760. *A New Type of Transition Metal–Cyclopentadiene Compound.**

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The reduction of cobalticenium and rhodicenium halides by sodium borohydride or by lithium aluminium hydride forms the neutral compound in which one π-cyclopentadienyl ring has been converted into a cyclopentadiene group, π-$C_5H_5(C_5H_6)M$. The deuteride π-$C_5H_5(C_5H_5D)Co$ was obtained by reduction with lithium aluminium deuteride, and a methyl derivative, π-$Me{\cdot}C_5H_4(Me{\cdot}C_5H_5)Co$, was obtained from 1,1′-dimethylcobalticenium bromide. A monomethyl derivative, π-C_5H_5(1-*endo*-$Me{\cdot}C_5H_5$)Co, was prepared by the action of methyl iodide on cobaltocene; a trichloromethyl compound obtained previously by reaction of carbon tetrachloride with cobaltocene is shown to be similar to the 1-*endo*-methyl derivative. Reduction of the 1-*endo*-trichloromethyl compound with lithium aluminium hydride gives a 1-*endo*-dichloromethyl analogue.

Infrared and high-resolution nuclear magnetic resonance spectra of these compounds and some related olefin–transition metal complexes are described, and the structures of the molecules are discussed.

REACTION of anhydrous cobalt chloride with sodiocyclopentadiene in tetrahydrofuran produces the paramagnetic neutral di-π-cyclopentadienylcobalt(II) cobaltocene.[1] In attempts some years ago to prepare similarly the rhodium analogue from rhodium trichloride, a small yield of stable orange-yellow crystals was obtained at 150° *in vacuo*. Analysis and molecular-weight determination gave the formula $C_{10}H_{11}Rh$, and magnetic-susceptibility measurements showed the compound to be diamagnetic.

It has been shown that essentially quantitative yields of this rhodium compound can be obtained by reduction of the di-π-cyclopentadienylrhodium(III) (rhodicenium) ion in aqueous ethanol by sodium borohydride. A cobalt compound, $C_{10}H_{11}Co$, was obtained similarly and by reduction of anhydrous cobalticenium halides with lithium aluminium hydride in tetrahydrofuran or 1,2-dimethoxyethane. The latter reaction has allowed the

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[1] Wilkinson, Birmingham, and Cotton, *J. Inorg. Nuclear Chem.*, 1956, **2**, 95.

preparation of the monodeuterium compound, $C_{10}H_{10}DCo$, by use of lithium aluminium deuteride.

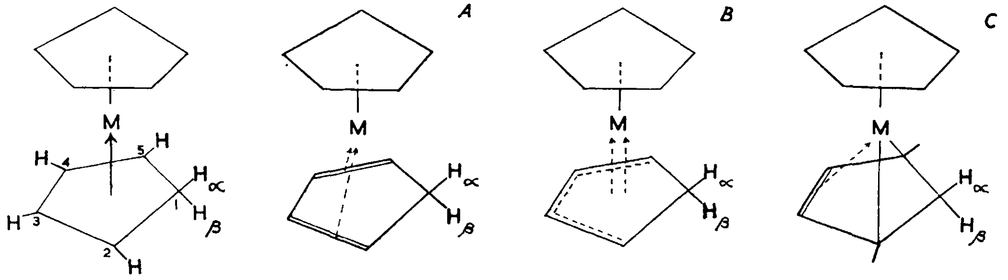
On the basis of the early studies, Liehr [2] suggested that the rhodium compound was a di-π-cyclopentadienylrhodium hydride, similar in stoicheiometry to the di-π-cyclopentadienylrhenium hydride,[3] but with a different type of metal–hydrogen bond. Detailed studies on a series of compounds of similar type (Table 1) now described show that this suggestion must be discarded.

TABLE 1. *Cyclopentadiene–metal complexes.*

Compound	Form	M. p.	Ultraviolet and visible absorption (λ in mμ)
π-$C_5H_5(C_5H_6)Co$	Wine-red crystals	98—99°	397 (ε 5·27 × 10^3), 327 (ε 9·27 × 10^3), 263·8 (ε 1·78 × 10^5)
π-$C_5H_5(C_5H_5D)Co$	,, ,,	78—79	398 (ε 4·2 × 10^3), 328 (ε 8·79 × 10^3), 264·7 (ε 2·10 × 10^5)
π-$CH_3{\cdot}C_5H_4(Me{\cdot}C_5H_5)Co$	Dark red oil	~ −5	—
π-C_5H_5(1-*endo*-$Me{\cdot}C_5H_5$)Co	Red oil	~ −10	—
π-C_5H_5(1-*endo*-$CHCl_2{\cdot}C_5H_5$)Co	Orange-red crystals	50—51	—
π-C_5H_5(1-*endo*-$CCl_3{\cdot}C_5H_5$)Co ...	,, ,,	79—80	400 (ε 9·94 × 10^3), 331 (ε 2·40 × 10^4), 272·5 (ε 1·34 × 10^5)
π-$C_5H_5(C_5H_6)Rh$	Orange-yellow crystals	121—122	396 (ε 2·84 × 10^3), 297 (ε 3·01 × 10^3), 236·5 (ε 1·97 × 10^4)

The infrared and high-resolution nuclear magnetic resonance spectra discussed below indicate that in the $C_{10}H_{11}M$ compounds there is one π-cyclopentadienyl ring bound to the metal atom as in other di- and mono-π-cyclopentadienyl-metal compounds.

FIG. 1.



The electronic requirements of the metal atom in known π-cyclopentadienylcobalt and rhodium compounds, *e.g.*, π-$C_5H_5Co(CO)_2$ [4] and π-C_5H_5(cyclo-octa-1,5-diene)Rh,[5] indicate that the remaining organic part of the $C_{10}H_{11}M$ compounds, a C_5H_6 group, must furnish four bonding electrons in order that the metal atom shall achieve the formal inert-gas configuration and that the observed diamagnetism be explained. The chemical properties of the compounds, and the interpretation given below of their infrared and nuclear magnetic resonance spectra, are in agreement with a molecular configuration shown in Fig. 1. The C_5H_6 grouping contains one methylene group in which the hydrogen atoms (H_α and H_β) are not equivalent, and four $\geqslant$C–H groups. In the substituted compounds, one hydrogen atom (H_α) is replaced by the substituent group. H_α and the groups replacing it are probably in the *endo*-configuration, *i.e.*, on the side of the C_5H_6 ring nearer to the metal atom. The hydrogen atoms on $C_{(2)}$ and $C_{(5)}$ are equivalent, but differ from the equivalent ones on $C_{(3)}$ and $C_{(4)}$. It is also probable that these four carbon atoms lie in the same plane and that the four electrons which bond the C_5H_6 group to the metal are associated with

[2] Liehr, *Naturwiss.*, 1957, **44**, 61.
[3] Green, Pratt, and Wilkinson, *J.*, 1958, 3916.
[4] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.
[5] Chatt and Venanzi, *J.*, 1957, 4735.

these carbon atoms. The detailed bonding of this group to the metal atom is discussed after the evidence for the molecular configuration has been presented.

Chemical Properties.—The π-cyclopentadienyl(cyclopentadiene)Co(or Rh) compounds could not be prepared by electrolysis of neutral or alkaline aqueous solutions of the (πt $C_5H_5)_2M^+$ ions, or by reduction of such solutions by sodium amalgam, sodium dithionite, or Devarda's alloy. The reduction solely by complex hydrides suggests that hydride-ion attack, either on the π-C_5H_5 ring or through initial attack on the metal atom, is involved. Since borohydride and aluminium hydride do not usually cleave carbon–carbon bonds, no opening of the five-membered ring is to be expected. Thus we can write $(\pi\text{-}C_5H_5)_2M^+ + H^-(\text{or } D^-) = (\pi\text{-}C_5H_5)MC_5H_5H(\text{or D})$.

The presence of the intact five-membered ring is also indicated by the reaction of the compounds with acids. With 2N-hydrochloric acid, $C_{10}H_{11}Rh$ gives about a 50% yield of the $(\pi\text{-}C_5H_5)_2Rh^+$ ion, which was characterised by precipitation reactions and by its absorption spectrum.[6] A gas is also evolved which has been found to consist of hydrogen (~50%) together with C_5 olefinic hydrocarbons (mass 68, probably mainly cyclopentene) and a trace of butenes; some insoluble matter containing metal is also produced, presumably associated with the degradation leading to olefins. This reaction has a parallel in the reaction of the compounds with carbon tetrachloride at room temperature to form chloroform and the respective $(\pi\text{-}C_5H_5)_2M^+$ chlorides as the main products, together with insoluble tar and some unidentified solvent-soluble olefins. From the products formed by air-oxidation of $C_{10}H_{11}Co$, considerable amounts of the cobalticenium ion can be recovered on extraction with water or dilute acid.

The simple hydrogen-transfer reactions, *e.g.*:

$$\pi\text{-}C_5H_5CoC_5H_6 + H^+_{aq.} = (\pi\text{-}C_5H_5)_2Co^+_{aq.} + H_2$$

$$\pi\text{-}C_5H_5CoC_5H_6 + CCl_4 = (\pi\text{-}C_5H_5)_2Co^+Cl^- + CHCl_3$$

suggest the presence in the molecules of a hydridic hydrogen atom.

The compounds are unaffected by hydrogenation in presence of Adams catalyst, and a Kuhn–Roth analysis for a *C*-Me group was negative. No reaction was observed with nitric oxide at room temperature and atmospheric pressure, and no hydrogen-transfer was obtained with acridine, the rhodium compound being recovered after three days. *N*-Bromosuccinimide in benzene with $C_{10}H_{11}Co$ gave cobalticenium bromide quantitatively, whilst benzaldehyde in alkaline solution gave the cobalticenium ion together with benzyl alcohol and benzoic acid.

The chemical properties thus show the presence of a cyclic C_5H_6 unit but indicate that the $-CH_2-$ group has unusual chemical behaviour, one of the hydrogen atoms being readily lost. In fact, the derivatives of the $C_{10}H_{11}Co$ compound have been prepared, where the substituent group, replacing H_α, is 1-*endo*.

π-Cyclopentadienyl-(1-*endo*-methylcyclopentadiene)cobalt was prepared by a different route from that used for the $C_{10}H_{11}M$ compounds. It was known [1] that cobaltocene reacts with organic halides to give cobalticenium salts and unidentified hydrocarbon-soluble red cobalt compounds without evolution of gas. It seemed reasonable to assume that with methyl iodide a methyl-substituted derivative similar to the $C_{10}H_{11}M$ compounds was formed, and this has proved to be the case, the reaction being:

$$2(\pi\text{-}C_5H_5)_2Co + CH_3I = (\pi\text{-}C_5H_5)_2CoI + \pi\text{-}C_5H_5(1\text{-Me}\cdot C_5H_5)Co$$

The spectra of this methyl derivative, which are discussed below, show that it contains a $-CHMe-$ group.

The 1-endo-*Chloromethyl Derivatives.*—Other workers [7] have recently reported a reaction between cobaltocene and carbon tetrachloride. We similarly obtained the orange-red crystalline product $C_{10}H_{10}(CCl_3)Co$. The infrared and nuclear magnetic resonance

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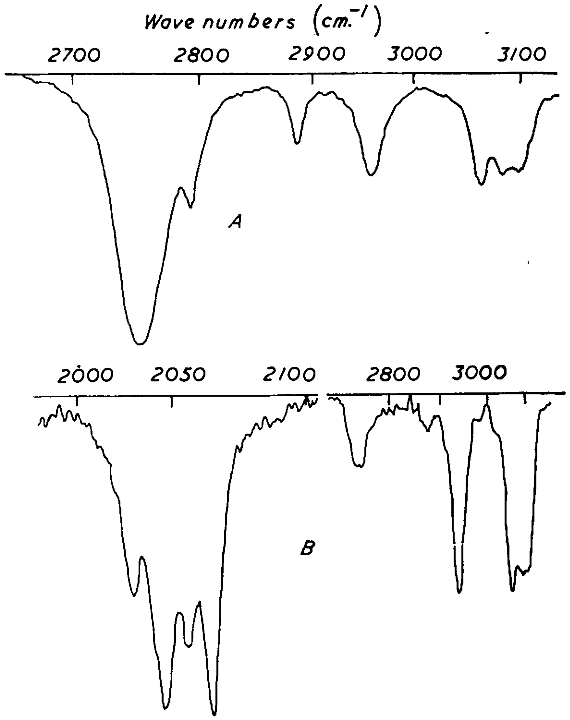
[6] Cotton, Whipple, and Wilkinson, *J. Amer. Chem. Soc.*, 1953, **75**, 3586.

[7] Katz, Weiher, and Voigt, *ibid.*, 1959, **80**, 6459.

spectra of this compound closely resemble those of the 1-*endo*-methyl derivative (Tables 2 and 3 and Fig. 3) and it must have a similar structure, with a $-CH(CCl_3)-$ group. In an attempt to reduce the 1-*endo*-trichloro-derivative with lithium aluminium hydride to the methyl analogue, the main product formed was the 1-*endo*-dichloromethyl compound, π-$C_5H_5(1\text{-}CHCl_2{\cdot}C_5H_5)Co$. Its properties agree with formulation as the $-CH(CHCl_2)-$ derivative.

Another compound, π-methylcyclopentadienyl(methylcyclopentadiene)cobalt, was obtained by reduction of 1,1′-dimethylcobalticenium chloride with sodium borohydride. It is a very reactive, thermally unstable liquid. Although isomers might have been expected from the method of formation, chromatography showed no evidence for them. This derivative develops hydrogen pressure in a sealed tube and eventually solidifies to form dark red-black crystals, m. p. ~33°; the reaction may be written thus:

FIG. 2. *Infrared spectra of* π-$C_5H_5(C_5H_6)Co$ (*A*) *and* π-$C_5H_5(C_5H_5D)Co$ (*B*) *in the* 2600—3200 *cm.*$^{-1}$ *region* (LiF *optics*).



$$\pi\text{-}Me{\cdot}C_5H_4(Me{\cdot}C_5H_5)Co \longrightarrow (\pi\text{-}Me{\cdot}C_5H_4)_2Co + \tfrac{1}{2}H_2$$

Infrared Spectra.—The spectra to 650 cm.$^{-1}$ are given in the Experimental section. High-resolution spectra in the region 2700—3300 cm.$^{-1}$ are given in Table 2 and Fig. 2. In the spectra of all the compounds there are bands characteristic of a π-C_5H_5-metal grouping (cf. ref. 8), including a single sharp C–H stretching band at 3100 cm.$^{-1}$. Both of the $C_{10}H_{11}M$ compounds show two bands in the region where aliphatic C–H stretching frequencies normally occur, at 2948 and 2882 cm.$^{-1}$ for the rhodium compound and 2942 and 2871 cm.$^{-1}$ for the cobalt compound. These bands have the appearance of those due to a methylene group.[9] In the deuterium compound π-$C_5H_5(C_5H_5D)Co$, however, the

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[8] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[9] Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen and Co., London, 1958.

2871 cm.$^{-1}$ band disappears and *does not* reappear in the expected region (2871/$\sqrt{2}$ cm.$^{-1}$); therefore it cannot be assigned as a fundamental C–H stretching frequency. In agreement with this, no band is observed near 2870 cm.$^{-1}$ in the trichloromethyl derivative. Similarly the peak at about 2780 cm.$^{-1}$ in the $C_{10}H_{11}M$ compounds is not found in the 1-*endo*-methyl or 1-*endo*-chloromethyl derivative or in similar arene–iron compounds, *e.g.*, $C_6H_6(C_5H_6)Fe$ (to be described in a later paper). It therefore seems reasonable to ascribe this band as an overtone or combination in the C_5H_6–metal system. The band at 2942 cm.$^{-1}$ remains in the same position in the deuterated compound but with a slightly increased intensity; this band could therefore be assigned as a C–H fundamental from the C_5H_6 group.

The bands at approximately 3050 and 3080 cm.$^{-1}$ which are found in the spectra of all the compounds are in the region of olefinic C–H stretching modes.

A most unusual feature of the $C_{10}H_{11}M$ compounds is a band at about 2750 cm.$^{-1}$, which is one of the strongest in their spectra. It may be noted that very few fundamental stretching frequencies in the region ~2750 cm.$^{-1}$ have been reported (cf. ref. 9), the most notable being that of the aldehyde group. Since this band at ~2750 shifts by approximately the expected value [ν_H(obs.)/ν_D(obs.) = 1·34] in π-$C_5H_5(C_5H_5D)Co$, it must be assigned as a fundamental C–H stretching frequency. The marked splitting of the C–D peaks, which is not observed for the corresponding C–H peak even under the highest resolution, may be attributed to coupling with other vibrational frequencies.

TABLE 2. *Infrared spectra in* 2700—3200 *cm.*$^{-1}$ *region* (*cm.*$^{-1}$).

π-$C_5H_5(C_5H_6)Rh$	π-$C_5H_5(C_5H_6)Co$	π-$C_5H_5(C_5H_5D)Co$ [a]	π-$C_5H_5(C_5H_5CH_3)Co$	π-$C_5H_5(C_5H_5CCl_3)Co$	Assignment [b]
3100m	3096m	3105m	3100m	3100m	1
3080m	3076m	3068m	3088m	3085m	2
—	—	—	3075m	—	2
3056m	3053m	3042m	3045m	3066m	2
—	—	—	2960s	—	3
—	—	—	2850m	—	3
—	—	—	—	2956w	4
2948m	2942m	2932m	2912s	2924m	5
2882w	2871w	—	—	—	4
2784w	2780w	—	—	—	4
2758s	2742s	2745w	—	—	6
—	—	2076s	—	—	7
—	—	2057s	—	—	7
—	—	2039s	—	—	7
—	—	2017s	—	—	7

[a] Isotopic purity ~95%. 1, C–H stretch of π-C_5H_5; 2, CH⁚CH stretch; 3, –Me stretch of CH_3; 4, probably overtone or combination band; 5, C–H$_\beta$ stretch; 6, C–H$_\alpha$ stretch; 7, C–D stretch.

In the formation of the deuterated derivative by reduction of the cobalticenium ion with lithium aluminium deuteride, it is probable that a –CHD– group is formed. Since the strong C–H peak is also absent in the monosubstituted cobalt derivatives, it may be assigned to the methylene proton which is replaced in these compounds and in the deutero-compound.

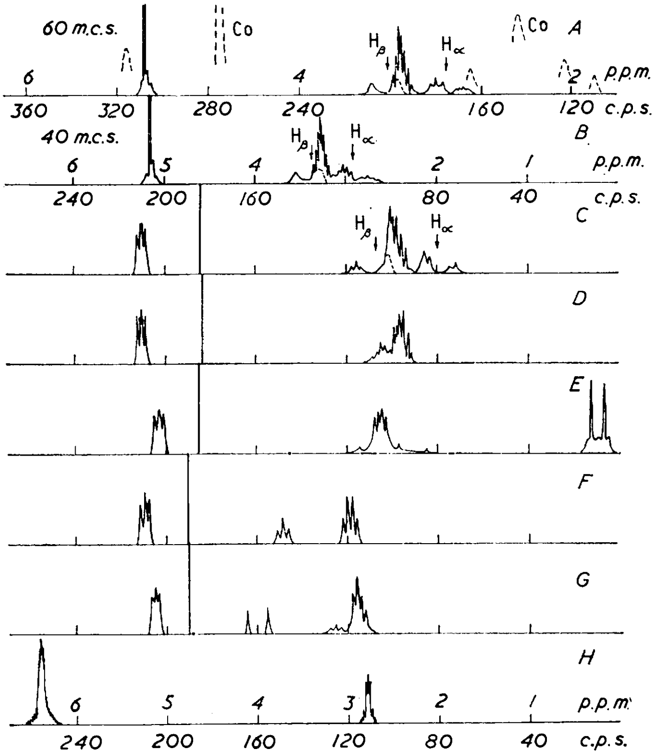
The other fundamental aliphatic C–H stretching frequency at 2948 cm.$^{-1}$ (Rh) and 2942 cm.$^{-1}$ (Co) which occurs at about the same place in all the compounds is assigned to the C–H stretching frequency of the other methylene proton. The marked difference in the two methylene C–H bands is confirmed by the nuclear magnetic resonance spectra. It seems likely that the unusually low and intense stretching frequency of the reactive methylene-hydrogen atom may be caused by the close approach of one of the protons, H_α, to the metal atoms causing steric or electrostatic interactions. Therefore we assign the bands at 2758 (Rh) and 2742 (Co) to the C–H_α stretching frequency and those at 2948 (Rh) and 2942 (Co) to the C–H_β stretching frequency (Fig. 2).

The 1-*endo*-methyl derivative shows that in addition to the C–H_β stretch at 2912 cm.$^{-1}$ there are two more strong bands in the aliphatic C–H stretching region, at 2960 and

2850 cm.$^{-1}$. These are assigned to the asymmetrical and symmetrical C–H stretching frequencies of the methyl group. Similarly in the 1-*endo*-dichloromethyl derivative there is a band at 2962 cm.$^{-1}$ which may be attributed to the C–H stretching frequency of the $CHCl_2$ group.

High-resolution Nuclear Magnetic Resonance Spectra.—The spectra were obtained at 40 and 60 Mc./sec. (Table 3) and are shown in Fig. 3. The sharpness of the lines in all the spectra shows that the pure compounds are diamagnetic (the broadened lines in the spectrum at 60 Mc./sec. of the $C_{10}H_{11}Co$ compound indicate that this particular sample contained some paramagnetic impurity).

FIG. 3. *High-resolution proton magnetic resonance spectra of cyclopentadiene compounds of rhodium and cobalt, relative to tetramethylsilane as internal reference.*



A, π-$(C_5H_5)(C_5H_6)Rh$ at 60 Mc./sec.; broken lines show line positions of π-$(C_5H_5)(C_5H_6)Co$ at 60 Mc./sec (All other spectra at 40 Mc./sec.)

B, π-$(C_5H_5)(C_5H_6)Rh$ } Broken line indicates "hidden component" of Hβ doublet. Arrows indicate approximate chemical shift positions for Hα and Hβ.
C, π-$(C_5H_5)(C_5H_6)Co$ }

D, π-$(C_5H_5)(C_5H_5D)Co$. *E*, π-(C_5H_5)(1-*endo*-Me·C_5H_5)Co. *F*, π-(C_5H_5)(1-*endo*-CCl_3·C_5H_5)Co.
G, π-(C_5H_5)(1-*endo*-$CHCl_2$·C_5H_5)Co. *H*, Cyclopentadiene.

In no case was a line observed in the region (7·5—17·5 p.p.m. on the high-field side of tetramethylsilane) where lines due to hydrogen atoms directly bound to a transition metal occur.[3]

All the spectra can be satisfactorily interpreted on the basis of the molecular structure of Fig. 1 for the $C_{10}H_{11}M$ compounds. They all show a strong, sharp line which is assigned to the five equivalent protons of the π-C_5H_5 group as in other metal–cyclopentadienyl compounds.[3,4] This line is single in the cobalt compounds, but in the rhodium compound it is a doublet with a separation 1·0 ± 0·2 cycles/sec. at both 40 and 60 Mc./sec. This splitting arises from the field-independent spin coupling interaction between the C_5H_5

TABLE 3. *Nuclear magnetic resonance data* (*see Fig.* 3).

Compound	Frequency (10^6 c.p.s.)	Band position (p.p.m. rel. to to $SiMe_4$)	Relative intensity	Structure		Assignment
				Multiplicity	Sepn. bet. components (c.p.s.)	
$Rh(C_5H_5)(C_5H_6)$	40	5·13	$7\{5$	2 (doublet)	1·0 ± 0·2	(C_5H_5) group
		~5·09	2	3 or 4	1—2	$H_{(3)} + H_{(4)}$
		3·54	$\sim\frac{1}{4}$	1	—	Part of doublet of Hβ; splitting 11·2 c.p.s.; chemical shift posn. ~3·34 p.p.m.
		3·26	$\sim2\frac{1}{4}$	⩾7	~1·1 ± 0·3	Remainder ($I = \frac{3}{4}$) of Hβ doublet + ($H_{(2)} + H_{(5)}$ at 3·25 p.p.m.
		3·02	$1\{\sim\frac{3}{4}$	~5	~2·2	Hα doublet; sepn. 11·2 c.p.s. chemical shift posn. ~2·92 p.p.m.
		2·74	$\sim\frac{1}{4}$	~4	~2	
$Rh(C_5H_5)(C_5H_6)$	60	5·14	$7\{5$	2 (doublet)	1·0 ± 0·2	(C_5H_5) group
		~5·09	2	3 or 4	1—2	$H_{(3)} + H_{(4)}$
		3·46	$\sim\frac{1}{4}$	1 (~6 broad)	—	Part of Hβ doublet; splitting 11·2 c.p.s.; chemical shift posn. ~3·34 p.p.m.
		~3·26	$\sim2\frac{1}{4}$	⩾7	~1·1 ± 0·3	Remainder of Hβ doublet ($I = \frac{3}{4}$) + ($H_{(2)} + H_{(5)}$) at 3·25 p.p.m.
		~2·99	$1\{\sim\frac{3}{4}$	3 to 5	~2	Hα doublet; splitting 11·2 c.p.s chemical shift posn. ~2·9 p.p.m.
		2·80	$\sim\frac{1}{4}$	3 or 4	~2	
$Co(C_5H_5)(C_5H_6)$	40	5·20	2	3 (triplet)	1·9 ± 0·2	$H_{(3)} + H_{(4)}$
		4·59	5	1		(C_5H_5) group
		2·87	$\sim\frac{1}{4}$	3 (triplet)	2·2 ± 0·3	Part of Hβ doublet; splitting 12·7 c.p.s.; chemical shift posn. at ~2·68 p.p.m.
		2·45	$\sim2\frac{1}{4}$	5 to 6	— 2·0 ± 0·3	Remainder of Hβ doublet ($I = \frac{3}{4}$) + ($H_{(2)} + H_{(5)}$); $I = 2$; possibly a quintuplet; centred at 2·43 p.p.m.
		2·08	$1\{\sim\frac{3}{4}$	2	~2·1 ± 0·3	Doublet of Hα; splitting = 12·7 c.p.s.; chemical shift posn. at ~2·01 p.p.m.
		1·81	$\sim\frac{1}{4}$	2	~2·1 ± 0·3	
$Co(C_5H_5)(C_5H_6)$	60	5·25	2	1 (broad)	—	$H_{(3)} + H_{(4)}$
		4·6	5	1 (broad)		(C_5H_5) group
		2·75	$\sim\frac{1}{4}$	1 (broad)		Part of Hβ doublet; splitting 12·7 c.p.s.; chem. shift posn. at ~2·6 p.p.m.
		2·4	$\sim2\frac{1}{4}$	1 (broad)		Remainder ($I = \frac{3}{4}$) of Hβ doublet + ($H_{(2)} + H_{(5)}$); at ~2·4 p.p.m.
		2·04	$\sim\frac{3}{4}$	1 (broad)		Hα doublet; splitting 12·7 c.p.s. chemical shift posn. at 1·95 p.p.m.
		1·82	$\sim\frac{1}{4}$	1 (broad)		
$Co(C_5H_5)(C_5H_5D)$	40	5·20	2	Triplet	2·0 ± 0·2	$H_{(3)} + H_{(4)}$
		4·58	5	Singlet		(C_5H_5) group
		2·64	1	Complex, pentuplet	2·1 ± 0·3	Hβ
		2·40	2	Complex, quartet	~2	$H_{(2)} + H_{(5)}$
$Co(C_5H_5)(C_5H_5Me)$ ...	40	5·07	2	Triplet	2·0 ± 0·2	$H_{(3)} + H_{(4)}$
		4·61	5	Singlet	—	(C_5H_5) group
		~2·63	3	Quartet main + others	~2 in quartet	Hβ + ($H_{(2)} + H_{(5)}$)
		0·23	3	Doublet + others	~5·8 ± 0·2	Me
$Co(C_5H_5)(C_5H_5{\cdot}CCl_3)$	40	5·23	2	Triplet	2·0 ± 0·2	$H_{(3)} + H_{(4)}$
		4·75	5	Singlet	—	(C_5H_5) group
		3·70	1	Triplet	2·5 ± 0·2	Hβ
		2·96	2	Quadruplet	bet. inner two peaks 2·0 ± 0·2 bet. outer pairs, 2·2	$H_{(2)} + H_{(5)}$
$Co(C_5H_5)(C_5H_5{\cdot}CH_2Cl_2)$	40	5·12	2	Triplet	2·0 ± 0·3	$H_{(3)} + H_{(4)}$
		4·75	5	Singlet		(C_5H_5) group
		4·12 3·89	~1	Doublet	8·9	H of $CHCl_2$ group
		3·14	$\sim\frac{1}{2}$	Triplet	2·3 ± 0·3	Part of Hβ " doublet "
		2·89	$\sim2\frac{1}{2}$	Complex, quadruplet	~2	Remainder of Hβ; $H_{(2)} + H_{(5)}$
C_5H_6	40	6·38	4	Complex, multiplet	<1	$H_{(2,\,3,\,4,\,5)}$
		2·79	2	Complex, pentuplet	~1·2	$H_{(1)}$ and $H_{(2)}$ (on $C_{(1)}$)

protons and the ^{103}Rh nucleus (100% abundance, spin $\frac{1}{2}$; each proton line of the π-C_5H_5 ring is split into $2 \times \frac{1}{2} + 1 = 2$ components). Similarly the $(\pi\text{-}C_5H_5)_2Rh^+$ ion in water shows a spectrum which is a sharp doublet with a separation of about 1·0 cycle/sec. The absence of splitting in the cobalt compounds is due to rapid relaxation of the ^{59}Co nucleus which has a quadrupole moment.[10] All the cobalt compounds show a band (at about 5·2 p.p.m. relative to $SiMe_4$) on the low-field side of the C_5H_5 line. This band has three main components and has an intensity (area) corresponding to two protons relative to the C_5H_5 lines whose intensity is taken as 5. This band cannot be observed separately for the rhodium compound, although there are some incompletely resolved lines at the base of the C_5H_5 doublet. Comparisons of the total intensity of the composite band, both with that of the other bands in the spectrum and with the intensity of the cyclopentadienyl line from ferrocene in an equimolar solution, indicate that there is a band of intensity 2 analogous to those in the cobalt compounds, which is largely obscured by the C_5H_5 doublet. This band is assigned to the two *equivalent* protons on $C_{(3)}$ and $C_{(4)}$. The resonance of each of these protons is split into a doublet by the nearest proton on $C_{(2)}$ (or $C_{(5)}$) and again into a doublet by the more distant proton of $C_{(5)}$ (or $C_{(2)}$). The two separate splittings are both roughly 2 cycles/sec., and the two middle lines of the doublets overlap, under the resolution obtained, to give the observed triplet structure with a total splitting of about 4 cycles/sec. The assignment of this band to resonances of the protons remote from the CH_2 group is supported by the absence of additional splitting.

Another common feature of the spectra is the presence on the high-field side of the C_5H_5 line of a band of intensity 2, with more fine structure than the one just described. This is assigned to two equivalent protons on $C_{(2)}$ and $C_{(5)}$. A simple interpretation of its structure can be given for the trichloromethyl-cobalt derivative, where complications due to the close proximity of other resonances are absent. The resonance of each proton is split into a doublet three times over, once by the nearest proton on $C_{(3)}$ (or $C_{(4)}$) (~2 cycles/sec.), again by the more distant proton on $C_{(4)}$ (or $C_{(3)}$) (~2 cycles/sec.) and, in addition, by the single proton H_β on $C_{(1)}$ (2·5 cycles/sec.). Within the resolution obtained, the inner components of the three doublets overlap to give the observed quartet. In agreement with this interpretation, the overall splitting (6·4 cycles/sec.) is, within the limits of experimental error, equal to the sum (6·5 cycles/sec.) of the three splittings contained in the lines from the three protons producing it. A similar group of lines appears in the spectra of the other compounds, although the simple quartet structure is made more complicated by additional factors. First, the H_β resonance lies closer to this group, so that the chemical shift between them is either not much greater than the splittings or is so small that the H_β line is obscured. In either case a simple interpretation of the splittings does not account for all the lines. Secondly, in the $C_{10}H_{11}M$ compounds there is also a splitting from the additional proton (H_α) and for the rhodium compound some further splitting by the ^{103}Rh nucleus may be present.

The remaining group in the spectrum of the trichloromethyl compound has unit intensity and is assigned to the H_β proton. The splitting into a 1 : 2 : 1 triplet, with a separation between components of 2·5 cycles/sec., is attributed to spin coupling with the two equivalent protons on $C_{(2)}$ and $C_{(5)}$. The chemical shift to markedly lower fields, compared with that for the other compounds, is probably due to an inductive effect of the electronegative chlorine atoms. In the other compounds, the lines from this proton are partly or completely obscured.

The spectra of the $C_{10}H_{11}M$ compounds show two complex lines at slightly higher fields than the strong band which, on the above assignment, contains the C_5H and C_2H resonances. These weaker lines, whose combined intensity is unity, are missing in the deutero-cobalt derivative, and hence they represent the contribution from the H_α proton. Also, the replacement of H_α by a deuterium atom changes the position and structure of the

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[10] Pople, *Mol. Phys.*, 1958, **1**, 168.

visible components of the H_β resonance which occur on the low-field side of the strong band.

These changes, and the doublet structure of the H_α resonance, can be interpreted as follows. The H_α and H_β protons are in different environments, and each splits the other into a doublet. However, the chemical shift between these protons (27 cycles/sec. for $C_{10}H_{11}Co$ and 17·5 cycles/sec. for $C_{10}H_{11}Rh$ at 40 Mc./sec.) is of the same order of magnitude as the spin–spin coupling between then (12·7 and 11·2 cycles/sec., respectively). In a group of this type (H_AH_B) it is known[11] that the spectrum appears as a symmetrical quartet with the outer peaks less intense than the inner ones. The inner peak of the H_β doublet lies under the strong band and only its outer component is observed. In the $C_{10}H_{10}DCo$ derivative, the H_β proton no longer experiences the relatively large splitting by H_α, and its resonance is centred at a position which should correspond with that calculated from the lines assigned to the quadruplet in the $C_{10}H_{11}Co$ compound. The small arrows indicate the calculated positions of the unsplit resonances for H_α and H_β in the $C_{10}H_{11}M$ compounds. The calculated position of the H_β resonance in the cobalt compound does in fact agree with that observed in the deutero-derivative.

The above interpretation and calculations were assisted by measurements of the spectra at 60 Mc./sec., since chemical shifts (in cycles/sec.) are directly proportional to field strength, and spin–spin couplings are field-independent. As expected for an H_AH_B group, the splitting of each doublet is the same as at 40 Mc./sec., whilst the chemical shift separation between the doublets increases in the expected manner.

Part of the additional structure on the main components of the H_α and the H_β resonance arises from smaller splittings produced by coupling with the protons on $C_{(2)}$ and $C_{(5)}$.

In the spectrum of the $CHCl_2$ derivative the doublet (intensity equivalent to 1 proton) at 4·05 p.p.m. is assigned to the single proton of the $CHCl_2$ group. The resonance of this proton is shifted to lower fields by the adjacent chlorine atoms, and split into a doublet by H_β. Conversely, the resonance of H_β should be a doublet of the same separation (9 cycles/sec.). This doublet appears to be centred at ~3·1 p.p.m., with one component obscured by the group of lines from ($H_{(2)}$,$H_{(5)}$). The observed component shows a triplet structure, probably due to coupling with the protons on $C_{(2)}$ and $C_{(5)}$.

In the 1-*endo*-methyl derivative the resonance of the methyl protons, which occurs at a comparatively high field (0·23 p.p.m.), is more shielded than the resonances in normal aliphatic methyl groups, which may be due to the metal atom. The main doublet structure of this resonance (separation 6·8 cycles/sec.) is probably caused by coupling with the H_β proton; the additional structure may be the result of restricted rotation of the group about the C–C axis. The resonance of H_β should conversely be split by the three methyl protons into a quadruplet with the same separation between the components. This group cannot be observed, but must lie under the lines of ($H_{(2)}$,$H_{(5)}$). Intensity measurements are consistent with this interpretation.

π-Methylcyclopentadienyl(methylcyclopentadiene)cobalt.—The infrared spectrum of this compound is similar to those of the $C_{10}H_{11}M$ compounds, showing again a strong band at ~2750 cm.$^{-1}$, and therefore a $-CH_2-$ group must be present in the ($Me{\cdot}C_5H_5$) ring. This is to be expected since a hydride ion attack on the 1,1′-dimethylcobalticenium ion would probably occur at carbon atoms remote from the methyl group. The nuclear magnetic resonance spectrum shows a complicated pattern of lines, which are broadened by the presence of paramagnetic impurities. The spectrum was not analysed although the general features are consistent with the compound having the same basic molecular structure.

Butadiene-iron Carbonyl Compounds.—It is probable that the structures of the cyclopentadiene compounds discussed above are related to that of butadiene-iron carbonyl, $C_4H_6{\cdot}Fe(CO)_3$,[12] in which the C_4H_6 group supplies four electrons to the iron atom. This

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[11] Pople, Schneider, and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1060.

[12] Hallam and Pauson, *J.*, 1958, 642.

group would correspond to the $C_{(2)}C_{(3)}C_{(4)}C_{(5)}$ group in the cyclopentadiene compounds. The infrared spectrum of the butadiene compound shows a main strong peak at 3050 cm.$^{-1}$ (assigned to the olefinic C–H stretching frequencies) and a weak peak at 2925 cm.$^{-1}$ (probably an overtone or combination band).

The nuclear magnetic resonance spectrum of the butadiene compound shows three symmetrical complex bands, each of an intensity corresponding to two protons. Comparison of the spectra at 40 and 60 Mc./sec. shows that the separations between the bands are chemical shifts. The low-field band at 5·28 p.p.m. is assigned to the two equivalent protons on the central carbon atoms. The bands in the high-field region are assigned to the four protons on the terminal carbon atoms. The symmetry of all the band patterns indicates that the terminal $=CH_2$ groups are equivalent, but that the two protons of this group are not equivalent. The spectrum of the 1,2,3,4-tetraphenyl derivative supports this assignment, since it shows a doublet band (separation 10 cycles/sec., intensity ~20) at low fields (6·92 + 7·16 p.p.m.) assigned to the protons on the phenyl groups, and an unresolved band (width ~3 cycles/sec., intensity ~2) at higher fields (2·38 p.p.m.), which is assigned to the two protons on the terminal carbons.

DISCUSSION

It has been seen that the evidence given above suggests the molecular configuration shown in Fig. 1. The bonding in that part of the molecule consisting of $C_{(3)}$,$C_{(3)}$,$C_{(4)}$,$C_{(5)}$, and the metal atom can be represented in several ways, and three extreme formal structures may be considered. These are structure A, in which each double bond of a cyclopentadiene molecule independently donates two electrons to the metal; a structure B with delocalisation of these electrons; and structure C, which would result from a Diels–Alder type addition of the conjugated system of a cyclopentadiene molecule to the metal atom, with a donation of two electrons from the remaining double bond.

Similar structures can be considered for the butadiene-iron carbonyl compound for which a structure of the type B has been proposed.

It does not seem possible to arrive at a definite conclusion about the bonding in these compounds from the data at present available.

The infrared data are less consistent with structures of type C. For the $C_{10}H_{11}M$ compounds, apart from the bands which have been assigned to C–H stretching frequencies of the 1-CH_2 group, there are no strong bands in the region associated with aliphatic (sp^3) CH groups, which would be present at $C_{(2)}$ and $C_{(5)}$. For the butadiene compound also a strong band with a doublet structure would be expected for aliphatic-type methylene groups at $C_{(2)}$ and $C_{(5)}$, but this is not observed. The infrared data indicate the presence of hydrogen atoms bonded to sp^2-hybridised carbon atoms, but can be interpreted equally well by structure A or B.

These interpretations assume that the normal infrared correlation rules for C–H bonds in simple organic molecules are still valid for C–H bonds in groups which are bonded to a metal atom in organometallic compounds. This assumption is probably correct since the vibration frequency of a C–H bond depends mainly on the carbon-atom hybridisation; provided that the hybridisation is essentially sp^2, the C–H stretching frequency will not be greatly altered by variations in π-electron density at the carbon atom.

For simple organic molecules, similar correlations are found experimentally between the chemical environment of a hydrogen atom and the relative position of its nuclear (*i.e.*, proton) resonance line. If the present data are interpreted with these correlations, they agree better with structures of the type C, with only the protons on $C_{(3)}$ and $C_{(4)}$ in the lower field region associated with normal olefinic protons.

However, the correlation rules for simple organic molecules may not be valid as a criterion of bond type in organometallic compounds. The relative position of a proton resonance at a constant applied frequency depends on the extent to which it is shielded from the field by the local magnetic fields produced by the induced motions of the electrons around it. In an olefin group there appears to be a paramagnetic contribution to the proton-shielding from the π-electrons (ref. 13), and if the π-electrons are involved in bonding to a metal atom this contribution could be altered so as to make the resonances of protons on *sp*^{2}-hybridised carbon atoms appear at higher fields than in simple olefins. In several compounds which contain non-conjugated olefin molecules bonded to metal atoms, we have observed (Table 4) that the resonance lines of protons in the " olefin " groups do not always appear in the olefin region, as has already been reported in the compounds π-cyclopentadienyl(cyclopentadiene)rhenium dicarbonyl and its reduced derivative.[14] In metal derivatives of conjugated olefins, such as those of cycloheptatriene and those discussed in the present paper, only some of the normal olefinic proton resonances of the parent olefin are shifted to higher fields, which may indicate that the π-electrons are localised between certain carbon atoms and not as much delocalised as was suggested previously.[15] However, the shifts cannot be interpreted solely in terms of π-electrons, since it is probable that there is an additional contribution to the shielding from

TABLE 4. *Nuclear magnetic resonance data at* 40 *Mc./sec.*

Compound	Band posn. (p.p.m. rel. to $Si(CH_3)_4$	Rel. int.	Structure; splitting (c.p.s.)	Assignment
Butadiene (liquid)	$\sim$6·2	2	Complex quadruplet	Centre =CH–, $C_{(2)}$, $C_{(3)}$
	$\sim$5·11	4	Complex triplet	End =CH_2 $C_{(1)}$, $C_{(4)}$
Butadiene-iron tricarbonyl [12]	5·28	2	Symmetrical complex triplet; 6·9	$C_{(2)}$ $C_{(3)}$ protons
	1·68	2	Double: 4·1; 2·5	$C_{(1)}$ and $C_{(4)}$ protons
	0·22	2	Double doublet: 4·1; 2·1	
1,2,3,4-Tetraphenylbutadiene-iron tricarbonyl	7·16	20	Doublet ($\sim$10)	Phenyl protons
	6·92			
	2·38	2	Singlet (width 3)	$C_{(1)}$ and $C_{(4)}$ protons
Norbornadiene	6·62	4	Triplet	Olefin protons
	3·50	2	Septuplet	Tertiary protons
	1·95	2	Triplet	Bridging CH_2 group
Norbornadiene-iron tricarbonyl [a]	3·12	$\sim$6	Complex, doublet + unresolved line	" Olefin " and tertiary protons
	1·25	2	Triplet	Bridging CH_2 group
Norbornadiene-rhodium chloride dimer [b]	3·88	$\sim$6	Weak doublet	" Olefin " and tertiary protons
	1·20	$\sim$2	Weak singlet, unresolved	Bridging CH_2 group
Cyclo-octa-1,5-diene	5·5	4	Unresolved, singlet	Olefin protons
	2·25	8	Quadruplet	Aliphatic CH_2 protons
Cyclo-octa-1,5-diene-rhodium dimer [c]	4·25	$\sim$4	Unresolved singlet	" Olefin " protons
	2·17	$\sim$8	Broad quadruplet	? Aliphatic protons
Cyclopentadiene	6·38	4	Complex multiplet	Protons on C at posns. 2—5
	2·79	2	Complex pentuplet	Protons of CH_2 group
$(C_5H_5)(C_5H_6)Re(CO_2)$ [11]	$\sim$6·9	1	Complex band	Protons on non-bonded double bond
	$\sim$5·9	1	Complex band	
	$\sim$5·6	5	Singlet	C_5H_5 protons
	$\sim$4·7	1	Doublet ($\sim$7)	Protons of olefin group bonded to metal
	$\sim$4·3	1	Complex band	
	$\sim$3·3	2	Complex	Protons of CH_2 group
$(C_5H_5)(C_5H_8)Re(CO)_2$ [11]	$\sim$6·1	5	Singlet	C_5H_5 protons
	$\sim$4·05	2	Single band	Protons of bonded olefin group
	$\sim$2·7	4	Complex	Protons of 3-CH_2 and 5-CH_2
	$\sim$1·2	2	Complex	Protons of 4-CH_2

[a] Burton, Green, Abel, and Wilkinson, *Chem. and Ind.*, 1958, 1592. [b] Abel, Bennett, and Wilkinson, unpublished work. [c] Chatt and Venanzi, *J.*, 1957, 4735.

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[13] Jackman, personal communication.

[14] Green and Wilkinson, *J.*, 1958, 4314.

[15] Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.

the electrons of the metal atom, and as yet there are insufficient data for organometallic compounds of known structure to allow definite conclusions concerning the bonding to be made. Hence in either of the two types of compound the infrared and nuclear magnetic resonance data suggest different structures, but they can be reconciled on the basis of structure A or B rather than C because it is felt that at present infrared must be preferred to nuclear magnetic resonance data as a criterion of bond type.

The extent to which the diene of structure A is delocalised (as in B) is not determined by the spectroscopic evidence. Since the bond order of the 2,3-bond in butadiene and probably also that of the 3,4-bond in cyclopentadiene is essentially that of a single bond, the bonding in structure A can be roughly pictured in the manner described [16] for the bonding between unconjugated olefins and metal atoms, in which it is believed that there is a feedback of electrons from filled *d*-orbitals of the metal to the anti-bonding orbitals on the carbon atoms of the double bond. For the conjugated olefins an additional bonding could result from a further overlap between the resultant (d–p_π*) orbitals at the adjacent carbon atoms $C_{(3)}$ and $C_{(4)}$.

It is not at first evident that a large group such as CCl_3 can replace the hydrogen atom H_α whose proximity to the metal atom is suggested above as the cause of the unusual behaviour of the C–H stretching frequency. However, the cyclopentadiene group is not necessarily planar or parallel to the π-cyclopentadienyl ring, and rough calculations based on simple models for the structure show that large groups substituted in this position on $C_{(1)}$ can be accommodated by a bending of the 1,2- and/or 1,5-bonds, or by a pivoting of the whole C_5 ring, although such groups may not be able to rotate freely about the $C_{(1)}$–C axis.

[Added in proof]: recently, in this laboratory, Dr. R. Watterson has prepared the compound π-C_5H_5(1-*endo*-CF_3·C_5H_5)Co by the reaction between cobaltocene and trifluoromethyl iodide. It is a blood-red oil at ~20° and decomposes only slowly in air. Its proton resonance spectrum is very similar to that of the trichloromethyl derivative, with lines at 5·01 p.p.m. (triple, $H_{(3)} + H_{(4)}$), 4·48 p.p.m. (single, C_5H_5), and 2·34 p.p.m. (quadruple, $H_{(2)} + H_{(5)}$). However, the resonance of H_β, which is centred at 3·08 p.p.m., shows an additional splitting from the three equivalent fluorine (^{19}F) nuclei in the CF_3 group, and appears as a symmetrical quartet (1 : 3 : 3 : 1) of triplets (1 : 2 : 1). The separation between components is 7·4 ± 0·2 c.p.s. in the quartet and 2·4 ± 0·2 c.p.s. in each triplet. The fluorine resonance, which is split by H_β, is a doublet with the same separation (7·3 ± 0·2 c.p.s.).

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College. Preparations, reaction, and chromatographic separations were carried out in nitrogen or in a vacuum; solvents were degassed before use. Light petroleum is " AnalaR " material of b. p. <40°.

π-Cyclopentadienyl(cyclopentadiene)rhodium.—Preparation. (*A*) Rhodium trichloride trihydrate (7 g., 0·03 mole) (no product was obtained from the insoluble anhydrous halide) was added to a freshly prepared solution of sodiocyclopentadiene [1] (0·2 mol.) in tetrahydrofuran (250 ml.) under nitrogen; the mixture was stirred under reflux for 2 hr. Solid sodium borohydride (5 g.) was added in small portions and after 2 hours' refluxing the solvent was removed. Sublimation from the dry reaction mixture in a vacuum at 130° gave orange-yellow crystals.

Without addition of the borohydride the material was obtained in much lower yield and contaminated with oil which was not readily removed. The product from the borohydride reaction was purified by chromatography on alumina with light petroleum as eluant, and by crystallisation from isopentane (yield ~40% based on rhodium) [Found: C, 51·4; H, 5·0; Rh, 44·3%; *M* (isopiestic in ether with azobenzene as standard) 233, (ebullioscopic in benzene) 233. $C_{10}H_{11}Rh$ requires C, 51·3; H, 4·7; Rh, 43·95%; *M*, 234·1].

(*B*) A solution of rhodicenium chloride [6] (0·5 g.) was evaporated to dryness in a vacuum and the residue was dissolved in 80% ethanol (5 ml.). Sodium borohydride (~2 g.) was added in portions; after ½ hr. the solvent was removed and the oily residue extracted with light

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[16] Dewar, *Bull. Soc. chim. France*, 1951, **18**, C71; Chatt and Duncanson, *J.*, 1953, 2939.

petroleum. After drying, the solution was evaporated and the product recovered by vacuum-sublimation in ~80% yield.

Properties. The compound decomposes in air, only about 50% being recoverable after 2 days. It is soluble in benzene, light petroleum, and similar organic solvents; these solutions decompose within a few hours in air, and even in absence of air the benzene solutions darken in a few days, presumably owing to photochemical decomposition. The compound has a strong camphoraceous odour and readily sublimes in a vacuum at 50°. It is stable indefinitely in absence of air.

In carbon tetrachloride solution, decomposition sets in within a few minutes; infrared spectra show that chloroform and one or more olefins are formed. The precipitate obtained on treatment with water or dilute acids gives a solution of the rhodicenium ion. Carbon disulphide solutions also decompose quite rapidly, but the products have not been studied. With carbon monoxide at 100°/250 atm. extensive decomposition occurs.

With 3N-hydrochloric acid (5 ml.) the compound (7·755 mg.) gave 218 ml. of gas (at N.T.P.). Of this 50% was hydrogen. The infrared spectrum of the remainder showed peaks at 3080m, 2950s, 2870s, 1625m, 1458m, 1447m, 1345w, 1287w, 1215w, 1060w, 1047m, 1030m, 918w, 896m, 708m, 693s, 675m, among which bands due to C=C, $=CH_2$, and $-CH=CH_2$ groups can be recognised. Mass-spectrography showed that the main constituent had mass 68; a trace (0·2%) of butenes was also present.

π-Cyclopentadienyl(cyclopentadiene)cobalt.—Anhydrous cobalticenium tribromide (5 g.) (prepared in the same way as the methyl derivative below but from sodiocyclopentadiene [1]) in 1,2-dimethoxyethane (150 ml.) was treated with an excess of sodium borohydride (5 g.) in small portions with stirring. Hydrogen was evolved and a green coating formed on the sodium borohydride (probably cobalticenium borohydride). On warming to 60°, or on addition of water (2 ml.), the mixture became deep wine-red. After 1 hr., the solution was filtered and the residue washed with the ether. (If the solution is not filtered at this stage, sublimation of the dried mixture gives a high yield of the purple-black cobaltocene; reduction of the cobalticenium ion with lithium aluminium hydride in this way has previously been shown to give cobaltocene.[17]) The filtrate was reduced to a few ml. in a vacuum and extracted with light petroleum. This solution was concentrated and the product separated on a 20-cm. alumina column. The first red band eluted by light petroleum was evaporated and the residue sublimed in a vacuum to a probe at −70° to give the product (yield 80%) [Found: C, 63·0; H, 6·2%; *M* (ebullioscopic in benzene), 193. $C_{10}H_{11}Co$ requires C, 63·2; H, 5·8%; *M*, 190]. The compound is less stable than the rhodium analogue. It can be handled in air only for a few minutes and in organic solvents rapidly decomposes on exposure to air; even degassed solutions in organic solvents show notable decomposition within a few hours. The compound is more volatile than the rhodium compound and has a similar odour. The reactions with aqueous acid and carbon tetrachloride are similar to those of the rhodium analogue.

The Deutero-compound, π-$C_5H_5(C_5H_5D)Co$.—To a solution of lithium aluminium deuteride (0·2 g.) (Metal Hydrides Inc., Beverley, Mass.) was added solid anhydrous cobalticenium chloride in small portions until no effervescence occurred. The product was isolated as above (yield, ~80% based on $LiAlD_4$). An estimate of the isotopic purity by infrared measurements gave over 90% deuterium.

The anhydrous cobalticenium chloride was obtained by evaporating hydrochloric acid solutions on a steam-bath to give a dark green oil. This was triturated with tetrahydrofuran, and the residual crystals were then dissolved in and crystallised from tetrahydrofuran; it forms large pale green crystals and is as an etherate.

Equilibration of $C_{10}H_{11}Co$ *with* $LiAlD_4$.—The cobalt compound (~0·05 g.) was set aside in tetrahydrofuran solution at 25° with an excess of $LiAlD_4$. After 3 hr. the solvent was removed and the compound extracted and purified. The infrared spectrum was identical with that of the starting material.

Preparation of 1,1′-*Dimethylcobalticenium Salts.*—To sodiomethylcyclopentadiene [18] (1·0 mole) in tetrahydrofuran (300 ml.) was added anhydrous cobaltous chloride (0·5 mole). After 2 hours' stirring at the b. p. the solvent was removed and the residue treated with 1 : 1 hydrochloric acid (100 ml.). The yellow aqueous layer was separated, washed twice with ether, and filtered. To a portion of the filtrate was added a solution of Reinecke's

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[17] Birmingham, Fischer, and Wilkinson, *Naturwiss.*, 1955, **42**, 96.
[18] Reynolds and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86.

salt; the pale pink *salt* precipitated was centrifuged, washed, and dried {Found: C, 34·7; H, 3·6. $[C_{12}H_{14}Co][Cr(NH_3)_2(SCN)_4],H_2O$ requires C, 34·6; H, 3·9%}. The remainder of the solution was treated with bromine water and the precipitated tribromide was removed and dried at 80° in a vacuum to leave a pale yellow powder.

π-Methylcyclopentadienyl(methylcyclopentadiene)cobalt.—This *compound* was prepared from the tribromide as for the unsubstituted compound. On evaporation of the eluate from the chromatographic column, a deep red oil was obtained. On an 80-cm. alumina column, further treatment gave only a single sharp elution band. The oil melted sharply at ~−5°; it was purified by vacuum-distillation (Found: C, 65·1; H, 6·8. $C_{12}H_{15}Co$ requires C, 66·0; H, 6·9%).

*π-Cyclopentadienyl(*1-endo-*methylcyclopentadiene)cobalt.*—Cobaltocene [1] (3 g.) and methyl iodide (5 ml.) were heated in a sealed tube at 80° for 2 hr. The excess of methyl iodide was then removed and the residue extracted with a 7 : 3 mixture of light petroleum (b. p. 40—60°) and anhydrous ether. The *product* was chromatographed twice with the petroleum–ether mixture as eluant; it was finally distilled at $40°/10^{-3}$ mm. to an ice-cooled probe to give a red oil (yield, ~30% based on $C_{10}H_{10}Co$; theor., 50%) [Found: C, 64·7; H, 6·4%; *M* (ebullioscopic in benzene), 204. $C_{11}H_{13}Co$ requires C, 64·8; H, 6·7%; *M*, 204·6].

Reaction of cobaltocene with methyl iodide was very slow at room temperature, no product being isolated after 12 hr., and ultraviolet irradiation did not increase the reaction rate.

The compound is readily soluble in all organic solvents, but the solutions and the pure compound decompose in air fairly rapidly to give traces of paramagnetic species, as shown by loss of nuclear magnetic resonance resolution.

*π-Cyclopentadienyl(*1-endo-*trichloromethylcyclopentadiene)cobalt.*—Cobaltocene (3 g.) was treated with carbon tetrachloride (5 ml.); after 1 hr. the tetrachloride was removed and the residue extracted with light petroleum (b. p. 40—60°). After chromatography with light petroleum–ether the eluate was evaporated and the *product* (45% based on $C_{10}H_{10}Co$) crystallised at low temperatures from isopentane [Found: C, 43·2; H, 3·7%; *M* (ebullioscopic in benzene), 306. $C_{11}H_{10}Cl_3Co$ requires C, 42·9; H, 3·2%; *M*, 307·6]. It is considerably more stable than its methyl analogue and is freely soluble in organic solvents; carbon tetrachloride solutions are stable in air for 24 hr.

*π-Cyclopentadienyl(*1-endo-*dichloromethylcyclopentadiene)cobalt.*—π-Cyclopentadienyl-(1-*endo*-trichloromethylcyclopentadiene)cobalt (0·5 g.) in tetrahydrofuran was treated with an excess of lithium aluminium hydride (1·0 g.). After ½ hr. a large excess of water was carefully added to the mixture, and the solution extracted with light petroleum. The orange petroleum layer was separated, washed thoroughly with water, dried ($CaCl_2$), and evaporated to a small volume which was chromatographed in ether–petroleum on a 3 ft. alumina column. The eluate was evaporated and the *product* (75%) crystallised at low temperatures from isopentane [Found: C, 48·6; H, 4·3; Cl, 26·1%; *M* (ebullioscopic in benzene), 278·7. $C_{11}H_{11}Cl_2Co$ requires C, 48·4; H, 4·1; Cl, 26·0%; *M*, 273]. It is very similar to the 1-*endo*-trichloromethyl analogue.

Infrared Spectra.—Measurements were made with a Perkin–Elmer Model 21 spectrometer with sodium chloride and calcium fluoride optics. High-resolution spectra in the 2500—3200 $cm.^{-1}$ region were obtained by using a modified Grubb–Parsons instrument with lithium fluoride optics. The compounds were run in carbon tetrachloride and carbon disulphide; although the $C_{10}H_{11}M$ compounds decompose in these solvents, consecutive spectra taken in a 10-minute period immediately after preparation of the solution were the same. Spectra were also taken in tetrachloroethylene and in 1,1,2-trichlorotrifluoroethane which do not react as rapidly as the above solvents. The spectrum of the methyl derivatives was taken on a thin film of the pure liquid.

Details of the spectra (excluding bands listed in Table 2) are:

π-$C_5H_5(C_5H_6)Co$ (in CS_2 and C_2Cl_4), 3880w, 3720vw, 2440w, 2380w, 1737w, 1700w, 1664w, 1609w, 1518m, 1443w, 1412w, 1384w, 1370w, 1350w, 1330w, 1240m, 1107m (π-C_5H_5), 1066m, 1037w, 1006s (π-C_5H_5), 993m, 984m, 920m, 810s (π-C_5H_5), 780s.

π-$C_5H_5(C_5H_5D)Co$ (in CS_2 and C_2Cl_4), 3900w, 1964w, 1945w, 1775w, 1742w, 1705w, 1665w, 1590w, 1426w, 1412m, 1372w, 1336m, 1301m, 1251w, 1245w, 1216m, 1105m (π-C_5H_5), 1070s, 1046m, 1010s (π-C_5H_5), 996s.

π-$C_5H_5(C_5H_6)Rh$ (in CS_2 and $CF_2Cl{\cdot}Cl_2F$), 3860w, 2462w, 2425w, 2040w, 1820w, 1765w, 1665m, 1384m, 1372m, 1345m, 1335m, 1252m, 1234m, 1105s (π-C_5H_5), 1065s, 1034m, 1006s (π-C_5H_5), 995s, 923m, 898w, 865m, 828vw, 822s (π-C_5H_5), 785vs.

π-Me·C_5H_4(Me·C_5H_5)Co (pure liquid and in CS_2), 3860w, 3095m, 3056m, 2935s, 2885s, 2720s, 2050vw, 1474m, 1445s, 1416m, 1374m, 1363m, 1340w, 1264m, 1230w, 1188w, 1107w, 1035s, 998m, 1067w, 934w, 920m, 780m.

π-C_5H_5(1-*endo*-CH_3·C_5H_5)Co (pure liquid and in CS_2), 3850w, 2760vw, 1764vw, 1659vw, 1612vw, 1587vw, 1451m (CH_3 def.), 1415m, 1385w (CH_3 def.), 1355w, 1342w, 1317m, 1272vw, 1254w, 1126m, 1100m (π-C_5H_5), 1055w, 1036m, 1024m (π-C_5H_5), 929vw, 917vw, 868w, 858w, 825s (π-C_5H_5), 790vw, 726vw.

π-C_5H_5(1-*endo*-$CHCl_2$·C_5H_5)Co (in CCl_4 and CS_2), 3100m, 3080m, 2962s, 2946s, 2880m, 1752w, 1710w, 1377w, 1348w, 1330w, 1314w, 1262vw, 1220m, 1187w, 1105w (π-C_5H_5), 1065w, 1042w, 1009m, 996m (π-C_5H_5), 823s, 806s (π-C_5H_5), 794s, 739m, 725w, 698m.

π-C_5H_5(1-*endo*-CCl_3·C_5H_5)Co (in CCl_4 and CS_2), 1872w, 1788w, 1741w, 1692w, 1640w, 1577w, 1385w, 1380w, 1351w, 1343w, 1292m, 1214m, 1166m (π-C_5H_5), 1072m, 1049m, 1010s, 1001s (π-C_5H_5), 912s, 1844s, 863s (π-C_5H_5), 757m, 732s.

Nuclear Magnetic Resonance Spectra.—The spectra at 40 Mc./sec. were obtained on a Varian Associates Model 4300B spectrometer; spectra at 60 Mc./sec. were obtained on a similar instrument through the courtesy of the Varian staff at the Brussels World Exhibition. Measurements were made at 22° ± 2° in strong solutions in benzene and cyclohexane contained in spinning tubes of 5 mm. outside diameter. A small amount of tetramethylsilane was added to each sample as an internal reference. Line positions were measured by the conventional side-band technique.

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