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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XXVI*. TETRAFLUOROBENZOBARRELENE COMPLEXES OF Mn, Co, Rh, Pd AND Pt

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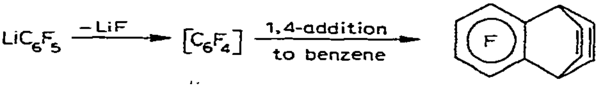
SUMMARY

The non-conjugated diolefin ligand tetrafluorogenzobarrelene (5,6,7,8-tetrafluoro-1,4-ethenonaphthalene) forms air-stable complexes with Mn, Co, Rh, Pd and Pt. In the complex formed from cyclopentadienylmanganese tricarbonyl, $C_6F_4C_6H_6MnC_5H_5(CO)_2$, tetrafluorobenzobarrelene coordinates to the metal using only one of the olefinic bonds; in all the other complexes the ligand behaves as a chelating diolefin.

The thermal decomposition of either pentafluorophenyllithium or pentafluorophenylmagnesium halides in the presence of benzene produces tetrafluorobenzobarrelene** in high yield[2]:



Methyl-substituted benzenes give similar products.

Tetrafluorobenzobarrelene and its methyl derivatives are powerful, non-conjugated diolefinic ligands which readily form iron tricarbonyl complexes when treated with triiron dodecacarbonyl in refluxing hydrocarbon solvents:

We have recently reported[3] the results of an X-ray structure determination on (tetrafluorobenzobarrelene)iron tricarbonyl which show that both olefinic bonds are coordinated to the iron atom.

When tetrafluorobenzobarrelene is refluxed under UV irradiation with cyclopentadienylmanganese tricarbonyl in cyclohexane as solvent, carbon monoxide is evolved and a yellow complex analysing as π-$C_5H_5(CO)_2MnC_6H_6C_6F_4$, can be

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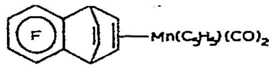
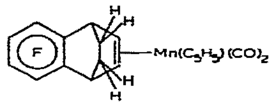
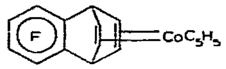
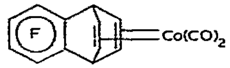
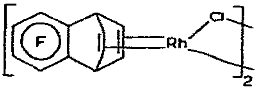
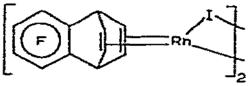
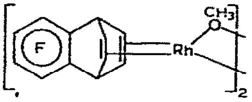
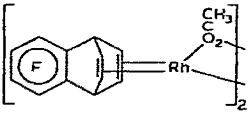
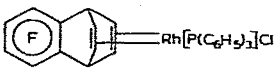
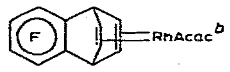
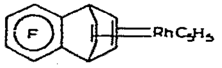
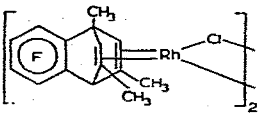
[*] For Part XXV see ref. 1.

[**] *Chem. Abstr.*'s name: 5,6,7,8-tetrafluoro-1,4-ethenonaphthalene.

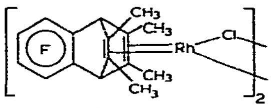
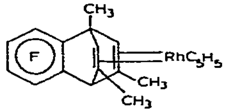
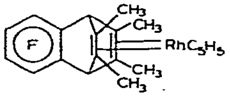
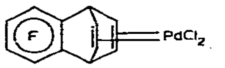
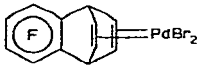
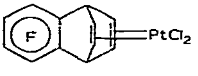
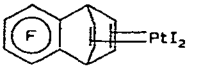
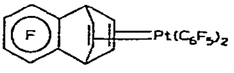
TABLE 1

ANALYTICAL DATA ON THE BARRELENE COMPLEXES

Complex	Colour	M.p. (°C)	Analyses, found (calcd.) (%)		
			C	H	X
	Yellow	188–190 dec.	56.7 (56.85)	2.65 (2.7)	
	Yellow	195	56.6 (56.4)	3.1 (3.2)	
	Orange	194.5–196	59.3 (58.3)	3.2 (3.1)	F, 21.9 (F, 21.7)
	Orange- yellow		49.3 48.6	1.9 1.8	
	Yellow		39.4 (39.5)	1.5 (1.6)	Cl, 9.5 (Cl, 9.7)
	Brown	240 dec.	31.8 (31.7)	1.3 (1.3)	I, 27.6 (I, 27.9)
	Yellow	180 dec.	43.4 (43.3)	2.3 (2.5)	
		220 dec.	43.2 (43.2)	2.1 (2.3)	
	Yellow	230–240 dec.	57.9 (57.6)	3.2 (3.2)	
 [a]	Red	255	45.7 (46.1)	2.5 (2.3)	N, 4.7 (N, 5.1)
 [b]	Yellow	225–235 dec.	47.3 (47.6)	3.3 (3.0)	
	Yellow	210	51.6 (51.8)	2.7 (2.8)	
	Yellow	>270	44.2 (44.7)	2.75 (2.95)	

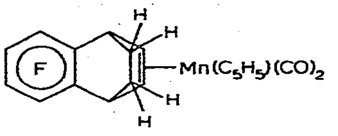
(*continued*)

TABLE 1 (*Continued*)

Complex	Colour	M.p. (°C)	Analyses, found (calcd.) (%)		
			C	H	X
	Yellow		54.6 (54.4)	3.3 (3.3)	
		112	55.3 (55.0)	4.1 (3.9)	
		219–220	56.2 (56.0)	4.2 (4.2)	
	Yellow	>250	35.9 (35.7)	1.5 (1.5)	Cl, 17.55 (Cl, 17.6)
	Orange-yellow	127 d	31.2 (29.8)	1.35 (1.2)	Br, 33.0 (Br, 33.1)
	White	>300	29.4 (29.3)	1.25 (1.2)	Cl, 14.4 (Cl, 14.4)
	Yellow		21.5 (21.3)	0.95 (0.9)	I, 36.7 (I, 36.5)
	White		38.6 (38.1)	0.8 (0.7)	F, 36.0 (F, 35.2)

[a] Bipy = 2,2′-bipyridine. [b] Acac = acetylacetonate.

isolated from the solution; the heaviest ion in the mass spectrum corresponds to $MnC_{19}H_{11}F_4O_2^+$ showing that the complex is probably monomeric. If the effective atomic number of manganese is to remain equal to that of krypton then the tetrafluorobenzobarrelene must be coordinated to the manganese by only one of the olefinic bonds. In accordance with this the proton NMR spectrum of the complex shows four peaks (ratio 2/2/5/2) at τ 6.15, 4.80, 4.54 and 4.18 ppm; the peak at 6.15 ppm is in the region expected for protons attached to olefinic carbon atoms. The infra-red spectrum contains a strong band at 760 cm^{-1} which is also present in the free ligand. In the ligand this band has been assigned to a *cis*-disubstituted olefin frequency[4] and is absent from the spectra of all the tetrafluorobenzobarrelene–metal derivatives in which the ligand is bidentate. Hydrogenation of the free double bond can be achieved at room temperature by bubbling hydrogen through an ethanolic solution of $C_{12}H_6F_4Mn(C_5H_5)(CO)_2$ in the presence of a Raney nickel catalyst. The product was shown to be $C_{12}H_8F_4Mn(C_5H_5)(CO)_2$ (I) by analysis and mass spectrometry; its infra-red spectrum was notable for the absence of a peak at 760 cm^{-1}.

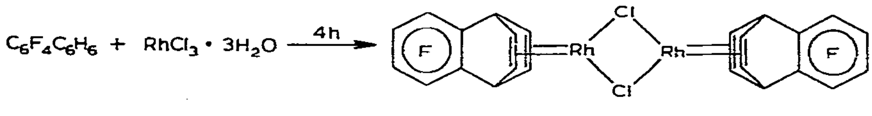


(I)

No evidence could be found for the formation of the binuclear complex $C_{12}H_6F_4[Mn(C_5H_5)(CO)_2]_2$, in which both double bonds on the ligand are used for π-bonding to manganese, when $C_{12}H_6F_4Mn(C_5H_5)(CO)_2$ was heated either alone *in vacuo* or in the presence of $C_5H_5Mn(CO)_3$. This is in contrast to the closely related non-conjugated olefins norbornadiene and 1,5-cyclooctadiene, both of which form binuclear complexes with ease[5].

In contrast, tetrafluorobenzobarrelene substitutes both carbon monoxide groups in cyclopentadienylcobalt dicarbonyl when the two are refluxed, under ultraviolet irradiation, in methylcyclohexane. The resulting orange complex, cyclopentadienyl(tetrafluorobenzobarrelene)cobalt, is monomeric and very stable; it can be dissolved in concentrated sulphuric acid and recovered unchanged on dilution. The complex does not react with de-oxygenated hydrochloric acid but is instantly decomposed by HCl in the presence of air to give high yields of tetrafluorobenzobarrelene.

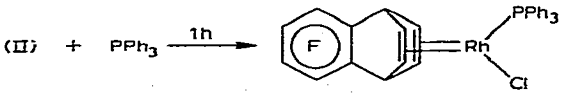
Tetrafluorobenzobarrelene and rhodium trichloride trihydrate react readily in refluxing methanol:



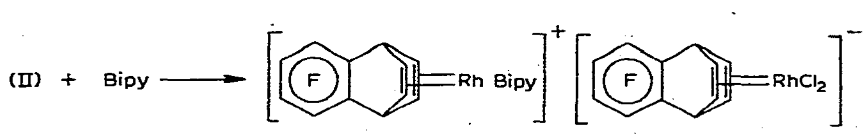
(II) 80 % yield

The reaction occurs in one hour in boiling ethanol or within four days if the mixture is stirred at room temperature. The bridging chlorine atoms in the yellow complex (II) can be substituted for iodine, methoxy or acetoxy groups by treatment with potassium iodide, sodium carbonate in methanol, or sodium acetate, respectively. An ethanolic solution of (II) gives no precipitate, even on standing, when treated with silver nitrate at room temperature. Complex (II) is regenerated in essentially 100% yield when concentrated hydrochloric acid is added to the methoxy- or acetoxy-bridged complexes.

The chlorine bridges in (II) can be split open by treating (II) either with triphenylphosphine in dichloromethane at room temperature:

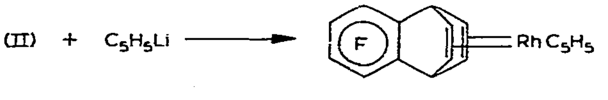


or with 2,2′-bipyridine (Bipy) in dichloromethane:

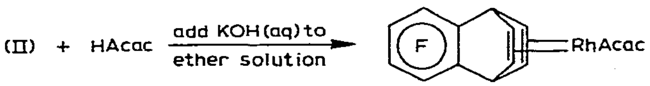


(III)

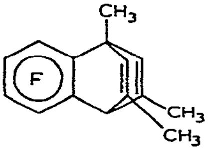
The red complex (III) is given the ionic structure shown on the basis of the elemental analysis, which gave the correct stoichiometry, and by analogy with Chatt's work on similar complexes derived from 1,5-cyclooctadiene[6]. The dimeric structure of (II) is also destroyed when it is treated with either cyclopentadienyllithium:



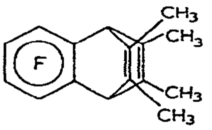
or acetylacetone (HAcac) in the presence of potassium hydroxide:



Analogues of all the above rhodium complexes have been prepared in which the tetrafluorobenzobarrelene ligand has been replaced by either (IV) or (V):

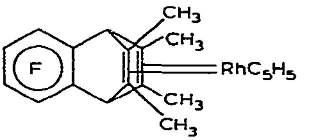


(IV)



(V)

thus, although the methyl groups on the olefinic bonds no doubt interfere sterically with coordination to the rhodium atom (see ref. 7 for a study of such steric interaction in the case of Fe complexes), the complexes formed from (IV) and (V) are still capable of existence. Indeed (VI) is only partially decomposed even after being heated at



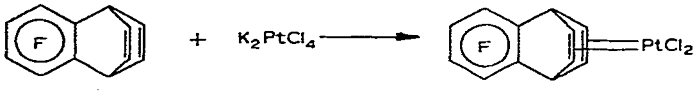
(VI)

200° for 24 hours in a sealed, evacuated tube; the main isolable decomposition product was 1,2,3,4-tetrafluoro-7,8-dimethylnaphthalene. It is noteworthy that while tetrafluorobenzobarrelene reacts with rhodium trichloride to give an 80% yield of (II) within four hours, ligand (IV) requires two days and ligand (V) requires five days to react to the same extent.

The NMR spectra of the compounds DiolefinM(C_5H_5) [M = Co, Rh; Diolefin = tetrafluorobenzobarrelene, (IV), (V)] showed some interesting features. (Tetrafluorobenzobarrelene)cyclopentadienylcobalt gave a singlet at δ 4.73 ppm due to the

C_5H_5 protons, a broad peak at 4.85 ppm assigned to the bridge-head protons, and a four-line multiplet at 2.74 ppm assigned to the olefinic protons. The rhodium analogue gave a more complex spectrum in which the C_5H_5 peak was split into a doublet [J(Rh–H) 0.8 Hz] and the olefinic protons showed an extra coupling of 2.5 Hz. Double resopance experiments showed that this extra coupling could be attributed to the ^{103}Rh nucleus ($I=\frac{1}{2}$; 100% abundance). The rhodium complexes of ligands (IV) and (V) showed similar rhodium couplings on the olefinic and C_5H_5 protons; in addition the protons on the olefinic methyl groups were also coupled to the rhodium (J 1.1 Hz).

Tetrafluorobenzobarrelene and K_2PtCl_4 react together when stirred in aqueous acetic acid for three days forming the highly insoluble complex (VII):



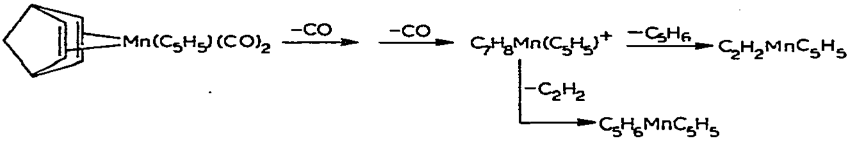
(VII)

The analogous palladium complex results when tetrafluorobenzobarrelene is treated with bis(benzonitrile)palladium dichloride in benzene at room temperature. The infra-red spectra of the platinium complexes show the presence of terminal chlorine groups (Pt complex: very strong bands at 343 and 320 cm^{-1}; Pd complex: very strong bands at 333 and 310 cm^{-1}); in both complexes the diolefin ligand can be displaced by triphenylphosphine to give the known $(Ph_3P)_2MCl_2$; M = Pt, Pd. The chlorine atoms in the platinium complex (VII) are quite labile, for example, (VII) reacts within minutes when treated with an acetone solution of potassium iodide giving $C_{12}H_6F_4PtI_2$. This iodide is sufficiently soluble in acetone to allow molecular weight determination to be carried out; these showed it to be monomeric. In contrast, $C_{12}H_6F_4PdCl_2$ gave very poor yields of the corresponding dibromide when treated with KBr and was completely decomposed by the presence of potassium iodide. A better yield of what appeared to be $C_{12}H_6F_4PdBr_2$ could be obtained by the addition of tetrafluorobenzobarrelene to methanolic K_2PdBr_4 although the complex did not give very satisfactory analyses even after several attempted purifications. Basic methanol reacted with $C_{12}H_6F_4PtCl_2$ and $C_{12}H_6F_4PdCl_2$ to give complete decomposition, in contrast to other DiolefinMX$_2$ derivatives which give [DiolefinMX(OCH$_3$)]$_2$[7].

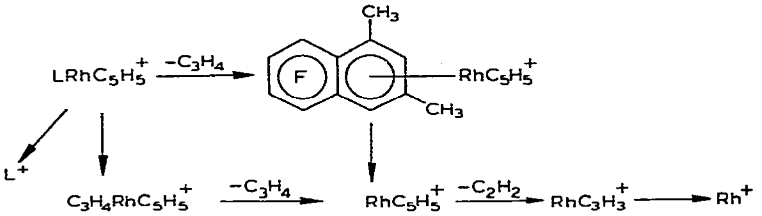
Treatment of (VII) with "pentafluorophenylmagnesium bromide" gave only a low yield (*ca.* 10%) of the white complex $C_{12}H_6F_4Pt(C_6F_5)_2$ even when the Grignard reagent was used in vast excess. The ^{19}F NMR spectrum of this compound exhibited five peaks: two at 156.6 and 148.3 ppm (relative to CCl_3F) we attribute to the fluorine atoms on the tetrafluorobenzobarrelene ligand while the three very complex peaks at 120.2, 158.2 and 162.7 ppm we assign to the *ortho*, *para* and *meta* C_6F_5 ring fluorine atoms.

Fragmentation of the manganese complex $C_{12}H_6F_4Mn(C_5H_5)(CO)_2$ in a mass spectrometer is relatively simple, involving the step-wise loss of carbon monoxide and then further breakdown to give L^+, $Mn(C_5H_5)^+$ and Mn^+ (where L = tetrafluorobenzobarrelene). This is a much more simple breakdown pattern than was observed for the corresponding norbornadiene complex[9] $C_7H_8Mn(C_5H_5)(CO)_2$

which gave several ions arising from "reverse Diels–Alder" reactions:



The cobalt and rhodium complexes, Diolefin MC_5H_5, gave a complex breakdown pattern, *e.g.* for M = rhodium, Diolefin = (IV):



Metastable peaks were observed for all the above transitions. No metastable loss of MF_2 or C_5H_5MF fragments could be detected in the spectra of any of these complexes.

EXPERIMENTAL

Reactions were normally carried out under dry nitrogen; analyses were performed by the microanalytical laboratory at Queen Mary College. The tetrafluorobenzobarrelene ligands were prepared as described in a previous paper[7].

ACKNOWLEDGEMENTS

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