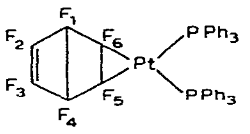
Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

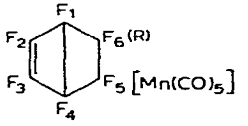
A hexafluoro(*para*-bonded benzene) platinum complex

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.

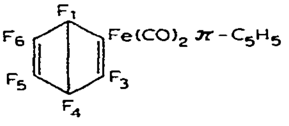
When tetrakis(triphenylphosphine)platinum[3], which reacts[4,5] readily with chloro- or fluoro-olefins, is stirred with hexafluorobicyclo[2,2,0]hexa-2,5-diene at room temperature in benzene the colourless solid (53 % yield: m.p. 168° with decomposition) produced has a molecular weight (952, 894 by osmometry in different solvents) and an elemental analysis for C, H, F, and P consistent with the molecular formula $(Ph_3P)_2Pt(C_6F_6)$ [mol. wt., 905]. The ^{19}F 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 $CF_3 \cdot CO_2H$ 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 ^{195}Pt–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 consistent[5] 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]-hexane[1] in low yield.



(I)



(II)



(III)

---

* Unpublished observations.

The compounds $RMn(CO)_5$ [R = H, Me, or Ph] also react with hexafluorobicyclo[2,2,0]hexa-2,5-diene to give insertion compounds which appear to be of the type $RC_6F_6Mn(CO)_5$ (II) in which only one double bond undergoes insertion, the other double bond and the *para*-bond being unaffected. The compound where R = 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 (CF=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 $CF_3\cdot CO_2H$; 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 $[Fe(CO)_2\pi\text{-}C_5H_5]^-$, $[Re(CO)_5]^-$ and $[Mn(CO)_5]^-$. The ^{19}F NMR spectrum of the compound $C_6F_5Fe(CO)_2\pi\text{-}C_5H_5$ (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 CF_3CO_2H, and its IR spectrum has strong bands at 1740 cm^{-1} (CF=CF), 1600 cm^{-1} (CF=CFe) and ν(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.

Department of Chemistry,
The University of Manchester
Institute of Science and Technology,
Manchester (Great Britain)

B. L. BOOTH
R. N. HASZELDINE
N. I. TUCKER

1 G. CAMAGGI, F. GOZZO AND G. CEVIDALLI, *Chem. Commun.*, (1966) 313.
2 I. HALLER, *J. Amer. Chem. Soc.*, 88 (1966) 2070.
3 L. MALATESTA AND C. CARIELLO, *J. Chem. Soc.*, (1958) 2323.
4 W. J. BLAND AND R. D. W. KEMMITT, *Nature*, 211 (1966) 963.
5 M. GREEN, R. B. L. OSBORN, A. J. REST AND F. G. A. STONE, *Chem. Commun.*, (1966) 502.
6 L. CAVALLI, *J. Chem. Soc.*, B, (1967) 384.

Received September 29th, 1967