Metal Carbonyl Chemistry. Part XVIII.[1,2] Preparation and Reactions of Some Transition Metal Derivatives of Hexafluorobicyclo[2.2.0]hexa-2,5-diene

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Hexafluorobicyclo[2.2.0]hexa-2,5-diene reacts with $[M(Ph_3P)_4]$ (M = Pt or Pd) to afford air-stable complexes of the type $[(C_6F_6)M(PPh_3)_2]$. These compounds react further with $[Pt(Ph_3P)_4]$ or $[Pd(Ph_3P)_4]$ to give the compounds $[(C_6F_6)\{Pt(PPh_3)_2\}_2]$ and $[(C_6F_6)\{Pd(PPh_3)_2\}_2]$, respectively; the latter complex is also obtained on thermal decomposition of $[(C_6F_6)Pd(PPh_3)_2]$ in solution at 90 °C. The *para*-bonded benzene also reacts with an excess of acetylacetonatobis(ethylene)rhodium to give $[(C_2H_4)(acac)Rh(C_6F_6)]$ and $[\{(C_2H_4)(acac)Rh\}_2(C_6F_6)]$. The mono-rhodium complex reacts with 1,2-bis(diphenylphosphino)ethane to yield a compound which is thought to be $[(C_6F_6)Rh(acac)(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)]$. Reactions of the *para*-bonded benzene with carbonylmetal anions to yield the compounds $[(C_6F_5)M(CO)_5]$ (M = Mn or Re) and $[(C_6F_5)Fe(CO)_2(\pi\text{-}C_5H_5)]$ are also described, together with the preparation of the adducts $[(RC_6F_6)Mn(CO)_5]$ (R = H, Me, or Ph) obtained by reaction of hexafluorobicyclo[2.2.0]hexa-2,5-diene with $[HMn(CO)_5]$, $[MeMn(CO)_5]$, or $[PhMn(CO)_5]$. In all complexes described the *para*-bond is retained.

As part of a general study [1,3,4] of the reactions of *para*-bonded benzene derivatives with transition-metal compounds we have investigated the reactions of hexafluorobicyclo[2.2.0]hexa-2,5-diene [5,6] with various metal complexes, and this work is now described.

Hexafluorobicyclo[2.2.0]hexa-2,5-diene reacts readily with $[Pt(Ph_3P)_4]$ or $[Pd(Ph_3P)_4]$ in benzene to afford the compounds (Ia) and (Ib) in 56 and 90% yield respectively. The compound (Ia) has been reported elsewhere [7] since our preliminary note.[1] The i.r. spectrum of (Ib) shows the characteristic $\nu(CF{:}CF)$ band at

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[1] Preliminary communication, B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J. Organometallic Chem.*, 1968, **11**, P5.

[2] Part XVII, R. E. Banks, R. N. Haszeldine, M. Lappin, and A. B. P. Lever, *J. Organometallic Chem.*, 1971, 427.

[3] B. L. Booth, R. N. Haszeldine, and M. Hill, *J. Chem. Soc.* (*A*), 1969, 1299.

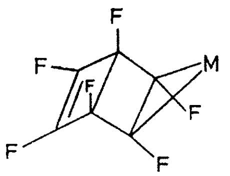
[4] B. L. Booth, R. N. Haszeldine, and M. Hill, *J. Organometallic Chem.*, 1969, **16**, 491.

[5] G. Camaggi, F. Gozzo, and G. Cevidalli, *Chem. Comm.*, 1966, 313; *J. Chem. Soc.* (*C*), 1969, 489.

[6] I. Haller, *J. Amer. Chem. Soc.*, 1966, **88**, 2070.

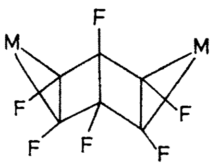
[7] D. J. Cook, M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1771.

1 752 cm^{-1},* and its ^{19}F n.m.r. spectrum * shows multiplets at 48.4, 86.5, and 93.0 p.p.m. to high field of trifluoroacetic acid in the intensity ratio of 1 : 1 : 1. The band at 48.4 p.p.m. is assigned to the fluorine atoms $F^{2,3}$ attached to the free olefinic bond, and the band at 93.0 p.p.m., which is broader and more complex than that at 86.5 p.p.m., is assigned to the fluorine atoms $F^{5,6}$ attached to the complexed olefinic bond; the increased complexity of this band is probably due to P–F long-range coupling, as previously observed in similar fluoro-olefin platinum complexes.[8,9] The platinum complex (Ia) also shows three complex bands in its ^{19}F n.m.r. spectrum centred at 47.5, 87.2, and 97.9 p.p.m. relative to external trifluoroacetic acid. Under high resolution (100 MHz in benzene) the two high-field bands both show ^{195}Pt-satellite systems with coupling constants [$J(^{195}\text{Pt–F}) = 185 \pm 5$ Hz; band at 87.2 p.p.m.] and [$J(^{195}\text{Pt–F}) = 180 \pm 5$ Hz; band at 97.9 p.p.m.], and the band at 97.9 p.p.m. is significantly broader and more complex than that at 87.2 p.p.m., indicative of ^{31}P–F long-range coupling. This suggests that the band at 97.9 p.p.m. is caused by the fluorine atoms F^5 and F^6, and not, as previously reported,[1,7] the bridgehead fluorine atoms F^1 and F^4; the latter are now considered to give rise to the band at 87.2 p.p.m. The ^{195}Pt satellites observed for this last band, which probably arise by a ' through-space ' coupling, support an *exo*-structure for complex (Ia), and by analogy, the palladium complex (Ib).



(I)

a; M = $Pt(PPh_3)_2$
b; M = $Pd(PPh_3)_2$
c; M = $Rh(C_2H_4)(acac)$



(II)

a; M = $Pt(PPh_3)_2$
b; M = $Pd(PPh_3)_2$
c; M = $Rh(C_2H_4)(acac)$

Pyrolysis of compound (Ia) at 275 °C/0.5 mmHg gave an almost quantitative yield of hexafluorobenzene together with a mixture of a red solid and a yellow solid, which were identified by i.r. spectroscopy as $[Pt(Ph_3P)_2]$ (yellow)[10] and its trimer $[\{Pt(Ph_3P)_2\}_3]$ (red).[10] Bromine reacts rapidly with compound (Ia) to give the previously unreported compound $[Pt(Ph_3P)_2Br_4]$ in 97% yield. Irradiation of the filtrate from this reaction gave a low yield of 2,3,5,6-tetrabromohexafluorobicyclo[2.2.0]hexane, which was identified by i.r. spectroscopy,[5] and is presumably formed by radical bromination of hexafluorobicyclo[2.2.0]hexa-2,5-diene obtained on initial cleavage of (Ia); a similar cleavage with iodine has also been reported,[7] although the nature of the platinum complex formed during this reaction was not commented on. The palladium complex (Ib) is also readily cleaved with iodine at room temperature to give hexafluorobicyclo[2.2.0]hexa-2,5-diene and di-iodobis(triphenylphosphine)palladium in 90% yield.

The platinum complex (Ia) reacts rapidly with $[Pt(Ph_3P)_4]$ in benzene at room temperature to afford $[(C_6F_6)\{Pt(PPh_3)_2\}_2]$ (IIa) in 55% yield as an air-stable white solid, which is relatively insoluble in most common organic solvents. The palladium complex (Ib) reacts with $[Pd(Ph_3P)_4]$ under similar conditions to give the analogous dipalladium complex (IIb) in 82% yield. The same compound was also obtained in 16% yield on heating (Ib) with 2,2'-bipyridyl at 90 °C in benzene in an attempt to cleave the mono-palladium adduct. It is probable that the 2,2'-bipyridyl plays no part in this reaction, as compound (IIb) was obtained in similar yield on heating a benzene solution of (Ib) under the same conditions; on heating (Ib) under reflux in toluene solution hexafluorobenzene was observed. These reactions probably occur by initial dissociation of (Ib) into the *para*-bonded benzene and $[Pd(Ph_3P)_2]$, which then reacts further with (Ib) to form the di-palladium complex (IIb) (see Scheme). The reaction is complicated by the fact that molecular-weight evidence suggests that compound (IIb) is dissociated in solution, and this is supported by the fact that initially colourless solutions of (IIb) in benzene acquire a pale yellow colour, possibly due to the formation of $[Pd(Ph_3P)_2]$ after 5—10 min. It therefore appears that the formation of the di-palladium complex from the mono-palladium complex is governed by a series of equilibria which are kinetically controlled. It is noteworthy that the mono-platinum complex (Ia) does not exhibit the same behaviour and may be recovered unchanged after being heated at 80—90 °C for 20 h in benzene solution.

The ^{19}F n.m.r. spectrum of the di-palladium complex (IIb) could not be obtained due to its low solubility. However, that of the di-platinum complex (IIa) showed two bands centred at 52.7 and 93.3 p.p.m. relative to external trifluoroacetic acid. The presence of only two bands in the spectrum suggests that the structure is symmetrical, *i.e.* either *exo–exo* or *endo–endo*, but not *exo–endo*. As both bands show ^{195}Pt-satellite splitting the most probable structure is *exo–exo* for the reasons discussed above for the mono-platinum compound. The general broadness and complexity of the band centred at 93.3 p.p.m. [$J(^{195}\text{Pt–F})$ 220 ± 40 Hz], which is probably caused by ^{31}P–F coupling, supports the assignment of this band to the fluorine atoms F^2, F^3, F^5, and F^6. The low-field band is, therefore, assigned to the bridgehead fluorines. When the chemical shift of these bridgehead fluorines (52.7 p.p.m.) is compared

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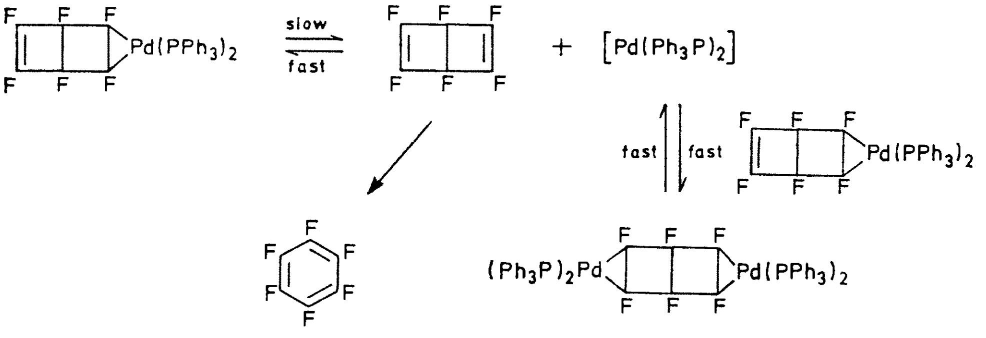
* Detailed i.r. spectral data for compounds (Ib), (IIa—c), (III), (IVa), and (Va—c) and ^{19}F n.m.r. spectral data for compounds (Ib), (IIa), (IVa), and (Va—c) are deposited as a Supplementary Publication (SUP No. 21366, 4 pp); see *J.C.S. Dalton*, 1974, Index issue for details of the Scheme.

[8] M. Green, B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

[9] F. L. Bowden, R. N. Haszeldine, and B. H. J. Williamson, unpublished data from this Department.

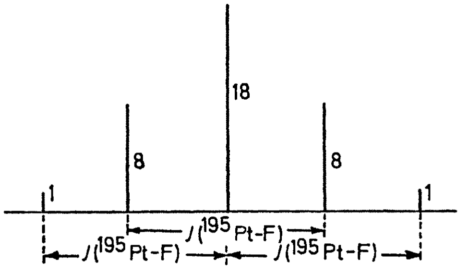
[10] R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Comm.*, 1966, 869.

with the values for the bridgehead fluorines in the mono-adduct (Ia) (87.2 p.p.m.; $\Delta = 34.5$ p.p.m.) and in hexafluorobicyclo[2.2.0]hexa-2,5-diene (116.2 p.p.m.; $\Delta = 63.5$ p.p.m.) it becomes apparent that the deshielding effect of the spacially close platinum atoms is cumulative and again supports an *exo–exo* structure. The introduction of a further platinum atom also alters the appearance of the ^{195}Pt-satellite bands. The abundance of the n.m.r. active ^{195}Pt isotope is *ca.* 33% and three possible combinations of n.m.r. active and inactive Pt isotopes may act on the bridgehead fluorines, *viz.*: (Pt,Pt) which is inactive; (Pt,^{195}Pt) which will produce a doublet of separation $J(^{195}\text{Pt–F})$; and (^{195}Pt,^{195}Pt) which will produce a triplet of overall spacing $2 \times J(^{195}\text{Pt–F})$. Thus a five-line spectrum is possible and probability theory predicts that their intensities will be in the ratio 1 : 8 : 18 : 8 : 1 (see Figure). The actual spectrum clearly shows the inner satellites and gives $J(^{195}\text{Pt–F}^{1,4}) = 190 \pm 20$ Hz, but the weaker outer satellites are barely discernible above the background noise and give $J(^{195}\text{Pt–F}) = 200 \pm 40$ Hz.



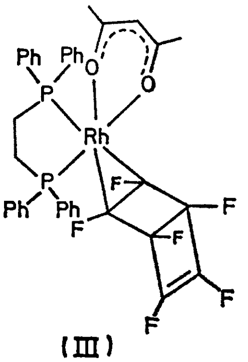
SCHEME

Acetylacetonatobis(ethylene)rhodium has previously been reported[7] to react with hexafluorobicyclo[2.2.0]-hexa-2,5-diene to give the mono-substituted complex (Ic), and we can confirm these findings. When this reaction is carried out using an excess of [Rh(acac)(C_2H_4)$_2$] compound (Ic) is obtained together with a small amount of a yellow solid. Although this solid could not be fully characterised by elemental analysis, its molecular weight and i.r. spectrum suggest that it is the di-substituted derivative (IIc). The mass spectrum obtained by direct insertion at 200 °C shows weak peaks at *m/e* 258 [(acac)Rh(C_2H_4)$_2$]$^+$, 230 [(acac)Rh(C_2H_4)]$^+$, 202 [(acac)Rh]$^+$, 186 (C_6F_6)$^+$, and 100 (Hacac)$^+$, which are probably the result of thermal decomposition in the ionisation chamber. When compound (IIc) is treated with cyclo-octa-1,5-diene displacement of hexafluorobicyclo[2.2.0]hexa-2,5-diene occurs to give an amount of acetylacetonato(cyclo-octa-1,5-diene)rhodium equivalent to two atoms of Rh per molecule of (IIc), thus confirming its formulation as a di-rhodium complex.



Theoretical splitting diagram for the coupling of two Pt atoms to a ^{19}F nucleus

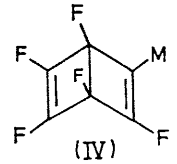
The mono-rhodium compound (Ic) has been shown to react with 1,2-bis(diphenylphosphino)ethane (diphos) to give yellow crystals of a compound believed to have structure (III). Its i.r. spectrum shows an absorption of medium intensity at 1 745 cm^{-1} [ν(CF:CF)] and other bands assignable to the acetylacetonato and diphos ligands. Its mass spectrum, obtained by direct insertion of the sample at 200 °C, shows a parent ion at *m/e* 786, and other peaks at *m/e* 600 [(acac)Rh(diphos)]$^+$, 501 [(diphos)Rh]$^+$, 202 [(acac)Rh]$^+$, and 186 [C_6F_6]$^+$; other peaks in the spectrum arise from fragmentation of the ligand ions [C_6F_6]$^+$ and [diphos]$^+$ and to a lesser extent from fragmentation of [(acac)Rh]$^+$ and [Hacac]$^+$, produced by hydrolysis in the spectrometer. The attempted reactions of di-μ-chloro-tetrakis(ethylene)dirhodium and π-cyclopentadienylbis(ethylene)rhodium with hexafluorobicyclo[2.2.0]hexa-2,5-diene failed to give any isolable complexes. The reaction of [{(C_2H_4)$_2$RhCl}$_2$] in methanol at room temperature gave a dark brown solid, which could not be purified and which decomposed on chromatography. Elemental analysis confirmed the presence of Cl and F, and its i.r. spectrum showed a



(III)

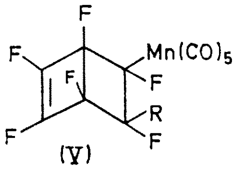
band at 1 750 cm^{-1} [ν(CF:CF)], indicating that it was possibly a *para*-bonded benzene complex, but insufficient data were available to assign a structure to this compound.

The carbonylmetal anions $[Mn(CO)_5]^-$, $[Re(CO)_5]^-$, and $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ react with hexafluorobicyclo[2.2.0]hexa-2,5-diene with displacement of a vinylic fluorine to give complexes (IVa—c). The compounds (IVb) and (IVc) have been reported[7] since our preliminary communication.[1] The compound (IVa) was obtained in low yield (6%) as an unstable pale yellow oil, which shows four bands in its i.r. spectrum for terminal metal carbonyl groups. Its ^{19}F n.m.r. spectrum is in general agreement with the spectra reported[7] for the similar compounds (IVb) and (IVc). A weak band in the spectrum at *ca.* 82 p.p.m. may also indicate the presence of some pentacarbonylpentafluorophenylmanganese,[11] but the poor quality of the spectrum prevented a definite assignment. It has previously been noted[7] that formation of compounds (IVc) and particularly compound (IVb) is accompanied by the formation of some of the corresponding pentafluorophenylmetal complex. This has been attributed to collapse of the intermediate carbanion formed on initial nucleophilic attack of the carbonylmetal anion on the CF:CF bond. Although this is certainly a feasible explanation an alternative possibility which cannot be ignored is that the formation of the pentafluorophenylmetal complexes arises from the inherent thermal instability of the *para*-bonded benzene complexes. When complex (IVb) is allowed to stand in an n.m.r. tube at 34.5 °C the percentage of the pentafluorophenyl isomer increases from 16 to 22% during 2 h. Furthermore, a sample of the *para*-bonded benzene complex rearranges quantitatively to the aromatic compound during 3 weeks at room temperature in the absence of light. It is noteworthy that complex (IVc), which appears to be indefinitely stable in the solid state and for several weeks in solution at room temperature, gives only a low yield of the pentafluorophenyl derivative on reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with *para*-hexafluorobenzene. It is thus possible that some of the rearrangement of these *para*-benzene complexes occurs during the purification of the reaction product.



(IV)

a; M = Mn(CO)5
b; M = Re(CO)5
c; M = Fe(CO)2(π-C5H5)



(V)

a; R = Me
b; R = Ph
c; R = H

A number of reactions have been reported in which fluoro-olefins insert into σ-alkyl transition-metal bonds.[12] We have now shown that u.v. irradiation of methyl- or phenyl-pentacarbonylmanganese with hexafluorobicyclo[2.2.0]hexa-2,5-diene leads to low yields of the adducts (Va) and (Vb) respectively. The i.r. spectra of these compounds show a characteristic band in the region of 1 750 cm^{-1} for ν(CF:CF), and both show five bands in the metal carbonyl region. The ^{19}F n.m.r. spectrum of (Va) shows the anticipated six complex bands, in accordance with the strong deshielding influence of the $Mn(CO)_5$ group, the band at lowest field is assigned to F^6, and the bands at 40.4 and 45.4 p.p.m. can be assigned to the vinylic fluorines F^2 and F^3. The bands at 81.0 (or 74.2) and 110.0 p.p.m. can be assigned to the bridgehead fluorines F^1 and F^4 respectively. The apparent deshielding of these nuclei when compared with the chemical shifts observed for compound (IVa) is in accordance with the $Mn(CO)_5$ and CH_3 groups being *cis* to the bridgehead fluorines. This deshielding effect is more noticeable in the n.m.r. spectrum of (Vb), where the bridgehead fluorines have chemical shifts of 103.1 p.p.m. (F^4) and either 83.6 or 81.6 p.p.m. (F^1), and is again in accordance with the addition of $[PhMn(CO)_5]$ occurring in a *cis* manner from above the ring. The mass spectrum of (Va) shows no parent ion, or $(P - CO)^+$ peak, and peaks corresponding to $[P - 2CO]^+$ m/e 340, $[P - 3CO]^+$ m/e 312, $[P - 4CO]^+$ m/e 286, and $[P - 5CO]^+$ m/e 256 are of low intensity. The major fragmentation pathway involves loss of $Mn(CO)_xF$ ($x = 0$—5) from a manganese-containing fragment to give $[C_6F_5CH_3]^+$ at m/e 182. The mass spectrum of compound (Vb) shows a parent ion at m/e 458, followed by stepwise loss of five CO groups, thus confirming the presence of an $Mn(CO)_5$ group.

Pentacarbonylhydridomanganese reacts with the *para*-bonded benzene to give a low yield (*ca.* 1%) of an air-stable pale yellow oil, identified spectroscopically as (Vc); no evidence was found for hydrogenation of the *para*-bonded benzene. Its i.r. spectrum shows a strong absorption at 1 745 cm^{-1} [ν(CF:CF)], and five bands in the ν(CO) region typical of a $Mn(CO)_5$ group bonded to an asymmetric fluorocarbon ligand. The ^1H n.m.r. spectrum shows a weak doublet centred at *ca.* τ 4.7 (J_{HF} *ca.* 50 Hz), and the ^{19}F n.m.r. spectrum shows several very weak bands at 38.6, 42.5, 45.0, 55.0, 64.0, 81.0, 103.0, and 115.0 p.p.m. Although the spectrum shows that a mixture is present several assignments may be made. In agreement with the previously reported spectrum of this compound, prepared by a different route,[7] the ill-defined doublet (J_{HF} *ca.* 50 Hz) at highest field may be assigned to the CHF group, and the bands at 42.5 and 45.0 p.p.m. are in the anticipated region for the vinylic fluorines. In contrast to the previous report,[7] we assign the band at lowest field (38.6 p.p.m.) to the fluorine atom adjacent to the metal atom, by comparison with the spectra of compounds (Va) and (Vb), leaving the bands at 81.0 and 103.0 p.p.m. assignable to the bridgehead fluorine atoms F^1 and F^4 respectively; the remaining bands at 55.0 and 64.0 p.p.m. are due to some impurity. The

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[11] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459.

[12] J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119.

mass spectrum of (Vc) shows a parent ion of low abundance at *m/e* 382, and stepwise loss of five carbonyl groups giving rise to peaks at *m/e* 354, 326, 298, 270, and 242 confirms the presence of a $Mn(CO)_5$ group. The base peak (*m/e* 168) arises from loss of $Mn(CO)_xF$ ($x = 0$—5) from a $[C_6F_6(H)Mn(CO)_x]^+$ ion.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer model 257 grating spectrometer, and n.m.r. spectra were recorded on a Varian HA 100 instrument operating at 100.0 MHz for protons and 94.1 MHz for ^{19}F nuclei. Mass spectra were obtained on an A.E.I. MS 902 mass spectrometer operating at an ionising energy of 70 eV. Molecular-weight determinations were carried out using a Mechrolab vapour-pressure osmometer. Hexafluorobicyclo[2.2.0]hexa-2,5-diene was prepared by the photochemical rearrangement of hexafluorobenzene,[5] and was separated from unchanged hexafluorobenzene as described elsewhere.[13] Tetrakis(triphenylphosphine)platinum,[14] tetrakis(triphenylphosphine)palladium,[15] acetylacetonatobis(ethylene)rhodium,[16] decacarbonyldimanganese,[17] pentacarbonylhydridomanganese,[17] and methyl- and phenyl-pentacarbonylmanganese [18] were prepared by previously reported methods. Decacarbonyldirhenium and di-μ-carbonyl-bis[carbonyl(π-cyclopentadienyl)iron] were commercial samples used without further purification. Except where stated, all manipulations were carried out under an atmosphere of dry nitrogen.

Reactions of Hexafluorobicyclo[2.2.0]*hexa*-2,5-*diene*.—(a) *With tetrakis(triphenylphosphine)platinum.* Hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.98 g, 5.3 mmol) was added to a solution of tetrakis(triphenylphosphine)platinum (3.0 g, 2.4 mmol) in benzene (30 ml), and the mixture was stirred at room temperature for 6 h, and then left for a further 48 h at this temperature. Filtration of the pale yellow solution and evaporation of the filtrate to *ca.* 4 ml under reduced pressure gave, on addition of ethanol (50 ml), a white precipitate of hexafluorobicyclo[2.2.0]hex-2-ene-5,6-diylbis(triphenylphosphine)platinum (Ia) (1.19 g, 1.3 mmol, 56%), m.p. 170—172 °C (decomp.) (reported [7] 173 °C), which was filtered, washed with several portions of diethyl ether, and dried *in vacuo* [Found: C, 56.0; H, 3.5; F, 12.6; P, 6.85%; *M*, 894 (benzene), 952 (1,2-dichloroethane). Calc. for $C_{42}H_{30}F_6P_2Pt$: C, 55.7; H, 3.3; F, 12.7; P, 6.85%; *M*, 905].

(b) *With tetrakis(triphenylphosphine)palladium.* A mixture of tetrakis(triphenylphosphine)palladium (3.1 g, 2.7 mmol), hexafluorobicyclo[2.2.0]hexa-2,5-diene (1.0 g, 5.8 mmol), and dry benzene (25 ml) was shaken at room temperature for 16 h in a tube (50 ml) sealed *in vacuo*. The deep red solution was reduced to *ca.* 5 ml by evaporation of the solvent under reduced pressure, and addition of ethanol (25 ml) and cooling afforded *hexafluorobicyclo*[2.2.0]-*hex*-2-*ene*-5,6-*diylbis(triphenylphosphine)palladium* (Ib) as white crystals (2.1 g, 2.4 mmol, 90%), m.p. 156—157 °C, which may be recrystallised from a 1 : 3 mixture of dichloromethane–n-pentane at −20 °C [Found: C, 61.0; H, 3.4; P, 7.55%; *M*, 791 (ethyl methyl ketone), 839 (benzene). $C_{42}H_{30}F_6P_2Pd$ requires C, 61.7; H, 3.7; P, 7.60%; *M*, 816].

(c) *With acetylacetonatobis(ethylene)rhodium.* A mixture of acetylacetonatobis(ethylene)rhodium (0.62 g, 2.4 mmol) and a sample (1.0 g) of a mixture containing hexafluorobicyclo[2.2.0]hexa-2,5-diene contaminated with some hexafluorobenzene in dry ether (20 ml) was sealed *in vacuo* in a Pyrex tube (50 ml) and shaken for 17 h at room temperature, whereupon a yellow solid (1.05 g) precipitated. Chromatography of the solid on Florisil gave, on elution with light petroleum, yellow crystals of acetylacetonato(ethylene)hexafluorobicyclo[2.2.0]hex-2-ene-5,6-diylrhodium (Ic) (0.06 g, 0.14 mmol, 6%) [Found: C, 37.8; H, 3.0%; *M*, 527 (benzene), 528 (ethyl methyl ketone). Calc. for $C_{13}H_{11}F_6O_2Rh$: C, 37.5; H, 2.7%; *M*, 416], which had an identical i.r. spectrum to that of an authentic sample prepared according to a previously reported procedure.[7] Further elution with a 4 : 1 mixture of light petroleum (b.p. 40—60°) and dichloromethane gave an orange-yellow solid, which on recrystallisation from dichloromethane at −20 °C afforded μ-*hexafluorobicyclo*[2.2.0]*hexane*-2,3:5,6-*tetrayl-bis[acetylacetonato(ethylene)rhodium]* (IIc) (0.05 g, 0.007 mmol, 2%) [Found: C, 35.8; H, 3.5%; *M*, 692 (ethyl methyl ketone). $C_{20}H_{22}F_6O_4Rh_2$ requires C, 37.6; H, 3.4%; *M*, 646]. The mass spectrum suggested the presence of CH_2Cl_2, possibly as solvent of crystallisation ($C_{20}H_{22}F_6O_4Rh_2 \cdot 0.5CH_2Cl_2$ requires C, 35.7; H, 3.3%; *M*, 689).

(d) *With sodium pentacarbonylmanganate.* Hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.98 g, 5.3 mmol) was added in one portion to a solution of the sodium salt [prepared from decacarbonyldimanganese (1.0 g, 2.6 mmol) and 1% sodium amalgam] in dry tetrahydrofuran (30 ml), and the mixture was stirred at room temperature for 3 h. Chromatographic separation of the mixture on alumina [light petroleum (b.p. 40—60 °C) as eluant] gave an unstable, pale yellow oil (0.12 g), which was identified by i.r. and ^{19}F n.m.r. spectroscopy as impure pentacarbonyl(pentafluorobicyclo[2.2.0]hexa-2,5-dien-2-yl)rhodium (IVa) (*ca.* 6% yield).

(e) *With sodium pentacarbonylrhenate.* A solution of the sodium salt [prepared from decacarbonyldirhenium (2.27 g, 3.5 mmol) and 1% sodium amalgam] in tetrahydrofuran (50 ml) was added dropwise during 40 min to a stirred solution of hexafluorobicyclo[2.2.0]hexa-2,5-diene (1.37 g, 7.4 mmol) in tetrahydrofuran (5 ml) maintained at *ca.* −72 °C, and the mixture was then kept at this temperature for 3 h and for a further 1 h at ambient temperature. Removal of the solvent and unchanged diene under reduced pressure gave an orange, waxy residue which, on extraction with a 1 : 3 mixture of dichloromethane–light petroleum (3 × 20 ml), gave a pale orange oil (0.41 g) on removal of the solvent from the combined extracts at 20 °C/50 mmHg. ^{19}F N.m.r. spectroscopy indicated that the oil was a mixture of pentafluorophenylrhenium and (IVb) in the ratio of 1 : 5.25, respectively. Chromatography of the oil on Florisil (light petroleum eluant) gave pentacarbonyl(pentafluorobicyclo[2.2.0]hexa-2,5-dien-2-yl)rhenium (IVb) (0.30 g, 0.61 mmol, 9%), m.p. 29.5—30 °C (reported [7] 31.5—32 °C), as a pale yellow, waxy solid [Found: C, 27.2; H, 0.2%; *M*, 519 (benzene). Calc. for $C_{11}F_5O_5Re$: C, 27.0; H, 0.0%; *M*, 493].

(f) *With sodium dicarbonyl(π-cyclopentadienyl)ferrate(−1).*

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A solution of the sodium salt {from di-μ-carbonyl-bis-[carbonyl(π-cyclopentadienyl)iron] (0.90 g, 2.5 mmol) with 1% sodium amalgam} in tetrahydrofuran (25 ml), added during 20 min to a stirred solution of the diene (1.03 g, 5.5 mmol) in tetrahydrofuran (5 ml) at 0—5 °C, was kept at this temperature for 4.5 h and for a further 0.5 h at room temperature. Chromatography on alumina (light petroleum eluant) gave dicarbonyl(π-cyclopentadienyl)(pentafluorobicyclo[2.2.0]hexa-2,5-dien-2-yl)iron (IVc) (0.96 g, 2.8 mmol, 56%), m.p. 58—59 °C (lit.,[7] 59—60°), which was recrystallised from n-pentane at −20 °C [Found: C, 45.7; H, 1.7%; *M*, 346 (benzene). Calc. for $C_{13}H_5F_5O_2Fe$: C, 45.4; H, 1.5%; *M*, 344].

(g) *With pentacarbonylmethylmanganese.* When a mixture of pentacarbonylmethylmanganese (0.5 g, 2.35 mmol) and hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.6 g, 3.2 mmol) in hexafluorobenzene (11.7 g) was sealed in a silica tube (100 ml) *in vacuo*, and irradiated (Hanovia UVS 500 light source) at room temperature for 19 h, removal of the solvent left a pale yellow solid (*ca.* 0.20 g). Sublimation of this solid at 20 °C/1 mmHg gave unchanged pentacarbonylmethylmanganese (0.16 g) which sublimed onto the probe cooled to −72 °C; a further quantity of pentacarbonylmethylmanganese (0.25 g; total recovery 0.41 g, 82%) was recovered from the hexafluorobenzene solvent. Sublimation of the yellow oily residue at 40 °C/1 mmHg gave a colourless oil (0.01 g, 0.002 mmol, 1%) identified spectroscopically as *pentacarbonyl(5-methylhexafluorobicyclo*[2.2.0]*hex-2-en-6-yl)manganese* (Va).

(h) *With pentacarbonylphenylmanganese.* When a mixture of pentacarbonylphenylmanganese (0.72 g, 2.65 mmol), hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.50 g, 2.7 mmol), and dry n-hexane (8 ml) was irradiated for 22 h at room temperature, removal of the volatiles left an orange oil (0.75 g), which on chromatography (alumina; light petroleum eluant) yielded unchanged pentacarbonylphenylmanganese (0.25 g), and further fractions which were shown by i.r. spectroscopy to be mixtures of pentacarbonylphenylmanganese and a complex. Sublimation of these latter fractions at 20—30 °C/0.5 mmHg to remove the volatile pentacarbonylphenylmanganese, gave a waxy, orange solid residue (0.05 g, 0.01 mmol, 4%) identified spectroscopically as *pentacarbonyl(5-phenylhexafluorobicyclo*[2.2.0]*hex-2-en-6-yl)manganese* (Vb), which on repeated recrystallisation from n-hexane at −20 °C gave a small amount of pure material as a pale lemon solid, m.p. 62.5—63.5 °C [Found: *M*, 484 (1,2-dichloroethane), 458 (mass spectroscopy). $C_{17}H_5F_6MnO_5$ requires *M*, 458].

(i) *With pentacarbonylhydridomanganese.* Hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.40 g, 2.15 mmol) and pentacarbonylhydridomanganese (0.40 g, 2.0 mmol) were sealed under vacuum in a tube (25 ml) and set aside at room temperature for 3 days. Removal of the volatiles [shown by i.r. spectroscopy to be unchanged starting materials (0.50 g)] under reduced pressure gave an orange liquid (0.20 g) which on sublimation at 20 °C/1 mmHg yielded a pale yellow oil identified spectroscopically as *pentacarbonyl(hexafluorobicyclo*[2.2.0]*hex-2-en-6-yl)manganese* (Vc) (0.01 g, 0.002 mmol, 1%) [Found: *M*, 382 (mass spectroscopy). $C_{11}HF_6MnO_5$ requires *M*, 382].

(j) *With π-cyclopentadienylbis(ethylene)rhodium.* When a mixture of π-cyclopentadienylbis(ethylene)rhodium [19] (0.45 g, 2.0 mmol), hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.50 g, 2.7 mmol), and dichloromethane (10 ml) was heated at 50 °C for 5 h in a tube sealed under vacuum no reaction occurred and the starting materials were recovered quantitatively.

(k) *With di-μ-chloro-tetrakis(ethylene)dirhodium.* Di-μ-chloro-tetrakis(ethylene)dirhodium [20] (0.20 g, 0.51 mmol), hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.22 g, 1.2 mmol), and methanol (5 ml) were shaken at room temperature for 3 h in a tube sealed under vacuum. A brown solid formed during the reaction was filtered off, washed with light petroleum (b.p. 40—60 °C), and dried in air [Found: C, 28.5 (26.3); H, 2.7 (2.5); Cl, 8.5; F, 20.1 (19.6)%]. The solid, which decomposed at 160 °C, showed the following bands in its i.r. spectrum: 3 700—2 760s,br, 2 060w, 1 870w, 1 750s (C:C), 1 615m,br, 1 505m, 1 455m,br, 1 370m,sh, 1 348s, 1 324m,sh, 1 300m, 1 143m, 1 084m, 1 065m, 1 009m,br, 962m, 935m, 870w,br, 820w, 790m, 734m,br, and 683w cm^{-1}.

Reactions of Hexafluorobicyclo[2.2.0]*hex-2-ene-5,6-diylbis(triphenylphosphine)platinum.*—(a) *With tetrakis(triphenylphosphine)platinum.* A solution of (Ia) (0.16 g, 0.19 mmol) and tetrakis(triphenylphosphine)platinum (0.22 g, 0.18 mmol) in dry benzene (8 ml) was kept at room temperature for 20 h. The pale yellow solution was reduced to *ca.* 3 ml under reduced pressure and poured into ethanol (20 ml), and this solution was cooled at 0 °C to give an off-white solid. Recrystallisation from a 1 : 10 mixture of dichloromethane–n-pentane at −20 °C yielded colourless crystals of *hexafluorobicyclo*[2.2.0]*hexane-2,3:5,6-tetraylbis[bis(triphenylphosphine)platinum]* (IIa) (0.16 g, 0.1 mmol, 55%), which decomposed at 230 °C [Found: C, 57.9; H, 4.1; P, 7.4%; *M*, 1 705 (benzene). $C_{78}H_{60}F_6P_4Pt_2$ requires C, 57.6; H, 3.7; P, 7.63%; *M*, 1 624].

(b) *On pyrolysis.* A sample of (Ia) (0.09 g, 0.1 mmol) was heated at a rate of 10 °C min^{-1} to 275 °C and maintained at this temperature for 1.5 h, while any volatile products were continuously removed by pumping at 0.5 mmHg and trapped at −196 °C. The volatile material collected in this way was identified as hexafluorobenzene [2.2 ml (of gas), 0.009 mmol, 95%]. A yellow solid (0.02 g) which had sublimed onto the cooler parts of the reaction tube was collected and, on the basis of its i.r. spectrum, was tentatively identified as bis(triphenylphosphine)platinum. A dark red, lustrous solid (0.05 g) which remained was identified spectroscopically as tris[bis(triphenylphosphine)platinum]. The total amount of solid (0.07 g) corresponded to 95% of that expected for $[Pt\{(C_6H_5)_3P\}_2]$.

(c) *With bromine.* When a solution of bromine (0.16 g, 1.0 mmol) in dry carbon tetrachloride (2 ml) was added dropwise to a stirred solution of (Ia) (0.16 g, 0.18 mmol) in carbon tetrachloride (15 ml) at room temperature and the mixture was set aside overnight, orange crystals precipitated. These were filtered, washed with light petroleum (b.p. 30—40 °C), and dried in air to yield *tetrabromobis(triphenylphosphine)platinum* (0.18 g, 0.17 mmol, 97%), which decomposed when heated at 195 °C (Found: C, 41.6; H, 3.2. $C_{36}H_{30}Br_4P_2Pt$ requires C, 41.5; H, 2.9%).

When the filtrate was sealed in a silica tube (50 ml) under vacuum and irradiated at room temperature for 15 h, removal of the volatile materials gave a white solid residue identified as 2,3,5,6-tetrabromohexafluorobicyclo[2.2.0]hexane (0.01 g) by i.r. spectroscopy.[5]

Reactions of Hexafluorobicyclo[2.2.0]*hex-2-ene-5,6-diylbis(triphenylphosphine)palladium* (Ib).—(a) *With tetrakis(triphenylphosphine)palladium.* A mixture of (Ib) (0.12 g,

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0.15 mmol), tetrakis(triphenylphosphine)palladium (0.17 g, 0.15 mmol), and dry benzene (8 ml) was sealed under vacuum in a Pyrex tube (20 ml), which was shaken for 5 min to give a homogeneous solution, and was then left at room temperature for 14 h during which time large colourless crystals deposited on the side of the reaction vessel. On decantation of the solution the remaining solid was washed with light petroleum (b.p. 40—60 °C), and air-dried to yield *hexafluorobicyclo*[2.2.0]*hexane*-2,3:5,6-*tetraylbis*[*bis*-(*triphenylphosphine*)*palladium*] (IIb) (0.16 g, 0.11 mmol), which decomposed at 155—160 °C; evaporation of the filtrate to *ca.* 1 ml and addition of ethanol (10 ml) afforded a further crop of the white solid (0.02 g; total yield 82%). The product was recrystallised from a 1 : 10 mixture of dichloromethane–light petroleum (b.p. 40—60 °C) at −20 °C [Found: C, 64.0; H, 4.1; P, 8.4%; *M*, 717, 724 (benzene). $C_{78}H_{60}F_6P_4Pd_2$ requires C, 64.7; H, 4.1; P, 8.6%; *M*, 1 447].

(b) *With iodine.* A solution of iodine (0.03 g, 0.13 mmol) in bromobenzene (5 ml) was added dropwise to a solution of (Ib) (0.10 g, 0.12 mmol) in bromobenzene (15 ml) at room temperature. The volatile material, which was removed at 20 °C/1 mmHg and collected in a trap cooled to −196 °C, was shown by i.r. spectroscopy to be hexafluorobicyclo[2.2.0]hexa-2,5-diene. The remaining brown solution was evaporated to dryness under reduced pressure and the solid residue was recrystallised from dichloromethane at −5 °C to yield a mixture of yellow-orange and brick-red crystals of *di-iodobis*(*triphenylphosphine*)*palladium* (0.11 g, 0.11 mmol, 90%), m.p. 270—274 °C (Found: C, 48.4; H, 3.4. $C_{36}H_{30}I_2P_2Pd$ requires C, 48.6; H, 3.4%).

(c) *With* 2,2′-*bipyridyl.* A mixture of (Ib) (0.12 g, 0.15 mmol), 2,2′-bipyridyl (0.05 g, 3.2 mmol), and dry benzene (8 ml) were sealed under vacuum in a tube (20 ml), which was then heated at 70 °C for 4 h and at 90 °C for a further 16 h. The resulting pale yellow solution was reduced to *ca.* 1 ml under reduced pressure, and on addition of ethanol (15 ml) a cream solid (0.03 g, 0.02 mmol, 16%) precipitated, which had an i.r. spectrum identical to that of (IIb). Removal of the solvent from the filtrate gave unchanged 2,2′-bipyridyl (0.03 g, 60% recovery).

(d) *On heating in solution.* When a solution of (Ib) (0.18 g, 0.22 mmol) in toluene (10 ml) was heated at 90 °C for 20 h in a tube (20 ml) sealed under vacuum, and the resulting orange solution was reduced to 1 ml by evaporation of the solvent under reduced pressure, addition of ethanol (15 ml) precipitated an off-white solid, identified by i.r. spectroscopy as (IIb) (0.05 g, 0.03 mmol, 14%). Examination of the solvent by i.r. spectroscopy showed the presence of hexafluorobenzene. Evaporation to dryness of the pale orange filtrate gave a deep orange solid (0.07 g), which was shown by i.r. spectroscopy to be a triphenylphosphineplatinum complex, but no bands attributable to starting material were observed.

When this reaction was repeated at 90 °C for 5 days, only metallic palladium and triphenylphosphine were obtained.

Reaction of Acetylacetonato(*ethylene*)*hexafluorobicyclo*[2.2.0]-*hex*-2-*ene*-5,6-*diylrhodium with* 1,2-*Bis*(*diphenylphosphino*)-*ethane.*—When a solution of 1,2-bis(diphenylphosphino)-ethane (0.03 g, 0.008 mmol) in chloroform (5 ml) was added to a solution of acetylacetonato(ethylene)hexafluorobicyclo-[2.2.0]hex-2-ene-5,6-diylrhodium (0.03 g, 0.008 mmol) in chloroform (5 ml), the colour of the solution changed from yellow-orange to straw; the mixture was left at room temperature for 20 min. Removal of the solvent under reduced pressure gave a yellow solid, which was redissolved in a small quantity of chloroform, and upon addition of n-hexane acetylacetonato[1,2-bis(diphenylphosphino)-ethane]hexafluorobicyclo[2.2.0]hex-2-ene-5,6-diylrhodium (III) (0.06 g, 0.07 mmol, 92%) precipitated as a straw yellow solid, which decomposed at *ca.* 160 °C [Found: *M*, 775 (ethyl methyl ketone), 786 (mass spectroscopy). $C_{37}H_{31}F_6O_2P_2Rh$ requires *M*, 786].

Reaction of Hexafluorobicyclo[2.2.0]*hexane*-2,3:5,6-*tetraylbis*[*acetylacetonato*(*ethylene*)*rhodium*] (IIb) *with Cyclo-octa*-1,5-*diene.*—Cyclo-octa-1,5-diene (0.200 g, 1.90 mmol) was added to a solution of (IIc) (0.011 g, 0.017 mmol) in dichloromethane (0.5 ml). An immediate colour change from orange to yellow occurred and the solution was shaken for 10 min at room temperature. Removal of the volatiles at 25 °C/1 mmHg yielded acetylacetonato(cyclo-octa-1,5-diene)rhodium (0.010 g, 0.032 mmol, 96%) as a yellow solid, m.p. 114 °C (reported[21] 125—128 °C). Its i.r. spectrum was identical to that of an authentic sample (m.p. 114 °C) prepared from acetylacetonatobis(ethylene)rhodium and cyclo-octa-1,5-diene.

[4/1877 *Received*, 16*th September*, 1974]

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