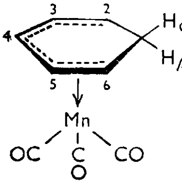
738. *π-Cyclohexadienylmanganese Tricarbonyl and Related Compounds.*[1]

By G. WINKHAUS, L. PRATT, and G. WILKINSON.

The reduction of the manganese tricarbonyl cations of benzene and other aromatic hydrocarbons, $ArMn(CO)_3^+$, by sodium borohydride and other reagents has given π-cyclohexadienylmanganese tricarbonyl derivatives, $(ArH)Mn(CO)_3$. Infrared and high-resolution nuclear magnetic resonance spectra of the derivatives are given.

DURING studies of the interaction of cyclohexa-1,3-diene with metal carbonyls it was observed that with dimanganese decacarbonyl in a rather critical temperature range, 140—160°, small quantities of a monomeric diamagnetic compound of stoicheiometry $C_6H_7Mn(CO)_3$ were obtained. High-resolution nuclear magnetic resonance and infrared spectral studies showed that the compound had to be regarded as π-cyclohexadienyl-manganese tricarbonyl (I) in which a new type of partially delocalised ring system is bound to the metal atom. It was then shown that this compound, the corresponding deuterium compound, and substituted derivatives can best be obtained by reduction of the appropriate arenemanganese tricarbonyl ions or their salts.



(I)

Arenemanganese Tricarbonyl Salts.—Although the mesitylenemanganese tricarbonyl ion has been isolated as the iodide[2] and the benzene and toluene derivatives have been mentioned, no preparative details or properties of these ions are available. We have prepared the cations with benzene, toluene, mesitylene, hexamethylbenzene, and naphthalene as ligands by the interaction of manganese pentacarbonyl chloride with an excess of the aromatic hydrocarbon at 60—80° in the presence of aluminium chloride. Hydrolysis of the reaction mixtures gives yellow aqueous solutions of the ions $ArMn(CO)_3^+$ which can be isolated as the perchlorates, polyiodides, tribromides, mercuric chlorides, etc. Solutions of the salts are fairly stable at room temperature, even in air, but decompose slowly losing carbon monoxide; the compounds are more stable in acid solutions but are decomposed on addition of sodium hydroxide or other base. The infrared spectra of the salts are all similar and show a sharp band in the region 3100—3080 cm.$^{-1}$ characteristic of aromatic C–H stretch, two very strong carbonyl stretching modes at *ca.* 2070 and 2010 cm.$^{-1}$ as well as bands due to the co-ordinated arenes (cf. ref. 2).

π-Cyclohexadienylmanganese Tricarbonyl Complexes.—Cyclohexa-1,3-diene has been shown to form olefin complexes with iron,[3] molybdenum,[4] and cobalt carbonyls,[5] but with manganese carbonyl a compound of stoicheiometry and molecular weight $C_6H_7Mn(CO)_3$ was obtained. This compound could be considered to arise by loss of a hydrogen atom from the cyclohexadiene just as π-cyclopentadienyl derivatives arise by loss of hydrogen

---

[1] Preliminary note: Winkhaus and Wilkinson, *Proc. Chem. Soc.*, 1960, 311.
[2] Coffield, Sandel, and Closson, *J. Amer. Chem. Soc.*, 1957, **79**, 5826.
[3] Hallam and Pauson, *J.*, 1958, 642.
[4] Fischer and Frohlich, *Z. Naturforsch.*, 1960, **15b**, 266.
[5] Winkhaus and Wilkinson, *Chem. and Ind.*, 1960, 1083; *J.*, 1961, 602.

in the interaction of cyclopentadiene with metal carbonyls.[6] Although this reaction may well proceed through an intermediate olefin complex we have been unable to isolate such a complex in the direct reaction, which proceeds only at about 150° and gives only low yields of the compound. Reduction of the arenemanganese tricarbonyl cations with sodium borohydride in aqueous solution, or, more conveniently, reduction of the anhydrous perchlorates in ether suspension by lithium aluminium hydride, provides a general method for the preparation of $C_6H_7Mn(CO)_3$, the deuterium compound, $(C_6H_6D)Mn(CO)_3$ (by use of lithium tetradeuteroaluminate), and of substituted derivatives, in good yields. The complexes so far prepared have been derived from benzene, toluene, mesitylene, hexamethylbenzene and naphthalene. Although the mechanism of these hydrogen-transfer reactions is not yet elucidated, it seems likely that a metal–hydrogen bond is first formed, followed by transfer to the hydrocarbon ring (cf. also refs. 7, 8).

Chemical Properties.—The chemical properties of the π-cyclohexadienyl compounds are very similar. They are yellow or orange crystalline solids or oils, which readily sublime in a vacuum and are readily soluble in common organic solvents but insoluble in, and unaffected by, water; they have strong camphoraceous odours. In air they are reasonably stable but their solutions in benzene or other hydrocarbons decompose extensively within an hour or two in air, giving brown paramagnetic material.

The compounds possess a reactive hydrogen atom, considered to be the H_α atom of the methylene group formed in the reduction (see below) and in this respect closely resemble the cyclopentadiene–metal complexes which possess such a reactive hydrogen atom.[7,8] Thus they react with carbon tetrachloride and with other hydride-abstracting reagents such as triphenylmethyl tetrafluoroborate. In these reactions salts of the arenemanganese tricarbonyl ion are re-formed so that the reaction

$$\mathrm{ArMn(CO)_3^+} \underset{-\mathrm{H}^-}{\overset{+\mathrm{H}^-}{\rightleftharpoons}} \mathrm{(ArH)Mn(CO)_3}$$

is reversible. With carbon tetrachloride the complex $C_6H_7Mn(CO)_3$ gives some unidentified, white, insoluble, organic material and red crystals; the latter dissolve in water and the solution gives precipitates which were shown to be identical with those given by $C_6H_6Mn(CO)_3^+$ with large anions. Chloroform and some carbonyl chloride are also formed in the reaction, as shown by infrared spectra and gas chromatography; the deutero-compound gives deuterochloroform. The compounds also react with 5N-hydrochloric acid, to give yellow solutions which do not give precipitates with large anions. Acetyl chloride reacts with the complex $C_6H_7Mn(CO)_3$ only in presence of aluminium chloride and after hydrolysis the $C_6H_6Mn(CO)_3^+$ ion was isolated and characterised. The substituted derivatives are thermally less stable than $C_6H_7Mn(CO)_3$, which is unchanged up to *ca.* 160°, and also react more rapidly. It is of interest that in some of the hydride-abstraction reactions, *e.g.*, of $C_6H_7Mn(CO)_3$ with carbon tetrachloride, transient red colours are observed but the nature of any intermediate species is not at present known.

The toluene compound, as directly prepared, is an isomeric mixture which was separated chromatographically into two main fractions, each of which still appears from its nuclear magnetic resonance to be complex.

Spectroscopic Properties and Structure.—The infrared spectra of the various compounds and of the salts from which they were obtained are listed in the Experimental section.

In the $(ArH)Mn(CO)_3$ compounds, a sharp band of weak or medium intensity is observed in the region 3080—3010 cm.$^{-1}$, shifted to lower wavenumbers than in the corresponding $ArMn(CO)_3^+$ salts. In $C_6H_7Mn(CO)_3$ and $(C_6H_6D)Mn(CO)_3$ there is a band at *ca.* 2970 cm.$^{-1}$ which can be clearly assigned [7,8] to the C–H_β stretching mode of the methylene group;

---

[6] For references see Wilkinson and Cotton, " Progress in Inorganic Chemistry," Interscience Publishers Inc., New York, 1959, Vol. I, p. 1.

[7] Green, Pratt, and Wilkinson, *J.*, 1959, 3753.

[8] Davison, Green, and Wilkinson, *J.*, 1961, 3172.

in the methyl-substituted complexes this band is obscured by the methyl group stretches at *ca.* 2970 and 2880 cm.$^{-1}$. In $C_6H_7Mn(CO)_3$ the single strong band at 2830 cm.$^{-1}$ shifts to 2120 cm.$^{-1}$ in $(C_6H_6D)Mn(CO)_3$ [ν_H(obs.)/ν_D(obs.) $\approx$ 1·34] and can be assigned as before [7,8] to the C–H$_\alpha$ stretch of the methylene group. As with the cyclopentadiene system it is clear that the hydrogen atom of the methylene group originating in the hydride reductant is the one which is responsible for the unusually low and strong C–H stretching frequency and is the one removed by chemical attack. The substituted derivatives show a similar band at *ca.* 2820 cm.$^{-1}$.

In the carbonyl region, two very strong bands are always observed at 2020—2000 and 1950—1920 cm.$^{-1}$, respectively. The lower band, though broad, has not been resolved; it may be complex. All of the compounds show three bands in the region 4070—3870 cm.$^{-1}$ which appear to be overtones of the C–O stretching fundamentals, and this suggests that the lower carbonyl band is in fact a doublet. Three C–O stretches would be expected for molecules of the type (I), since free rotation of the organic portion relative to the $Mn(CO)_3$ group is not likely to occur; it happens in the case of π-$C_5H_5Mn(CO)_3$ where the symmetry is higher.

There is no absorption in the 1600 and 1500 cm.$^{-1}$ regions where the C=C stretching modes of aromatic hydrocarbons are found or where cyclohexadiene absorbs (1600, 1577 cm.$^{-1}$). Instead, bands appear in the region 1450—1400 cm.$^{-1}$ which can be reasonably assigned as the ring C–C stretching modes, lowered by conjugation and bonding to the metal; in the methyl-substituted complexes, C–H deformation frequencies obscure this region. Bands at *ca.* 1300 cm.$^{-1}$ for $C_6H_7Mn(CO)_3$ [1277 cm.$^{-1}$ for $(C_6H_6D)Mn(CO)_3$] appear to be the deformation modes of the $>CH_\alpha H_\beta$ group.

The high-resolution nuclear magnetic resonance spectra of the complex $C_6H_7Mn(CO)_3$ and its substituted derivatives, details of which, with assignments, are given in the Experimental section, agree with the proposed structure (I). The C_6H_7 group has a plane of symmetry through $C_{(1)}$—$C_{(4)}$, perpendicular to the ring, and is symmetrical about this plane. However, there is a marked non-equivalence between the hydrogen atoms $H_{(4)}$, $H_{(5,3)}$, and $H_{(2,6)}$. The relative shifts could be the result of changes in the long-range shielding contribution of the π-electrons, not necessarily involving different π-electron densities at positions 2, 3, and 4. There are, however, appreciable solvent shifts in polar solvents, suggesting that there are slight differences in charge density at these positions, and it may be noted that similar solvent effects have been observed for the π-allyl–metal complexes.[9,10]

The two methylene protons in $C_6H_7Mn(CO)_3$ are not equivalent chemically or in the infrared spectrum, and they are not equivalent here; one of them (H_β) is obscured by the band due to $H_{(2)} + H_{(6)}$, while the other (H_α), which occurs at $\tau = 8{\cdot}4$, is absent for the deuterium compound, confirming its assignment as that closer to the metal atom. In the hexamethyl compound, the 4- and 3(5)-methyl group are very nearly equivalent. The 2(6)-methyl groups differ from the others and show in addition a small doublet separation, presumably due to splitting by the single H_α proton on $C_{(1)}$. The 1-methyl group shows a larger doublet splitting, 6·9 c./sec., as would be expected from a single proton on $C_{(1)}$. The lines due to this single proton could not be observed, but rough estimates based on the relative intensities of the 1-methyl doublet at 40 and 56·4 Mc./sec. indicate that the resonance lies in the region $\tau = 8{\cdot}0$—$8{\cdot}5$, *i.e.*, where the high-field methylene proton occurs for $C_6H_7Mn(CO)_3$.

The other methyl-substituted compounds are less stable in solution and their spectra were not so well resolved owing to the presence of traces of paramagnetic material resulting from decomposition. In the product from 1,3,5-trimethylbenzene, the presence of a band at $\tau = 4{\cdot}9$ indicates the presence of a proton in a position *para* to the reduced carbon atom [*i.e.*, corresponding to $H_{(4)}$ in $C_6H_7Mn(CO)_3$], so that the added hydrogen atom should have formed a $>CH_\alpha Me$ group, although such a group (giving a methyl line

---

[9] Dehm and Chien, *J. Amer. Chem. Soc.*, 1960, **82**, 4429.

[10] Jones and Wilkinson, unpublished results.

split into a doublet of about 7 c./sec.) could not be observed in the high-field region. The relative intensities of the high- and the low-field band suggest, however, that there is a mixture of the two possible isomeric products.

In the case of the monomethyl derivative, isomers are again to be expected and chromatography on alumina in this case showed two main components. For the fraction eluted first there are two different major methyl resonances, so that this fraction itself appears to contain more than one isomer; since neither of the isomers shows a splitting of more than 1·5 c./sec. there is hence very little of the isomer with a >CHMe group present. However, we have been unable to separate further the isomers, and the complexities of the spectra do not allow us to rule out the possibility of up to 10% of an isomer with a >CHMe grouping. The fraction eluted second, which we have been unable to separate further, has a similarly complex spectrum. Although this fraction appears to contain small amounts of the two isomers of the first fraction, the major component has a methyl resonance at a position different from those of the other two isomers, and, like them, does not have a >CHMe grouping. Hence the three major products appear to be the three isomers with methyl groups at positions 2, 3, and 4. These are the ones to be expected on chemical grounds, since hydride ion attack would be more likely at positions remote from the methyl group.

[*Added in proof:* The nuclear magnetic resonance spectrum of the compound $C_{11}H_{12}Fe$ [11] appeared to be very similar to those of cyclopentadiene complexes [7] at 40 Mc./sec. and was accordingly formulated as $C_6H_6FeC_5H_6$. However, at 56·4 Mc./sec. additional bands can be observed [10] which, together with intensities of the lines measured on an integrator, show unequivocally that the compound must be re-formulated as π-cyclopentadienyl-π-cyclohexadienyliron(II), π-C_5H_5Fe-π-C_6H_7. An unstable π-cyclohexadienyliron tricarbonyl cation has also recently been obtained by hydrogen abstraction from cyclohexa-1,2-diene-iron tricarbonyl.[12]

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College, and the Mikroanalytisches Laboratorium, Max-Planck Institut, Mülheim. Molecular weights were determined cryoscopically in cyclohexane or ebullioscopically in benzene.

All preparations and most operations were carried out in a nitrogen atmosphere or *in vacuo.*

Benzenetricarbonylmanganese Ion and Salts.—Manganese pentacarbonyl chloride [13] (3·45 g., 15 mmoles) and anhydrous aluminium chloride (3 g.) were refluxed for 6 hr. in anhydrous benzene (30 ml.). Carbon monoxide and a trace of hydrogen chloride were evolved and two layers separated, the lower being orange and containing the organomanganesecarbonyl–aluminium chloride complex. After addition of ice-water (40 ml.) the yellow acidic aqueous solution was filtered; the benzene layer, which is yellow, contained some unchanged $Mn(CO)_5Cl$, and also $Mn_2(CO)_{10}$, as shown by infrared spectra. An excess of 30% perchloric acid was added to the aqueous solution and the precipitated pale yellow *perchlorate* (dec. *ca.* 160°) (Table 1) was

TABLE 1. *Analyses of arenemanganese tricarbonyl salts.*

	Found (%)			Required (%)		
	C	H	Cl	C	H	Cl
$C_6H_6Mn(CO)_3ClO_4$	34·1	1·8	—	34·15	1·9	—
$C_7H_8Mn(CO)_3ClO_4$	36·1	2·4	10·95	36·3	2·4	10·7
$C_9H_{12}Mn(CO)_3ClO_4$	40·0	3·6	9·9	40·2	3·4	9·9
$C_{12}H_{18}Mn(CO)_3[Cr(NH_3)_2(SCN)_4]$...........	36·9	4·2	13·45 (N)	36·8	3·9	13·6 (N)
$C_{10}H_8Mn(CO)_3ClO_4$	41·0	3·3		42·6	2·2	

---

[11] Green, Pratt, and Wilkinson, *J.*, 1960, 989.

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

[13] Abel and Wilkinson, *J.*, 1959, 1501.

filtered off, washed with methanol and ether, and dried *in vacuo* [yield, 2·1 g., 45% based on $Mn(CO)_5Cl$]. Addition of the appropriate anion gave a pink reineckate, white tetraphenylborate, and brown polyiodide; precipitates were also given by $PtCl_6^{2-}$, bromine water, mercuric chloride, etc.

Addition of hydrogen peroxide to the aqueous solution, after an induction period, gives a red colour which is stable for some hours.

Substituted Arenemanganesetricarbonyl Ions and Salts.—The toluene, mesitylene, hexamethylbenzene, and naphthalene *derivatives* (Table 1) were prepared as above, except that light petroleum (b. p. 50—70°) was added to the reaction mixture in order to avoid high reaction temperatures which cause rearrangement and decomposition of the arenes under the influence of aluminium chloride.

Under the prescribed conditions, fluorobenzene gives only the benzene derivative, as shown by analysis, infrared spectrum, and reduction.

π-Cyclohexadienylmanganese Tricarbonyl.—*Method* 1, *from cyclohexa*-1,3-*diene*. Manganese carbonyl (3·9 g., 10 mmole) and cyclohexa-1,3-diene (4 g., 50 mmoles) were heated in mesitylene (50 ml.) at about 145° for 12 hr. After removal of solvent at 20°/10^{-3} mm., the residue was chromatographed on alumina with light petroleum (b. p. 30—40°)–ether as eluant; the first band contained unchanged $Mn_2(CO)_{10}$; the second fraction, on evaporation, left *π-cyclohexadienylmanganese tricarbonyl* (0·09 g., 2%) which was purified by vacuum-sublimation and crystallisation from light petroleum, forming yellow square plates, m. p. 78°, decomp. *ca.* 160° (Table 2). The low yield is probably due in part to decomposition at the reaction temperature, but no reaction occurs in lower-boiling solvents in a convenient time.

Method 2. To the aqueous chloride solution of the $C_6H_6Mn(CO)_3^+$ obtained as above from 3·45 g. of $Mn(CO)_5Cl$ was added in portions sodium borohydride (3 g.). The solution was extracted with n-pentane (6 × 50 ml.) as rapidly as possible and, after drying (Na_2SO_4), the yellow pentane solution was reduced to a few ml. *in vacuo*. This residue was transferred to an alumina column which was eluted with pentane–ether. The first yellow band, after removal of solvent and sublimation of the residue at 40°/10^{-3} mm., gave π-cyclohexadienylmanganese tricarbonyl [0·59 g.; overall averaged yields based on $Mn(CO)_5Cl$, 18%]. A very small yield (*ca.* 20 mg.) of a second product which is eluted after the main component is formed; the nature of this substance has not been elucidated.

Method 3. To a suspension of anhydrous $C_6H_6Mn(CO)_3ClO_4$ (2·1 g.) in ether (50 ml.) was added lithium aluminium hydride (1 g.) in small portions. The solution gradually became yellow and after 15 min. an excess of water (15 ml.) was carefully added in portions. More ether was added and the layers were separated. The ether layer was dried (Na_2SO_4) and reduced, after which the product was chromatographed as before [1st band, 0·55 g. (41% based on perchlorate); 2nd band, 12 mg.]. This method was utilized to prepare the deuterium compound $(C_6H_6D)Mn(CO)_3$ by lithium tetradeuteroaluminate.

TABLE 2. *Analyses of π-cyclohexadienylmanganese carbonyls.*

			Found (%)			Required (%)		
	M. p.	Colour	C	H	M	C	H	M
$C_6H_7Mn(CO)_3$ * ...	78°	Yellow	49·5	3·5	218	49·6	3·2	218
$(C_6H_6DMn)(CO)_3$ ...	79	,,				49·3	3·7	
$C_7H_9Mn(CO)_3$ (A) ...	Oil	,,	51·6	3·8	258	51·7	3·9	232
$C_7H_9Mn(CO)_3$ (B) ...	Oil	Yellow-orange	52·0	4·1		51·7	3·9	
$C_9H_{13}Mn(CO)_3$	Oil	Orange	56·1	5·8		55·4	5·0	
$C_{12}H_{19}Mn(CO)_3$	70	,,	60·6	7·1		59·6	6·3	
$C_{10}H_9Mn(CO)_3$	*ca.* 10	,,	56·9	5·0		58·2	3·4	

* Found: O, 21·4. Required: O, 22·0%.

Method 4. To the aqueous solution, as in method 2, were added magnesium turnings (2 g.) and concentrated hydrochloric acid (3 ml.); the red-brown solution was extracted with ether (4 × 50 ml.), and the products were isolated as before [1st band, 60 mg. (2%)]; the 2nd band was poorly defined.

Substituted π-Cyclohexadienylmanganese Tricarbonyls.—The substituted *derivatives* were prepared from the aqueous solutions of their ions by method 2; methods 3 and 4 gave much lower yields than in the benzene case. The compounds were isolated as for $C_6H_7Mn(CO)_3$ except that the liquid derivatives were " molecularly " distilled to a dry ice-cooled probe from which after warming they were allowed to run into a small container within the sublimation apparatus.

The toluene complex has isomers which were partially separated by chromatography on alumina.

In all cases traces of a second band were obtained for the substituted derivatives.

Infrared Spectra.—A Perkin–Elmer model 21 instrument with calcium fluoride and sodium chloride optics was used. Spectra of the perchlorates of polyiodides were taken in potassium bromide discs; bands due to perchlorate are omitted.

$C_6H_6Mn(CO)_3{}^+$: 3086s, 2083vs, 2024vs, 1453s, 1433m, 1385w, 1169m, 1013s, 827m, 645s,br.

$C_7H_9Mn(CO)_3{}^+$: 3086s, 3003w, 2940w, 2469w, 2075vs, 2004vs, 1549m, 1468s, 1449m, 1383m, 1208m, 1164s, 1000m, 855m, 783m, 650s,br.

$C_9H_{12}Mn(CO)_3{}^+$: 3115m, 3071s, 2941w, 2483w, 2070vs, 2016vs, 1564m, 1462s, 1383s, 1305s, 1038m, 999w, 928m, 666m, 651s,br.

$C_{12}H_{18}Mn(CO)_3{}^+$: 3100w, 2950w, 2049vs, 1988vs, 1439w, 1381s, 1284w, 1068w, 1000m, 655s.

$C_{10}H_8Mn(CO)_3{}^+$: 3096s, 2949w, 2075vs, 2012vs, 1554m, 1468s, 1431m, 1385m, 998w, 931w, 649s.

Spectra of the π-cyclohexadienyl compounds were taken in carbon tetrachloride (rapidly), tetrachloroethylene (which reacts more slowly), and carbon disulphide solutions.

$C_6H_7Mn(CO)_3$: 4065w, 3960m, 3884w, 3080w, 2968m, 2830s, 2410w, 2020vs, 1942vs, 1453m, 1405m, 1307s, 1154m, 1052s, 918m, 839m, 657s, 636s.

$(C_6H_6D)Mn(Co)_3$: 4060w, 3975m, 3876w, 3080w, 2967m, 2874w, 2412w, 2150sh, 2119s, 2018vs, 1937vs, 1455m, 1403m, 1323m, 1277s, 1153w, 1015s, 977w, 896w, 824m, 656s, 639s.

$C_7H_9Mn(CO)_3$: 4065w, 3968m, 3876w, 3058m, 2972m, 2890m, 2809s, 2404w, 2010vs, 1933vs, 1449m, 1383s, 1323w, 1307m, 1290w, 1194w, 1039m, 906w, 660s.

$C_9H_{13}Mn(CO)_3$: 4050w, 3968m, 3876w, 3012m, 2967m, 2907m, 2825s, 2420w, 2008vs, 1923vs, 1534m, 1491m, 1460m, 1439m, 1379s, 1324s, 1258m, 1187w, 1172w, 1156m, 1047s, 1038s, 1012s, 972m, 833w, 684w, 662s.

$C_{12}H_{19}Mn(CO)_3$: 3960w, 3003sh, 2959s, 2809m, 2000vs, 1931vs, 1381s, 1313m, 1214m, 1058w, 663m?

$C_{10}H_9Mn(Co)_3$: 4065w, 3952m, 3906w, 3049w, 2959s, 2825s, 2404w, 2326w, 2004vs, 1938vs, 1492m, 1425m, 1035m.

High-resolution Proton Resonance Spectra.—Spectra were recorded on a Varian instrument operating at 56·45 and 40 mc./sec. Samples were measured in 10% solutions in benzene, containing a little tetramethylsilane as reference; the C_6H_7 compound was also measured in other solvents. Line positions in τ values; splittings accurate to about ±0·2 c./sec.

$C_6H_7Mn(CO)_3$: Band A, 4·80, triple triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ (5·1 c./sec.), and by $H_{(2)} + H_{(6)}$ (1·2 c./sec.); band B, 5·84, complex, approx. triplet (6·5 c./sec.), $H_{(3)} + H_{(5)}$ each split by $H_{(4)}$ and by adjacent proton of $H_{(2)}$ and $H_{(6)}$; band C, 7·65, complex, $H_{(2)} + H_{(6)}$; $7{\cdot}7_5$ (H_β) and 8·44 (H_α) (band D), two protons (AB pair) of CH_2 group, mutual splitting ~11 c./sec.; additional splitting by $H_{(2)} + H_{(6)}$.

In the solvents C_6H_{12}, CCl_4, $CHCl_3$, Me_2CO, and Me_2SO, band A is centred at 4·24, 4·15, 4·08, 3·83, and 3·86, respectively, and band B at 5·33, 5·20, 5·17, 4·98, and 4·95, respectively. In CCl_4 and $CHCl_3$, band C is at 7·1 and band D at 7·4.

$(C_6H_6DMn)(CO)_3$: 4·83, $H_{(4)}$ (same as band A above); 5·84, approx. main triplet (5·5 c./sec.), $H_{(3)} + H_{(5)}$, each split by $H_{(4)}$ and by $H_{(2)}$ or $H_{(6)}$; ~7·7, complex band (two main double peaks, one with peaks at 132·1 and 130·7 c./sec. from the reference, the other (more intense) with peaks at 126·5 and 124·3 c./sec., $H_{(2)} + H_{(6)}$ and H_β of $\rangle$CHD group.

$C_9H_{13}Mn(CO)_3$: Spectrum poorly resolved. Weak bands at $4{\cdot}9_5$ and 5·8 may represent small proportions of protons at positions $H_{(4)}$ and ($H_{(3)} + H_{(5)}$) respectively, and that at 7·7, protons in $H_{(2)} + H_{(6)}$ positions; 7·9, (?) single peak, possibly methyl groups of trimethyl benzene as impurity; 8·2—8·8, unresolved band, peaks at 8·54 and 8·67 (chemical shifts), methyl groups in manganese compound.

$C_{12}H_{19}Mn(CO)_3$: 8·31 and 8·33, 4-methyl and (3 + 5)-methyl groups, 8·73, doublet (1 c./sec.), (2 + 6)-methyl groups, split by H_α of $\rangle$CHMe group; 8·88, doublet, components at 65·9 (stronger) and 59 (weaker) c./sec. from reference; methyl protons of $\rangle$CHMe group.

$C_7H_9Mn(CO)_3$ (first fraction): 4·89, triplet, $H_{(4)}$ split by $H_{(3)} + H_{(5)}$ [asymmetry suggests this may be a mixture of a triplet with a doublet, from the isomer with a methyl group at the

3 or 5 position]; 4·16, five components, $H_{(2)} + H_{(6)}$, again representing more than one isomer, since the overall width is less at 40 mc./sec. (18 c./sec.) than at 56·4 mc./sec. (21·5 c./sec.); 7·5—8, $H_{(2)} + H_{(6)}$ (peaks at 136, 122, 123·5, and 118 c./sec. from reference); 8·1—9·1, complex band, incompletely resolved, main singlet peaks at 8·58 and 8·88, probably methyl groups in two isomers, neither having a $CH{\cdot}CH_3$ group; one of them probably is the 3-methyl isomer.

$C_7H_9Mn(CO)_3$ (second fraction): 4·96, unsymmetrical triplet, $H_{(4)}$; 5·57, 5 components, unsymmetrical ($H_{(3)} + H_{(5)}$); 7·7 to 9·1, unresolved complex band, main singlet peak at 8·40, probably methyl group of third isomer, again without a $>$CHMe group, weaker peaks at 8·62 and 8·86 probably represent smaller proportions of the other two isomers found in first fraction (other peaks at 132, 127·3, 120·3, 114, 80, 70, 56, and 51·3 c./sec. from reference).

We thank the Ethyl Corporation for a fellowship (G. Winkhaus) and for supplies of manganese carbonyl, and Professor Feher, Cologne, for providing laboratory facilities for part of this work.

CHEMISCHES INSTITUT DER UNIVERSITÄT, COLOGNE, GERMANY.
INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[*Received, April 5th,* 1961.]