adduct itself. Conversely, for iron, a metallacycle of type C finds a large energy barrier along the pathway to its formation due to the destabilization of some filled orbitals. Ultimately, this is due to the difficulty of transferring electrons from the metal to the acetylene carbon atom.

Acknowledgment. We thank MRT for financial support of the form of scholarship (F.C.) and the CNRS for partial financial support. We are indebted to Dr. Brevard for recording NMR spectra on a Bruker AM 400 spectrometer and stimulating discussions.

We are grateful to NATO for its generous support of this research through Grant No. 200.81, which made this collaboration possible. J.L. would like to express her thanks to the members of ISSECC for their hospitality during her stay in Florence. We thank Joyce Barrows for the production of this manuscript and Jane Jorgensen and Elisabeth Fields for the drawings.

Registry No. **1**, 112803-32-4; **2**, 119382-09-1; **3**, 119382-10-4; **4**, 119382-11-5; **5**, 119382-13-7; **6**, 119434-98-9; **7**, 119382-14-8; **8**, 121056-08-4; **9**, 5512-84-5; dmad, 762-42-5; $CF_3C{\equiv}CCF_3$, 692-50-2; $HC{\equiv}CCN$, 1070-71-9.

Supplementary Material Available: Tables of anisotropic thermal parameters for 2, 4, 6, and 7 and hydrogen atom coordinates for 4, 6, and 7 (7 pages); listings of structure factors for 2, 4, 6, and 7 (44 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of Some New (η^6-Arene)cobalt Complexes

Helmut Bönnemann,* Richard Goddard, Joachim Grub, Richard Mynott, Eleonore Raabe, and Stefan Wendel

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,
D-4330 Mülheim a. d. Ruhr, Federal Republic of Germany

Received December 15, 1988

The preparation of several new types of (η^6-arene)cobalt complexes is described. (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene)cobalt (**1**) reacts with H_2 in the presence of arenes and N bases such as piperidine to form (η^6-arene)(η^1,η^2-cyclooctenyl)cobalt complexes (**2**). The structure of the 1-η^1,4,5-η^2-cyclooctenyl ligand was determined by 2D NMR techniques. Complexes **2** react with $HBF_4{\cdot}Et_2O$ in the presence of dienes to give (η^6-arene)(diene)cobalt tetrafluoroborates (**5**, **6**, **8**, **10**), which in turn react with $NaBEt_3H$ to afford (η^6-arene)(η^3-allyl)cobalt complexes. When the latter are treated with $HBF_4{\cdot}Et_2O$ in the presence of dienes, then (η^6-arene)(diene)cobalt tetrafluoroborates are re-formed. (η^6-Arene)(butadiene)cobalt tetrafluoroborates can be prepared by treating (5-methylheptadienyl)(η^4-butadiene)cobalt with $HBF_4{\cdot}Et_2O$ in the presence of arenes. The reaction of **1** with $HBF_4{\cdot}Et_2O$ and arene results in the synthesis of (η^6-arene)(η^1,η^3-cyclooctenediyl)cobalt(III) tetrafluoroborate complexes (**18**). The NMR evidence for this structure is discussed. The arene ligand in **18** is easily displaced by acetonitrile to give (η^1,η^3-cyclooctenediyl)tris(acetonitrile)cobalt tetrafluoroborate (**21**), which is a versatile compound for the synthesis of neutral cobalt complexes with η^1,η^3-cyclooctenediyl ligands. The crystal structures of (η^5-cyclopentadienyl)(η^1,η^3-cyclooctenediyl)cobalt (**22**) and (acetylacetonato)(η^1,η^3-cyclooctenediyl)cobalt (**23**) were confirmed by X-ray diffraction techniques. Crystals of **22** are tetragonal, space group $P\bar{4}$, with $a = b =$ 16.583 (2) Å, c = 7.995 (1) Å, and Z = 8; R = 0.031 for 2525 unique observed reflections. Crystals of **23** are triclinic, space group $P\bar{1}$, with a = 8.4165 (8) Å, b = 8.9539 (9) Å, c = 9.3770 (5) Å, α = 72.588 (5)°, β = 72.224 (5)°, γ = 70.521 (8)°, and Z = 2; R = 0.033 for 3160 unique observed reflections. Both complexes are monomeric and contain similar $C_8H_{12}Co$ fragments.

Introduction

In the past 30 years a number of neutral and cationic η^6-arene complexes of cobalt[1] have been synthesized in which the arene is benzene, an alkylated benzene, or an annelated arene. However, only a few examples of arene–cobalt complexes are known where the arene ligands bear functional groups.[2] In this paper we wish to report some novel cationic and neutral arene–cobalt complexes with arenes and functionized arenes. We also report some compounds containing ligands that are η^1,η^2-, η^3-, or η^1,η^3-bound to cobalt, some of which are of types previously unknown for this metal.

Results and Discussion

1. (η^6-Arene)(η^1,η^2-cyclooctenyl)cobalt Complexes (2). The reaction of (η^3-cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (**1**)[3,4] with H_2 at room temperature in benzene solution leads to hydrogenation and decomposition of **1** to metallic cobalt, cyclooctane, and cyclohexane (eq 1). However, when basic auxiliary ligands (for example, an amine such as piperidine) are added, the formation of metallic cobalt is suppressed almost completely and the

---

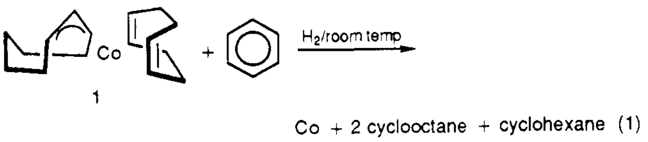
[1] (a) Silverhorn, W. E. *Adv. Organometal. Chem.* **1975**, *13*, 47. (b) Gastinger, R. G.; Klabunde, K. J. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 1. (c) Kemmitt, R. D. W.; Russel, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 5. (d) Geiger, W. E.; Edwin, J. *Organometallics* **1984**, *3*, 1910. (e) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. (f) Bönnemann, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248.

[2] (a) Efraty, A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1967**, *89*, 3744. (b) Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1531.

[3] Otsuka, S.; Rossi, M. *J. Chem. Soc. A* **1968**, 2630.

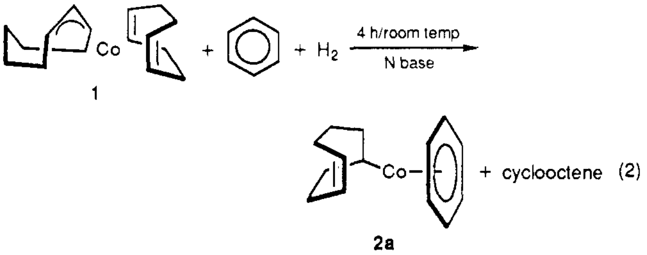
[4] Grard, Ch. Dissertation, Ruhr-Universität Bochum, 1967.

0276-7333/89/2308-1941$01.50/0 © 1989 American Chemical Society



(1)

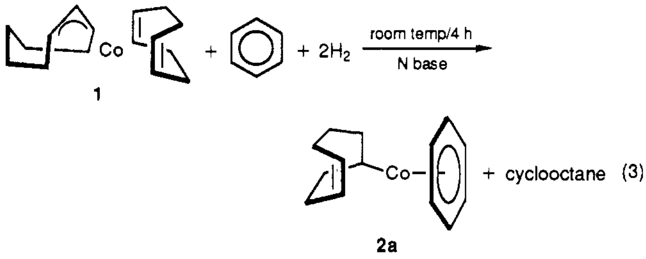
new cobalt complex **2a** can be isolated from the reaction solution as dark red crystals (eq 2). The structure of **2a** was determined unambiguously and the spectrum assigned by ^{13}C NMR by means of a 2D INADEQUATE spectrum[5] (see section 5).



(2)

N base: piperidine, 85% (**2a**)

In addition to a η^6-benzene ring, this compound contains a C_8 ring which is bound to the central metal atom by a metal–olefin bond and a metal–carbon σ-bond. This 1-η^1,4,5-η^2-enyl structure element is known for Ni,[6] Pd,[7] and Pt[8] compounds. Cobalt complexes with a η^1,η^2-bound C_8 ring have been previously postulated as intermediates,[4] but this is the first time that such compounds have been isolated or their structures determined spectroscopically. The effect of adding other amines such as triethylamine and quinuclidine was investigated. It was found that when the ratio of amine to **1** was 5:1, the yield of **2a** is strongly dependent upon the basicity of the amine added (eq 3). Thus in the case of triethylamine, the yield of **2a** is about 50%, but with quinuclidine and piperidine (eq 2) the yield increases to over 80%.

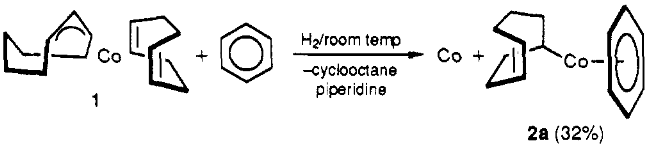


(3)

N base: pyridine, 42% (**2a**); triethylamine, 48% (**2a**)

Since triethylamine and quinuclidine have almost identical pK_B values,[9] this must mean that steric effects must play a role in the influence of the amines. Clearly, quinuclidine is better at stabilizing the cobalt complexes formed as intermediates during the reaction. Surprisingly, in contrast to triethylamine and quinuclidine, when piperidine is added, then only 7 mol of H_2/mol of cobalt complex is taken up and one of the C_8 rings is liberated as cyclooctene (eq 2).

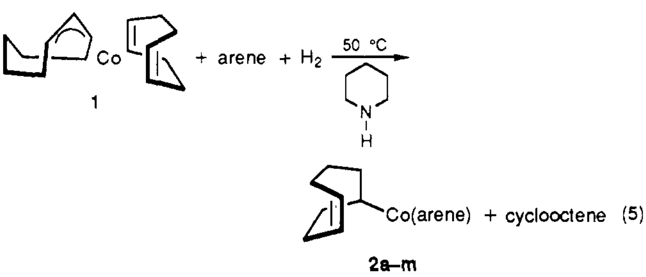
Further studies showed that the yield is not affected if the molar ratio of **1** to piperidine is less than 2:1. However, when this ratio is exceeded, then the parallel reaction is no longer suppressed. For example, when the molar ratio of **1** to piperidine is 10:1, then metallic cobalt is produced and the yield of **2a** is only 32%. Twenty-one percent of the starting material **1** remains unchanged (eq 4).



(4)

1: piperidine = 10:1

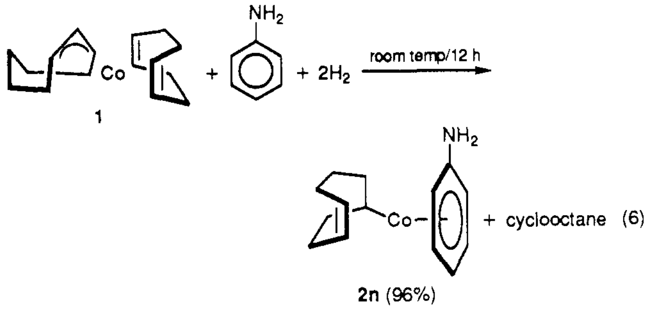
The synthetic method in eq 2 accommodates a wide range of arene components. Thus at 50 °C with piperidine added, the (η^6-arene)(η^1,η^2-cyclooctenyl)cobalt compounds (**2a–m**) are obtained in very good yields (eq 5). The reaction to form the analogous aniline complex **2n** proceeds at room temperature in almost quantitative yield (eq 6).



(5)

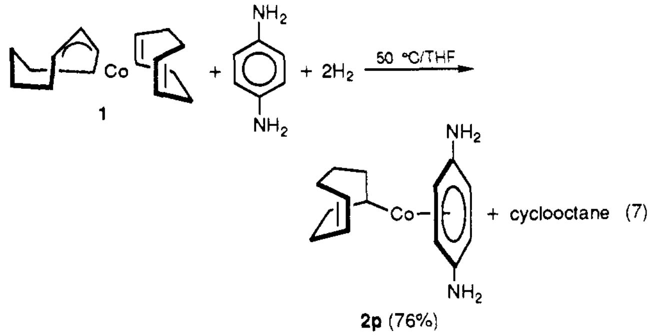
arene: benzene, 88% (**2a**); hexamethylbenzene, 15% (**2b**); mesitylene, 81% (**2c**); pseudocumene, 76% (**2d**); biphenyl, 65% (**2e**); diphenylmethane, 72% (**2f**); 9,10-dihydroanthracene, 35% (**2g**); anisole, 96% (**2h**); *p*-anisidine, 72% (**2i**); 1,4-dimethoxybenzene, 57% (**2j**); *p*-methoxybenzoic acid methyl ester, 56% (**2k**); fluorobenzene, 23% (**2m**)

Here the aniline not only appears in the final product but also acts as the auxiliary ligand. Similarly, with *p*-phenylenediamine, the corresponding *p*-phenylenediamine complex **2p** is formed without another amine having to be added.



(6)

However, since *p*-phenylenediamine only melts at 142 °C, at 50 °C the reaction has to be carried out in a 1:1 mixture of the aromatic compound and THF (eq 7).



(7)

When the

---

(5) For general references, see: Ernst, R. R.; Bodenhausen, C.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Pergamon: Oxford, 1987. Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* **1981**, *43*, 478.

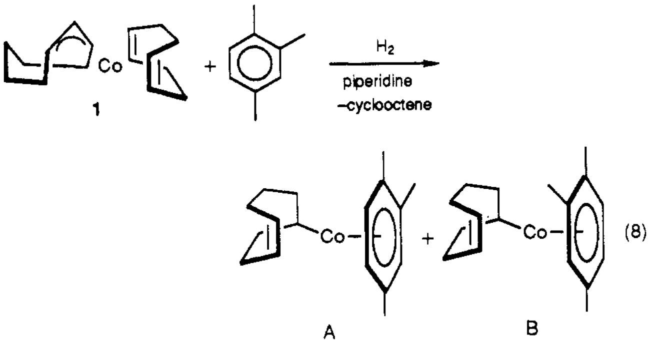
(6) Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, 1973; Vol. 1, p 350.

(7) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413. Maitlis, P. M.; Espiret, P.; Russel, M. J. H. In *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 6, p 365.

(8) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496.

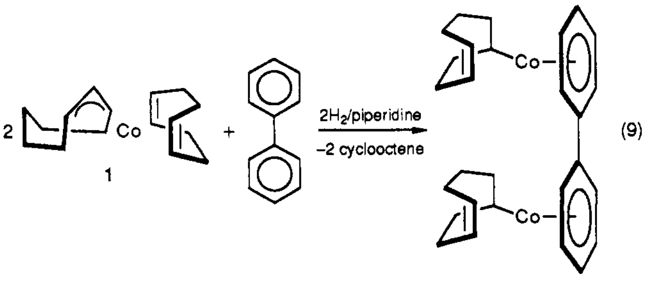
(9) (a) Grob et al. *Chem. Ind.* (*London*) **1957**, 598. (b) Weast, C. W.; Astle, M. J.; Beyer, W. H. In *Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Cleveland, 1983–1984.

pseudocumene complex **2d** is prepared by the route in eq 5, the two diastereomeric pairs of compounds A and B are obtained. The ratio A/B is strongly dependent upon the temperature (eq 8). The reaction of a 1:1 mixture of 1



T = 50 °C, A:B = 2:1
T = 0 °C, A:B = 4,5:1

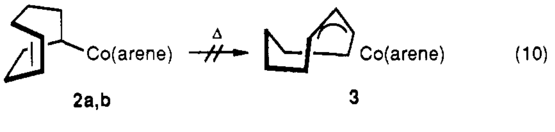
with biphenyl gives the mononuclear complex **2e**. The binuclear complex **2q** can be obtained in 8% yield by taking a twofold excess of 1 (eq 9). The meso form and



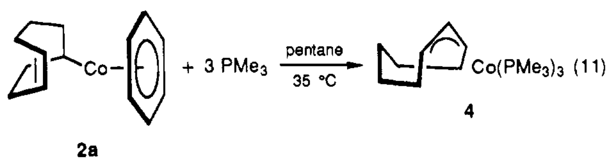
2q

the *d/l* racemate are formed in a 1:1 ratio. The new cobalt complexes **2a–q** are isolated as orange to deep red crystals. They are stable at room temperature in an inert atmosphere. Their characterization by NMR is discussed in section 5.

Wilke et al.[6] discovered that η^1,η^2-cyclooctenyl ligands in Ni complexes undergo thermal isomerization to form the corresponding η^3-allyl systems. No similar reaction could be found for the (η^6-arene)(η^1,η^2-cyclooctenyl)cobalt complexes **2**, nor did differential thermal analysis of **2a** and **2b** produce any indication of such an isomerization reaction. Clearly the arene stabilizes the complex. Only after the arene has been replaced (for example, by PMe_3 ligands) does isomerization of the η^1,η^2-enyl ligand take place.

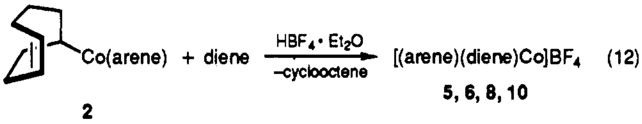


arene: C_6H_6 (**2a**); $C_6(CH_3)_6$ (**2b**)

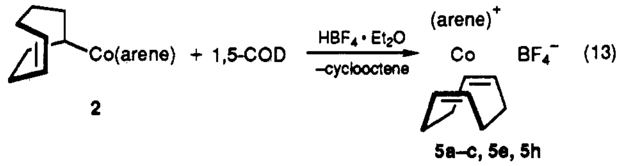


2a

2. [(η^6-Arene)(diene)Co]BF_4 Complexes. A general method of preparing the [(η^6-arene)(diene)Co]$^+$ systems **5**, **6**, **8**, and **10** is to treat the appropriate complex **2** with $HBF_4 \cdot Et_2O$ in the presence of the corresponding diene. Protolysis of the Co–C σ-bond occurs with displacement of the C_8 ring by a diene (eq 12). For example, the complexes **5a–c**, **5e**, and **5h** are obtained as orange-red crystals



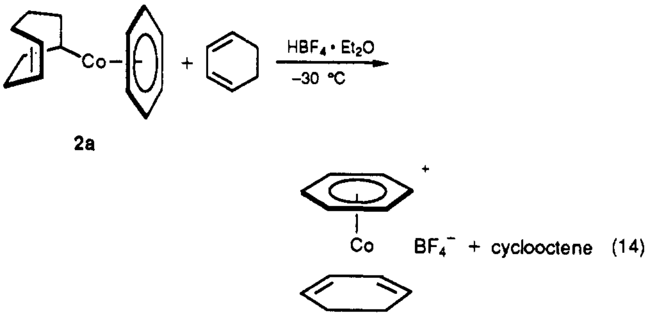
when **2** reacts with cyclooctadiene-1,5 (eq 13). These



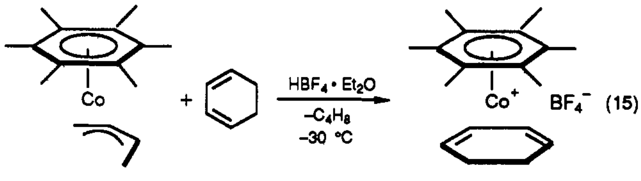
arene: benzene, 67% (**5a**); hexamethylbenzene, 63% (**5b**); mesitylene, 74% (**5c**); biphenyl, 82% (**5e**); anisole, 41% (**5h**)

cations, with the exception of **3b**, dissolve with decomposition in polar solvents such as ethanol, acetone, and acetonitrile. **3c** and **3h** are soluble in CH_2Cl_2 below –30 °C without decomposition while **3a** decomposes above –50 °C and **3e** above –70 °C. The hexamethylbenzene–cobalt complex **3b**, which has been prepared by Geiger et al.[1d] from [bis(hexamethylbenzene)cobalt] hexafluorophosphate[10] and COD-1,5, is stable in CH_2Cl_2 at room temperature.

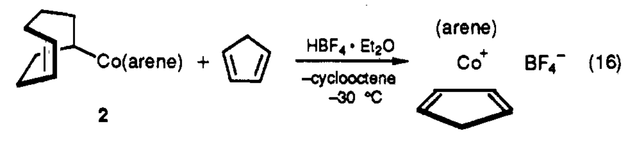
Treatment of **2a** with $HBF_4 \cdot Et_2O$ in the presence of cyclohexadiene-1,3 produces the benzene–cobalt complex **6a** (eq 14). In contrast, the analogous hexamethylbenzene–cobalt complex **6b** is best prepared by treating complex **7b**, which will be described later, with cyclohexadiene-1,3. The η^3-allyl ligand undergoes protolysis (eq 15). The reaction of cyclopentadiene-1,3 with the complexes **2** affords the corresponding cyclopentadienyl complexes **8a–c** (eq 16). Whereas complexes **8b** and **8c** are obtained pure in good yields, compound **8a** is always contaminated with cobalticenium tetrafluoroborate, which is formed together with metallic cobalt as a product of the



6a



7b **6b**



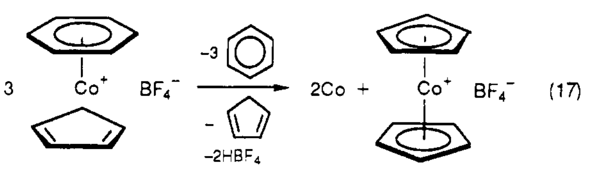
8a–c

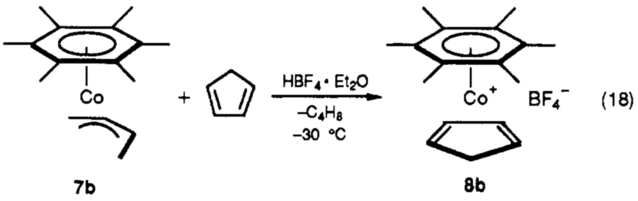
arene: benzene (**8a**); hexamethylbenzene (**8b**); mesitylene (**8c**)

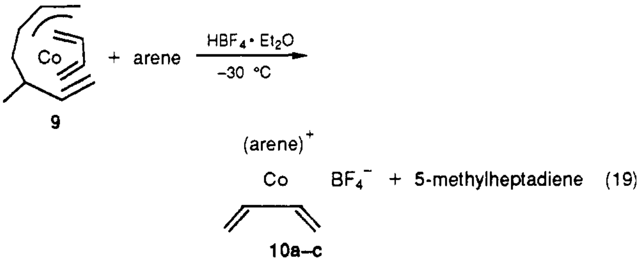
---

(10) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307.

disproportionation of **8a** (eq 17). The hexamethylbenzene complex **8b** can be prepared from the crotyl complex **7b** (eq 18). On the other hand, [(η^6-arene)(η^4-butadiene-1,3)Co]$^+$ systems are formed in good yields from (5-methylheptadienyl)(η^4-butadiene)cobalt (**9**)[11] and HBF$_4$·Et$_2$O in the presence of the arene (eq 19). Here one observes that, similar to complexes **5a–c**, the thermal stability of the complexes **10** increases with increasing alkyl substitution. The complex of unsubstituted benzene (**10a**) is stable in CH$_2$Cl$_2$ only to about −60 °C. Solutions of **10c** and **10b** in CH$_2$Cl$_2$ are stable to −30 and to 10 °C, respectively.





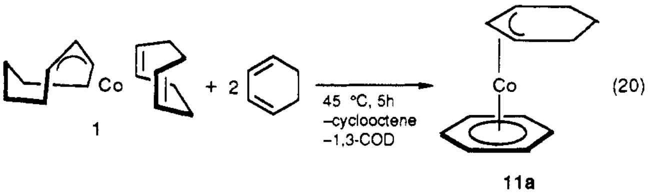


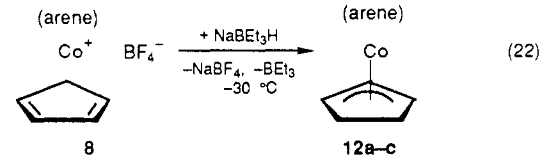
arene: benzene (**10a**); hexamethylbenzene (**10b**); mesitylene (**10c**)

3. (η^6-Arene)(η^3-allyl)cobalt Complexes. Previously no general method was known for preparing complexes of the type (η^6-arene)(η^3-allyl)cobalt. Indeed, the only reported example was described by Cibura,[12] who prepared (η^6-benzene)(η^3-cyclohexenyl)cobalt (**11a**) by reacting **1** with cyclohexadiene-1,3 (eq 20). However, the reaction of the [(η^6-arene)(η^4-1,3-diene)Co]$^+$ cations with NaBEt$_3$H[13] is a general method of preparing (η^3-allyl)Co complexes (eq 21). The η^3-cyclopentenyl complexes **12a–c** are obtained

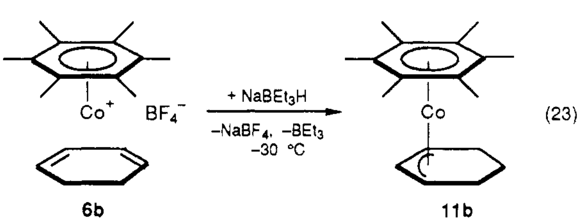
$$\underset{\mathbf{6,\ 8,\ 10}}{[(\text{arene})(1,3\text{-diene})\text{Co}]\text{BF}_4} \xrightarrow[-\text{NaBF}_4,\ -\text{BEt}_3]{+\text{NaBEt}_3\text{H}} \underset{\mathbf{7,\ 11,\ 12}}{(\eta^3\text{-allyl})(\text{arene})\text{Co}} \qquad (21)$$

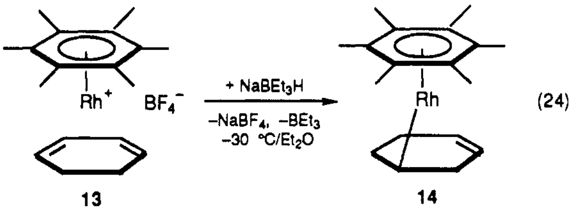
in good yields starting from the cationic cyclopentadiene-1,3 complexes **8a–c** at −30 °C (eq 22). In contrast, the reaction of the cyclohexadiene-1,3 complex **6b** gives complex **11b** in only 20% yield with most of complex **6b** undergoing decomposition (eq 23). By comparison, treatment of the analogous rhodium complex **13**[14] with NaBEt$_3$H at −30 °C leads to the formation of the isomeric (η^6-benzene)(1-η^1,3,4-η^2-cyclohexenyl)rhodium **14** (eq 24). However, at room temperature the η^3-cyclohexenyl complex **15** is produced (eq 25). The reaction of the butadiene complex **10b** at −30 °C gives the η^3-butenyl complex **7b** already mentioned, together with approximately the same amount of the isomeric 1-η^1,3,4-η^2-3-butenyl complex **16** (eq 26). When the reaction temperature is raised to 20 °C, the product contains no **16** and the yield of **7b** increases to about 60% (eq 27). It can be assumed that any of the 1-η^1,3,4-η^2-3-butenyl isomer **16** that may be formed during the reaction is converted to the ther-

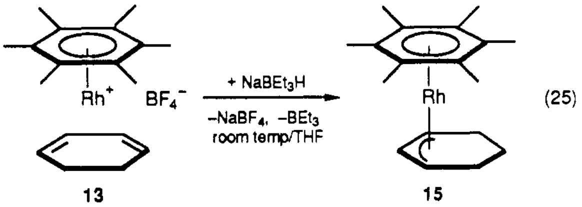


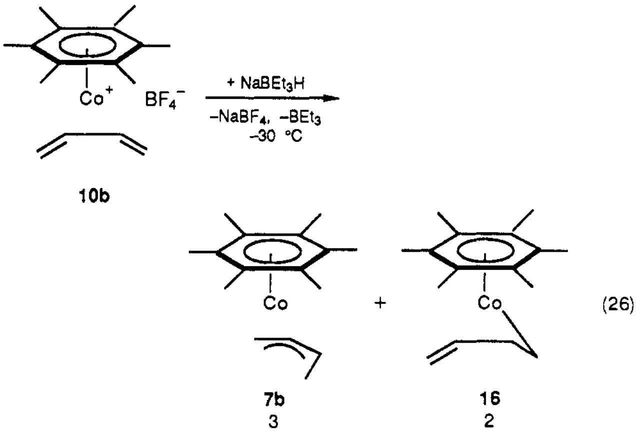


arene: benzene (**12a**); hexamethylbenzene (**12b**); mesitylene (**12c**)









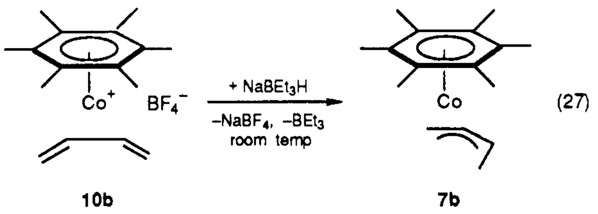
---

[11] Natta, G., et al. *Chim. Ind.* (*Milan*) **1965**, *47*, 524.

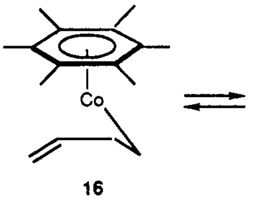
[12] Cibura, K. Dissertation, Ruhr-Universität Bochum, 1985.

[13] Binger, P.; Benedikt, B.; Rotermund, G. W.; Köster, R. *Liebigs Ann. Chem.* **1968**, *717*, 21–40.

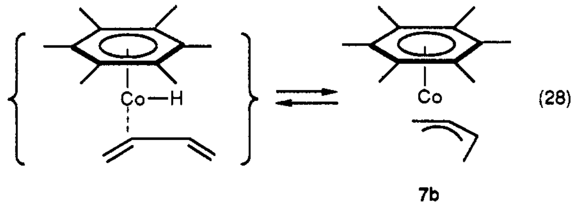
[14] Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 832.

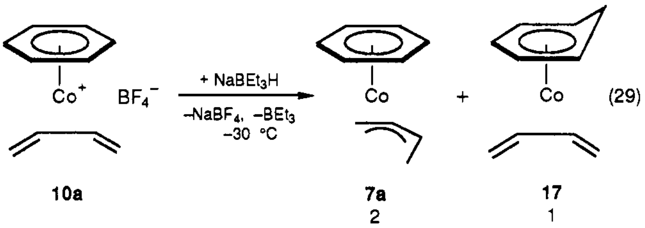


modynamically more stable η^3-allyl isomer **7b** by decomplexation of the C=C double bond and β-H elimination (eq 28). This isomerization has been studied thoroughly in the case of (η^5-cyclopentadienyl)(1-η^1,3,4-η^2-3-butenyl)nickel systems.[15] However, when the unsubstituted complex **10a** is treated with $NaBEt_3H$ at −30 °C, a mixture of isomers consisting of (η^6-benzene)(η^3-crotyl)cobalt (**7a**) and (η^5-cyclohexadienyl)(η^4-butadiene)cobalt (**17**) in the ratio 2:1 is formed and the overall yield is only 10% (eq 29).

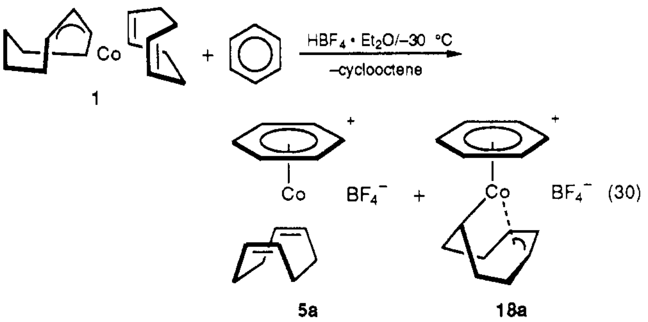


16

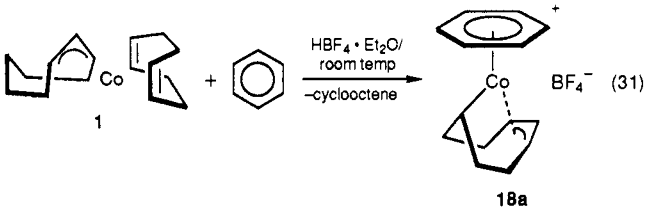




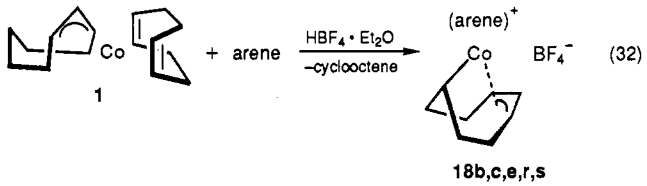
4. **[(η^6-Arene)(η^1,η^3-cyclooctenediyl)Co]BF_4 Complexes and Their Chemistry.** The protolysis of **1** in the presence of aromatic hydrocarbons might be expected to provide an alternative method of preparing [(η^6-arene)(η^2,η^2-COD-1,5)Co]BF_4 complexes. However, the reaction of **1** with $HBF_4{\cdot}Et_2O$ in the presence of benzene at −70 °C affords a mixture of two isomeric benzene–cobalt cations in a 1:1 ratio. One of these compounds is the expected [(η^6-benzene)(η^2,η^2-COD-1,5)Co]BF_4 (**5a**), already obtained from (η^6-benzene)(η^1,η^2-cyclooctenyl)cobalt (**2a**) according to eq 13, while the other is the (η^6-benzene)(η^1,η^3-cyclooctenediyl)cobalt(III) tetrafluoroborate complex (**18a**) (eq 30). The presence of the η^1,η^3-cyclooctenediyl ligand was established by ^{13}C NMR (see section 5). Complexes containing such a C_8 ring bonded by a σ-bond and a η^3-enyl group to the central atom have been reported for individual cases on iron, ruthenium, and osmium.[16] Low-temperature chromatography on Al_2O_3 (7% H_2O) at −78 °C with acetone as eluent yielded the pure cyclooctenediyl complex **18a** in 35% yield; the cation **5a** decomposes under these conditions.



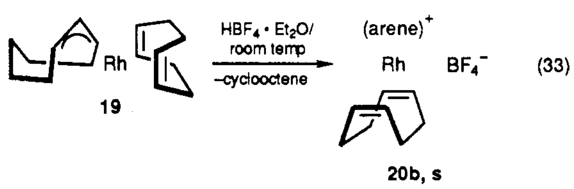
When the reaction is carried out at room temperature, **18a** is obtained after low-temperature chromatography and recrystallization from $Et_2O{\cdot}CH_2Cl_2$ in 72% yield as orange crystals which are not stable at room temperature (eq 31). When the reaction temperature is raised, the ratio of isomers shifts in favor of **18a**.



The (η^6-arene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt(III) monocations **18b,c,e,r,s** can be prepared the same way in similarly good yields (eq 32). This method of preparing arene–cobalt monocations from **1** (eq 32) can also be applied to the analogous rhodium compounds[17] **19** (eq 33).

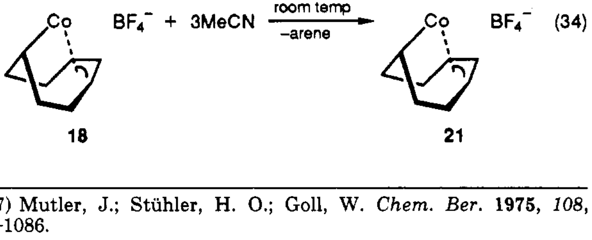


arene: hexamethylbenzene, 58% (**18b**); mesitylene,72% (**18c**); biphenyl, 30% (**18e**); naphthalene, 48% (**18r**); 1,4-dihydroxybenzene, 67% (**18s**)



arene: hexamethylbenzene (**20b**); 1,4-dihydroxybenzene (**20s**)

However, as opposed to cobalt, the cation with η^2,η^2-bound COD is formed selectively. With the exception of the hexamethylbenzene complex **18b**, the aromatic ring in complexes **18** can be displaced easily by acetonitrile to afford the tris(acetonitrile) complex **21** (eq 34). Even in



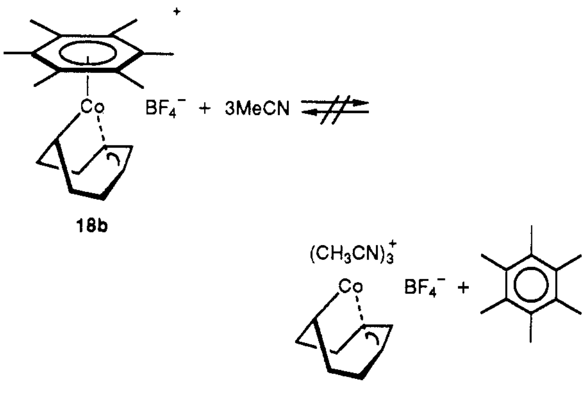
---

[15] (a) Lehmkuhl, H.; Rufinska, A.; Benn, R.; Schroth, G.; Mynott, R. *J. Organomet. Chem.* **1980**, *188*, C36–C40. (b) Lehmkuhl, H.; Rufinska, A.; Benn, R.; Schroth, G.; Mynott, R. *Liebigs Ann. Chem.* **1981**, 317.

[16] (a) Cotton, F. A.; LaPrade, M. D.; Johnson, B. F. G.; Lewis, J. *J. Am. Chem. Soc.* **1971**, *93*, 4626. (b) Cotton, F. A.; Deeming, A. J.; Jasty, P. L.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Am. Chem. Soc.* **1971**, *93*, 4624.

[17] Mutler, J.; Stühler, H. O.; Goll, W. *Chem. Ber.* **1975**, *108*, 1074–1086.

boiling acetonitrile neither is the hexamethylbenzene ring of **18b** exchanged nor does the reverse reaction with complexation of hexamethylbenzene take place (eq 35).

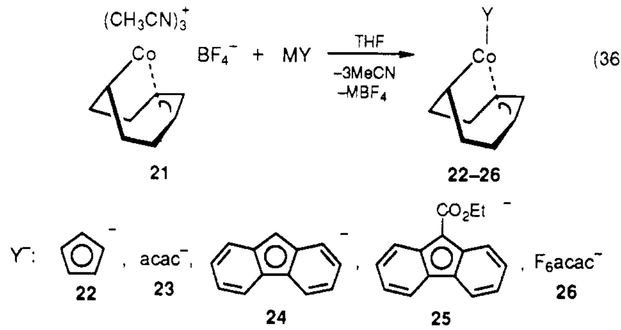


18b

21

(35)

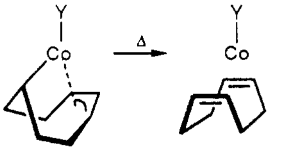
Treatment of **21** with anionic ligands X⁻ leads to formation of the neutral (1-η^1,4-6-η^3-cyclooctenediyl)cobalt complexes **22–26** (eq 36). Complexes **22** and **23** can be converted to the isomeric η^2,η^2-COD-1,5 complexes **27** and **28** (eq 37).



21 **22–26**

22 **23** **24** **25** **26**

(36)

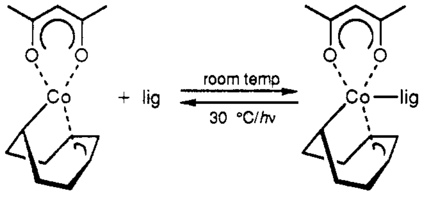


27, 28

(37)

Y: Cp (**27**), 160 °C; fluorenyl (**28**), 75 °C

With strongly solvating solvents such as THF and DMF, the green 16e complex **23** undergoes color changes with the reversible formation of solvent adducts **29** (eq 38). **23**, like **21**, reacts with anionic ligands to form neutral η^1,η^3-cyclooctenediyl complexes. For example, the reaction of **23** with C_5H_7Li at room temperature in THF gives **30** (eq 39).

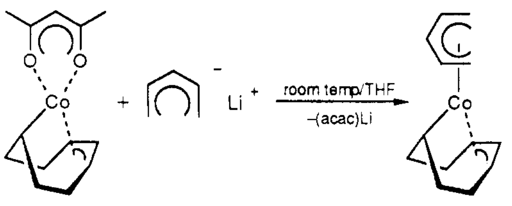


23 **29**

(38)

lig: THF, DMF

5. NMR and X-ray Crystallography. (a) (η^6-Arene)(η^1,η^2-cyclooctenyl)cobalt Complexes. The structure of the η^1,η^2-cyclooctenyl ligand in the complexes **2** was confirmed with the help of a ^{13}C 2D NMR INADEQUATE measurement of **2a**. This showed that the complexed double bond lies between C-4 and C-5. The chemical shifts of the η^1,η^2-cyclooctenyl group are affected little by variation of the arene and the signals of all the other complexes in this series (**2b–2q**) can be assigned without ambiguity.



23 **30**

(39)

The ^{13}C NMR data for the new cobalt complexes **2a–q** in THF-d_8 solution are collected in Table I. These NMR data including the number of signals in the spectra are fully consistent with the given structures. C-1 in the (η^1,η^2-cyclooctenyl)cobalt group is chiral. **2q** contains two such groups and the observation of two sets of signals for this compound in the ratio 1:1 is explained by the presence of diastereomers. Similarly, when the pseudocumene ring is complexed, this is also chiral (see C-10); here the diastereomers are present in a 2:1 ratio. In the complexes with one substituent in the complexed aromatic ring (**2e, 2f, 2h, 2m, 2n, 2q**) the ortho and the meta carbon atoms are diastereotopic. Similarly, the ortho carbons are diastereotopic in the para-disubstituted compounds **2i, 2j, 2k,** and **2p**.

(b) (η^6-Arene)(η^1,η^3-cyclooctenediyl)cobalt Complexes. The ^{13}C NMR data for the cationic and neutral 1-η^1,4–6-η^3-cyclooctenediyl complexes are collected in Table II.

In the ^{13}C NMR spectra of complexes **18** the number of signals, their intensities, multiplicities, and values of ^1J(C,H) all suggest that a 1-η^1,4–6-η^3-cyclooctenediyl ring is present. However, in the ^{13}C NMR spectra of transition-metal complexes of symmetrically substituted η^3-allyl groups the resonance of the meso carbon atom is usually found well to a lower field of that of the terminal carbon atoms, as observed here for the cyclopentenyl and cyclohexenyl compounds **12** and **15**. The chemical shifts of the η^3-allyl carbon atoms of **18** are very unusual because the signal of the meso carbon atom is found to *higher* field than that of the terminal carbons.

The structure of the C_8 ring in **18a** and the signal assignments were therefore checked by further experiments. The assignment in the ^{1}H NMR spectrum of H-5 (triplet) and H-4 (quartet) is unambiguous. A 2D ^{13}C,^{1}H shift correlated NMR spectrum[18] showed that the ^{1}H and ^{13}C assignments are completely consistent. Further confirmation of the structure was obtained from a 1D INADEQUATE NMR spectrum.[19]

The other complexes containing this η^1,η^3-cyclooctenediyl ligand in which the η^6-arene has been replaced by Cp, acac, or other ligands (**21–26, 30**) show the usual pattern of chemical shifts, with the meso resonance at a lower field of that of the other allyl carbon atoms.

An X-ray crystallographic analysis was carried out on complexes **22** and **23**; their molecular structures are illustrated in Figure 1.

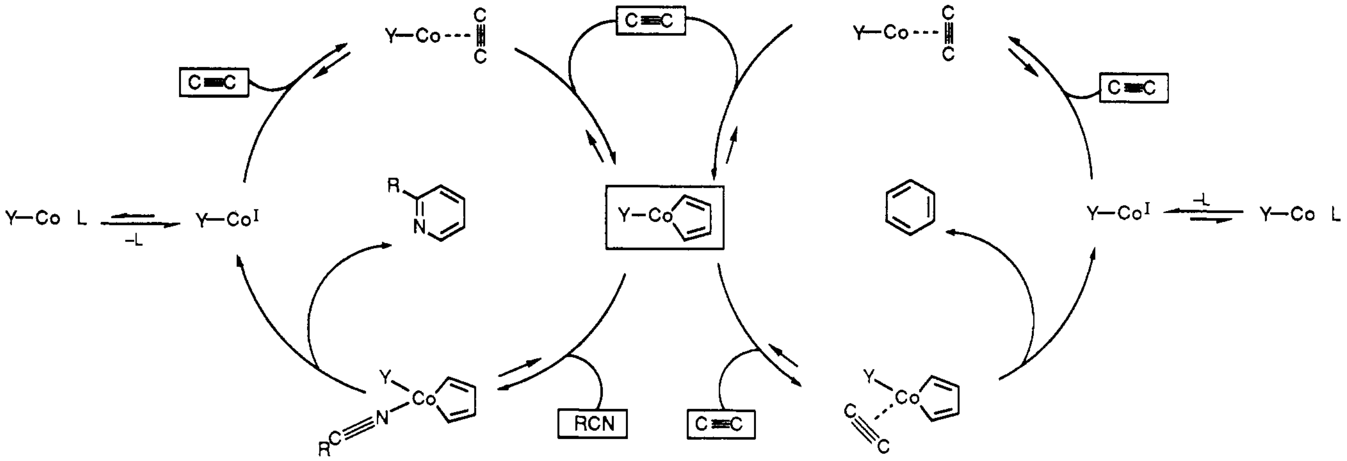
The atomic fractional coordinates for both compounds are given in Table III and selected distances and angles are given in Table IV. In **22** there are two independent molecules in the asymmetric unit. They are essentially similar and differ only by a rotation of the η^5-cyclopentadienyl ring about the metal–ring axis.

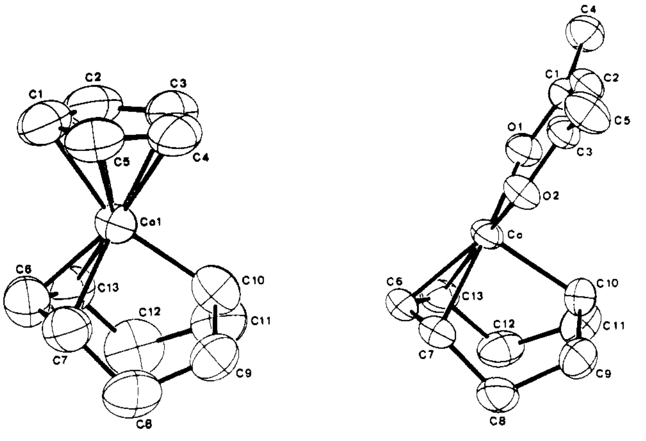
---

(18) For a general review, see: Bax, A. *Top. Carbon-13 NMR Spectrosc.* **1984**, *4*, 197.

(19) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849.

Scheme I





(22) (23)

Figure 1. Molecular structures of complexes 22 and 23.

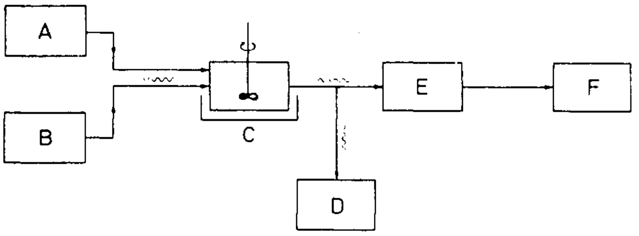
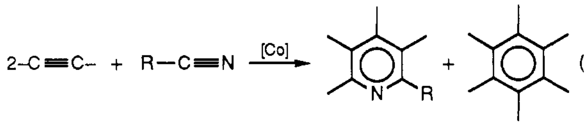


Figure 2. Continuous-flow apparatus for optimation of homogeneous catalytic processes: A, catalyst solution; B, educts; C, thermostated reactor; D, trap; E, gas chromatograph; F, data interpretation.

Replacement of the C_5H_5 ring in **22** by the acetylacetonate ligand (acac) in **23** results in no significant change in the geometry in the remainder of the molecule, the acac ligand merely adopts a position such that the atoms Co, C7, C13, O1, and O2 lie in a plane (±0.02 Å). It is clear from the observed geometry that the coordination about the metal atom is not determined by steric effects alone. The square-pyramidal ligand geometry can be attributed to the six d electrons on the metal, which force the metal to retain its octahedral origins.[20] The favorable delocalization afforded by the coordinated acac ligand appears to play a minor role, since a similar square-pyramidal geometry is observed for bis(butadiene)monocarbonyliron,[21] which has no equivalent π-acceptor orbitals in the basal plane.

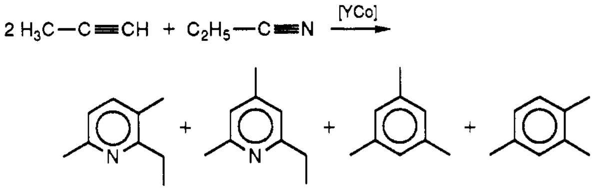
In both compounds there are no intermolecular distances shorter than 3.0 Å between non-hydrogen atoms. The molecules of **23** crystallize in pairs across centers of symmetry with the coordination planes containing the acac ligand lying 3.4 Å apart. As a result, the free coordination site of the cobalt atom points approximately toward C2 of the neighboring molecule. The Co···C2 distance is 3.444 (2) Å and is too large to indicate strong interaction between the two molecules.

6. Test of Complexes 1, 2b, 7b, 11a–c, 12b, and 22 as Catalysts in the Pyridine Synthesis. Complexes of the type [YCoL], where Y is a univalent anionic ligand and L is a neutral ligand, catalyze the cyclotrimerization of alkynes with nitriles (eq 40). In the initial step of the catalysis the stabilizing neutral ligand is eliminated to form the catalytically active species.[22] The Y ligand, which remains bound to the metal during the catalytic cycle, acts as a steering ligand (Scheme I). Reaction 41 is used to characterize the catalysts. The catalytic properties of the YCoL complexes are described by three characteristic quantities. 1. **The Activity of the Catalyst**: this is given indirectly as the temperature required in a continuous-flow reactor to achieve 65% conversion of propyne in the test reaction (eq 41). The higher the temperature required, the lower the activity. 2. **Chemoselectivity**: the ratio of heterocyclics to carbocyclics in the product. 3. **Regioselectivity**: the proportions of symmetric and asymmetric products in the heterocyclic and carbocyclic fractions.



(40)

R = H, alkyl, aryl, functional groups



(41)

Complexes 1, **2b**, **7b**, **11a–c**, **12b**, and **22** were investigated to see whether the catalytic trimerization (eq 41)

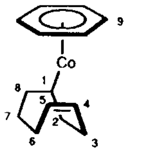
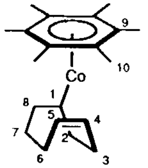
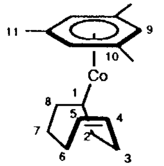
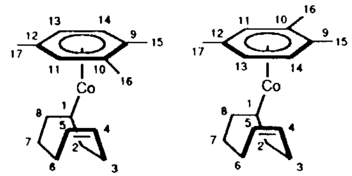
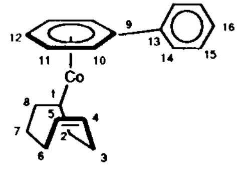
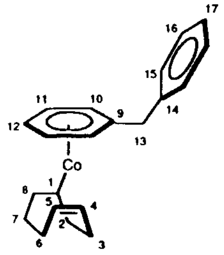
---

(20) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.

(21) Whiting, D. A. *Cryst. Struct. Commun.* **1972**, *1*, 379–381.

(22) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R.; von Philipsborn, W.; Egolf, T. *J. Organomet. Chem.* **1984**, *272*, 231–249.

Table I. ^{13}C NMR Data of Complexes 2a–2q in THF-d_8 Solution

									arene								
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}
 **2a** (243 K)	28.5[e] d[f] *a*	44.1 t 123[g]	29.9 t 124	65.5 d 151	54.9 d 147	29.6 t 123	27.4 t 126	38.6 t 122	94.3 d 170								
 **2b** (243 K)	31.5 d *a*	41.6 t 122	30.5 t *a*	66.2 d *a*	56.5 d 144	29.4 t *a*	27.6 t *a*	36.7 t 121	101.8 s	15.6 q 127							
 **2c** (203 K)	30.2 d 132	42.89 t 123	30.61 t 123	66.7 d 149	56.4 d 144	29.75 t 122	27.00 t 124	38.55 t 121	94.16 d 167	105.72 s	19.67 q 127						
 **2d** (213 K)	29.8 d *a*	42.6 t 122	30.5 t 124	65.8 d 156	56.3 d 144	30.1 t 122	27.2 t 122	37.9 t 121	102.8[b] s	102.7[b] s	97.1 d 165	104.7 s	93.3 d 167	96.5 d 168	17.1[c] q 127	17.5[c] q 127	19.1 q 127
	29.6 d	42.5 t	30.5 t	65.7 d	56.4 d	30.0 t	27.2 t	38.1 t	104.9[b] s	101.7[b] s	96.4 d	103.9 s	94.8 d	95.6 d	17.0[c] q	18.0[c] q	18.9 q
 **2e** (213 K)	28.8 d *a*	43.2 t 123	30.0 t 124	67.0 d 146	56.4 d 144	29.6 t 122	26.7 t 124	38.5 t 121	106.6 s	93.0[d] d 168 92.1[d] d 169	94.5[d] d 171 94.0[d] d 171	94.4 d 170	139.4 s	127.9 d 157	129.6 d 159	128.2 d 161	
 **2f** (243 K)	≃29.0 d *a*	43.8 t 122	30.0 t 125	66.3 d 150	55.8 d 145	29.6 t 122	27.5 t 124	38.4 t 121	109.4 s	94.3[d] d 170 93.4[d] d 169	94.8[d] d 171 94.5[d] d 171	94.5 d 169	41.0 t 128	141.4 s	129.5 d 158	128.2 d 160	127.0 d 159

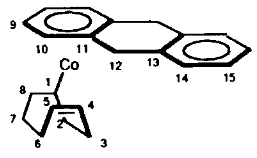
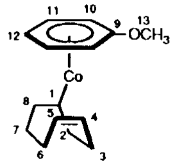
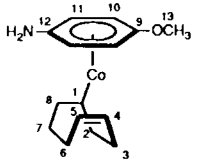
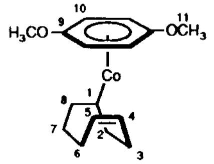
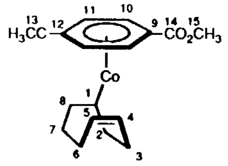
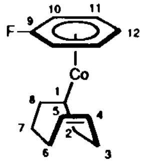
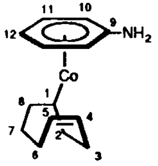
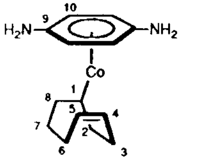
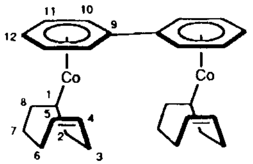
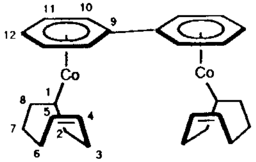
 **2g** (243 K)	28.4 d *a*	42.8 t 123	30.3 t 125	66.5 d 142	56.2 d 146	29.1 t 124	26.5 t *a*	38.0 t 122	92.4^d d 168 91.7^d d *a*	93.8^d d 165 93.6^d d 166	105.8^d s 105.6^d s	34.8^d t 128 34.3^d t 128	136.6^d s 136.4^d s	128.4^d d 156 128.3^d d 156	126.8^d d 160 126.75^d d 160
 **2h** (243 K)	30.2 d 132	43.9 t 123	30.5 t 123	65.3 d 150	55.7 d 146	29.8 t 123	27.7 t 124	39.1 t 122	138.2 s	79.7^d d 170 79.0^d d 170	95.3^{b,d} d 170 94.8^{b,d} d 170	87.1 d 170	55.3 q 145		
 **2i** (243 K)	32.0 d *a*	43.7 t 123	31.3 t 124	63.7 d 150	58.3 d 146	30.7 t 123	28.6 t 123	39.4 t 121	130.2 s	80.5^{b,d} d 168 79.0^{b,d} d 168	78.9^{b,d} d 168 76.9^{b,d} d 167	121.5 s	55.1 q 144		
 **2j** (243 K)	30.5 d 128	44.0 t 123	31.1 t 122	65.7 d 150	57.9 d 142	30.6 t 122	28.0 t 122	39.2 t 121	132.1 s	79.0^d d 169 78.6^d d 171	55.5 q 144				
 **2k** (213 K)	32.8 d *a*	43.2 t 124	30.1 t 123	68.4 d 152	58.8 d 148	30.1 t 123	27.0 t 125	38.9 t 122	83.6 s	96.1^{b,d} d 173 95.8^{b,d} d 172	81.2^d d 172 79.2^d d 172	139.4 s	56.1 q 145	166.8 s	52.3 q 147
 **2m** (213 K)	30.7 d 132	43.5 t 123	30.3 t 123	67.0 d 152	57.0 d 146	29.9 t 123	26.9 t 125	39.1 t 123	141.0 s J_{CF} = 260	82.3^d d 176 J_{CF} = 21 81.1^d d 176 = 21	95.8^d d 172 = 8 95.2^d d 170 = 8	87.3 d 172			
 **2n** (243 K)	33.7 d 128	43.5 t 122	31.0 t 124	62.8 d 150	54.6 d 144	30.0 t 123	28.1 t 126	39.5 t 121	128.9 s	79.1^d d 168 77.8^d d 166	95.7^d d 168 95.6^d d 168	83.4 170			

Table I (Continued)

	C1	C2	C3	C4	C5	C6	C7	C8	arene C9	C10	C11	C12	C13	C14	C15	C16	C17
 **2p** (243 K)	34.6 d 132	43.3 t 123	31.3 t 124	61.4 d 150	57.7 d 146	30.8 t 123	29.1 t 125	39.6 t 121	118.6 s	79.7[d] d 166 79.2[d] d 164							
	≃28.9 d *a*	43.3 t 123	30.0 t 121	67.0 d 154	56.4 d 145	29.7 t 122	26.7 t *a*	38.4 t 121	104.0 s	93.2 d 168 92.5 d 168	94.1 d 171 93.8 d 171	94.5 d 171					
 **2q** (193 K)	≃28.9 d *a*	43.2 t 123	30.0 t 121	67.0 d 154	56.4 d 145	29.7 t 122	26.7 t *a*	38.4 t 121	103.9 s	93.1 d 169 94.0 d 169	92.4 d 171 93.8 d 171	94.5 d 171					

[a] Not determined (signal obscured). [b or c] These assignments can be reversed. [d] Diastereotopic. [e] Chemical shifts in ppm. [f] Multiplicity. [g] Coupling constant in hertz.

could be controlled by the allyl group. The results are summarized in Table V.

(η^5-Cyclopentadienyl)(η^1,η^3-cyclooctenediyl)Co (**22**) shows the same activity and chemoselectivity as the reference complex (η^5-Cp)(η^2,η^2-COD)Co (**28**). Thus the η^1,η^3-cyclooctenediyl ligand can be regarded as an isomer of cyclooctadiene. The η^1,η^3-cyclooctenediyl ligand is clearly more easily displaced by the alkyne/nitrile under catalytic conditions than the η^5-cyclopentadienyl ligand.

The new allyl–Co complexes **7b**, **11a**, and **11b** all have a low activity similar to that of η^3-cyclooctenyl–Co–COD (**1**). Just like **1**, they direct the catalysis toward the production of carbocyclics and the ratios of isomers (72:28 for the pyridine derivatives and 43:57 for the benzene derivatives) are the same as for **1**. Interestingly, the values for (η^6-C_6Me_6)(η^1,η^2-cyclooctenyl)Co (**2b**) are also similar to those for **7b**, **11a**, and **11b**, so that the major steering factor in all these complexes must be the same. Unlike for R–Cp–Co and R–Ind–Co complexes, no fine control was achieved by the introduction of substituents into the allyl group.

The behavior of the (η^3-cyclopentenyl)cobalt complexes **12b** and **12c** in the catalysis differs greatly from that of the others. They are much more active and produce more of the heterocyclic products. In addition, the isomer ratios of both the pyridine and the benzene derivatives differ from those obtained with the other allyl–Co systems. The catalytic characteristics suggest that the cyclopentenyl–Co compounds undergo partial dehydrogenation to form Cp–Co catalysts, so that in the reaction mixture the active species from both the original cyclopentenyl complex and [CpCo] are present. Taking the known characteristic values for (η^5-Cp)(η^2,η^2-COD)Co (**28**) and the other allyl–Co complexes, then the experimental values for the cyclopentenyl–Co–arene complexes are consistent with the conversion of ca. 60% of this compound to [CpCo]. A test experiment to check this result, using a mixture of 60% (η^5-cyclopentadienyl)(η^4-butadiene)cobalt and 40% (η^6-benzene)(cyclohexenyl)cobalt (**11a**) produced data which are in satisfactory agreement with this supposition (see Table VI).

Experimental Section

All preparations were carried out in an atmosphere of purified argon. The solvents were carefully dried and distilled in an argon atmosphere. The Al_2O_3 for column chromatography was degassed in vacuum and transferred under argon. ^1H NMR spectra were recorded on a Bruker WP 80 FT spectrometer and ^{13}C NMR spectra on a Bruker WM 300 spectrometer (75.5 MHz). IR spectra were recorded on a Nicolet 7199 FT-IR spectrometer. Mass spectra were recorded on Varian MAT CH 5 and CH7 spectrometers. Elemental analyses were carried out by Dornis and Kolbe, Mülheim a.d. Ruhr. (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (**1**) was prepared as described in the literature.[22]

X-ray Crystallographic Analyses of 22 and 23. Details of data collection are given in Table VII. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα X-radiation (λ = 0.71069 Å). Lattice parameters were determined by a least-squares fit to the θ values of 74 (75 for **23**) reflections in the range $9.97 < \theta < 17.2°$ ($13.7 < \theta < 28.3$). The structures of **22** and **23** were solved by Patterson methods and refined to convergence. For **22**: $R = 0.031$ ($R_w = 0.036$) for 2525 unique observed reflections (error of fit = 1.61). For **23**: $R = 0.033$ ($R_w = 0.049$) for 3160 unique observed reflections (error of fit = 2.98). Refinement was by least squares where the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Hydrogen atoms were included in the refinement at calculated positions (C–H = 0.95 Å) with fixed isotropic thermal parameters (U_H = 0.06 Å^2 for **22** and U_H = 0.05 Å^2 for **23**). The scattering factors were taken from ref 23 and those for Co were corrected for the effects of anomalous dispersion ($\Delta f' = 0.299$; $\Delta f'' = 0.0973$). Refinement of the enantiomorphic structure in the case of **22** gave $R_w = 0.044$, indicating the chosen enantiomorph to be the correct one.

Synthesis of (η^6-Arene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt Complexes (2). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) was dissolved in 50 mL of arene and 3 mL (30 mmol) of piperidine. After the reaction solution had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 230 mL (9.4 mmol) of hydrogen gas at 323 K (reaction time: 4 h). The color of the solution changed from brown to deep red. The solvent was removed under vacuum, and the residue was redissolved in pentane and filtered over Al_2O_3 (7% H_2O) at room temperature.

(η^6-Benzene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt (2a). The crystallization at 195 K gave 2.0 g (8.1 mmol) (89% of theory) of **2a** as red crystals, mp 365 K. Mass spectrum: *m/z* 246 (98%, $[M]^+$), 168 (22%, $[C_8H_{13}Co]^+$), 166 (30%, $[C_8H_{11}Co]^+$), 164 (61%, $[C_8H_9Co]^+$), 137 (100%, $[C_6H_6Co]^+$), 78 (58%, $[C_6H_6]^+$, 59 (30%, $[Co]^+$). Anal. Calcd for $C_{14}H_{19}Co$: C, 68.29; H, 7.72; Co, 23.98. Found: C, 68.39; H, 7.76; Co, 23.81.

(η^6-Hexamethylbenzene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2b). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) and 2.5 g (15.4 mmol) of hexamethylbenzene were dissolved in 60 mL of hexane and 3 mL (30 mmol) of piperidine. After the reaction solution had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 550 mL (22.4 mmol) of hydrogen gas at 323 K. The solvent was removed under vacuum, and the residue was chromatographed on Al_2O_3 (7% H_2O). **2b** was eluted with pentane. Crystallization at 243 K gave **2b** as red crystals: yield 0.4 g (1.2 mmol) (13% of theory); mp 437 K. Mass spectrum: *m/z* 300 (65%, $[M]^+$), 221 (53%, $[C_{12}H_{18}Co]^+$), 220 (100%, $[C_{12}H_{17}Co]^+$), 162 (30%, $[C_{12}H_{18}]^+$). Anal. Calcd for $C_{20}H_{31}Co$: C, 72.73; H, 9.39; Co, 17.88. Found: C, 72.89; H, 9.30; Co, 17.82.

(η^6-Mesitylene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt (2c). Crystallization at 195 K gave 2.1 g (7.3 mmol) (80% of theory) of **2c**, mp 375 K. Mass spectrum: *m/z* 288 (80%, $[M]^+$), 179 (100%, $[C_9H_{12}Co]^+$), 168 (15%, $[C_8H_{13}Co]^+$), 120 (25%, $[C_9H_{12}]^+$), 59 (35%, $[Co]^+$). Anal. Calcd for $C_{17}H_{25}Co$: C, 70.83; H, 8.68; Co, 20.49. Found: C, 70.86; H, 8.53; Co, 20.48.

(η^6-Pseudocumene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt (2d). Crystallization at 193 K gave 2.0 g (6.9 mmol) (76% of theory) of **2d**. **2d** is a mixture of two diastereomers in the ratio of 2:1. The same preparation at 273 K gave the two diastereomers in a ratio of 4.5:1. Melting point: liquid at room temperature, decomposition at 413 K. Mass spectrum: *m/z* 288 (20%, $[M]^+$), 179 (20%, $[C_9H_{12}Co]^+$), 120 (45%, $[C_9H_{12}]^+$), 105 (100%, $[C_8H_9]^+$). Anal. Calcd for $C_{17}H_{25}Co$: C, 70.82; H, 8.74; Co, 20.44. Found: C, 70.92; H, 8.95; Co, 20.08.

(η^6-Biphenyl)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2e). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) and 3.5 g (22.7 mmol) of biphenyl were combined with 3 mL (30 mmol) of piperidine. After the reaction mixture had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 223 mL (9.1 mmol) of hydrogen gas at 323 K. The liquid components were removed under vacuum, and the residual biphenyl was sublimed off in high vacuum at room temperature over 16 h. The residue was dissolved in pentane and filtered over Al_2O_3 (7% H_2O). Crystallization in pentane gave 1.9 g (5.9 mmol) (65% of theory) of **2e** as dark red crystals, mp 329–331 K. Mass spectrum: *m/z* 322 (40%, $[M]^+$), 213 (50%, $[C_{12}H_{10}Co]^+$), 168 (10%, $[C_8H_{13}Co]^+$), 154 (100%, $[C_{12}H_{10}]^+$), 59 (35%, $[Co]^+$). Anal. Calcd for $C_{20}H_{23}Co$: C, 74.52; H, 7.19; Co, 18.28. Found: C, 74.69; H, 6.96; Co, 18.38.

(η^6-Diphenylmethane)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2f). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) was dissolved in 6 mL (36.4 mmol) of diphenylmethane and 3 mL (30 mmol) of piperidine. After the reaction mixture had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 223 mL (9.1 mmol) of hydrogen gas at 323 K. All liquid components including unreacted diphenylmethane were removed in high vacuum at room temperature over 16 h. The residue was dissolved in pentane and filtered over Al_2O_3 (7% H_2O). Crystallization in pentane at 193 K gave 2.2 g (6.5 mmol) (72% of theory) of **2f** as orange crystals. Melting point: **2f** is liquid at room temperature, decomposition at 393 K. Mass spectrum: *m/z* 336 (20% $[M]^+$), 227 (45%, $[C_{13}H_{14}Co]^+$), 168 (98%, $[C_8H_{13}Co]^+$ and $[C_{13}H_{12}]^+$), 167 (100%, $[C_8H_{12}Co]^+$ and $[C_{13}H_{11}]^+$), 59 (25%, $[Co]^+$). Anal. Calcd for $C_{21}H_{25}Co$: C, 74.99; H, 7.49; Co, 17.52. Found: C, 74.84; H, 7.55; Co, 17.54.

(η^6-9,10-Dihydroanthracene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2g). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) and 3.3 g (18.2 mmol) of 9,10-dihydroanthracene were dissolved in 3 mL (30 mmol) of piperidine and 5 mL of THF. After the reaction solution had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 223 mL (9.1 mmol) of hyrogen gas at 323 K. All liquid components were removed under vacuum, the residual 9,10-dihydroanthracene was sublimed off in high vacuum at 313 K over 16 h. The residue was dissolved in pentane and filtered; crystallization in pentane at 193 K gave 1.1 g (3.2 mmol) (35% of theory) of **2g** as orange-red crystals, mp 349–351 K, decomp 423 K. Mass spectrum: *m/z* 348 (45%, $[M]^+$), 238 (40%, $[C_{14}H_{11},co]^+$), 180 (45%, $[C_{14}H_{12}]^+$), 179 (100%, $[C_{14}H_{11}]^+$), 178 (70%, $[C_{14}H_{10}]^+$). Anal. Calcd for $C_{22}H_{25}Co$: C, 75.85; H, 7.23; Co, 16.92. Found: C, 75.65; H, 6.99; Co, 19.70.

(η^6-Anisole)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2h). Crystallization at 243 K gave 2.4 g (8.7 mmol) (96% of theory) of **2h** as red crystals, mp 306 K. Mass spectrum: *m/z* 276 (59%, $[M^+]$), 168 (25%, $[C_8H_{13}Co]^+$), 167 (12%, $[C_8H_{12}Co]^+$), 108 (10%, $[C_7H_8O]^+$). Anal. Calcd for $C_{15}H_{21}CoO$: C, 65.22; H, 7.61; Co, 21.38. Found: C, 65.06; H, 7.64; Co, 21.37.

(η^6-*p*-Anisidine)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2i). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) and 2.5 g (20.6 mmol) of *p*-anisidine were combined with 3 mL (30 mmol) of piperidine. After the reaction mixture had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 223 mL (9.1 mmol) of hydrogen gas at 323 K. The liquid components were removed under vacuum; the unreacted *p*-anisidine was removed by sublimation in high vacuum at 313 K over 16 h. The residue was dissolved in ether and filtered over Al_2O_3 (7% H_2O). Crystallization in ether/heptane at 273–193 K gave 1.9 g (6.6 mmol) (72% of theory) of **2i** as orange crystals, mp 333–335 K. Mass spectrum: *m/z* 291 (7%, $[M]^+$), 182 (5%, $[C_7H_9CoNO]^+$), 123 (65%, $[C_7H_9NO]^+$), 108 (100%, $[C_8H_{12}]^+$ and $[C_6H_6NO]^+$). Anal. Calcd for $C_{15}H_{22}CoNO$: C, 61.85; H, 7.61; Co, 20.23; N, 4.81. Found: C, 61.80; H, 7.66; Co, 20.19; N, 4.76.

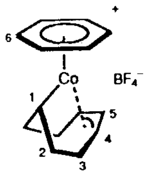
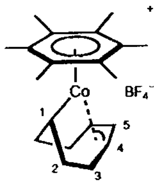
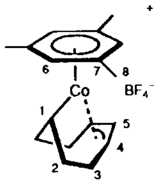
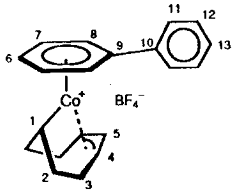
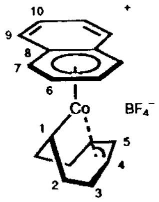
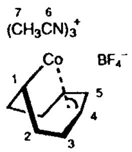
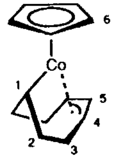
(η^6-Hydroquinol dimethyl ether)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2j). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol), 5 g (36.3 mmol) of hydroquinol dimethyl ether, and 3 mL (30 mmol) of piperidine were frozen with liquid nitrogen. The reaction vessel was evacuated and then filled with 223 mL (9.1 mmol) of hydrogen gas at 323 K. The liquid components were removed under vacuum; the residual hydroquinol dimethyl ether was sublimed off in high vacuum at room temperature over 12 h. The residue was dissolved in pentane and filtered over Al_2O_3 (7% H_2O). Crystallization in pentane at 193 K gave 1.6 g (5.2 mmol) (57% of theory) of **2j** as orange crystals, mp 288 K. Mass spectrum: *m/z* 306 (100%, $[M]^+$), 197 (50%, $[C_8H_{10}O_2Co]^+$), 167 (55%, $[C_8H_{12}Co]^+$), 138 (60%, $[C_8H_{10}O_2]^+$), 123 (95%, $[C_7H_7O_2]^+$), 59 (40%, $[Co]^+$). Anal. Calcd for $C_{16}H_{23}CoO_2$: C, 62.74; H, 7.57; Co, 19.24. Found: C, 62.76; H, 7.49; Co, 19.06.

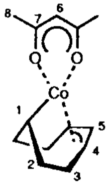
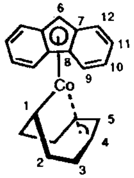
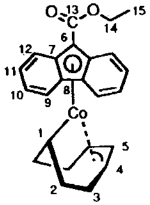
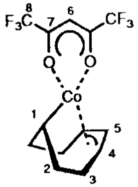
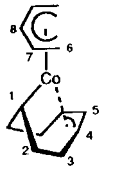
(η^6-*p*-Carbomethoxyanisole)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2k). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol), 9 g (54 mmol) of *p*-carbomethoxyanisole, and 3 mL (30 mmol) of piperidine were frozen with liquid nitrogen. After the reaction vessel had been evacuated, it was filled with 223 mL (9.1 mmol) of hydrogen gas at 323 K. The liquid components were removed under vacuum; the residual *p*-carbomethoxyanisole was sublimed off in high vacuum at room temperature over 16 h. The residue was dissolved in pentane, filtered over Al_2O_3 (7% H_2O), and crystallized at 193 K. Yield: 1.7 g (5.1 mmol) (56% of theory) of dark red crystals of **2k**, mp 344–346 K. Mass spectrum: *m/z* 334 (3%, $[M]^+$), 224 (3%, $[M - C_8H_{14}]^+$), 166 (25%, $[C_9H_{10}O_3]^+$), 135 (100%, $[C_8H_7O_2]^+$). Anal. Calcd for $C_{17}H_{23}CoO_3$: C, 61.08; H, 6.93; Co, 17.63. Found: C, 61.20; H, 6.98; Co, 17.65.

---

(23) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 99–102, 149.

Table II. ^{13}C NMR Data of Complexes **18a**–**18r** and **21**–**30**

	no.	LM[a]	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
	**18a** (213 K)	A	59.4[b] d[c] 139[d]	47.9 t 127	26.0 t 130	92.4 d 157	87.6 d 163	103.7 d 178									
	**18b** (313 K)	A	64.5 d 136	45.9 t 126	27.3 t 130	92.8 d 158	92.7 d 158	113.6 s	16.5 q 129								
	**18c** (213 K)	A	60.9 d 138	46.6 t 127	26.2 t 129	92.1 d 158	89.4 d 162	102.7 d 173	116.7 s	19.0 q 130							
	**18e** (193 K)	A	61.0 d 139	47.4 t 127	26.2 t 129	93.5 d 158	89.0 d 162	102.2 d 179	103.9 d 177	100.5 d 174	118.5 s	131.7 s	129.8[e] d 163	127.2[e] d 160	131.1 d 163		
	**18r** (193 K)	A	61.1 d 142	46.4 t 127	25.7 t 129	94.5 d 158	92.0 d 162	100.9 d.d 176	98.7 d 176	111.0 s	126.4 d 167	133.2 d.d 166					
	**21** (313 K)	B	43.5 d 144	42.2 t 126	24.7 t 128	76.9 d 154	105.5 d 157	127.3 s	2.5 q								
	**22** (313 K)	C	42.3 d ≃133	49.1 t 123	29.2 t 126	75.8 d 152	80.4 d 157	84.1 d 175									

	**23** (313 K)	B	42.9 d 141	41.6 t 125	26.6 t 126	68.3 d 155	105.1 d 155	97.5 d 156	187.2 s	28.3 q 126							
	**24** (313 K)	D	44.9 d 136	45.45 t 124	28.40 t 126	81.75 d 151	90.32 d 158	61.69 d 178	97.75[e] s	108.14[e] s	122.63[f] d 160	122.98[f] d 159	124.85[f] d 160	126.31[f] d 158			
	**25** (243 K)	D	50.27 d 139	43.92 t 124	28.02 t 127	82.69 d 152	90.96 d 158	61.40 s	100.40[e] s	108.89[e] s	122.51[f] d 160	124.03[f] d 160	126.76[f] d 167	127.78[f] d 160	171.72 s	59.92 t 146	14.87 q 126
	**26** (313 K)	D	50.2 d 143	40.56 t 128	25.62 t 129	73.47 d 156	102.63 d 154	90.98 d 167	175.56 s $^1J_{CF}$ = 35 Hz	118.97 s $^1J_{CF}$ = 284 Hz							
	**30** (243 K)	D	46.7 d 138	50.78 t 124	28.88 t 126	79.26 d 153	87.16 d 159	58.61 t 154/158	101.48 d 159	96.22 d 163							

[a] LM: A, CD_2Cl_2; B, THF-d_8; C, benzene-d_6; D, toluene-d_8. [b] Chemicals shifts in ppm. [c] Multiplicity. [d] Coupling constants in hertz. [e or f] These assignments can be reversed.

Table III. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}
		22		
Co1	0.0405 (1)	0.2742 (1)	0.1737 (1)	0.049
Co2	0.4556 (1)	0.2261 (1)	0.3414 (1)	0.044
C1	0.1306 (4)	0.3520 (4)	0.0814 (8)	0.076
C2	0.0573 (5)	0.3951 (4)	0.1136 (8)	0.081
C3	−0.0021 (4)	0.3638 (4)	0.017 (1)	0.080
C4	0.0323 (6)	0.3001 (5)	−0.0747 (7)	0.094
C5	0.1158 (4)	0.2938 (4)	−0.0351 (8)	0.078
C6	0.0966 (4)	0.2399 (4)	0.3788 (8)	0.073
C7	0.0927 (3)	0.1713 (3)	0.2747 (8)	0.067
C8	0.0314 (4)	0.1039 (3)	0.2806 (8)	0.078
C9	−0.0389 (4)	0.1227 (3)	0.1711 (8)	0.074
C10	−0.0613 (3)	0.2101 (3)	0.1757 (8)	0.063
C11	−0.1099 (3)	0.2316 (4)	0.3306 (9)	0.077
C12	−0.0544 (4)	0.2421 (4)	0.4830 (8)	0.080
C13	0.0234 (4)	0.2830 (4)	0.4318 (7)	0.068
C21	0.4636 (5)	0.1518 (5)	0.5565 (9)	0.089
C22	0.5293 (5)	0.2053 (4)	0.5494 (9)	0.088
C23	0.5724 (4)	0.1942 (4)	0.404 (1)	0.084
C24	0.5332 (4)	0.1306 (4)	0.3174 (8)	0.074
C25	0.4662 (4)	0.1029 (4)	0.4092 (9)	0.083
C26	0.3471 (3)	0.2672 (3)	0.3658 (8)	0.067
C27	0.3468 (3)	0.2292 (3)	0.2184 (8)	0.073
C28	0.3554 (4)	0.2646 (4)	0.0461 (9)	0.088
C29	0.4413 (4)	0.2689 (4)	−0.0057 (7)	0.071
C210	0.4946 (3)	0.2872 (3)	0.1425 (8)	0.061
C211	0.4973 (4)	0.3756 (3)	0.1865 (9)	0.073
C212	0.4245 (4)	0.3994 (3)	0.2858 (7)	0.076
C213	0.3996 (4)	0.3308 (3)	0.4043 (7)	0.071
		23		
Co	0.3109 (1)	0.1845 (1)	0.1756 (1)	0.042
O1	0.2439 (2)	0.1420 (2)	0.0172 (2)	0.048
O2	0.4002 (2)	−0.0398 (2)	0.2640 (2)	0.051
C1	0.2519 (2)	0.0005 (2)	0.0059 (2)	0.044
C2	0.3116 (3)	−0.1449 (2)	0.1055 (2)	0.051
C3	0.3847 (2)	−0.1578 (2)	0.2251 (2)	0.045
C4	0.1947 (3)	−0.0026 (3)	−0.1305 (2)	0.059
C5	0.4572 (4)	−0.3237 (3)	0.3169 (3)	0.070
C6	0.3759 (3)	0.3727 (2)	0.1782 (3)	0.057
C7	0.3747 (3)	0.2728 (3)	0.3267 (3)	0.059
C8	0.2245 (3)	0.2882 (3)	0.4669 (2)	0.067
C9	0.1089 (3)	0.1817 (3)	0.4777 (3)	0.064
C10	0.0817 (3)	0.1988 (3)	0.3199 (2)	0.051
C11	−0.0404 (3)	0.3553 (3)	0.2536 (3)	0.061
C12	0.0449 (3)	0.4951 (3)	0.1907 (3)	0.060
C13	0.2334 (3)	0.4357 (2)	0.1099 (2)	0.054

Table IV. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

molecule 1		molecule 2	
	22		
	(a) Distances		
Co1–C6	1.969 (6)	Co2–C26	1.934 (6)
Co1–C7	2.076 (6)	Co2–C27	2.057 (6)
Co1–C10	1.996 (5)	Co2–C210	1.994 (6)
Co1–C13	2.089 (5)	Co2–C213	2.034 (6)
C6–C7	1.41 (1)	C26–C27	1.34 (1)
C6–C13	1.47 (1)	C26–C213	1.40 (1)
C7–C8	1.51 (1)	C27–C28	1.51 (1)
C8–C9	1.49 (1)	C28–C29	1.49 (1)
C9–C10	1.50 (1)	C29–C210	1.51 (1)
C10–C11	1.52 (1)	C210–C211	1.51 (1)
C11–C12	1.54 (1)	C211–C212	1.50 (1)
C12–C13	1.51 (1)	C212–C213	1.54 (1)
	(b) Angles		
C13–Co1–C10	85.1 (3)	C213–Co2–C210	84.9 (2)
C13–Co1–C7	74.3 (2)	C213–Co2–C27	72.3 (2)
C13–Co1–C6	42.4 (3)	C213–Co2–C26	41.3 (2)
C10–Co1–C7	84.9 (2)	C210–Co2–C27	83.7 (2)
C10–Co1–C6	103.8 (2)	C210–Co2–C26	101.7 (2)
C7–Co1–C6	40.7 (2)	C27–Co2–C26	39.0 (2)
C13–C6–C7	121.6 (5)	C213–C26–C27	123.4 (5)
C13–C6–Co1	73.2 (3)	C213–C26–Co2	73.1 (3)
C7–C6–Co1	73.7 (3)	C27–C26–Co2	75.5 (4)
C8–C7–C6	127.5 (5)	C28–C27–C26	128.6 (5)
C8–C7–Co1	109.9 (4)	C28–C27–Co2	111.4 (4)
C6–C7–Co1	65.5 (3)	C26–C27–Co2	65.5 (3)
C9–C8–C7	110.7 (5)	C29–C28—C27	111.4 (5)
C10–C9–C8	112.4 (5)	C210–C29–C28	110.7 (5)
C11–C10–C9	112.3 (5)	C211–C210–C29	113.3 (5)
C11–C10–Co1	109.3 (4)	C211–C210–Co2	108.5 (4)
C9–C10–Co1	107.8 (4)	C29–C210–Co2	109.5 (4)
C12–C11–C10	110.8 (5)	C212–C211–C210	110.8 (5)
C13–C12–C11	110.3 (5)	C213–C212–C211	110.4 (5)
C12–C13–C6	124.3 (5)	C212–C213–C26	126.0 (5)
C12–C13–Co1	110.6 (4)	C212–C213–Co2	111.0 (4)
C6–C13–Co1	64.5 (3)	C26–C213–Co2	65.5 (3)
	23		
	(a) Distances		
Co–O1	1.914 (1)	Co–O2	1.915 (1)
Co–C6	1.947 (2)	Co–C7	2.083 (2)
Co–C10	1.979 (2)	Co–C13	2.074 (2)
O1–C1	1.281 (3)	O2–C3	1.273 (2)
C1–C2	1.394 (3)	C1–C4	1.509 (3)
C2–C3	1.395 (3)	C3–C5	1.508 (3)
C6–C7	1.412 (3)	C6–C13	1.404 (3)
C7–C8	1.524 (3)	C8–C9	1.539 (4)
C9–C10	1.521 (3)	C10–C11	1.522 (4)
C11–C12	1.527 (4)	C12–C13	1.523 (4)
	(b) Angles		
C13–Co–C10	87.0 (1)	C13–Co–O2	169.0 (1)
C13–Co–O1	96.4 (1)	C10–Co–C7	86.4 (1)
C10–Co–C6	104.6 (1)	C10–Co–O2	93.3 (1)
C10–Co–O1	94.8 (1)	C7–Co–O2	95.3 (1)
C7–Co–O1	170.0 (1)	O2–Co–O1	94.6 (1)
C1–O1–Co	124.7 (1)	C3–O2–Co	124.6 (1)
C4–C1–C2	119.6 (2)	C4–C1–O1	115.0 (2)
C2–C1–O1	125.3 (2)	C3–C2–C1	124.4 (2)
C5–C3–C2	119.3 (2)	C5–C3–O2	115.1 (2)
C2–C3–O2	125.7 (2)	C13–C6–C7	124.8 (2)
C8–C7–C6	125.9 (2)	C9–C8–C7	109.6 (2)
C10–C9–C8	110.3 (2)	C11–C10–C9	117.5 (2)
C12–C11–C10	111.7 (2)	C13–C12–C11	110.5 (2)
C12–C13–C6	126.3 (2)		

(η^6-Fluorobenzene)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2m). Crystallization at 193 K gave 550 mg (2.1 mmol) (23% of theory) of **2m** as orange crystals, mp 379–381 K. Mass spectrum: m/z 264 (50%, $[M]^+$), 164 (50%, $[C_8H_9Co]^+$), 155 (20%, $[C_6H_5FCo]^+$), 138 (50%, $[C_6H_7Co]^+$), 124 (100%, $[C_5H_5Co]^+$), 96 (30%, $[C_6H_5F]^+$), 59 (70%, $[Co]^+$). Anal. Calcd for $C_{14}H_{18}CoF$: C, 63.64; H, 6.87; Co, 22.30; F, 7.19. Found: C, 63.49; H, 6.89; Co, 22.37; F, 7.18.

(η^6-Aniline)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2n). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) was dissolved in 40 mL of aniline. After the reaction solution had been frozen in liquid nitrogen, the reaction vessel was evacuated and then filled with 446 mL (18.2 mmol) of hydrogen gas at 20 °C (reaction time: 10 h). The solvent was removed; the residue redissolved in ether and filtered over Al_2O_3 (7% H_2O). Crystallization in pentane/ether gave 2.3 g (8.8 mmol) (96% of theory) of **2n** as orange-red crystals, mp 321 K. Mass spectrum: m/z 261 (36%, $[M]^+$), 168 (11%, $[C_8H_{13}Co]^+$), 166 (5%, $[C_8H_{11},co]^+$), 164 (13%, $[C_8H_9Co]^+$), 152 (45%, $[C_6H_7NCo]^+$), 93 (100%, $[C_7H_6N]^+$), 59 (14%, $[Co]^+$). Anal. Calcd for $C_{14}H_{20}CoN$: C, 64.37; H, 7.66; N, 5.36. Found: C, 64.45; H, 7.80; N, 5.28.

(η^6-p-Phenylenediamine)(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I) (2p). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) (2.5 g, 9.1 mmol) and 4 g (37 mmol) of p-phenylenediamine were dissolved in 5 mL of THF. After the reaction solution had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 446 mL (18.2 mmol) of hydrogen gas at 323 K. The solvent was removed under vacuum; the residual p-phenylenediamine was sublimed off at 313 K in high vacuum over 24 h. The residue was dissolved in ether and filtered over Al_2O_3 (7% H_2O). Crystallization in heptane/ether gave 1.9 g (6.9 mmol) (76% of theory) of **2p** as red crystals, mp 430 K. Mass spectrum:

Table V

complex	reaction temp, °C (65% unsat)	chemoselect. Py/Be	regioselect.			
			Py		Be	
			% sym	% asym	% sym	% asym
η^5-CpCo–η^2,η^2-COD (**27**)	147	1.8	63.1	36.9	27.2	72.8
η^5-CpCo–η^1,η^3-COD (**22**)	147	2.3	62.5	37.5	26.6	73.4
η^3-C_8H_{13}Co–η^2,η^2-COD (**1**)	130 (15%)	0.5	69.9	30.1	41.0	59.0
η^1,η^2-cycloctenyl–Co–C_6Me_6 (**26**)	165 (28.6%)	0.45	72.0	28.0	42.6	57.4
η^3-cyclohexenyl–Co–C_6H_6 (**11a**)	155 (31.5%)	0.43	71.5	28.5	42.4	57.6
η^3-cyclohexenyl–Co–C_6Me_6 (**11b**)	162 (28%)	0.47	72.1	27.9	42.7	57.3
η^3-crotyl–Co–C_6Me_6 (**7b**)	169 (34%)	0.76	72.1	27.9	42.6	57.4
η^3-cyclopentenyl–Co–$C_6H_3Me_3$ (**12c**)	158	1.54	65.8	34.2	32.7	67.3
η^3-cyclopentenyl–Co–C_6Me_6 (**12b**)	160	1.38	67.5	32.5	33.3	66.7

Table VI

	Py/Be	% P_{sym}	% P_{asym}	% B_{sym}	% B_{asym}
CpCo–butadiene					
cyclohexenyl–Co–benzol (**11a**)	1.45	67	33	27	73
theor (3:2)	1.26	67	33	32	68

Table VII. Crystal Data and Details of Data Collection

	22	**23**
empirical formula	$C_{13}H_{17}Co$	$C_{13}H_{19}O_2Co$
mol wt	232.2	266.2
crystal color	brown-red	black
a, Å	16.583 (2)	8.4165 (8)
b, Å	16.583 (2)	8.9539 (9)
c, Å	7.995 (1)	9.3770 (5)
α, deg	90.0	72.588 (5)
β, deg	90.0	72.224 (5)
γ, deg	90.0	70.521 (8)
V, Å^3	2198.4	618.9
Z	8	2
cryst size, mm	0.30 × 0.28 × 0.28	0.36 × 0.54 × 0.54
space group	$P\bar{4}$	$P\bar{1}$
μ(Mo Kα), cm^{-1}	15.15	13.66
absorptn correctn	empirical	
correctn factors	1.11–0.75	
scan type	ω–2θ	ω–2θ
2θ_{max}, deg	24.9	29.9
data collected	$\pm h,\pm k,\pm l$	$\pm h,\pm k,+l$
reflctns measd	9006	3564
independent reflctns	3824	3563
R_{av}	0.020	
reflctns with $I > 2.0\sigma(I)$	2525	3160
R	0.031	0.033
R_w	0.036	0.049
error of fit	1.61	2.98
max Δ/σ	0.01	0.002
residual density, e/Å^3	0.45	0.65

m/z 276 (20%, $[M]^+$), 168 (20%, $[C_8H_{13}Co]^+$), 167 (19%, $[C_6H_8N_2Co]^+$), 108 (100%, $[C_6H_8N_2]^+$). Anal. Calcd for $C_{14}H_{21}CoN_2$: C, 60.87; H, 7.66; Co, 21.33; N, 10.14. Found: C, 60.89; H, 7.66; Co, 21.27; N, 10.10.

(μ-Biphenyl)bis[(1-η^1,4,5-η^2-cyclooctenyl)cobalt(I)] (2q). Biphenyl (3 g, 19.5 mmol) and 12.4 g (45 mmol) of (η^3-cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (1) were dissolved in 15 mL (150 mmol) of piperidine. After the reaction mixture had been frozen with liquid nitrogen, the reaction vessel was evacuated and then filled with 1225 mL (50 mmol) of hydrogen gas at 323 K. All liquid components were removed under vacuum. The residue was dissolved in ether and filtered; the solvent was again removed under vacuum. The residue was washed three times with pentane. The binuclear complex **2q** remained as a deep red, nearly black powder: yield, 750 mg (1.5 mmol) (7.8% of theory); mp 328–330 K, decomp 338–343 K. Mass spectrum: m/z 322 (1%, $[C_{20}H_{23}Co]^+$), 213 (2.5%, $[C_{12}H_{10}Co]^+$), 154 (100%, $[C_{12}H_{10}]^+$). Anal. Calcd for $C_{28}H_{36}Co_2$: C, 68.57; H, 7.40; Co, 24.03. Found: C, 68.40; H, 7.53; Co, 23.89.

Synthesis of [(η^6-Arene)(diene)Co]BF_4 Complexes (5, 6, 8, 10). (η^6-Benzene)(η^2,η^2-cyclooctadiene-1,5)cobalt Tetrafluoroborate (5a). (η^6-Benzene)(η^1,η^2-cyclooctenyl)cobalt(I) (**2a**) (5 g, 20.37 mmol) was dissolved in 25 mL of diethyl ether and 20 mL of cyclooctadiene at room temperature. After the reaction solution had been cooled to 243 K, 2.75 mL (20.3 mmol) of $HBF_4 \cdot Et_2O$ was added dropwise to the solution with vigorous stirring. The reaction solution was removed, and the orange residue was solved in cold CH_2Cl_2 (195 K). The deep red solution was filtered under cooling (195 K). Ether was added, and orange crystals precipitated from the solution kept at 195 K overnight. [In CH_2Cl_2 **5a** decomposes above 223 K]. Yield: 4.5 g (13.6 mmol) (67% of theory) of **5a**, mp 332 K. ^{13}C NMR (CD_2Cl_2, 193 K): 100.6 (d, $^1J_{CH}$ = 177 Hz), 78.9 (d, $^1J_{CH}$ = 158 Hz), 30.1 ppm (t, $^1J_{CH}$ = 130 Hz). Anal. Calcd for $C_{14}H_{18}CoBF_4$: C, 50.60; H, 5.42; F, 22.89. Found: C, 50.53; H, 5.54; F, 22.72.

(η^6-Hexamethylbenzene)(η^2,η^2-cyclooctadiene-1,5)cobalt Tetrafluoroborate (5b).[14] **5b** was synthesized from **2b** as described for **5a** from **2a**. Yield: 63% of theory. ^{13}C NMR (CD_2Cl_2, 193 K): 110.0 (s), 81.7 (d, $^1J_{CH}$ = 155 Hz), 30.0 (t, $^1J_{CH}$ = 130 Hz); 15.5 ppm (q, $^1J_{CH}$ = 129 Hz). Anal. Calcd for $C_{20}H_{30}CoBF_4$: C, 57.69; H, 7.21; F, 18.27. Found: C, 57.75; H, 7.35; F, 18.10.

(η^6-Mesitylene)(η^2,η^2-cyclooctadiene-1,5)cobalt Tetrafluoroborate (5c). **5c** was prepared from **2c** in the same way as **5a** from **2a**; yield, 74% of theory. ^{13}C NMR (CD_2Cl_2, 243 K): 114.3 (s), 101.0 (d, $^1J_{CH}$ = 172 Hz); 80.8 (d, $^1J_{CH}$ = 156 Hz), 30.5 (t, $^1J_{CH}$ = 130 Hz), 18.8 ppm (q, $^1J_{CH}$ = 130 Hz). Anal. Calcd for $C_{17}H_{24}CoBF_4$: C, 54.55; H, 6.42; F, 20.32. Found: C, 54.42; H, 6.51; F, 20.15.

(η^6-Biphenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt Tetrafluoroborate (5e). **5e** was prepared from **2e** in the same way as **5a** from **2a**; yield 82% of theory. ^{13}C NMR (CD_2Cl_2, 193 K): 132.8 (s); 130.4 (d, $^1J_{CH}$ = 162 Hz), 129.3 (d, $^1J_{CH}$ = 160 Hz), 127.5 (d, $^1J_{CH}$ = 158 Hz), 118.5 (s), 102.7 (d, $^1J_{CH}$ = 178 Hz), 98.8 (d, $^1J_{CH}$ = 174 Hz), 96.7 (d, $^1J_{CH}$ = 174 Hz), 80.6 (d, $^1J_{CH}$ = 158 Hz), 29.9 ppm (t, $^1J_{CH}$ = 129 Hz). Anal. Calcd for $C_{20}H_{22}BCoF_4$: C, 58.86; H, 5.43; Co, 14.44; F, 18.62. Found: C, 58.76; H, 5.38; Co, 14.31; F, 18.43.

(η^6-Anisole)(η^2,η^2-cyclooctadiene-1,5)cobalt Tetrafluoroborate (5h). **5h** was prepared from **2h** in the same way as **5a** from **2a**: yield, 41% of theory; mp 360 K dec. ^{13}C NMR (CD_2Cl_2, 243 K): 141.1 (s), 99.8 (d, $^1J_{CH}$ = 179 Hz), 95.0 (d, $^1J_{CH}$ = 178 Hz), 87.9 (d, $^1J_{CH}$ = 176 Hz), 80.4 (d, $^1J_{CH}$ = 156 Hz), 57.5 (q, $^1J_{CH}$ = 148 Hz), 30.8 ppm (t, $^1J_{CH}$ = 130 Hz). Anal. Calcd for $C_{15}H_{20}CoBF_4O$: C, 49.72; H, 5.52; F, 20.99. Found: C, 49.65; H, 5.61; F, 20.85.

(η^6-Benzene)(η^4-cyclohexadiene-1,3)cobalt Tetrafluoroborate (6a). **6a** was prepared from **2a** as mentioned above; yield, 71% of theory. **6a** decomposes above 373 K. ^{13}C NMR (CD_2Cl_2, 243 K): 98.7 (d, $^1J_{CH}$ = 178 Hz), 86.2 (d, $^1J_{CH}$ = 174 Hz), 71.5 (d, $^1J_{CH}$ = 162 Hz), 23.6 ppm (t, $^1J_{CH}$ = 132 Hz). Anal. Calcd for $C_{12}H_{14}CoBF_4$: C, 47.37; H, 4.61; Co, 19.41; F, 25.00. Found: C, 47.53; H, 4.48; Co, 19.35; F, 24.97.

(η^6-Hexamethylbenzene)(η^4-cyclohexadiene-1,3)cobalt Tetrafluoroborate (6b). **6b** was prepared from **7b** as above; yield, 64.8% of theory. ^{1}H NMR (CD_2Cl_2, 213 K): 5.11 (m, 2 H), 3.05 (m, 2 H), 2.25 (s, 18 H), 1.36 (m, 2 H), 0.56 ppm (m, 2 H). Anal. Calcd for $C_{18}H_{26}BCoF_4$: C, 55.70; H, 6.75; Co, 15.18; F, 19.58. Found: C, 55.67; H, 6.66; Co, 15.11; F, 19.74.

(η^6-Benzene)(η^4-cyclopentadiene-1,3)cobalt Tetrafluoroborate (8a). **8a** was prepared from **2a** as mentioned above, but with only a 10% excess of cyclopentadiene; yield, 25.5% of theory, unpurified with about 30% of $[Cp_2Co]BF_4$. Nevertheless, it is a suitable starting material for the preparation of **12a**. ^{1}H NMR

(CD_2Cl_2, 193 K): 6.50 (s, 6 H), 6.16 (m, 2 H), 3.86 (m, 2 H), 2.75 (m, 1 H), 1.81 ppm (m, 1 H).

(η^6-Hexamethylbenzene)(η^4-cyclopentadiene-1,3)cobalt Tetrafluoroborate (8b). (a) From 2b. **8b** was prepared from **2b** as above, except that a fourfold excess of cyclopentadiene was taken; yield, 52.8% of theory. ^1H NMR (CD_2Cl_2, 193 K): 5.67 (t, *J* = 2 Hz, 2 H), 2.96 (p, *J* = 2 Hz, 2 H), 2.44 (m, 1 H), 2.20 (s, 18 H), 1.69 ppm (m, 1 H). ^{13}C NMR (CD_2Cl_2, 193 K): 107.5 (s), 86.8 (d, $^1J_{CH}$ = 180 Hz), 57.4 (d, $^1J_{CH}$ = 176 Hz), 39.9 (t, $^1J_{CH}$ = 134 Hz, 140 Hz), 16.5 ppm (q, $^1J_{CH}$ = 129 Hz). Anal. Calcd for $C_{17}H_{24}BCoF_4$: C, 54.58; H, 6.47; Co, 15.75. Found: C, 54.70; H, 6.56; Co, 15.65.

(b) From 7b. **8b** was also prepared from **7b** as above, except that a fourfold excess of cyclopentadiene was taken; yield 82.4% of theory. ^1H NMR: see above. Anal. Calcd for $C_{17}H_{24}BCoF_4$: C, 54.58; H, 6.47; Co, 15.75; F, 20.31. Found: C, 54.41; H, 6.48; Co, 15.91; F, 20.19.

(η^6-Mesitylene)(η^4-cyclopentadiene-1,3)cobalt Tetrafluoroborate (8c). **8c** was prepared from **2c** as above, but with only a 10% excess of cyclopentadiene; yield, 53.3% of theory. ^1H NMR (CD_2Cl_2, 253 K): 6.19 (s, 3 H), 6.09 (m, 2 H), 3.56 (m, 2 H), 2.74 (m, 1 H), 2.33 (s, 9 H), 1.88 ppm (m, 1 H). Anal. Calcd for $C_{14}H_{18}BCoF_4$: C, 50.64; H, 5.46; Co, 17.75; F, 22.89. Found: C, 50.56; H, 5.36; Co, 17.72; F, 22.69.

(η^6-Benzene)(η^4-butadiene-1,3)cobalt Tetrafluoroborate (10a). (5-Methylheptadienyl)(η^4-butadiene)cobalt (**9**)[11] (2.5 g, 11.3 mmol) was dissolved in 20 mL of benzene and 30 mL of ether at 273 K. After the mixture was cooled to 243 K, 1.57 mL (11.5 mmol) $HBF_4{\cdot}Et_2O$ was added dropwise to the reaction solution with vigorous stirring. The reaction solution was removed and the brown residue washed twice with cold ether (243 K). The residue was redissolved in CH_2Cl_2 (195 K), filtered, and precipitated with cold ether at 195 K. **10a** crystallized from CH_2Cl_2/Et_2O as red crystals at 195 K: mp 351 K dec; yield, 1.2 g (4.3 mmol) (38% of theory). ^{13}C NMR (CD_2Cl_2, 193 K): 98.8 (d, $^1J_{CH}$ = 179 Hz), 88.4 (d, $^1J_{CH}$ = 173 Hz), 46.1 ppm (t, $^1J_{CH}$ = 164 Hz). Anal. Calcd for $C_{10}H_{12}CoBF_4$: C, 43.17; H, 4.32; Co, 21.22; F, 27.34. Found: C, 43.18; H, 4.35; Co, 21.24; F, 27.26%.

(η^6-Hexamethylbenzene)(η^4-butadiene-1,3)cobalt Tetrafluoroborate (10b). (5-Methylheptadienyl)(η^4-butadiene)cobalt (**9**) (2.5 g, 11.3 mmol) and 2.2 g (13.6 mmol) of hexamethylbenzene were dissolved in ether at 243 K. $HBF_4{\cdot}Et_2O$ (1.47 mL, 11.5 mmol) was added dropwise to the cooled reaction solution with vigorous stirring. After being stirred for another hour at room temperature, the reaction solution was removed and the red residue washed three times with ether. The residue was dissolved with CH_2Cl_2 (193 K), filtered, and precipitated with cold ether at 193 K. **10b** crystallizes from CH_2Cl_2/ether as red crystals at 193 K; yield, 55% of theory. ^1H NMR (CD_2Cl_2, 213 K): 5.33 (m, 2 H), 2.30 (s, 18 H), 1.96 (m, 2 H), 0.63 ppm (m, 2 H). ^{13}C NMR (CD_2Cl_2, 213 K): 108.9 (s), 88.4 (d, $^1J_{CH}$ = 171 Hz), 47.9 (t, $^1J_{CH}$ = 161 Hz); 17.0 ppm (q, $^1J_{CH}$ = 129 Hz). Anal. Calcd for $C_{16}H_{24}BCoF_4$: C, 53.07; H, 6.68; Co, 16.28. Found: C, 53.34; H, 6.66; Co, 16.15.

(η^6-Mesitylene)(η^4-butadiene-1,3)cobalt Tetrafluoroborate (10c). **10c** was prepared analogously to **10a**: yield, 47% of theory; mp 370 K dec. ^{13}C NMR (CD_2Cl_2, 243 K): 114.1 (s), 98.0 (d, $^1J_{CH}$ = 174 Hz), 88.6 (d, $^1J_{CH}$ = 173 Hz), 47.8 (t, $^1J_{CH}$ = 161 Hz), 20.1 ppm (q, $^1J_{CH}$ = 129 Hz). Anal. Calcd for $C_{13}H_{18}CoBF_4$: C, 48.75; H, 5.63; F, 23.75. Found: C, 48.90; H, 5.56; F, 23.96.

Synthesis of Substituted (η^6-Arene)(η^3-allyl)cobalt Complexes. (η^6-Benzene)(η^3-crotyl)cobalt(I) (7a) and (η^5-Cyclohexadienyl)(η^4-butadiene)cobalt(I) (17). [(η^6-Benzene)(η^4-butadiene-1,3)Co]BF_4 (9.2 g, 33.1 mmol) (**10a**) and 200 mL of ether were combined and cooled down to 243 K. $NaHBEt_3$ in ether (33.1 mL of a 1 M solution) was added with vigorous stirring. The solvent was removed at 243 K under reduced pressure, and the residue was dissolved in pentane at 243 K and filtered. Crystallization at 193 K gave 650 mg (3.4 mmol, 10.3% of theory) of a deep red substance, which was liquid at room temperature and contained the two isomers **7a** and **17** in a 2:1 ratio. Mass spectrum: *m/z* 192 (60%, $[M]^+$), 164 (15%, $[C_6H_6CoC_2H_3]^+$), 137 (100%, $[C_6H_6Co]^+$), 114 (12%, $[C_4H_7Co]^+$), 78 (89%, $[C_6H_6]^+$), 59 (39%, $[Co]^+$). ^{13}C NMR (THF-d_8, 173 K): for **7a**, 30.4 (t, $^1J_{CH}$ = 154 Hz), 79.2 (d, $^1J_{CH}$ = 162 Hz); 46.6 (d, $^1J_{CH}$ = 147 Hz), 17.2 (q, $^1J_{CH}$ = 125 Hz), 87.5 ppm (d, $^1J_{CH}$ = 170 Hz); for **17**, 35.0 (t, $^1J_{CH}$ = 155 Hz), 80.4 (d, $^1J_{CH}$ = 163 Hz), 84.7 (d, $^1J_{CH}$ = 166 Hz), 81.1 (d, $^1J_{CH}$ = 170 Hz), 93.0 (d, $^1J_{CH}$ = 164 Hz), 95.7 (d, $^1J_{CH}$ = 166 Hz), 40.5 (d, $^1J_{CH}$ = 162 Hz), 50.7 (d, $^1J_{CH}$ = 168 Hz), 26.5 ppm (t, $^1J_{CH}$; obscured).

(η^6-Hexamethylbenzene)(η^3-crotyl)cobalt(I) (7b). **7b** was prepared from **10b** in the same way as **12b** except that the reaction was carried out at room temperature instead of at 243 K. Fractional crystallization between 273 K and 193 K gave **7b** in form of deep red crystals: yield, 62% of theory; mp 366–368 K; decomp >428 K. Spectra: see above. Anal. Calcd for $C_{16}H_{25}Co$: C, 69.55; H, 9.12; Co, 21.33. Found: C, 69.49; H, 9.23; Co, 21.18.

(η^6-Hexamethylbenzene)(η^3-crotyl)cobalt(I) (7b) and (η^6-Hexamethylbenzene)(1-η^1,3,4-η^2-butenyl)cobalt(I) (16). **10b** was treated with $NaHBEt_3$ in the same way as described for preparation of **12b**. After crystallization in pentane at 193 K, the two isomers **7b** and **16** were isolated in a 3:2 ratio as deep red crystals: yield, 35% of theory for both isomers; mp 365–366 K; decomp > 428 K. Mass spectrum: *m/z* 276 (32%, $[M]^+$), 221 (30%, $[C_{12}H_{18}Co]^+$), 220 (34%, $[C_{12}H_{17}Co]^+$), 162 (49%, $[C_{12}H_{18}]^+$), 147 (100%, $[C_{11}H_{15}]^+$). ^{13}C NMR (THF-d_8, 193 K): for isomer **7b**, 96.3 (s), 78.6 (d, $^1J_{CH}$ = 162 Hz), 45.7 (d, $^1J_{CH}$ = 146 Hz), 30.7 (t, $^1J_{CH}$ = 151 Hz), 17.0 (q, $^1J_{CH}$ = 127 Hz), 14.8 ppm (q, $^1J_{CH}$ = 124 Hz); for isomer **16**, 101.1 (s), 46.1 (t, $^1J_{CH}$ = 151 Hz), 34.7 (d, $^1J_{CH}$ = 156 Hz), 29.8 (t, $^1J_{CH}$ = 128 Hz), 16.3 (q, $^1J_{CH}$ = 127 Hz), −16.5 ppm (t, $^1J_{CH}$ = 139 Hz). Anal. Calcd for $C_{16}H_{25}Co$: C, 69.55; H, 9.12; Co, 21.33. Found: C, 69.46; H, 9.23; Co, 21.28.

(η^6-Benzene)(η^3-cyclohexenyl)cobalt(I) (11a)[12] was prepared as described in the literature.[12]

(η^6-Hexamethylbenzene)(η^3-cyclohexenyl)cobalt(I) (11b). **11b** was prepared from **6b** in the same way as **12b**. Fractional crystallization in pentane between 273 K and 193 K gave **11b** as red crystals: Yield, 20% of theory; mp 351 K; decomp 403 K. Mass spectrum: *m/z* 302 (97%, $[M]^+$), 220 (100%, $[C_{12}H_{17}Co]^+$), 162 (25%, $[C_{12}H_{18}Co]^+$), 147 (62%, $[C_{11}H_{15}]^+$). ^1H NMR (THF-d_8, 203 K): 4.64 (t, *J* = 5.5 Hz, 1 H), 2.1 (s, 18 H), 1.68 (m, 2 H), 1.34–0.58 ppm (m, 6 H). ^{13}C NMR (THF-d_8, 193 K): 97.1 (s), 74.0 (d, $^1J_{CH}$ = 164 Hz), 49.3 (d, $^1J_{CH}$ = 149 Hz), 25.8 (t, $^1J_{CH}$ = 123 Hz); 25.2 (t, $^1J_{CH}$ = 123 Hz); 17.0 ppm (q, $^1J_{CH}$ = 127 Hz). Anal. Calcd for $C_{18}H_{27}Co$: C, 71.51; H, 9.00; Co, 19.49. Found: C, 71.61; H, 9.00; Co, 19.43.

(η^6-Mesitylene)(η^3-cyclopentenyl)cobalt(I) (12c). **12c** was prepared from **8c** in the same way as **12b**: yield, 92% of theory; mp 300 K; decomp >408 K. Mass spectrum: *m/z* 246 (87%, $[M]^+$), 244 (100%, $[C_{14}H_{17}Co]^+$), 179 (92%, $[C_9H_{12}Co]^+$), 178 (61%, $[C_9H_{11}Co]^+$), 124 (58%, $[C_5H_5Co]^+$), 119 (17%, $[C_9H_{11}]^+$), 105 (46%, $[C_8H_9]^+$), 59 (55%, $[Co]^+$). ^1H NMR (THF-d_8, 213 K): 5.15 (s, 3 H), 4.51 (t, *J* = 3 Hz, 1 H), 2.34 (m, 2 H); 2.10 (s, 9 H), 1.08 ppm (m, 4 H). ^{13}C NMR (THF-d_8, 193 K): 100.4 (s), 88.7 (d, $^1J_{CH}$ = 167 Hz), 73.8 (d, $^1J_{CH}$ = 174 Hz), 51.5 (d, $^1J_{CH}$ = 158 Hz), 31.8 (t, $^1J_{CH}$ = 129 Hz), 20.9 ppm (q, $^1J_{CH}$ = 127 Hz). Anal. Calcd for $C_{14}H_{19}Co$: C, 68.29; H, 7.78; Co, 23.93. Found: C, 68.15; H, 7.78; Co, 23.67.

(η^6-Benzene)(η^3-cyclopentenyl)cobalt(I) (12a). **12a** was prepared from **8a** in the same way as **12b**. The product still contained (η^5-Cp)(η^5-C_5H_6)Co. Sublimation of (η^4-Cp)(η^4-C_5H_6)Co in high vacuum at room temperature gave pure **12a** in a yield of 48%: mp 244–346 K; decomp >373 K. Mass spectrum: *m/z* 204 (38%, $[M]^+$), 202 (36%, $[C_{11}H_{11}Co]^+$), 137 (40%, $[C_6H_6Co]^+$), 124 (100%, $[C_5H_5Co]^+$), 78 (16%, $[C_6H_6]^+$), 59 (55%, $[Co]^+$). ^1H NMR (THF-d_8, 193 K): 5.06 (s, 6 H), 4.64 (t, *J* = 3 Hz, 1 H), 2.65 (m, 2 H), 1.13 (m, 2 H), 0.96 ppm (m, 2 H). ^{13}C NMR (THF-d_8, 193 K): 88.1 (d, $^1J_{CH}$ = 170 Hz), 73.0 (d, $^1J_{CH}$ = 174 Hz), 51.9 (d, $^1J_{CH}$ = 159 Hz), 32.4 ppm (t, $^1J_{CH}$ = 130 Hz). Anal. Calcd for $C_{11}H_{13}Co$: C, 64.72; H, 6.42; Co, 28.87. Found: C, 64.63; H, 6.43; Co, 28.97.

(η^6-Hexamethylbenzene)(η^3-cyclopentenyl)cobalt(I) (12b). **34** (2.5 g, 6.7 mmol) and 200 mL of ether were combined and cooled to 243 K. $NaHBEt_3$ (6.7 mL of a 1 M solution) in ether was added with vigorous stirring. The solvent was removed at 243 K; the residue was dissolved at room temperature in pentane and filtered. Crystallization at 193 K gave 1.4 g (4.86 mmol) (72.5% of theory) of **12b** as red crystals: mp 412–414 K; decomp >431 K. Mass spectrum: *m/z* 288 (93% $[M]^+$), 286 (69%, $[C_{17}H_{23}Co]^+$), 221 (57%, $[C_{12}H_{18}Co]^+$), 220 (100%, $[C_{12}H_{17}Co]^+$), 161 (24%, $[C_{12}H_{17}]^+$), 147 (28%, $[C_{11}H_{15}]^+$). ^1H NMR (THF-d_8, 243 K) 4.28 (t, *J* = 3 Hz, 1 H), 2.08 (s, 18 H), 1.86 (m, 2 H), 0.95 ppm (m, 4 H). ^{13}C NMR (THF-d_8, 193 K): 97.1 (s), 71.7 (d, $^1J_{CH}$ = 173 Hz), 50.1 (d, $^1J_{CH}$ = 156 Hz), 30.4 (t, $^1J_{CH}$ = 128 Hz), 16.9

ppm (q, $^1J_{CH}$ = 127 Hz). Anal. Calcd for $C_{17}H_{25}Co$: C, 70.82; H, 8.74; Co, 20.44. Found: C, 70.88; H, 8.76; Co, 20.28.

(η^6-Hexamethylbenzene)(1-η^1,3,4-η^2-cyclohexenyl)rhodium (14). (η^6-Hexamethylbenzene)(η^2,η^2-cyclohexadiene-1,3)rhodium tetrafluoroborate (**13**)[14] (775 mg, 1.78 mmol) were combined with 25 mL of ether, and the mixture was cooled to 243 K. Under vigorous stirring 1.78 mL of a 1 M solution of $NaHBEt_3$ in ether was added. The solvent was removed at 243 K; the residue was dissolved at 243 K in pentane, filtered, and crystallized at 193 K. Yield: 375 mg (1.08 mmol) (60.7% of theory) of **14**. Mass spectrum: m/z 346 (68%, $[M]^+$), 264 (98%, $[C_{12}H_{17}Rh]^+$), 162 (42%, $[C_{12}H_{18}]^+$), 147 (100%, $[C_{11}H_{15}]^+$). ^{1}H NMR (THF-d_8, 223 K): 2.71 (m, 1 H, H on C-4), 2.68 (m, 1 H, H on C-3), 2.51 (m, 1 H, H_{exo} on C-2), 2.39 (m, 1 H, H_{endo} on C-2), 2.18 (s, 18 H, CH_3), 1.91 (m, 1 H, H_{endo} on C-5), 1.76 (m, 1 H, H_{exo} on C-5), 1.28 (m, 1 H, H_{endo} on C-6), 1.02 (m, 1 H, H_{exo} on C-6), 0.75 (m, 1 H, H on C-1). ^{13}C NMR (THF-d_8, 193 K): 14.2 (d, $^1J_{CH}$ = 145 Hz, J_{RhC} = 21.1 Hz), 38.7 (t, $^1J_{CH}$ = 128 Hz, J_{RhC} = 6.1 Hz), 36.1 (d, $^1J_{CH}$ = 162 Hz, J_{RhC} = 10.7 Hz), 65.2 (d, $^1J_{CH}$ = 151 Hz, J_{RhC} = 20.4 Hz), 28.2 (t, $^1J_{CH}$ = 124 Hz, J_{RhC} = 1.9 Hz), 37.4 (t, $^1J_{CH}$ = 124 Hz), 105.5 (s, J_{RhC} = 2.7 Hz), 16.8 ppm (q, $^1J_{CH}$ = 127 Hz). Anal. Calcd for $C_{18}H_{27}Rh$: C, 62.43; H, 7.86; Rh, 29.71. Found: C, 62.51; H, 7.78; Rh, 29.10.

(η^6-Hexamethylbenzene)(η^3-cyclohexenyl)rhodium (15). (η^6-Hexamethylbenzene)(η^4-cyclohexadiene-1,3)rhodium tetrafluoroborate (**13**)[14] (1.32 g, 3.06 mmol) was combined with 100 mL of THF. Under vigorous stirring 3.06 mL of a 1 M solution of $NaHBEt_3$ in ether was added dropwise. The solution was stirred for another 4 h at room temperature, the solvent was removed, and the residue was dissolved in pentane, filtered, and crystallized at 193 K: yield, 700 mg (2.02 mmol) (66% of theory) of **15**. ^{1}H NMR (THF-d_8, 213 K): 4.30 (t(d), ^3J = 5.5 Hz, J_{HRh} = 2 Hz, 1 H), 2.56 (m, 2 H), 1.09 (m, 6 H), 2.23 ppm (s, 18 H). Anal. Calcd for $C_{18}H_{27}Rh$: C, 62.43; H, 7.86; Rh, 29.71. Found: C, 62.50; H, 8.01; Rh, 29.54.

Synthesis of (η^6-Arene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt(III) Tetrafluoroborate Complexes. (η^6-Benzene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt(III) Tetrafluoroborate (18a). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (**1**) (5 g, 18.1 mmol) was dissolved in 100 mL of benzene and 100 mL of diethyl ether at room temperature. $HBF_4{\cdot}Et_2O$ (26 mL, 19.0 mmol) was added dropwise to the reaction solution with vigorous stirring. The reaction solution was removed from the orange precipitate. The orange residue was dissolved in acetone (195 K) and filtered over Al_2O_3 (7% H_2O) at 196 K. **18a** was precipitated by addition of cold ether (243 K) to the filtrate. Recrystallization from CH_2Cl_2/Et_2O gave **18a** as red crystals: mp 394 K dec; yield, 4.4 g (13.3 mmol) (74% of theory). Anal. Calcd for $C_{14}H_{18}CoBF_4$: C, 50.60; H, 5.42; Co, 17.77; F, 22.89. Found: C, 50.51; H, 5.50; Co, 17.65; F, 23.21.

(η^6-Hexamethylbenzene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt(III) Tetrafluoroborate (18b). **1** (3 g, 10.9 mmol) and 1.9 g (11.7 mmol) of hexamethylbenzene were dissolved in 100 mL of ether at room temperature. $HBF_4{\cdot}Et_2O$ (1.7 mL, 12.2 mmol) was added with vigorous stirring. The orange residue was dissolved in CH_2Cl_2 and chromatographed over Al_2O_3 (7% H_2O). First hexamethylbenzene is separated with diethyl ether, and then **18b** is eluated with ethanol. Red needles precipitated from the solution kept at 273 K overnight; yield, 2.6 g (6.3 mmol) (58% of theory). Anal. Calcd for $C_{20}H_{30}CoBF_4$: C, 57.69; H, 7.21; F, 18.27. Found: C, 57.80; H, 7.15; F, 18.38.

(η^6-Mesitylene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt(III) Tetrafluoroborate (18c). **18c** was prepared as described for **18a**: yield, 72% of theory; mp 396 K dec. Anal. Calcd for $C_{17}H_{24}CoBF_4$: C, 54.55; H, 6.42; F, 20.32. Found: C, 54.78; H, 6.44; F, 20.18.

(η^6-Biphenyl)(1-η^1,4–6-η^3-cyclooctendiyl)cobalt(III) Tetrafluoroborate (18e). **18e** was prepared from **1** in the same way as **18r**; yield, 30% of theory. Anal. Calcd for $C_{20}H_{22}CoBF_4$: C, 58.86; H, 5.43; Co, 14.44; F, 18.62. Found: C, 58.78; H, 5.45; Co, 14.45; F, 18.34.

(η^6-Naphthalene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt Tetrafluoroborate (18r). (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)cobalt (**1**) (5 g, 18.1 mmol) and 2.5 g (19.5 mmol) of naphthalene were dissolved in 50 mL of ether at room temperature. The reaction solution was cooled to 273 K, and 2.4 mL (17.6 mmol) of $HBF_4{\cdot}Et_2O$ was added with vigorous stirring. The reaction solution was removed and the orange residue was dissolved in CH_2Cl_2 (195 K). After filtration over Al_2O_3 (7% H_2O) at 195 K **18r** was precipitated as a red solid by addition of cold ether (195 K): mp 322 K dec; yield, 45% of theory. Anal. Calcd for $C_{18}H_{20}CoBF_4$: C, 56.64; H, 5.24; F, 19.90. Found: C, 56.39; H, 4.96; F, 20.08.

(η^6-1,4-Dihydroxybenzene)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt Tetrafluoroborate (18s). **1** (2 g, 7.2 mmol) and 1 g (9.1 mmol) of hydroquinone were dissolved in 40 mL of diethyl ether. $HBF_4{\cdot}Et_2O$ (1.3 mL, 9.5 mmol) was added dropwise to the reaction solution with vigorous stirring at room temperature. After being stirred for 1 h, the reaction solution was removed from the orange residue. The orange solid was dissolved in methanol and stirred for 1 h. After filtration of the orange solution most of the solvent was removed under vacuum and ether was added. An orange solid precipitated from the solution kept at 243 K overnight: yield, 1.0 g (2.7 mmol) (30% of theory); mp 311 K dec. ^{1}H NMR (acetonitrile-d_3): –0.10 (m, 2 H), 0.60–1.19 (m, 2 H), 1.50–2.64 (m), 3.41 (m, 1 H), 4.80 (m, 1 H), 5.36 (m, 2 H), 6.32 (br s, 2 H, OH), 6.64 ppm (s, 4 H, aromatic H, free 1,4-dihydroxybenzene). Anal. Calcd for $C_{14}H_{18}CoBF_4O_2$: C, 46.15; H, 4.95; F, 20.88. Found: C, 46.39; H, 5.08; F, 21.04.

(η^6-Hexamethylbenzene)(η^2,η^2-cyclooctadiene-1,5)rhodium Tetrafluoroborate[1d] (20b) from (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)rhodium[17] (19). **19** (0.3 g, 0.9 mmol) and 0.3 g (1.85 mmol) of hexamethylbenzene were dissolved in 30 mL diethyl ether. After addition of 0.13 mL (0.9 mmol) of $HBF_4{\cdot}Et_2O$ the solution was stirred for 1 h. The reaction solution was removed and redissolved in CH_2Cl_2. **20b** precipitated as yellow needles on addition of ether; yield, 0.42 g (0.9 mmol).

(η^6-1,4-Dihydroxybenzene)(η^2,η^2-cyclooctadiene-1,5)rhodium Tetrafluoroborate (20s) from (η^3-Cyclooctenyl)(η^2,η^2-cyclooctadiene-1,5)rhodium (19). **20s** was prepared as described for **20b**: yield, 78% of theory; mp 463 K dec. ^{1}H NMR (CD_2Cl_2): 7.55 (s, 2 H), 6.59 (s, 4 H), 4.62 (m, 4 H), 2.59–2.0 ppm (m, 8 H). Anal. Calcd for $C_{14}H_{10}RhBF_4O_2$: C, 41.18; H, 4.41; F, 18.63. Found: C, 41.15; H, 4.27; F, 18.60. IR (KBr): 3350 (vs, OH–), 1550, 1505 (s, aromatic C=C), 1225 (s, C—O), 1100–950 cm^{-1} (vs, BF_4^-).

Tris(acetonitrile)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt(III)] Tetrafluoroborate (21). **18a** (4.4 g, 13.3 mmol) was dissolved in 50 mL of acetonitrile and the mixture stirred at room temperature for 1 h. The deep brown solution was filtered and most of the solvent removed under vacuum. After addition of ether the solution was filtered and stored at 243 K overnight. **21** precipitated from the solution as brown needles: yield, 5.0 g (13.3 mmol); mp 367 K. ^{1}H NMR (acetonitrile-d_3): –0.06 (m, 2 H), 0.59–1.18 (m, 2 H), 1.50–2.61 (m), 3.40 (m, 1 H), 4.80 (m, 1 H), 5.36 ppm (m, 2 H). Anal. Calcd for $C_{14}H_{21}CoBF_4N_3$: C, 44.56; H, 5.57; N, 11.14. Found: C, 44.53; H, 5.54; N, 11.26. IR (KBr): 1060 (s, BF_4^-), 2280–2360 cm^{-1} (vw, -CN).

(η^5-Cyclopentadienyl)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt (22). **21** (1 g, 2.7 mmol) and 0.3 g (3.4 mmol) of NaCp were suspended in 50 mL of ether and the mixture stirred at room temperature overnight. The solution was filtered, and the solvent was removed under vacuum. The red residue was dissolved in pentane and filtered. Red crystals precipitated from the solution kept at 195 K overnight: yield, 0.5 g (2.2 mmol) (81% of theory); mp 382 K. Mass spectrum: m/z 232 (56%, $[M]^+$), 230 (43%, $[C_{13}H_{15}Co]^+$), 202 (76%, $[C_{11}H_{11}Co]^+$), 124 (100%, $[C_5H_5Co]^+$), 59 (30%, $[Co]^+$). Anal. Calcd for $C_{13}H_{17}Co$: C, 67.24; H, 7.38; Co, 25.38. Found: C, 67.34; H, 7.29; Co, 25.24.

(Acetylacetonato)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt (23). **6** (1 g, 2.7 mmol) and 0.4 g (3.3 mmol) of sodium acetylacetonate were dissolved in 30 mL of tetrahydrofuran and the mixture stirred at room temperature overnight. After addition of 30 mL of pentane the solution was filtered off and the solvent was removed under vacuum; this was accompanied by a color change from red to green. The green residue was recrystallized from pentane at 243 K to give 0.6 g (2.3 mmol) (85% of theory) of black crystals, mp 385 K dec. Mass spectrum: m/z 266 (20%, $[M]^+$), 158 (100%, $[C_5H_7CoO_2]^+$), 59 (10%, $[Co]^+$). Anal. Calcd for $C_{13}H_{19}CoO_2$: C, 58.65; H, 7.19; Co, 22.14. Found: C, 58.54; H, 7.17; Co, 22.02.

(η^5-Fluorenyl)(1-η^1,4–6-η^3-cyclooctenediyl)cobalt (24). **21** (1.5 g, 4.0 mmol) was suspended in 50 mL of diethyl ether. After addition of 1.0 g (5.3 mmol) of sodium fluorenyl[13] the reaction solution was stirred at room temperature overnight. After filtration the solvent was removed under vacuum. The residue was redissolved in pentane and filtered. Crystallization at 195 K gave **24** as violet crystals: yield, 0.9 g (2.7 mmol) (68% of theory); mp 385 K. Mass spectrum: m/z 332 (25%, $[M]^+$), 225 (20%, $[C_{13}H_{10}Co]^+$), 224 (30%, $[C_{13}H_9Co]^+$), 165 (100%, $[C_{13}H_9]^+$), 59 (7%, $[Co]^+$). Anal. Calcd for $C_{21}H_{21}Co$: C, 75.90; H, 6.33; Co, 17.77. Found: C, 75.85; H, 6.60; Co, 17.61.

(η^5-9-Carbethoxyfluorenyl)(1-η^1,4-6-η^3-cyclooctenediyl)cobalt (25). **25** was prepared as described for **24**: yield, 68% of theory; mp 379 K. Mass spectrum: m/z 404 (40%, $[M]^+$), 298 (20%, $[C_{16}H_{15}CoO_2]^+$), 297 (50%, $[C_{16}H_{14}CoO_2]^+$), 252 (40%, $[C_{14}H_9CoO]^+$), 224 (35%, $[C_{13}H_9Co]^+$), 165 (100%, $[C_{13}H_9]^+$), 59 (25%, $[Co]^+$). Anal. Calcd for $C_{24}H_{25}CoO_2$: C, 71.29; H, 6.19; Co, 14.60. Found: C, 71.10; H, 6.05; Co, 14.72.

(1-η^1,4-6-η^3-Cyclooctenediyl)(hexafluoroacetylacetonato)cobalt (26). **6** (1.0 g, 2.7 mmol) and 0.7 g (3.0 mmol) of sodium hexafluoroacetylacetonate were dissolved in 30 mL of tetrahydrofuran and the mixture stirred at room temperature overnight. After removal of the solvent the red solid was sublimed off under vacuum at 313 K to give 0.9 g (2.4 mmol) (89% of theory) of **26** as red crystals, mp 347–350 K. Mass spectrum: m/z 374 (62%, $[M]^+$), 266 (25%, $[C_5HCoF_6O_2]^+$), 216 (60%, $[C_4HCoF_4O_2]^+$), 79 (100%), 59 (38%, $[Co]^+$). Anal. Calcd for $C_{13}H_{13}CoF_6O_2$: C, 41.71; H, 3.48; F, 30.48. Found: C, 41.79; H, 3.60; F, 30.58.

(η^5-Pentadienyl)(1-η^1,4-6-η^3-cyclooctenediyl)cobalt (30). **23** (1 g, 3.8 mmol) was dissolved in tetrahydrofuran. After addition of 5.0 mmol of pentadienyllithium in tetrahydrofuran the reaction solution was stirred at room temperature overnight. The solution was filtered, and the solvent was removed under vacuum. Crystallization from pentane gave 0.6 g (2.6 mmol) (68% of theory) of **30**: mp 368 K; mass spectrum: m/z 234 (35%, $[M]^+$), 164 (63%), 138 (60%), 137 (53%), 124 (100%, $[C_5H_5Co]^+$), 59 (34%, $[Co]^+$). Anal. Calcd for $C_{13}H_{19}Co$: C, 66.67; H, 8.12; Co, 25.21. Found: C, 66.80; H, 8.38; Co, 24.99.

Catalytic Measurements. All measurements were made in a continuous-flow reactor under stationary conditions. The evaluation was made by on-line process chromatography. Concentrations: catalyst, 4.3 mmol/L; propyne, 6.6 mol/L; propionitrile, 3.9 mol/L; toluene, 345 g/L. Pressure: 35–40 bar. Temperature: the temperature for 65% propyne conversion was determined. If 65% propyne conversion was not attained, the temperature for maximum propyne conversion was determined.

Acknowledgment. We thank Dr. Henneberg and his co-workers for the mass spectra and R. Galonska, S. Hagenbach, W. Hofstadt, and E. Rickers for technical assistance.

Registry No. 1, 34829-55-5; **2a**, 120967-09-1; **2b**, 120967-10-4; **2c**, 120967-11-5; **2d** (isomer A), 120967-12-6; **2d** (isomer B), 121053-57-4; **2e**, 120967-13-7; **2f**, 120967-14-8; **2g**, 120967-15-9; **2h**, 120967-16-0; **2i**, 120967-17-1; **2j**, 120967-18-2; **2k**, 120967-19-3; **2m**, 120967-20-6; **2n**, 120967-21-7; **2p**, 120967-22-8; **2q**, 120967-49-9; **5a**, 120967-24-0; **5b**, 120967-25-1; **5c**, 120967-27-3; **5e**, 120967-29-5; **5h**, 120967-31-9; **6a**, 120967-33-1; **6b**, 120967-35-3; **7a**, 120989-90-4; **7b**, 120967-48-8; **8a**, 120967-37-5; **8b**, 120967-39-7; **8c**, 120967-41-1; **9**, 12154-10-8; **10a**, 120967-43-3; **10b**, 120967-45-5; **10c**, 120967-47-7; **11a**, 120967-78-4; **11b**, 120967-52-4; **12a**, 120967-54-6; **12b**, 120967-82-0; **12c**, 120967-53-5; **13**, 120967-58-0; **14**, 120967-55-7; **15**, 120967-56-8; **16**, 120967-51-3; **17**, 120967-50-2; **18a**, 120967-60-4; **18b**, 120967-62-6; **18c**, 120967-64-8; **18e**, 120967-66-0; **18r**, 120989-92-6; **18s**, 120967-68-2; **19**, 31798-33-1; **20b**, 36644-49-2; **20s**, 120967-70-6; **21**, 120967-72-8; **22**, 120967-73-9; **23**, 120967-79-5; **24**, 120989-93-7; **25**, 120989-94-8; **26**, 120967-80-8; **27**, 12184-35-9; **28**, 120967-77-3; **29** (lig = THF), 120967-75-1; **29** (lig = DMF), 120967-76-2; **30**, 120967-74-0; $[Cp_2Co]BF_4$, 52314-53-1; benzene, 71-43-2; hexamethylbenzene, 87-85-4; mesitylene, 108-67-8; pseudocumene, 95-63-6; biphenyl, 92-52-4; diphenylmethane, 101-81-5; 9,10-dihydroanthracene, 613-31-0; anisole, 100-66-3; *p*-anisidine, 104-94-9; fluorobenzene, 462-06-6; aniline, 62-53-3; *p*-phenylenediamine, 106-50-3; cyclooctadiene, 111-78-4; 1,3-cyclohexadiene, 592-57-4; cyclopentadiene, 542-92-7; naphthalene, 91-20-3; hydroquinone, 123-31-9; (9-carbethoxyfluorenyl)lithium, 120967-81-9; propyne, 74-99-7; propionitrile, 107-12-0; 2-ethyl-3,6-dimethylpyridine, 40946-38-1; 2-ethyl-4,6-dimethylpyridine, 1124-35-2; 1,4-dimethoxybenzene, 150-78-7; methyl *p*-methoxybenzoate, 121-98-2.

Supplementary Material Available: Molecular structures and tables of crystal data and data collection, hydrogen atom positions, anisotropic thermal parameters, and bond distances and angles for **22** and **23** (11 pages); listings of observed and calculated thermal parameters and standard deviation for **22** and **23** (23 pages). Ordering information is given on any current masthead page.