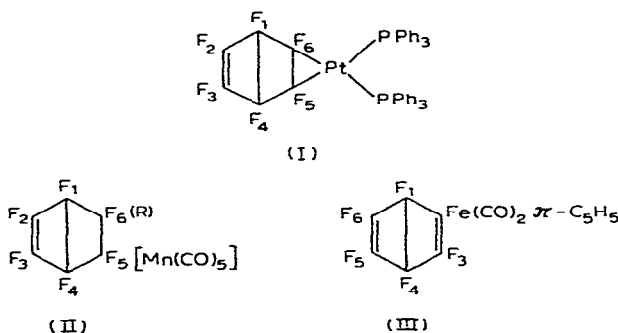


PRELIMINARY COMMUNICATION

A hexafluoro(*para*-bonded benzene) platinum complex

The synthesis of hexafluorobicyclo[2,2,0]hexa-2,5-diene by irradiation of hexafluorobenzene has recently been described^{1,2}, but little is known of the reactions of this *para*-bonded benzene derivative. The first examples of its reactions with transition metal complexes are now described.

When tetrakis(triphenylphosphine)platinum³, which reacts^{4,5} readily with chloro- or fluoro-olefins, is stirred with hexafluorobicyclo[2,2,0]hexa-2,5-diene at room temperature in benzene the colourless solid (53 % yield: m.p. 168° with decomposition) produced has a molecular weight (952, 894 by osmometry in different solvents) and an elemental analysis for C, H, F, and P consistent with the molecular formula $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_6\text{F}_6)$ [mol. wt., 905]. The ¹⁹F NMR spectrum of this compound shows three bands of equal intensity centred at 48.0 (apparent singlet), 88.0 (complex multiplet) and 99.8 ppm (complex multiplet) in CH_2Cl_2 relative to external $\text{CF}_3\cdot\text{CO}_2\text{H}$ increasing to high field, and assigned to the vinylic F nuclei (F_2, F_3), the F nuclei bonded to the carbon atoms attached to platinum (F_5, F_6), and the bridgehead F nuclei (F_1, F_4) respectively (I) on the basis of the chemical shifts. The shift of the



bridgehead F nuclei is to lower field than found in the free *para*-bonded benzene, and in related compounds^{6*}. The spectrum was insufficiently well resolved for detailed analysis, but from the band at 88.0 ppm the ¹⁹⁵Pt-F coupling constant was approximately 220 c/sec. The IR spectrum, which shows a strong double bond absorption at 1752 cm^{-1} , but no absorption attributed to the co-ordinated double bond, is consistent⁵ with a rigid σ -bonded 3-membered ring system to platinum as in (I). It is not yet known whether the compound has the *endo* or the *exo* structure, although the low field shift of the bridgehead fluorines in the NMR spectrum would suggest the latter. Pyrolysis of the compound at 275°/0.5 mm gives a >90 % yield of hexafluorobenzene, and bromination gives 2,3,5,6-tetrabromohexafluorobicyclo[2,2,0]-hexane¹ in low yield.

* Unpublished observations.

The compounds $\text{RMn}(\text{CO})_5$ [$\text{R} = \text{H}, \text{Me}, \text{or Ph}$] also react with hexafluorobicyclo[2,2,0]hexa-2,5-diene to give insertion compounds which appear to be of the type $\text{RC}_6\text{F}_6\text{Mn}(\text{CO})_5$ (II) in which only one double bond undergoes insertion, the other double bond and the *para*-bond being unaffected. The compound where $\text{R} = \text{Me}$ is a pale yellow liquid with an IR spectrum which shows bands at 2122s, 2065m, 2034vs, 2021vs, 2004s, in the metal carbonyl region and 1750s ($\text{CF}=\text{CF}$), and its ^{19}F NMR spectrum in CHCl_3 has six bands of equal intensity at 36.6 (F_5), 41.4 (F_3), 45.4 (F_2), 72.4 (F_6), 81.0 (F_4) and 109.0 (F_1) ppm relative to $\text{CF}_3\cdot\text{CO}_2\text{H}$; as in the Pt complex described above the high chemical shifts for F_1 and F_4 indicate the retention of the *para*-bonded structure.

Hexafluorobicyclo[2,2,0]hexa-2,5-diene reacts at the 2-position with the anions $[\text{Fe}(\text{CO})_2\pi\text{-C}_5\text{H}_5]^-$, $[\text{Re}(\text{CO})_5]^-$ and $[\text{Mn}(\text{CO})_5]^-$. The ^{19}F NMR spectrum of the compound $\text{C}_6\text{F}_5\text{Fe}(\text{CO})_2\pi\text{-C}_5\text{H}_5$ (m.p. 56–57°; III) shows five bands of equal intensity at 29.8 (F_3), 45.2 (F_6), 46.0 (F_5), 97.6 (F_1), and 109.0 (F_4) relative to external $\text{CF}_3\text{CO}_2\text{H}$, and its IR spectrum has strong bands at 1740 cm^{-1} ($\text{CF}=\text{CF}$), 1600 cm^{-1} ($\text{CF}=\text{CFe}$) and $\nu(\text{CO})$ bands at 2030 and 1984 cm^{-1} ; the chemical shifts for F_1 and F_4 again indicate that the *para*-bond is retained in this compound.

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