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Some ruthenium complexes of fluorinated alkynylcyclopentenes

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ABSTRACT

Reactions between 1,2-dichlorohexafluorocyclopentene and Ru(C≡CH)(dppe)Cp* or Ru(C≡CC≡CLi)(dppe)Cp* have given Ru(C≡C-*c*-C_5F_6Cl-2)(dppe)Cp* **4** and Ru(C≡CC≡C-*c*-C_5F_6Cl-2)(dppe)Cp* **7**, respectively. Ready hydrolysis of **4** to the ketone Ru{C≡C[*c*-$C_5F_4Cl(O)$]}(dppe)Cp* **5** occurs, which can be converted to Ru{C≡C(*c*-C_5F_4Cl[=$C(CN)_2$])}(dppe)Cp* **6** by treatment with $CH_2(CN)_2$/basic alumina. Spectroscopic, electrochemical and XRD structural studies for **4**–**7** are reported: for **6**, these suggest that the cyanated fluorocarbon ligand is a very powerful electron-withdrawing group.

1. Introduction

Replacement of hydrogen by fluorine in organic compounds leads to significant changes in chemical and biological activities. In particular, the ready nucleophilic attack upon unsaturated fluorocarbons (vinyls, aromatics) provides an entry into derivatives for which the non-fluorinated analogues are not so readily available [1].

Recent studies of ethynyl compounds bearing electron-rich substituents, exemplified by Ru(C≡CH)(dppe)Cp* **1**, have shown that these complexes behave as strong nucleophiles. For example, reactions with tetracyanoethene result in replacement of one CN group by the –C≡CRu(dppe)Cp* fragment to give Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp*, rather than the usual [2+2]-cycloaddition reaction [2]. Subsequent chemistry involves reactions which lead to replacement of the CN group *gem* to the metal substituent, or to coordination of a second metal–ligand group to the CN group *trans* to the metal moiety.

Earlier studies by one of us showed that 1,2-dichlorohexafluorocyclopentene ($C_5F_6Cl_2$, **2**) is susceptible to nucleophilic attack by anionic metal carbonyls, with displacement of one of the Cl atoms to give complexes {ML_n}C_5F_6Cl [ML_n = $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2Cp$] [3]. In an extension of this chemistry, we have examined the reactions of **2** with Ru(C≡CH)(dppe)Cp*, and also with the lithiated butadiynyl LiC≡CC≡CRu(dppe)Cp* **3** [4]. The results are described below, together with some further chemistry of the fluorinated cyclopentenyl group which resulted in preparation of a strongly electron-withdrawing cyanated fluorocarbon ligand.

2. Results

In the reaction between Ru(C≡CH)(dppe)Cp* and **2**, concomitant elimination of HCl results in the formation of [Ru(=C=CH_2)(dppe)Cp*]$^+$, which does not react further with **2**, in a competing reaction. Addition of base to remove HCl often results in other reactions, addition of NEt_3, for example, giving a rapid reaction producing not only the desired ruthenium complex, but also unwanted by-products. A clean but slow (10 d) reaction occurs at 50 °C in the presence of K_2CO_3 to give orange Ru(C≡C-*c*-C_5F_6Cl-2)(dppe)Cp* **4** (Scheme 1) in 87% yield.

This complex was characterised by microanalysis, spectroscopically and by a single-crystal XRD structure determination (see below). The IR spectrum contains ν(C≡C) at 2030, ν(C=C) at 1572 and ν(CF) bands between 1301 and 1024 cm^{-1} The usual peaks at δ_H 1.55, δ_C 10.29, 94.31 (Cp*), δ_H 1.89, 2.66, δ_C 29.17–29.78 (CH_2) and δ_H 7.02–7.67, δ_C 127.7–138.1 (Ph) for the Ru fragment are found in the ^{1}H and ^{13}C NMR spectra, with an ^{31}P NMR peak at δ_P 80.9. The fluorinated alkynyl ligand also gives rise to peaks at δ_C 101.71 (C≡C) and 176.45 (RuC), while resonances for the CF_2 groups are found at δ_F −112.4, −113.0 and −132.0. In the electrospray mass spectrum (ES-MS) from a solution containing MeCN, M$^+$, [Ru(NCMe)(dppe)Cp*]$^+$ and [Ru(dppe)Cp*]$^+$ are found at *m/z* 868, 676 and 635, respectively.

The spectroscopic data may be compared with values recorded for **2**, for which the IR spectrum has ν(C=C) at 1630 cm^{-1} and ν(CF) bands between 1327 and 1006 cm^{-1}. The ^{13}C NMR spectrum of **2**

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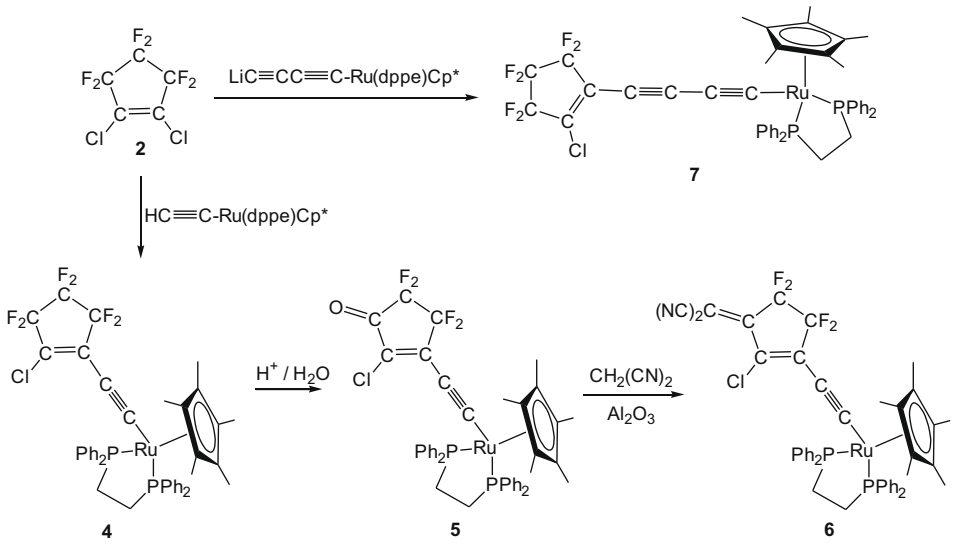


Scheme 1.

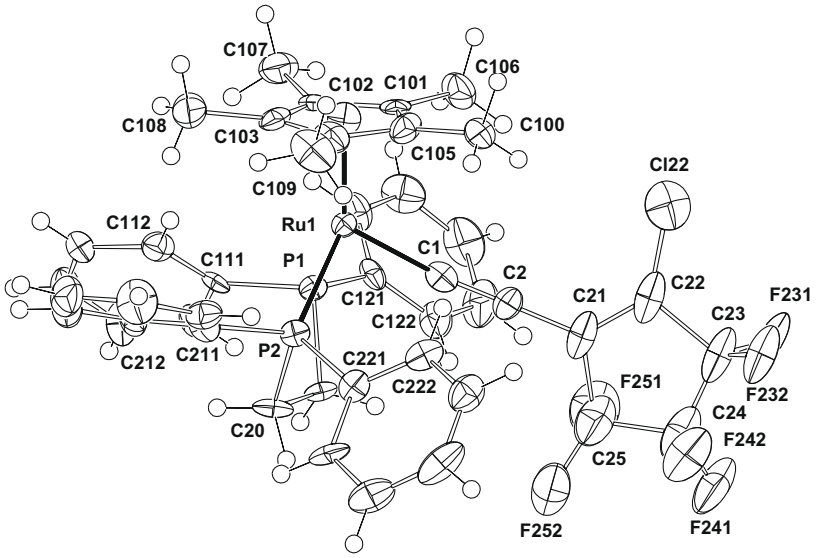


Fig. 1. Plot of a molecule of Ru(C≡CC_5F_6Cl-2)(dppe)Cp* **4**. Only one set of atoms of the disordered cyclopentene ring is shown.

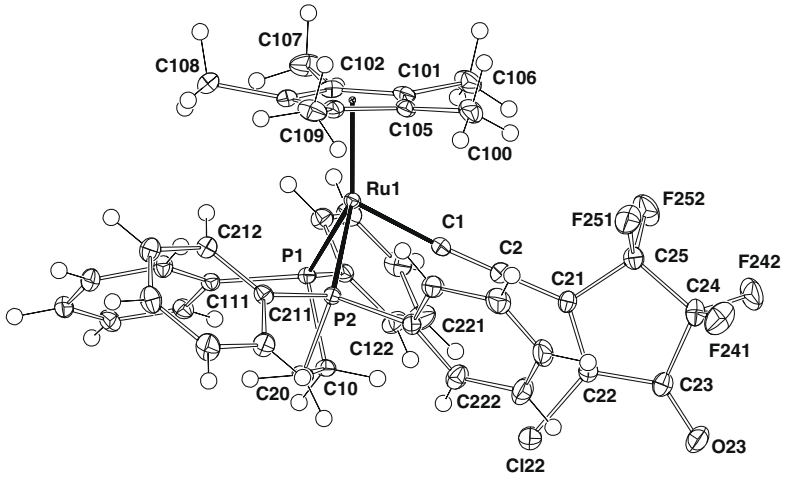


Fig. 2. Plot of a molecule of Ru{C≡$CC_5F_4Cl(O)$}(dppe)Cp* **5**.

contains two signals for the CF_2 groups (at δ_C 110.80 and 113.69) and for =CCl at δ_C 134.93, while the ^{19}F NMR spectrum contains two signals at δ_F −115.5 and −131.5 (intensities 2/1).

During attempts to purify **4**, it was noted that the colour changed rapidly to red on chromatographic supports (silica gel, Florisil, basic alumina). Subsequent isolation of this compound showed that regioselective hydrolysis of **4** to the cyclic ketone Ru{C≡C-*c*-$C_5F_4Cl(O)$}(dppe)Cp* **5** had occurred. Treatment of a solution of **4** in dichloromethane with 10% aqueous acetic acid over 4 d, followed by neutralisation (NEt_3) and subsequent work-up, afforded **5** in 79% yield.

Initial characterisation of **5** was by a single-crystal XRD structure determination, later supported by microanalysis and spectroscopy. The IR spectrum contains ν(C≡C) at 2007, ν(C=O) at 1685, ν(C=C) at 1517 and ν(CF) between 1323 and 1022 cm^{-1}. In addition to the expected resonances for the Ru(dppe)Cp* group, additional peaks were found at δ_C 109.51, 113.98 and 140.06 [ring C(sp^2)], 118.66 (C≡C), 179.64 (RuC) and 210.95 (acyl CO), while two equal intensity triplet signals at δ_F −115.9 and −128.1 were present in the ^{19}F NMR spectrum. The ES-MS contained $[M+Na]^+$ at *m/z* 869.

Knoevenagel condensation of **5** with malononitrile in the presence of basic alumina slowly produced the expected deep blue dicyanomethylene compound Ru{C≡CC_5F_4Cl[=C$(CN)_2$]}(dppe)Cp* **6** in 93% yield. Crystals have a metallic purple sheen. The structure of **6** was determined by a single-crystal XRD determination. Spectroscopic properties include ν(CN) at 2209, ν(C≡C) at 1969 and ν(C=C) at 1535, 1467 and 1433 and ν(CF) between 1307 and 1019 cm^{-1}. In addition to the usual resonances for the Ru(dppe)Cp* group, signals for CF_2 (δ_C 112.95, 115.24 [both tt with *J*(CF) = 258,

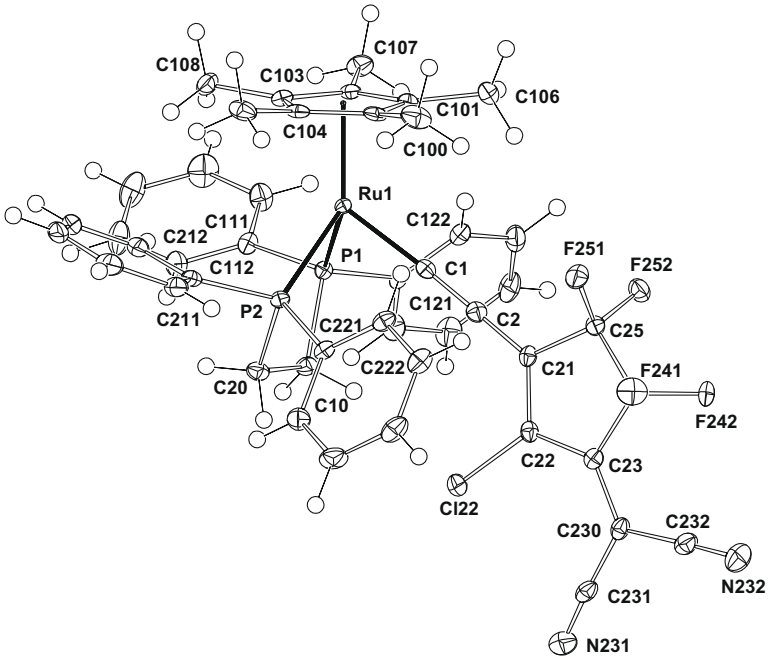


Fig. 3. Plot of a molecule of Ru{C≡CC_5F_4Cl[=C$(CN)_2$]}(dppe)Cp* **6**.

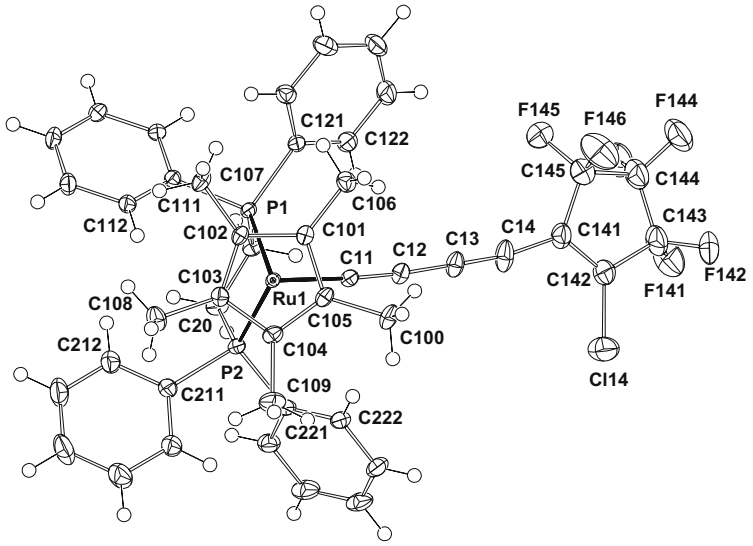


Fig. 4. Plot of the major component of molecule **1** of Ru(C≡CC≡CC_5F_6Cl-2)(dppe)Cp* **7**. Molecule **2** is similar.

24 Hz], δ_F −115.2, −117.9), CN (δ_C 114.49, 114.75) and RuC [δ_C 231.95, J(CP) = 20 Hz] were present in the ^{13}C and ^{19}F NMR spectra. The ES-MS contained $[M+Na]^+$ and $[M+H]^+$ at m/z 917 and 895, respectively.

The reaction between **2** and LiC≡CC≡CRu(dppe)Cp* proceeded cleanly to give orange Ru(C≡CC≡C-*c*-C_5F_6Cl-2)(dppe)Cp* **7** in 84% yield. In addition to a single-crystal XRD structure determination, this compound was characterised by analysis and spectroscopically. The IR spectrum contains ν(C≡C) (2132, 2119, 1996 cm^{-1}), ν(C=C) (1590 cm^{-1}) and ν(CF) bands (between 1322 and 994 cm^{-1}), while the ^{13}C NMR spectrum contained resonances at δ_C 94.42, 101.71, 128.54 (for C≡C), 111.67, 114.76, 115.15 (CF_2) and 163.74 (RuC). The ^{19}F signals were at δ_F −112.3, −113.9 and −131.9. The ES-MS contained M^+ at m/z 892.

2.1. Molecular structures

Figs. 1–4 show projections of individual molecules of complexes **4**–**7**, with selected bond parameters collected in Tables 1 and 2. The structures are consistent with the chemistry, with a central fluorinated cyclopentenyl ring bearing –C≡C–Ru(dppe)Cp* (**4**–**6**) or –C≡CC≡C–Ru(dppe)Cp* (**7**) groups attached to C(3) of the C=C double bond, and a remaining Cl atom attached to the other doubly-bonded carbon C(4). In **4** and **7**, the remaining three carbon atoms of the ring each carry two F atoms, while for **5** and **6**, two F atoms are replaced by O(6) (for **5**) or the =C(CN)$_2$ group (in **6**).

The Ru(dppe)Cp* fragments are similar to many others which have been described, with Ru–P [2.249(1)–2.299(1) Å], Ru–C(cp) [2.218–2.299(1) Å] and P(1)–Ru–P(2) [82.24(1)–84.71(2)°], P(1,2)–Ru–C(1) [81.64(4)–89.5(1)°] in the normal ranges. For **4**–**6**, the alkynyl groups are attached to Ru [Ru–C(1) 1.913(2)–1.930(5) Å] and the C(1)≡C(2)–C(3) separations are as expected for the triple bond between C(1)–C(2) [1.240(2)–1.248(7) Å]. These bonds are notably shorter and longer, respectively, than the corresponding bonds in **1** [Ru–C(1) 2.015(2), C(1)–C(2) 1.202(3) Å] [5]. In **7**, Ru–C(1) [1.944(2), 1.959(2) Å, values for molecules **1**, **2**] is somewhat longer than those in **4**–**6**, while the C–C separations have the expected short–long–short–long separations, and long

Table 1
Selected bond parameters for **4**–**6**.

Compound	**4**	**5**[a]	**6**[b]
Bond distances (Å)			
Ru(1)–P(1)	2.249(1)	2.2867(3)	2.2798(4)
Ru(1)–P(2)	2.299(1)	2.2936(3)	2.2945(5)
Ru(1)–C(cp)	2.239–2.289(5)	2.234–2.299(1)	2.254–2.275(2)
(av.)	2.26	2.266	2.265
Ru(1)–C(1)	1.930(5)	1.926(1)	1.913(2)
C(1)–C(2)	1.248(7)	1.240(2)	1.242(2)
C(2)–C(21)	1.405(7)	1.367(2)	1.367(2)
C(2)–C(3)	–	–	–
C(3)–C(4)	–	–	–
C(21)–C(22)	1.345(9)	1.383(2)	1.390(2)
C(22)–C(23)	1.568(12), 1.415(12)	1.428(2)	1.401(2)
C(23)–C(24)	1.51(1), 1.53(1)	1.537(2)	1.507(2)
C(24)–C(25)	1.549(11), 1.600(11)	1.540(2)	1.551(2)
C(25)–C(21)	1.536(10)	1.512(2)	1.503(2)
C(22)–Cl(22)	1.644(8)	1.714(1)	1.710(2)
C–F	1.342–1.436(7)	1.344–1.359(2)	1.352–1.358(2)
(av.)	1.38	1.352	1.354
Bond angles (°)			
P(1)–Ru(1)–P(2)	82.98(5)	84.43(1)	84.71(2)
P(1)–Ru(1)–C(1)	83.3(1)	82.93(4)	84.72(4)
P(2)–Ru(1)–C(1)	89.5(1)	86.52(3)	84.22(5)
Ru(1)–C(1)–C(2)	173.8(5)	176.0(1)	173.9(2)
C(1)–C(2)–C(21)	176.9(5)	170.1(1)	167.4(2)
C(2)–C(21)–C(22)	127.1(7)	129.6(1)	130.3(2)
C(2)–C(21)–C(25)	121.6(6)	122.2(1)	121.8(2)
C(21)–C(22)–C(23)	110.5(7), 117.5(8)	114.3(1)	114.3(1)
C(22)–C(23)–C(24)	103.4 (7), 102.4(7)	105.9(1)	106.4(1)
C(23)–C(24)–C(25)	106.5(7), 110.0(7)	105.6(1)	105.5(1)
C(21)–C(25)–C(24)	103.0(5), 98.9(5)	105.4(1)	104.7(1)
C(21)–C(22)–Cl(22)	130.5(5)	123.9(1)	121.5(1)

[a] For **5**: C(23)–O(23) 1.220(2) Å; C(24)–C(23)–O(23) 123.3(1)°.
[b] For **6**: C(23)–C(230) 1.376(2), C(230)–C(231,232) 1.433, 1.431(2) Å; C(22,24)–C(23)–C(230) 131.5(2), 122.1(1), C(23)–C(230)–C(231,232) 123.8(1), 121.6(2)°.

Table 2
Selected bond parameters for **7** (molecule **1**).

Bond distances (Å)	
Ru(1)–P(1)	2.2710(4)
Ru(1)–P(2)	2.2834(4)
Ru(1)–C(cp)	2.225–2.283(2)
(av.)	2.256
Ru(1)–C(11,21)	1.944(2)
C(11)–C(12)	1.238(2)
C(12)–C(13)	1.344(2)
C(13)–C(14)	1.220(2)
C(14)–C(141)	1.431(6)
C(141)–C(142)	1.344(6)
C(141)–C(145)	1.498(6)
C(142)–C(143)	1.475(5)
C(143)–C(144)	1.536(6)
C(144)–C(145)	1.543(6)
C(142)–Cl(14)	1.698(4)
C–F	1.297–1.365(5)
(av.)	1.338
Bond angles (°)	
P(1)–Ru(1)–P(2)	82.24(1)
P(1)–Ru(1)–C(11)	81.64(4)
P(2)–Ru(1)–C(11)	89.37(5)
Ru(1)–C(11)–C(12)	173.7(1)
C(11)–C(12)–C(13)	176.2(2)
C(12)–C(13)–C(14)	179.7(2)
C(13)–C(14)–C(141)	170.5(3)
C(14)–C(141)–C(142)	124.7(4)
C(14)–C(141)–C(145)	126.2(4)
C(141)–C(142)–C(143)	114.4(4)
C(141)–C(145)–C(144)	104.2(4)
C(142)–C(143)–C(144)	103.1(3)
C(143)–C(144)–C(145)	105.3(3)
C(141)–C(142) Cl(14)	127.1(3)

Table 3
Electrochemistry of complexes **4**–**7**.

Compound	Reduction V (i_a/i_c)	Oxidation V (i_a/i_c)	
Ru(C≡CPh)(dppe)Cp*		+0.30	+1.15[a]
Ru(C≡CC_5F_6Cl)(dppe)Cp* **4**		+0.65	+1.23 (0.9)[b]
Ru(C≡CC≡CC_5F_6Cl-2)(dppe)Cp* **7**		+0.66 (0.9)[b]	+1.38[a]
Ru{C≡CC_5F_4Cl(O)}(dppe)Cp* **5**	−1.30 (0.9)[b]	+0.82	+1.32 (0.3)[b]
Ru{C≡CC_5F_4Cl[=C(CN)$_2$]} (dppe)Cp* **6**	−0.81	+0.91	+1.30[a]

[a] Non-reversible.
[b] Partially reversible. All values in V versus SCE.

Table 4
Selected spectroscopic and structural data for complexes **4**–**7**.

Compound	λ_{max} (nm) (ε/l mol^{-1} cm^{-1})	ν(CC) (cm^{-1})	δ(Ru–C)	Ru–C (Å)	C≡C (Å)
1	334 (4200)	1925	120.58	2.015(2)	1.202(3)
4	383 (17400)	2030	176.45	1.930(5)	1.248(7)
7	442 (16300)	2132, 2119, 1966	163.74	1.944(2)	1.238(2)
5	488 (31300)	2007	179.64	1.926(1)	1.240(2)
6	610 (73600)	1969	222.07	1.913(2)	1.242(2)

Table 5
Crystal data and refinement details.

Complex	**4**	**5**	**6**	**7**
Formula	$C_{43}H_{39}ClF_6P_2Ru.C_6H_6$	$C_{43}H_{39}ClF_4OP_2Ru$	$C_{46}H_{39}ClF_4N_2P_2Ru$	$C_{45}H_{39}ClF_6P_2Ru$
Molecular weight	946.31	846.2	894.25	892.22
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	8.6190(5)	12.0863(3)	12.2173(3)	24.6638(3)
b (Å)	26.5123(15)	17.2597(5)	16.4428(3)	12.6837(3)
c (Å)	19.3133(11)	18.4941(4)	20.3970(8)	26.2274(3)
β (°)	90.413(4)	105.447(2)	105.798(4)	99.363(1)
V (Å^3)	4413.2(4)	3718.6(2)	3942.7(2)	8095.4(2)
ρ_c	1.424	1.511	1.507	1.464
Z	4	4	4	8
$2\theta_{max}$ (°)	60.5	75	65	75
μ (Mo Kα) (mm^{-1})	0.55	0.63	0.60	0.59
$T_{min/max}$	0.87/0.97	0.77/0.89	0.81/0.98	0.87/0.97
Crystal dimensions (mm^3)	0.17 × 0.14 × 0.05	0.28 × 0.25 × 0.19	0.51 × 0.20 × 0.04	0.41 × 0.28 × 0.05
N_{tot}	24742	83891	51806	291506
N (R_{int})	10935 (0.065)	18686 (0.029)	13265 (0.045)	41760 (0.074)
N_o	7550	14064	9279	27344
R_1, wR_2 [$I > 2\sigma(I)$]	0.061, 0.126	0.031, 0.082	0.031, 0.056	0.038, 0.081
R_1, wR_2 (all data)	0.094, 0.141	0.047, 0.093	0.058, 0.059	0.078, 0.089
T (K)	150	100	100	100

separations, the C(1)≡C(2) triple bond being longer than C(3)–C(4) by **6** s.d. The cyclopentenyl ring has C–C distances consistent with single bonds between C(5)–C(6)–C(7) (sp^3–sp^3) and C(3)–C(7) and C(4)–C(5) (sp^2). The C–F bond lengths are normal [ca. 1.35 Å], as are the C–Cl bonds [1.71 Å]. In **4** and **7**, the C_5F_6Cl groups are essentially superimposable. For **5**, the C(6)=O(6) group is a normal ketone [1.220(2) Å], while for **6**, the C=C(CN)$_2$ group also has no unexpected features, having C(23)–C(230) 1.376(2) Å.

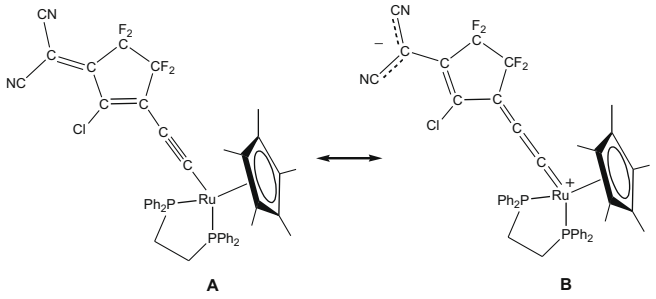
2.2. Electrochemistry

Table 3 summarises the redox potentials measured for **4**–**7**, together with those for Ru(C≡CPh)(dppe)Cp* for comparison. Replacement of the Ph group by the fluorinated cyclopentenyl group in **4** results in significantly higher oxidation potentials, as expected from the presence of the electron-withdrawing F atoms. Introduction of oxygen or dicyanomethylene substituents in **5** and **6**, respectively, results in further increases in the oxidation potentials, these stronger electron-withdrawing substituents serving to remove additional electron density from the metal centre.

Whereas **4** and **7**, like the phenylalkynyl complex, do not show any reduction processes, it proved to be possible to reduce both **5** (partially reversible) and **6** (reversible) to species in which the extra negative charge can be stabilised on the O or =C(CN)$_2$ substituents. These complexes are therefore examples of "push–pull" systems in which the electron-rich metal centre is linked to an electron-attracting fluoro-ketone or fluoro–cyano-carbon ligand via the C_2 or C_4 bridges.

2.3. UV–Vis spectroscopy

Table 4 relates features of the UV–Vis, IR and ^{13}C NMR spectra and the Ru–C bond lengths of complexes **4**–**7**. In particular, the λ_{max} values of the metal-to-ligand charge transfer (MLCT) absorption bands show red shifts as the Ru–C bond order increases with the increase in electron attracting power of the ligand. In **4**, λ_{max} is at 383 nm, while the extra C≡C triple bond in **7** results in broadening of this band, with a shift to 442 nm. Replacement of a CF_2 group by C=O and C=C(CN)$_2$ results in progressive red-shifting of the MLCT absorption, the compounds being red and dark blue, with λ_{max} at 488 and 610 nm, respectively. The molar absorption also increases along this series. Parallel changes in the IR ν(C≡C) band positions and in the ^{13}C chemical shifts of the Ru–C atom are all consistent with a contribution from resonance structure **B** (shown for **6**) in which the allenylidene, C=C double bond and substituent are conjugated. There is a small shift in the λ_{max} of **6** in different solvents: CH_2Cl_2 610, PhMe 590, hexane-CH_2Cl_2 (24/1) 574 nm, which may be attributed to a polar excited state which is stabilised in the more polar solvents [6].



3. Discussion

Reactions between 1,2-dichlorohexafluorocyclopentene **2** and anionic metal carbonyls result in displacement of one of the Cl atoms to form complexes such as M(C_5F_6Cl)L_n [ML_n = Mn(CO)$_5$, Re(CO)$_5$, Fe(CO)$_2$Cp] [3]. The high nucleophilic character of the neutral ethynyl Ru(C≡CH)(dppe)Cp* is further exemplified by its reaction with **2** to give Ru(C≡CC_5F_6Cl)(dppe)Cp* **4**. Similarly, the lithiated diynyl complex Ru(C≡CC≡CLi)(dppe)Cp* affords Ru(C≡CC≡CC_5F_6Cl)(dppe)Cp* **7**. While phosphorus and sulfur nucleophiles often displace more than one Cl from **2** [7,8], the present studies provided no evidence for the formation of poly-substituted products. Reactions of perfluorocyclopentene with carbon nucleophiles (organolithiums) generally result in substitution of one or both F atoms attached to the C=C double bond, although the reaction with Na[CH(CO$_2$Et)$_2$] also afforded a bis(ethoxycarbonyl)vinyl derivative [9]. Ring-opening occurs in the reaction of **2** with cyanide to produce the [C(CN)$_2$=C(CN)CF=NC(CN)$_2$]$^-$ anion [10].

Ready hydrolysis of **4** to give the cyclic ketone **5** occurred, either when adsorbed on chromatographic supports (which probably contained water), or deliberately in solution in the presence of

acetic acid. We recall the earlier observations of the reactions between $C_5F_6Cl_2$ and NaOR, which gave the trisubstituted compounds 1,3,3-$C_5F_4Cl(OR)_3$ [3,11]. In the present case, formation of a *gem*-dihydroxy derivative would be followed by rapid elimination of water. We note that in all cases, regioselective reactions are occurring.

Further derivatisation of **4** was achieved by the Knoevenagel reaction with malononitrile, which afforded the dicyanomethylene derivative Ru{C≡CC$_5$F$_4$Cl[=C(CN)$_2$]}(dppe)Cp* **6**. As expected, the cyanated fluorocarbon ligand is strongly electron-withdrawing, as shown by the oxidation potentials of the complexes described above, that of **6** being the highest so far observed of any neutral complex in the Ru(dppe)Cp* series. In comparison, the value for Ru(C≡CH)(dppe)Cp* is +0.34 V, while that found for cationic [Ru(=C=CH$_2$)(dppe)Cp*]$^+$ is +1.68 V [5]. The high E° for **6** agrees with the allenylidene tautomer **B** being a significant contributor to the overall structure.

4. Conclusions

Reactions between 1,2-dichlorohexafluorocyclopentene and Ru(C≡CH)(dppe)Cp* and Ru(C≡CC≡CLi)(dppe)Cp* have resulted in substitution of one Cl to give Ru{(C≡C)$_x$C$_5$F$_6$Cl}(dppe)Cp* (x = 1 **4**, 2 **7**). Hydrolysis of **4** gives the cyclic ketone Ru{C≡CC$_5$F$_4$Cl(O)}(dppe)Cp* **5**, which was converted to the dicyanomethylene derivative Ru{C≡CC$_5$F$_4$Cl[=C(CN)$_2$]}(dppe)Cp* **6**. Trends in oxidation potentials, λ_{max} (MLCT) and δ(Ru–C) are related to the increasing electron acceptor power of the fluoro- or fluoro(cyano)-ligands in **4**–**7**, the cyanated fluorocarbon group in **6** being very strongly electron-accepting to give an extreme example of a donor–acceptor molecule. In particular, the large down-field shift of the C(1) resonance to δ 222.07 (C_6D_6), together with the high oxidation potential of **6**, suggests that there is a substantial contribution from allenylidene structure **B** to the overall structure of this molecule. Such highly polarised complexes may have unusual electrical and optical (including non-linear) properties.

5. Experimental

5.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm^2) coated with silica gel (Merck, 0.5 mm thick) or by flash chromatography on silica gel (Davisil 40–63 μm) or alumina (Fluka, 0.05–0.15 mm, activity 1, pH 7.0 ± 0.5).

5.2. Instruments

IR spectra were obtained from Nujol mulls or liquid films (**2**) mounted between NaCl discs using a Bruker IFS28 FT-IR spectrometer. UV–Vis spectra were obtained with a Varian-Cary 5000 UV–Vis-NIR spectrophotometer, with fused quartz cells of path-length 1 cm. NMR spectra were recorded on a Varian Gemini 2000 instrument (^{1}H at 300.145 MHz, ^{13}C at 75.479 MHz, ^{19}F at 282.388 MHz, ^{31}P at 121.501 MHz) or Varian Unity Inova 600 instrument, equipped with a cryo-probe (^{1}H at 599.653 MHz, ^{13}C at 150.796 MHz). Unless otherwise stated, samples were dissolved in C_6D_6 contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C NMR spectra, C_6F_6 (δ_F −162.9) for ^{19}F NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH. Solutions were injected into a Varian Platform II spectrometer *via* a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Peaks listed are the most intense of the isotopic clusters. Electrochemistry was performed on samples (1 mM) in CH_2Cl_2 containing 0.1 M [NBu$_4$]PF$_6$ as the supporting electrolyte. CVs were recorded using a PAR Model 263A potentiostat, scan rate 100 mV s^{-1}. The cell contained Pt-mesh working, Pt wire counter and pseudo-reference electrodes. Decamethylferrocene was used as an internal reference ($FeCp^*_2$/[$FeCp^*_2$]$^+$ = −0.02 V versus SCE). Elemental analyses were by Campbell Microanalytical Centre, University of Otago, Dunedin, New Zealand.

5.3. Reagents

The compounds Ru{(C≡C)$_x$H}(dppe)Cp* (x = 1 [5], 2 [12]) were prepared by the cited methods. 1,2-$C_5F_6Cl_2$ was obtained from Sigma–Aldrich, all other reagents were used as received from Sigma–Aldrich or Fluka without further purification.

5.3.1. Spectroscopic data for 1,2-$C_5F_6Cl_2$

IR (neat, film/cm^{-1}): ν(C=C) 1631w, ν(CF) 1328m, 1180m, 1252m, 1209m, 1168m, 1109m, 1007m. ^{13}C NMR: δ 110.80 [t quin, J(CF) = 277.25 Hz, $CF_2CF_2CF_2$], 113.69 [tt, J(CF) = 261, 25 Hz, $CF_2CF_2CF_2$], 134.93 [br t, J(CF) = 28 Hz, =CCl]. ^{19}F NMR: δ −115.5 (s, 4F, 2 × CF_2), −131.5 (m, 2F, $CF_2CF_2CF_2$). Lit. [3]: 114.4t (2F), 130.4q (1F), J(FF) = 3.21 Hz.

5.3.2. Ru(C≡CC$_5$F$_6$Cl-2)(dppe)Cp* **4**

A mixture of Ru(C≡CH)(dppe)Cp* (200 mg, 0.303 mmol), K_2CO_3 (420 mg, 3.04 mmol) and $C_5F_6Cl_2$ (148 mg, 0.606 mmol) in thf (15 ml) was heated at 50 °C for 10 d in a sealed Schlenk tube. After reduction in volume to about 2 ml, petroleum spirit (30 ml) was added and the mixture was filtered. Solvent was removed from the filtrate and the residue was purified by column chromatography (neutral alumina, hexane-Et$_2$O, 1/1) to give Ru(C≡CC$_5$F$_6$Cl-2)(dppe)Cp* **4** as an orange crystalline solid (228 mg, 87%). X-ray quality crystals were grown from C_6D_6. *Anal.* Calc. ($C_{43}H_{39}ClF_6P_2Ru$): C, 59.48; H, 4.53; M, 868. Found: C, 59.58; H, 4.63%. IR (nujol/cm^{-1}): ν(C≡C) 2030s, ν(C=C) 1572m, 1436m, ν(CF) 1301m, 1259s, 1180m, 1159w, 1134m, 1110m, 1095m, 1081m, 1042w, 1024w, 954m. ^{1}H NMR: δ 1.55 (s, 15H, Cp*), 1.89, 2.66 (2 × m, 2 × CH_2, dppe), 7.02–7.67 (m, Ph). ^{13}C NMR: δ 10.29 (C_5Me_5), 29.17–29.78 (m, CH_2), 94.31 (s, C_5Me_5), 101.71 (s, ≡C), 127.75–138.14 (Ph), 176.45 (m, Ru–C). ^{19}F NMR: δ −112.4, −113.0 (2 × s, 2 × 2F, 2 × CF_2), −132.0 (m, 2F, $CF_2CF_2CF_2$). ^{31}P NMR: δ 80.9 [s, Ru(dppe)]. ES-MS (positive ion, MeCN, m/z): 868, M$^+$; 676, [Ru(NCMe)(dppe)Cp*]$^+$; 635, [Ru(dppe)Cp*]$^+$.

5.3.3. Ru(C≡CC≡CC$_5$F$_6$Cl-2)(dppe)Cp* **7**

BuLi (0.082 ml, 1.78 M in hexanes, 0.146 mmol) was added to a stirred solution of Ru(C≡CC≡CH)(dppe)Cp* (100 mg, 0.146 mmol) in thf (15 ml) at −78 °C. After 30 min $C_5F_6Cl_2$ (72 mg, 0.044 ml, 0.293 mmol) was added, upon which the solution changed from yellow to dark orange. After warming to room temperature and stirring for 1 h, solvent was removed under reduced pressure. The residue was purified by column chromatography (neutral alumina, petroleum spirit-ether 1/1). The first orange band contained Ru(C≡CC≡CC$_5$F$_6$Cl-2)(dppe)Cp* **7** (110 mg, 84%), obtained as a dark orange solid. X-ray quality crystals were grown from Et$_2$O/hexane. *Anal.* Calc. ($C_{45}H_{39}ClF_6P_2Ru$): C, 60.58; H, 4.41; M, 892. Found: C, 60.86; H, 4.47%. IR (nujol/cm^{-1}): ν(C≡C) 2132 (sh), 2119s, 1996m, ν(C=C) 1590m, ν(CF) 1322m, 1264s, 1190m, 1138s, 1095m, 1083m, 1026w, 994m. ^{1}H NMR: δ 1.47 (s, 15H, Cp*), 1.71, 2.35 (2 × m, 2 × CH_2, dppe), 7.00–7.70 (m, Ph). ^{13}C NMR: δ 9.98 (C_5Me_5), 29.38–29.69 (m, CH_2), 94.42, 101.71,

128.54 (3 × s, ≡C), 94.52 (s, C_5Me_5), 111.67 [t quin, J(CF) = 273, 25 Hz, $CF_2CF_2CF_2$], 114.76 [tt, J(CF) = 259, 24 Hz, CF_2], 115.15 [tt, J(CF) = 256, 24 Hz, CF_2], 127.68–137.70 (Ph) 163.74 [t, J(CP) = 23 Hz, Ru–C]. ^{19}F NMR: δ −112.3, −113.9 (2 × s, 2 × 2F, 2 × CF_2), −131.9 (m, 2F, $CF_2CF_2CF_2$). ^{31}P NMR: δ 80.2 [s, Ru(dppe)]. ES-MS (positive ion, MeCN, *m/z*): 892, M^+; 676, [Ru(NCMe)(dppe)Cp*]$^+$; 635, [Ru(dppe)Cp*]$^+$.

5.3.4. Ru{C≡CC$_5$F$_4$Cl(O)}(dppe)Cp **5***

A solution of Ru(C≡CC$_5$F$_6$Cl)(dppe)Cp* (30 mg, 0.034 mmol) in CH_2Cl_2 (10 ml) was treated with acetic acid–water (1/9, 10 ml). After stirring in air for 4 d, the solution was neutralised (NEt_3). Removal of solvent from the red organic layer and purification of the residue by column chromatography (silica, CH_2Cl_2), gave a fraction containing Ru{C≡CC$_5$F$_4$Cl(O)}(dppe)Cp* **5** (23 mg, 79%), obtained as a red solid. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/hexane. *Anal.* Calc. ($C_{43}H_{39}ClF_4OP_2Ru$): C, 61.03; H, 4.65; M, 846. Found: C, 61.29; H, 4.90%. IR (nujol, cm^{-1}): ν(C≡C) 2007s, ν(C=O) 1684br, ν(C=C) 1517s, ν(CF) 1323w, 1297s, 1274m, 1158s, 1115m, 1094m, 1056w, 1022w. ^{1}H NMR: δ 1.50 (s, 15H, Cp*), 1.87, 2.70 (2 × m, 2 × CH_2, dppe), 7.02–7.56 (m, Ph). ^{13}C NMR: δ 9.95 (C_5Me_5), 29.12–29.78 (m, CH_2), 95.95 (s, C_5Me_5), 109.51, 113.98 [2 × tt, J(CF) = 258, 23 Hz, CF_2CF_2], 118.66 (s, C), 127.75–138.14 (Ph), 140.06 [t, J(CF) = 25 Hz, C=C], 179.64 [t, J(CP) = 24 Hz, Ru–*C*], 210.95 [t, J(CF) = 22 Hz, C=O]. ^{19}F NMR: δ −115.9 [t, J(FF) = 2.5 Hz, CF_2], −128.1 [t, J(FF) = 2.5 Hz, CF_2CF_2CO). ^{31}P NMR: δ 80.6 [s, Ru(dppe)]. ES-MS (positive ion, MeOH, *m/z*): 869, [M+Na]$^+$; 635, [Ru(dppe)Cp*]$^+$.

5.3.5. Ru{C≡CC$_5$F$_4$Cl[=C(CN)$_2$]}(dppe)Cp **6***

A mixture of Ru{C≡CC$_5$F$_4$Cl(O)Cl}(dppe)Cp* (42 mg, 0.050 mmol), $CH_2(CN)_2$ (500 mg, 7.576 mmol) and basic alumina (30 mg) in thf-NEt_3 (5/1, 6 ml) was heated at reflux point for 6 d, adding more $CH_2(CN)_2$ (26 mg, 0.378 mmol) and basic alumina (30 mg) each day, maintaining the solvent volume. The solution changed colour from red to black to blue. The reaction was monitored by TLC to determine when most of the starting material had been consumed. The reaction mixture was separated by column chromatography (silica gel, acetone–hexane, 1/4). The first red fraction contained recovered starting material (3 mg), the second blue band afforded the title compound (35 mg, 93%) as a metallic purple solid, which formed blue films on glass. X-ray quality crystals were from MeOH/C_6D_6. *Anal.* Calc. ($C_{46}H_{39}ClF_4N_2P_2Ru$): C, 61.28; H, 4.40; N, 3.13; M, 894. Found: C, 61.34; H, 4.50; N, 3.33%. IR (nujol/cm^{-1}): ν(CN) 2209 m, ν(C≡C) 1969s, ν(C=C) 1535s, 1467s, 1433s, ν(CF) 1305w, 1281m, 1212m, 1186m, 1156w, 1124m, 1091m, 1019w. ^{1}H NMR: δ 1.43 (s, 15H, Cp*), 1.91, 2.65 (2 × m, 2 × CH_2, dppe), 7.02–7.43 (m, Ph). ^{13}C NMR ($CDCl_3$): δ 9.81 (C_5Me_5), 28.90–29.68 (m, CH_2), 97.97 (s, C_5Me_5), 112.95, [tt, J(CF) = 258, 24 Hz, CF_2CF_2], 114.49, 114.75 (2 × s, CN), 115.24 [tt, J(CF) = 265, 25 Hz, CF_2CF_2], 127.88–135.28 (Ph), 139.51 (s, C), 151.81 [t, J(CF) = 23 Hz, ring C], 231.95 [t, J(CP) = 20 Hz, Ru–C] (δ_{RuC} = 222.07 in C_6D_6). ^{19}F NMR: δ −117.9, −115.2 (2 × s, CF_2CF_2). ^{31}P NMR: δ 80.4 [s, Ru(dppe)]. HR-MS (positive ion, MeOH, m/*z*): found 917.115, calc. 917.115 [M+Na]$^+$; found 895.136, calc. 895.134, [M+H]$^+$.

5.4. Molecular structures

Crystal data for **4**–**7** are summarised in Table 5 and the plots of individual molecules are depicted in Figs. 1–4, where ellipsoids have been drawn at the 50% probability level. Selected coordination geometries are shown in Tables 1 and 2. Crystallographic data for the structures were collected at 100(2) K [150 K for **4**] on an Oxford Diffraction Xcalibur or Gemini [for **6**] diffractometers fitted with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) yielding N_{tot} reflections, these merging to N unique after multiscan absorption correction (R_{int} cited), with N_o reflections having $I > 2\sigma(I)$. The structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97 [13]. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the isotropic displacement parameter of the parent atom.

5.5. Variata

4. The cyclopentene ring is rotationally disordered with site occupancies set at 0.5 after trial refinement for both components.

7. Two crystallographically independent molecules in the asymmetric unit. In both molecules the cyclopentene ring is rotationally disordered about the C(n3)–C(n4) vector with site occupancies for the pairs of components being refined to 0.583(2), 1–0.583(2) (molecule **1**) and 0.875(2), 1–0.875(2) (molecule **2**).

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Appendix A. Supplementary material

CCDC 742438 (**4**), 742437 (**5**), 742439 (**6**) and 742440 (**7**) contain the supplementary crystallographic data for compounds **4**–**7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.050.

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