Journal of Organometallic Chemistry, 226 (1982) 289—299
Elsevier Sequoia S A , Lausanne — Printed in The Netherlands

REACTIONS INVOLVING TRANSITION METALS

XIX *. SOME REACTIONS OF PERFLUORONORBORNADIENE WITH LOW VALENT TRANSITION METAL COMPLEXES

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(Received September 25th, 1981)

Summary

Perfluoronorbornadiene reacts with the compounds $[M(PPh_3)_4]$ (M = Pt, Pd) and $[IrCl(CO)(PMePh_2)_2]$ to give the adducts $[(C_7F_8)M(PPh_3)_2]$ and $[(C_7F_8)$-$IrCl(CO)(PMePh_2)_2]$ in which one of the double bonds is coordinated to the metal atom. The platinum complex reacts further with $[Pt(PPh_3)_4]$ to give $[(C_7F_8)\{Pt(PPh_3)_2\}_2]$ having both double bonds coordinated to a Pt atom. The carbonylmetal anions $[M^-]$ react to form the mono-substitution products $[(C_7F_7)M]$ (M = $Mn(CO)_5$, $Re(CO)_5$, $Ir(CO)_2(PPh_3)_2$, $Rh(CO)_2(PPh_3)_2$), but the use of an excess of $[Fe(CO)_2(\eta\text{-}C_5H_6)]^-$ leads to substitution of one fluorine atom on each of the double bonds The complex having M = $Mn(CO)_5$ reacts with $[Pt(PPh_3)_4]$ to afford the derivative $[(C_7F_7)\{Mn(CO)_4(PPh_3)\}$-$\{Pt(PPh_3)_2\}]$, and the compound where M = $Ir(CO)_2(PPh_3)_2$ undergoes an oxidative addition reaction with acetyl chloride. Oxidative coupling products have been isolated on UV irradiation of a mixture of perfluoronorbornadiene and $[Fe(\eta^4\text{-}CH_2{=}CRCH{=}CH_2)(CO)_3]$ (R = H, Me), and under similar conditions the reaction with $Fe(CO)_5$ affords $[(C_7F_8)Fe(CO)_4]$ in very low yield.

Introduction

The strained, bicyclic diene, norbornadiene, has been of interest to organic and organometallic chemists for many years. It is well known that the proximity of the non-conjugated double bonds leads to rearrangement products via non-classical carbocation and nortricyclyl radical intermediates on reaction

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* For part XVIII see ref. 20.

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0022-328X/82/0000—0000/$02 75

with electrophiles and radicals respectively [1,2]. Also, it behaves as a bidentate ligand capable of stabilising many low valent transition metal ions [3]. A few years ago the synthesis of the fluorinated analogue, perfluoronorbornadiene, was achieved in this Department [4]. It has been of interest to explore the chemistry of this compound to see if this is also capable of behaving as a bidentate ligand, and whether, like the hydrocarbon analogue, it can form rearrangement products. We now describe some of its reactions with low valent transition metal complexes.

Results and discussion

Perfluoronorbornadiene reacts with the complexes $[M(PPh_3)_4]$ (M = Pt, Pd) at room temperature to give the compounds 1 and 2. The palladium complex is not stable in benzene and the colourless solution rapidly turns orange. A molecular weight determination (Table 1) suggests that there is appreciable dissociation, similar to that noted previously for the bis(triphenylphosphine)palladium derivative of hexafluorobicyclo[2.2.0]hexa-2,5-diene [5]. For this reason the ^{19}F NMR spectrum was not obtained and the compound was characterised by microanalysis (Table 1) and IR spectroscopy (Table 2) only. The platinum complex 1 does not dissociate in benzene solution, and the ^{19}F NMR spectrum (Table 2) confirms that only one of the CF=CF bonds of the diene has coordinated to the platinum atom. The large, through-space, Pt—F^8 coupling indicates that the $Pt(PPh_3)_2$ moiety is *exo* to the CF_2 bridge. The non-coordinated CF=CF bond in 1 is still sufficiently electrophilic to react with a further molecule of $[Pt(PPh_3)_4]$ over 24 h at room temperature to give 3 in 86% yield. This is expected to have the *exo,exo* structure shown, but this could not be confirmed by a ^{19}F NMR spectrum as it is almost insoluble in all common solvents. The IR spectrum of 3 confirms the disappearance of the band at 1740 cm^{-1}

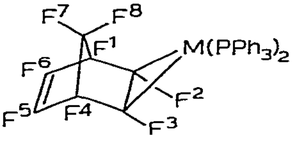
TABLE 1

MELTING POINT, ANALYTICAL (%) AND MOLECULAR WEIGHT DATA FOR THE PERFLUORONORBORNADIENE DERIVATIVES

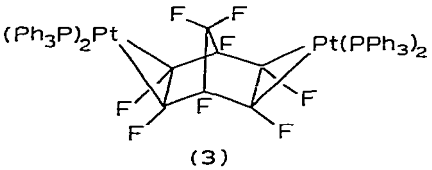
Compound	M p (°C)	Analysis (Found (calcd) (%))			Mol.wt. [a]
		C	H	F	
1	205—206 [b]	54 2(54 0)	3 3(3 2)	15 5(15 6)	944(955) [c]
2	170	59 2(59 5)	3.4(3 5)	17 0(17 5)	444(866) [c]
3	—	56 9(56 6)	3 6(3 6)	8 9(9 1)	
4	—	46 2(45 8)	3 1(2 9)	16 7(17 1)	
5	38—39	35 2(35 0)		32 4(32 3)	
6	60—61	26 6(26 5)		25 5(24 5)	
7	98—99 [b]	53 7(54 2)	2 9(3 0)	11 2(11 5)	
8	85—87	57 4(57 4)	3 6(3 4)	14 2(14 7)	
9	150	45 2(44 8)	2 0(1.8)	20 7(20 0)	540(552) [c]
10		55 5(57 1)	3 5(3 4)	8 4(9.7)	
11	230—232 [b]	54 0(53 2)	3 1(3 2)	12 8(12 2)	
12	140	39 0(39 1)	1.4(1.4)	35 0(35 3)	
13	166—167	40 6(40 6)	1 8(1 8)	33 6(34 1)	

[a] Calculated figures are given in parentheses. [b] With decomposition. [c] In $CHCl_3$

(ν(CF=CF)) observed in the spectrum of 1. No reaction occurred between perfluoronorbornadiene and [IrCl(CO)(PPh_3)$_2$] either at room temperature over 3 days or on heating at 50°C for 4 h However, the more nucleophilic iridium(I) complex [IrCl(CO)($PMePh_2$)$_2$] reacted to give 4 even at room temperature. The IR spectrum of 4 confirmed the presence of an uncomplexed CF=CF



(1) M = Pt
(2) M = Pd



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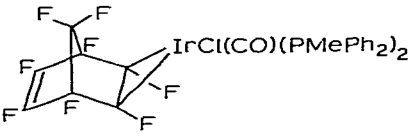
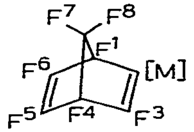


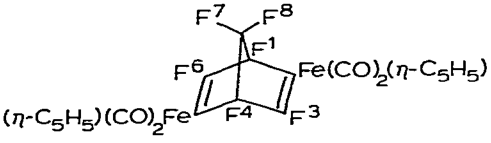
(4)

group, and also showed the expected single metal carbonyl absorption at 2050 cm^{-1}. There was no evidence in the ^{1}H NMR spectrum for virtual coupling between the ^{31}P nuclei of the two phosphine ligands indicating that they occupy *cis*-sites [6]. No reaction occurred between perfluoronorbornadiene and [$PdCl_2$(PhCN)$_2$], [Rh(CO)$_2$Cl]$_2$, [Rh(C_2H_4)$_2$(acac)] (acac = acetylacetonate) or [Rh(η-C_5Me_5)(cod)] (cod = cycloocta-1,5-diene) at room temperature.

The carbonylmetal anions [Mn(CO)$_5$]$^-$, [Re(CO)$_5$]$^-$, [Ir(CO)$_2$(PPh_3)$_2$]$^-$ and [Rh(CO)$_2$(PPh_3)$_2$]$^-$ react with perfluoronorbornadiene to give the compounds 5—8. The best yields were obtained by addition of a solution of the anion in tetrahydrofuran to an excess of the diene in the same solvent, the weak nucleophile [Co(CO)$_4$]$^-$ [7,8] did not react under similar conditions. The IR spectra of these products (Table 2) all show a strong band in the region of 1750—1759 cm^{-1} for an uncoordinated CF=CF bond, and a new, strong band in the region of 1612—1615 cm^{-1} for the CF=C[metal] bond. In addition, the spectra of 5 and 6 show five metal carbonyl absorptions at 2076s, 2045vs, 2025s, 2012m, and 2000m cm^{-1} (compound 5) and 2072s, 2040vs, 2023s,



(5) M = Mn(CO)$_5$
(6) M = Re(CO)$_5$
(7) M = Ir(CO)$_2$(PPh_3)$_2$
(8) M = Rh(CO)$_2$(PPh_3)$_2$



(9)

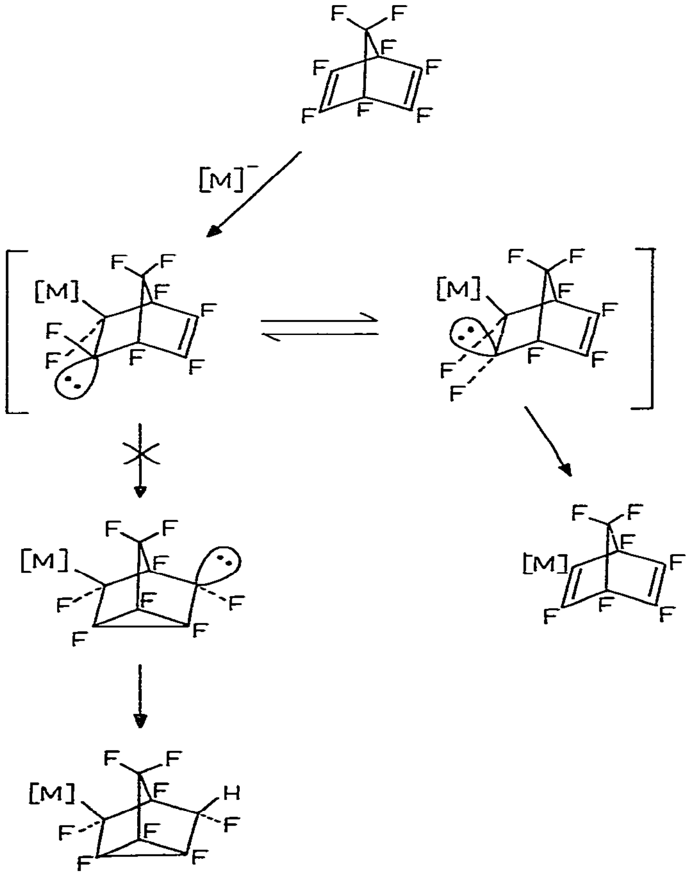
TABLE 2

IR(cm^{-1}) AND ^{19}F NMR [a, b] (ppm upfield from trifluoroacetic acid) OF THE COMPLEXES OF PERFLUORONORBORNADIENE

Compound	ν(CF = CF)	ν(CF = Cmetal)	F^1	F^2	F^3	F^4	F^5	F^6	F^{7,8} [c]	Coupling constants (Hz)
C_7F_8 [d]	1748	—	139,1	74.2	74.2	139.1	74.2	74.2	53	
1	1740	—	132	110	110	132	72	72	53	$J(P—F^{2,3})30$, $J(F^7—F^8)155$, $J(Pt—F^8)233$
2	1741	—	—	—	—	—	—	—	—	
4	1750s	—	—	—	—	—	—	—	—	
5	1759s	1615s	114	—	48	135	82	73	55	$J(F^7—F^8)164$
6	1756s	1613s	111	—	46	133	80	71	54	$J(F^7—F^8)169$
7	1750s	1612s	113	—	45	129	80	72	53	$J(F^7—F^8)152$
8	1752s	1613s	112	—	46	131	81	70	55	$J(F^7—F^8)164$
9	—	1613s	112	—	52	112	—	52	55	$J(F^7—F^8)155$
10	—	1650s	—	—	—	—	—	—	—	
11	1750s	1612s	—	—	—	—	—	—	—	
12	1758s	—	149	109	105	134	85	99	56	$J(F^7—F^8)160$
13	1750s	—	149	109	104	134	84	97	55	$J(F^7—F^8)160$

[a] In the majority of cases spectra were weak and poorly resolved. [b] In $CDCl_3$ [c] Centre of an AB quartet [d] From ref 4

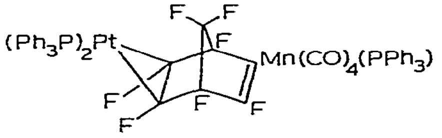
2009m, and 1995m cm^{-1} (compound 6), respectively. The iridium and rhodium complexes show only one strong band in this region at 2010 and 2015 cm^{-1} respectively, suggesting a *trans* arrangement for the carbonyl ligands as found previously for similar complexes [9,10]. The reaction with Na[Fe(CO)$_2$-(η-C$_5$H$_5$)] was carried out using an excess of anion over perfluoronorbornadiene and gave a low yield of a product 9 which showed three bands at 2035s, 1998s and 1980s cm^{-1} in the metal carbonyl region of the IR spectrum, a strong band at 1613 cm^{-1} (ν(CF=C metal)) and no band in the region expected for a CF=CF bond. The ^{19}F NMR spectrum (Table 2) showed only three bands in the intensity ratio 1/1/1 suggesting a compound having the structure shown, and this was confirmed by elemental analysis and molecular weight determination (Table 1). The mechanism of nucleophilic attack on fluoro olefins is well-established [11], and the lone pair of electrons on the developing carbanion centre are *anti* to the incoming nucleophile to minimise electron-pair repulsion. Inversion at the carbanion centre must take place before F$^-$ elimination can occur so that the lone pair electrons are *anti* to the leaving group. This is shown in Scheme 1 assuming that *exo* attack by the nucleophile on the perfluoronorbornadiene is preferred. It seemed possible that the carbanion intermediate



SCHEME 1

shown might rearrange to give a tricyclane product in a similar way to rearrangement of the norbornenyl cation and radical. Tricyclane products have not been detected in the reactions with carbonylmetal anions, or, indeed, any reactions of nucleophiles with perfluoronorbornadiene investigated to date. Possibly the tetrahedral geometry of the sp^3-hybridised carbanion centre prevents overlap with the second CF=CF bond. Overlap will be less favourable than that between an sp^2-hybridised carbocation or radical centre and a CH=CH bond.

The manganese complex **5** reacts with $[Pt(PPh_3)_4]$ at room temperature to give a low yield of a compound believed to have structure **10**. Elemental analysis indicates that it is slightly impure, but it was almost insoluble in all common solvents and could not be recrystallised, for the same reasons a ^{19}F NMR spectrum could not be obtained. The IR spectrum shows four bands at 2070m, 2026w, 1995sh and 1970s in the metal carbonyl region for a compound of type



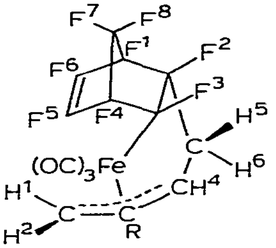
(10)

(11)

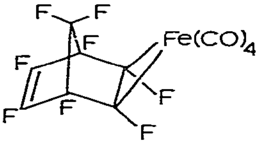
cis-$MnL^1L^2(CO)_4$ [12]: a strong band at 1650 cm^{-1} (ν(CF=C metal)), but no band in the region of 1750—1760 cm^{-1}. A second product from this reaction was $[Pt(CO)(PPh_3)_3]$, and it would appear that a PPh_3 molecule from dissociation of $[Pt(PPh_3)_4]$ substitutes a carbonyl ligand of the $Mn(CO)_5$ group, but it is not known whether this occurs prior to or after reaction of **5** with $[Pt(PPh_3)_4]$ It has not proved possible to prepare **10** by the alternative reaction between **1** and $[Mn(CO)_5]^-$. A complex product mixture was obtained from this reaction, and a similar complex reaction occurred on treatment of **1** with $[Re(CO)_5]^-$.

Acetyl chloride adds to the iridium(I) complex **7** at room temperature to give a 55% yield of **11**. The IR spectrum of this adduct shows a single, strong metal carbonyl absorption at 2075 cm^{-1}, and a band at 1570m cm^{-1} (ν(C=O) of COMe group), in addition to bands due to ν(CF=CF) and ν(CF=C metal) (Table 2). A colour change from colourless to yellow in $CDCl_3$, and a ^1H NMR band at δ 1.23 ppm in addition to the expected bands at δ 2.1 ($COCH_3$) and 7.4 ppm (C_6H_5) suggests that **12** may decarbonylate to $[C_7F_7IrMeCl(CO)(PPh_3)_2]$ in solution. There was no reaction between **7** and iodomethane at room temperature, but at 60° C trifluoroacetic acid reacted to give a low yield of $[IrH(O_2CCF_3)_2(CO)(PPh_3)_2]$. This possibly arises by oxidative-addition to give $[C_7F_7IrH(O_2CCF_3)(CO)(PPh_3)_2]$ followed by reductive elimination to form C_7F_7H and $[Ir(O_2CCF_3)(CO)(PPh_3)_2]$; this last compound with more acid would give the observed product.

Oxidative-coupling reactions between fluorinated olefins and $[Fe(\eta^4\text{-diene})(CO)_3]$ are well-known [13,14]. It has now been shown that UV irradiation of mixture of norbornadiene and the compounds $[Fe(\eta^4\text{-}CH_2{=}CRCH{=}CH_2)(CO_3)]$ (R = H, Me) gives the compounds **12** and **13**. These are stable at room temperature and the IR spectra show the expected three strong metal carbonyl vibrations at 2090, 2049, and 2018 (compound **12**) and 2080, 2040, and 2012 cm^{-1} (compound **13**), and a band in the region of 1750—1760 cm^{-1} for a free



(12) R = H
(13) R = Me



(14)

CF=CF group. The ^1H NMR spectra were very similar to those reported for the products of reaction between C_2F_4 and $[Fe(\eta^4\text{-}CH_2{=}CRCH{=}CH_2)(CO)_3]$ [14]. Tentative assignments of the bands observed in the ^{19}F NMR spectra are given in Table 2 It is known from other work [14,15] that the fluoro olefin in these reactions probably coordinates to the iron atom first and forms an *endo* link with the butadiene ligand Intuitively it might be expected on this basis that the complexes **12** and **13** will have the stereochemistry shown, but without X-ray crystallography this cannot be confirmed Irradiation of a mixture of perfluoronorbornadiene and $[Fe(CO)_5]$ gave 1% yield of a yellow solid thought to be **14**. There was insufficient sample for elemental analysis or NMR spectroscopy The IR spectrum shows four strong bands at 2149, 2099, 2060 and 2049 cm^{-1} in the metal carbonyl region, and a band at 1760 cm^{-1} (ν(CF=CF)). The mass spectrum did not give a molecular ion, but gave an intense ion at *m/e* 376 $[C_7F_8Fe(CO)_3]^+$, and peaks at *m/e* 168 $[Fe(CO)_4]^+$, 140 $[Fe(CO)_3]^+$, 112 $[Fe(CO)_2]^+$ and 84 $[Fe(CO)]^+$.

Experimental

Perfluoronorbornadiene was prepared by a modification of the method described in the literature [4]. Products were identified by elemental analysis and by IR (Perkin—Elmer spectrophotometer model 621), NMR (Perkin—Elmer R10) instrument operating at 60 MHz for ^1H (int Me_4Si reference) and 56.46 MHz for ^{19}F (ext. CF_3CO_2H reference, positive shifts to high field) spectroscopy. Molecular weights were determined using a Perkin—Elmer model 115 apparatus by the isopiestic method. Except where stated all reactions were carried out under dry, oxygen-free nitrogen, and solvents were purified and dried by standard procedures.

Reaction with $[Pt(PPh_3)_4]$

Perfluoronorbornadiene (0.46 g, 1.99 mmol) was added to a solution of freshly-prepared $[Pt(PPh_3)_4]$ (2.40 g, 1.93 mmol) in benzene (100 cm^3) and the mixture was stirred at room temperature for 3 days during which time triphenylphosphine (0.12 g, 0.43 mmol) precipitated. This was removed by filtration, and the volume of the filtrate was reduced to ca. 10 cm^3 before addition of cold ethanol (10 cm^3) which precipitated unreacted platinum complex (0.23 g, 0.17 mmol). This was filtered off and the solvent was removed from the filtrate to give compound **1** (0.5 g, 0.53 mmol, 26%) as a white solid.

Reaction with [Pd(PPh$_3$)$_4$]

Under similar conditions reaction between perfluoronorbornadiene (0.47 g, 1 99 mmol) and a suspension of the palladium complex (2.3 g, 1.98 mmol) in benzene (40 cm^3) gave white crystals of compound 2 (1.2 g, 1.39 mmol, 71%) which were washed with hot ethanol (10 cm^3) and dried in vacuo.

Reaction with [IrCl(CO)(PMePh$_2$)$_2$]

When a solution of perfluoronorbornadiene (0 8 g, 3 38 mmol) and the iridium complex (0.6 g, 0.92 mmol) in benzene (30 cm^3) was stirred at room temperature, then, after 24 h, the solvent was removed, a yellow oil was obtained. This was dissolved in the minimum amount of dichloromethane and methanol was added to give pale yellow crystals of compound 4 (0 55 g, 0.62 mmol, 68%). (^{1}H NMR (CDCl$_3$) δ 2 09 (d, 3 H, CH$_3$, J(P—H) 5 Hz) and 7 6 (m, 10 H, C$_6$H$_5$))

Reaction between compound 1 and [Pt(PPh$_3$)$_4$]

A solution of 1 (0.1 g, 0.1 mmol) in benzene (10 cm^3) was added dropwise to a stirred solution of [Pt(PPh$_3$)$_4$] (0 14 g, 0.11 mmol) in the same solvent, and after 24 h the orange solution was reduced to half volume before addition of ethanol (10 cm^3). Over several days small white crystals of compound 3 (0 15 g, 0.09 mmol, 86%) formed, and these were filtered, washed with ethanol, and ether, and finally dried in vauo.

Reaction with Na[Mn(CO)$_5$]

Decacarbonyldimanganese (1 0 g, 2 55 mmol) was converted into its sodium salt by stirring in dry tetrahydrofuran (50 cm^3) with dilute sodium amalgam for 3 h according to a reported procedure [16]. After removing the excess of amalgam, this solution was added dropwise to a stirred solution of perfluoronorbornadiene (2.0 g, 8.5 mmol) in tetrahydrofuran at room temperature. The mixture was stirred for 60 h, the solvent was then removed, and the residue was chromatographed (florisil (100—200 mesh), petroleum ether (b.p. 30—40°C) eluant) to give small white crystals of compound 5 (0.82 g, 1.9 mmol, 80%)

Reaction with Na[Re(CO)$_5$]

Using a similar procedure reaction between Na[Re(CO)$_5$] (1.5 mmol) and perfluoronorbornadiene (1.4 g, 5 9 mmol) in tetrahydrofuran at room temperature gave, after chromatography, white crystals of 6 (0.25 g, 0.46 mmol, 31%).

Reaction with Na(Ir(CO)$_2$(PPh$_3$)$_2$]

Carbon monoxide was bubbled through a stirred solution of [IrCl(CO)(PPh$_3$)$_2$] (1.0 g, 1.28 mmol) in tetrahydrofuran (100 cm^3) to give a pale yellow precipitate of [IrCl(CO)$_2$(PPh$_3$)$_2$] (1 0 g, 1.24 mmol, 97%) This was treated with dilute sodium amalgam (sodium (2 g): mercury (25 cm^3)) for 4 h under a slow stream of carbon monoxide. The excess of amalgam was then removed, and the solution of the sodium salt was added dropwise over 1 h under an atmosphere of carbon monoxide to a stirred solution of perfluoronorbornadiene (1.25 g, 5.16 mmol) in tetrahydrofuran (25 cm^3). The mixture was stirred for a further 48 h before removal of the solvent, and chromatography

(Florisil; 80/20 mixture of petroleum ether (b p 60—80°C). dichloromethane as eluant) to give yellow crystals of compound 7 (0 5 g, 5.05 mmol, 39%) recrystallised from dichloromethane/methanol. Further elution with acetone gave $[IrCl(CO)(PPh_3)_2]$ (0 3 g).

With $Na[Rh(CO)_2(PPh_3)_2]$

Hexadecacarbonylhexarhodium (0.46 g, 0 44 mmol) [17] triphenylphosphine (0.40 g, 5.3 mmol) and benzene (20 cm^3) were stirred at 45°C, while a stream of carbon monoxide was passed through the solution After 2 h the yellow $[Rh(CO)(PPh_3)_2]_2$ (1 2 g, 0.84 mmol) was dried in a stream of carbon monoxide. This was converted into its sodium salt by stirring with dilute sodium amalgam (sodium (3 g), mercury (30 cm^3)) in tetrahydrofuran at room temperature for 3 h under a slow stream of carbon monoxide. After removal of the excess of amalgam and filtration, this solution was added dropwise under an atmosphere of carbon monoxide to a stirred solution of perfluoronorbornadiene (1.3 g, 9 2 mmol) over 45 min. The mixture was then stirred at room temperature for 2 days and a wine-red colour developed The mixture was filtered, and the volume of the filtrate was reduced to 10 cm^3 before addition of light petroleum (10 cm^3) to precipitate a brown solid (0.5 g) which was removed by filtration. Cold methanol (20 cm^3) was added to the filtrate to give yellow crystals of compound 8 (0.10 g, 0 11 mmol, 16%), which were washed with light petroleum and dried in vacuo. Chromatography of a brown residue (0.5 g) using acetone as eluant gave $[RhCl(CO)(PPh_3)_2]$ (0 3 g, 0 44 mmol)

With $Na[Fe(CO)_2(n\text{-}C_5H_5)]$

A solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ in tetrahydrofuran (100 cm^3), prepared from $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$ (2 0 g, 5 65 mmol) and sodium amalgam, was added dropwise over 1 h to a stirred solution of perfluoronorbornadiene (1.2 g, 1 20 mmol) in tetrahydrofuran at room temperature. The mixture was stirred for 18 h and a brown solid decomposition product which precipitated was filtered off The solvent was then removed from the filtrate and the residual maroon oil was dissolved in the minimum amount of ethanol before addition of light petroleum ether (b p. 30—40°C) to give yellow crystals of compound 9 (0 61 g, 1.7 mmol, 21%).

With $[Fe(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)(CO)_3]$

A mixture of the iron complex (1 0 g, 8 25 mmol), perfluoronorbornadiene (2.0 g, 8.5 mmol) and hexane (20 cm^3) sealed in vacuo in a Pyrex tube (capacity 100 cm^3) and irradiated with a 250 W Hanovia U.V. lamp for 48 h gave yellow crystals of compound 12 (0.5 g, 1.16 mmol, 20%) (^1H NMR ($CDCl_3$)· δ 2 33 (m, H^6), 2.47 (m, H^5), 2.96 (m, H^1), 3 43 (m, H^2) 4.44 (m, H^4), and 5.20 (m, H^3) ppm) which were washed with light petroleum and dried in vacuo

A repeat of this reaction using a 2/1 and a 4/1 mol ratio of iron complex to norbornadiene and irradiation for 8 days gave 34 and 36% yield respectively of compound 12.

With $[Fe(\eta^4\text{-}CH_2{=}CMeCH{=}CH_2)(CO)_3]$

Irradiation of a mixture of perfluoronorbornadiene (2.0 g, 8.5 mmol) and the iron complex (1.4 g, 6.73 mmol) in hexane (20 cm^3) for 3 days gave yellow crystals of 13 (0.6 g, 1.35 mmol, 20%) (^{1}H NMR ($CDCl_3$). δ 2.08 (broad s, CH_3 + H^6), 2.50 (m, H^5), 3.00 (m, H^1), 4.03 (m, H^2) and 4.43 (m, H^4) ppm).

With [Fe(CO)$_5$]

A solution of pentacarbonyliron (1.0 g, 5.10 mmol) in an excess of perfluoronorbornadiene (3 0 g, 12.7 mmol) sealed under vacuum in a silica reaction tube was irradiated with a 500 W Hanovia UV lamp for 5 days to give nonacarbonyldiiron (0.27 g, 0.81 mmol, 16%) and a brown oil, which on chromatography (Florisil, light petroleum (b.p. 30—40°C) as eluant) gave small, yellow crystals of compound 14 (10.0 mg, 0.03 mmol, 1%), which were washed with diethyl ether and dried in air.

Reaction between compound 5 and [Pt(PPh$_3$)$_4$]

A solution of [$Pt(PPh_3)_4$] (3 6 g, 2.89 mmol) in benzene (150 cm^3) was added dropwise to a stirred solution of compound 5 (1.2 g, 2.91 mmol), and the mixture was stirred at room temperature for 24 h. During this period an intense red colour developed. The solvent was removed and the residue was chromatographed (Florisil; ethanol eluant). The volume of the eluate was reduced to ca. 15 cm^3 to give [$Pt(CO)(PPh_3)_3$] (0.1 g, 0.13 mmol) m p. 308°C (lit. [18] 310°C) which was removed by filtration. Addition of light petroleum to the residue gave compound 10 (0.25 g, 0.18 mmol, 6%) as a pale yellow solid

Reactions of compound 7

(a) With acetyl chloride A mixture of compound 7 (0.26 g, 2.63 mmol) and acetyl chloride (0.62 g, 7.94 mmol) in dichloromethane (20 cm^3) was sealed under vacuum in a Pyrex reaction tube, and was allowed to stand at room temperature for 3 days. Removal of most of the solvent and addition of ethanol (10 cm^3) and petroleum ether (b.p. 60—80°C, 5 cm^3) gave white crystals of compound 11 (0 15 g, 0.014 mmol, 55%)

(b) With trifluoroacetic acid A mixture of compound 7 (0.26 g, 2.63 mmol), trifluoroacetic acid (1.0 g, 8.8 mmol) and dichloromethane (10 cm^3) was kept in a sealed tube for 4 days at room temperature, and then heated at 60°C for a further 2 days. Removal of the solvent and addition of ethanol gave white crystals of [$IrH(O_2CCF_3)_2(CO)(PPh_3)_2$] (50 mg, 0.05 mol, 20%) m p. 208—213°C decomp. (lit. [19] 210—215°C) (Found: C, 50.0; H, 3.2; F, 11.6. $C_{41}H_{31}F_6O_5P_2Ir$ calcd.: C, 50.6; H, 3.2; F, 11.7%). The IR and ^{1}H NMR spectra of this compound agreed with those reported [19].

Acknowledgements

Thanks are due to Mr. F. Vennels, Mr. F. Fitton, and Mr. J.V. Latham for assistance in the preparation of perfluoronorbornadiene.

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