though its solubility is very high, the crystals have a tendency to stick to one another, forming flocks when in contact with water, and this makes the dissolution comparatively slow. In the rate study of B′ $\rightleftarrows$ BH′ $\rightarrow$ AH′, therefore, a stock solution containing a known amount of B′ was prepared and stored ice-cold, and a certain amount of this stock solution, after being brought to the desired temperature, was mixed with a certain amount of a solution containing perchloric acid and sodium perchlorate. Because of this manipulation the temperature control was not as satisfactory as in the study of AH′ $\rightarrow$ BH′ or AH′ $\rightarrow$ C′.

The pH was measured by a Beckman Model G pH meter calibrated by using Beckman standard buffer solutions of pH 4.00 and 6.86.

The epr measurements were carried out with a Varian V-4500 spectrometer with 100-kc/sec modulation, operating at 9500-Mc/sec and room temperature. In contradistinction to any of the other paramagnetic compounds of cobalt, the binuclear cobalt–peroxo complexes show strong epr absorption even at room temperature.

Fitting of straight lines to the experimental points was done with the aid of a least-squares computer program (IBM 1620).

Acknowledgments. It is the authors' pleasure to acknowledge Dr. Minoru Okada for discussions and his cooperation in the epr measurements. The authors' gratitude is also expressed to Mrs. Judith K. Kinnaird and to Mr. Adolph Venters for the dehydration experiments, and to Mr. Yoshihisa Yamamoto for the susceptibility measurement. Some of the compounds were analyzed through the kindness of Dr. Bane's group.

Cyclobutadiene–Metal Complexes. IX.[1] Tetraphenylcyclobutadienecobalt(I) Complexes[2]

A. Efraty and P. M. Maitlis[3]

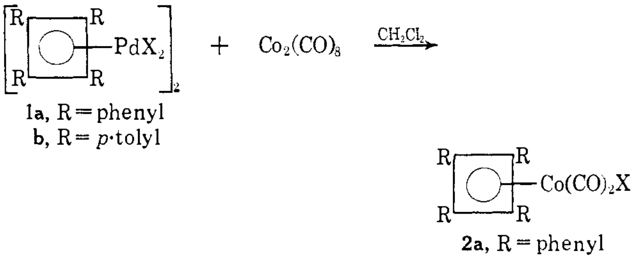
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received February 28, 1967*

Abstract: The complexes $R_4C_4Co(CO)_2X$ (R = C_6H_5, p-$CH_3C_6H_4$; X = halogen) have been prepared by ligand-transfer reactions from $[R_4C_4PdX_2]_2$. The reactions of $R_4C_4Co(CO)_2X$ show considerable similarity to those of π-$C_5H_5Fe(CO)_2X$, and evidence for a very strong metal–ring bond in the cobalt complex is presented. Reaction of $R_4C_4Co(CO)_2Br$ with C_6F_5Li gave the very stable σ-pentafluorophenyl complex $R_4C_4Co(CO)_2C_6F_5$. With aromatic hydrocarbons in the presence of $AlCl_3$, $R_4C_4Co(CO)_2Br$ gave the stable $[R_4C_4Co(arene)]^+$; cycloheptatriene also reacted with $R_4C_4Co(CO)_2Br$ in the absence of a catalyst to give $[R_4C_4CoC_7H_8]^+$. Nucleophilic attack occurred readily at the C_7H_8 ring in $[R_4C_4CoC_7H_8]^+$ and less easily at the benzene ring in $[R_4C_4CoC_6H_6]^+$ to give the $(R_4C_4)Co$(cycloheptadienyl) and the $(R_4C_4)Co$(cyclohexadienyl) complexes, respectively. The order of susceptibility of π-complexed ligands in metal d^8 complexes toward nucleophilic attack, cycloheptatriene > benzene > (R_4C_4) > cyclopentadienyl, is proposed. A novel method for effecting hydride abstraction is reported. Aniline in $[Ph_4C_4Co(aniline)]^+$ is less basic than aniline itself by approximately 1.5 pK units.

A general method for the preparation of tetraphenylcyclobutadiene (Ph_4C_4) metal complexes by ligand transfer from the readily accessible (Ph_4C_4)–palladium halide complexes[4] (**1a**) has been developed.[5] In these reactions the palladium complex (**1a**) is allowed to react with a metal carbonyl, and transfer of the (Ph_4C_4) group, frequently in high yield, onto the other metal occurs. No detailed studies have yet been carried out on these reactions but a possible mechanism has been outlined.[6] A particularly interesting and fruitful application of this reaction has been to the synthesis of the (tetraphenylcyclobutadiene)cobalt dicarbonyl halides (**2a**) by reaction of **1a** with dicobalt octacarbonyl in dichloromethane at 25°.

Results

The complexes **2a** (X = Cl, Br, and I) were obtained from the (Ph_4C_4)–palladium halide complexes **1a** (X = Cl, Br, and I) in yields ranging from 65 to 17% (Table I). The analogous tetrakis(p-tolyl)cyclobutadienecobalt dicarbonyl bromide (**2b**, X = Br) was obtained similarly. As obtained, the complexes **2** were usually analytically pure but, as they showed quite a high paramagnetism, it was at first thought that they represented a new type of paramagnetic Co(I) complex.[2a] After very careful purification, however, it has now been possible to obtain this material with quite low magnetic susceptibilities. Solutions of the complexes also show



1a, R = phenyl
b, R = p-tolyl

2a, R = phenyl
b, R = p-tolyl

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[1] Part VIII: D. F. Pollock and P. M. Maitlis, *Can. J. Chem.*, **44**, 2673 (1966).

[2] Part of the work described here has been the subject of preliminary communications: (a) P. M. Maitlis and A. Efraty, *J. Organometal. Chem.* (Amsterdam), **4**, 175 (1965); and (b) A. Efraty and P. M. Maitlis, *Tetrahedron Letters*, 4025 (1966).

[3] Author to whom any correspondence should be addressed.

[4] A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964).

[5] P. M. Maitlis and M. L. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963); *Chem. Ind.* (London), 1624 (1963); P. M. Maitlis and A. Efraty, *J. Organometal. Chem.* (Amsterdam), **4**, 172 (1965).

[6] P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 109 (1966).

Table I

Complex[a]	No.	Mp, °C	Yield, %	Prepared from	Calculated, % C	Calculated, % H	Calculated, % Other	Found, % C	Found, % H	Found, % Other
$Ph_4C_4Co(CO)_2Br$	**2a**, X = Br	259–265 dec	59	**1a**, X = Br	65.38	3.66	Co, 10.69; Br, 14.49; O, 5.78; M, 551	65.60	3.63	Co, 10.81; Br, 14.28; O, 6.08; M, 538
$To_4C_4Co(CO)_2Br$	**2b**, X = Br	258–260 dec	35	**1b**, X = Br	67.20	4.49	...	67.05	4.47	...
$Ph_4C_4Co(CO)_2Cl$	**2a**, X = Cl	200 dec	65	**1a**, X = Cl	71.06	3.98	...	71.26	4.10	...
$Ph_4C_4Co(CO)_2I$	**2a**, X = I	268–271 dec	17	**1a**, X = I	60.20	3.37	...	60.38	3.41	...
$Ph_4C_4CoCO \cdot PPh_3Br$	**4**, X = Br	225–230 dec	72	**2a**, X = Br	71.87	4.49	Br, 10.17	72.45	4.76	Br, 9.67
$Ph_4C_4CoCO \cdot PPh_3Cl$	**4**, X = Cl	210–215 dec	85	**2a**, X = Cl	76.25	4.76	...	76.15	4.75	...
$Ph_4C_4Co(CO)_2C_6F_5$	**5a**	164 dec	53	**2a**, X = Br	67.73	3.16	F, 14.88; M, 638	67.99	3.22	F, 14.80; M, 625
$To_4C_4Co(CO)_2C_6F_5$	**5b**	172–173 dec	78	**2b**, X = Br	69.20	4.07	F, 13.67; M, 695	68.96	3.94	F, 13.87; M, 687
$[Ph_4C_4CoC_6H_6]^+Br^-$	**10a**	180–190 dec	55	**2a**, X = Br	71.20	4.57	Co, 10.27; Br, 13.93	71.28	4.62	Co, 9.75; Br, 13.45
$[Ph_4C_4CoC_6H_6]^+PF_6^-$	**13**, Y = H	370–378 dec	..	**10a**	63.90	4.11	...	64.06	4.30	...
$[To_4C_4CoC_6H_6]^+Br^-$	**10b**	145–147 dec	86	**2b**, X = Br	72.50	5.44	...	72.35	5.49	...
$[Ph_4C_4CoC_6H_5CH_3]^+$-Br^-	**6**, arene, toluene,	170–172 dec	62	**2a**, X = Br	71.69	4.64	Co, 10.05; Br, 13.62	71.61	4.89	Co, 10.12; Br, 13.56
$[Ph_4C_4CoC_6H_5Bu\text{-}n]^+$-$PF_6^-$	**13**, Y = *n*-Bu	229–230 dec	63 62	**12a**, **2a**, X = Bu	65.70	4.96	...	65.57	4.75	...
$[Ph_4C_4CoC_6H_5NH_2]^+$-Br^-	**7**, X = Br	220–230 dec	60	**2a**, X = Br	69.40	4.61	...	69.17	4.96	...
$[Ph_4C_4CoC_6H_5NH_2]^+$-PF_6^-	**7**, X = PF_6	330–334 dec	90	7, X = Br	62.50	4.16	N, 2.14	62.87	4.05	N, 1.95
$[Ph_4C_4CoC_6H_4$-$(CH_3)_2]^+Br^-$	**6**, arene, *p*-xylene	215 dec	53	**2a**, X = Br	72.00	5.03	Co, 9.81; Br, 13.29	72.20	5.02	Co, 10.01; Br, 13.29
$[Ph_4C_4Co(C_6H_5)_2]^+Br^-$	**6**, arene, biphenyl	138–140 dec	40	**2a**, X = Br	74.00	4.65	Br, 12.30	73.87	4.81	Br, 12.06
$[Ph_4C_4CoC_6H_3(CH_3)_3]^+$-$Br^-$	**6**, arene, mesitylene	160 dec	72	**2a**, X = Br	72.20	5.24	Br, 12.98; Co, 9.57	72.10	5.40	Br, 12.88; Co, 9.62
$Ph_4C_4CoC_6H_7$	**11**	134–135	20	**10a**	82.57	5.56	M, 494	82.91	5.70	M, 494
$Ph_4C_4CoC_6H_6Bu\text{-}n$	**12a**	140	53	**10a**	82.89	6.41	M, 550	82.81	6.49	M, 556
$To_4C_4CoC_6H_6Bu\text{-}n$	**12b**	129–131	42	**10b**	83.20	7.31	...	83.16	7.29	...
$[Ph_4C_4CoC_7H_8]^+Br^- \cdot 1.1CoBr_2$	**8a** (A)	...	25	**2a**, X = Br	50.77	3.41	Br, 30.88 Co, 14.94	50.69	3.69	Br, 31.00; Co, 14.84
$[ToC_4CoC_7H_8]^+Br^- \cdot 1.5CoBr_2$	**8b** (A)	...	40	**2b**, X = Br	48.21	3.74	...	48.18	4.12	...
$[Ph_4C_4CoC_7H_8]_2^+$-$[Co(NCS)_4]^{2-}$	**8a**, X = 0.5-$[Co(NCS)_4]$	110–120 dec	27	**8a**	68.00	4.32	...	68.55	4.42	...
$[Ph_4C_4CoC_7H_8]^+ PF_6^-$	**8a**, X = PF_6	284–288	56	**8a**	64.41	4.33	...	64.28	4.19	...
$[To_4C_4CoC_7H_8]^+PF_6^-$	**8b**, X = PF_6	248–251	22	**8b**	66.20	5.12	...	66.00	5.12	...
$[Ph_4C_4CoC_7H_8]^+ I^-$	**8a**, X = I	195–202 dec	44	**8a**	66.23	4.45	...	66.52	4.48	...
$Ph_4C_4CoC_7H_9$	**9a**, Y = H	187–188	16	**8a**	82.64	5.75	M, 508	82.76	5.90	M, 510
$Ph_4C_4CoC_7H_8OH$	**9a**, Y = OH	135–137 dec	64	**8a**	80.14	5.58	Co, 11.22	80.09	5.95	Co, 11.03
$Ph_4C_4CoC_7H_8OMe$	**9a**, Y = OMe	190–195 dec	62	**8a**	80.30	5.80	M, 538	80.08	5.95	M, 536
$To_4C_4CoC_7H_8OMe$	**9b**, Y = OMe	175–178 dec	36	**8b**	80.80	6.61	M, 594	80.67	6.45	M, 616

[a] Ph = phenyl; To = *p*-tolyl.

reasonably sharp phenyl proton nmr resonances with no detectable shifts. We are therefore reasonably certain that we are indeed dealing with diamagnetic Co(I) complexes and that the observed paramagnetism is due to impurities which are very difficult to eliminate completely.

Complexes **2** are red-brown crystalline compounds which appear to be reasonably air stable when dry but which are rapidly oxidized in solution. The infrared spectra of the complexes showed two strong terminal carbonyl stretching frequencies at *ca.* 2025 and 2060 cm^{-1}; the other bands in the spectra were very similar to those of other Ph_4C_4 complexes which we have prepared. The pmr spectrum of **2a** (X = Br) showed an unresolved multiplet at τ 2.60 (26 cps wide) due to the phenyl protons, while that of the tetrakis(*p*-tolyl)-cyclobutadiene (To_4C_4) complex (**2b**, X = Br) showed a fairly well-resolved AB quartet (J_{AB} = 8 cps) (with some paramagnetic broadening) due to the phenyl protons and a singlet at τ 7.67 due to the methyl protons (Table II). This indicated that a cyclobutadiene group was in fact present since otherwise the four *p*-tolyl groups are not equivalent with consequent loss of the AB pattern in the spectrum. This occurs, for example, in the various tetrakis(*p*-tolyl)cyclobutenyl complexes (**3**, R = *p*-tolyl) which we have prepared and studied.[7] Additional proof for the presence of a $(Ph_4C_4)Co$ complex in **2a** was obtained from the ligand-transfer reaction with cyclopentadienyliron dicarbonyl dimer, $[(C_5H_5)Fe(CO)_2]_2$, to give the known (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)cobalt.[8]

Reaction of **2a** with triphenylphosphine in benzene at 25° led to the replacement of one carbonyl group by

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(7) D. F. Pollock, A. Efraty, and P. M. Maitlis, unpublished results. It should also be noted that, since the remainder of the molecule in each case does not have the fourfold axis of symmetry of the tetrakis(*p*-tolyl)cyclobutadiene group, free rotation of the cyclobutadiene ring about the ring to metal axis is also implied when the four *p*-tolyl groups are said to be equivalent.

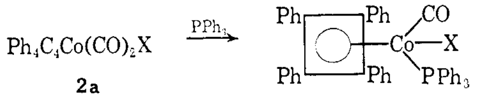
(8) P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, **87**, 719 (1965).

Table II. Nmr Spectra (in τ units; in $CDCl_3$ solution)

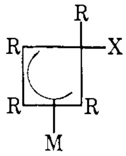
	Phenyl protons	Methyl protons	Others
$Ph_4C_4Co(CO)_2Br$ (**2a**, X = Br)	2.60[a]		
$To_4C_4Co(CO)_2Br$ (**2b**, X = Br)	2.69	7.67	
$Ph_4C_4CoCO \cdot PPh_3Br$ (**4**, X = Br)	2.76[a]		
$Ph_4C_4CoC_5H_5$	2.63, 2.78		5.36[c]
$To_4C_4CoC_5H_5$	2.88[b]	7.87	5.50[c]
$[Ph_4C_4CoC_6H_6]Br^-$ (**10a**)	2.50		3.35[d]
$[To_4C_4CoC_6H_6]Br^-$ (**10b**)	2.74[b]	7.66	3.51[d]
$[Ph_4C_4CoC_6H_5CH_3]^+ Br^-$ (**6a**)	2.50	8.13	3.25, 3.50[e]
$[Ph_4C_4CoC_6H_5C_4H_9]^+Br^-$ (**6a**)	2.59		. . .[f]
$[Ph_4C_4CoC_6H_4(CH_3)_2]^+Br^-$ (**6a**)	2.52	8.18	3.48[e]
$[Ph_4C_4CoC_6H_3(CH_3)_3]^+Br^-$ (**6a**)	2.51	7.97	3.76[e]
$[Ph_4C_4Co(C_6H_5)_2]^+ Br^-$ (**6a**)	2.83[a]		
$Ph_4C_4CoC_6H_7$ (**11**)	2.8[a]		g
$Ph_4C_4CoC_6H_6 \cdot C_4H_9$ (**12a**)	2.79[a]		h
$To_4C_4CoC_6H_6 \cdot C_4H_9$ (**12b**)	2.84[b]	7.70	h
$Ph_4C_4CoC_7H_9$ (**9a**, Y = H)	2.83[a]		g
$Ph_4C_4CoC_7H_8OMe$ (**9a**, Y = OMe)	2.77[a]	6.90[i]	g
$To_4C_4CoC_7H_8OMe$ (**9b**, Y = OMe)	2.86[b]	6.88,[i] 7.73	
$Ph_4C_4Co(CO)_2C_6F_5$ (**5a**)	2.70		j
$To_4C_4Co(CO_2)C_6F_5$ (**5b**)	2.80[b]	7.76	j

[a] Unresolved multiplet. [b] AB quartet (J_{AB} = 8.0 cps). [c] Singlet due to π-C_5H_5. [d] Singlet due to π-C_6H_6. [e] Peak(s) due to π-R_n-C_6H_{6-n}. [f] Unresolved multiplets at τ 3.36, 3.64 (π-phenyl), and 8.05, 8.80, 9.28 (*n*-butyl). [g] See text. [h] Unresolved multiplets at τ 4.5, 5.7, 7.2, and 9.1. [i] Methoxy protons. [j] F^{19} nmr spectrum, see Experimental Section.

one triphenylphosphine to give **4** (X = Cl, Br) in 72–85% yield. 4 was previously also reported to be paramagnetic; however, we have succeeded in reducing the observed paramagnetism by careful purification here too, and we are now of the opinion that complexes 4 are also diamagnetic but contain persistent impurities which are very difficult to remove. In addition to the bands expected from the organic ligands, the infrared spectra of 4 (X = Cl, Br) show a strong terminal carbonyl band at 2000 cm^{-1}. The decrease in ν_{CO} by comparison with **2a** implies a higher Co–CO bond order in 4 than in **2a**, as is expected.



2a **4**



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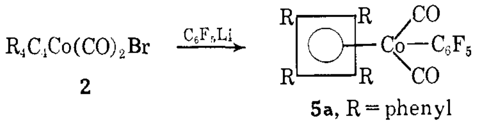
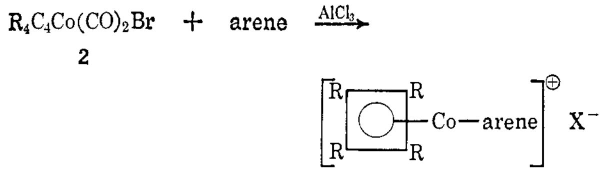


2

5a, R = phenyl
b, R = *p*-tolyl

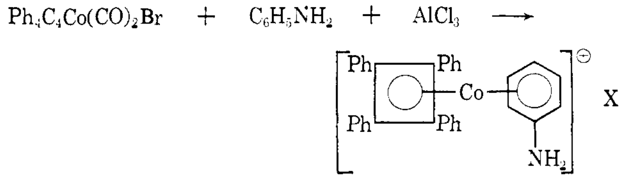
The halogen in **2** (X = Br) was also replaceable by reaction with pentafluorophenyllithium[9] to give the very stable yellow crystalline and diamagnetic (σ-pentafluorophenyl)dicarbonyl(π-tetraphenylcyclobutadiene)cobalt (**5a**). The structure of **5** was again verified by analysis and infrared, H^1, and F^{19} nmr spectra, the latter showing the characteristic large low-field shift of the *ortho* fluorines in the pentafluorophenyl group when bonded to a transition metal.[10] Additional confirmation that attack of the pentafluorophenyl group had indeed occurred on the metal and not on the cyclobutadiene ring was obtained from the H^1 nmr spectrum of the *p*-tolyl analog **5b**. This again showed the AB quartet characteristic of molecules with all four *p*-tolyl groups equivalent and hence implied the presence of a cyclobutadiene ring.

Metal carbonyl halides readily undergo an aluminum chloride catalyzed reaction with aromatic hydrocarbons in which two carbonyls and the halogen are replaced to give the cationic arene π complex. The cobalt complex **2a** (X = Br) readily underwent these reactions with a number of aromatic hydrocarbons to give the cations **6**, which were then treated with saturated aqueous KBr or ammonium hexafluorophosphate to prepare the pure compounds **6**, X = Br, and **6**, X = PF_6, respectively. The complexes **6** were characterized by their analyses (Table I), their infrared spectra, and their pmr spectra (Table II) which were in agreement with the postulated structures. The pmr spectrum of the *p*-tolyl complex **6b** (X = Br) showed conclusively that the cyclobutadiene ring was still intact in these complexes.



6a, R = C_6H_5; arene = benzene, toluene, *n*-butylbenzene, *p*-xylene, mesitylene, biphenyl
b, R = *p*-tolyl; arene = benzene

The aniline complex **7** (X = Br, PF_6) was also prepared. The infrared spectrum showed the presence of a free NH_2 group with ν_{NH} at 3390 and 3497 cm^{-1} (Nujol). A potentiometric titration of the aniline complex in 50% aqueous methanol with 0.1 *N* sodium hydroxide gave a value for pK_b of the complex **7** (X = Br) of 11.00 ± 0.10. Aniline under the same conditions had a measured pK_b of 9.51 ± 0.04, showing that the basicity of aniline was appreciably reduced in the complex.



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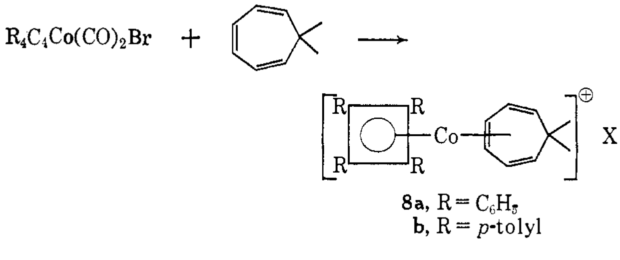

8a, R = C_6H_5
b, R = *p*-tolyl

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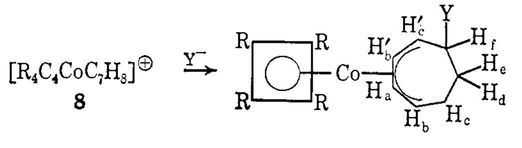
(9) P. M. Treichel, M. A. Chaudhari, and F. G. A. Stone, *J. Organometal. Chem.* (Amsterdam), 1, 98 (1963).

(10) See F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc., Sect. A*, 1326 (1966), and references therein.

The cobalt complexes **2a** (X = Br) and **2b** (X = Br) reacted with cycloheptatriene on heating in the absence of a catalyst to give the cycloheptatriene complexes (**8**) in rather low yield. The green complex (A) initially obtained was not pure and could not be purified without decomposition. From its analysis, A appeared to contain **8** (X = Br) together with varying amounts of $CoBr_2$ (1.1 moles for **8a** and 1.5 moles for **8b**). The presence of this extra cobalt associated with the anion was verified by treatment of A with aqueous potassium thiocyanate, whereupon the complex **8** (X = 0.5Co-$(NCS)_4$) was obtained. This showed the presence of a single strong bond due to a terminal NCS group at 2066 cm^{-1}; Sabatini and Bertini quote a value of 2065 cm^{-1} for ν_{NCS} in $(Et_4N)_2Co(NCS)_4$.[11] Treatment of the crude complex A with aqueous KI or ammonium hexafluorophosphate gave the pure complexes **8a** (X = I and PF_6) and **8b** (X = PF_6). Unfortunately these were all too insoluble to permit the measurement of H^1 nmr spectra; however, their analyses, infrared spectra, and properties were in agreement with the proposed structures which were assigned by analogy with those of the π-arene complexes **6**.

The complexes **6** and **8** are yellow crystalline solids, insoluble in nonpolar solvents, and moderately soluble in polar solvents such as alcohol–water mixtures. They are air stable and in most cases thermally stable to over 150°. Their melting and decomposition points depend on the anion present, the hexafluorophosphates having particularly high melting and decomposition temperatures.

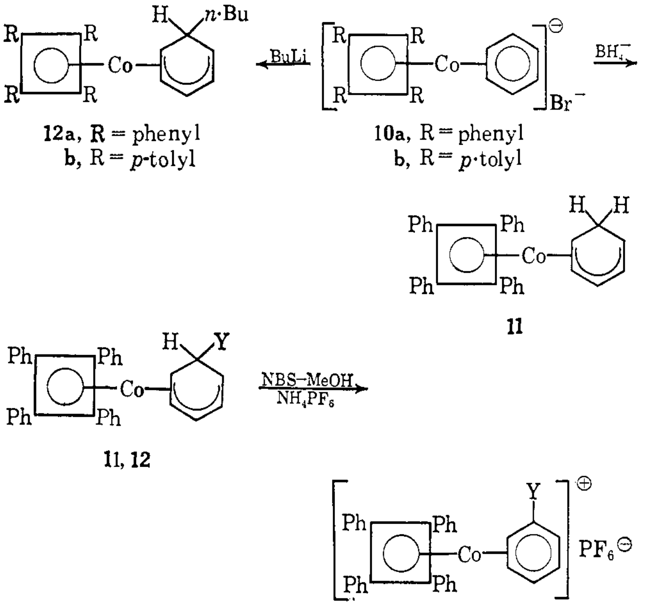
The cycloheptatriene sandwich complexes **8** readily underwent nucleophilic attack, for example, by water in the presence of triethylamine, alkoxide, or borohydride.[12]



9a, R = phenyl
b, R = *p*-tolyl

The pmr spectrum of the *p*-tolyl complex **9b** (Y = OMe) showed the AB quartet in the phenyl proton region (Table II); this implies attack of the methoxide on the cycloheptatriene ring, and we presume attack to have occurred at one end of the triene to give a cycloheptadienyl complex **9** with five of the seven carbon atoms coordinated to the cobalt. The nmr spectrum of the cycloheptadienyl protons was extremely complex. For **9a** (Y = H) the pairs of protons H_b and H_b', H_c and H_c', H_d and H_f, and H_e and Y are equivalent, and five multiplets were observed at τ 4.2 (H_a), 5.2 (H_b), 6.0 (H_c), and 7.5 and 8.5 (CH_2). That at τ 4.2 was just resolvable into a triplet, as expected for H_a. Due to the even lower symmetry of the cycloheptadienyl ring in **9a** (Y = OMe), the spectrum observed was even more complex since now H_b and H_b', H_c and H_c', etc., are all different; multiplets were observed at τ 4.35 (triplet, H_a) 5.2, 5.6, 6.3, 6.95, 7.9, and 8.8. These observations are basically in agreement with the results reported from other π-2,4-cycloheptadienyl complexes;[13,14] the low solubility of our complexes, however, prevented a more detailed assignment.

By contrast, the π-benzene complexes **10** were very inert to nucleophilic attack and could be recovered even after reaction with potassium methoxide or methylmagnesium bromide. Reaction of **10a** with sodium borohydride in aqueous methanol gave a 20% yield of the (π-cyclohexadienyl)(π-tetraphenylcyclobutadiene)-cobalt(I) complex (**11**). This was characterized by analysis, molecular weight measurements, and spectra. The pmr spectrum was particularly significant since it did not show the sharp singlet at τ 3.35 due to the π-complexed benzene, but instead showed five multiplets at τ 4.1, 5.4, 6.1, 7.7, and 8.5 which we assign to the π-cyclohexadienyl protons. Because of the low solubility of the complex, these multiplets could not be resolved; however, the general form of the spectrum was similar to that reported by Winkhaus and Wilkinson for π-cyclohexadienylmanganese tricarbonyl.[15] Reaction of **10** with *n*-butyllithium in hexane gave the (π-1-butyl-2,4-cyclohexadienyl) complexes **12**; the pmr spectrum of **12b** showed an AB quartet in the phenyl proton region, and neither **12a** nor **12b** showed a singlet due to π-complexed benzene. This confirmed our conclusion that nucleophilic attack on **10** occurs on the benzene rather than on the tetraphenylcyclobutadiene ring.



12a, R = phenyl
b, R = *p*-tolyl

10a, R = phenyl
b, R = *p*-tolyl

11

11, 12

13, Y = H or *n*-Bu

A further check on this conclusion was obtained by removal of hydride from the complexes **11** and **12a**. A number of reagents have been used to effect this type of reaction including Ph_3C^+,[13] air in the presence of acid, or H_2O_2 in acid.[16] Attempts to effect the reaction using the latter reagents were not successful here, but N-bromosuccinimide in methanol gave the cations **13** which were precipitated as the hexafluorophosphates, on addition of ammonium hexafluorophosphate, in

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[11] A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

[12] It was earlier reported in error that the complexes **8a** and **8b** reacted with acetate ion to give the complexes **9** (Y = $OCOCH_3$).[2b]

[13] H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961); see also D. J. Bertelli, Ph.D. Dissertation.

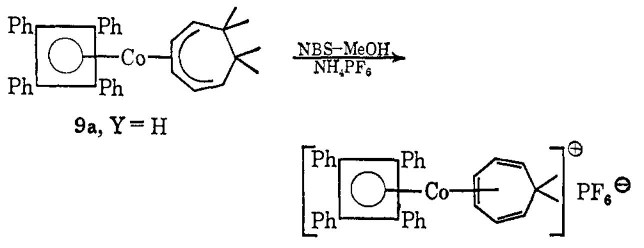
[14] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind.* (London), 553 (1961); *J. Chem. Soc.*, 4821 (1962).

[15] G. Winkhaus and G. Wilkinson, *Proc. Chem. Soc.*, 311 (1960); G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961).

[16] M. L. H. Green, L. Pratt, and G. Wilkinson, *ibid.*, 3753 (1959); R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, **85**, 3733 (1967).

82% (**13**, Y = H) and 63% (**13**, Y = *n*-Bu) yields. Both of these complexes were identified by comparison with authentic samples prepared directly from **2a** and benzene or *n*-butylbenzene.

The hydride abstraction by N-bromosuccinimide in methanol was also used to convert the cycloheptadienyl complex **9a** (Y = H) back to the cycloheptatriene complex **8a**, isolated as the hexafluorophosphate in 18% yield. This was identical with a sample prepared directly from the cycloheptatriene complex A.

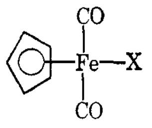


9a, Y = H

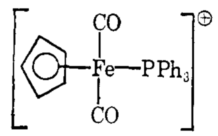
8a, X = PF$_6$

Discussion

The chemistry of the tetraphenylcyclobutadienecobalt dicarbonyl halides (**2**) shows many similarities to that of the cyclopentadienyliron dicarbonyl halides (**14**), and both the $(Ph_4C_4)Co$ and the $(C_5H_5)Fe$ act as units which can stabilize a large number of complexes. Thus the halide in **2** is replaced by pentafluorophenyl to give the σ-pentafluorophenyl complexes **5** analogous to **14** (X = C_6F_5),[17] and the dicarbonyl halide in **2** is replaced by aromatic hydrocarbons to give the complexes **6** analogous to the (π-benzene)(π-cyclopentadienyl)iron cations.[18]



14



15

The cobalt complex **2a** (X = I) shows two strong terminal carbonyl stretching bands in the infrared at 2020 and 2055 cm^{-1}, slightly higher than those in **14** (X = I) at 2000 and 2044 cm^{-1}.[19] A direct comparison is not strictly valid since the metals, their oxidation states, and their d-electron configurations are different. Since the iron in **14** is formally in the +2 (d^6) state, whereas the cobalt in **2** is formally in the +1 (d^8) state, a greater degree of back-bonding from the metal to the carbonyl would be expected for the cobalt complex than for the iron one. This implies a stronger Co–CO bond and hence a lower ν_{CO} in **2** than in **14**. Since the opposite is found, this means that the cobalt is bonding elsewhere, namely to the cyclobutadiene ring, very strongly indeed. This conclusion is in agreement with the prediction of Longuet-Higgins and Orgel that a metal–cyclobutadiene bond is likely to be stronger than a metal–cyclopentadienyl bond.[20]

The stronger M–CO bonding in the iron complex **14** is also shown by its reaction with triphenylphosphine to give **15**, where the halogen has been substituted.[21] The cobalt complex **2a**, in contrast, reacts much more easily with triphenylphosphine and substitution of a carbonyl occurs to give **4**.

Reaction of **2** with pentafluorophenyllithium gave the expected σ-pentafluorophenyl complexes **5**, the cyclobutadiene ring not being attacked. These complexes are very stable, and as in the case of the iron complex **15** (X = C_6F_5) there appears to be very little difference in ν_{CO} between **5** and the halide complexes **2**.

Reaction of **2** under Friedel–Crafts conditions with aromatic hydrocarbons led to the (π-benzene)(π-cyclobutadiene)cobalt cations **6**. These are diamagnetic and very stable. There is some evidence that the presence of electron-releasing substituents on the benzene ring causes an increase in the yield of **6**. An interesting compound is the aniline complex **7**. The only other π complex containing aniline as a ligand reported is the (π-aniline)chromium tricarbonyl.[22] Potentiometric titration of **7** and aniline under the same conditions shows that the complex **7** is less basic than the free amine by about 1.5 p*K* units. This is nearly the same as the difference between the (aniline)chromium tricarbonyl and aniline found by Fischer, *et al.*,[22a] and suggests that the $(Ph_4C_4)Co$ group has approximately the same effect as the $Cr(CO)_3$ group. Since the complex **7** bears a positive charge and might be expected to have a much greater tendency to lower the basicity of the aniline, this is somewhat surprising. One possible reason why this is not observed is that the positive charge is delocalized over the whole molecule and hence its net effect on the NH_2 will be small.[23]

The cycloheptatriene complexes **8** are formulated by analogy to the benzene complexes. Because of the small yields obtained in the initial reaction and the insolubility of the salts **8**, a more complete characterization has not been possible. The exact nature of the initial complex A obtained from the reaction of **2** and cycloheptatriene is not clear, but A may well be nonstoichiometric. The cycloheptatriene complexes A and **8** reacted very readily with nucleophiles (BH_4^-, OH^-, OMe^-) to give the covalent cycloheptadienyl complexes **9**. By contrast the π-benzene complexes **10** underwent nucleophilic addition with much greater difficulty; borohydride or butyllithium, however, did convert **10** into the covalent complexes **11** and **12**. Attack was shown to occur on the benzene ring, and the products are formulated as π-cyclohexadienyl complexes by analogy with those prepared by Wilkinson and his coworkers.[18] In agreement with these workers, we also observed the relatively intense ν_{CH} at 2762 cm^{-1} in **11**; this was absent in the π-butyl complexes **12**. The results of X-ray structure determinations on the products obtained from nucleophilic attack on various π-com-

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[17] M. D. Rausch, *Inorg. Chem.*, **3**, 300 (1964); R. B. King and M. Bisnette, *J. Organometal. Chem.* (Asterdam), **2**, 38 (1964).

[18] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 989 (1960); D. Jones and G. Wilkinson, *Chem. Ind.* (London), 1408 (1961); D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962); R. Mason and G. Wilkinson, *Experientia Suppl.*, **9**, 233 (1964).

[19] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

[20] H. C. Longuet-Higgins and L. Orgel, *J. Chem. Soc.*, 1969 (1956).

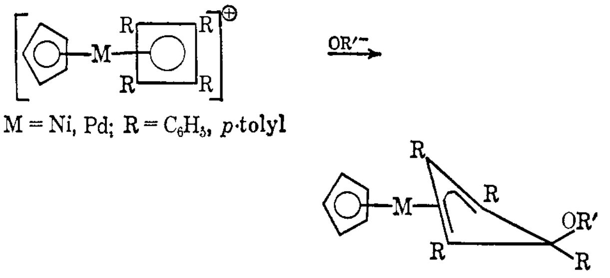
[21] A. Davison, M. L. H. Green, and G. Wilkinson, *ibid.*, 3172 (1961).

[22] (a) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J P. Mortensen, and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958); (b) B. Nicholls and M. Whiting, *J. Chem. Soc.*, 551 (1959); 469 (1960); (c) G. Natta, F. Calderazzo, and E. Santambrogio, *Chim. Ind.* (Milan), **40**, 287 (1958).

[23] An alternative explanation is that since carbonyl groups are better π acceptors than π-complexed hydrocarbons they would be expected to decrease the basicity of π-complexed aniline to a greater extent, other factors being equal. The charge on the complex (**7**) therefore must just compenesate for this. We are indebted to a referee for this suggestion.

plexed ring systems show that the attacking group is *exo* to the metal.[24] We presume the same to have happened in the substituted cyclohexadienyl and cycloheptadienyl complexes described here. This argument need not necessarily hold for the complexes **9a** (Y = H) and **11**, however, since the reaction of **8a** and **10a** with borohydride may proceed *via* a cobalt hydride which then rearranges to give the products with the entering H now *endo* to the metal. Wilkinson, *et al.*, have given evidence for this type of process in other cases.[18]

The ready nucleophilic attack on the cycloheptatriene complexes **8** is not surprising since addition to one end of the conjugated triene, which is presumed to occur, would not be a very unfavorable process. Similarly, the inertness of the benzene complexes **10** to nucleophiles is not unexpected; however, the direction of attack, namely that it is the π-benzene rather than the π-tetraphenylcyclobutadiene which is attacked, is very unexpected. This is particularly so in view of the facility with which the isoelectronic Ni(II) and Pd(II) complexes **16** are attacked by alkoxide ion on the cyclobutadiene ring to give the π-cyclobutenyl complexes **17**.[8]



16, M = Ni, Pd; R = C_6H_5, *p*-tolyl

17

This suggests that an order of reactivity of π-complexed organic ligands toward nucleophiles can now be proposed: cycloheptatriene > benzene > tetraphenylcyclobutadiene > cyclopentadienyl, the last being the most stable. Confirmation of this is provided by the observations (a) of Wilkinson, *et al.*,[18] that the (π-benzene)(π-cyclopentadienyl)iron cation undergoes attack on the benzene to give the (π-cyclohexadienyl)(π-cyclopentadienyl)iron, and (b) of Fischer and Kohl[25] that borohydride attack on $[(C_5H_5)W(C_6H_6)(CO)]^+PF_6^-$ occurs on the π-complexed benzene ring as well as on the metal. Green, *et al.*,[26] have also shown that cations such as $[(C_5H_5)Fe(CO)_2(C_2H_4)]^+$ and $[(C_5H_5)Mo(CO)_3C_2H_4]^+$ are attacked at the π-ethylene to give the σ-ethyl compounds. An explanation of this order of reactivity must await calculations of the localization energies of various positions in these molecules.

The novel method we have used to effect the reconversion of the cyclohexadienyl complexes **11** and **12a** to the cations **13** (Y = H, *n*-Bu) is probably capable of considerable extension and provides a convenient method of carrying out a hydride abstraction. As is evident from the much poorer yield of the cycloheptatriene complex **8a** obtained from **9a** (Y = H), the use of N-bromosuccinimide in methanol is only likely to be of synthetic utility when the product is sufficiently stable.

Experimental Section

Reactions were carried out under an atmosphere of purified nitrogen. Only typical preparations are described in detail here. The tetrakis(*p*-tolyl)cyclobutadiene complexes were obtained from tetrakis(*p*-tolyl)cyclobutadienepalladium bromide (**1b**, X = Br) which was prepared by standard methods from bis(*p*-tolyl)acetylene.[7] The yields, decomposition points, and analyses of the complexes are listed in Table I. H^1 nmr spectra are listed in Table II.

Tetraphenylcyclobutadienecobalt Dicarbonyl Bromide (2a, X = Br). Tetraphenylcyclobutadienepalladium bromide dimer (**1a**, X = Br), 3.0 g (2.4 mmoles), was refluxed with stirring in 500 ml of methylene chloride for 1 hr. The solution was cooled at 25°, a large excess (2.5 g, 7.3 mmoles) of dicobalt octacarbonyl was added, and the solution was stirred at 25° for 48 hr. It was then filtered, the volume reduced to *ca.* 20 ml on a rotary evaporator, and 500 ml of light petroleum (bp 30–60°) added. The complex **2a** (X = Br) crystallized out as dark red crystals, yield 1.33 g (50%, based on the palladium complex), ν_{CO} 2020, 2060 (C_6H_6 solution), 2028, 2062 (KBr) cm^{-1}. As obtained it had mp 255–262° dec and was analytically pure. It still, however, contained a comparatively large amount of paramagnetic impurity, as shown by the measured magnetic susceptibilities per gram; $\chi^{296°} = +0.64 \times 10^{-6}$, $\chi^{78°} = +3.66 \times 10^{-6}$, $\chi^{4.2°} = +32 \times 10^{-6}$. Attempts to measure the pmr spectrum of this material in solution gave only a very broad signal. Purification was achieved by careful recrystallization from methylene chloride–methanol. This material was now diamagnetic at room temperature ($\chi^{296°} = -0.15 \times 10^{-6}$) but still somewhat paramagnetic at lower temperatures ($\chi^{78°} = +0.25 \times 10^{-6}$, $\chi^{4.2°} = +4.8 \times 10^{-6}$); the pmr spectrum was much sharper and the phenyl protons appeared as a multiplet, of width 26 cps at half-height. ν_{CO}'s for the related complexes **2** are as follows (cm^{-1}): (**2a**, X = Cl) 2028, 2062 (KBr); (**2a**, X = I) 2020, 2055 (C_6H_6 solution); 2028, 2062 (KBr); (**2b**, X = Br) 2020, 2055 (C_6H_6 solution).

(Tetraphenylcyclobutadiene)(triphenylphosphine)cobalt Carbonyl Bromide (4, X = Br). Tetraphenylcyclobutadienecobalt dicarbonyl bromide (**2a**, X = Br), 0.6 g (1.09 mmoles), was dissolved in 50 ml of benzene and 0.4 g (1.5 mmoles) of triphenylphosphine was added. The solution was stirred at 25° for 7 hr, then filtered, and concentrated to a volume of 25 ml on a rotary evaporator; the product (**4**, X = Br) crystallized on the addition of light petroleum. Brown crystals (0.62 g, 73%) of (tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl bromide (**4**, X = Br), mp 225–230° dec, were obtained, ν_{CO} 2000 cm^{-1} (KBr). The compound was also found to be slightly paramagnetic ($\chi^{292°} = +0.6 \times 10^{-6}$) and could not be completely freed from the impurities which caused this paramagnetism. Both it and the chloro analog (**4**, X = Cl) decomposed rapidly in solution, making molecular weight determinations impracticable.

(σ-Pentafluorophenyl)dicarbonyl(π-tetraphenylcyclobutadiene)cobalt (5a). Tetraphenylcyclobutadienecobalt dicarbonyl bromide (**2a**, X = Br), 0.45 g (0.82 mmole), was added to a solution of pentafluorophenyllithium (prepared at −78° from 0.4 g (1.6 mmoles) of bromopentafluorobenzene and *n*-butyllithium[9]) in 50 ml of ether at 0°. The suspension was allowed to warm up to 25° and stirred for 12 hr. The yellow precipitate which formed slowly was filtered off, washed with ether, and crystallized from methylene chloride–methanol to give 0.27 g (53%) of the σ-pentafluorophenyl complex **5a**, mp 164° dec, ν_{CO} 2008 and 2050 cm^{-1} ($CHCl_3$ solution). **5b** showed ν_{CO} at 2010 and 2050 cm^{-1} ($CHCl_3$ solution). The pmr spectrum showed a sharp singlet at τ 2.70 (in the phenyl region) and indicated the complex to be diamagnetic. The F^{19} nmr spectrum of **5a**, relative to $CFCl_3$ as internal standard, showed multiplets at 108.5 (*ortho* fluorines), 163.4 (*para* fluorines), and 164.7 ppm (*meta* fluorines); $J_{o,m} = 24.6$ and $J_{m,p} = 19.2$ cps. That of **5b** was similar and showed multiplets at 107.1, 162.0, and 163.2 ppm; $J_{o,m} = 22.8$ and $J_{m,p} = 18.7$ cps.

(π-Benzene)(π-tetraphenylcyclobutadiene)cobalt(I) Bromide (10a). Tetraphenylcyclobutadienecobalt dicarbonyl bromide, 0.70 g (2.0 mmoles), and aluminum chloride, 0.28 g (2.1 mmoles), were refluxed in 30 ml of dry benzene for 45 min. The reaction mixture was cooled to 25°, 20 ml of a saturated aqueous solution of KBr was added, and the mixture was stirred vigorously for 30 min. The

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(24) M. R. Churchill and R. Mason, *Proc. Roy. Soc.* (London), **A279**, 191 (1964); W. E. Oberhansli and L. F. Dahl, *Inorg. Chem.*, **4**, 150 (1965); L. F. Dahl and W. E. Oberhansli, *ibid.*, **4**, 629 (1965); M. R. Churchill, *J. Organometal. Chem.* (Amsterdam), **4**, 258 (1965); N. W. Alcock, *Chem. Commun.*, 177 (1965); P. E. Baikie, O. S. Mills, P. L. Pauson, G. H. Smith, and J. Valentine, *ibid.*, 425 (1965); W. A. Whitla, H. M. Powell, and L. M. Venanzi, *ibid.*, 310 (1966).

(25) E. O. Fischer and F. J. Kohl, *Chem. Ber.*, **98**, 2134 (1965).

(26) M. L. H. Green and P. L. I. Nagy, *J. Am. Chem. Soc.*, **84**, 1310 (1962); M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

yellow solid obtained was then filtered off, dried, dissolved in methylene chloride, and filtered to remove KBr. The solution was evaporated to dryness and the solid crystallized from aqueous methanol to give 0.62 g (55%) of yellow crystals of (π-benzene)(π-tetraphenylcyclobutadiene)cobalt bromide, mp 180–190° dec. The complex was soluble in methanol and methylene chloride but insoluble in nonpolar solvents and appeared to be air stable both in the solid and in solution. The infrared spectrum was in agreement with the proposed structure, and the H^1 nmr spectrum showed two sharp singlets at τ 2.50 (phenyl protons) and 3.35 (π-complexed benzene protons) with the expected intensity ratio of 20:6.

On addition of a saturated methanolic solution of ammonium hexafluorophosphate to a methanolic solution of the bromide **10a**, the insoluble hexafluorophosphate salt precipitated out in 70% yield.

The other complexes (**6**) were prepared analogously.

(π-Aniline)(π-tetraphenylcyclobutadiene)cobalt Bromide (7, X = Br). Tetraphenylcyclobutadienecobalt dicarbonyl bromide, 0.5 g (0.9 mmoles), aluminum chloride, 0.72 g (5.6 mmoles), and aniline, 0.45 g (4.8 mmoles), were refluxed in 30 ml of isooctane for 1 hr. The reaction mixture was cooled and 30 ml of saturated aqueous KBr was added and the mixture stirred for 4 hr at 25°. The yellow insoluble product was washed with ether and a little water and then recrystallized from aqueous methanol to give 0.32 g (60%) of yellow crystals of (π-aniline)(π-tetraphenylcyclobutadiene)cobalt bromide (7, X = Br), mp 220–230° dec. On treatment of a methanolic solution of **7** (X = Br) with ammonium hexafluorophosphate in methanol, a 90% conversion into the hexafluorophosphate salt (7, X = PF_6) was obtained. A Nujol mull of this salt showed ν_{NH} at 3390 (m) and 3497 (w) cm^{-1}.

A potentiometric titration of the bromide **7** (X = Br) in 0.1 *N* 50% aqueous methanolic hydrochloric acid against 0.1 *N* sodium hydroxide solution gave a value of pK_b of 11.00 ± 0.10. Under similar conditions, aniline had a pK_b of 9.51 ± 0.04. The decrease in basicity on complexing of the aniline is therefore about 1.5 pK units.

(π-Cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt Cations (8a). Tetraphenylcyclobutadienecobalt dicarbonyl bromide, 0.22 g (0.39 mmole), was refluxed in 15 ml of cycloheptatriene for 30 min. The solution was cooled to 25° and light petroleum (bp 30–60°) added to precipitate 0.09 g (25%) of a green solid which on analysis was shown to be $[Ph_4C_4CoC_7H_8]^+Br^- \cdot 1.1CoBr_2$ (A), Table I.

A 0.035-g sample of A was dissolved in 10 ml of methanol and filtered to give a yellow solution. On addition of 0.3 g of potassium thiocyanate the solution turned green, and after filtration and addition of 50 ml of water, 0.015 g (27% based on A) of the tetrathiocyanatocobaltate salt **8a** (X = $0.5Co(NCS)_4$) was obtained, ν_{NCS} 2066 cm^{-1} (KBr).

Addition of methanolic potassium iodide or ammonium hexafluorophosphate to a methanolic solution of A gave the iodide and hexafluorophosphate salts **8a** (X = I and PF_6) in 44 and 56% yields, respectively, based on A. The infrared spectra of all three salts (**8a**, X = $0.5Co(NCS)_4$, I, and PF_6) were all identical with that of A, except for bands associated with the anions, showing that the organic moiety was unchanged in these interconversions.

(π-2,4-Cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt (11). A solution of 0.13 g (3.3 mmoles) of sodium borohydride in 2 ml of water was added to a solution of 0.2 g (0.35 mmole) of (π-benzene)(π-tetraphenylcyclobutadiene)cobalt bromide (**10a**) in 20 ml of methanol at 25°. A red precipitate formed which was filtered and dried. This was extracted with light petroleum and crystallized from light petroleum–methanol to give 0.035 g (20%) of red crystals of (π-2,4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt (**11**), mp 134–135°. The infrared spectrum showed, in addition to the expected bands, a relatively strong ν_{CH} at 2762 cm^{-1} (KBr) which has been ascribed to the *endo*-CH of the methylene group.[18]

(π-1-Butyl-2,4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt (12a). (π-Benzene)(π-tetraphenylcyclobutadiene)cobalt bromide (**10a**), 0.10 g (0.17 mmole), was added to 15 ml of a 15% solution of *n*-butyllithium in hexane, and the mixture was stirred for 3 hr at 25°. Ammonium chloride was added to destroy the excess butyllithium, and the hexane solution was then evaporated to dryness. The solid was washed with water, dried, and extracted with and crystallized from hexane to give 0.05 g (53%) of orange-red crystals of **12a**, mp 140°. The infrared spectrum did not show the band at 2762 cm^{-1} observed for **11** above.

(π-3,5-Cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt (9a, Y = H). A solution of 0.1 g (2.7 mmoles) of sodium borohydride in 0.6 ml of water was added to a solution of 0.14 g (0.16 mmole) of the cycloheptatriene complex A in 50 ml of methanol. The deep red solid which precipitated was filtered off, dried, and crystallized from hexane to give 0.014 g (16.3%) of the cycloheptadienyl complex **9a** (X = H), mp 187–188°.

(π-2-Methoxy-3,5-cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt (9a, X = OMe). A solution containing 1 mmole of sodium methoxide in 2 ml of methanol was added to a solution of 0.27 g (0.33 mmole) of the cycloheptatriene complex A in 20 ml of methanol and stirred for 5 min at 25°. The orange solid which precipitated was extracted with hexane and crystallized from methylene chloride and methanol to give 90 mg (62%) of orange-red crystals of the methoxycycloheptadienyl complex **9a** (Y = Me), mp 190–195° dec.

The hydroxycycloheptadienyl complex **9a** (Y = OH) was prepared in 64% yield by treatment of complex A with triethylamine in wet benzene and crystallizing the product from ether–light petroleum.

Conversion of the π-Cyclohexadienyl Complexes 11 and 12a to the π-Benzene Complexes 13. A 0.050-g (0.09 mmole) portion of the *n*-butylcyclohexadienyl complex **12a** was dissolved in a mixture of 3 ml of light petroleum and 20 ml of methanol. Addition of 0.03 g (0.17 mmole) of N-bromosuccinimide gave a yellow solution to which was then added 10 ml of a saturated methanolic solution of ammonium hexafluorophosphate. The solvent was removed in a rotary evaporator, and the solid remaining was washed with water and recrystallized from aqueous methanol to give 0.040 g (63%) of the (π-butylbenzene)(tetraphenylcyclobutadiene)cobalt hexafluorophosphate (**13**, Y = *n*-Bu), mp 220–230°, mmp (with a sample prepared from *n*-butylbenzene and the cobalt complex **2a** (X = Br) of mp 229–233°) 228–230°. The infrared spectra of the samples were identical.

The π-cyclohexadienyl complex **11** was converted to the π-benzene complex **13** (Y = H) in an analogous manner in 80% yield.

Conversion of the π-Cycloheptadienyl Complex 9a (Y = H) to the π-Cycloheptatriene Complex 8a (X = PF_6). A mixture of 0.030 g (0.06 mmole) of the cycloheptadienyl complex **9a** (Y = H) and 0.050 g (0.33 mmole) of ammonium hexafluorophosphate in 2 ml of light petroleum and 5 ml of methanol was stirred at 25°, and 0.030 g (0.17 mmole) of N-bromosuccinimide was added slowly. An immediate color change occurred and a small amount of a yellow solid precipitated. This was filtered, washed with water, and crystallized from methylene chloride–light petroleum to give 7 mg (18%) of the π-cycloheptatriene complex **8a** (X = PF_6), mp 272–282°, mmp (with an authentic sample of mp 284–288°) 281–285°. The infrared spectra of both samples were identical.

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