

## New Polynuclear Carbonyl Complexes containing Iron with Cobalt or Rhodium

By J. Knight and M. J. Mays,\* University Chemical Laboratory, Lensfield Road, Cambridge

The reaction of  $\text{Fe}_2(\text{CO})_9$  with  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  ( $\text{M} = \text{Co}$  or  $\text{Rh}$ ) has led to the preparation of five new polynuclear carbonyl complexes containing iron with cobalt or rhodium. The structure of these new 'mixed-metal' complexes has been inferred from a combination of i.r., n.m.r., and Mössbauer spectroscopic data and is discussed in relation to the structures of known polynuclear carbonyls such as  $\text{Fe}_3(\text{CO})_{12}$  and  $(\pi\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3$ .

It has now been conclusively proved by a single-crystal X-ray analysis that tri-iron dodecacarbonyl, in the solid state, has the molecular structure shown in (1).<sup>1</sup> There is a close relationship between the structure of this molecule and the structure<sup>2</sup> of one of the two isomers of  $(\pi\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3$  shown in (2) (which we shall call type A in the following discussion). This is not unexpected since a  $\pi\text{-C}_5\text{H}_5$  group is, in terms of number of electrons, formally equivalent to an  $\text{Fe}(\text{CO})_3$  group. The other isomer of  $(\pi\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3$  (type B) in (3) is clearly of comparable thermodynamic stability to the isomer of type A.<sup>3</sup> Two isomers have also been shown to exist for  $(\pi\text{-C}_5\text{H}_5)_3\text{Co}_3(\text{CO})_3$  and these may be of analogous structure to the isomers of  $(\pi\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3$ .<sup>4</sup> For  $\text{Fe}_3(\text{CO})_{12}$  there is no evidence for a second isomer in the solid state but it has been pointed out<sup>1</sup> that the

solution i.r. spectrum of this complex is better accounted for by a structure of type B than by one of type A, and, if this is correct, the difference in energy between the two types of isomer must again be small.

If we regard the complexes  $[(\text{CO})_3\text{Fe}]_3(\text{CO})_3$  and  $[(\pi\text{-C}_5\text{H}_5)\text{M}]_3(\text{CO})_3$  ( $\text{M} = \text{Co}$  or  $\text{Rh}$ ) as the end members of a series, it would be of interest to examine the structure of intermediate complexes in the series, and here we describe the preparation and a structural investigation by i.r., Mössbauer, and n.m.r. spectroscopy of complexes of this type. Tetranuclear complexes containing iron and rhodium have also been isolated and their structures are discussed.

Reaction of an excess of  $\text{Fe}_2(\text{CO})_9$  in refluxing light petroleum during 20 min. with  $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and  $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$  gave the complexes  $(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$  and  $(\pi\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_9$  respectively.

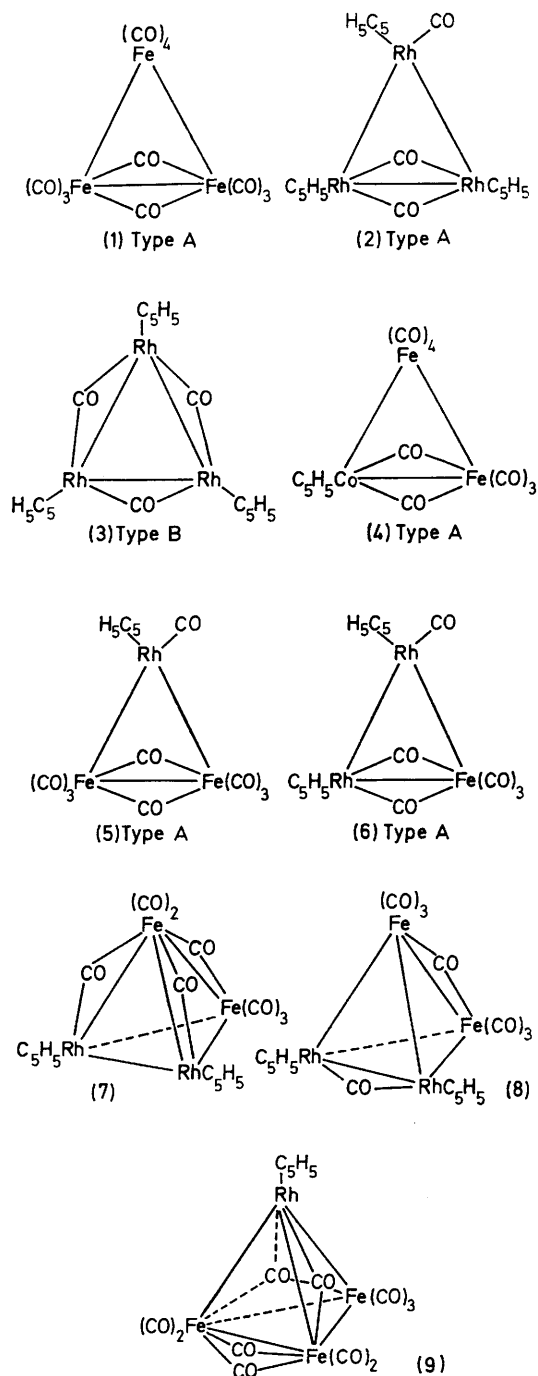
<sup>1</sup> C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 1351.

<sup>2</sup> E. O. Fischer, H. P. Fritz, E. F. Paulus, and H. Schuster-Woldan, *J. Organometallic Chem.*, 1967, **10**, P3.

<sup>3</sup> O. S. Mills and E. F. Paulus, *J. Organometallic Chem.*, 1967, **10**, 331.

<sup>4</sup> R. B. King, *Inorg. Chem.*, 1966, **5**, 2227.

In the latter reaction, trace quantities of  $(\pi\text{-C}_5\text{H}_5)\text{-RhFe}_3(\text{CO})_{11}$ ,  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_6$ , and  $(\pi\text{-C}_5\text{H}_5)_2\text{-Rh}_2\text{Fe}_2(\text{CO})_8$  were also formed; larger quantities of these last three complexes were isolated when the

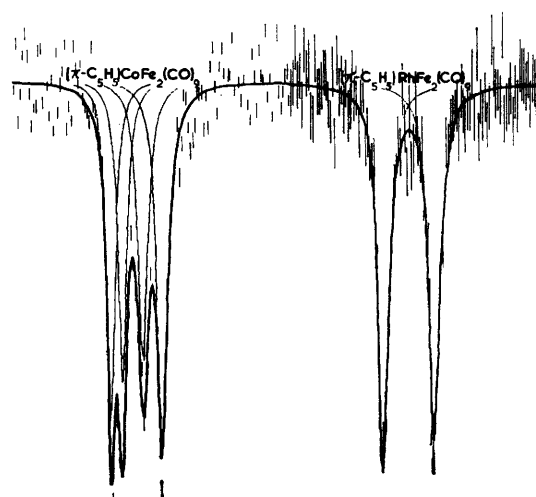


reaction period was extended to 5 hr. All the complexes were obtained as black crystals after chromatography of the reaction residues on silica gel, with light

petroleum as eluant. Their stoichiometry was established by observation of molecular ions in their mass spectra and by chemical analysis.

Enneacarbonyl di-iron, when heated alone under the above conditions, slowly decomposed to give  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$ . When  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  was also present, formation of  $(\pi\text{-C}_5\text{H}_5)\text{MFe}_2(\text{CO})_9$  almost ceased after all the  $\text{Fe}_2(\text{CO})_9$  had decomposed. This, together with the fact that  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_3(\text{CO})_{12}$  reacts extensively with  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  only under much more drastic conditions, indicates that a reactive intermediate in the decomposition of  $\text{Fe}_2(\text{CO})_9$  is probably responsible for the reaction. The properties of the new trinuclear and tetranuclear complexes which we have prepared are now considered.

**Trinuclear Complexes.**—(a)  $(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$  and  $(\pi\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_9$ . Trinuclear complexes containing



FIGURE

two iron atoms and one other transition-metal atom include  $\text{MnFe}_2(\text{CO})_{12}$ ,<sup>5</sup>  $\text{ReFe}_2(\text{CO})_{12}$ ,<sup>6</sup> and  $\text{RuFe}_2(\text{CO})_{12}$ .<sup>7</sup> These are believed to have a structure which is derived from that of  $\text{Fe}_3(\text{CO})_{12}$  by replacement of the  $\text{Fe}(\text{CO})_4$  group by  $\text{Mn}(\text{CO})_4^-$ ,  $\text{Re}(\text{CO})_4^-$ , and  $\text{Ru}(\text{CO})_4$  respectively.  $(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$  cannot have an analogous structure, however, since although the i.r. spectrum of the complex, both as a Nujol mull and in solution, shows that bridging carbonyl groups are present, the Mössbauer spectrum, which was recorded for the solid complex and for a frozen solution in benzene at the same temperature, shows that the two iron atoms are in different environments (Figure). Two quadrupole-split doublets were observed (Table 2) of equal intensity. The magnitude of the quadrupole splitting of one of the doublets was slightly different in the solution spectrum from its value in the solid-state spectrum indicating that a true frozen solution had been obtained and that the complex had not crystallised out from the solvent matrix. The

<sup>5</sup> U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 291.

<sup>6</sup> G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Comm.*, 1967, 186.

<sup>7</sup> F. G. A. Stone and D. B. W. Yawney, *J. Chem. Soc. (A)*, 1969, 502; J. Knight and M. J. Mays, *Chem. and Ind.*, 1968, 1159.

different environments of the two iron atoms cannot, therefore, be due to a crystal effect. The only structure which does not violate the inert-gas rule and is in accord with the Mössbauer and i.r. data is shown in (4). The highest possible symmetry for this complex is  $C_s$  for which seven terminal carbonyl stretching frequencies

further opportunity of assessing the relative strength of metal-metal bonds between two transition metals from the same series (3d) and from different series (3d and 4d). In agreement with previous data<sup>8</sup> for the series  $Mn_2(CO)_{10}$ ,  $Re_2(CO)_{10}$ , and  $MnRe(CO)_{10}$  (3d, 5d) which indicates (mass and vibrational spectroscopy) that the

TABLE 1  
Analytical data and i.r. and n.m.r. spectra

Compound	Found (%)		Required (%)		Colour	$\nu(CO)$ (cm. <sup>-1</sup> )	$\tau(C_5H_5)$
	C	H	C	H			
$(\pi-C_5H_5)CoFe_2(CO)_9$	34.5	1.2	34.5	1.0	Brown	2080s, 2033s, 2013s, 2001sh, 1981m, 1848w, 1812m	4.77
$(\pi-C_5H_5)RhFe_2(CO)_9$	31.5	1.1	31.6	1.0	Green	2079s, 2037s, 2032sh, 2015s, 1999s, 1982sh, 1844w, 1803m	4.59
$(\pi-C_5H_5)RhFe_3(CO)_{11}$	29.9	1.0	29.9	0.8	Red	2069s, 2033sh, 2025s, 1993s, 1977m, 1957m, 1945sh, 1873m, 1826w	5.14
$(\pi-C_5H_5)_2Rh_2Fe(CO)_8$	34.2	2.1	34.3	1.8	Green	2054s, 2002s, 1989s, 1980s, 1839w, 1792m	4.50
$(\pi-C_5H_5)_2Rh_2Fe_2(CO)_8$	32.4	1.7	32.2	1.6	Purple	2039s, 2005s, 1972m, 1956m, 1935m, 1849w, 1788w	4.28

and two bridging frequencies are allowed. All except two of the terminal absorptions are observed.

For the rhodium complex,  $(\pi-C_5H_5)RhFe_2(CO)_9$ , the i.r. spectrum again reveals the presence of bridging carbonyl groups but the Mössbauer spectrum indicates that the two iron atoms are equivalent. This complex is, therefore, assigned structure (5) which is analogous to that previously proposed for the corresponding manganese-iron, rhenium-iron, and ruthenium-iron clusters. The cobalt-iron and rhodium-iron complexes

TABLE 2  
Mössbauer spectra

Compound	Chemical shift * (mm./sec.)	Quadrupole splitting (mm./sec.)	Form temp. (°K)
$(\pi-C_5H_5)CoFe_2(CO)_9$	0.29	0.99	Solid 293°
	0.21	0.40	
	0.35	1.01	
	0.27	0.43	Solid 78
	0.35	1.00	
$(\pi-C_5H_5)RhFe_2(CO)_9$	0.29	0.35	Solid 293
$(\pi-C_5H_5)RhFe_3(CO)_{11}$	0.25	1.04	
$(\pi-C_5H_5)_2Rh_2Fe(CO)_8$	0.22 †	0.89 †	Solid 293
$(\pi-C_5H_5)_2Rh_2Fe_2(CO)_8$	0.24	1.05	Solid 293
$(\pi-C_5H_5)_2Rh_2Fe_2(CO)_8$	0.27 †	0.80 †	Solid 293
$Fe_3(CO)_{12}$ <sup>14</sup>	0.30	0.98	Solid 293
	0.22	0	

\* Chemical shifts quoted relative to sodium nitroprusside.

† More than one quadrupole-split doublet is probably present.

therefore, whilst differing in the position of the bridging carbonyl groups, both have a type A structure. There was no evidence for a second isomer of type B structure for either the cobalt or rhodium complexes. This more symmetrical  $C_{2v}$  structure would, in fact, satisfy the Mössbauer data for the rhodium complex but is eliminated on i.r. grounds since five terminal and three bridging carbonyl absorptions are allowed for this structure whilst six terminal and two bridging carbonyl absorptions are observed.

The isolation of these two complexes provides a

<sup>8</sup> G. A. Junk and H. J. Svec, *J. Amer. Chem. Soc.*, 1967, **89**, 2836; H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.*, 1966, 616.

manganese-rhenium bond is the strongest of the three metal-metal bonds, we find that the rhodium-iron complex is thermodynamically the more stable of the two. Thus reaction of  $(\pi-C_5H_5)CoFe_2(CO)_9$  with  $(\pi-C_5H_5)Rh(CO)_2$  at reflux point rapidly gives  $(\pi-C_5H_5)RhFe_2(CO)_9$  and  $(\pi-C_5H_5)Co(CO)_2$  as the major products of the reaction (which is irreversible). This, in itself, is not sufficient evidence to determine conclusively the relative strengths of the Co-Fe and Rh-Fe bonds, since this factor is only one of several which affect the position of equilibrium. The stability order  $Rh-Fe > Co-Fe$  is, however, supported by the fact that, compared to the base peak  $C_5H_5M^+$  in the mass spectra of the two complexes, the average abundance of trimetallic ions is higher in the rhodium complex than in the cobalt complex (Table 3). A further point of interest in the mass spectra of the complexes is the relatively high abundance of the ion  $C_5H_5M(CO)_2^+$  in both. Although these ions could well arise from the unsymmetrical cleavage of bridging carbonyl groups which may be present in the positively charged parent ion  $C_5H_5MFe_2(CO)_9^+$ , it is clearly not a worthwhile exercise to attempt to deduce the structure of the neutral molecule (different for  $M = Co$  and  $Rh$ ) from this data, as has been done for  $Fe_3(CO)_{12}$  (ref. 1.) and  $Ru_3(CO)_{12}$  (ref. 9).

(b)  $(\pi-C_5H_5)_2Rh_2Fe(CO)_8$ . The most likely structure for this complex is shown in formula (6). This proposal is based on i.r. evidence which indicates the presence of bridging carbonyl groups and on the magnitude of the Mössbauer quadrupole splitting. The environment of the iron atoms in the complexes  $(\pi-C_5H_5)CoFe_2(CO)_9$ ,  $(\pi-C_5H_5)RhFe_2(CO)_9$  and  $(\pi-C_5H_5)_2Rh_2Fe(CO)_8$  will be similar either to that of the unique iron atom in  $Fe_3(CO)_{12}$  or to that of the other two iron atoms in this molecule which are linked by bridging carbonyl groups. Values for the quadrupole splittings of the compounds mentioned are given in Table 2. The quadrupole splittings for  $(\pi-C_5H_5)RhFe_2(CO)_9$  and for one of the iron atoms in  $(\pi-C_5H_5)CoFe_2(CO)_9$  are very close to the

<sup>9</sup> J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc. (A)*, 1966, 1663.

value for the carbonyl-bridged iron atoms of  $\text{Fe}_3(\text{CO})_{12}$  as predicted from the structural assignments given above. The quadrupole splittings of the other iron atom of  $(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$  and of the unique iron atom of  $\text{Fe}_3(\text{CO})_{12}$  are much smaller. Since the quadrupole splitting for  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_8$  is also very close to the value for the carbonyl-bridged iron atoms of  $\text{Fe}_3(\text{CO})_{12}$ , its environment is likely to be similar to these, as in formula (6), rather than to the environment of the unique iron atom of  $\text{Fe}_3(\text{CO})_{12}$  as in a structure having the bridging carbonyl groups linking the two rhodium atoms. Both of the possible type A structures are consistent with the i.r. spectrum in solution but the observation of four terminal and two bridging carbonyl

and the mixed clusters which we have been able to prepare, structures of type A appear the more stable. In solution, conclusive evidence is more difficult to obtain. The frozen solution Mössbauer spectrum of  $(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$  suggests that its structure is not changed from that found in the solid state; similar behaviour has been found for  $(\pi\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_9$ . We have had the same solubility problems as other workers<sup>10</sup> in attempting to record the frozen solution Mössbauer spectrum of  $\text{Fe}_3(\text{CO})_{12}$ . It is hoped, however, that a study at liquid helium temperature which is shortly to be undertaken<sup>11</sup> will provide the answer to these difficulties, since a much lower concentration of iron will be required to obtain a spectrum.

TABLE 3  
Mass spectra  
Compound and source temperature

$(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$ , 50°		$(\pi\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_9$ , 60°		$(\pi\text{-C}_5\text{H}_5)\text{RhFe}_3(\text{CO})_{11}$ , 80°		$(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_8$ , 90°		$(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_8$ , 110°	
(Relative peak height)		(Relative peak height)		(Relative peak height)		(Relative peak height)		(Relative peak height)	
Ion		Ion		Ion		Ion		Ion	
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_9^+$	(3)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_9^+$	(10)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_{11}^+$	(0.3)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_8^+$	(5)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_8^+$	(0.2)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_8^+$	(2)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_8^+$	(6)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_{10}^+$	(1.1)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_7^+$	(4)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_7^+$	(0.9)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_7^+$	(3)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_7^+$	(10)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_9^+$	(0.5)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_6^+$	(18)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_6^+$	(0.1)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_6^+$	(1)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_6^+$	(6)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_8^+$	(0.2)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_5^+$	(8)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_5^+$	(0.2)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_5^+$	(0.3)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_5^+$	(2)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_7^+$	(0.6)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_4^+$	(10)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_4^+$	(0.1)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_4^+$	(2)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_4^+$	(10)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_6^+$	(0.6)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_3^+$	(40)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_3^+$	(0.2)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_3^+$	(5)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_3^+$	(26)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_5^+$	(2)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}^+$	(20)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})_2^+$	(1.4)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})_2^+$	(1)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_2^+$	(25)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_4^+$	(3)	$(\text{C}_5\text{H}_5)_2\text{Rh}^+$	(67)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_3(\text{CO})^+$	(0.4)
$\text{C}_5\text{H}_5\text{CoFe}_2(\text{CO})^+$	(2)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})^+$	(24)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_3^+$	(0.6)	$\text{C}_5\text{H}_5\text{Rh}(\text{CO})_3^+$	(35)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2^+$	(0.5)
$\text{C}_5\text{H}_5\text{CoFe}_2^+$	(0.6)	$\text{C}_5\text{H}_5\text{RhFe}_2^+$	(29)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_2^+$	(2)	$\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2^+$	(37)	$(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_3^+$	(5)
$\text{C}_5\text{H}_5\text{Co}(\text{CO})_2^+$	(90)	$\text{C}_5\text{H}_5\text{RhFe}(\text{CO})^+$	(7)	$\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})^+$	(3)	$\text{C}_5\text{H}_5\text{Rh}^+$	(100)	$(\text{C}_5\text{H}_5)_2\text{Fe}_3(\text{CO})_3^+$	(10)
$\text{C}_5\text{H}_5\text{Co}(\text{CO})^+$	(60)	$\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2^+$	(39)	$(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4^+$	(0.9)	$\text{Rh}^+$	(12)	$(\text{C}_5\text{H}_5)_2\text{Fe}_3(\text{CO})_2^+$	(5)
$\text{C}_5\text{H}_5\text{Co}^+$	(100)	$\text{C}_5\text{H}_5\text{Rh}(\text{CO})^+$	(37)	$\text{C}_5\text{H}_5\text{RhFe}^+$	(4)	$\text{Fe}(\text{CO})^+$	(10)	$(\text{C}_5\text{H}_5)_2\text{Fe}_3(\text{CO})^+$	(15)
		$\text{C}_5\text{H}_5\text{Rh}^+$	(100)	$(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3^+$	(0.3)	$\text{Fe}^+$	(4)	$(\text{C}_5\text{H}_5)_2\text{Fe}_3(\text{CO})$	(5)
		$\text{Fe}_2(\text{CO})^+$	(23)	$\text{C}_5\text{H}_5\text{RhFe}_2(\text{CO})_3^+$	(2)			$(\text{C}_5\text{H}_5)_2\text{Fe}_3^+$	(30)
		$\text{Rh}^+$	(12)	$(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2^+$	(0.8)			$(\text{C}_5\text{H}_5)_2\text{Rh}^+$	(30)
		$\text{Fe}(\text{CO})^+$	(16)	$\text{C}_5\text{H}_5\text{RhFe}_2^+$	(3)			$\text{C}_5\text{H}_5\text{Rh}(\text{CO})_3^+$	(*)
		$\text{Fe}^+$	(9)	$\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2^+$	(59)			$\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2^+$	(*)
				$\text{C}_5\text{H}_5\text{Rh}(\text{CO})^+$	(68)			$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	(*)
				$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	(22)			$\text{C}_5\text{H}_5\text{Rh}^+$	(*)
				$\text{C}_5\text{H}_5\text{Rh}^+$	(100)			$\text{Rh}^+$	(100)
				$\text{C}_5\text{H}_5\text{Fe}^+$	(23)			$\text{Fe}^+$	(70)
				$\text{Rh}^+$	(17)				
				$\text{Fe}(\text{CO})^+$	(23)				
				$\text{Fe}^+$	(16)				

• Very large abundance.

absorptions means that the type B structure, for which no more than three terminal absorptions are expected, can be ruled out. The only piece of evidence which is not in accord with the structure shown in formula (6) is the n.m.r. spectrum in deuteriochloroform solution, which shows only a single, sharp resonance attributable to the  $\text{C}_5\text{H}_5$  protons. This may, however, be explained if we postulate that the isomer (6) is in rapid equilibrium with a small concentration of an unbridged isomer, thus rendering the two proton sites in (6) equivalent on the n.m.r. time scale. Confirmation of the crystal structure of this complex must await the result of an X-ray diffraction study. The corresponding cobalt complex, if formed at all, could not be isolated, the action of prolonged heating on  $(\pi\text{-C}_5\text{H}_5)\text{CoFe}_2(\text{CO})_9$  and  $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  giving predominantly  $\text{Fe}_3(\text{CO})_{12}$ .

The result of our study of trinuclear complexes of iron and rhodium, therefore, has been to show that only for  $(\pi\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3$  are the isomers of type A and B of comparable stability in the solid state. For  $\text{Fe}_3(\text{CO})_{12}$

**Tetranuclear Complexes.**—(a)  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$ . Two reasonable structures for this molecule are shown in formulae (7) and (8). Both obey the inert-gas rule individually for each metal atom and are consistent with the n.m.r. spectrum of the complex which shows a single resonance. In addition, the expected number of carbonyl stretching frequencies in the i.r. spectrum [five terminal and three bridging for formula (7) and five terminal and two bridging for formula (8)] are both compatible with the observed spectrum which contains five terminal and two bridging carbonyl absorptions. The Mössbauer spectrum consists of two absorptions the relatively large half-widths of which suggest that there are two different iron sites in the molecule, thus favouring structure (7). Structure (8) can be regarded as derived from  $\text{Fe}_2(\text{CO})_9$  by replacement of two of the bridging carbonyl groups by rhodium fragments just as the structure of  $(\pi\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_9$  is derived by replacement of one bridging carbonyl group. Interestingly, this tetranuclear complex is the major product of the reaction between  $(\pi\text{-C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_9$  and  $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ .

<sup>10</sup> R. H. Herber, *Progr. Inorg. Chem.*, 1967, **8**, 30.

<sup>11</sup> G. M. Bancroft *et al.*, personal communication.



(b)  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_3(\text{CO})_{11}$ . A possible structure for this complex is shown in formula (9). The inert-gas rule is obeyed for each individual metal atom which is difficult to achieve in other configurations. It also offers a satisfactory explanation for the physical data we have obtained, *e.g.* for the Mössbauer spectrum which shows that more than one iron site is present. The fitting of two quadrupole-split doublets to the two relatively broad absorptions obtained gives a significant lowering of the standard deviations. In the i.r. spectrum in solution, seven terminal, two edge-bridging and two face-bridging carbonyl absorptions are expected; a total of nine absorptions is observed.

#### EXPERIMENTAL

Analyses were carried out by the Microanalytical Department of the University Chemical Laboratory.

Mass spectra were recorded on an AEI MS 9 mass spectrometer and n.m.r. spectra on a Varian 100 Mc./sec. spectrometer.

I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer to an accuracy of  $\pm 1\text{ cm}^{-1}$  with carbon monoxide as calibrant.

Mössbauer spectra were fitted to smoothed curves and chemical shift and quadrupole splitting values are quoted to an accuracy of  $\pm 0.01\text{ mm./sec.}$

Reactions were carried out in an atmosphere of dry, oxygen-free nitrogen and solvents were degassed before use.

Enneacarbonyl-di-iron and  $\pi$ -cyclopentadienyldicarbonylcobalt were prepared by literature methods.<sup>12</sup>  $\pi$ -Cyclopentadienyldicarbonylcobalt was fractionated under reduced pressure (15 mm. Hg).

$\pi$ -Cyclopentadienyldicarbonylrhodium was prepared according to a variation of the method of Fischer and Bittler<sup>13</sup> as follows. To a solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (13.7 g.) in light petroleum (b.p. 30–40°; 800 ml.) was added thallium(I) cyclopentadienide (30 g.) and the mixture was shaken vigorously at room temperature until an i.r. spectrum of the orange solution in the carbonyl region showed that all the starting material had reacted. The mixture was filtered and solvent was removed at 15 mm. Hg. The residual oil was fractionated at room temperature under reduced pressure to give a clear orange liquid (11 g.).

$(\pi\text{-C}_5\text{H}_5)_2\text{CoFe}_2(\text{CO})_9$ . A solution of  $(\pi\text{-C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$  (2 g.) in light petroleum (b.p. 60–80°) was added to  $\text{Fe}_2(\text{CO})_9$  (5 g.) and the mixture was stirred magnetically at 65° for 15 min. when all the  $\text{Fe}_2(\text{CO})_9$  had reacted. Solvent was removed from the cool solution together with  $\text{Fe}(\text{CO})_5$  and excess of  $(\pi\text{-C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$ . The residue was extracted with light petroleum and the solution was filtered and then chromatographed on silica gel. Elution with light petroleum (b.p. 40–60°) gave  $\text{Fe}_3(\text{CO})_{12}$  as a green band followed by  $(\pi\text{-C}_5\text{H}_5)_2\text{CoFe}_2(\text{CO})_9$  (black). The bulk of the

solvent was removed and the concentrated solution was filtered and cooled to  $-30^\circ$  when black crystals separated (900 mg.).

$(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_2(\text{CO})_9$ .  $\text{Fe}_2(\text{CO})_9$  (2.5 g.) was added to a solution of  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}(\text{CO})_2$  (0.5 g.) in light petroleum ether (b.p. 60–80°; 50 ml.) and the mixture was stirred and heated under reflux for 20 min. The mixture was cooled and solvent was removed under reduced pressure together with  $\text{Fe}(\text{CO})_5$  and excess of  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}(\text{CO})_2$ . The residue was extracted with light petroleum and the solution was filtered and chromatographed on silica gel. Elution with light petroleum ether (b.p. 40–60°) gave  $\text{Fe}_3(\text{CO})_{12}$  as a green band; this was followed by a very dark green band of  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_2(\text{CO})_9$  which was collected. The solution was concentrated, filtered, and cooled to give black crystals of  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_2(\text{CO})_9$  (70 mg.).

$(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_3(\text{CO})_{11}$ ,  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_6$ , and  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$ .—A solution of  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}(\text{CO})_2$  (5.5 g.) in light petroleum (b.p. 60–80°; 350 ml.) was added to  $\text{Fe}_2(\text{CO})_9$  (16.5 g.) and the mixture was heated under reflux for 5 hr. When cooled slowly to room temperature, the solution deposited crystals of  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$  on the walls of the flask. The mother liquor was filtered and the combined residues were washed with light petroleum (b.p. 30–40°; 20 ml.) and then dissolved in a minimum quantity of chloroform. The purple solution was filtered and then added to light petroleum at room temperature. Crystals formed immediately and more crystals separated when the solution was cooled to  $-30^\circ$ . The mother liquor after separation of the crude product was chromatographed on silica gel. Elution with light petroleum (b.p. 40–60°) gave  $\text{Fe}(\text{CO})_5$ ,  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}(\text{CO})_2$ , and  $\text{Fe}_3(\text{CO})_{12}$ ; finally  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_2(\text{CO})_9$  was obtained as a slow-moving dark green band. Increasing proportions of benzene in the eluant then gave the other components of the reaction mixture as follows:  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_3(\text{CO})_{11}$  (red band in 20 : 1 light petroleum–benzene),  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_6$  (green band in 10 : 1 light petroleum–benzene) and finally a mixture containing mainly  $[(\pi\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$  and  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$  (1 : 1 light petroleum–benzene). Evaporation of the solutions of  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_2(\text{CO})_9$ ,  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_3(\text{CO})_{11}$ , and  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_6$  followed by recrystallisation from dichloromethane–light petroleum mixtures gave the following pure products as black crystals:  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_2(\text{CO})_9$  (1150 mg.),  $(\pi\text{-C}_5\text{H}_5)_2\text{RhFe}_3(\text{CO})_{11}$  (10 mg.),  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8$  (400 mg.), and  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}(\text{CO})_6$  (55 mg.).

We thank Messrs. Johnson-Matthey Ltd. for a loan of rhodium trichloride, Drs. G. M. Bancroft and B. E. Prater for helpful discussion of the Mössbauer data, and the S.R.C. for a maintenance award (to J. K.).

[9/1280 Received, July 28th, 1969]

<sup>13</sup> K. Bittler and E. O. Fischer, *Z. Naturforsch.*, 1961, **16b**, 225.

<sup>14</sup> W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, 1968, **90**, 3293.

<sup>12</sup> R. B. King, 'Organometallic Syntheses,' Academic Press, New York and London, vol. 1, pp. 93 and 115.