863. *π-Cyclohexadienyl Compounds of Manganese, Rhenium, Iron, and Ruthenium.*

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The interaction of salts of arene-metal cations with sodium borohydride or lithium aluminium hydride has given π-cyclohexadienyl derivatives of rhenium, iron, and ruthenium. In the case of ruthenium the isomer of the di-π-cyclohexadienyl compound $(\pi\text{-}C_6H_7)_2Ru$, *viz.*, benzenecyclohexa-1,3-dieneruthenium, $C_6H_6RuC_6H_8$, is also obtained. The interaction of phenyl-lithium with arene-metal salts gives 1-*endo*-π-cyclohexadienyl derivatives such as π-(1-*endo*-$C_6H_5{\cdot}C_6H_6)_2Ru$.

The high-resolution nuclear magnetic resonance spectra of the compounds, and of $\pi\text{-}C_6H_7Fe(CO)_3BF_4$, have been measured and are discussed.

FOLLOWING the recognition that the partially delocalized π-electron system of the carbanion $C_6H_7^-$ can be stabilized by bonding to a metal atom as in $\pi\text{-}C_6H_7Mn(CO)_3$ and related compounds,[1] we have attempted to prepare similar compounds of other transition metals [2] by the same method, *viz.*, the interaction of salts of arene-metal cations with hydride ion, *e.g.*,

$$(C_6H_6)_2Re^+ + H^- = C_6H_6(\pi\text{-}C_6H_7)Re$$

and also with phenyl-lithium, *e.g.*,

$$(C_6H_6)_2Ru(ClO_4)_2 + 2C_6H_5Li = \pi\text{-}(C_6H_5{\cdot}C_6H_6)_2Ru + 2LiClO_4$$

The new compounds prepared in the present work are:

$$\pi\text{-}(C_6H_5{\cdot}C_6H_6)Mn(CO)_3(\text{I}),\ C_6H_6(\pi\text{-}C_6H_7)Re(\text{I}),\ \pi\text{-}(C_6H_5{\cdot}C_6H_6)(\pi\text{-}C_5H_5)Fe(\text{II}),$$
$$\pi\text{-}(C_6H_5{\cdot}C_6H_6)_2Ru(\text{II}),\ C_6H_6(C_6H_8)Ru(0),\ (\pi\text{-}C_6H_7)_2Ru(\text{II}).$$

The compound previously formulated [3] as $C_6H_6(C_5H_6)Fe(0)$ on the basis of its infrared spectrum and its high-resolution proton resonance spectrum, at 40 Mc./sec., has been reformulated as $\pi\text{-}C_6H_7(\pi\text{-}C_5H_5)Fe(\text{II})$ on the basis of a more accurate determination of its proton resonance spectrum, measured at 56·45 Mc./sec.

The phenyl-cyclohexadienyl derivatives are much less reactive than the corresponding unsubstituted cyclohexadienyl compounds, presumably because the reactive hydrogen, believed to be the H_α of (I) [1,3] is replaced by the phenyl group (1-*endo*). Thus they are quite stable in air and carbon tetrachloride solution. They do not sublime.

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[1] Winkaus, Pratt, and Wilkinson, *J.*, 1961, 3807.
[2] Jones and Wilkinson, *Chem. and Ind.*, 1961, 1408.
[3] Green, Pratt, and Wilkinson, *J.*, 1960, 989.

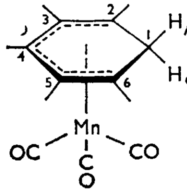
The reduction of bisbenzeneruthenium perchlorate with sodium borohydride in tetrahydrofuran gives a yellow-green compound which is rapidly decomposed in carbon tetrachloride solution and in air. The proton resonance spectrum of this compound is very similar to that of tricarbonylcyclohexa-1,3-dieneiron[4] and it is clearly benzenecyclohexa-1,3-dieneruthenium. Reduction of the perchlorate with lithium aluminium hydride in ethylene glycol dimethyl ether gives a different product, namely, yellow crystals (from ligroin), the analysis of which corresponds to the empirical formula $C_{12}H_{14}Ru$. The proton resonance spectrum of this material clearly shows that it is mainly the cyclohexa-1,3-diene derivative (*ca.* 75%) and that the remainder is the isomeric di-(π-cyclohexadienyl)-ruthenium, $(\pi\text{-}C_6H_7)_2Ru$.

Attempts to separate the latter in a pure state have failed; crystallization gives little if any separation, and the products decompose on chromatographic columns of alumina, even with rigorous exclusion of air. When the mixture is heated *in vacuo* at temperatures up to about 100° there is no apparent change in the solid but the product which condenses on a cold probe is exclusively the greenish-yellow cyclohexa-1,3-diene complex. Reduction of the perchlorate $(C_6H_6)_2Ru(ClO_4)_2$ with lithium aluminium deuteride, and sublimation of the resulting product, gave a mixture of isomers and the proton resonance spectrum was not useful.

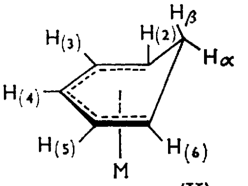
An attempt was made to remove one hydrogen atom from the cyclohexa-1,3-diene complex by using triphenylmethyl tetrafluoroborate in methylene chloride. The product was exclusively $(C_6H_6)_2Ru(BF_4)_2$ even when an excess of the olefin complex was present.

Infrared and High-resolution Nuclear Magnetic Resonance Spectra.—Details of the spectra are given in the Experimental section.

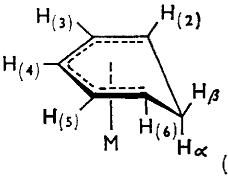
The characteristics of the infrared spectra of the π-cyclohexadienyl compounds in the 2750—3100 cm.$^{-1}$ region have been discussed before.[1] The main features are a band of medium intensity at *ca.* 3080 cm.$^{-1}$ (*ca.* 3120 for the parent arene-cation), and the appearance of bands below 3000 cm.$^{-1}$ at *ca.* 2970 and *ca.* 2800 cm.$^{-1}$, assigned to H_β and H_α, respectively. The latter band is exceptionally strong, as in the cyclopentadiene compounds.[3] The main difference in the infrared spectra of $C_6H_6RuC_6H_8$ and $(\pi\text{-}C_6H_7)_2Ru$ is the presence in the latter of an exceedingly strong band at 2772 cm.$^{-1}$. It is curious that the solid-state spectrum of the salt $\pi\text{-}C_6H_7Fe(CO)_3{}^+BF_4{}^-$ does not show this strong band at *ca.* 2800 cm.$^{-1}$; its absence may be attributable, in a way not yet understood, to the charge on the complex cation.



(I)



(II)



(III)

There are differences in the 800—1500 cm.$^{-1}$ region between π-cyclohexadienyl and π-cyclopentadienyl compounds. Characteristic absorptions of the C_5H_5 ring occur at 1420—1430m, 1360w, 1100w, 1005—1015m, and 800—850vs. Characteristic absorptions of the C_6H_7 ring occur at 1450—1490ms, 1288—1307m, and 1045—1052ms. $\pi\text{-}C_6H_7(\pi\text{-}C_5H_5)Fe$ absorbs in the regions 1483m, 1290s, and 1055s. The infrared data are thus in good agreement with the present formulation of this compound.

The high-resolution proton resonance spectrum of $\pi\text{-}C_6H_7Mn(CO)_3$ has been interpreted previously.[1] The spectrum of $\pi\text{-}C_6H_7Fe(CO)_3BF_4$ provides a simpler picture of the line patterns typical of a cyclohexadienyl grouping since the bands are more widely separated.

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[4] Burton, Pratt, and Wilkinson, *J.*, 1961, 594.

The complex high-field line in π-$C_6H_7Mn(CO)_3$ which was assigned to H_α, H_β, $H_{(2)}$, and $H_{(6)}$ is separated into three distinct components in π-$C_6H_7Fe(CO)_3BF_4$.

One of the typical features of the spectra of the π-C_6H_6X (X = 1-*endo*-D,C_6H_5) grouping is the presence of three "triplet" bands with relative intensities 1 : 2 : 2, the triplet of unit intensity occurring at lowest field. These bands are assigned, as for π-$C_6H_7Mn(CO)_3$, to $H_{(4)}$, $H_{(3)}H_{(5)}$, and $H_{(2)}H_{(6)}$, respectively, *i.e.*, to the protons attached to the π-bonded part of the cyclohexadienyl ring. The component splittings in each band, due to coupling with adjacent protons, are nearly the same for all the compounds.

In π-C_6H_7 compounds, H_α and H_β are approximately an AB pair and would be expected to give rise to a quartet. In π-$C_6H_7Fe(CO)_3BF_4$ one of these protons gives two sharp bands, at τ 7·85 and 8·11, and the other gives two "triplets," at τ 7·09 and 6·86. The difference in structure of the bands suggests that H_α and H_β are coupled in different ways to $H_{(2)}$ and $H_{(6)}$. This difference can be explained if we assume that the π-C_6H_7 ring is not completely planar but that the methylene carbon, $C_{(1)}$, is bent out of the plane of the other carbons. The methylene group may point either away from (as in II) or towards (as in III) the metal atom. If we consider (III) with the protons as labelled, then H_α will make a dihedral angle of *ca.* 90° with $H_{(2)}$ and $H_{(6)}$ and, as is found for simple organic molecules, there should be no coupling between them. H_β, however, will make a dihedral angle of *ca.* 30° with $H_{(2)}$ and $H_{(6)}$, and these protons would therefore be expected to couple. This is observed, and in the case of π-$C_6H_7Fe(CO)_3BF_4$ the coupling is of the expected order (6·5 c./sec.).[5]

The compounds (π-$C_6H_6D)Mn(CO)_3$, π-$(C_6H_5{\cdot}C_6H_6)(\pi$-$C_5H_5)Fe$, π-$(C_6H_5{\cdot}C_6H_6)Mn(CO)_3$, and π-$(C_6H_5{\cdot}C_6H_6)_2Ru$ do not have a band assignable as above to H_α, but show a complex band at high field (in some cases not separated from the band due to $H_{(2)}$ and $H_{(6)}$) which can be assigned to H_β. It seems reasonable to assume that in these compounds and the corresponding unsubstituted derivatives the methylene carbon is as in (III).

For the rhenium compound, $C_6H_6(\pi$-$C_6H_7)Re$, the general features of the proton resonance spectrum are similar to those of the other compounds except that the bands due to H_α and H_β are apparently interchanged. This could be explained on the basis of (II), where H_α is now "*cis*" to $H_{(2)}$ and $H_{(6)}$ and H_β is "*trans*" to $H_{(2)}$ and $H_{(6)}$, resulting in a reversal of the couplings of H_α and H_β with $H_{(2)}$ and $H_{(6)}$.

The proton resonance spectrum of the compound obtained by reduction of the salt $(C_5H_6)_2Ru(ClO_4)_2$ with sodium borohydride resembles that of tricarbonylcyclohexa-1,3-dieneiron and is satisfactorily interpreted on the basis of the structure $C_6H_6RuC_6H_8$.

The spectrum, in benzene solution, of the mixture obtained by lithium aluminium hydride reduction of $(C_6H_6)_2Ru(ClO_4)_2$ contains bands identical with those for $C_6H_6RuC_6H_8$, but has additional bands which are assigned to the compound $(\pi$-$C_6H_7)_2Ru$, present in the mixture in *ca.* 25% abundance.

The spectrum of the compound formulated as $C_6H_6FeC_5H_6$ on the basis of data at 40 Mc./sec. has been re-examined at 56·4 Mc./sec. and the compound is reformulated as π-$C_6H_7(\pi$-$C_5H_5)Fe$. The low-field triple triplet of intensity 1 can be assigned to H_4. Had the compound been benzenecyclopentadieneiron(0) this band would have had intensity 2 and the structure of an overlapping double doublet, *i.e.*, a "triplet" assignable to the central diene protons of the C_5H_6 ring. The band at τ 5·93 (benzene solution) which has side structure and is of intensity 7 we now assign to the five π-cyclopentadienyl protons plus $H_{(3)} + H_{(5)}$. This band would have been a singlet of intensity 6 had the compound been $C_6H_6FeC_5H_6$, assignable to the benzene protons.

We have also reduced the π-cyclopentadienylmesityleneiron(II) cation with lithium aluminium hydride in ethylene glycol dimethyl ether; but although three isomers could be produced we have been unable to separate them, and the proton resonance data are ambiguous.

[5] Jackman, personal communication; see also Conroy, in "Advances in Organic Chemistry," Interscience Publ., Inc., New York, London, 1960, Vol. II, p. 311.

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College.

Dibenzeneruthenium(II) *Perchlorate.*—The cation (mesitylene)$_2$Ru^{2+} has been reported and the benzene analogue mentioned, although experimental details and analytical data were not provided for the latter.[6] We have prepared the perchlorate as follows. A mixture of anhydrous ruthenium trichloride (4·15 g.), finely ground anhydrous aluminium trichloride (6·6 g.), dry aluminium powder (1·0 g.), and benzene (20 ml.) was heated at 140° for 12 hr. in a sealed tube. The tube was cooled and opened and the contents were carefully hydrolysed with a mixture of ice (30 g.), water (100 ml.), and methanol (50 ml.). It was not necessary to exclude air during this and subsequent operations. After 5 hr. the mixture was filtered through acid-washed kieselguhr. The clear yellow filtrate gave precipitates with large anions. An excess of perchloric acid (30%, *ca.* 30 ml.) was added and the pale yellow precipitate collected and washed with water, methanol, and ether, and dried *in vacuo* (4 g., 45% based on $RuCl_3$) (Found: C, 32·0; H, 2·8. $C_{12}H_{12}Cl_2O_8Ru$ requires C, 31·5; H, 2·6%). The *salt* is stable in air but explodes at high temperatures.

Benzenecyclohexa-1,3-*dieneruthenium*(0).—To dibenzeneruthenium perchlorate (4 g.) suspended in ethylene glycol dimethyl ether (50 ml.) was added, in small portions during *ca.* 10 min., sodium borohydride (*ca.* 5 g.). After 12 hr., light petroleum (b. p. 60—80°) (100 ml.) was added and the organic phase washed with water (3 × 50 ml.), dried ($CaCl_2$), and filtered, the solvent being then removed *in vacuo*. The residue was purified by sublimation to give green crystals of the *compound*, m. p. 114—115° [0·5 g., 23% based on $(C_6H_6)_2Ru(ClO_4)_2$] [Found: C, 55·4; H, 5·3%; *M* (ebullioscopic in benzene), 250. $C_{12}H_{14}Ru$ requires C, 55·5; H, 5·4%; *M*, 270]. The compound is completely decomposed in air in 2 hr. It is soluble in all common organic solvents, and the solutions are air sensitive. It decomposes rapidly (30 min.) in carbon tetrachloride solution in the absence of air.

When the above preparation was repeated with lithium aluminium hydride instead of sodium borohydride, or was carried out with the latter reagent in moist tetrahydrofuran containing lithium chloride (*ca.* 2 g.), the petroleum phase, after it had been washed with water (3 × 50 ml.) and dried ($CaCl_2$), gave yellow crystals (Found: C, 55·8; H, 5·7. Calc. for $C_{12}H_{14}Ru$: C, 55·5; H, 5·4%). This substance is a mixture of di-(π-cyclohexadienyl)-ruthenium(II) and $C_6H_6(C_6H_8)Ru(0)$, as shown by spectroscopic studies.

Benzenecyclohexa-1,3-dieneruthenium in methylene chloride was treated with either a deficiency or an excess of triphenylmethyl tetrafluoroborate. The yellow crystalline product was in both cases *dibenzeneruthenium*(II) *tetrafluoroborate* (Found: C, 33·0; H, 3·0; F, 35·8. $C_{12}H_{12}B_2F_8Ru$ requires C, 33·4; H, 3·0; F, 35·0%).

Benzene-π-cyclohexadienylrhenium(I).—The dibenzenerhenium ion has been reported previously and characterised as the tetraphenylborate.[7] Although rhenium pentachloride was used previously, we have used the trichloride, and isolated the ion as the tri-iodide. These modifications give a slightly increased yield (4% in place of 2%); the reason for the low yields is not clear.

To the dibenzenerhenium tri-iodide (0·5 g.) suspended in ethylene glycol dimethyl ether (20 ml.) was added, during *ca.* 5 min. in small portions, lithium aluminium hydride (*ca.* 1·5 g.). After 2 hr. light petroleum (b. p. 60—80°) (20 ml.) was added and the mixture filtered, the solvent being then removed *in vacuo*. Sublimation of the residue at 100° *in vacuo* gave orange-red crystals of the *compound* (*ca.* 40 mg.), m. p. 195° (Found: C, 42·1; H, 4·3. $C_{12}H_{13}Ru$ requires C, 42·0; H, 3·6%).

The compound is unstable in air and decomposes immediately in carbon tetrachloride. It is soluble in petroleum and benzene.

π-Cyclohexadienyl-π-cyclopentadienyliron(II).—This compound was made as before.[3] The deuteride has been found to react with carbon tetrachloride to give both deutero- and hydrogenohalides such as deuteromethylene chloride and chloroform. Thus the specific behaviour observed for the cyclopentadiene compounds [3] where the reactive hydrogen atom appears to be the *endo*-substituted one, H_α, does not appear to hold in this case.

Tricarbonyl-π-cyclohexadienyliron(II) *Tetrafluoroborate.*—This was prepared by interaction

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[6] Fischer and Böttcher, *Z. anorg. Chem.*, 1957, **291**, 305.

[7] Fischer and Wirzmuller, *Chem. Ber.*, 1957, **90**, 1725.

of tricarbonylcyclohexa-1,3-dieneiron [made by interaction of cyclohexadiene with $Fe_3(CO)_{12}$ in refluxing light petroleum (b. p. 100—120°)] in methylene chloride solution with triphenyl tetrafluoroborate.[8,9]

Bis-(1-endo-*phenyl-π-cyclohexadienyl)ruthenium*(II).—The perchlorate $(C_6H_6)_2Ru(ClO_4)_2$ (2 g.) dissolved exothermally in an ether solution of phenyl-lithium (two-fold excess) at 0°. The resulting clear yellow solution was washed with water, dried ($CaCl_2$), and filtered, and the solvent was removed *in vacuo*. The residue was extracted with light petroleum (b. p. 30—40°) from which were obtained yellow crystals of the *compound*, m. p. 158° [0·5 g., *ca.* 25% based on $(C_6H_6)_2Ru(ClO_4)_2$] (Found: C, 69·9; H, 5·4. $C_{24}H_{22}Ru$ requires C, 69·9; H, 5·4%). The compound is stable in air and carbon tetrachloride solution for several days.

*Tricarbonyl-*1-endo-*phenyl-π-cyclohexadienylmanganese*(I).—This compound was prepared, in a similar manner to $\pi(C_6H_5{\cdot}C_6H_6)_2Ru$, from $C_6H_6Mn(CO)_3ClO_4$. Crystallization from light petroleum gave pale yellow crystals of the *compound* (30%), m. p. 110—112° (Found: C, 61·1; H, 4·1. $C_{15}H_{11}MnO_3$ requires C, 61·2; H, 4·1%). It decomposes very slowly (days) in air or in carbon tetrachloride solution.

1-endo-*Phenyl-π-cyclohexadienyl-π-cyclopentadienyliron*(II).—Benzene-π-cyclopentadienyliron(II) tribromide was slowly added to an excess (*ca.* two-fold) of phenyl-lithium in ether at 0°. After 0·5 hr. the solvent was removed *in vacuo* and the large amount of biphenyl produced in the reaction was sublimed at 40°/0·1 mm. on to a water-cooled probe. The residue was purified by chromatography on Brockmann grade 2 alumina, with light petroleum (b. p. 30—40°) as eluant. Removal of solvent from the main band left red crystals of the *compound* (*ca.* 30%), m. p. 157—158° (Found: C, 74·3; H, 6·2. $C_{17}H_{16}Fe$ requires C, 73·9; H, 5·8%). The compound is less stable in air than the phenyl-manganese and -ruthenium compounds.

Infrared Spectra.—A Perkin–Elmer model 21 instrument with calcium fluoride optics and a Perkin–Elmer Infracord instrument with sodium chloride optics were used. Spectra of neutral compounds were recorded in carbon tetrachloride and carbon disulphide solutions, and spectra of cations were recorded in Nujol and Fluorolube mulls.

$(C_6H_6)_2Ru(BF_4)_2$: 3123m, 2940vw, 1445m, 1282w, 1175sh, 1070vs, 1004sh,vs, 872m, 852m.

π-$C_6H_7Fe(CO)_3BF_4$: 3080m, 2910m, 2850w, 2115vs, 2053vs, (broad), 1453s, 1404m, 1306m, 1202w, 1260w, 1158sh, 1050vvs, 957m, 902w, 880w, 815w, 700w.

$C_6H_6(C_6H_8)Ru$: 3070m, 3030m, 2980s, 2928s, 2907m, 2883m, 2864s, 2830vs, 2770w, 1475w, 1425m, 1380w, 1312w, 1283w, 1250m, 1230w, 1175s, 1135w, 1103m, 1058w, 1025m, 1003s, 973s, 925m, 880w, 840m, 785s.

Mixture of $C_6H_6(C_6H_8)Ru$ and $(\pi$-$C_6H_7)_2Ru$: 3075m, 3050s, 2980s, 2925s, 2905sh, 2883m, 2860m, 2827s, 2772vs, 1474w, 1430m, 1380w, 1312w, 1283m, 1250m, 1220w, 1175s, 1130w, 1100w, 1055w, 1045m, 1025w, 1000s, 972s, 940w, 920m, 850m, 785s.

$C_6H_6(\pi$-$C_6H_7)Re$: 3026s, 2900w, 2850vw, 2750vs, 1488s, 1460w, 1420w, 1360w, 1288m, 1125m, 1047m, 995m, 965m, 870w, 810s, 785w.

π-$(C_6H_5{\cdot}C_6H_6)Mn(CO)_3$: 3910w, 3840w, 3026m (broad), 2970m, 2918m, 2864sh, 2420vw, 2045vs, 1936vs (broad), 1320m, 1387vw, 1272msh, 1258vs, 1175m (broad), 1149m, 1085s (broad), 1015vs (broad, shoulder at 1001vs), 978sh, 958m, 897w, 875vs, 797vs, 743s (broad), 688s, 667m, 648s.

π-$(C_6H_5C_6{\cdot}H_6)_2Ru$: 3050sh, 3033vs, 2940sh, 2890m, 1956sh, 1938w, 1872sh, 1858w, 1793w, 1755w,sh, 1708w, 1661w, 1500m, 1483m, 1440m, 1375w, 1309m, 1282sh, 1200s (broad), 1176m, 1127s, 1094m (broad), 1067s, 1026ms, 992vs, 957m, 930w, 897m, 860m, 829m, 805vs, 768s, 730ms, 690vs, 667m.

π-$(C_6H_5{\cdot}C_6H_6)(\pi$-$C_5H_5)Fe$: 3104sh, 3066sh, 3044s, 2875m, 1930vw, 1728vw, 1565s, 1470sh, 1455sh, 1435s, 1306vw, 1250m, 1170w, 1125w, 1105s, 1065w, 1027m, 997vs, 954w, 855m, 805vs, 730ms, 670m.

High-resolution Nuclear Magnetic Resonance Spectra.—Spectra were recorded at 56·45 Mc./sec. on a Varian instrument. Samples were measured in *ca.* 10% solutions (solvents in brackets) containing tetramethylsilane as reference. Line positions were determined by the side-band technique and are given in τ values. Splittings are accurate to *ca.* $\pm 0{\cdot}3$ c./sec.

π-$C_6H_7(\pi$-$C_5H_5)Fe$ (in benzene): 4·13, intensity 1, triple triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (5·6 c./sec.) and $H_{(2)} + H_{(6)}$ (1·5 c./sec.); 5·93, intensity 7, sharp with side structure, cyclopentadienyl protons plus $H_{(3)} + H_{(5)}$; 7·41 to 8·44, intensity 4, complex with nine main bands;

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[8] Fischer and Fischer, *Angew. Chem.*, 1960, **72**, 919.

[9] Dauben and Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 498.

at 8·23 and 8·44, two bands (intensity 1), H_α split by H_β (12·0 c./sec.), rest of bands H_β plus $H_{(2)} + H_{(6)}$.

$\pi\text{-}C_6H_6D(\pi\text{-}C_5H_5)Fe$ (in CCl_4): 4·01, intensity 1, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (4·8 c./sec.); 5·82, intensity 7, sharp with side structure, cyclopentadienyl protons plus $H_{(3)} + H_{(5)}$; 7·4 to 8·72, intensity 3, complex, with six main bands, H_β plus $H_{(2)} + H_{(6)}$.

$\pi\text{-}C_6H_7Fe(CO)_3BF_4$ (in liquid SO_2): 2·66, intensity 1, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (5·5 c./sec.); 4·08, intensity 2, " triplet " which is actually an overlapping double doublet, $H_{(3)} + H_{(5)}$ split by $H_{(4)}$ and $H_{(2)}$ or $H_{(6)}$ (6·0 c./sec.); 5·66, intensity 2, " triplet " which is actually an overlapping double doublet, $H_{(2)} + H_{(6)}$ split by H_β and $H_{(5)}$ or $H_{(5)}$ (6·0 c./sec.); 7·09 and 6·86, intensity 1, double triplet, H_β split by H_α (16·0 c./sec.) and $H_{(2)} + H_{(6)}$ (6·5 c./sec.), 7·85 and 8·11, intensity 1, two single sharp bands H_α split by H_β (15·0 c./sec.).

$C_6H_6(C_6H_8)Ru$ (in CCl_4): 5·0, intensity 6, sharp band, benzene protons; 5·48 to 5·6, intensity 2, central diene protons (A_2X_2 assumed) each split by other (3·4 c./sec.) and by nearest (5·6 c./sec.) and farthest (1·1 c./sec.) terminal protons; 7·16 to 7·31, intensity 2, broad unresolved band, terminal diene protons split by adjacent methylene protons and adjacent central diene protons; 8·73, intensity 4, " triplet " poorly resolved, methylene protons.

$C_6H_6(C_6H_8)Ru$ plus $(\pi\text{-}C_6H_7)_2Ru$ (in benzene): assigned for mixture in 3 : 1 ratio, respectively. $C_6H_6RuC_6H_8$ components as above (estimated relative intensities) with line positions altered owing to solvent shifts: 5·07 (benzene protons); 5·10 (central diene); 6·79 (terminal diene); 8·25 (methylene). $(\pi\text{-}C_6H_7)_2Ru$ components: 4·91, intensity 1, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (5·0 c./sec.); 5·63, intensity 2, double doublet, $H_{(3)} + H_{(5)}$ split by $H_{(4)}$ plus $H_{(2)}$ or $H_{(6)}$; 7·00 and 7·09, intensity 4, two partially overlapping bands in which fine structure not resolved, assigned to $(H_{(2)} + H_{(6)})$ and $(H_\alpha + H_\beta)$.

$C_6H_6(\pi\text{-}C_6H_7)Re$ (in benzene): 4·13, intensity 1, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (5·0 c./sec.); 5·10, intensity 2, " triplet " (overlapping double doublet), $H_{(3)} + H_{(5)}$ split by $H_{(4)}$ and $H_{(2)}$ or $H_{(6)}$ (5·0 c./sec.); 5·35, intensity 6, single sharp band, benzene protons; 5·96 and 6·00, total intensity 1, H_β split by H_α (11·5 c./sec.); 6·81, intensity 2, " triplet " (overlapping double doublet), $H_{(2)} + H_{(6)}$ split by H_α and $H_{(3)}$ or $H_{(5)}$ (6·0 c./sec.); 7·48 (centre), " quintuplet " (overlapping double triplet), H_α split by H_β (11·5 c./sec.) and $H_{(2)} + H_{(6)}$ (5·5 c./sec.).

$\pi\text{-}(C_6H_5\cdot C_6H_6)_2Ru$ (in CCl_4): 3·0, intensity 5, single band with some side structure, phenyl protons; 4·77, intensity 1, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (5·0 c./sec.); 5·37, intensity 2, " triplet " (overlapping double doublet), $H_{(3)} + H_{(5)}$ split by $H_{(4)}$ and $H_{(2)}$ or $H_{(6)}$ (5·3 c./sec.); 6·6 to 5·98, intensity 3, complex band, very approximately two overlapping triplets, H_β and $H_{(2)} + H_{(6)}$.

$\pi\text{-}(C_6H_5\cdot C_6H_6)Mn(CO)_3$ (in CCl_4): 2·75 to 3·35, intensity 5, complex band, phenyl protons; 4·33, intensity 1, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (7·5 c./sec.); 5·18, intensity 2, " triplet " (overlapping double doublet), $H_{(3)} + H_{(5)}$ split by $H_{(4)}$ plus $H_{(2)}$ or $H_{(6)}$ (9·5 c./sec.); 6·27, intensity 1, " triplet," H_β split by $H_{(2)} + H_{(6)}$ (5·5 c./sec.); 6·61, intensity 2, " triplet," $H_{(2)} + H_{(6)}$ split by H_β and $H_{(3)}$ or $H_{(5)}$ (8·0 c./sec.).

$\pi\text{-}(C_6H_5\cdot C_6H_6)(\pi\text{-}C_5H_5)Fe$ (in CCl_4): 3·1 and 3·33, total intensity 5, unsymmetrical doublet plus unsymmetrical quartet each with side structure, phenyl protons; 4·2, intensity 1, " triplet," $H_{(4)}$ split by $H_{(2)} + H_{(6)}$ (5·0 c./sec.); 5·7, intensity 7, single sharp line with side structure, π-cyclopentadienyl protons plus $H_{(3)} + H_{(5)}$; 6·51, intensity 1, unsymmetrical triplet, H_β split by $H_{(2)} + H_{(6)}$ (6·5 c./sec.); 7·27, intensity 2, unsymmetrical triplet, $H_{(2)} + H_{(6)}$ split by H_β and $H_{(3)}$ or $H_{(5)}$ (6·5 c./sec.).

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