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REACTIONS INVOLVING TRANSITION METALS

XX *. A COMPARISON OF THE REACTIONS OF 1,2,3,4,7,7-HEXAFLUOROBICYCLO[2.2.1]HEPTADIENE, AND 2,3-BIS(TRIMETHYLTIN)- AND 2,3-DICHLORO-1,4,5,6,7,7-HEXAFLUOROBICYCLO[2.2.1]HEPTA-2,5-DIENES WITH LOW VALENT TRANSITION METAL COMPLEXES

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Summary

1,2,3,4,7,7-Hexafluorobicyclo[2 2 1]heptadiene (1) and 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexafluorobicyclo[2 2.1]hepta-2,5-diene (2) react with $[M(Ph_3P)_4]$ (M = Pt, Pd) to afford air-stable adducts 2,3-Dichloro-1,4,5,6,7,7-hexafluorobicyclo[2.2.1]hepta-2,5-diene (**3**) gives only $[PtCl_2(PPh_3)_2]$ with $[Pt(Ph_3P)_4]$, but a low yield of an adduct was obtained with $[Pd(PPh_3)_4]$ The diene **1** also reacts with $Fe(CO)_5$ to form the complex $[(C_7H_2F_6)Fe(CO)_4]$, and with $[Rh(C_2H_4)_2(acac)]$ to give $[(C_7H_2F_6)Rh(acac)]$ in which the diene acts as a bidentate ligand. Similar products could not be isolated from the reactions of **2** and **3**. A stable adduct, believed to be $[\{C_7F_6(SnMe_3)_2\}Rh(CO)_2(\mu\text{-}Cl)_2\text{-}Rh(CO)_2]$ has been isolated from the reaction between **2** and $[Rh(CO)_2Cl]_2$. This adduct reacts with PPh_3 to give the bridge-cleavage product $[\{C_7F_6(SnMe_3)_2\}RhCl(CO)(PPh_3)_2]$. Reaction of **1** with $[Rh(CO)_2Cl]_2$ gives an unstable adduct which could not be isolated, and **2** does not react at room temperature. The chloro derivative **3** reacts with $[PdCl_2(PhCN)_2]$ to give the adduct $[(C_7F_6Cl_2)PdCl(PhCN)]$, but **1** and **2** do not react under similar conditions Stable substitution products $[(C_7F_6R_2)M]$ (R = H, M = $Fe(CO)_2(\eta\text{-}C_5H_5)$, R = $SnMe_3$, M = $Fe(CO)_2(\eta\text{-}C_5H_5)$, $Mn(CO)_5$, $Ir(CO)_2(PPh_3)_2$, $Rh(CO)_2(PPh_3)_2$; R = Cl, M = $Ir(CO)_2(PPh_3)_2$, $Rh(CO)_2(PPh_3)_2$) have been isolated from the reactions of the dienes with carbonylmetal anions. Insertion of the CH=CH bond occurs when **1** is heated with $[MnMe(CO)_5]$ to give $[\{C_7F_6H_2C(\overline{O)Me\}Mn}(CO)_4]$,

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and this, on reaction with either PPh_3 or $[Pt(PPh_3)_4]$, gives $[(C_7F_6H_2COMe)Mn(CO)_4PPh_3]$.

Introduction

As a continuation of our studies of the organometallic chemistry of fluorinated norbornadienes [1] we have investigated some reactions of the 2,3-disubstituted hexafluorobicyclo[2.2.1]hepta-2,5-dienes (**1**—**3**), which are intermediates in the multi-stage synthesis of perfluoronorbornadiene from hexafluorocyclopentadiene [2]. We now report their reactions with a number of low valent platinum, palladium, and rhodium complexes, pentacarbonyliron, carbonylmetal anions and $[MnMe(CO)_5]$.

Results and discussion

Dienes **1** and **2** react readily with $[M(PPh_3)_4]$ (M = Pt, Pd) in benzene at room temperature to afford the adducts **4**—**7** in good yields. The compounds were characterised by elemental analysis (Table 1), and IR spectroscopy. Reaction occurs at the fluorinated double bond in all cases, as evidenced by the disappearance of the characteristic ν(CF=CF) bands at 1761 and 1750 cm^{-1} present in the IR spectra of **1** and **2**, respectively. The platinum complex **6** was so insoluble in common solvents that an NMR spectrum could not be obtained. A weak, poorly-resolved ^{19}F NMR spectrum was obtained for **4** (Table 2), and

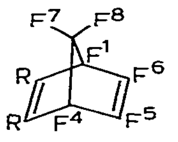
TABLE 1

MELTING POINT ANALYTICAL (%) AND MOLECULAR WEIGHT DATA FOR THE NEW COMPLEXES

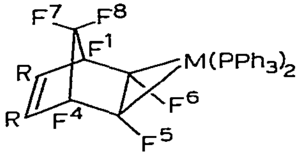
Compound	M p (°C)	Analysis (Found/calcd) (%)			mol. wt [a]
		C	H	F	
4	170[b]	58.5(56.7)	3.9(3.5)	10.4(12.5)	
5	140[b]	61.8(62.1)	3.7(3.8)	13.3(13.7)	
6	240—241[b]	47.9(47.2)	4.1(3.9)	8.9(9.2)	
7	125[b]	51.1(50.9)	4.4(4.2)	9.8(9.8)	684(1156)[c]
8	—	56.7(57.3)	4.1(3.8)	11.7(11.9)	310(889)[c]
9	—	35.7(35.8)	2.3(2.3)	28.8(28.4)	
10	—	23.0(22.3)	2.3(2.0)		899(915)[d]
11	—	49.3(49.5)	3.8(3.9)	9.2(9.4)	
12	—	33.1(32.7)	1.1(1.0)	21.4(22.2)	
14	—	47.1(47.2)	1.95(2.0)	26.6(26.4)	
15	—	33.9(34.5)	2.9(3.3)	13.6(13.9)	
16	—	29.9(30.5)	2.8(2.5)	13.0(13.5)	720(702)[d]
17	163	47.8(47.8)	4.0(3.7)	7.6(7.4)	
18	142	51.8(51.5)	4.3(4.0)	8.1(7.9)	
19	152	52.1(52.8)	2.7(2.9)	9.0(9.3)	
21	80[b]	38.2(38.0)	1.1(1.2)	27.3(27.8)	
22	—	55.6(55.9)	3.1(3.1)	17.8(17.7)	

[a] Calculated figures are given in parentheses. [b] With decomposition. [c] In dichloromethane. [d] In chloroform

shows bands at 58, 110, and 121 ppm to high field of trifluoroacetic acid in the intensity ratio of 1/1/1 The bands at 58 and 121 ppm are assigned to the bridging fluorine atoms ($F^{7,8}$) and fluorine atoms ($F^{1,4}$) respectively by analogy with the spectrum of **1** The band at 110 ppm is therefore assigned to the fluorine atoms $F^{5,6}$ which have been shifted upfield by 30 ppm upon coordination to the platinum atom. Shifts of a similar magnitude have been noted previously [1,3]. Details of coupling constants could not be determined from the spectrum, but by analogy with products from perfluoronorbornadiene these compounds are expected to have the *exo*-structure shown [1]. Colourless solutions of the palladium complexes **5** and **7** in various solvents under an atmosphere of nitrogen rapidly turned orange. A molecular weight determination on a dichloromethane solution of **7** clearly shows that appreciable dissociation is occurring (Table 1) as found for analogous palladium derivatives of perfluoronorbornadiene [1] and hexafluorobicyclo[2.2 0]hexa-2,5-diene [3]. For this reason ^{19}F NMR spectra of compounds **5** and **7** were not obtained. The immediate development of a deep red colour was observed on addition of the dichloro-compound **3** to $[Pt(PPh_3)_4]$ in benzene at room temperature, and the only product which could be isolated was *cis*-$[PtCl_2(PPh_3)_2]$. A similar result was obtained when this reaction was repeated at 0°C, and special care was taken to exclude air at all stages of the reaction and subsequent work-up. Reaction between **3** and the palladium complex, $[Pd(PPh_3)_4]$, gave a low yield of the adduct **8**. This, like the other palladium derivatives, was unstable in solution, and it was characterised by elemental analysis and IR spectroscopy only One possible explanation for these results is that in the reaction of **3** there is competition between attack at the CF═CF and CCl═CCl bonds. It is well known that chloro- or bromo-substituted olefins coordinated to palladium or platinum readily rearrange to *o*-vinyl derivatives [4,5], and, perhaps, the sequence of reactions shown in Scheme 1 could account for the formation of *cis*-$[PtCl_2(PPh_3)_2]$ and the low yield of adduct from the palladium reaction. Due to the small scale employed we have so far been unable to isolate any organic product from this reaction which might confirm this mechanism.



(1) R = H
(2) R = SnMe3
(3) R = Cl

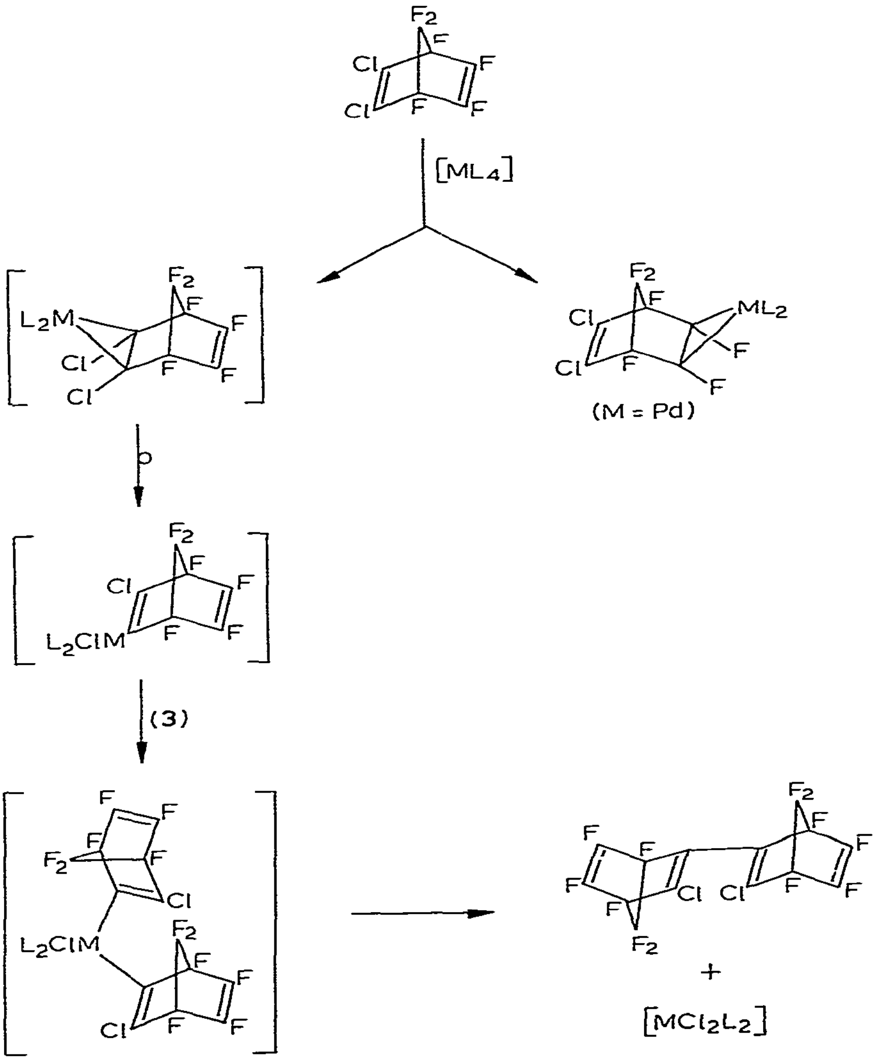


(4) M = Pt R = H
(5) M = Pd, R = H
(6) M = Pt, R = SnMe3
(7) M = Pd R = SnMe3
(8) M = Pd, R = Cl

Neither **2** nor **3** reacted with $[Ni\{P(OEt)_3\}_4]$ at room temperature over several hours, and **1** failed to react with $[IrCl(CO)(PPh_3)_2]$ after 8 h in boiling toluene. There was no reaction between **3** and $[Rh(C_2H_4)_2(acac)]$ at room temperature, and in this respect this diene behaves like perfluoronorbornadiene [1]. An intense red colour developed upon mixing **2** and $[Rh(C_2H_4)_2(acac)]$ at −25°C in dichloromethane. When this reaction in $CDCl_3$ was monitored by ^1H

NMR it was observed that addition of one equivalent of **2** caused the intensity

SCHEME 1



of the band at δ 2.96 ppm for the ethylenic protons of [$Rh(C_2H_4)_2(acac)$] to decrease to one half of its original value suggesting that [{$C_7F_6(SnMe_3)_2$}(C_2H_4)-Rh(acac)] had been formed. When a further equivalent of the diene was added the band at δ 2 96 ppm disappeared consistent with the formation of [{C_7F_6-($SnMe_3)_2$}$_2$Rh(acac)]. These adducts appear to be very unstable and attempts to isolate them have resulted only in recovery of **2** and an intractable brown solid. In contrast, the dihydro derivative **1** reacts with [$Rh(C_2H_4)_2(acac)$] to give the adduct **9** as an air stable yellow solid. The IR spectrum of **9** shows no evidence of a ν(CF=CF) band at 1761 cm^{-1} or ν(CH=CH) band at 1541 cm^{-1} present in the spectrum of **1**. The olefinic protons appear in the ^1H NMR spectrum at δ 4.21 ppm, i.e. an upfield shift of 2.54 ppm from the olefinic protons in the spectrum of the free diene (δ 6.75 ppm). The ^{19}F NMR spectrum (Table

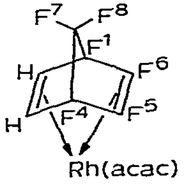
TABLE 2

^{19}F NMR SPECTRA OF THE COMPLEXES OF 1 2 3 4 7 7-HEXAFLUOROBICYCLO[2 2 1]HEPTADIENE (ppm to high field of trifluoroacetic acid)

Compound	F^1	F^4	F^5	F^6	$F^{7\ 8}$ [a]	Coupling constants (Hz)
1	131 42	131 42	80 0	80 0	57 51	$J(F^7—F^8)$ 147
4 [c]	121	121	110	110	58	
9 [d]	123 38	123 38	128 6	128 6	70 6	$J(F^7—F^8)$ 166 $J(Rh—F^{5\ 6})$ 19
13 [c]	127 35	127 35	148 3	148 3	74 1	$J(F^7—F^8)$176
14 [d]	104	125	54	—	56	
22 [c]	136	136	85	85	65	

[a] Centre of an AB quartet [b] Neat liquid [c] In dimethylformamide at 100°C [d] In $CDCl_3$ [e] In $CHCl_3$

2) also shows quite clearly that the vinylic fluorine atoms have been shifted upfield by 48 6 ppm as a result of coordination to the rhodium atom. In this complex the diene is behaving as a bidentate ligand with both double bonds coordinated to the rhodium atom, and it resembles the complex $[Rh(C_2H_4)(C_2F_4)(acac)]$ first isolated by Cramer and Parshall [6] Tetrafluoroethylene [6] and hexafluorobicyclo[2.2.0]hexa-2,5-diene [3,7] displace only one ethylene molecule on reaction with $[Rh(C_2H_4)_2(acac)]$ and the remaining ethylene ligand is not displaced even on prolonged treatment Our results show that by having a fluoro-olefin and a comparatively electron-rich olefin in the same molecule both ethylene ligands can be displaced, although steric factors also play an important role in these reactions as noted previously [8]. This might explain the instability of the complexes from **2**, and also, perhaps, the failure of perfluoronorbornadiene and **3** to form stable mono-substitution complexes with $[Rh(C_2H_4)_2(acac)]$.



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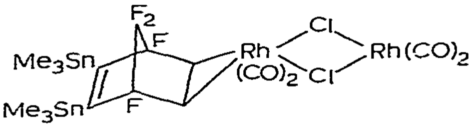
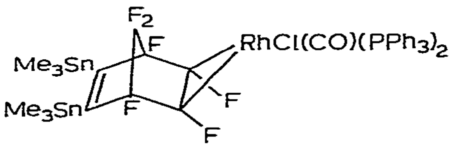


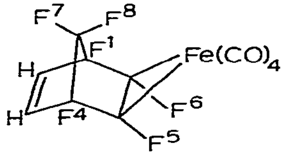
(10)

When the reaction between **1** and $[Rh(CO)_2Cl]_2$ in tetrahydrofuran at room temperature was monitored by IR spectroscopy over 24 h the $\nu(CF{=}CF)$ band at 1761 cm^{-1} was seen to decrease in intensity and a new band at 1725 cm^{-1} developed until it was approximately as intense as that at 1761 cm^{-1}. During this period there was no obvious change in the intensity of the metal carbonyl bands at 2040 and 2095 cm^{-1}, and a ^{19}F NMR spectrum taken over the same time period showed no obvious changes. The ^1H NMR spectrum, however, showed the development of a new band at δ 5.2 ppm in addition to the band at δ 6.24 ppm for the diene. The evidence suggests that some complex is formed, but all attempts to isolate it have resulted only in failure. Addition of triphenylphosphine to the mixture gave only $[RhCl(CO)(PPh_3)_2]$. Under similar conditions diene **2** reacted with $[Rh(CO)_2Cl]_2$ in benzene to give a brown crystalline product, which analysed for structure **10** The molecular weight is consistent with a dimer rather than a monomer of type [(diene)RhCl(CO)$_3$], and the IR spectrum shows bands at 360 and 310 cm^{-1} indicative of bridging chlorines [9]. The analytical and molecular weight data do not distinguish between the structure shown and one having only 3 or even 2 carbonyl ligands. The IR spectrum was not very helpful on this point. It showed only two bands at 2050(sh) and 2130s cm^{-1} in the metal carbonyl region, but the band at 2130 cm^{-1} was very broad and probably consisted of two or more overlapping bands. Addition of an excess of triphenylphosphine to a solution of **10** in acetone caused the evolution of approximately 2 mols of carbon monoxide per mol of **10** and gave the chlorine bridge-cleavage product **11** together with [RhCl(CO)(PPh$_3$)$_2$]. This confirms that **10** must have had four carbonyl ligands as shown. The chloro compound **3** did not react with [Rh(CO)$_2$Cl]$_2$ at room temperature over 24 h, and on heating to 60°C decomposition occurred to give a black intractable solid.

As with perfluoronorbornadiene there was no reaction between the dienes **1** and **2** and [PdCl$_2$(PhCN)$_2$] at room temperature over several hours, and on heating decomposition occurred to give palladium metal A low yield of small purple crystals, which analysed for [(C$_7$F$_6$Cl$_2$)PdCl(PhCN)] (**12**), were isolated from the reaction between **3** and [PdCl$_2$(PhCN)$_2$] at room temperature after 2 days. The IR spectrum showed a band at 2280 cm^{-1} {ν(C≡N) of benzonitrile ligand) and one broad band at 330—360 cm^{-1} (ν(Pd—Cl)}. The absence of a band at 1745 cm^{-1} (ν(CF=CF) of diene **3**) suggests that reaction has occurred at the fluorinated double bond The complex was too insoluble for NMR spectroscopy or molecular weight determination, and without such information any structure would be highly speculative. Displacement of the benzonitrile ligands of [PdCl$_2$(PhCN)$_2$] by electron-rich olefins is well-established [10], but displacement by a fluoro-olefin is unusual.



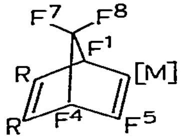
(**11**)



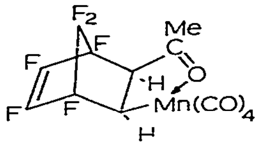
(**13**)

It has been reported previously [1] that UV irradiation of a mixture of perfluoronorbornadiene with [Fe(CO)$_5$] over several days gives a very low yield of a product believed to be [Fe(η^2-C$_7$F$_8$)(CO)$_4$]. It is now reported that under similar conditions **1** reacts with [Fe(CO)$_5$] to give a low yield of **13**. There was insufficient pure material for elemental analysis, but the IR spectrum shows the expected four metal carbonyl absorptions at 2140m, 2130m, 2075vs, and 2020vs cm^{-1}. The ^{19}F NMR spectrum shows only three bands in the intensity ratio of 1/1/1 consistent with the structure assigned (Table 2). The AB quartet at 70.6 ppm can be clearly assigned to the bridging fluorines (F^{7,8}) and the multiplet at 127.35 ppm is slightly downfield of the chemical shift of the fluorines (F^{1,4}) in the spectrum of **1**. Previous work has shown [7,11] that coordination of an Fe(CO)$_4$ moiety to a fluorinated double bond causes a marked upfield shift of the olefinic fluorine atoms and usually a slight downfield shift of the β-fluorines i.e. those on carbon atoms adjacent to the olefinic fluorines. On this basis the multiplet at 148.3 ppm is tentatively assigned to F^{5} ^{6}; an upfield shift of 68 ppm from that of F^{5} ^{6} in the spectrum of **1**. Analogous products could not be isolated from the reactions of **2** and **3** with $Fe(CO)_5$ under similar conditions

The dihydro derivative **1** did not react readily with carbonylmetal anions, and no substitution product could be isolated from the reaction with $Na[Mn(CO)_5]$ after 48 h at room temperature The stronger nucleophile $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ [12] gave only a low yield of **14**. The yields of the substitution products **15** and **16** obtained from the reaction of **2** with $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and $Na[Mn(CO)_5]$, respectively, were also low, but the products were easily isolated The IR spectra of the iron complexes **14** and **15** showed two metal carbonyl absorptions at 2038vs and 1975vs cm^{-1} (compound **14**) and 2050vs and 200vs cm^{-1} (compound **15**). There was no absorption in the region of 1750—1760 cm^{-1} (ν(CF=CF)), but instead a new band of medium intensity at 1614 cm^{-1} (compound **14**) and 1615 cm^{-1} (compound **15**) for ν(CF=Cmetal) was present. The IR spectrum of **16** showed bands at 2070s, 2040vs, 2023s, 2009m, and 1990m in the metal carbonyl region, and a band at 1614m cm^{-1} for the CF=CMn bond. The solubility of complexes **15** and **16** was too low for the determination of ^{1}H and ^{19}F NMR spectra. Weak spectra were obtained for compound **14**, and the ^{1}H NMR spectrum clearly shows the olefinic protons at δ 6.6 ppm while the ^{19}F NMR spectrum (Table 2) shows four bands with chemical shifts comparable to those found for the analogous perfluoronorbornadiene derivative [1]. The chlorinated diene **3** proved to be very reactive towards $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ and $[Mn(CO)_5]^-$, but attack appears to take place at the CCl=CCl bond giving $[ClFe(CO)_2(\eta\text{-}C_5H_5)]$ and $[ClMn(CO)_5]$, respectively. The anions $[M(CO)_2(PPh_3)_2]^-$ (M = Rh, Ir) react with both **2** and **3** to give low yields of the substitution products (**17**—**20**). With **3** competing reaction at the CCl=CCl bond also occurred as the product mixtures always contained *trans*-$[MCl(CO)(PPh_3)_2]$ (M = Rh or Ir) in addition to the products **19** and **20**. The IR spectra of the complexes (**17**—**20**) showed only a single metal carbonyl absorption in the region 2000—2020 cm^{-1}, consistent with a *trans*-arrangement of the carbonyl ligands [13], and a band of medium intensity in the region of 1610—1611 cm^{-1} (ν(CF=C metal)). ^{19}F and ^{1}H NMR



(14) M = $Fe(CO)_2(\eta\text{-}C_5H_5)$ R = H
(15) M = $Fe(CO)_2(\eta\text{-}C_5H_5)$, R = $SnMe_3$
(16) M = $Mn(CO)_5$, R = $SnMe_3$
(17) M = $Ir(CO)_2(PPh_3)_2$, R = $SnMe_3$
(18) M = $Rh(CO)_2(PPh_3)_2$ R = $SnMe_3$
(19) M = $Ir(CO)_2(PPh_3)_2$, R = Cl
(20) M = $Rh(CO)_2(PPh_3)_2$, R = Cl



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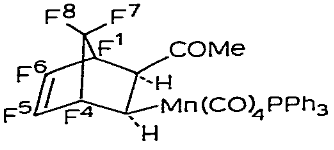

(22)

spectra could not be obtained for these compounds as they were insoluble in all the usual solvents

When methylpentacarbonylmanganese was heated with **1** at 100° C for 15 h in tetrahydrofuran the adduct **21** was obtained in 57% yield. The IR spectrum of **21** shows four bands at 2059m, 1974s, 1966vs, and 1929vs in the metal carbonyl region characteristic [14] of *cis*-[$RMn(CO)_4L$] compounds There was no band at 1592 cm^{-1} for the CH=CH bond, but the band at 1754 cm^{-1} (ν(CF=CF)) was still prominent. In addition the spectrum showed a medium band at 1650 cm^{-1} assigned to a keto-group coordinated to the manganese atom [15]. Attempts to add [$Pt(PPh_3)_4$] to the CF=CF bond of this complex resulted only in the formation of the triphenylphosphine derivative **22** The same compound was also prepared in higher yield by reaction of **21** with triphenylphosphine in tetrahydrofuran at room temperature The IR spectrum of **22** showed metal carbonyl absorptions at 2003vs, 1921s, and 1896s cm^{-1}, a band at 1750m cm^{-1} (ν(CF=CF)), and a band at 1720 cm^{-1} for the carbonyl stretching vibration of the uncoordinated acetyl group A weak ^{19}F NMR spectrum obtained in dimethylformamide (Table 2) confirms the presence of the vinylic fluorines, $F^{5\ 6}$, at 85 ppm upfield from trifluoroacetic acid The formation of **21** can be explained by a mechanism similar to that proposed for the reactions of dicyclopentadiene with methyl- and phenyl-pentacarbonylmanganese [15]. There is no reaction at the CF=CF bond as insertion of fluoro olefins into [$MnMe(CO)_5$] usually requires UV light and probably take place by a radical mechanism [16].

Experimental

IR spectra were recorded on mulls in Nujol and hexachlorobutadiene using a Perkin—Elmer model 621 spectrophotometer; metal carbonyl absorptions were recorded on solutions in dichloromethane using expanded scale (X 10) NMR spectra were recorded on a Perkin—Elmer R10 instrument (^1H, 60 MHz, internal Me_4Si reference; ^{19}F, 56 46 MHz, CF_3CO_2H external reference, positive shifts to high field). Molecular weights were determined using a Perkin—Elmer model 115 apparatus by the isopiestic method 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexafluorobicyclo[2.2 1]hepta-2,5-diene [2], 2,3-dichloro-1,4,5,6,7,7-hexafluorobicyclo-[2.2.1]hepta-2,5-diene [2], and 1,2,3,4,7,7-hexafluorobicyclo[2 2 1]heptadiene [17,18] were prepared by previously reported procedures. Except where stated all reactions were carried out under dry, oxygen-free nitrogen, and solvents were purified and dried by standard procedures.

Reactions of 1,2,3,4,7,7-hexafluorobicyclo[2 2 1]heptadiene

(a) With [$Pt(PPh_3)_4$] The diene (0.1 g, 0 5 mmol) in benzene (5 cm^3) was added to a stirred solution of [$Pt(PPh_3)_4$] (0.6 g, 0.5 mmol) in benzene (25 cm^3), and the mixture was stirred at room temperature for 13 h. The volume of the solution was reduced to 10 cm^3 and light petroleum (b.p. 30—40°C, 30 cm^3) was added to give white crystals of **4** (0.46 g, 0.48 mmol, 96%) (^1H NMR ($CDCl_3$) δ 5.4 (m, 2 H, =CH) and 7 25 (m, 30 H, C_6H_5) ppm).

(b) With [$Pd(PPh_3)_4$] Under similar conditions reaction between the diene (0.86 g, 4.30 mmol) and [$Pd(PPh_3)_4$] (5.0 g, 4 30 mmol) in tetrahydrofuran (55

cm^3) gave white crystals of **5** (1 9 g, 2 24 mmol, 52%) which were recrystallised from a mixture of dichloromethane and light petroleum (b.p 40—60° C) (^{1}H NMR ($CDCl_3$) δ 6 22 (m, 2 H, =CH) and 6 9 (m, 30 H, C_6H_5) ppm).

(c) With Na[Fe(CO)$_2$(η-C$_5$H$_5$)] The sodium salt, prepared from $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ (0.89 g, 2 5 mmol) and 1% sodium amalgam in tetrahydrofuran (20 cm^3), was added dropwise with stirring to the diene (1 0 g, 5 0 mmol) in the same solvent The mixture was stirred at room temperature for 13 h, before removal of the solvent and chromatography (florisil; light petroleum (b p. 40—60°C) eluant) to give yellow crystals of **14** (0 25 g, 0 65 mmol, 13%) (^{1}H NMR ($CDCl_3$) δ 5 0 (s, 5 H, C_5H_5) and 6.6 (m, 2 H, =CH) ppm)

(d) With [Fe(CO)$_5$]. A mixture of the diene (4.3 g, 21.5 mmol) and pentacarbonyliron (4 3 g, 22.0 mmol) sealed under vacuum in a Pyrex tube (250 cm^3 capacity) was irradiated (500 W Hanovia UV lamp) for 6 days Removal of unchanged starting materials and addition of chloroform gave deep yellow platelets of nonacarbonyldiiron (0 63 g), which were removed by filtration. The solvent was removed from the filtrate and the residue was chromatographed (silica; light petroleum (b p. 40—60° C) eluant) to give a yellow oil thought to be **13** (0.25 g, 0.65 mmol, 3%).

(e) With [Rh(C$_2$H$_4$)$_2$(acac)] A solution of the diene (0.78 g, 3.9 mmol) in tetrahydrofuran (5 cm^3) was added to a stirred solution of the rhodium complex (1.0 g, 3 9 mmol) in the same solvent at 0° C, and the mixture was then stirred at room temperature for 13 h Removal of the solvent and recrystallisation of the residue from light petroleum (b p. 30—40° C) gave yellow crystals of **9** (1 35 g, 3 35 mmol, 86%) (^{1}H NMR ($CDCl_3$) δ 2 00 (s, 6 H, 2 × CH_3), 4 21 (m, 2 H, =CH) and 5.47 (s, 1 H, CH) ppm).

(f) With [MnMe(CO)$_5$]. A mixture of the diene (0.6 g, 3 0 mmol), pentacarbonylmethylmanganese (0 6 g, 2.9 mmol) and tetrahydrofuran (10 cm^3) was heated at 100° C for 15 h in a Pyrex tube sealed under vacuum The solvent was removed, and the residue was extracted with light petroleum (b p 30—40°C, 50 cm^3) to give yellow crystals of **21** (0 69 g, 1 65 mmol, 57%), which were recrystallised from dichloromethane/light petroleum at —78° C.

Reactions of 1,2,3,4,7,7-hexafluorobicyclo[2 2.1]hept-2-ene-5-acetyltetracarbonylmanganese

(a) With [Pt(PPh$_3$)$_4$] A solution of **21** (0 31 g, 0 75 mmol) in tetrahydrofuran (10 cm^3) was added dropwise with stirring to the platinum complex (1 29 g, 1.13 mmol) in tetrahydrofuran (50 cm^3), and the mixture was stirred at room temperature for 24 h. The solvent was removed and the residue was chromatographed to give yellow crystals of **22** (0 2 g, 0 29 mmol, 40%), recrystallised from light petroleum

(b) With triphenylphosphine. Addition of a solution of **21** (0.97 g, 2.4 mmol) in tetrahydrofuran (30 cm^3) to triphenylphosphine (0.66 g, 2 5 mmol) in the same solvent, and stirring at room temperature for 13 h gave **22** (0 88 g, 1 31 mmol, 55%).

Reactions of 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexafluorobicyclo[2.2.1]hepta-2,5-diene

(a) With [Pt(PPh$_3$)$_4$] A solution of the tin complex (5.3 g, 1.0 mmol) in

benzene (30 cm^3) was added to a solution of [$Pt(PPh_3)_4$] (1.2 g, 1.0 mmol) in benzene (40 cm^3), and the mixture was stirred at room temperature for 3 days. Partial removal of the solvent and addition of hexane (10 cm^3) gave white crystals of **6** (0.95 g, 0.76 mmol, 79%), which were washed with hot ethanol, and dried under vacuum.

(b) With [$Pd(PPh_3)_4$] Following a similar procedure reaction between the tin compound (0.5 g, 0.95 mmol) and [$Pd(PPh_3)_4$] (1.0 g, 0.88 mmol) in toluene (45 cm^3) at room temperature for 5 h gave white crystals of **7** (0.91 g, 0.79 mmol, 88%) recrystallised from a mixture of dichloromethane and hexane.

(c) With Na[$Fe(CO)_2(\eta$-$C_5H_5)$] A solution of the tin complex (1.5 g, 2.85 mmol) in tetrahydrofuran (15 cm^3) was added dropwise to a stirred solution of the sodium salt prepared from [$Fe(CO)_2(\eta$-$C_5H_5)$]$_2$ (0.9 g, 2.54 mmol) and sodium amalgam (Na, 3 g, Hg, 30 cm^3) in tetrahydrofuran (50 cm^3). The mixture was then stirred at room temperature for 16 h before removal of the solvent, and chromatography (alumina, light petroleum eluant) of the residue to give yellow crystals of **15** (0.2 g, 2.93 mmol, 15%). Further elution with dichloromethane gave [$Fe(CO)_2(\eta$-$C_5H_5)$]$_2$ (0.4 g, 1.13 mmol).

(d) With Na[$Mn(CO)_5$] Addition of a solution of the tin derivative (4.0 g, 8.71 mmol) in tetrahydrofuran (20 cm^3) to a solution of the sodium salt from [$Mn_2(CO)_{10}$] (2.0 g, 5.5 mmol) and sodium amalgam (Na, 2 g; Hg, 25 cm^3) in tetrahydrofuran (75 cm^3), followed by stirring for 12 h at room temperature, gave, after chromatography (alumina, 1/1 light petroluem/CH_2Cl_2 eluant) gave yellow crystals of **16** (0.8 g, 1.14 mmol, 22%) and [$Mn_2(CO)_{10}$] (0.5 g, 1.28 mmol).

(e) With Na[$Ir(CO)_2(PPh_3)_2$]. A solution of the sodium salt prepared from [$IrCl(CO)(PPh_3)_2$] (2.0 g, 2.48 mmol) and sodium amalgam (Na, 2 g; Hg, 25 cm^3) in tetrahydrofuran under 1 atm carbon monoxide was added to a stirred solution of the tin compound (1.0 g, 1.94 mmol) in the same solvent. After 24 h at room temperature the mixture was filtered, and most of the solvent was removed from the filtrate before addition of ethanol precipitated pale yellow crystals of **17** (0.5 g, 3.9 mmol, 25%) (ν(CO) 2020s; ν(CF=CIr) 1610 cm^{-1}).

(f) With Na[$Rh(CO)_2(PPh_3)_2$]. Reaction between the sodium salt (1.0 g, 0.73 mmol) and the tin compound (1.5 g, 2.85 mmol) in tetrahydrofuran (25 cm^3) at room temperature for 48 h under a slow stream of carbon monoxide gave, after chromatography (florisil; light petroleum eluant), triphenylphosphine (0.5 g, 1.90 mmol). Elution with ethanol gave yellow crystals of **18** (0.3 g, 0.25 mmol, 34%) (ν(CO) 2000s; ν(CF=CRh) 1611m cm^{-1}).

(g) With [$Rh(CO)_2Cl$]$_2$. Reaction between the tin compound (0.3 g, 0.57 mmol) and bis(μ-chlorodicarbonylrhodium) (0.25 g, 0.64 mmol) in benzene (45 cm^3) at room temperature gave a light brown solution, from which light brown crystals of **10** (0.25 g, 0.27 mmol, 48%) precipitated on addition of a 1/1 mixture of hexane and diethyl ether, and were recrystallised from a mixture of dichloromethane and hexane.

Addition of triphenylphosphine (5.72 g, 3.64 mmol) in dry acetone to a solution of **10** (0.44 g, 0.48 mmol) in dry acetone contained in a flask connected to a gas burette caused evolution of carbon monoxide (0.79 mmol), and formation of a deep yellow precipitate of **11** (0.2 g, 0.16 mmol, 34%), which was filtered off and washed with acetone. The solvent was removed from the filtrate and the residue was chromatographed (Florisil; light petroleum b.p 60—80°C eluant) to give triphenylphosphine (2.5 g, 0.96 mmol), and further elution with dichloromethane gave chlorocarbonylbis-(triphenylphosphine)rhodium (0.24 g, 0.35 mmol, 73%).

Reactions of 2,3-dichloro-1,4,5,6,7,7-hexafluorobicyclo[2 2 1]hepta-2,5-diene

(a) With [Pd(PPh$_3$)$_4$]. Addition of the diene (0.27 g, 1.0 mmol) to a solution of [Pd(PPh$_3$)$_4$] (1.15 g, 1.0 mmol) in toluene (30 cm^3) at room temperature, followed by stirring for 6 h gave an orange solution. The volume was then reduced to 10 cm^3 before addition of diethyl ether to give small orange crystals of **8** (0.25 g, 0.28 mmol, 28%).

(b) With Na[Fe(CO)$_2$(η-C$_5$H$_5$)] The diene (1.05 g, 3.85 mmol) was added to Na[Fe(CO)$_2$(η-C$_5$H$_5$)] (3.96 mmol) in tetrahydrofuran (75 cm^3) at room temperature and the mixture was stirred for 18 h. Chromatography (Florisil, hexane eluant) of the residue after removal of the solvent gave a deep yellow solid (80 mg, 0.38 mmol, 9%) identified as [FeCl(CO)$_2$(η-C$_5$H$_5$)]. Further elution with light petroleum and dichloromethane gave [Fe(CO)$_2$(η-C$_5$H$_5$]$_2$ (0.2 g, 0.56 mmol).

(c) With Na[Mn(CO)$_5$] Under similar conditions reaction between the diene (1.0 g, 3.72 mmol) and Na[Mn(CO)$_5$] (2.55 mmol) in tetrahydrofuran (50 cm^3) gave [MnCl(CO)$_5$] (0.46 g, 2.0 mmol, 78%)

(d) With Na[Ir(CO)$_2$(PPh$_3$)$_2$] A solution of the sodium salt in tetrahydrofuran (100 cm^3), prepared from [IrCl(CO)$_2$(PPh$_3$)$_2$] (2.0 g, 2.48 mmol) and sodium amalgam under an atmosphere of carbon monoxide, was added to a stirred solution of the diene (1.2 g, 2.11 mmol) in tetrahydrofuran (20 cm^3) and the mixture was stirred at room temperature for 18 h. The insoluble material was removed by filtration, and the volume of the filtrate was reduced to ca. 10 cm^3 before addition of diethyl ether to precipitate pale yellow crystals of [IrCl(CO)-(PPh$_3$)$_2$] (0.62 g, 8.0 mmol, 60%). After filtration, removal of the remaining solvent gave a residue which was recrystallised from dichloromethane and ethanol to afford yellow crystals of **19** (0.2 g, 7.0%). Triphenylphosphine (0.8 g, 3.05 mmol) was also isolated from the residue

(e) With Na[Rh(CO)$_2$(PPh$_3$)$_2$]. The diene (1.01 g, 4.4 mmol) was added to a stirred solution of the sodium salt, prepared by reaction of [Rh(CO)(PPh$_3$)$_2$]$_2$ (0.6 g, 4.4 mmol) with sodium amalgam under carbon monoxide, and the mixture was stirred for 18 h at room temperature. Chromatography (Florisil, light petroleum eluant) gave [RhCl(CO)(PPh$_3$)$_2$] (0.21 g, 3.0 mmol, 70%). Further elution with ethanol gave small yellow-green crystals of **20** (80 mg, 0.08 mmol, 20%), followed by triphenylphosphine (0.39 g, 1.47 mmol).

(f) With [PdCl$_2$(PhCN)$_2$]. A mixture of the diene (0.5 g, 1.86 mmol), [PdCl$_2$(PhCN)$_2$] (0.5 g, 1.31 mmol) and benzene (10 cm^3) were sealed in vacuo in a Pyrex tube (100 cm^3 capacity), and the tube was shaken at room temperature for 2 days. After filtration, hexane (10 cm^3) was added to the filtrate to give small purple crystals of **12** (0.2 g, 0.42 mmol, 32%).

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