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A Study of the Syntheses and Properties of the Cobalt Triad of Metal Complexes of [2_n]Cyclophanes

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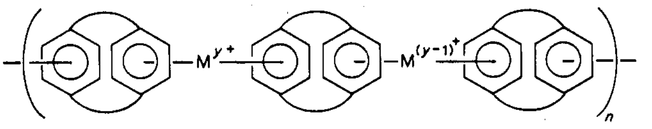
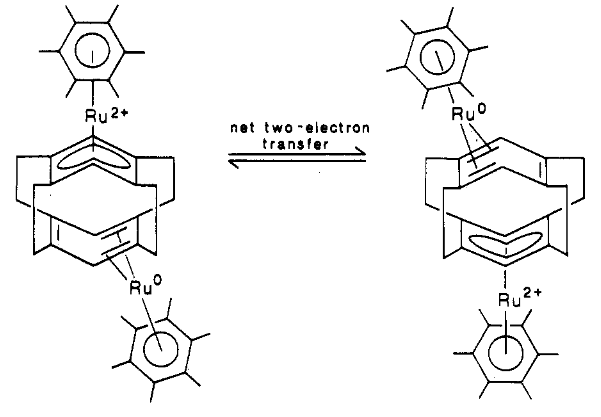
Various known methods for the syntheses of cyclopentadienyl (Cp) and pentamethylcyclopentadienyl ($CpMe_5$) cobalt complexes of arenes have been investigated for preparing cobalt complexes of [2_n]cyclophanes. The most general and most efficient method found was that of generating the solvated ions of (η^5-Cp)Co^{2+}, (η^5-$CpMe_5$)Co^{2+}, and (η^5-$CpMe_5$)Co^+, by the reaction of [(η^5-Cp)CoI_2]$_2$ or [(η^5-$CpMe_5$)$CoCl_2$]$_2$ with silver tetrafluoroborate in solvent or the reaction of [(η^5-$CpMe_5$)CoCl]$_2$ with thallium hexafluorophosphate in solvent, and then allowing these solvated ions to react with individual [2_n]cyclophanes. In this manner the mono(capped) (η^5-Cp)Co^{2+}, (η^5-$CpMe_5$)Co^{2+}, and (η^5-$CpMe_5$)Co^+ complexes were made with [2_2](1,4)cyclophane (compounds **6**, **22**, and **30**), 4,5,6,7,8,12,13,15,16-octamethyl-[2_2](1,4)cyclophane (**8**, **25**, and **33**), 12,13,15,16-tetramethyl-[2_2](1,4)cyclophane (**16**, **24**, and **32**), 5,8,12,15-tetramethyl-[2_2](1,4)cyclophane (**15**, **23**, and **34**), *anti*-[2_2](1,3)cyclophane (**13**, **26**, and **31**), [2_3](1,3,5)cyclophane (**14** and **27**), [2_4](1,2,4,5)cyclophane (**28** and **35**), and 4,5,7,8-tetramethyl[2_2](1,4)cyclophane (**16**). In addition, the bis(capped) (η^5-$CpMe_5$)Co^{2+} complexes were made with [2_2](1,4)cyclophane (**36**), 4,5,7,8-tetramethyl-[2_2](1,4)cyclophane (**37**), and 5,8,12,15-tetramethyl-[2_2](1,4)cyclophane (**38**). In a similar fashion, the (η^5-$CpMe_5$)Rh^{2+} and (η^5-$CpMe_5$)Ir^{2+} solvates were made and used to synthesize the mono(capped) complexes of [2_2](1,4)cyclophane (**42** and **45**), [2_4](1,2,4,5)cyclophane (**43** and **46**), and *anti*-[2_2](1,3)cyclophane (**44** and **47**). Also the (η^5-$CpMe_5$)$_2Ir^{2+}$ complex of [2_2](1,4)cyclophane (**48**) was prepared. The physical properties and electrochemical behavior of these metal complexes were examined, and comparisons were made between the individual members of the cobalt triad.

Polymers having macroscopic properties related to electrical conductivity or magnesium could be of significant practical value. One approach to such substances is to control the synthetic design such that the requirements for the desired electrical or magnetic properties are inherent in the individual molecules themselves. Our goal, in exploring this approach, has been the synthesis of a polymer having as its monomer unit a mixed-valence, dimetallic [2_n]cyclophane complex, as shown by **1**.[1] A polymer having a class III mixed-valence ion as its monomeric unit would be expected to show electron delocalization over the whole of the polymer molecule, and our effort has been directed toward the synthesis of such molecules.



1

An enormous amount of work has been reported on the theory and experimental examples of one-electron transfers for mixed-valence ions of the class II and class III types, particularly for dimetallic complexes involving ruthenium and iron in the oxidation states (Ru(II)–Ru(III))[2-4] and Fe(II)–Fe(III).[5] For synthetic reasons ruthenium was chosen as the transition metal for the first model monomer units related to **1** that we prepared.[6-8] Unfortunately, the binding of transition metals, in the oxidation state III, to arenes is so weak that solvolysis of the arene occurs immediately. Thus, it was not possible to prepare a mixed-valence ion related to **1** containing the Ru(II)–Ru(III) oxidation states. However, reduction of the corresponding Ru(II)–Ru(II) ion does lead to a mixed-valence ion, class II, as shown by structures **2a** and **2b**.[8] The equilibrium shown by **2a** ⇌ **2b** is exceptional in being the first example of a net, two-electron intervalence transfer in a discrete mixed-valence organometallic complex.



2a **2b**

It is well-known that, when ruthenium bound to arenes changes its oxidation state from II to O, a change in geometry normally occurs changing the binding of the arene from η^6 to η^4.[9] Presumably, this change in geometry is

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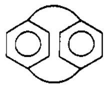
(1) The following is a generalized structure representing any one of the possible [2_n]cyclophanes. (See: Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87-143).



(2) (a) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357–391. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

(3) (a) Wong, K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369–449. (b) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94–100.

(4) (a) Taube, H. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 481–495. (b) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107–129.

(5) (a) Cowan, D. O.; LeVanda, C.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1–7. (b) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhof, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181–3187.

(6) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415–1420.

(7) (a) Swann, R. T.; Boekelheide, V. *Tetrahedron Lett.* **1984**, *25*, 899–900. (b) Swann, R. T.; Hanson, A. W.; Boekelheide, V. *J. Am. Chem. Soc.* **1986**, *108*, 3324–3334.

(8) Voegeli, R. H.; Kang, H. C.; Finke, R. G.; Boekelheide, V. *J. Am. Chem. Soc.* **1986**, *108*, 7010–7016.

(9) (a) Fischer, E. O.; Elschenbroich, Ch. *Chem. Ber.* **1970**, *103*, 162–172. (b) Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 7425–7428.

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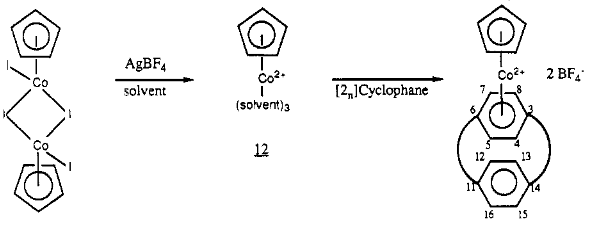
Scheme I



11

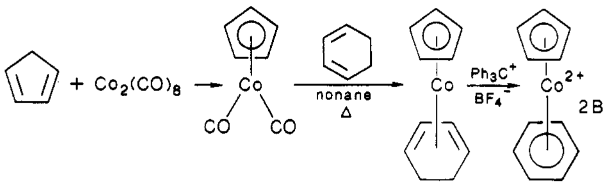
6	[2$_2$](1,4)cyclophane
8	4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)cyclophane
13	anti-[2$_2$](1,3)cyclophane
14	[2$_3$](1,3,5)cyclophane
15	5,8,12,15-tetramethyl-[2$_2$](1,4)-cyclophane
7	4,5,7,8-tetramethyl-[2$_2$](1,4)-cyclophane
16	12,13,15,16-tetramethyl-[2$_2$]-(1,4)cyclophane

largely responsible for the slow rate of intervalence electron transfer observed for the equilibrium **2a** $\rightleftharpoons$ **2b**. Since strong binding for transition-metal–arene complexes is associated with the lower oxidation states of these metals, it seemed desirable to explore metals that undergo one-electron reductions but require little change in the geometry of the arene ligand. This type of behavior is typical of the first-row elements iron[10] and cobalt[11,12] but not of the second- and third-row elements. We chose cobalt, rather than iron, because it offered a greater number of low-valent oxidation states and its 20-electron complexes are much easier to handle.[10b] For example, Fischer and Lindner prepared bis(η^6-hexamethylbenzene)cobalt(II) (**3**) and found that it spontaneously disproportionated to give the more stable bis(η^6-hexamethylbenzene)cobalt(I) (**4**), a paramagnetic 20-electron complex having two unpaired electrons.[11] Furthermore, an X-ray analysis of **4** has shown that it has two planar aromatic decks with essentially D_{6h} symmetry.[12]

$$\underset{\mathbf{3}}{[C_6(CH_3)_6]_2Co^{2+}} \rightarrow \underset{\mathbf{4}}{[C_6(CH_3)_6]_2Co^{+}} + \text{other products}$$

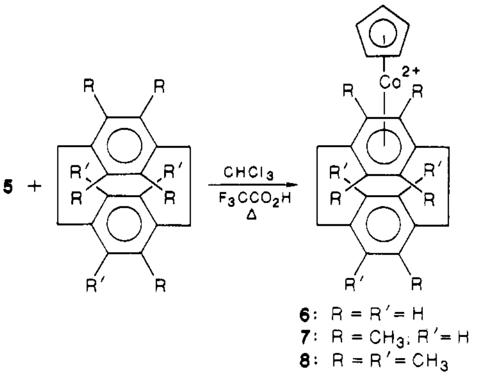
Since the properties of the bis(arene)cobalt complex **4** seemed well-suited for the type of model monomer unit of **1**, which we were seeking, we undertook a systematic study of the synthesis and properties of cobalt complexes of the [2$_n$]cyclophanes. Although bis(arene)cobalt(III) complexes are unknown, the corresponding (η^5-cyclopentadienyl)(η^6-arene)cobalt(III) complexes are well-known, but unstable unless substituted by electron-donating groups. We turned, therefore, to the use of CpCo^{2+} as a capping agent for [2$_n$]cyclophanes. Fischer and Fischer first prepared (η^5-Cp)(η^6-benzene)Co^{2+} (**5**) in 1961,[13] but its insolubility in noncoordinating solvents and instability in all coordinating solvents caused it to be neglected as a reagent. However, Fairhurst and White in 1979 showed that heating **5** with arenes in trifluoroacetic acid resulted in displacement of the benzene by the arene.[14]

Fischer–Fischer Method[13]



5

Fairhurst–White Exchange[14]



As shown below, application of this method readily led to the syntheses of the mono(capped) (η^5-Cp)(η^6-cyclophane)Co^{2+} complexes **6**, **7**, and **8** in good yields.[15]

However, a more versatile method was needed. Koelle et al. have reported that the reaction of dimeric halides of cobalt(III), such as [(CpMe$_5$)CoCl$_2$]$_2$, with arenes in the presence of Friedel–Crafts catalysts gives (η^5-CpMe$_5$)(η^6-arene)Co^{2+} complexes.[19] In view of our extensive experience in using [(η^6-hexamethylbenzene)RuCl$_2$]$_2$ as a precursor for capping [2$_n$]cyclophanes with the (η^6-hexamethylbenzene)Ru^{2+} moiety,[6-8] this route for preparing cobalt complexes was particularly attractive. The necessary dimeric halide precursor was readily prepared by the reaction of CpCo(CO)$_2$ with iodine to form CpCo(CO)I$_2$ which, on heating, gave the iodo dimer [CpCoI$_2$]$_n$ (**11**).[16] When a mixture of **11** and the appropriate cyclophane was heated in the presence of fluoroboric acid in trifluoroacetic acid as solvent, the previously described cobalt complexes **6**, **7**, and **8** were formed, but in poor yield.

Alternatively, though, treatment of the iodo dimer **11** with silver tetrafluoroborate in an appropriate solvent (acetone, trifluoroacetic acid, or propylene carbonate) readily gave the solvated CpCo^{2+} ion **12**, analogous to our experience in the ruthenium series.[6] The solvated CpCo^{2+} ion is quite unstable and must be generated in the presence of a [2$_n$]cyclophane if capping is to be successful. However, when this requirement is observed, capping of [2$_n$]-cyclophanes with the CpCo^{2+} moiety occurs readily and in good yield, as summarized in Scheme I.

The CpCo^{2+} complexes of the unsubstituted [2$_n$]-cyclophanes **6** and **13** are subject to very easy solvolysis in polar solvents, behaving much like the (η^5-Cp)(η^6-benzene)Co^{2+} ion in this respect. Thus, it was not possible to find a suitable solvent for examining the electrochemical behavior of **6** and **13**. Substitution of the [2$_n$]cyclophanes

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(10) (a) Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Oswald, N.; Michaud, P.; Hamon, J. R.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400–2407. (b) Fischer, E. O.; Rohrscheid, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *B17*, 483.

(11) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307–317.

(12) Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979–2986.

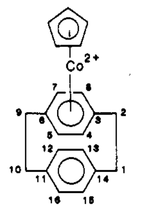
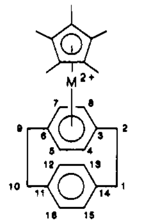
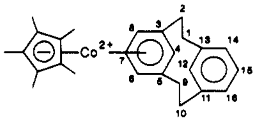
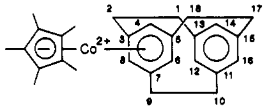
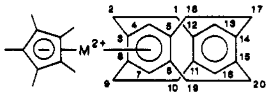
(13) Fischer, E. O.; Fischer, R. D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *B16*, 556–557.

(14) Fairhurst, G.; White, C. *J. Chem. Soc. D* **1979**, 1531–1538.

(15) In the case of **7**, two products are possible depending on which cyclophane deck is complexed to the cobalt ion. Only one product was isolated, and the ^{13}C NMR spectrum of this product clearly shows that it has structure **7**.

(16) Substance **11** is commonly referred to as the "iodo dimer", but in fact it is probably polymeric.

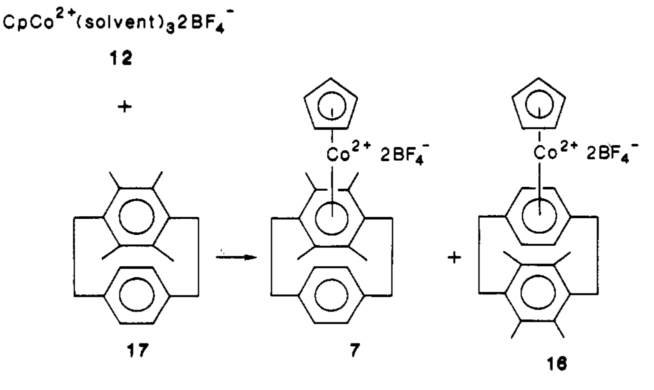
Table I. Chemical Shift Values (δ) and Assignments for the ^{13}C NMR Spectra of the M^{2+} Complexes[a,b]

	6	144.7 (11, 14),[c] 141.0 (3, 6), 135.9 (12, 13, 15, 16), 96.9 (4, 5, 7, 8), 93.7 Cp), 35.6 (1, 10), 34.6 (2, 9)
	8	146.3 (11, 14), 136.3 (12, 13, 15, 16), 135.5 (3.6), 106.2 (4, 5, 7, 8), 94.7 (Cp), 30.3 (1, 10), 28.3 (2, 9), 19.8 and 17.5 (CH$_3$)
	7	142.9 (11, 14), 139.9 (3, 6), 131.1 (12, 13, 15, 16), 108.3 (4, 5, 7, 8), 94.4 (Cp), 32.8 (1, 10), 30.4 (2, 9), 19.4 (CH$_3$)
	15	142.5 (11, 14), 138.8 (3.6), 138.4 (13, 16), 134.3 (12, 15), 109.7 (5, 8), 95.9 (4, 7), 94.1 (Cp), 31.2 (1, 10), 30.5 (2, 4), 19.9 and 19.2 (CH$_3$)
	22 (Co)	141.1 (11, 14), 139.7 (3, 6), 135.7 (12, 13, 15, 16), 109.5 (Cp), 99.8 (4, 5, 7, 8), 35.3 (1, 10), 33.2 (2, 9), 11.4 (CH$_3$)
	42 (Rh)	142.7 (11, 14), 141.3 (3, 6), 135.7 (12, 13, 15, 16), 112.9 (Cp), 102.4 (4, 5, 7, 8), 35.4 (1, 10), 33.4 (2, 9), 11.1 (CH$_3$)
	45 (Ir)	141.0 (11, 14), 140.2 (3, 6), 135.8 (12, 13, 15, 16), 106.3 (Cp), 92.3 (4, 5, 7, 8), 35.1 (1, 10), 33.2 (2, 9), 10.7 (CH$_3$)
	25 (Co)	142.1 (11, 14), 135.9 (12, 13, 15, 16), 135.8 (3, 6), 106.7 (4, 5, 7, 8), 106.5 (Cp), 29.3 (1, 10), 27.8 (2, 9), 17.6, 17.3, and 9.9 (CH$_3$)
	23 (Co)	138.5 (11, 14), 138.4 (12, 15), 138.0 (3, 6), 133.9 (13, 16), 109.3 (5, 8), 108.3 (Cp), 99.1 (4, 7), 30.7 (1, 10), 29.3 (2, 9), 19.2, 17.8, and 10.8 (CH$_3$)
	24 (Co)	139.2 (11, 14), 137.4 (12, 13, 15, 16), 137.2 (3, 6), 109.5 (Cp), 96.4 (4, 5, 7, 8), 30.8 (1, 10), 29.1 (2, 9), 17.4 and 11.4 (CH$_3$)
	26	139.3 (15), 138.4 (11, 13), 134.0 (12), 128.7 (14, 16), 128.5 (3, 5), 110.6 (Cp), 103.7 (7), 102.3 (6, 8), 99.2 (4), 39.4 (1, 10), 38.6 (2, 9), 11.1 (CH$_3$)
	27	146.1 (11, 13, 15), 137.1 (12, 14, 16), 135.4 (3, 5, 7), 109.0 (Cp), 95.4 (4, 6, 8), 37.7 (1, 10, 17), 34.3 (2, 9, 18), 11.7 (CH$_3$)
	28 (Co)	143.8 (11, 12, 14, 15), 142.2 (13, 16), 129.1 (3, 5, 6, 8), 108.7 (Cp), 98.9 (4, 7), 33.7 (1, 10, 17, 20), 30.9 (2, 9, 18, 19), 11.5 (CH$_3$)
	46 (Ir)	143.8 (11, 12, 14, 15), 142.8 (13, 16), 126.7 (3, 5, 6, 8), 105.8 (Cp), 90.5 (4, 7), 33.3 (1, 10, 17, 20), 30.6 (2, 9, 18, 19), 10.8 (CH$_3$)

[a] All spectra were measured on a 360-MHz instrument using CD$_3$NO$_2$ as solvent. [b] Partially coupled spectra were also measured, and the coupling with attached protons observed is in accord with the assignments made. [c] The numbers in parentheses refer to the numbers of the carbons in the cyclophane structures.

by methyl groups improved the stability of these complexes toward solvolysis very markedly, and this was the reason for our choice of the methylated complexes shown.

The CpCo^{2+} capping of 4,5,7,8-tetramethyl[2$_2$](1,4)-cyclophane (**17**) may lead to two different products: either **7**, in which the Co^{2+} ion is attached to the methyl-substituted deck, or **16**, in which the Co^{2+} ion is attached to the unsubstituted deck. In the Fairhurst–White exchange of **5** with **17**, the only product isolated is **7**. Similarly, the Friedel–Crafts catalyzed reaction of [CpCoI$_2$]$_n$ with **17** gives only **7**. However, the reaction of **12** with **17** gives a 1:1 mixture of **7** and **16**. Presumably, the more drastic conditions of the Fairhurst–White exchange and the Friedel–Crafts catalyzed reactions result in the thermodynamically more stable product as the sole isomer to be isolated, whereas the more reactive reagent **12** leads to a kinetically controlled reaction resulting in a mixture of isomers.



The assignment of structures to **7** and **16** could not be made by a simple comparison of their respective ^{1}H NMR spectra. However, in the course of our synthetic work we compiled a collection of ^{13}C NMR spectra of (η^5-Cp)(η^6-[2$_n$]cyclophane)M^{2+} and (η^5-CpMe$_5$)(η^6-[2$_n$]cyclophane)M^{2+} complexes, and this is presented in Table I. In their review,[17] Chisholm and Godleski comment that π-arene complexation by metals leads to an upfield shift for the carbon resonances of the arene. We found this upfield shift occurred on ruthenium(II) complexation of [2$_n$]-cyclophanes,[18] and it is evident again in the case of the cobalt(III) complexation of [2$_n$]cyclophanes presented in Table I. Thus, the ^{13}C NMR chemical shift for cobalt(III)-complexed ArCH is generally about δ 96, whereas that of the noncomplexed ArCH is about δ 132; similarly, the signal for the cobalt(III)-complexed ArC(CH$_3$) appears at about δ 109, whereas the noncomplexed ArC(CH$_3$) is at δ 138. Since the compound assigned structure **7** has ^{13}C NMR signals at δ 108.3 (s) and 131.1 (d), these data provide clear evidence that the structural assignment made for **7** is correct.

Although the use of **12** was quite effective for mono(capping) of the [2$_n$]cyclophanes, all attempts to accomplish bis(capping) with this reagent were unsuccessful. Also, the CpCo^{2+} complexes of the [2$_n$]cyclophanes were subject to solvolysis in coordinating solvents. In an attempt to solve both these problems, we investigated the pentamethylcyclopentadienyl–cobalt(2+) moiety,

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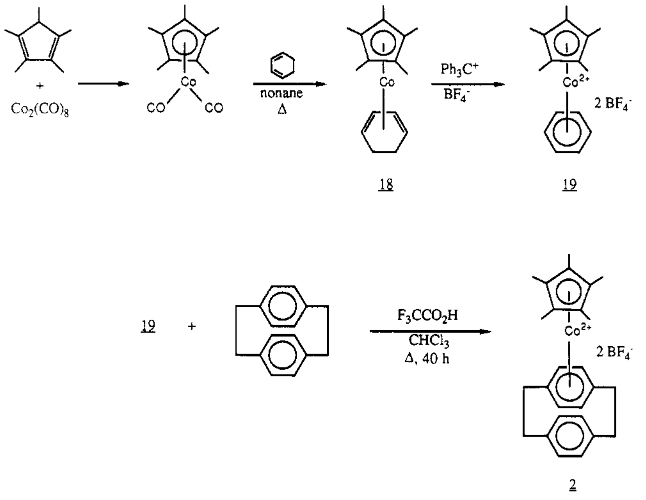
(17) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299–419.

(18) Rohrbach, W. D.; Boekelheide, V. *J. Org. Chem.* **1983**, *48*, 3673–3678.

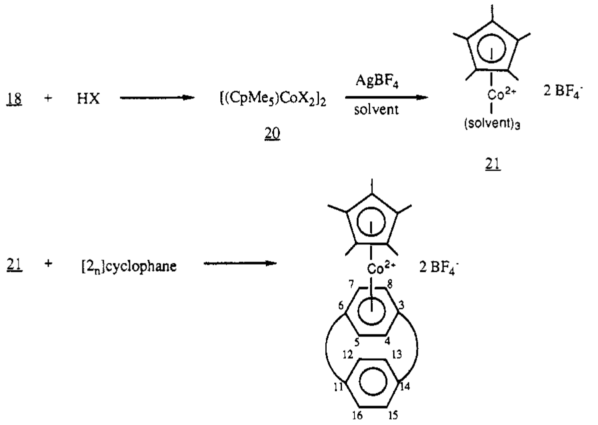
Scheme II



$(CpMe_5)Co^{2+}$, to see whether it would be a better complexing agent. As shown in Scheme II, the Fischer–Fischer method readily gave $(\eta^5\text{-}CpMe_5)(\eta^6\text{-benzene})Co^{2+}(BF_4^-)_2$ (**19**).[19] The presence of the $(CpMe_5)Co^{2+}$ moiety had two obvious effects: (1) compound **19** is much more stable toward solvolysis than **5**, but (2) the exchange reaction, involving displacement of benzene by $[2_2](1,4)$cyclophane to give **20**, is more difficult, being slow and incomplete (Scheme II).

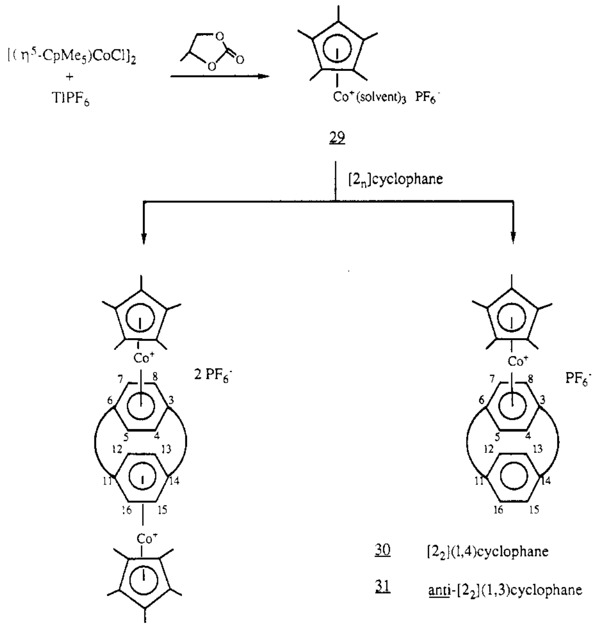
As an alternative to other methods of preparing halogen dimers, Grundy and Maitlis have shown that the reaction of $(\eta^6$-hexamethylbenzene$)(\eta^4$-cyclohexadiene$)$Ru(0) with hydrogen chloride gives cyclohexene plus the $(\eta^6$-hexamethylbenzene$)Ru^{2+}$ chloro dimer.[22] We have used this type of conversion to advantage in our syntheses of $(\eta^6\text{-}[2_n]\text{cyclophane})_2Ru^{2+}$ complexes.[7] Thus, as expected, we found that treatment of the cyclohexadiene complex **18** with either hydrogen chloride or hydrogen bromide provided a convenient route for preparing $[(\eta^5\text{-}CpMe_5)CoX_2]_2$. In addition, the iodo dimer could be prepared from $(CpMe_5)Co(CO)_2$ by reaction with iodine, analogous to the behavior of the corresponding cyclopentadiene case, as discussed earlier. As shown in Scheme III, the reaction of $[(\eta^5\text{-}CpMe_5)CoX_2]_2$, where X = Cl, Br, or I, with silver tetrafluoroborate in an appropriate solvent (acetone, trifluoroacetic acid, or propylene carbonate) gave the solvated complex **21**, which proved to be an excellent reagent for capping $[2_n]$cyclophanes.

Scheme III



22	$[2_2](1,4)$cyclophane
23	5,8,12,15-tetramethyl-$[2_2](1,4)$-cyclophane
24	12,13,15,16-tetramethyl-$[2_2](1,4)$-cyclophane
25	4,5,7,8,12,13,15,16-octamethyl-$[2_2](1,4)$-cyclophane
26	anti-$[2_2](1,3)$cyclophane
27	$[2_3](1,3,5)$cyclophane
28	$[2_4](1,2,4,5)$cyclophane

Scheme IV



36	$[2_2](1,4)$cyclophane
37	4,5,7,8-tetramethyl-$[2_2](1,4)$-cyclophane
38	5,8,12,15-tetramethyl-$[2_2](1,4)$-cyclophane

30	$[2_2](1,4)$cyclophane
31	anti-$[2_2](1,3)$cyclophane
32	12,13,15,16-tetramethyl-$[2_2](1,4)$-cyclophane
33	4,5,7,8,12,13,15,16-octamethyl-$[2_2](1,4)$cyclophane
34	5,8,12,15-tetramethyl-$[2_2](1,4)$-cyclophane
35	$[2_4](1,2,4,5)$cyclophane

Even though **21** was a more effective capping agent than **12**, we were still unsuccessful in achieving bis(capping) of $[2_n]$cyclophanes. In view of the fact that cobalt in its lower oxidation states is much more strongly bonded to arenes,[11] we then examined the $(\eta^5\text{-}CpMe_5)Co^+$ ion as a capping agent. In this case silver tetrafluoroborate cannot be used to generate the solvated $(\eta^5\text{-}CpMe_5)Co^+$ ion because silver ion oxidizes the cobalt(II) ion. However, treatment of $[(\eta^5\text{-}CpMe_5)CoCl]_2$, prepared as described by Koelle et al.,[19] with thallium hexafluorophosphate in propylene carbonate readily generated the solvated $(\eta^5\text{-}CpMe_5)Co^+$ ion (**29**). Without isolation, **29** underwent reaction in solution with $[2_n]$cyclophanes at room temperature to give the mono(capped) complexes shown in Scheme IV. Furthermore, when **29** was used in excess, the corresponding bis(capped) cobalt(II) complexes were formed in good yield.

Since the series of mono(capped) cobalt(II) complexes presented in Scheme IV differ from the corresponding

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(19) Koelle, U.; Fuss, B.; Rajasekharan, M. V.; Ramakrishna, B. L.; Ammeter, J. H.; Böhm, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 4152–4160.

(20) (a) Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 743–752. (b) *Ibid.* **1984**, *117*, 753–762.

(21) Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem.* **1982**, *94*, 132; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131.

(22) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379–380.

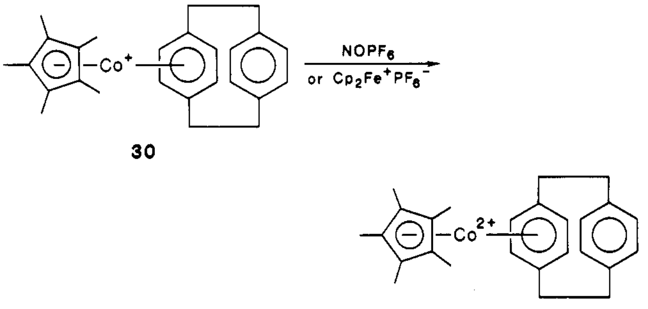
Table II. Electrochemical Data for the M^{2+}[2$_n$]Cyclophane Complexes[a,b]

		2+/+						+/0						
compd	cyclophane[c]	E_{p_c}	E_{p_a}	ΔE_p (mV)	i_a/i_c	$E_{1/2}$	n	E_{p_c}	E_{p_a}	ΔE_p (mV)	i_a/i_c	$E'_{1/2}$	n	$(E_{1/2} - E'_{1/2})$
						$CpCo^{2+}$ Complexes								
8	OMCP	+0.172	+0.294	122	0.99	+0.233	1	−0.817	−0.719	98	0.93	−0.768	1	1.001
15	TMCP	+0.305	+0.362	57	0.96	+0.344	1	−0.837	−0.780	57	0.78	−0.809	1	1.114
7	TCP	+0.242	+0.333	91	0.93	+0.288	1	−0.915	−0.816	99	0.93	−0.866	1	1.154
6	pCp	dec							dec					
13	mCp	dec							dec					
						$CpMe_5Co^{2+}$ Complexes								
22	pCP	−0.005	+0.072	47	0.99	+0.035	1	−0.902	−0.816	56	0.97	−0.860	1	0.895
25	OMCP	−0.043	+0.024	62	1.05	−0.009	1	−1.143	−1.078	63	0.87	−1.110	1	1.101
23	TMCP	−0.026	+0.044	53	1.00	+0.009	1	−1.033	−0.961	56	0.96	−0.991	1	1.006
24	TeMCP	−0.029	+0.057	69	1.03	+0.015	1	−0.941	−0.862	63	0.92	−0.902	1	0.917
26	mCp	−0.023	+0.059	43	1.02	+0.018	1	−0.891	−0.815	37	0.92	−0.853	1	0.871
27	TBCP	−0.114	−0.044	63	0.99	−0.078	1	−1.059	−0.996	53	0.89	−1.027	1	0.949
28	TeBCP	+0.031	+0.099	54	1.04	+0.065	1	−0.556	−0.485	57	0.96	−0.521	1	0.586

		$CpMe_5Rh^{2+}$ complexes							$CpMe_5Ir^{2+}$ complexes					
		2+/0							2+/0					
		E_{p_c}	E_{p_a}	ϵE_p (mV)	i_a/i_c	$E_{1/2}$	n		E_{p_c}	E_{p_a}	ΔE_p (mV)	i_a/i_c	$E_{1/2}$	n
42	pCP	−0.535	−0.452	68	0.99	−0.494	2	**45**	−0.469	−0.390	71	0.92	−0.430	2
43	TeBCP	−0.331	−0.272	36	0.88	−0.307	2	**46**	−0.282	−0.189	60	0.78	−0.235	2

[a] Cyclic voltammograms were measured in propylene carbonate at a scan rate of 100 mV/s; n was measured by coulometry. [b] All voltage measurements have a probable error of ±0.005 V and are referred to SCE, based on simultaneous measurement of the ferrocene redox potential (+0.383 V). [c] pCP = [2$_2$](1,4)cyclophane; OMCP = 4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)cyclophane; TMCP = 5,8,12,15-tetramethyl-[2$_2$](1,4)cyclophane; TCP = 4,5,7,8-tetramethyl-[2$_2$](1,4)cyclophane; TeMCP = 12,13,15,16-tetramethyl-[2$_2$](1,4)cyclophane; mCp = *anti*-[2$_2$](1,3)cyclophane; TBCP = [2$_3$](1,3,5)cyclophane; TeBCP = [2$_4$](1,2,4,5)cyclophane.

series of cobalt(III) complexes in Scheme III only in the oxidation state of the cobalt ion, correlation between the two series is readily evident from cyclic voltammogram studies, as will be discussed shortly. Correlation between the two series can also be done chemically. For example, oxidation of the (η^5-CpMe$_5$)(η^6-[2$_2$](1,4)cyclophane)Co$^+$ ion (**30**) by 1 equiv of either NOPF$_6$ or ferrocenium hexafluorophosphate readily gives the (η^5-CpMe$_5$)(η^6-[2$_2$](1,4)cyclophane)Co^{2+} ion (**22**) identical with a sample of **22** synthesized earlier (Scheme III). Correlation by this means is important because the cobalt(II) complexes are paramagnetic, highly reactive, and not easy to characterize, and so this correlation was made for each of the cobalt(II) complexes. Useful comparisons between analogous cobalt(III) and the paramagnetic cobalt(II) complexes by analysis of NMR data are not possible.



30

22

For purposes of comparison we have also prepared some examples of (η^5-CpMe$_5$)Rh^{2+} and (η^5-CpMe$_5$)Ir^{2+} complexes of the [2$_n$]cyclophanes. These were synthesized following the same general procedure presented in Scheme I for preparing the (η^5-Cp)Co^{2+} complexes. Although the rhodium and iridium dimeric chlorides **40** have been previously described and used,[23,24] the procedure presented in Scheme V, in which pentamethylcyclopentadiene (**39**) is heated with either rhodium or iridium trichloride was exceptionally convenient. The procedure of Bercaw et al. is an excellent route for preparing pentamethylcyclopentadiene (**39**).[25] Since the arene π-bonding ability of iridium is very strong, it was possible, using an excess of the capping agent, to prepare the bis(capped) diiridium(III) complex **48**.

The ^{13}C NMR spectra of complexes **42**, **45**, and **46** were also measured and are included in Table I. There is very little change in the ^{13}C NMR chemical shift values with a change in the transition metal except for those carbons directly bonded to the metal. For these carbons, both in the Cp ring and in the bound deck of the cyclophane, there is a consistent pattern that with the iridium-bound carbons the highest upfield shift is seen, whereas the corresponding rhodium-bound carbons show the greatest downfield shift and the cobalt-bound carbons are in between.

Electrochemistry

A summary of our electrochemical data for the cobalt, rhodium, and iridium complexes of the [2$_n$]cyclophanes is presented in Table II. The sensitivity of (η^5-Cp)(η^6-arene)Co^{2+} complexes toward solvolysis in polar solvents, when the arene is unsubstituted or only partially alkylated, has been previously noted.[19] In the case of (η^5-Cp)(η^6-[2$_2$](1,4)cyclophane)Co^{2+} (**6**) and (η^5-Cp)(η^6-*anti*-[2$_2$](1,3)cyclophane)Co^{2+} (**13**), solvolysis occurs so readily in polar solvents that it was not possible to find a suitable solvent for conducting cyclic voltammetry (this is indicated in Table I as decomposition). Methylation of the cyclophane moiety improves the stability of the metal complex toward solvolysis, and methylation of the cyclopentadiene

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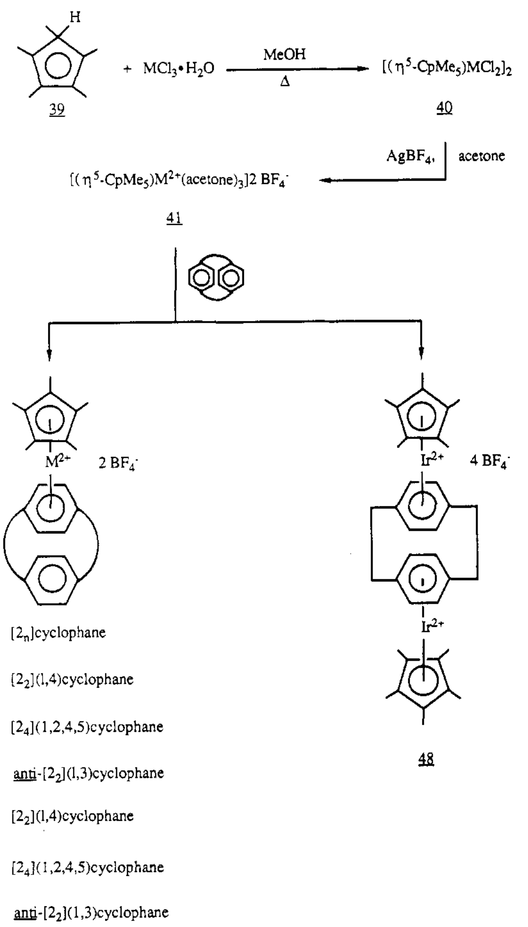
(23) (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1964**, *91*, 5970–5977. (b) Thompson, S. J.; Bailey, P. M.; White, C.; Maitlis, P. M. *Angew. Chem.* **1976**, *88*, 506–507.

(24) Booth, B. L.; Hazeldine, R. N.; Hill, M. *J. Chem. Soc. A* **1964**, 1299–1303. (b) Rybinskaya, M. F.; Kudinov, A. R.; Kaganovich, V. S. *J. Organomet. Chem.* **1983**, *246*, 279–285.

(25) Kende, A. S. *Org. Synth.* **1986**, *64*, 228 (unchecked procedure no. 2359 by R. S. Threlkel, J. E. Bercaw, P. F. Seidler, J. M. Stryker, and R. G. Bergman).

Scheme V



ring, as in the $CpMe_5$ series, improves the stability much more. Even so, some solvolysis is still likely to occur and must be taken into account in conducting cyclic voltammetry. The $(CpMe_5)Co^{2+}$ (solvent)$_3$ ion is deep blue in color, and so its formation by solvolysis is readily detected.

Koelle et al. have reported that small-sample electrolysis on the plateau of the second reduction wave for (η^5-Cp)(η^6-arene)Co^{2+} complexes leads to dark solutions with precipitation of elementary cobalt along with drastically decreased cyclic voltammetric peaks.[19] We observed a similar behavior for the second reduction waves of our (η^5-Cp)(η^6-[2_n]cyclophane)Co^{2+} complexes. Even though the second wave seemed nearly reversible, its peak current ratio deviated from unity at sweep rates ≤100 mV/s. Thus, the neutral complex must be short-lived on the electrochemical time scale.

Cyclic voltammograms for (η^5-$CpMe_5$)(η^6-[2_2](1,4)-cyclophane)$Co^{2+}(BF_4^-)_2$ (**22**) and (η^5-$CpMe_5$)(η^6-[2_4]-(1,2,4,5)cyclophane)$Co^{2+}(BF_4^-)$ (**28**) are shown in Figure 1. These are typical of the cobalt(III) cyclophane complexes, showing two reversible waves which, by coulometry, correspond to the transfer of one electron for each wave. In the $(CpMe_5)Co^{2+}$ series, the [2_4](1,2,4,5)cyclophane complex **28** shows the most positive redox potentials ($E_{1/2}{}^{2+/+}$ = +0.65 V and $E_{1/2}{}^{+/0}$ = −0.521 V) and the smallest separation (586 mV) between them.

These data for *28* provide an interesting comparison with the (η^6-hexamethylbenzene)Ru^{2+} cyclophane series, where again the [2_4](1,2,4,5)cyclophane example **49** shows the most positive redox potential ($E_{1/2}{}^{2+/0}$ = −0.50 V) of the series.[6] In general, reduction of the mono(capped) ruthenium(II) cyclophane complexes by cyclic voltammetry shows a single, reversible wave corresponding to a net, two-electron transfer. It was shown that reduction of **49** leads to a change in the bonding of ruthenium to the cyclophane from η^6 to η^4, as illustrated by **49** → **50**.[8] Even though the reduction of the cobalt(III) series does not require a change in geometry of an attached arene, as does the ruthenium(II) series, the inherent boat-shaped geometry of the [2_4](1,2,4,5)cyclophane ligand apparently enhances the ease of reduction in the cobalt(III) series just as it does in the ruthenium(II) series.

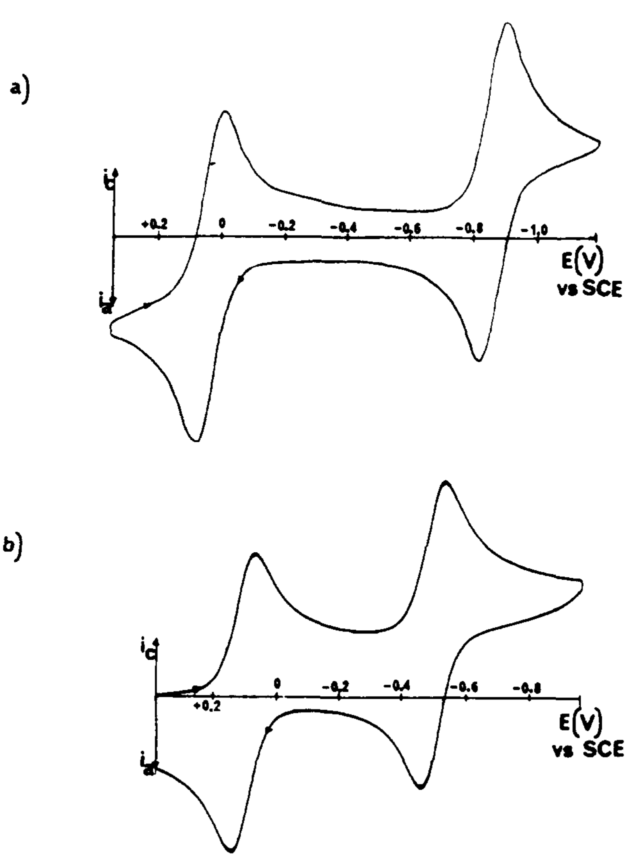
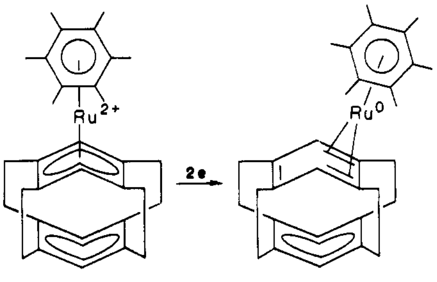


Figure 1. Cyclic voltammograms for (a) (η^5-$CpMe_5$)(η^6-[2_2]-(1,4)cyclophane)cobalt(III) bis(tetrafluoroborate) (**22**) and (b) (η^5-$CpMe_5$)(η^6-[2_4](1,2,4,5)cyclophane)cobalt(III) bis(tetrafluoroborate) (**28**) measured in propylene carbonate (ν = 100 mV/s).



49 50

Other than for the example of **28**, just cited, our observations for the mono(capped) cobalt(III) cyclophane complexes are quite analogous to those reported by Koelle et al. for the cobalt(III) arene complexes. Methylation of the benzene deck of a cyclophane leads to a negative shift of about 30 mV/Me in the redox potential, just as it does in the arene series. Similarly, methyl substitution of the cyclopentadienyl ring leads to a negative shift of 70 mV/Me, again comparable to the arene series.

The bis(capped) cobalt(II) complexes **36**, **37**, and **38** present a complicated picture. They are all paramagnetic and provide no useful NMR spectra. Furthermore, the cyclic voltammograms of these bis(capped) complexes

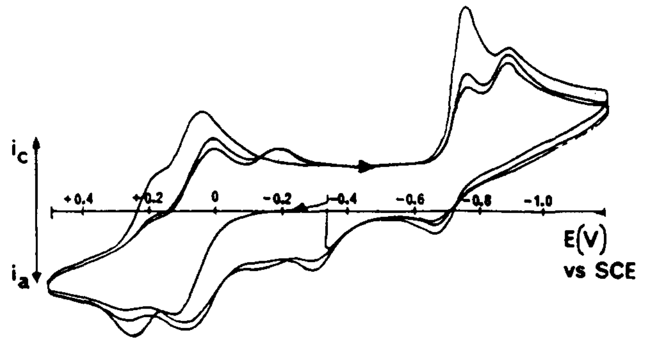


Figure 2. Cyclic voltammogram for bis(η^5-CpMe$_5$)(η^6,η^6-[2$_2$](1,4)cyclophane)dicobalt(II,II) bis(tetrafluoroborate) (**36**) measured in propylene carbonate (ν = 100 mV/s) after three scans.

taken in propylene carbonate at room temperature show a multitude of peaks, suggesting that extensive, unknown electrochemical events are occurring during these experiments. The cyclic voltammogram for bis(η^5-CpMe$_5$)(η^6,η^6-[2$_2$](1,4)cyclophane) dicobalt(II,II) bis(tetrafluoroborate) (**36**), shown in Figure 2, is typical for these bis(capped) complexes. The complicated cyclic voltammogram observed for **36** is not simplified even at sweep rates of 1000 mV/s. Upon repetitive scan the development of a peak due to the (CpMe$_5$)Co^{2+}(solvent)$_3$ ion can readily be recognized.

When a sample of **36** was allowed to stand in a nitromethane solution, there was isolated a product having the correct elemental composition for the oxidation product, [bis(η^5-CpMe$_5$)(η^6,η^6-[2$_2$](1,4)cyclophane)dicobalt(II,III)]$^{3+}$ tris(tetrafluoroborate) (**51**). Compound **51** is paramagnetic and gave essentially the same cyclic voltammogram as that shown for **36** in Figure 2. Thus, **51** appears to be a mixed-valence ion derived from **36**, but, again, there is little that can be deduced about the intramolecular electron-transfer process for **51**.

Finally, as presented in Table II, the mono(capped) rhodium(III) complexes **42** and **43** and the mono(capped) iridium(III) complexes **45** and **46** present cyclic voltammograms that show a single, reversible wave corresponding to a net two-electron reduction. As expected, their behavior is quite analogous to that of the mono(capped) ruthenium(II) complexes. The iridium(III) complexes are somewhat easier to reduce than the corresponding rhodium(III) complexes.

Experimental Section[26]

(η^5-Cp)(η^6-4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)-cyclophane)cobalt(III) Bis(tetrafluoroborate) (8). (A) Fairhurst–White Exchange. A mixture of 60 mg (0.87 mmol) of (η^5-Cp)(η^6-benzene)Co^{2+}(BF$_4^-$)$_2$ and 15 mg (0.047 mmol) of 4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)cyclophane[27,28] in 5 mL of chloroform and 2.5 mL of trifluoroacetic acid was boiled under reflux for 6 h. Then the cold mixture was poured into 125 mL of ether. The resulting reddish brown precipitate was collected by filtration and dried. This solid was redissolved in nitromethane and again precipitated by addition of ether. This gave 16.9 mg (73%) of a reddish brown solid. When a sample was dissolved in nitromethane and slow vapor diffusion of ether was allowed, **8** was isolated as shiny dark red crystals: melting point with decomposition; ^{1}H NMR (CD$_3$NO$_2$) δ 6.10 (5 H, s, Cp*H*), 3.69–3.55 (8 H, m, CH$_2$), 2.76 (12 H, s, ArCH$_3$), 2.24 (12 H, s, ArCH$_3$).

Anal. Calcd for C$_{29}$H$_{37}$CoB$_2$F$_8$·CH$_3$NO$_2$: C, 53.05; H, 5.94. Found: C, 52.92; H, 6.03.

(B) Friedel–Crafts Catalyzed Exchange. A mixture of 383 mg (0.507 mmol) of (CpCoI$_2$)$_2$[31] and 30.7 mg (0.095 mmol) of 4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)cyclophane in 2 mL of trifluoroacetic acid was boiled under reflux for 2 h. After the mixture had cooled to room temperature, a few drops of fluoroboric acid were added and the whole was poured into ether. The precipitate was collected by filtration, dried, and redissolved in nitromethane. Addition of ether, followed by collection of the precipitate, gave 23.7 mg (40%) of a dark red solid whose ^{1}H NMR spectrum was identical with that of the product isolated from (A).

(C) Use of the (η^5-Cp)Co^{2+}(solvent)$_3$ Ion for Capping. A mixture of 60 mg (0.187 mmol) and 10 mL of trifluoroacetic acid was cooled to 0 °C, and 78 mg (0.401 mmol) of AgBF$_4$ plus 75.6 mg (0.100 mmol) of (η^5-CpCoI$_2$)$_2$ were added. The solution first became a deep blue, due to the solvated (η^5-Cp)Co^{2+} ion, and then slowly became a greenish brown. After 2 h, the mixture was warmed to room temperature and poured into 150 mL of ether. The precipitate was collected by filtration, dried, and redissolved in nitromethane. Addition of ether caused the separation of 47 mg (41%) of a reddish brown solid whose ^{1}H NMR spectrum was identical with that of the products from (A) and (B).

(η^5-Cp)(η^6-[2$_2$](1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (6). (A) Fairhurst–White Exchange. This was carried out as described for the preparation of **8**. From 1.386 g (6.64 mmol) of [2$_2$](1,4)cyclophane and 250 mg (0.664 mmol) of (η^5-Cp)(η^6-benzene)Co^{2+}(BF$_4^-$)$_2$ heated in 12 mL of chloroform and 6 mL of trifluoroacetic acid for 7 h, there was isolated 215 mg (64%) of a reddish solid: melting point with decomposition; ^{1}H NMR (CD$_3$NO$_2$) δ 7.00 (4 H, s, ArH), 6.86 (5 H, s, CpH), 6.48 (4 H, s, ArH), 3.45 (8 H, m, CH$_2$). Compound **6** was too unstable to provide a satisfactory elemental analysis.

(B) Use of the (η^5-Cp)Co^{2+}(solvent)$_3$ Ion for Capping. This was carried out as described for the preparation of **8** by method (C). From 250 mg (1.20 mmol) of [2$_2$](1,4)cyclophane, 400 mg (0.529 mmol) of (η^5-CpCoI$_2$)$_2$, and 414 mg (2.13 mmol) of AgBF$_4$, after stirring for 2 h in 5 mL of trifluoroacetic acid, there was isolated 300 mg (50%) of a reddish solid whose ^{1}H NMR spectrum was identical with that of **6** isolated from (A).

(η^5-Cp)(η^6-*anti*-[2$_2$](1,3)cyclophane)cobalt(III) Bis(tetrafluoroborate) (13). This was prepared by method (C) as described for the preparation of **8**. From 125 mg (0.600 mmol) of *anti*-[2$_2$](1,3)cyclophane, 200 mg (0.265 mmol) of (η^5-CpCoI$_2$)$_2$, and 207 mg (1.063 mmol) of AgBF$_4$, which was held at 0 °C for 2 h, there was isolated 198.5 mg (65%) of a yellow solid: melting point with decomposition; ^{1}H NMR (CD$_3$NO$_2$) δ 7.75 (1 H, t, ArH), 7.66 (2 H, d, ArH), 7.46 (1 H, t, ArH), 7.37 (2 H, d, ArH), 6.60 (5 H, s, CpH), 4.97 (1 H, t, ArH), 3.80 (1 H, t, ArH), 3.72–3.50 (4 H, m, CH$_2$), 2.64–2.40 (4 H, m, CH$_2$). Compound **13** was too unstable to provide a satisfactory elemental analysis.

(η^5-Cp)(η^6-[2$_3$](1,3,5)cyclophane)cobalt(III) Bis(tetrafluoroborate) (14). This was prepared by method (C) as described for the preparation of **8**. From 40 mg (0.171 mmol) of [2$_3$](1,3,5)cyclophane,[29] 64.5 mg (0.171 mmol) of (η^5-CpCoI$_2$)$_2$, and 66.5 mg (0.341 mmol) of AgBF$_4$ in 1.5 mL of trifluoroacetic acid, which was stirred at room temperature for 30 min, there was isolated 60 mg (66%) of a red solid: melting point with decomposition; ^{1}H NMR (CD$_3$NO$_2$) δ 6.57 (5 H, s, CpH), 6.36 (3 H, s, ArH), 5.89 (3 H, s, ArH), 3.34 (12 H, m, CH$_2$).

Anal. Calcd for C$_{23}$H$_{23}$CoB$_2$F$_8$·H$_2$O: C, 50.23; H, 4.57. Found: C, 50.82; H, 4.36.

(η^5-Cp)(η^6-5,8,12,15-tetramethyl-[2$_2$](1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (15). This was prepared by method (C) as described for the preparation of **8**. From 70 mg

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[26] All NMR spectra were measured on a Nicolet 360-MHz instrument. Melting points were taken in sealed, evacuated, melting point capillaries and are uncorrected. Elemental analyses were done by Micanal Analyses, Tucson, AZ. Electrochemical measurements were made using a Princeton Applied Research electrochemical station (Model 175 universal programmer, Model 173 potentiostat–galvanostat, and a Model 174A polargraphic analyzer). The supporting electrolyte was tetra-*n*-butylammonium hexafluorophosphate, and the electrodes employed were platinum.

[27] Longone, D. T.; Simanyi, L. H. *J. Org. Chem.* **1964**, *29*, 3245–3249.

[28] Eltamany, S. H.; Hopf, H. *Tetrahedron Lett.* **1980**, *21*, 4901–4904.

[29] Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3201–3208.

[30] Otsubo, T.; Horita, H.; Misumi, S. *Synth. Commun.* **1976**, *6*, 591–592.

[31] Roe, D. M.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3173–3175.

(0.265 mmol) of 5,8,12,15-tetramethyl-$[2_2]$(1,4)cyclophane,[30] 100 mg (0.265 mmol) of $(\eta^5\text{-CpCoI}_2)_2$, and 103 mg (0.530 mmol) of $AgBF_4$ in 3 mL of trifluoroacetic acid, which was stirred at room temperature for 20 min, there was isolated 82 mg (55%) of a red solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.86 (2 H, s, ArH), 6.81 (2 H, s, ArH), 6.42 (5 H, s, CpH), 3.65–3.0 (8 H, m, CH_2), 2.65 (6 H, s, $ArCH_3$), 2.23 (6 H, s, $ArCH_3$).

Anal. Calcd for $C_{25}H_{29}CoB_2F_8$: C, 53.43; H, 5.20. Found: C, 52.96; H, 5.34.

$(\eta^5$-Cp)$(\eta^6$-4,5,7,8-tetramethyl-$[2_2]$(1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (7). This was prepared following method (A) as described for the synthesis of 8. From 500 mg (1.89 mmol) of 4,5,7,8-tetramethyl-$[2_2]$(1,4)cyclophane,[18] 177.6 mg (0.473 mmol) of $(\eta^5\text{-CpCoI}_2)_2$, and 12 mL of trifluoroacetic acid in 25 mL of chloroform, boiled under reflux for 6 h, there was isolated 283 mg (67%) of a red solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 7.04 (4 H, s, ArH), 6.23 (5 H, s, CpH), 3.48–3.39 (8 H, m, CH_2), 2.67 (12 H, s $ArCH_3$).

Anal. Calcd for $C_{25}H_{29}CoB_2F_8$: C, 53.43; H, 5.20. Found: 53.62; H, 5.08.

Compound 7 was also prepared by method (B) as described for the preparation of 8. From 31 mg (0.117 mmol) of 4,5,7,8-tetramethyl-$[2_2]$(1,4)cyclophane[18] and 468 mg (0.619 mmol) of $(\eta^5\text{-CpCoI}_2)_2$, in 2 mL of trifluoroacetic acid, boiled under reflux for 2 h, there was isolated 29 mg (30%) of a red solid, whose ^{1}H NMR spectrum was identical with that of 7 as prepared by method (A) above.

Preparation of 7 and $(\eta^5$-Cp)$(\eta^6$-12,13,15,16-tetramethyl-$[2_2]$(1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (16). This preparation was carried out as described under method (C) for the synthesis of 8. From 35 mg (0.132 mmol) of 4,5,7,8-tetramethyl-$[2_2]$(1,4)cyclophane,[18] 50 mg (0.132 mmol) of $(\eta^5\text{-CpCoI}_2)_2$, and 61.8 mg (0.317 mmol) of $AgBF_4$ in 1.5 mL of trifluoroacetic acid, stirred at room temperature for 15 min, there was isolated 52 mg (70%) of a 1:1 mixture of 7 and 16. The sample of 7 had a ^{1}H NMR spectrum identical with that of the previous preparations of 7. The sample of 16 was a reddish solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.84 (4 H, s, ArH), 6.49 (5 H, s, CpH), 3.48–3.39 (8 H, m, CH_2), 2.14 (12 H, s, $ArCH_3$).

Anal. Calcd for $C_{25}H_{29}CoB_2F_8$: C, 53.43; H, 5.20. Found: C, 53.57; H, 5.12.

$[(\eta^5\text{-CpMe}_5)CoCl_2]_2$ (20). Although 20 has been previously described,[20,21] the method we found most convenient, based on earlier work,[7,22] is the following. Anhydrous hydrogen chloride was bubbled through a solution of 153 mg (0.556 mmol) of $(\eta^5$-CpMe$_5)(\eta^4$-cyclohexadiene)cobalt(I)[32] in 5 mL of pentane, causing the immediate precipitation of a green solid. This was collected by filtration, washed with pentane, and dried to give 147 mg (100%) of 20 as a green powder whose properties were identical with those described for 20 in the literature.[20,21] It is preferable that 20 be prepared just prior to use.

Similarly, the corresponding bromo dimer 20 (X = Br) can be prepared by substituting hydrogen bromide for hydrogen chloride in the above preparation.

$(\eta^5$-CpMe$_5)(\eta^6$-$[2_2]$(1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (22). A mixture of 500 mg (2.40 mmol) of $[2_2]$(1,4)cyclophane, 1.0 g (2.23 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$,[20] and 870 mg (4.47 mmol) of $AgBF_4$ in 25 mL of propylene carbonate was stirred at room temperature for 4 h. It was then poured into ether, and the resulting precipitate was collected by filtration. After the precipitate had been washed with ether, it was dissolved in nitromethane and again precipitated by addition of ether. The orange precipitate was collected by filtration, washed with ether, and dried to give 800 mg (62%) of an orange solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.87 (4 H, s, ArH), 6.51 (4 H, s, ArH), 3.49–3.35 (8 H, m, CH_2), 2.01 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{26}H_{31}CoB_2F_8$: C, 54.21; H, 5.42. Found: C, 54.20; H, 5.53.

Compound 22 was also prepared by heating a mixture of 31 mg (0.059 mmol) of $[(\eta^5\text{-CpMe}_5)CoCl_2]_2$,[20] 118 mg (0.57 mmol) of $[2_2]$(1,4)cyclophane, and a few drops of fluoroboric acid in 1 mL of trifluoroacetic acid for 2 h. After the mixture was poured into ether, the resulting orange precipitate was collected by filtration, washed with ether, and dried to give 41.3 mg (61%) of an orange solid, whose ^{1}H NMR spectrum was identical with that of 22 as described above. The Friedel–Crafts catalyzed reaction of the chloro dimer 20 (X = Cl) with $[2_2]$(1,4)cyclophane was also investigated by using aluminum chloride in hexane. Again, 22 was isolated but only in 25% yield.

$(\eta^5$-CpMe$_5)(\eta^6$-5,8,12,15-tetramethyl-$[2_2]$(1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (23). This was prepared following the same procedure described for synthesizing 22. Use of 133 mg (0.503 mmol) of 5,8,12,15-tetramethyl-$[2_2]$(1,4)cyclophane, 205 mg (0.458 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$, and 179 mg (0.920 mmol) of $AgBF_4$, warmed in 5 mL of trifluoroacetic acid for 2 h, there was isolated on workup 231 mg (75%) of an orange solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.75 (2 H, s, ArH), 6.36 (2 H, s, ArH), 3.58–3.01 (8 H, m, CH_2), 2.50 (6 H, s, $ArCH_3$), 2.16 (6 H, s, $ArCH_3$), 1.93 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{30}H_{39}CoB_2F_8$: C, 56.54; H, 6.20. Found: C, 56.36; H, 6.15.

$(\eta^5$-CpMe$_5)(\eta^6$-12,13,15,16-tetramethyl-$[2_2]$(1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (24). This was prepared following the same procedure described for synthesizing 22. Use of 265 mg (1.00 mmol) of 4,5,7,8-tetramethyl-$[2_2]$(1,4)cyclophane, 408 mg (0.911 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$, and 355 mg (1.824 mmol) of $AgBF_4$ in 6 mL of boiling trifluoroacetic acid for 4 h gave 518 mg (90%) of a light brown solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.47 (4 H, s, ArH), 3.51–3.22 (8 H, m, CH_2), 2.07 (12 H, s, $ArCH_3$), 2.01 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{30}H_{39}CoB_2F_8$: C, 57.00; H, 6.22. Found: C, 56.82; H, 6.40.

$(\eta^5$-CpMe$_5)(\eta^6$-4,5,7,8,12,13,15,16-octamethyl-$[2_2]$(1,4)cyclophane)cobalt(III) Bis(tetrafluoroborate) (25). This was prepared following the same procedure described for synthesizing 22. Use of 35 mg (0.109 mmol) of 4,5,7,8,12,13,15,16-octamethyl-$[2_2]$(1,4)cyclophane, 49 mg (0.109 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$, and 47 mg (0.240 mmol) of $AgBF_4$ in 1.5 mL of trifluoroacetic acid for 0.5 h at room temperature gave on workup 26.4 mg (35%) of a reddish brown solid: melting point with decomposition: ^{1}H NMR (CD_3NO_2) δ 3.59–3.32 (8 H, m, $CH)_2$, 2.52 (12 H, s, $ArCH_3$), 2.24 (12 H, s, $ArCH_3$), 1.73 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{34}H_{47}CoB_2F_8$: C, 59.33; H, 6.88. Found: C, 59.47; H, 7.02.

$(\eta^5$-CpMe$_5)(\eta^6$-*anti*-$[2_2]$(1,3)cyclophane)cobalt(III) Bis(tetrafluoroborate) (26). This was prepared following the same procedure described for synthesizing 22. Use of 300 mg (1.440 mmol) of *anti*-$[2_2]$(1,3)cyclophane, 586.5 mg (1.309 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$, and 510 mg (2.620 mmol) of $AgBF_4$ in 9 mL of trifluoroacetic acid, after standing at room temperature for 4.5 h, gave on workup 680 mg (90%) of a yellow solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 7.61 (1 H, t, J_{AB} = 7.9 Hz, ArH), 7.36 (2 H, dd, J_{AB} = 7.9 Hz, J_{BX} = 1.4 Hz, ArH), 7.31 (1 H, J_{AB} = 6.8 Hz, ArH), 7.00 (2 H, dd, J_{AB} = 6.8 Hz, ArH), 4.79 (1 H, t, J_{BX} = 1.8 Hz), 3.65–3.48 (4 H, m, CH_2), 3.27 (1 H, s, ArH), 2.51–2.35 (4 H, m, CH_2), 2.01 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{26}H_{31}CoB_2F_8 \cdot H_2O$: C, 52.58; H, 5.27. Found: C, 51.99; H, 5.07.

$(\eta^5$-CpMe$_5)(\eta^6$-$[2_3]$(1,3,5)cyclophane)cobalt(III) Bis(tetrafluoroborate) (27). This was prepared following the procedure described for synthesizing 22. Use of 43 mg (0.184 mmol) of $[2_3]$(1,3,5)cyclophane, 76 mg (0.169 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$, and 66 mg (0.337 mmol) of $AgBF_4$ in 2.5 mL of propylene carbonate, allowed to stand at room temperature for 2 h, gave on workup 58 mg (53%) of an orange solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.20 (3 H, s, ArH), 5.62 (3 H, s, ArH), 3.31–3.18 (12 H, m, CH_2), 2.09 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{28}H_{33}CoB_2F_8$: C, 55.86; H, 5.52. Found: C, 55.56; H, 5.81.

$(\eta^5$-CpMe$_5)(\eta^6$-$[2_4]$(1,2,4,5)cyclophane)cobalt(III) Bis(tetrafluoroborate) (28). This was prepared by the same procedure described for the synthesis of 22. Use of 40 mg (0.154 mmol) of $[2_4]$(1,2,4,5)cyclophane, 63 mg (0.140 mmol) of $[(\eta^5\text{-CpMe}_5)CoI_2]_2$, and 54 mg (0.279 mmol) of $AgBF_4$ in 2 mL of propylene carbonate, allowed to stand at room temperature for 2 h, gave on workup 30 mg (34%) of an orange solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.61 (2 H, s, ArH), 6.10 (2 H, s, ArH),

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(32) Lai, Y.-H.; Tam, W.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *261*, 97–101.

3.68–3.45 (8 H, m, CH_2), 3.25–3.03 (8 H, m, CH_2), 1.99 (15 H, s, $CpCH_3$).

Anal. Calcd for $C_{30}H_{35}CoB_2F_8$: C, 57.36; H, 5.62. Found: C, 57.25; H, 5.49.

(η^5-CpMe$_5$)(η^6-4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)-cyclophane) cobalt(II) Hexafluorophosphate (33). A mixture of 40 mg (0.087 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$,[20,33] 61 mg (0.192 mmol) of 4,5,7,8,12,13,15,16-octamethyl-[2$_2$](1,4)cyclophane,[30] and 61 mg of thallium(I) hexafluorophosphate in 2.5 mL of propylene carbonate was stirred for 45 h at room temperature. During this period the initial dark brown color of the mixture changed to a grayish green and TlCl precipitated. The mixture was then passed through a bed of Celite on a fine frit to remove the finely divided TlCl, and the Celite bed was washed with a small amount of acetone followed by dichloromethane until the washings were colorless. After concentration of the combined filtrate and washings, the viscous residue was added to 50 mL of ether. The resulting green-gray precipitate was collected by filtration, washed with ether, and redissolved in dichloromethane. After addition of ether to the dichloromethane solution, the precipitate was collected and dried to give 90 mg (78%) of a green-gray solid. Since **33** is paramagnetic, no useful NMR spectra could be obtained. Characterization of **33** was made by cyclic voltammetry, in which it showed the same behavior as **25**. Also, as described below, chemical oxidation of **33** gave a product identical with **25**.

Anal. Calcd for $C_{34}H_{47}CoPF_6$: C, 61.91; H, 7.18. Found: C, 61.64; H, 7.55.

Oxidation of 33 To Give 25. To a solution of 24 mg of **33** in 6 mL of acetone was added 7 mg of $NOPF_6$ under an inert atmosphere. After a short time, ether was added and the resulting precipitate was collected by filtration and dried to give 26.3 mg (90%) of a reddish brown solid, in all respects identical with the hexafluorophosphate salt of **25**. Similarly, when the above oxidation experiment was carried out, but with ferrocenium hexafluorophosphate substituted for $NOPF_6$, the hexafluorophosphate salt of **25** was isolated in 95% yield.

(η^5-CpMe$_5$)(η^6-[2$_2$](1,4)cyclophane)cobalt(II) Hexafluorophosphate (30). This was prepared following the procedure described for the synthesis of **33**. Use of 136 mg (0.653 mmol) of [2$_2$](1,4)cyclophane, 64 mg (0.140 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, and 100 mg (0.286 mmol) of $TlPF_6$ in 3 mL of propylene carbonate, stirred for 16.5 h at room temperature, gave 76 mg (50%) of a gray-green solid. Again, no useful NMR spectra of this solid could be obtained. However, its cyclic voltammogram was the same as **22**, and, on oxidation with $NOPF_6$, it gave a sample of the hexafluorophosphate salt of **22**, whose ^1H NMR spectrum was identical with that obtained previously for **22**.

Anal. Calcd for $C_{26}H_{31}CoPF_6$: C, 57.05; H, 5.71. Found: C, 56.48; H, 5.32.

(η^5-CpMe$_5$)(η^6-12,13,15,16-tetramethyl-[2$_2$](1,4)-cyclophane)cobalt(II) Hexafluorophosphate (32). This was prepared following the procedure described for the synthesis of **33**. Use of 115 mg (0.436 mmol) of 4,5,7,8-tetramethyl-[2$_2$]-(1,4)cyclophane, 40 mg (0.087 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, and 60 mg (0.174 mmol) of $TlPF_6$ in 4 mL of propylene carbonate, stirred at room temperature for 24 h, gave 76 mg (73%) of a gray-green solid. The cyclic voltammogram of this product in propylene carbonate was identical with that of **24**, and, on oxidation with ferrocenium hexafluorophosphate, it gave a product whose ^1H NMR spectrum was identical with that of **24**.

Anal. Calcd for $C_{30}H_{39}CoPF_6$: C, 59.70; H, 6.51. Found: C, 59.93; H, 6.52.

(η^5-CpMe$_5$)(η^6-5,8,12,15-tetramethyl-[2$_2$](1,4)cyclophane)-cobalt(II) Hexafluorophosphate (34). This was prepared following the procedure described for the synthesis of **33**. Use of 158 mg (0.598 mmol) of 5,8,12,15-tetramethylcyclophane, 87 mg (0.189 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, and 133 mg (0.379 mmol) of $TlPF_6$ in 2.5 mL of propylene carbonate, stirred at room temperature for 4.5 h, gave 110 mg (48%) of a gray solid. The cyclic voltammogram of this solid in propylene carbonate was identical with that of **23**, and, on oxidation with $NOPF_6$, it gave a product whose ^1H NMR spectrum was identical with that of **23**.

Anal. Calcd for $C_{30}H_{39}CoPF_6$: C, 59.70; H, 6.51. Found: C, 59.32; H, 6.73.

(η^5-CpMe$_5$)(η^6-*anti*-[2$_2$](1,3)cyclophane)cobalt(II) Hexafluorophosphate (31). This was prepared following the procedure described for the synthesis of **33**. Use of 82 mg (0.394 mmol) of *anti*-[2$_2$](1,3)cyclophane, 45 mg (0.098 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, and 69 mg (0.196 mmol) of $TlPF_6$ in 5 mL of propylene carbonate, stirred at room temperature for 3.5 h, gave 80 mg (75%) of a purple solid. The cyclic voltammogram of this solid in propylene carbonate was identical with that of **26**, and, on oxidation with $NOPF_6$, it gave an orange solid whose ^1H NMR spectrum was identical with that of **26**.

Anal. Calcd for $C_{26}H_{31}CoPF_6$: C, 57.05; H, 5.71. Found: C, 56.72; H, 5.43.

(η^5-CpMe$_5$)(η^6-[2$_4$](1,2,4,5)cyclophane)cobalt(II) Hexafluorophosphate (35). This was prepared by the procedure described for the synthesis of **33**. Use of 30 mg (0.115 mmol) of [2$_4$](1,2,4,5)cyclophane, 24 mg (0.052 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, and 37 mg (0.104 mmol) of $TlPF_6$ in 1.5 mL of propylene carbonate, stirred at room temperature for 20 h, gave 58 mg (93%) of a blue-gray solid. The cyclic voltammogram of this solid in propylene carbonate was identical with that of **28**, and, on oxidation with ferrocenium hexafluorophosphate, it gave an orange solid, whose ^1H NMR spectrum was identical with that of **28**.

Anal. Calcd for $C_{30}H_{35}CoPF_6$: C, 60.10; H, 5.88. Found: C, 60.04; H, 6.01.

Bis(η^5-CpMe$_5$)(η^6,η^6-[2$_2$](1,4)cyclophane)dicobalt(II,II) Bis(hexafluorophosphate) (36). A mixture of 100 mg (0.218 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, 36 mg (0.174 mmol) of [2$_2$](1,4)-cyclophane, and 152 mg (0.435 mmol) of $TlPF_6$ in 3 mL of propylene carbonate was stirred at room temperature for 24 h. The initial dark brown mixture changed within 1 h to a dark green. The mixture was then filtered through a bed of Celite on a fine frit, followed by washing of the Celite bed with dichloromethane until the washings became colorless. The combined filtrate and washings were concentrated and then poured into 75 mL of ether. The dark green precipitate was collected, redissolved in dichloromethane, and again precipitated by addition of ether. The resulting green precipitate was collected by filtration and dried to give 110 mg (70%) of a deep green powder. This air-sensitive, paramagnetic compound, by a quick measurement in CD_3NO_2, showed in its ^1H NMR spectrum a broad hump in the region of δ 2.0 (CH_2?), a broad singlet around δ 9.6 (ArH?), and a broad singlet around δ 19.5 ($CpCH_3$?). Due to oxidation of **36** by CD_3NO_2, this spectrum disappeared fairly rapidly. The cyclic voltammogram of **36** in propylene carbonate is shown in Figure 2.

Anal. Calcd for $C_{36}H_{46}Co_2P_2F_{12}$: C, 48.77: H, 5.23. Found: C, 48.55; H, 5.27.

When a solution of **36** was alllowed to stand in nitromethane for several days and then ether was added, a green powder separated that was collected and dried. This powder was paramagnetic, and no useful ^1H NMR spectrum could be observed. Its cyclic voltammogram could be measured, using propylene carbonate as solvent, and was very similar to that of **36** shown in Figure 2. Elemental analysis of this product indicates that it is (η^5-CpMe$_5$)(η^6,η^6-[2$_2$](1,4)cyclophane)dicobalt(II,III) tris(hexafluorophosphate).

Anal. Calcd for $C_{36}H_{46}Co_2P_3F_{18}$: C, 41.92; H, 4.50. Found: C, 41.93, 42.28; H, 4.61, 4.23.

Bis(η^5-CpMe$_5$)(η^6,η^6-4,5,7,8-tetramethyl-[2$_2$](1,4)-cyclophane)dicobalt(II,II) Bis(hexafluorophosphate) (37). This was prepared following the procedure described for the synthesis of **36**. Use of 150 mg (0.327 mmol) of [(η^5-CpMe$_5$)CoCl]$_2$, 82 mg (0.311 mmol) of 4,5,7,8-tetramethyl-[2$_2$](1,4)cyclophane, and 228 mg (0.654 mmol) of $TlPF_6$, stirred at room temperature, gave a green solid. Crystallization of this by solution in dichloromethane followed by slow vapor diffusion of ether gave 142 mg (49%) of dark green microcrystals. No useful NMR spectra could be obtained from these crystals.

Anal. Calcd for $C_{40}H_{54}Co_2P_2F_{12}\cdot 2H_2O$: C, 49.09; H, 5.96. Found: C, 48.86; H, 5.69.

Bis(η^5-CpMe$_5$)(η^6,η^6-5,8,12,15-tetramethyl-[2$_2$](1,4)-cyclophane)dicobalt(II,II) Bis(hexafluorophosphate) (38). This was prepared following the procedure given for the synthesis of **36**. Use of 66 mg (0.248 mmol) of 5,8,12,15-tetramethyl-

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(33) Koelle, U.; Fuss, B.; Belting, M.; Raahe, E. *Organometallics* **1986**, *5*, 980–987.

$[2_2](1,4)$cyclophane, 131 mg (0.285 mmol) of $[(\eta^5\text{-CpMe}_5)\text{CoCl}]_2$, and 199 mg (0.570 mmol) of TlPF_6 in 6 mL of propylene carbonate, stirred at room temperature for 7.5 h, gave 129 mg (55%) of a green solid. No useful NMR spectra could be obtained. A cyclic voltammogram of **38** in propylene carbonate was very similar to that of **34**.

Anal. Calcd for $\text{C}_{40}\text{H}_{54}\text{Co}_2\text{P}_2\text{F}_{12}\cdot\text{H}_2\text{O}$: C, 50.01; H, 5.82. Found: C, 49.87; H, 5.68.

$(\eta^5$-CpMe$_5)(\eta^6$-[2$_2$](1,4)cyclophane)rhodium(III) Bis(tetrafluoroborate) (42). A mixture of 100 mg (0.162 mmol) of $[(\eta^5\text{-CpMe}_5)\text{RhCl}_2]_2$[23a] and 126 mg (0.647 mmol) of AgBF_4 in 6 mL of acetone was stirred at room temperature for 30 min. The precipitate of silver chloride was collected and washed with acetone. The combined filtrate and washings were concentrated, and to the gummy residue was added 202 mg (0.971 mmol) of $[2_2](1,4)$cyclophane, 3 mL of acetone, and 3 mL of trifluoroacetic acid. This mixture was boiled under reflux for 2 h. It was then filtered to remove excess $[2_2](1,4)$cyclophane, and the filtrate was poured into ether. The resulting yellow precipitate was collected by filtration, washed with ether, and then crystallized by dissolving it in nitromethane and slowly allowing vapor diffusion of ether into the solution. This gave 142 mg (71%) of pale yellow crystals: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.98 (4 H, s, ArH), 6.56 (4 H, s, ArH), 3.49–3.32 (8 H, m, CH_2), 2.17 (15 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{RhB}_2\text{F}_8$: C, 50.36; H, 5.04. Found: C, 50.30; H, 5.01.

$(\eta^5$-CpMe$_5)(\eta^6$-[2$_4$](1,2,4,5)cyclophane)rhodium(III) Bis(tetrafluoroborate) (43). This was prepared following the procedure described for the synthesis of **42**. Use of 111 mg (0.175 mmol) of $[(\eta^5\text{-CpMe}_5)\text{RhCl}_2]_2$ and 140 mg (0.719 mmol) of AgBF_4 in 10 mL of acetone to give the solvate **41**, followed by heating with 15.6 mg (0.060 mmol) of $[2_4](1,2,4,5)$cyclophane in 3 mL of trifluoroacetic acid for 24 h, gave on workup 37 mg (91%) of a gray-green solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.7 (2 H, s, ArH), 6.07 (2 H, s, ArH), 3.73–3.64 (4 H, m, CH_2), 3.52–3.44 (4 H, m, CH_2), 3.28–3.19 (4 H, m, CH_2), 3.05–2.96 (4 H, m, CH_2), 2.17 (15 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{RhB}_2\text{F}_8$: C, 53.61; H, 5.25. Found: C, 53.94; H, 5.16.

$(\eta^5$-CpMe$_5)(\eta^6$-*anti*-[2$_2$](1,3)cyclophane)rhodium(III) Bis(tetrafluoroborate) (44). This was prepared following the procedure described for the synthesis of **42**. Use of 54 mg (0.085 mmol) of $[(\eta^5\text{-CpMe}_5)\text{RhCl}_2]_2$ and 68 mg (0.350 mmol) of AgBF_4 in 10 mL of acetone to give the solvate **41**, followed by heating this with 40 mg (0.192 mmol) of *anti*-$[2_2](1,3)$cyclophane in 3 mL of trifluoroacetic acid for 2.5 h, gave 76 mg (78%) of a nearly white solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 7.59 (1 H, t, J_{AB} = 7.8 Hz, ArH), 7.33 (2 H, d, J_{AB} = 7.8 Hz, ArH), 7.29 (1 H, t, J_{AB} = 6.0 Hz, ArH), 7.20 (2 H, d, J_{AB} = 6.0 Hz, ArH), 5.13 (1 H, s, ArH), 3.64–3.57 (2 H, m, CH_2), 3.50 (1 H, s, ArH), 3.47–3.41 (2 H, m, CH_2), 2.62–2.49 (4 H, s, CH_2), 2.17 (15 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{RhB}_2\text{F}_8$: C, 50.36; H, 5.04. Found: C, 49.94; H, 5.26.

$(\eta^5$-CpMe$_5)(\eta^6$-[2$_2$](1,4)cyclophane)iridium(III) Bis(tetrafluoroborate) (45). This was prepared following the same procedure described for the synthesis of **42**. Use of 81 mg (0.102 mmol) of $[(\eta^5\text{-CpMe}_5)\text{IrCl}_2]_2$[23a,34] and 80 mg (0.410 mmol) of AgBF_4 in 5 mL of acetone to form the solvate **41**, followed by heating this with 48 mg (0.228 mmol) of $[2_2](1,4)$cyclophane in 4 mL of trifluoroacetic acid for 2 h, gave 143 mg (99%) of a white solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 7.07 (4 H, s, ArH), 6.56 (4 H, s, ArH), 3.56–3.34 (8 H, m, CH_2), 2.28 (15 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{IrB}_2\text{F}_8$: C, 44.02; H, 4.41. Found: C, 43.72; H, 4.11.

$(\eta^5$-CpMe$_5)(\eta^6$-[2$_4$](1,2,4,5)cyclophane)iridium(III) Bis(tetrafluoroborate) (46). Use of 133 mg (0.168 mmol) of $[(\eta^5\text{-CpMe}_5)\text{IrCl}_2]_2$ and 131 mg (0.670 mmol) of AgBF_4 in 10 mL of acetone to form the solvate **41**, followed by heating this with 21 mg (0.081 mmol) of $[2_4](1,2,4,5)$cyclophane in 3 mL of trifluoroacetic acid for 5 h, gave 45 mg (74%) of a tan solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 6.81 (2 H, s, ArH), 6.12 (2 H, s, ArH), 3.77–3.68 (4 H, m, CH_2), 3.60–3.51 (4 H, m, CH_2), 3.31–3.22 (4 H, m, CH_2), 3.00–2.91 (4 H, m, CH_2), 2.29 (15 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{30}\text{H}_{35}\text{IrB}_2\text{F}_8$: C, 47.32; H, 4.63. Found: C, 47.76; H, 4.53.

$(\eta^5$-CpMe$_5)(\eta^6$-*anti*-[2$_2$](1,3)cyclophane)iridium(III) Bis(tetrafluoroborate) (47). This was prepared following the procedure described for the synthesis of **42**. Use of 43 mg (0.052 mmol) of $[(\eta^5\text{-CpMe}_5)\text{IrCl}_2]_2$ and 43 mg (0.210 mmol) of AgBF_4 in 8 mL of acetone to form the solvate **41**, followed by heating this with 25 mg (0.120 mmol) of *anti*-$[2_2](1,3)$cyclophane in 3 mL of trifluoroacetic acid for 2.5 h, gave 50 mg (64%) of a gray-green solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 7.58 (1 H, t, J_{AB} = 7.5 Hz, ArH), 7.49 (2 H, s, ArH), 7.37 (1 H, t, J_{AB} = 7.5 Hz, ArH), 7.26 (2 H, s, ArH), 5.50 (1 H, s, ArH), 3.64–3.58 (2 H, m, CH_2), 3.57 (1 H, s, ArH), 3.42–3.37 (2 H, m, CH_2), 2.73–2.58 (4 H, m, CH_2), 2.29 (15 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{IrB}_2\text{F}_8$: C, 44.02; H, 4.41. Found: C, 44.56; H, 4.27.

Bis$(\eta^5$-CpMe$_5)(\eta^6,\eta^6$-[2$_2$](1,4)cyclophane)diiridium(III) Tetrakis(tetrafluoroborate) (48). This was prepared following the same general procedure described for **42** except that an excess of the capping reagent was employed. Use of 133 mg (0.167 mmol) of $[(\eta^5\text{-CpMe}_5)\text{IrCl}_2]_2$ and 131 mg (0.670 mmol) of AgBF_4 in 8 mL of acetone to form the solvate **41**, followed by heating this with 20 mg (0.096 mmol) of $[2_2](1,4)$cyclophane in 3 mL of trifluoroacetic acid for 4 h, gave a 1:1 mixture of mono- and bis(capped) products. When this was washed with acetone, in which **48** is not soluble, there was isolated 53 mg (45%) of a white solid: melting point with decomposition; ^{1}H NMR (CD_3NO_2) δ 7.08 (8 H, s, ArH), 3.80 (8 H, s, CH_2), 2.37 (30 H, s, CpCH_3).

Anal. Calcd for $\text{C}_{36}\text{H}_{46}\text{Ir}_2\text{B}_4\text{F}_{16}$: C, 35.72; H, 3.83. Found: 35.05; H, 3.24.

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Registry No. **6**, 114299-97-7; **7**, 114299-99-9; **8**, 114300-01-5; **11**, 78789-50-1; **12**, 114300-02-6; **13**, 114300-04-8; **14**, 114300-06-0; **15**, 114300-08-2; **16**, 114300-10-6; **18**, 114300-55-9; **19**, 72339-84-5; **20** (X = Br), 82595-78-6; **20** (X = Cl), 82595-77-5; **20** (X = I), 72339-52-7; **22**, 114300-12-8; **22** (hexafluorophosphate salt), 114300-59-3; **23**, 114300-14-0; **24**, 114300-16-2; **25**, 114300-18-4; **25 (hexafluorophosphate salt)**, 114300-58-2; **26**, 114300-20-8; **27**, 114300-22-0; **28**, 114300-24-2; **28** (hexafluorophosphate salt), 114300-60-6; **30**, 114300-26-4; **31**, 114300-28-6; **32**, 114300-30-0; **33**, 114300-32-2; **34**, 114300-34-4; **35**, 114300-36-6; **36**, 114300-38-8; **37**, 114300-40-2; **38**, 114300-62-8; **40** (M = Ir), 12354-84-6; **40** (M = Rh), 12354-85-7; **41** (M = Ir), 96097-01-7; **41** (M = Rh), 94058-31-8; **42**, 114300-42-4; **43**, 114300-44-6; **44**, 114300-46-8; **45**, 114300-48-0; **46**, 114300-50-4; **47**, 114300-52-6; **48**, 114300-54-8; mCP, 51744-98-0; OMCP, 77897-20-2; TBCP, 27165-88-4; TMCP, 35233-71-7; TCP, 65304-59-8; pCP, 1633-22-3; TeBCP, 54100-59-3; $[(\eta^5\text{-CpMe}_5)(\eta^6\eta^6\text{-pCP})\text{Co}^{\text{II,III}}{}_2](\text{PF}_6)_3$, 114300-57-1.

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(34) Booth, B. L.; Hazeldine, R. N.; Hill, M. *J. Chem. Soc. A* **1964**, 1299–1304.