306 (3.19), 378 (2.70); IR (KBr) 3493, 2920, 1601, 1504, 1223, 1152, 828, 807, 572. HRMS (EI, 70 eV) calcd for $C_{32}H_{33}CoF_2O$ *m/z* 530.1831, found *m/z* 530.1790.

1-(Diphenylhydroxymethyl)ferrocene (6). To a solution of 1.05 g (2.5 mmol) of 1-(chloromercurio)ferrocene in 50 mL of ether was added dropwise 3.9 mL of a 1.6 M solution of *n*-butyllithium at room temperature. The mixture became homogeneous and turned deep red. The solution was stirred for 30 min, and then 910 mg (5 mmol) of benzophenone was added. The reaction mixture was stirred for an additional 30 min and then quenched with 50 mL of water. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers and extracts were washed with saturated NaHCO$_3$ solution, dried over MgSO$_4$, concentrated in vacuo, and absorbed on Celite. The product was purified by column chromatography (alumina, 6% water/1:20 ether−*n*-pentane) and yielded 818 mg (93%) of **6** as a yellow solid. **6**: ^{1}H-NMR (300 MHz, CDCl$_3$) δ = 7.31−7.25 (m; 10H), 4.29−4.27 (m; J = 1.9 Hz; 2H), 4.19 (s; 5H), 4.05−4.05 (m; J = 1.9 Hz; 2H), 3.48 (s; 1H); ^{13}C-NMR (75,4 MHz, CDCl$_3$) δ = 146.96 (C), 127.44 (CH), 127.01 (CH), 126.72 (CH), 99.37 (C), 77.35 (C), 68.69 (CH), 68.55 (CH), 68.35 (CH).

{**(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene**}{**η^5-(diphenylmethylium)cyclopentadienyl**}**cobalt Tetrafluoroborate (14a).** To a solution of 100 mg (0.20 mmol) of **13a** in 5 mL of ether was added 0.2 mL of a 54% tetrafluoroboric acid solution in ether at 0 °C. The yellow color instantly changed to deep violet. After stirring of the mixture for an additional 30 min at 0 °C, the precipitate was filtered out and recrystallized from ether/*n*-pentane at −10 °C. A 91 mg (0.16 mmol) amount of a deep violet solid was obtained in 80% yield. **14a**: Mp 168 °C (dec); ^{1}H-NMR (300 MHz, CDCl$_3$, 223 K) δ = 7.72−7.10 (m; 10H), 6.10 (m; 2H), 5.86 (m; 2H), 1.85−1.60 (m; 14H), 1.32−0.74 (m; 6H); ^{13}C-NMR (75.4 MHz, CDCl$_3$, 223 K): δ = 170.58 (C), 140.27 (C), 132.67 (CH), 131.85 (CH), 129.09 (CH), 110.78 (C), 103.45 (CH), 99.40 (C), 84.79 (CH), 29.84 (CH$_2$), 28.00(CH$_2$), 27.25 (CH$_2$); UV (CH$_2$Cl$_2$) λ_{max} [nm (log ϵ)] = 220 (4.38), 256 (4.41), 3.62 (4.42), 589 (4.01); IR (KBr) 3412, 2916, 2846, 1440, 1121, 1081, 697; HRMS (FAB+) calcd for $C_{32}H_{34}Co$ *m/z* 477.1992, found *m/z* 477.2033.

{**(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene**}{**η^5-(bis(*p*-methylphenyl)methylium)cyclopentadienyl**}**cobalt Tetrafluoroborate (14b).** To a solution of 100 mg (0.19 mmol) of **13b** in 5 mL of ether was added 0.2 mL of 54% tetrafluoroboric acid solution in ether at 0 °C. The working up procedure was carried out as described for **14a** yielding 104 mg (0.17mmol) (89%) of **14b** as deep violet crystals. **14b**: Mp 161 °C (dec); ^{1}H-NMR (300 MHz, CDCl$_3$, 223 K) δ = 7.42−7.18 (m; 8H), 6.12 (m; 2H), 5.82 (m; 2H), 2.33 (m; 6H), 2.09−1.36 (m; 14H), 1.16−0.71 (m; 6H); ^{13}C-NMR (75.4 MHz, CDCl$_3$, 223 K) δ = 175.32 (C), 145.00 (C), 137.52 (C), 132.76 (CH), 129.89 (CH), 108.39 (C), 101.83 (CH), 97.60 (C), 85.42 (CH), 28.92 (CH$_2$), 28.15(CH$_2$), 27.23 (CH$_2$), 22.06(CH$_3$); UV (CH$_2$Cl$_2$) λ_{max} [nm (log ϵ)] = 220 (4.25), 256 (4.21), 380 (4.37), 602 (3.85); IR (KBr) 3432, 2924, 2855, 2361, 1635, 1178, 1083; HRMS (FAB+) calcd for $C_{34}H_{38}Co$ *m/z* 505.2305, found *m/z* 505.2341.

{**(1,2,8,9-η)-Tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene**}{**η^5-(bis(*p*-fluorophenyl)methylium)cyclopentadienyl**}-**cobalt Tetrafluoroborate (14c).** To a solution of 100 mg (0.17 mmol) of **13c** in 5 mL of ether was added 0.2 mL of 54% tetrafluoroboric acid solution in ether at 0 °C. The working up procedure was carried out as described for **14a**, but no crystals could be obtained. **14c**: ^{1}H-NMR (300 MHz, CDCl$_3$, 223 K) δ = 7.48−7.09 (m; 8H), 5.98 (m; 2H), 5.89 (m; 2H), 1.92−1.68 (m; 16H), 1.21−0.80 (m; 4H); ^{13}C-NMR (75.4 MHz, $CDCl_3$, 263 K) δ = 179.36 (C), 171.22 (C), 168.41 (C); 134.81 (CH), 134.62 (CH), 117.38 (CH), 116.94 (CH), 102.17 (CH), 99.50 (C), 85.33 (CH), 77.19 (C), 28.93 (CH_2), 28.26 (CH_2), 27.43 (CH_2).

X-ray Crystallography and Structure Solution. Data were collected on a Siemens (Nicolet Syntex) R4m/V diffractometer, and relevant crystal data and data collection parameters are given in Table 4. The structures were solved by direct methods, least-squares refinement, and Fourier techniques. All calculations were performed with the SHELXTL PLUS[14] and SHELXT-93[15] programs.

$C_{34}H_{39}CoO$ (13b). A orange-red crystal of the dimensions 0.2 × 0.3 × 0.3 mm^3 was obtained from ether at −10 °C. The unit cell was determined and refined from 31 reflections (3.6 < 2θ < 46.0°).

$C_{34}H_{38}BCoF_4$ (14b). A deep violet crystal of the dimensions 0.1 × 0.2 × 0.4 mm^3 was obtained from ether/methylenechloride at −10 °C. The unit cell was determined and refined from 39 reflections (2.7 < 2θ < 54°).

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Supporting Information Available: Tables of atom coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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[14] SHELXTL PLUS: Sheldrick, G. M. University of Göttingen.

[15] SHELXT 93: Sheldrick, G. M. Program for Crystal Structure Refinement, University of Göttingen.