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# [$\eta^5$-CYCLOPENTADIEN-1-YL-$\eta^4$-TETRAPHENYLCYCLOBUTADIENE-COBALT]DIPHENYLMETHYLIUM HEXAFLUOROPHOSPHATE: A METAL-STABILIZED CARBONIUM ION SALT *

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## Summary

Mercuration of $\eta^5$-cyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt, followed by transmetalation with n-butyllithium and reaction of the lithium derivative with benzophenone gave $\eta^4$-$Ph_4C_4$—Co—$\eta^5$-$C_5H_4CPh_2OH$. Treatment of this alcohol produced the [$\eta^4$-$Ph_4C_4$—Co—$C_5H_4CPh_2$]$^+$ cation. This species reacted as a carbon electrophile with methanol, monomethylamine and *N*-methylpyrrole, as a cobalt electrophile with *N,N*-dimethylaniline and anisole. In the latter process the $C_5H_4CPh_2$ ligand was displaced and the $\eta^6$-arene-$\eta^4$-tetraphenylcyclobutadienecobalt complexes were formed. Similar reactions with benzene, toluene and mesitylene proceeded only in the presence of aluminum chloride. The bonding in the cation is discussed on the basis of this chemistry and $^{13}$C NMR studies.

## Introduction

Much effort has been devoted in recent years to the study of carbonium ions which are stabilized by complexation to a transition metal [1], in particular to ferrocenyl-substituted carbonium ions [2]. At the time the present study was begun, no studies of the ability of cyclopentadienyl complexes of cobalt to stabilize carbonium ions had been reported. During the course of our investigation, Sheats et al. [3] reported that in the diphenylmethylcobalticinium carbonium ion (I), there was no stabilizing influence due to the cobalticinium substituent. It is not surprising that an already positively charged metal center is not effective in stabilizing the positive charge of the carbonium ion center; a neu-

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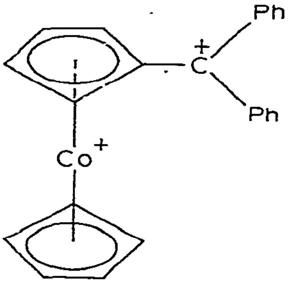
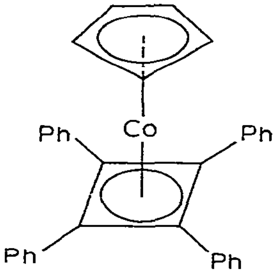
* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.



(I)

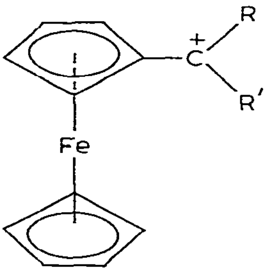
tral cyclopentadienyl complex of cobalt would be essential if delocalization of positive charge from carbon onto the metallocene substituent is to occur.

$\eta^5$-Cyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (II) is a neutral cobalt $\pi$-complex which is isoelectronic with ferrocene [4]. It is very stable,



(II)

decomposing at around 360° C when heated and is unreactive toward oxygen and moisture. In view of the high stability of ferrocenyl-carbonium ions III a study of carbonium ions derived from II, i.e., ions of type IV seemed worthwhile.



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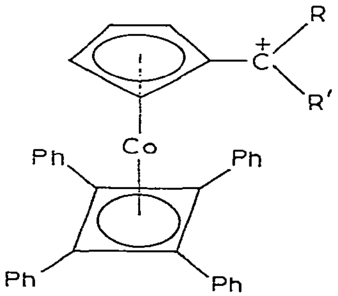
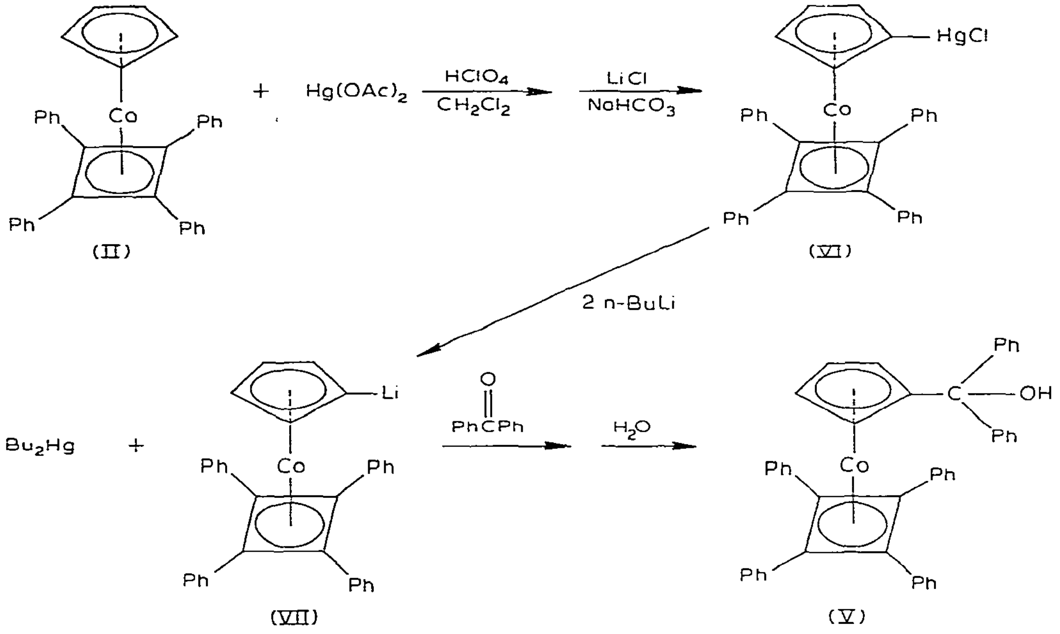


(IV)

## Results and discussion

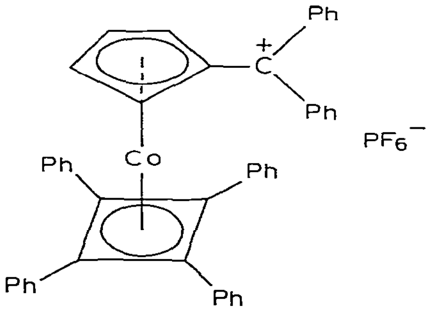
The synthesis of the alcohol V which served in the generation of [$\eta^5$-cyclopentadien-1-yl-$\eta^4$-tetraphenylcyclobutadienecobalt]diphenylmethyl carbonium

SCHEME 1



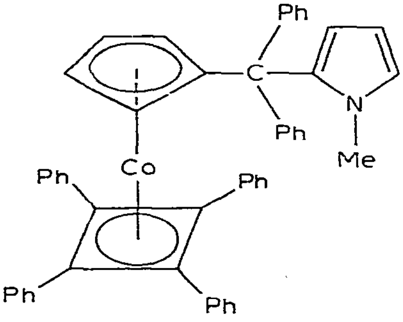
ion is summarized in Scheme 1. The mercuration of II had been demonstrated by Rausch and Genetti [5]. Transmetalation of the chloromercuri derivative VI with n-butyllithium in diethyl ether gave the organolithium reagent VII [5]. (Such a reaction had been utilized in these laboratories some years ago in the first preparation of lithioferrocene from chloromercuriferrocene [6].) Addition of lithium reagent VII to the C=O bond of benzophenone produced, after hydrolytic work-up, alcohol V, a yellow-orange solid, in excellent yield.

Treatment of a slurry of this alcohol in dichloromethane, under nitrogen, with diethyloxonium hexafluorophosphate, $Et_2OH^+PF_6^-$, produced an immediate and dramatic change: from a yellow-orange slurry in a brownish solution to a deep blue solution. Addition of diethyl ether precipitated a blue, crystalline solid which subsequent studies showed to be [$\eta^5$-cyclopentadien-1-yl-$\eta^4$-tetraphenylcyclobutadienecobalt]diphenylmethylium hexafluorophosphate (VIII).



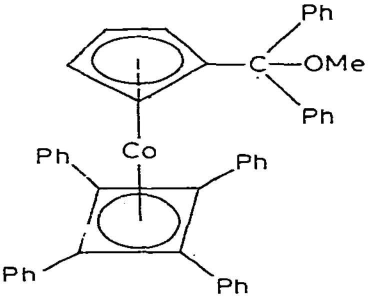
(VIII)

The chemistry of VIII did not develop straightforwardly. Thus methanol did not appear to react with solutions of VIII, although a carbonium ion salt would be expected to alkylate alcohols to form ethers. Treatment of VIII with diethylamine did result in discharge of the blue color, but subsequent work-up of the reaction mixture, which included column chromatography on alumina, yielded only the starting alcohol V. On the other hand, VIII did alkylate *N*-methylpyrrole to produce a high yield of IX.



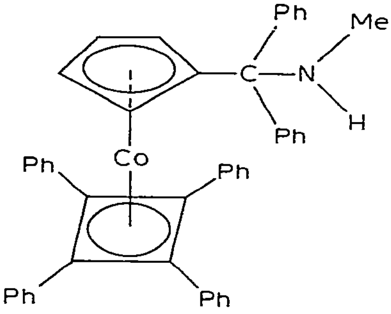
(IX)

The explanation of these observations resides in the fact that oxygen and nitrogen alkylations are reversible processes, whereas alkylations of aromatic nuclei in the absence of a Lewis acid are irreversible. The reaction of VIII with an alcohol is an equilibrium process and the stability of the carbonium ion apparently is such that the equilibrium lies far on the side of the carbonium ion. This equilibrium can be driven to the side of the ether by neutralization of the hexafluorophosphoric acid formed in the process. Thus, when VIII was treated with methanol in the presence of sodium carbonate, the blue color was discharged immediately and the methyl ether X could be isolated in good yield. While diethylamine, which was used in excess, did force the equilibrium to the right,



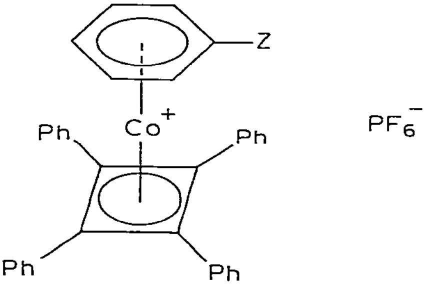
(X)

forming the *N*-diethyl derivative in high yield, it appears that the alumina used in chromatography was sufficiently acidic to convert the amine back to the carbonium ion which was eluted from the column as the alcohol. (Note that carbonium ions such as $Ph_3C^+$ can be formed from the alcohols on alumina or silica gel [7].) When VIII was allowed to react with an excess of monomethylamine and the product obtained was purified by fractional crystallization rather than by column chromatography, a high yield of XI was realized.



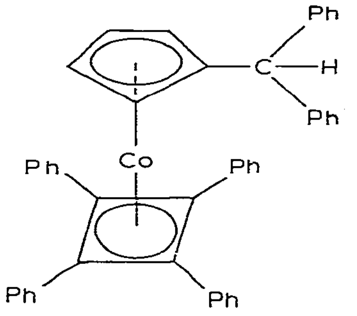
(XI)

In attempts to extend the scope of aromatic nucleophile alkylations with VIII, a more complex chemistry was discovered. Treatment of VIII with *N,N*-dimethylaniline at room temperature gave $\eta^6$-*N,N*-dimethylaniline-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate, XIIa. Although it required higher (100°C) temperatures to effect, the same type of reaction was found to occur with anisole, giving complex XIIb. Less reactive aromatic nucleophiles such as benzene, toluene and even mesitylene were inert toward VIII under these conditions. However, it was found that these aromatic hydrocarbons did react with alcohol V in the presence of an excess of aluminum chloride to give the respective $\eta^6$-arene-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate. That these aluminum chloride-induced reactions also proceed by way of the carbonium ion VIII but with a chloroaluminate counterion, is made apparent by the fact that the proton NMR spectrum of VIII is identical to that of alcohol V in the presence of aluminum chloride. Most certainly, it is not a reaction of the neutral complex V with the arene in the presence of aluminum chloride (in analogy to the known aluminum halide-catalyzed arene/ferrocene ligand exchange reaction [8]) since the neutral complex II does not react with benzene in the presence of aluminum chloride under these conditions.



(XII) a, Z = $NMe_2$
b, Z = OMe

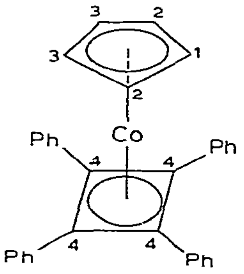
These reactivity patterns of VI can be better explained if the possible structure of and charge distribution in cation VIII are considered first. $^{13}C$ NMR spectroscopy has been applied by Olah et al. in investigations of wholly organic carbonium ions [9] and also has served in the study of transition metal-stabilized carbonium ions [10]. Furthermore, there is a large body of work on $^{13}C$ chemical shifts of many types of transition metal organic compounds [11]. In view of these available $^{13}C$ NMR data on neutral and charged transition metal complexes, a $^{13}$C NMR study of our cobalt system seemed worthwhile. The precursor alcohol V was unsatisfactory for the purpose of comparing the cation VIII with a neutral analog. The signal due to the α carbon bearing the OH function could not be located, possibly, due to its poor relaxation time or possibly because this resonance is obscured or hidden by some other signal. However, the α carbon atom resonance of XIII, which was prepared by reaction of VIII with triethyl-



(XIII)

TABLE 1

CARBON-13 CHEMICAL SHIFTS OF $\eta^5$-CYCLOPENTADIEN-1-YL-$\eta^4$-TETRAPHENYLCYCLOBUTADIENECOBALT COMPLEXES



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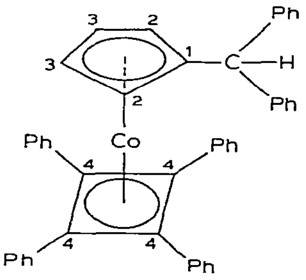

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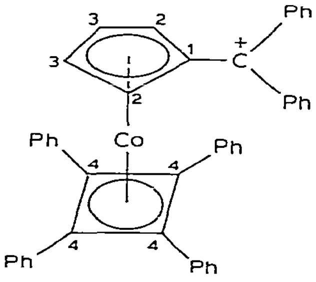


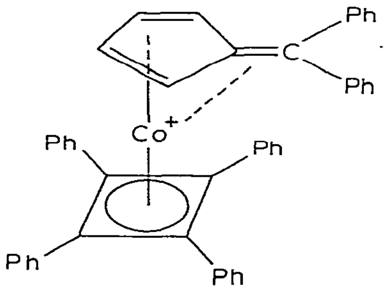
(VIII)

| Carbon | Chemical shift [a] | | |
|---|---|---|---|
| | II | XIII | VIII |
| α | | 48.6 | 184.0 |
| 1 | | 106.2 | 107.7 |
| 2 | 83.4 | 83.8 | 105.1 |
| 3 | | 83.0 | 90.8 |
| 4 | 75.0 | 74.8 | 88.1 |
| Aryl | 136.7, 129.1<br>128.1, 126.4 | 145.0, 136.4, 129.2<br>129.0, 128.3, 128.2,<br>126.3 | 139.5, 134.3, 131.4<br>129.2, 128.9 |

[a] Chemical shifts are reported in $\delta_C$ units, ppm downfield from TMS using the internal line of the carbon resonance of chloroform-*d* as 77.2 ppm downfield from TMS. Chloroform-*d* was used as solvent in all cases.

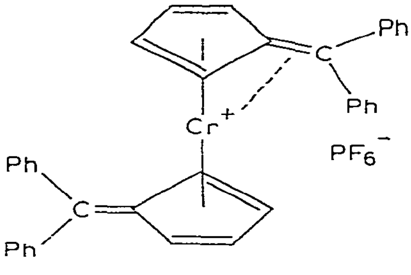
silane, was readily observable. The $^{13}C$ NMR spectrum of II also had to be recorded in order to help assign the resonances in the spectra of VIII and XIII. The pertinent data are given in Table 1. These spectral assignments are based on standard $^{13}C$ NMR correlations [11,12] and on gated-decoupled spectra.

The $\alpha$-carbon atom becomes deshielded on going from the neutral complex XIII to the cation VIII, with $\Delta\delta(\alpha)$ 135.4 ppm. For trialkyl carbonium ions, this $\Delta\delta$ value (for the process $R_3CH \rightarrow R_3C^+$) is around 300 ppm; for stabilized aryl-substituted carbonium ions, it is less (e.g., $Ph_2CH_2 \rightarrow Ph_2CH^+$, $\Delta\delta$ 163 ppm; $Ph_3CH \rightarrow Ph_3C^+$, $\Delta\delta$ 150 ppm [12]). While one must exercise caution in discussions of systems containing a metal center in assigning electron density at a given carbon atom using $^{13}C$ NMR chemical shifts, the available data [10] indicate that small $\Delta\delta$ values (for either of the processes (metal $\pi$-complex)—$CR_2H \rightarrow$ (metal $\pi$-complex)—$CR_2^+$ or (metal $\pi$-complex)—$CR_2OH \rightarrow$ (metal $\pi$-complex)—$CR_2^+$) are characteristic of highly stabilized transition metal-substituted carbonium ions. Thus $\Delta\delta$ is —49.4 ppm for $(C_5H_5)Fe(C_5H_4CHPhOH) \rightarrow (C_5H_5)Fe(C_5H_4CHPh)^+$ [10a], —70.1 ppm for $(OC)_3Fe(C_4H_3CHPhOH) \rightarrow (CO)_3Fe(C_4H_3CHPh)^+$ [10h]; —99.5 ppm for $(OC)_3Cr(C_6H_5CMe_2OH) \rightarrow (OC)_3Cr(C_6H_5CMe_2)^+$ [10k]. In the ferrocenylcarbonium ion series, these $\Delta\delta_C$ values for the $\alpha$(*exo*) carbon atom increase in the order: primary, $(C_5H_5)Fe(C_5H_4CH_2)^+$ < secondary, $(C_5H_5)Fe(C_5H_4CHR)^+$ < tertiary, $(C_5H_5)Fe(C_5H_4CR_2)^+$. The $\Delta\delta_C$ values for the tertiary ferrocenyl-substituted carbonium ions (R = alkyl) are in the range 90—120 ppm [10d]. The $\Delta\delta_C$ value for the alcohol/carbocation system $(OC)_3Mn(C_5H_4CPh_2OH)/(OC)_3Mn(C_5H_4CPh_2)^+$ is 123.8 ppm [10g]. Our $\Delta\delta_C$ value of 135.4 ppm thus is in the range observed for transition-metal-stabilized tertiary carbonium ions. Since $^{13}C$ chemical shifts depend on other factors in addition to the charge density at a carbon atom, a direct correlation between $^{13}C$ shieldings and charge distribution does not obtain. Consequently, a ranking of the stabilities of such carbonium ions which differ widely in metal and attached ligands cannot be made on the basis of these $\Delta\delta$ values. Thus, the most one can say on the basis of the $\Delta\delta_C$ value of 135.4 ppm for the XIII → VIII system is that it supports the idea that the carbonium ion is significantly stabilized by the $\eta^4$-tetraphenylbutadiene-$\eta^5$-cyclopentadienylcobalt substituent. Such stabilization would involve transfer of negative charge from the cobalt-containing substituent to the electron-deficient carbon center. In the extreme, the full positive charge could be transferred to cobalt and in that case, VIII could be regarded as a cobalt complex of the 6,6'-diphenylfulvene ligand, XIV.

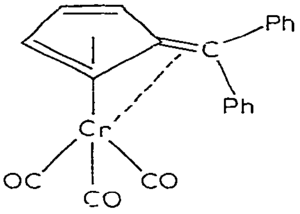


(XIV)

Complexes of this ligand, XV and XVI, have been prepared previously by Fischer et al. by reactions of 6,6′-diphenylfulvene with appropriate zerovalent transition metal species [13].



(XV)



(XVI)

Structure XIV is compatible with the $^{13}C$ chemical shifts of all of the carbon atoms in the cation. The α-carbon resonance is in the region of the neutral ligand resonance ($\delta_{\overset{*}{C}}$ for $C_5H_4{=}\overset{*}{C}Ph_2$ is 152.0 ppm [15]). The aryl resonances are essentially unchanged on going from XIII to VIII, so we conclude that the positive charge in VIII is not merely being delocalized through the two phenyl substituents on the α-carbon atom. The cyclopentadiene and cyclobutadiene carbon atom signals are shifted somewhat to lower field, and this is what one would expect on comparison of the shifts of ligands which are π-complexed to a neutral metal atom with the shifts of the same ligand coordinated to a positively charged metal center.

In order to gain further support for these structural arguments, we measured the $^{13}C$ NMR spectrum of XVI. A recent X-ray diffraction study had confirmed the coordination of the diphenylfulvene ligand to the chromium atom as shown in Fig. 1 [16]. The $^{13}C$ NMR data for XVI are recorded in Table 2 and compared with those of VIII. The similarities in the chemical shifts between the five-membered ring and the phenyl carbon atoms in XVI and VIII are striking. The *exo* carbon atom of XVI is deshielded, relative to the *exo* carbon atom in VIII, which may be understood in terms of the uncharged metal center in XVI vs. the charged metal center in VIII. Upon completion of this work, Russian

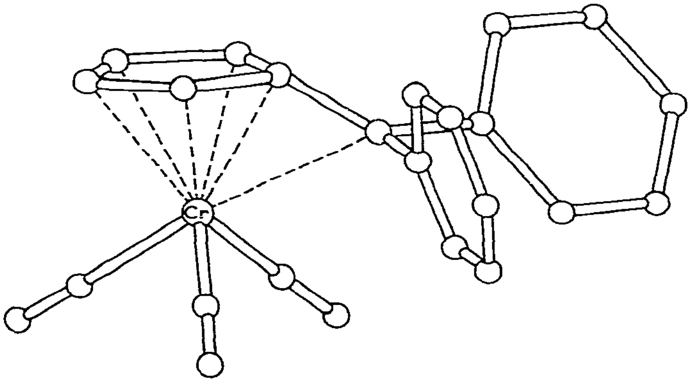
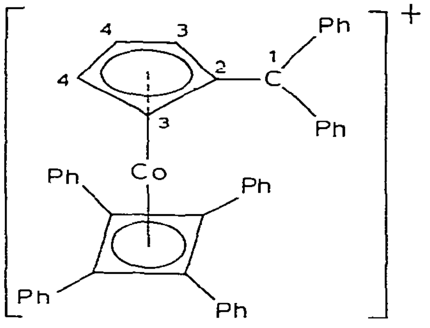
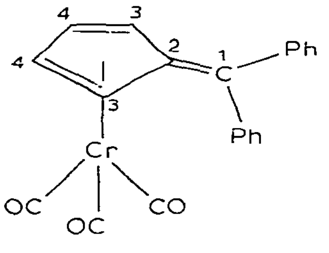


Fig. 1. Molecular structure of $[C_5H_4{=}CPh_2]Cr(CO)_3$ [16].

TABLE 2

COMPARISON OF THE CARBON-13 CHEMICAL SHIFTS BETWEEN XVI AND VIII





(XVI)

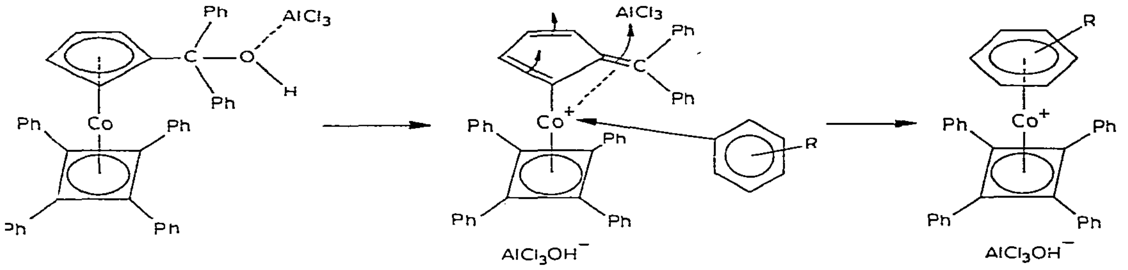
| Carbon | Chemical shift [a] | |
|---|---|---|
| | VIII | XVI |
| 1 | 184.0 | 132.5 |
| 2 | 107.7 | 107.5 |
| 3 | 105.1 | 93.5 |
| 4 | 90.8 | 89.0 |

[a] Chemical shifts are expressed in $\delta_C$ units, ppm downfield from TMS using the internal line of chloroform-*d* as 77.2 ppm. Solvent used was chloroform-*d*.

workers [15] also reported the $^{13}C$ NMR spectrum of XVI. They concluded that the data were consistent with the formulation of XVI as the "ylene" structure shown rather than as the cyclopentadienylide form in which the *exo* carbon atom is not coordinated to the cobalt atom.

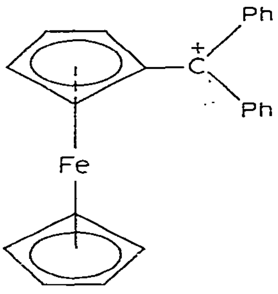
We return now to the reactivity of cation VIII. Its mode of reaction with various nucleophiles is readily understood in the context of the discussion above. Cation VIII is a poor carbon electrophile since a significant amount of the positive charge originally generated at the α-carbon atom by ionization of alcohol V is delocalized into the rest of the molecule, in large part onto the metal. With oxygen- and nitrogen-centered nucleophiles this results in unfavorable reaction equilibria. When cation VIII reacts with aromatic substrates which are sufficiently nucleophilic and which can be π-complexed to the metal center (i.e., *N,N*-dimethylaniline and anisole), displacement of the 6,6′-diphenylfulvene ligand occurs and the cationic $\eta^6$-arene-$\eta^4$-tetraphenylcyclobutadienecobalt complex is formed. In the reactions of *N,N*-dimethyaniline and anisole, the yields of these cationic complexes were low and there was spectroscopic evidence that C-alkylation of the aromatic nuclei had occurred to some extent as well. However, pure C-alkylated compounds could not be isolated. With less nucleophilic aromatic nucleophiles such as benzene, toluene and mesitylene, no reaction took place unless at least two molar equivalents of aluminum chloride per mole of alcohol V were present. One of these served to generate cation VIII (a deep blue solution resulted), but the second mole of $AlCl_3$ was essential. Assuming that the bonding interaction of the $C_5H_4CPh_2$ ligand in VIII is similar to that of the 6,6′-diphenylfulvene ligand in XVI, then all three double bonds

SCHEME 2



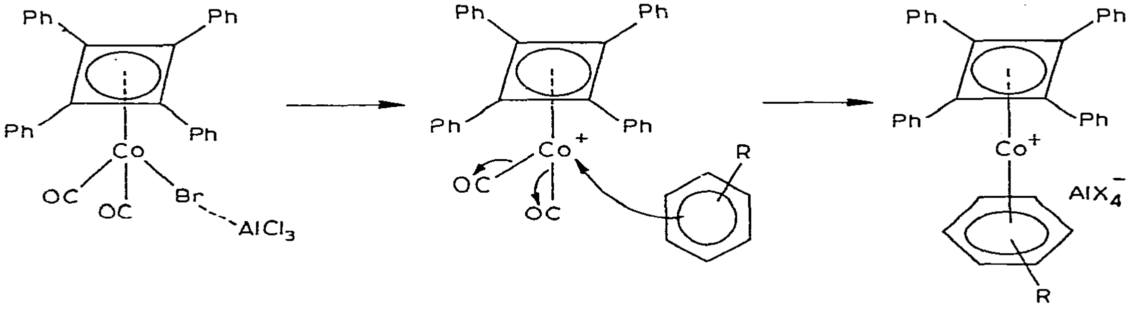
undergo π-complexation to cobalt. The stronger interaction should be that involving the C=C bonds of the $C_5$ ring, while the *exo* C=C bond should be more weakly bonded. The function of the second mole of $AlCl_3$ then may be to disrupt the latter interaction, thus making the cobalt more susceptible to nucleophilic attack by an arene (Scheme 2). Arenes less nucleophilic than benzene, such as chlorobenzene and nitrobenzene, did not react with VIII to form an $\eta^6$-arene complex even in the presence of aluminium chloride. A similar $AlCl_3$-induced ligand displacement process in which cationic $\eta^6$-arene-$\eta^4$-tetraphenylcyclobutadienecobalt complexes are formed was reported by Efraty and Maitlis (Scheme 3) [17].

As pointed out in the Introduction, $\eta^5$-cyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt and ferrocene are isoelectronic, and thus a comparison of cation VIII with its ferrocene analog, XVII would be of interest. A recent



(XVII)

SCHEME 3



communication [18] has reported an investigation of this species which was generated by dissolving the corresponding alcohol in concentrated sulfuric acid or in trifluoroacetic acid. Stable $BF_4^-$ and $ClO_4^-$ salts were reported; treatment of their acetonitrile solutions with aqueous NaOH and with NaOMe/MeOH gave the respective alcohol and methyl ether. Of special interest was the observation that acidic aqueous acetonitrile solutions of the $\eta^5$-$C_5H_5Fe$-$\eta^5$-$C_5H_4C(OH)Ph_2$ precursor decomposed on standing to give 6,6′-diphenylfulvene.

## Experimental

*General comments.* All reactions were carried out under an atmosphere of dry nitrogen in glassware which had been flame-dried in a stream of nitrogen. The solvents which were used were rigorously dried.

Proton NMR spectra were recorded using either a Varian Associates T-60, a Hitachi—Perkin—Elmer R-20B (60 MHz) or a Hitachi—Perkin—Elmer R-24 (60 MHz) spectrometer. $^{13}C$ NMR spectra were recorded using a JEOL FX-60Q spectrometer in the FT mode. Proton-coupled spectra were recorded using gated-decoupling to obtain the Nuclear Overhauser enhancement which measured the number of protons attached to the carbon. Infrared spectra were recorded using a Perkin—Elmer 457A infrared spectrophotometer. Melting points were obtained with a Mel—Temp melting point apparatus and are uncorrected.

*Starting materials.* Dicobalt octacarbonyl was purchased from Strem Chemicals, Inc., hexafluorophosphoric acid/diethyl etherate from Cationics, Inc. $\eta^5$-Cyclopentadienylcobalt dicarbonyl [5], $\eta^5$-cyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt [5] and 6,6′-diphenylfulvenechromium tricarbonyl [13] were prepared by the cited literature procedures.

### *Preparation of $\eta^5$-chloromercuricyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (VI)*

A 250 ml Erlenmeyer flask was charged with 3.8 g (7.9 mmol) of $\eta^5$-cyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (II), 1.1 g (3.5 mmol) of mercuric acetate, and 150 ml of dichloromethane. This mixture was stirred vigorously by means of a magnetic stirrer and 10 drops of 65% aqueous perchloric acid was added over a 15 min period until all of the mercuric acetate dissolved. The solution was stirred vigorously for 15 min; 1.0 g of lithium chloride was added, followed by stirring for 15 min; then 2.0 g of sodium bicarbonate was added. Next, the entire reaction mixture was poured onto a column of alumina (40 × 300 mm) and the entire mixture was eluted with dichloromethane. The first band to elute from the column was light yellow and yielded, after removal of solvent, 2.65 g of II (70% recovery). A second, darker yellow band was eluted from the column with dichloromethane containing 5% methanol. This yielded, after removal of solvent, 1.8 g (2.5 mmol) of VI, m.p. 233—234°C (lit. [5] 234—235°C). The yield was 70% based on the amount of unrecovered mercuric acetate.

### *Synthesis of $\eta^5$-diphenylhydroxymethylcyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (V)*

A 200 ml, three-necked, round-bottomed flask, equipped with nitrogen inlet and a magnetic stirrer, was charged with 3.40 g (4.75 mmol) of VI and 100 ml of anhydrous diethyl ether. The remaining two necks of the flask were closed with no-air stoppers. While the suspension of the orange cobalt complex was stirred magnetically, 5.0 ml of 2.4 *M* n-butyllithium in hexane (12.0 mmol) was added by syringe. The mixture became homogeneous and turned dark green-brown.

This solution was stirred for 30 min and then 1.84 g (10.0 mmol) of solid benzophenone was added. The solution was stirred for an additional 30 min. Then 1.0 ml of water was added, resulting in the formation of an orange precipitate. The latter was filtered to yield 3.50 g of yellow-orange solid. This was purified by Soxhlet extraction with chloroform to yield 2.80 g (4.20 mmol, 89% based on amount of chloromercuri complex) of V, m.p. 248—250°C. (Found: C, 83.35; H, 5.34. $C_{46}H_{35}CoO$ calcd.: 83.37; H, 5.32%.) NMR ($CDCl_3$): $\delta$ 2.76 (s, 1H, OH), 4.53 (m, 2H, Cp), 4.93 (m, 2H, Cp), 6.80 ppm (m, $C_6H_5$).

*Preparation of [$\eta^5$-cyclopentadien-1-yl-$\eta^4$-tetraphenylcyclobutadienecobalt]-diphenylmethylium hexafluorophosphate (VIII)*

A 50 ml round-bottomed flask, equipped with a side-arm and a magnetic stirrer, was charged with 0.80 g (1.20 mmol) of V in 10 ml of reagent-grade dichloromethane. The resulting mixture (yellow-orange slurry in a brown solution) was stirred magnetically and 0.4 ml of $HPF_6 \cdot Et_2O$ was added. The solution immediately changed from brown to deep blue in color and became homogeneous. It was stirred for 15 min and then anhydrous diethyl ether was added until a deep blue precipitate formed (ca. 20 ml). A frit attached to a 250 ml round-bottomed flask with a nitrogen inlet then was attached to the flask. The precipitate was filtered and washed three times with 10 ml-portions of ether until the washings were colorless, and dried in vacuo to give 0.85 g of blue solid (0.18 mmol, 90%). The compound was identified as VIII. (Found: C, 69.81; H, 4.37. $C_{46}H_{34}CoF_6P$ calcd.: C, 69.87; H, 4.33%.) NMR ($CDCl_4$): $\delta$ 5.75 (s, br, 4H), 7.0—7.5 ppm (m, 30H, $C_6H_5$).

*Reactions of VIII*

*1. With triethylsilane.* The carbonium ion salt was formed as described above from 1.00 g (1.51 mmol) of alcohol V and 0.5 ml of hexafluorophosphoric acid diethyl ether complex in 50 ml of dichloromethane. The salt was precipitated and washed several times with diethyl ether. It then was dissolved in 50 ml of dichloromethane and 2.0 ml (12.6 mmol) of triethylsilane was added. The solution was stirred at room temperature for 2 h at the end of which time the color of the reaction mixture had turned from blue to brown. The solvent was removed on a rotary evaporator and the residue was recrystallized from diethyl ether to yield 0.4 g (0.6 mmol, 41%) of a golden brown solid, m.p. 249—250°C, identified as $\eta^5$-diphenylmethylcyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (XIII). (Found: C, 85.14; H, 5.57. $C_{46}H_{35}Co$ calcd.: C, 85.43; H, 5.46%.) NMR ($CDCl_3$): $\delta$ 4.51 and 4.67 (both m, 4H, Cp), 4.78 (s, 1H, C<u>H</u>$Ph_2$) and 6.77—7.67 ppm (m, 30H, $C_6H_5$).

*2. With methanol.* The carbonium ion hexafluorophosphate was prepared from 1.00 g (1.51 mmol) of alcohol V and 0.5 ml of hexafluorophosphoric acid diethyl ether complex in 30 ml of dichloromethane. The blue salt was precipitated with diethyl ether and the solid was collected on a frit and washed with several portions of diethyl ether. It then was dissolved in 25 ml of dichloromethane and 10 ml of anhydrous methanol was added. The blue color was not discharged. To the blue solution was added 1.00 g (9.4 mmol) of anhydrous sodium carbonate, resulting in a color change to brown. The mixture was filtered and the filtrate was evaporated at reduced pressure to yield a dark brown solid. The latter was recrystallized from diethyl ether to yield 0.8 g (1.3 mmol, 88% yield) of $\eta^5$-diphenylmethoxymethylcyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (X), m.p. 210—211°C. (Found: C, 83.00; H, 5.55. $C_{47}H_{37}CoO$ calcd.: C, 83.42; H, 5.51%.) NMR ($CDCl_3$): $\delta$ 2.85 (s, 3H, OMe), 4.43 and 4.78 (both m, 4H, Cp) and 6.77—7.53 ppm (m, 30H, $C_6H_5$).

*3. With monomethylamine.* The carbonium ion hexafluorophosphate salt, prepared from 1.00 g (1.51 mmol) of alcohol V and 0.5 ml of hexafluorophosphoric acid diethyl ether complex in 30 ml of dichloromethane, was precipitated with diethyl ether, collected on a frit, and washed with several portions of diethyl ether. The blue salt was redissolved in 25 ml of dichloromethane. To this solution was added a saturated solution of monomethylamine in 30 ml of dichloromethane. The color immediately changed from blue to brown. To ensure complete reaction, 1.00 g (9.4 mmol) of anhydrous sodium carbonate was added to the solution. The mixture was filtered and the solvent was removed from the filtrate, yielding a brown solid. The latter was recrystallized from diethyl ether to yield 0.7 g (0.2 mmol, 77% yield) of $\eta^5$-diphenyl(methylamino)methylcyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (XI), m.p. 205—206°C. (Found: C, 83.40; H, 5.80. $C_{47}H_{38}CoN$ calcd.: C, 83.54; H, 5.67%.) NMR ($CDCl_3$): $\delta$ 1.63 (s, 3H, $CH_3$), 4.40 and 4.93 (both m, 4H, Cp) and 6.83—7.67 (m, 30H, $C_6H_5$). IR ($CHCl_3$): $\nu$(N—H) 3300w.

*4. With N-methylpyrrole.* The blue carbonium ion salt from 1.00 g (1.51 mmol) of alcohol V and 0.5 ml of hexafluorophosphoric acid diethyl ether complex in 30 ml of dichloromethane was precipitated and washed several times with diethyl ether. It was then dissolved in 30 ml of dichloromethane and 0.5 ml of *N*-methylpyrrole was added and the solution was stirred magnetically at room temperature for 10 h. The resulting brown solution was evaporated at reduced pressure, leaving a brown solid which was chromatographed on a short column of alumina. Benzene eluted a single brown band which yielded, after removal of solvent, a dark brown solid. This was recrystallized from a 50/50 benzene/hexane mixture to yield 0.8 g (1.1 mmol, 73% yield) of brown plates, m.p. 233—235°C identified as $\eta^5$-diphenyl(*N*-methylpyrrol-2-yl)methylcyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (IX). (Found: C, 84.91; H, 5.67. $C_{51}H_{46}CoN$ calcd.: C, 84.39; H, 5.56%.) NMR ($CDCl_3$): $\delta$ 3.26 (s, 3H, $CH_3$), 4.33 and 4.66 (both m, 4H, Cp), 5.48—5.78, 6.30 (m, 3H, pyrrole H), 6.60—7.50 ppm (m, 30H, $C_6H_5$).

*5. With N,N-dimethylaniline.* The blue carbonium ion hexafluorophosphate salt from 1.50 g (2.3 mmol) of alcohol V and 0.7 ml of hexafluorophosphoric acid diethyl ether complex in 30 ml of dichloromethane was precipitated and washed with several portions of diethyl ether. The salt then was dissolved in 15 ml of dichloromethane, 0.3 ml (2.3 mmol) of *N,N*-dimethylaniline was added and the solution was stirred magnetically at room temperature for 10 h. At the end of 10 h, the solution was brown. After removal of solvent, the brown residue was chromatographed on a short alumina column. Benzene eluted a brown band which yielded, after removal of solvent, 0.5 g of an orange-brown solid. The $^1$H NMR spectrum of this solid showed it to be a complex mixture of several components which could not be resolved, but appeared to contain some carbon-alkylated product.

Dichloromethane/1% methanol eluted a brown band which yielded, after removal of solvent, a gold-brown solid which was recrystallized from diethyl ether to give 0.4 g (0.59 mmol, 25% yield) of gold-brown prisms, m.p. 210—211°C, identified as $\eta^6$-*N*,*N*-dimethylaniline-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate (XIIa). (Found: C, 62.93; H, 4.66. $C_{36}H_{31}CoN$ calcd.: C, 63.44; H, 4.59%.) NMR (acetone-$d_6$): $\delta$ 2.80 (s, 6H, $CH_3$), 5.86—6.80 (m, 5H, $Me_2NC_6\underline{H}_5$) and 7.23—7.66 ppm (m, 20H, $C_6H_5$).

*6. With anisole.* The carbonium ion hexafluorophosphate salt from 1.00 g (1.51 mmol) of alcohol V and 0.5 ml of hexafluorophosphoric acid diethyl ether complex in 25 ml of dichloromethane was precipitated, washed with several portions of diethyl ether, and dissolved in 10 ml of dichloromethane. The resulting solution was transferred to a thick walled tube to which then was added 5.0 ml of anisole. The tube was evacuated, sealed, and placed in an oven at 100°C for 13 h. After this time, the solution color had changed from blue to dark brown. The solvent was removed to yield a dark brown solid which was chromatographed on a short alumina column. Benzene eluted a brown band which yielded, after removal of solvent, 0.5 g of a brown solid. The NMR spectrum of this solid showed it to be a complex mixture of several components which could not be resolved. Further elution with dichloromethane/1% methanol yielded, after removal of solvent, a gold-brown solid. The latter was recrystallized from diethyl ether to give 0.3 g (0.43 mmol, 30% yield) of $\eta^6$-anisole-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate (XIIb), m.p. 204—206°C. (Found: C, 62.47; H, 4.25. $C_{35}H_{28}CoO$ calcd.: C, 62.88; H, 4.22%.) NMR (DMSO-$d_6$): $\delta$ 3.36 (s, 3H, $CH_3$), 6.16—6.93 (m, 5H, $MeOC_6\underline{H}_5$), and 7.43 ppm (s, 20H, $C_6H_5$).

### *Aluminum chloride-induced reactions of $\eta^5$-diphenylhydroxymethylcyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (V)*

*1. With benzene.* A 100 ml, three-necked, round-bottomed flask, equipped with nitrogen inlet and magnetic stirrer, was charged with 1.00 g (1.50 mmol) of alcohol V in 50 ml of dichloromethane. Then, 0.6 g (4.5 mmol) of aluminum chloride was added and the solution became deep blue in color. After 5.0 ml of benzene had been added, the solution was stirred for 30 min. During this time the solution changed from deep blue to a brown red. The solution then was poured into 100 ml of water. The organic layer was taken and treated with 50 ml of saturated aqueous $KPF_6$ solution. The dichloromethane was removed on a rotary evaporator to yield an oily liquid. The oil was chromatographed on an alumina column with dichloromethane to yield two products. The first was eluted with dichloromethane and the solvent was removed on a rotary evaporator to yield a red, oily liquid. An NMR spectrum indicated this to be a complex mixture. The second product was eluted with dichloromethane/2% methanol to yield, following removal of solvent, 0.70 g (1.1 mmol, 75%) of $\eta^6$-benzene-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate, whose IR and

NMR spectra agreed with literature data [17].

The NMR spectrum in acetone-$d_6$ of the $PF_6$ salt is different from that reported for the bromide in $CDCl_3$. NMR (acetone-$d_6$): δ 6.91 (s, 6H, complexed benzene), 7.58 ppm (m, 20H, cyclobutadiene phenyls). An authentic sample of the bromide salt in $CDCl_3$ gave an NMR spectrum identical to that of the literature [17].

2. *With toluene.* The reaction flask was charged with 0.5 g (0.8 mmol) of alcohol V, 5 ml of toluene, and 50 ml of dichloromethane. This slurry was stirred magnetically and 1.0 g (7.5 mmol) of aluminum chloride was added. The solution became blue and homogeneous. After ca. 1 h, the solution had turned brown. It was poured into 100 ml of water, 1.0 g $KPF_6$ was added and the mixture was stirred vigorously for 1 h. The layers were separated, the organic layer was dried over magnesium sulfate, and the solvent removed. The residue was passed down a short alumina column and eluted with benzene to yield, after removal of solvent, 0.2 g of a dark brown material. This was shown to be a complex mixture by NMR.

Further elution with dichloromethane/1% methanol yielded, after removal of solvent, 0.24 g (0.4 mmol, 76%), of a yellow-brown solid, $\eta^6$-toluene-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate, which was identified by comparison of its IR and NMR spectra with those in the literature [17].

3. *With mesitylene.* The reaction flask was charged with 0.50 g (0.80 mmol) of alcohol V, 1.0 ml of mesitylene, and 50 ml of dichloromethane. Addition of 0.5 g (3.5 mmol) of $AlCl_3$ gave a deep blue solution. The solution was stirred for 2 h at the end of which time its color had changed to brown. The solution was poured into 100 ml of water and 50 ml of dichloromethane was added. The organic layer was taken and the solvent removed on a rotary evaporator. The residue was then treated with methanolic $KPF_6$ and passed down an alumina column. The first band, which was eluted with dichloromethane, had an NMR spectrum which indicated it to be a complex mixture.

The second band was eluted with dichloromethane/2% methanol. The solvent was removed to yield 0.31 g (0.46 mmol, 58%) of $\eta^6$-mesitylene-$\eta^4$-tetraphenylcyclobutadienecobalt hexafluorophosphate, identified on the basis of its IR and NMR spectra as compared to the literature [17].

### *Reaction between $\eta^5$-cyclopentadienyl-$\eta^4$-tetraphenylcyclobutadienecobalt (II) and benzene with aluminum chloride*

The reaction flask was charged with 1.00 g (2 mmol) of II in 50 ml of dichloromethane. The solution was stirred magnetically and 1.0 g (7.5 mmol) of aluminum chloride was added. The solution became a much darker brown. It was stirred for 1 h and then poured into 100 ml of water containing 1.0 g of $KPF_6$. The resulting mixture was stirred vigorously for 1 h. TLC examination of the dichloromethane layer indicated that there was no cationic benzene complex of cobalt present.

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