Some transition metal complexes derived from mono- and di-ethynyl perfluorobenzenes[†]

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Transition metal alkynyl complexes containing perfluoroaryl groups have been prepared directly from trimethylsilyl-protected mono- and di-ethynyl perfluoroarenes by simple desilylation/metallation reaction sequences. Reactions between Me₃SiC \equiv CC₆F₅ and RuCl(dppe)Cp' [Cp' = Cp, Cp*] in the presence of KF in MeOH give the monoruthenium complexes $Ru(C \equiv CC_6F_5)(dppe)Cp' [Cp' = Cp (2);$ Cp* (3)], which are related to the known compound $Ru(C \equiv CC_6F_5)(PPh_3)_2Cp$ (1). Treatment of $Me_3SiC \equiv CC_6F_5$ with $Pt_2(\mu$ -dppm)_2Cl_2 in the presence of NaOMe in MeOH gave the bis(alkynyl) complex $Pt_2(\mu$ -dppm)₂(C=CC₆F₅)₂ (4). The Pd(0)/Cu(I)-catalysed reactions between Au($C \equiv CC_6F_5$)(PPh₃) and Mo($\equiv CBr$)(CO)₂Tp* [Tp* = hydridotris(3.5-dimethylpyrazoyl)borate], $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$ or $IC \equiv CFc$ [Fc = $(\eta^5-C_5H_4)FeCp$] afford Mo($\equiv CC \equiv CC_6F_5)(CO)_7Tp^*$ (5), $Co_3(\mu_3-CC \equiv CC_6F_5)(\mu-dppm)(CO)_7$ (6) and $FcC \equiv CC \equiv CC_6F_5$ (7), respectively. The diruthenium complexes 1.4-{Cp'(PP)RuC=C} $_{2C_{6}F_{4}}$ [(PP)Cp' = (PPh_{3})_{2}Cp (8); (dppe)Cp (9); (dppe)Cp* (10)] are prepared from 1,4-(Me₃SiC=C)₂C₆F₄ in a manner similar to that described for the monoruthenium complexes 1–3. The non-fluorinated complexes 1,4-{ $Cp'(PP)RuC \equiv C$ }, C_6H_4 [(PP)Cp' = (PPh_3),Cp (11); (dppe)Cp (12); (dppe)Cp* (13)], prepared for comparison, are obtained from $1,4-(Me_3SiC=C)_2C_6H_4$. Spectro-electrochemical studies of the ruthenium aryl and arylene alkynyl complexes 2-3 and 8-13, together with DFT-based computational studies on suitable model systems, indicate that perfluorination of the aromatic ring has little effect on the electronic structures of these compounds, and that the frontier orbitals have appreciable diethynylphenylene character. Molecular structure determinations are reported for the fluoroaromatic complexes 1, 2, 3, 6 and 10.

Introduction

Substitution of ring hydrogens by fluorines in aromatic compounds results in dramatic differences in properties,¹ such as the marked increase in acidity of C₆F₅CO₂H when compared with benzoic acid ($K_a = 4.2 \times 10^{-4}$ vs. 6.2×10^{-5}),² and the tendency of the polyfluoroaromatics to undergo nucleophilic substitution.³ In addition, the introduction of strongly electron-withdrawing fluorine atoms at strategic points in a molecular structure might be expected to fine-tune electronic properties through stabilisation of

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the occupied frontier orbitals or destabilisation of the unoccupied frontier orbitals. Our interest in organometallic fluorine chemistry stems from early work concerning the displacement of an aromatic F atom by carbonylmetal anions.⁴ Later, the synthesis of the σ -alkynyl complex Ru(C=CC₆F₅)(PPh₃)₂Cp (1)⁵ from the corresponding chloride and pentafluorophenylacetylene, and its conversion to [Ru{=C=CX(C₆F₅)(PPh₃)₂Cp]⁺ (X = H, alkyl, Br, I, N₂Ar [Ar = aryl], C₇H₇),⁶ were reported.

Recent studies of the redox properties of the alkynyl systems M(C=CAr)(PP)Cp' [M = Fe, Ru, Os; PP = (PPh₃)₂, dppe; $Cp' = Cp, Cp^*$ groups,⁷⁻⁹ together with the growing spectrum of synthetic methods available for the preparation of organometallic compounds featuring alkynyl-based ligands, including in situ desilylation/metalation^{10,11} and palladium and/or coppercatalysed cross-couplings within the metal-ligand sphere,8,12-15 have led us to reconsider the synthetic chemistry of some fluorinated analogues. Below we describe the syntheses of a variety of complexes containing perfluorinated phenyl and phenylene ring systems that illustrate the use of in situ desilylation/metallation protocols and gold-enhanced cross-coupling reactions in the preparation of organometallic derivatives of pentafluorophenylacetylene and 1,4-diethynyltetrafluorobenzene. Computational studies indicate that the electronic structures of ruthenium alkynyl complexes featuring pentafluorobenzene substituents and bimetallic complexes featuring

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1,4-diethynyltetrafluorobenzene-based bridging ligands are comparable with the analogous aromatic hydrocarbon compounds. UV-Vis-NIR spectroelectrochemical studies are consistent with the conclusions drawn from the computational work, and indicate that the ethynylaromatic ligands are redox non-innocent.

Results and discussion

Complexes derived from Me₃SiC≡CC₆F₅

An earlier report has described the synthesis of $Ru(C \equiv CC_6 F_5)$ - $(PPh_3)_2Cp$ (1) in 76% yield by treatment of pentafluorophenylacetylene with RuCl(PPh₃)₂Cp in the presence of sodium methoxide.⁵ Here, the new analogues $Ru(C=CC_6F_5)(dppe)Cp'$ $(Cp' = Cp 2, Cp^* 3)$ were synthesised by reacting Me₃SiC=CC₆F₅ with RuCl(dppe)Cp' in the presence of potassium fluoride in 63% and 54% yields, respectively (Scheme 1). The latter route does not require prior deprotection of the alkyne and therefore avoids the additional desilylation/purification steps associated with the isolation of the terminal acetylene from the silylated precursor.¹⁶ Elemental analyses supported by spectroscopic data confirmed the formulations of these complexes. Thus, in the ¹⁹F NMR spectra, the five fluorine nuclei resonate as three signals with relative intensities 2/1/2 from AA'MXX' systems.17,18 The ortho and meta fluorines of 1 and 2 are found as multiplets at $\delta_{\rm F}$ -142.9, -145.6 and -166.3, -168.8, respectively, and the para-fluorines are observed as triplets at $\delta_{\rm F}$ -165.7, -168.3, due to coupling with the meta fluorine nuclei [J(FF) = 21 Hz]. This coupling is also observed in the central parts of the AA'XX' resonance assigned to the metafluorines. Replacing the Cp group by Cp* in 3 has little effect on the resonance from the ortho-fluorine atoms which is found at $\delta_{\rm F}$ –145.8, although unusually, the *para*-fluorine resonance ($\delta_{\rm F}$ -169.1) is observed upfield of that from the *meta*-fluorine atoms ($\delta_{\rm F}$ –168.9). Comparison of the ¹⁹F chemical shifts for HC=CC₆F₅ $[\delta - 134.2 (o-F), -149.9 (p-F), -159.6 (m-F)]$ with those of 2 shows that replacement of H by the Ru(dppe)Cp moiety results in shifts of -11.4, -18.4 and -9.2 ppm, reflecting the electron-donating properties of the Ru centre.

In the ³¹P NMR spectra, characteristic resonances at δ_P 87.0 (2) or 81.7 (3) were found. The electrospray-mass spectra (ES-MS) of these complexes contained M⁺ at m/z 756 (2) and 826 (3),

which fragmented by loss of F to give ions at m/z 738 (2) and 808 (3), respectively. The structures of 2 and 3 were confirmed by X-ray studies of crystals grown from dichloromethane/hexane (see below).

Two equivalents of Me₃SiC=CC₆F₅ react with Pt₂(μ $dppm)_2Cl_2^{19}$ in the presence of sodium methoxide to give $Pt_2(\mu$ $dppm)_2(C = CC_6F_5)_2$ (4). The non-fluorinated analogue has been made in a similar fashion on a previous occasion.²⁰ The IR spectrum of 4 contains a single v(CC) band at 2079 cm⁻¹. In the ¹H NMR spectrum, characteristic resonances are found for the dppm ligand at δ 4.62 (CH₂) and between δ 6.96 and 7.90 (Ph). In the ³¹P NMR spectrum the phosphine ligands give rise to a resonance at δ 2.13, with evident coupling to ¹⁹⁵Pt [J(PPt) = 2816 Hz]. In the ¹⁹F NMR spectrum the usual three multiplets are found at $\delta_{\rm F}$ –143.1, –165.7 and –168.2 for the ortho-, paraand *meta*-fluorines, respectively. The ES-MS contains $[M + H]^+$ at m/z 1541. As with the synthesis of 1, no evidence was found to suggest that the *para*-fluorine of **4** underwent nucleophilic attack by the methoxide present in the reaction mixture. This may be for kinetic reasons, with the metallation reaction and precipitation of the product taking place prior to fluoride substitution, but could also be due to electron-donation from the metal-acetylide fragment increasing the electron density at the para-carbon of the fluoroaromatic substituent.

Complexes derived from Au(C≡CC₆F₅)PPh₃

The Pd(0)/Cu(1)-catalysed reaction between phosphine-gold(1) alkynyls and C(sp² or sp³)–X (X = Br, I) bonds has recently been developed as a base-free analogue of the Sono-gashira reaction, which is useful in the preparation of novel metal-containing alkynyl and poly-ynyl derivatives.¹⁶ Using this methodology, reaction between Au(C=CC₆F₅)(PPh₃) and Mo(=CBr)(CO)₂Tp* [Tp* = hydridotris(3.5-dimethylpyrazoyl)-borate] gave the pentafluorophenyl-terminated C₃ complex, Mo(=CC=CC₆F₅)(CO)₂Tp* (**5**) (18%) (Scheme 2). Complex **5** was characterised by the usual array of spectroscopic methods, with ES-MS containing [M + Na]⁺ at *m*/*z* 677. The IR spectrum of **5** displays two *v*(CC) bands at 2110 and 2061 cm⁻¹ and two terminal *v*(CO) bands at 2006 and 1926 cm⁻¹. In the ¹⁹F NMR spectrum the *ortho-* and *meta*-fluorines are found at δ_F –136.8 and –163.9, with



Scheme 1



Scheme 2

the *para*-fluorine giving a triplet $\delta_{\rm F}$ –153.7 [*J*(FF) = 20 Hz]. The broadening of each line within this triplet suggests that there is also an unresolved coupling between the *para*- and *ortho*-fluorine nuclei.

The Pd(0)/Cu(1)-catalysed reaction between $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$ and Au(C=CC₆F₅)(PPh₃) afforded dark red $Co_3(\mu_3-CC=CC_6F_5)(\mu-dppm)(CO)_7$ (6) (36%) (Scheme 2), characterised by IR [ν (CC) at 2122 cm⁻¹, terminal ν (CO) between 2062 and 1976 cm⁻¹] and multinuclear NMR [CH₂ at δ_H 3.49, 4.24, δ_C 29.60, one C(sp) at δ_C 72.17, Ph between δ_H 7.18–7.73, δ_C 128.73–132.43, dppm (δ_P 34.7) and C₆F₅ [δ_F –139.8, –158.4, –165.5 (o-, p-, m-F)] spectroscopies, and ES-MS, with [M + Na]⁺ and [M + H]⁺ at m/z 983 and 961, respectively, being observed. In the negative ion ES-MS, [M – H]⁻ at m/z 959 was observed. The structure of the complex was also established by a single crystal X-ray diffraction study.

The Cadiot–Chodkiewicz reaction, in which a terminal alkyne RC=CH and a haloalkyne XC=CR' are cross-coupled in the presence of a copper catalyst, is a well-known route to the preparation of differentially substituted 1,4-buta-1,3-diynes, RC=CC=CR'.²¹ The reaction between Au(C=CC₆F₅)(PPh₃) and iodoethynylferrocene, IC=CFc, gives 1-ferrocenyl-4-pentafluorophenylbuta-1,3-diyne, FcC=CC=CC₆F₅ (7), accompanied by some FcC=CC=CFc. The composition of the former compound was readily established from elemental analysis and the usual spectroscopic data. Thus in the IR spectrum a single *v*(CC) band was observed at 2220 cm⁻¹. In the ¹³C NMR spectrum, resonances at δ_C 62.10, 69.53, 86.86 and 99.55 are assigned to the carbon nuclei of the butadiyne fragment. In the ¹⁹F NMR two multiplets at δ_F –137.7 and –163.8 and a triplet at δ_F –153.9 are found for the *o*-, *m*- and *p*-fluorines, respectively. The ES-MS contains M⁺ at *m/z* 400.

Ruthenium complexes derived from 1,4-(Me₃SiC≡C)₂C₆F₄

The pentafluorophenyl ring systems in complexes such as 1-3 are inert toward substitution reactions with common nucleophiles,

and our attempts to synthesise bis-metalla-1,4-diethynyltetrafluorobenzenes by reacting monometallic (pentafluorophenyl)ethynyl complexes 1-3 with alkynyl anions have been so far unsuccessful. Hence 1,4-bis[(trimethylsilyl)ethynyl]tetrafluorobenzene^{16,22} was treated with RuCl(PP)Cp' [where PP = (PPh₃)₂, dppe; $Cp' = Cp, Cp^*$ in the presence of KF to give the diruthenium complexes 1.4-{Cp'(PP)Ru(C=C)}₂C₆F₄ [PP = (PPh₃)₂, Cp' = Cp (8), PP = dppe, Cp' = Cp (9), Cp^* (10)] in 60, 26 and 63% yields, respectively (Scheme 3). Elemental analyses and ES-MS confirmed the formulations of these complexes with M^+ found at m/z 1578 (for 8) and 1326 (9), with $[M + H]^+$ being obtained as the highest molecular weight ion in the MS of the most electron-rich example, 10. For each compound 8–10 the IR spectra contain two v(CC)bands, which were closely spaced, between 2072 and 2032 cm⁻¹. In the ¹H NMR spectra, the usual resonances for the Cp ligands are found at $\delta_{\rm H}$ 4.86 (8) and 4.71 (9), and for Cp* at δ 1.68 (10). The ¹³C NMR of 10 contains resonances at $\delta_{\rm C}$ 10.7 and 93.7 (Cp*). In the ³¹P NMR spectra, characteristic resonances at δ_P 51.7 (8), 86.7 (9) and 80.9 (10) were found. The ¹⁹F NMR spectra each contain only one resonance at $\delta_{\rm F}$ -147.0 (8), -147.8 (9) and -148.0 (10), as expected for a symmetrically disubstituted C₆F₄ group.

Ruthenium complexes derived from 1,4-(Me₃SiC=C)₂C₆H₄

For purposes of comparison with the fluorinated complexes here, it was desirable to examine the hydrocarbon analogues Ru(C=CPh)(PP)Cp' and $1,4-\{Cp'(PP)RuC=C\}_2C_6H_4$. All three monoruthenium complexes Ru(C=CPh)(PP)Cp' have been reported elsewhere.^{8,23,24} Of the diruthenium complexes only the very insoluble compound $1,4-\{Cp(PPh_3)_2RuC=C\}_2C_6H_4$ (11) has been prepared previously.²⁵ The more soluble systems $1,4-\{Cp(dppe)RuC=C\}_2C_6H_4$ (12) and $1,4-\{Cp^*(dppe)RuC=C\}_2C_6H_4$ (13) were readily prepared from reactions of $1,4-(Me_3SiC=C)_2C_6H_4$ and two molar equivalents of the appropriate chloride precursor RuCl(PP)Cp' in the presence of KF (Scheme 3). The characterisation of these compounds was straightforward, and details of





the elemental analytical and spectroscopic results are given in the Experimental section.

Molecular structures

The structures of 1, 2, 3, 6 and 10 have been determined by single-crystal X-ray diffraction studies^{\dagger} and molecules of these complexes are depicted in Fig. 1–5. Table 1 contains selected structural parameters for all but 6, for which selected data are given in the caption to the associated Figure, whilst Table 2 summarises

F(26) F(26) F(26) F(22) F(22) F(22) F(23) F(24)

Fig. 1 Projection of a single molecule of $\operatorname{Ru}(C \equiv CC_6F_5)(PPh_3)_2Cp(1)$. In this, and subsequent plots, hydrogen atoms have been omitted for clarity.



Fig. 2 Projection of a single molecule of $Ru(C \equiv CC_6F_5)(dppe)Cp(2)$.



Fig. 3 Projection of a single molecule of $Ru(C \equiv CC_6F_5)(dppe)Cp^*$ (3).

details of the data collection. The Ru(dppe)Cp' fragments have the expected near-octahedral geometry, with Ru-P bond distances of 2.238(2)-2.2694(8) Å and Ru-C(Cp) 2.215(7)-2.269(3) Å. Along the carbon chain of 2 C(1)–C(2) is 1.205(9) Å and C(2)–C(21) is 1.432(9) Å, while in 3 C(1)–C(2) is 1.217(5) Å and C(2)–C(21) is 1.442(5) Å. The Ru-C(1) distance in 2 is 1.982(7) Å, similar to that reported for Ru(C=CC=CSiMe₃)(dppe)Cp* [1.983(2) Å];²⁶ in 3 the Ru–C(1) distance is 2.000(3) Å. The carbon chain of 2 is significantly less distorted than that of 3, with angles at C(1,2) of 178.7(6) and 177.2(7)° (for 2) compared with values of 168.9(3) and 170.2(3)° for 3. In 10 the Ru(dppe)Cp fragment has the expected geometry, with Ru–P(1,2) 2.2542(7) and 2.2607(7) Å and Ru-C(Cp) 2.223(3)-2.264(3) Å; the C(1)-C(2), C(2)-C(3) separations are 1.221(3), 1.427(3) Å and the Ru-C(1) distance is 1.996(2) Å. The carbon chain is again somewhat distorted, with angles at C(1,2) of 172.6(2) and 172.2(3)°, respectively. Surprisingly, compound 10 appears to represent the first bimetallic ruthenium complex of general type $L_n RuC = CArC = CRuL_n$ to be structurally characterised.

Comparison of closely related complexes containing Ph and C_6F_5 groups shows that there are few significant structural



Fig. 4 Projection of molecule 1 of $Co_3(\mu_3-CC\equiv CC_6F_3)(\mu-dppm)(CO)_7$ (6). Selected structural data: Bond distances (Å) Co(1)-Co(2,3) 2.4781(5), 2.4810(4), Co(2)-Co(3) 2.4805(4), Co(n)-P(n) (n = 1,2) 2.2014(5), 2.2035(4), Co(1)-C(1) 1.900(1), Co(2)-C(1) 1.914(2), Co(3)-C(1) 1.947(1), C(1)-C(2) 1.403(2), C(2)-C(3) 1.213(2), C(3)-C(131) 1.428(2), C(13n)-C(13n + 1) (av.) 1.385(9), C(13n)-F(13n) (av.) 1.343(3) Å. Bond angles (°) Co(1)-C(1)-C(2) 136.3(1), Co(2)-C(1)-C(2) 131.4(1), Co(3)-C(1)-C(2) 127.2(1), C(1)-C(2)-C(3) 179.1(2), C(2)-C(3)-C(131) 175.8(2), C(3)-C(131)-C(132) 121.9(1), C(3)-C(131)-C(136) 121.8(1)°. Molecule 2 is similar, differing only in the aromatic ring orientations.

differences. Considering the three pairs: $Ru(C=CC_6X_5)(PP)Cp'$ [X = H, F; (PP)Cp' = (PPh₃)₂Cp and (dppe)Cp, (dppe)Cp*, the Ru–P distances are experimentally the same in each pair, although they may differ with ligand set.^{8,23,24} The Ru–C(1) distance is longer in the phenylethynyl derivatives than in the

Table 1Selected bond parameters for 1–3 and 10



Fig. 5 Projection of a molecule of $1,4-\{Cp^*(dppe)Ru(C=C)\}_2C_6F_4$ (10).

 C_6F_5 analogues [2.017(5), 2.009(3), 2.011(4) (X = H) *vs.* 1.991(6), 1.982(7), 2.000(3) Å (X = F)], while the C(2)–C(21) distances are also shorter in two of the C_6F_5 compounds, but longer in the Cp* complex [1.463(8), 1.444(5), 1.431(5) (X = H) *vs.* 1.421(9), 1.432(9), 1.442(5) Å (X = F)]. However, the differences are only marginally significant. Within the C_6X_5 ring, average C–C separations are 1.395(8), 1.396(5), 1.373(9) (X = H) *vs.* 1.380(6), 1.373(10), 1.383(11) Å (X = F).

In **6** (Fig. 4), the carbon chains of the two independent molecules are essentially linear [C(2)–C(3)–C(131) 175.8(2), 173.5(2)°] with C(1)–C(2) [1.403(2), 1.404(2) Å] consistent with a carbon–carbon single bond and C(2)–C(3) [1.213(2), 1.208(2) Å] with C(1)–C(2) triple bond. The Co₃(μ -dppm)(CO)₇ clusters are similar to those found in many related examples,^{15,27-30} with Co–Co 2.4763(4)–2.4938(4), Co–P 2.2014(5)–2.2108(4) and Co–C(1) 1.893(2)–1.914(2) and 1.940(1), 1.947(1) Å, the latter involving Co(3), which is not attached to the dppm ligand.

Electrochemistry

Extensive studies of the redox properties of arylalkynyl complexes containing M(PP)Cp' [M = Fe, Ru; PP = (PPh₃)₂, dppe; Cp' = Cp, Cp* (not all combinations)] fragments have been made, with complementary spectroscopic and computational work used to analyse the physical and electronic structure of the redox-related species.⁷⁻⁹ In the case of arylalkynyl compounds of the Group 8 metals, the extensive mixing of the metal and alkynyl frontier orbitals leads to a significant degree of carbon ligand character in

Complex	1	2	3	10
Bond distances/Å				
Ru-P(1)	2.295(2)	2.238(2)	2.2694(8)	2.2542(7)
Ru-P(2)	2.282(2)	2.260(2)	2.2592(8)	2.2607(7)
Ru–C(Cp)	2.232(5) - 2.261(6)	2.215(7)-2.250(8)	2.224(3)-2.269(3)	2.223(3) - 2.264(3)
(Av.)	2.244(11)	2.234(14)	2.25(2)	2.250(16)
Ru-C(1)	1.991(6)	1.982(7)	2.000(3)	1.996(2)
C(1) - C(2)	1.225(9)	1.205(9)	1.217(5)	1.221(3)
C(2) - C(21)	1.421(9)	1.432(9)	1.442(5)	1.427(3)
C(2n) - F(2n)	1.329(8)-1.362(12)	1.329(9)-1.353(10)	1.338(5)-1.352(5)	1.342(3), 1.356(3)
(Av.)	1.344(14)	1.340(10)	1.344(6)	1.349(10)
Bond angles/°				
P(1)-Ru-P(2)	100.31(5)	83.48(6)	82.44(3)	82.62(3)
P(1)-Ru-C(1)	92.3(2)	87.2(2)	89.12(9)	86.38(7)
P(2)-Ru-C(1)	87.4(2)	81.6(2)	87.62(9)	85.45(7)
Ru - C(1) - C(2)	173.0(5)	178.7(6)	168.9(3)	172.6(2)
C(1) - C(2) - C(21)	169.2(6)	177.2(7)	170.2(3)	172.2(3)

Complex	1	2	3	6	10
Formula	$C_{49}H_{35}F_5P_2Ru\cdot 0.5C_6H_6$	$C_{39}H_{29}F_5P_2Ru$	$C_{44}H_{39}F_5P_2Ru$	$C_{41}H_{22}Co_3F_5O_7P_2$	$C_{82}H_{78}F_4P_4Ru_2$
MW	920.88	755.67	825.8	960.32	1465.55
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$	$P2_1/c$	$P\overline{1}$	$P2_1/n$
a/Å	10.1626(7)	8.988(1)	8.605(1)	11.617(1)	10.982(1)
b/Å	24.5128(2)	15.065(2)	25.438(3)	17.643(2)	18.486(2)
c/Å	17.0993(8)	23.420(3)	17.212(2)	19.108(3)	17.193(2)
$\alpha/^{\circ}$	_	_	_	97.855(9)	_
$\beta/^{\circ}$	96.323(5)	_	100.864(2)	91.445(11)	93.839(2)
$\gamma/^{\circ}$		_	_	93.438(7)	_
$V/Å^3$	4233.8(4)	3171.2(7)	3700.1(7)	3870.4(8)	3482.6(6)
Ζ	4	4	4	4	2
$\rho_{\rm c}/{\rm g~cm^{-3}}$	1.445	1.583	1.482	1.64_8	1.398
$2\theta_{\rm max}/^{\circ}$	58	58	58	68	62
μ (Mo- $K\alpha$)/mm ⁻¹	0.50	0.65	0.57	1.43	0.58
$T_{\rm min/max}$	0.92	0.91	0.91	0.92	0.92
Crystal dimensions/mm	$0.26 \times 0.21 \times 0.05$	$0.23 \times 0.15 \times 0.09$	$0.36 \times 0.13 \times 0.07$	$0.38 \times 0.28 \times 0.24$	$0.48 \times 0.32 \times 0.12$
$N_{ m tot}$	92469	30061	33123	76417	38966
$N(R_{\rm int})$	11272 (0.067)	4570 (0.048)	9336 (0.043)	29976 (0.024)	11272 (0.033)
No	11272	4127	7506	20530	8907
R	0.068	0.048	0.044	0.032 (<i>R</i> 1)	0.036
R _w	0.085	0.067	0.080	0.083 (wR2)	0.077
T/K	100	170	170	100	150

Table 2 Crystal data and refinement details[†]

the HOMOs of the resulting radical cations.^{8,9} Table 3 collects electrochemical data for the ruthenium σ -alkynyl complexes 2–3, 8–13 and the monoruthenium complexes Ru(C=CPh)(PP)Cp' described above, referenced against the ferrocene/ferrocenium couple. Given the contribution from the aryl ring to the redox-active orbital in these systems, it is unsurprising that perfluorination of the arylalkynyl ligand leads to less thermodynamically favourable oxidation (e.g., 2 +0.10 V, 3 -0.04 V) than found in the hydrocarbon analogues such as Ru(C≡CPh)(dppe)Cp (-0.08 V) and Ru(C≡CPh)(dppe)Cp* (-0.26 V).9,31,32 The fluorinated bimetallic complexes 8-10 and the hydrocarbon analogues 11-13 each undergo two reversible oxidation events, E_1 and E_2 with $\Delta E_p =$ $|E_2 - E_1|$ ca. 200–300 mV. The larger ΔE_p values are generally associated with the complexes featuring perfluorinated bridges, and indicate the greater stability of the mono-oxidised species with respect to disproportionation. This is likely a consequence of the higher thermodynamic barrier to the second oxidation brought

Table 3 Electrochemical data from 2-3, 8-13 and related systems^a

Compound	E_1	E_2	$\Delta E_{ m p}$
2	0.10		
3	-0.04		
$Ru(C \equiv CPh)(PPh_3)_2 Cp^b$	0.11	_	
Ru(C≡CPh)(dppe)Cp	-0.08	_	
Ru(C≡CPh)(dppe)Cp*	-0.26	_	
8	-0.09	0.21	0.30
9	-0.17	0.11	0.28
10	-0.35	-0.03	0.32
11	-0.30	-0.01	0.29
12	-0.32	-0.09	0.23
13	-0.50	-0.22	0.28

^{*a*} CH₂Cl₂/0.1 M [NBu₄]BF₄, Pt microdisk working, Pt wire counter, Pt wire pseudoreference electrodes, potentials in Volts *vs.* FeCp₂/[FeCp₂]⁺, *via* reference to FeCp₂, FeCp*₂ or CoCp₂⁺ internal standards. ^{*b*} Data from ref. 9.

about by the electron-withdrawing fluoro substituents. The first oxidation potentials follow the same trends as observed for the monometallic complexes, with oxidation of the fluorinated species being less thermodynamically favourable when compared with the hydrocarbon analogues.

Electronic structure calculations

In order to more fully probe the influence of perfluorination on the electronic structure of compounds such as $Ru(C \equiv CC_6X_3)(PP)Cp'$ and 1,4-{ $Cp'(PP)RuC \equiv C$ }₂C₆X₄ (X = H, F), a series of density functional theory (DFT) calculations (B3LYP/3–21G*) were carried out on the model systems $Ru(C \equiv CC_6F_3)(PH_3)_2Cp$ (1-F), $Ru(C \equiv CPh)(PH_3)_2Cp$ (1-H),⁹ 1,4-{ $Cp(PH_3)_2RuC \equiv C$ }₂C₆F₄ (8-F) and 1,4-{ $Cp(PH_3)_2RuC \equiv C$ }₂C₆H₄ (11-H). Results from the structural optimisations are summarised in Table 4, with relevant data from single crystal X-ray diffraction experiments of suitable compounds for comparison. Details of the orbital energies and compositions are summarised in Tables 5 and 6, and important orbitals are illustrated in Fig. 6–9. Whilst the basis set employed is relatively small, it has proven to be entirely satisfactory against other, larger, basis sets for $Ru(C \equiv CC_6X_3)(PP)Cp'$ type compounds.⁹

The electronic structures of pseudo-octahedral d⁶ metal alkynyl complexes such as **1-H** have been studied on previous occasions at various levels of theory,⁷⁻⁹ and only pertinent details are summarised here for completeness. The highest occupied molecular orbitals of the monometallic systems **1-H** and **1-F** essentially comprise the antibonding combinations of the orthogonal acetylene π -system with metal d-orbitals of appropriate symmetry (Fig. 6 and 7). The acetylide phenyl substituent is oriented either orthogonally (**1-H**) or co-planar (**1-F**) with a plane bisecting the P–Ru–P angle. However, the barrier to rotation around the C(2)–C(21) bond is small (estimated at 0.3 and 0.4 kcal mol⁻¹ for **1-H** and **1-F**, respectively, at B3LYP/3–21G*) and the preferential orientation

	1-H	$Ru(C=CPh)(PPh_3)_2Cp^a$	1-F	1	8-F	8	11-H
Ru-C(1)	2.018	2.016(3)	2.001	1.991(6)	2.005	1.996(2)	2.018
Ru–P	2.278	2.285(1), 2.303(1)	2.284	2.295(2), 2.282(2)	2.282	2.2542(7), 2.2607(7)	2.277
C(1) - C(2)	1.228	1.215(4)	1.226	1.225(9)	1.226	1.221(3)	1.228
C(2) - C(21)	1.426	1.456(4)	1.406	1.421(9)	1.407	1.427(3)	1.423
θ^{b}		_ ()	_	_	180.0	180	158.9

Table 4 Optimised structural data from 1-H, 1-F, 8-F and 11-H, with crystallographic data from related systems

^{*a*} Ref. 23*a* ^{*b*} $\theta = P(1)-Ru(1)\cdots Ru'-P(1)'$.

Table 5The energy (E/eV) and composition of selected frontier molecular orbitals in 1-F and 1-H

1-F	MO		Ε	Ср	\mathbf{PH}_{3}	Ru	C_{α}	C_{β}	C_6F_5
	109	L + 4	-0.02	0	0	0	0	0	100
	108	L + 3	-0.19	3	21	76	0	0	0
	107	L + 2	-0.43	17	14	59	8	1	1
	106	L + 1	-0.66	2	2	4	15	1	76
	105	LUMO	-1.05	24	27	49	0	0	0
	104	HOMO	-5.18	7	3	34	10	23	23
	103	H – 1	-5.68	8	5	60	6	19	1
	102	H – 2	-6.20	22	11	43	10	14	1
1-H	МО		Ε	Ср	PH_3	Ru	C_{α}	C_{β}	C ₆ H
	89	L + 4	0.57	0	2	6	0	0	92
	88	L + 3	0.09	2	12	27	10	1	48
	87	L + 2	-0.03	3	11	54	6	2	26
	86	L + 1	-0.15	16	13	62	8	0	0
	85	LUMO	-0.78	24	27	50	0	0	0
	84	HOMO	-4.91	2	1	30	16	22	29
	83	H = 1	-5.09	8	4	46	10	28	4
	05	11 1	5.07	0	-	40	10	20	

seems to depend more upon the level of theory employed or the starting point for the geometry optimisation than any significant electronic factor. In either case, the repulsive interactions between the filled M–C=C and phenyl fragment orbitals destabilise the more delocalised orbital, and therefore it is this that comprises the HOMO. The contribution from the arylalkynyl fragment to the HOMO is not negligible (*ca.* 56–67%),⁹ with fluorination of the



Fig. 6 Frontier orbitals of 1-H. Contour values are plotted at ± 0.04 (e bohr⁻³)^{1/2}.

ligand resulting in only a small decrease in the ligand character. Thus, for either system descriptions of the redox chemistry in terms of metal-localised behaviour is likely an oversimplification. In contrast to the delocalised nature of the HOMO, in both **1-H** and **1-F** the LUMO is centred on the metal fragment, without any significant contribution from the arylalkynyl moiety (Fig. 6 and 7). The aryl/alkynyl π^* systems lie above these empty metal orbitals, and, as would be expected, the π^* -system of the fluorinated ring is somewhat lower in energy than that of the analogous orbital from the aromatic hydrocarbon (Table 6).

Table 6 The energy (*E*/eV) and composition of selected frontier molecular orbitals in 8-F and 11-H

8-F	МО		Ε	Cp(1)	PH ₃ (1)	Ru(1)	C _α (1)	C _β (1)	C_6F_4	C _β (2)	C _α (2)	Ru(2)	PH ₃ (2)	Cp(2)
	168	L + 4	-0.16	9	7	30	4	0	0	0	4	29	7	9
	167	L + 3	-0.17	8	7	29	4	1	1	1	4	30	7	9
	166	L + 2	-0.48	1	1	3	12	1	63	1	12	3	1	1
	165	L + 1	-0.79	24	27	49	0	0	0	0	0	0	0	0
	164	LUMO	-0.79	0	0	0	0	0	0	0	0	49	27	24
	163	HOMO	-4.49	3	1	14	9	11	25	11	9	14	1	3
	162	H-1	-5.33	5	2	24	2	12	10	12	2	24	2	5
	161	H-2	-5.37	3	2	30	4	11	2	10	4	28	2	3
11 - H	МО		Ε	Cp(1)	PH ₃ (1)	Ru(1)	C _α (1)	$C_{\beta}(1)$	$\mathrm{C}_{6}\mathrm{H}_{4}$	$C_{\beta}(2)$	$C_{\alpha}(2)$	Ru(2)	PH ₃ (2)	Cp(2)
	152	L + 4	-0.02	1	2	4	11	2	59	2	11	4	2	1
	151	L + 3	-0.03	9	7	36	4	0	0	0	4	28	6	7
	150	L + 2	-0.04	7	5	28	3	0	0	0	4	36	7	9
	149	L + 1	-0.66	0	0	0	0	0	0	0	0	50	27	24
	148	LUMO	-0.67	24	27	50	0	0	0	0	0	0	0	0
	147	HOMO	-4.17	2	1	12	11	9	30	9	11	12	1	2
	146	H-1	-5.11	5	2	23	3	13	8	13	3	23	2	5
	145	H-2	-5.14	2	2	30	6	14	2	11	5	23	1	2



Fig. 7 Frontier orbitals of 1-F. Contour values are plotted at ± 0.04 (e bohr⁻³)^{1/2}.



Fig. 8 Frontier orbitals of 8-F. Contour values are plotted at ± 0.04 (e bohr^-3)^{1/2}.



Fig. 9 Frontier orbitals of 11-H. Contour values are plotted at ± 0.04 (e bohr⁻³)^{1/2}.

In general, perfluorination has little effect on the gross description of the electronic structure of the arylalkynyl complexes of ruthenium described here, save to stabilise the orbital manifold to some extent. A small elongation of the calculated Ru–P bond lengths is not reproduced within the level of precision of the structure determinations of Ru(C=CPh)(PPh₃)₂Cp²³ and **1**. However, the contraction of the Ru–C(1) bond length observed upon comparison of the optimised geometries of **1-H** and **1-F** is reflected at the limit of precision in the experimentally determined structures, and likely arises from the greater electrostatic attraction of the Ru and C(1) centres in the case of the fluorinated compound. The calculated electronic structures of the bimetallic systems **11-H** and **8-F**, which are similar to each other, merit consideration and discussion. Geometry optimisations for **11-H** and **8-F** show minima (type **A**) with the phenyl ring of the bridging ligand orthogonal to the plane bisecting the P–Ru–P angles and minima (type **B**) with the phenyl ring of the bridging ligand co-planar with the plane bisecting the P–Ru–P angle. Both minima **A** and **B** have the same energies at B3LYP/3–21G* for **11-H** and **8-F**. Similar behaviour for related systems has been noted elsewhere.³³ Here we focus on type **A** minima in detail for **11-H** and **8-F**, although similar conclusions for structure type **B** may also be made.

The HOMOs of 11-H and 8-F are, in each case, of comparable composition to those of the mononuclear models (Fig. 8 and 9), being delocalised over the metal centres, alkynyl fragment and aromatic ring system. Interestingly, the HOMO in 11-H and 8-F is 65-70% diethynyl aromatic ligand in character, and consequently the compounds are best described in terms of an organic diethynylarylene featuring strong π -donating substituents [the Ru(PP)Cp' fragments]. In each case, the HOMO is wellseparated in energy from the other occupied orbitals, in agreement with the electrochemical observation of two anodic events. The HOMO-1 can be described in terms of the various other inand out-of-phase combinations of the metal (d) and acetylide (π) orbitals, and being lower in energy in the case of the fluorinated derivative (Fig. 8 and 9, Table 6). Within the unoccupied orbital manifold the diethynylbenzene π^* system is interleaved within the unoccupied metal d orbitals, with the fluorinated system naturally lying lower in energy than the hydrocarbon analogue (Table 6). Interestingly, although Koopmans' theorem has no direct correlation with DFT-based methods of electronic structure calculation, the HOMO in 11-H is higher in energy than the HOMO in 8-F. This energy order maps with the differences in redox properties of 11 and 8, and supports the fairly intuitive observation than the introduction of the perfluoroaryl group leads to less thermodynamically favourable oxidation processes (vide supra).

UV-Vis-NIR spectroelectrochemistry

To provide an experimental check of the key conclusions drawn from the computational work (i.e. that the electronic structures of the bimetallic ruthenium complexes $1,4-\{Cp'(PP)RuC=C\}_2C_6X_4$ (X = H, F) are largely insensitive to fluorination of the alkynylaryl ring system, and that the HOMOs contain a very large amount of alkynylaryl character), UV-Vis-NIR spectroelectrochemical studies were conducted on complexes 10 and 13 (Fig. 10), chosen as samples representative of the series 8-13. The spectra of the neutral complexes 10 and 13 are similar, each being dominated by an intense band at 27100 (13) or 24900 (10) cm⁻¹. The red-shift of this band on fluorination of the phenylene ring is consistent with the assignment of the band to an MLCT transition, or perhaps more accurately to a bridge-based π - π * transition, albeit with the π -orbitals of the bridge admixed with some metal character (ML-LCT). In each case, this characteristic band collapses upon one-electron oxidation and is replaced by structured bands or composite band envelopes in the region 20000-17000 cm⁻¹ and 8000-5000 cm⁻¹.

Both $[10]^+$ and $[13]^+$ feature structured bands in the visible region that are similar to those observed in related radical



Fig. 10 The UV-Vis-NIR spectra of $[10]^{n+}$ (top) and $[13]^{n+}$ (bottom) (CH₂Cl₂/0.1M NBu₄BF₄).

complexes³⁴ and compounds³⁵ in which the phenylene ring systems are intimately involved in supporting the unpaired electron. When this experimental observation is considered alongside the DFT results, it is reasonable to describe oxidation of the ruthenium complexes 1,4-{Cp'(PP)RuC=C}₂C₆X₄ in terms of depopulation of the HOMO to give a SOMO of comparable character to those depicted in Fig. 8 and 9. The band envelope in the NIR region is similar in each of [10]⁺ and [13]⁺, and can be deconvoluted into the sum of two Gaussian-shaped components (Fig. 11), which contrasts with more complex deconvolutions associated with the NIR spectrum of the strongly coupled mixed valence complex 1,4-[{Cp*(dppe)FeC=C}₂C₆H₄]⁺ due to the pronounced "cut-off" on the high energy side, and potential complications arising from multiple IVCT transitions.³⁶ The almost identical band-shapes of



Fig. 11 The NIR region of $[10]^+$ (top) and $[13]^+$ (bottom) showing the deconvolution of the absorption envelope into a sum of two Gaussian shaped components ([10]⁺ : $\bar{\nu}_{max} = 5352 \text{ cm}^{-1}$, $\Delta \bar{\nu}_{\frac{1}{2}} = 1114 \text{ cm}^{-1}$, $\varepsilon = 6875 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; $\bar{\nu}_{max} = 6584 \text{ cm}^{-1}$, $\Delta \bar{\nu}_{\frac{1}{2}} = 2834 \text{ cm}^{-1}$, $\varepsilon = 6432 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; $\bar{\nu}_{max} = 5630 \text{ cm}^{-1}$, $\Delta \bar{\nu}_{\frac{1}{2}} = 1102 \text{ cm}^{-1}$, $\varepsilon = 12410 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; $\bar{\nu}_{max} = 6874 \text{ cm}^{-1}$, $\Delta \bar{\nu}_{\frac{1}{2}} = 2700 \text{ cm}^{-1}$, $\varepsilon = 16553 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

the components in the NIR band envelopes of $[10]^+$ and $[13]^+$ provides yet more evidence for the electronic similarity of these compounds. The absorption profile is red-shifted in the case of the fluorinated ring system, consistent with transfer of electron density to the phenylene-based orbitals in the transitions responsible for these bands, providing further evidence for the involvement of the phenylene ring in the redox active orbital. The deconvoluted NIR bands are also considerably narrower than predicted from the Hush model for weakly-coupled mixed-valence compounds,³⁷ and too intense to be simple dd bands associated with a d⁵ metal centre. Therefore, the lower energy component is assigned to the [HOMO–1] to SOMO transition, which has metal-ethynyl (d- π) to aryl (π) character. The higher energy component can be attributed to a transition from a lower-lying, more metal based orbital (or orbitals) to the SOMO (*i.e.* an M-MLCT transition).

Although an electrogenerated sample of the dication $[10]^{2+}$ decomposed before a reliable spectrum could be obtained, the UV-Vis-NIR spectrum of the dication $[13]^{2+}$ was satisfactorily obtained by controlled potential electrolysis in a spectroelectrochemical cell, as evidenced by the sequential re-reduction through $[13]^+$ to [13]. The spectrum of $[13]^{2+}$ (Fig. 10) is similar in profile to that of [Ru(C=CC₆H₄Me-4)(dppe)Cp*]⁺, and by analogy the major visible band in $[13]^{2+}$ can be assigned to a metal-to-metal/ligand (M-MLCT) transition.⁹ A weaker band is also present in the NIR region of $[13]^{2+}$, which is similar to that observed for the analogous mononuclear system $[3]^+$ and may therefore be assigned to a similar transition between approximately orthogonal orbitals with significant metal d/ethynyl π character.⁹

Taken as a whole, these UV-Vis-NIR spectroscopic data support the conclusions drawn from the DFT work, and indicate that the frontier/redox active orbitals in $1,4-\{Cp'(PP)RuC=C\}_2C_6X_4$ systems are heavily centred on the bridging ligand. It is therefore not appropriate to discuss the properties of these compounds in terms of mixed-valence models, but rather they should be regarded as further examples of bimetallic compounds featuring redox "non-innocent" bridging ligands.³⁸

Conclusions

This work has demonstrated the efficient syntheses of several complexes featuring mono- and di-ethynyl derivatives of perfluoroinated phenyl and phenylene ring systems, by treating the readily available SiMe₃-protected alkyne with equivalent amounts of the metal-halide precursor either in a fluoride- or NaOMe-initiated desilylation/metallation reaction sequence. Whilst nucleophilic substitution reactions are common in the chemistry of perfluoroaromatics, the introduction of a strong inductive electrondonating metal alkynyl fragment effectively turns off this reaction pathway. Gold-modified Sonogashira and Cadiot-Chodkiewicz coupling protocols are also effective as chain extension reactions involving perfluorophenyl rings. In the case of the monometallic (1-3) and bimetallic (8-13) ruthenium alkynyl complexes, perfluorination of the alkynyl-based ligand does not greatly affect the overall electronic structure of the compounds. Rather, perfluorination leads to a small stabilisation of the orbital manifold, and consequently less thermodynamically favourable oxidation. Interestingly, calculations reveal a significant (ca. 60–70%) contribution from the ethynyl aromatic moiety to the HOMOs in the ruthenium systems. This prediction is supported by UV-Vis-NIR spectroscopy, and raises questions about the nature of the oxidation events (metal- *vs.* ligand- centred) and "mixed valence" character of many similar ruthenium/alkynyl based systems. Further experiments directed at probing this point are in progress and will be reported elsewhere.

Experimental

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 nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates ($20 \times 20 \text{ cm}^2$) coated with silica gel (Merck, 0.5 mm thick).

Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer from samples mounted between NaCl windows. NMR spectra were recorded on a Varian 2000 instrument (1H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.503, ¹⁹F at 282.39 MHz). Unless otherwise stated, samples were dissolved in CDCl3 or C6D6 contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal SiMe₄ for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. ¹⁹F NMR spectra were referenced to CFCl₃, with internal C₆F₆ (δ_F –164.9) as the standard. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Fisons VG Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. NaOMe was used as an aid to ionisation when required.³⁹ Peaks listed are the highest intensity ions in the isotopic envelopes. Electrochemical samples (1 mM) were dissolved in CH₂Cl₂ containing 0.1 M [NBu₄]BF₄ as the supporting electrolyte. Cyclic voltammograms were recorded using a PAR Model 263 potentiostat and a cell with all Pt electrodes, and reported against ferrocene (FeCp₂/[FeCp₂]⁺ = +0.00 V). Under these conditions, the decamethylferrocene/decamethylferrocenium couple is -0.53 V, and cobaltocene/cobaltocenium -1.34 V. Elemental analyses were by CMAS, Belmont, Vic., Australia. Details of the spectroelectrochemical cell and conditions have been published elsewhere.9

Reagents

The compounds RuCl(dppe)Cp^{*},^{10d} Me₃SiC≡CC₆F₅,¹⁶ 1,4-(Me₃-SiC≡C)₂C₆F₄,^{16a,22} Pt₂(µ-dppm)₂Cl₂,¹⁹ Ru(C≡CC₆F₅)(PPh₃)₂Cp,⁵ 1,4-{Cp(PPh₃)₂Ru(C≡C)}₂C₆H₄ (11),⁴⁰ RuCl(dppe)Cp,⁴¹ RuCl-(PPh₃)₂Cp,⁴² Mo(≡CBr)(CO)₂Tp^{*},⁴³ Pd(PPh₃)₄,⁴⁴ Co₃(µ₃-CBr)(µ-dppm)(CO)₇,^{30a} IC≡CFc,⁴⁵ Au(C≡CC₆F₅)(PPh₃)⁴⁶ and Ru(C≡CPh)(dppe)Cp' (Cp' = Cp, Cp^{*})³¹ were all prepared as described previously.

$Ru(C \equiv CC_6F_5)(PPh_3)_2Cp(1)$

A sample of this complex was obtained as previously described,⁵ and recrystallised from dichloromethane/hexanes for the crystal-lographic study.

(a) Ru(C=CC₆F₅)(dppe)Cp (2). A mixture of Me₃SiC=CC₆F₅ (300 mg, 1.13 mmol), RuCl(dppe)Cp (456 mg, 0.76 mmol) and KF (44 mg, 0.15 mmol) in MeOH (20 ml) was heated under reflux for 5 h. The resulting yellow precipitate was collected and washed with MeOH followed by hexane to give Ru(C=CC₆F₅)(dppe)Cp (2) (575 mg, 63%). Anal. Calcd (C₃₉H₂₉F₅P₂Ru): C, 61.99; H, 3.87; *M*, 755. Found: C, 61.93; H, 3.83. IR (Nujol, cm⁻¹): v(CC) 2097 m, 2070 w. ¹H NMR (C₆D₆): δ 2.16, 2.71 (2 m, 2 × 2H, CH₂CH₂), 4.73 (s, 5H, Cp), 6.95–7.99 (m, 24H, Ph). ¹³C NMR: δ 27.8 [t, *J*(CP) 23 Hz, CH₂CH₂], 83.0 (s, Cp), 126.1–142.5 (m, Ph). ¹⁹F NMR: δ –145.6 (m, 2F, *o*-F), –168.3 [t, *J*(FF) = 21 Hz, 1F, *p*-F], –168.8 (m, 2F, *m*-F). ³¹P NMR: δ 87.0 (s, dppe). ES-MS (MeOH + NaOMe, *m*/*z*): 779, [M + Na]⁺; 756, [M + H]⁺; 738, [M – F]⁺; 593, [Ru(CO)(dppe)Cp]⁺; 565, [Ru(dppe)Cp]⁺.

(b) Ru(C=CC₆F₅)(dppe)Cp* (3). In a procedure similar to that used for 2, Me₃SiC=CC₆F₅ (200 mg, 0.76 mmol), RuCl(dppe)Cp* (508 mg, 0.76 mmol) and KF (44 mg, 0.76 mmol) and MeOH (20 ml) gave a pale green precipitate of Ru(C=CC₆F₃)(dppe)Cp* (3) (339 mg, 54%). Anal. Calcd (C₄₄H₃₉F₅P₂Ru): C, 64.00; H, 4.76; *M*, 826. Found: C, 63.98; H, 4.80. IR (Nujol, cm⁻¹): v(CC) 2078 m, 2033 s. ¹H NMR (C₆D₆): δ 1.66 (s, 15H, Cp*), 2.01, 2.81 (2 m, 2 × 2H, CH₂CH₂), 7.02–7.87 (m, 20H, Ph). ¹³C NMR: δ 10.6 (s, C₅*Me*₅), 29.9 [t, *J*(CP) = 23 Hz, CH₂CH₂], 92.7 (s, C=C), 93.84 (s, C₅Me₅), 127.1–144.7 (m, Ph). ¹⁹F NMR: δ –169.1 [t, *J*(FF) = 21 Hz, 1F, *p*-F], –168.9 (m, 2F, *p*-F), –145.8 (m, 2F, *o*-F). ³¹P NMR: δ 81.7 (s, dppe). ES-MS (MeOH + NaOMe, *m/z*): 848, [M + Na]⁺; 827, [M + H]⁺; 808, [M – F]⁺; 662, [Ru(CO)(dppe)Cp*]⁺; 635, [Ru(dppe)Cp*]⁺.

(c) $Pt_2(\mu-dppm)_2(C \equiv CC_6F_5)_2$ (4). To a stirred suspension of $Pt_2(\mu-dppm)_2Cl_2$ (100 mg, 0.08 mmol) in NaOMe [from Na (50 mg) in MeOH (10 ml)] was added an excess of Me₃SiC \equiv CC₆F₅ (50 mg). This mixture was stirred at r.t. for 6 h before the resulting precipitate was collected and washed with MeOH followed by hexane to give $Pt_2(\mu-dppm)_2(C \equiv CC_6F_5)_2$ (6) (33 mg, 26%). Anal. Calcd (C₆₆H₄₄F₁₀P₄Pt₂): C, 51.44; H, 2.88; *M*, 1540. Found: C, 51.39; H, 2.80. IR (Nujol, cm⁻¹): *v*(CC) 2079 m. ¹H NMR (C₆D₆): δ 4.62 (m, 4H, 2 × CH₂), 6.96–7.90 (m, 40H, Ph). ¹⁹F NMR: δ –168.2 (m, 2F, *m*-F), –165.7 [t, *J*(FF) = 21 Hz, 1F, *p*-F], –143.1 (m, 2F, *o*-F). ³¹P NMR: δ 2.1 [s, dppm, *J*(PtP) = 2816 Hz]. ES-MS (MeOH, *m/z*): 1541, [M + H]⁺.

Derivatives of Au(C≡CC₆F₅)(PPh₃)

(a) $Mo(=CC=CC_6F_5)(CO)_2Tp^*$ (5)

A mixture of Au(C=CC₆F₅)(PPh₃) (60 mg, 0.09 mmol), Mo(=CBr)(CO)₂Tp* (50 mg, 0.09 mmol), Pd(PPh₃)₄ (15 mg, 0.01 mmol) and CuI (5 mg, 0.02 mmol) in thf (10 ml) was stirred at r.t. for 2 h. The solvent was then removed and the residue purified by preparative t.l.c. using acetone–hexane (3 : 7, v/v) as eluent. The major fraction was collected as a green band which contained Mo(=CC=CC₆F₅)(CO)₂Tp* (5) (11 mg, 18%). IR (Nujol, cm⁻¹): v(CC) 2110 w, 2061 w, v(CO) 2006 s, 1926 s. ¹H NMR (CDCl₃): δ 2.33(s, 6H, pz-Me), 2.38 (s, 6H, pz-Me), 2.56 (s, 6H, pz-Me), 5.73 (s, 1H, H⁴), 5.89 (s, 2H, H⁴). ¹³C NMR: δ 12.8, 14.8, 15.9 (3 × s, pz-CMe), 94.1, 108.9 (2 s, C=C), 106.7/107.5, 144.9/145.6, 151.55/151.60 (6 × s, pz-ring C), 227.4 (s, CO), 248.8 (s, Mo=C). ¹⁹F NMR: δ –136.8 (m, 2F, *o*-F), –153.7 [t, *J*(FF) = 21 Hz, 1F, *p*-F], –163.9 (m, 2F, *m*-F). ES-MS (MeOH + NaOMe, *m*/*z*): 677, [M + Na]⁺; 487, [MC₆F₅]⁺.

(b) $Co_3(\mu_3-CC=CC_6F_5)(\mu-dppm)(CO)_7$ (6). A mixture of Au(C=CC₆F₅)(PPh₃) (60 mg, 0.09 mmol), $Co_3(\mu_3-CBr)(\mu$ dppm)(CO)₇ (30 mg, 0.09 mmol), Pd(PPh₃)₄ (15 mg, 0.01 mmol) and CuI (5 mg, 0.02 mmol) in thf (10 ml) was stirred at r.t. for 2 h. Solvent was removed and the residue was purified by preparative t.l.c. (acetone-hexane, 3 : 7, v/v). The major fraction was collected as a brown-green band ($R_{\rm f} = 0.52$) to give $Co_3(\mu_3 - CC \equiv CC_6F_5)(\mu - dppm)(CO)_7$ (6) (10 mg, 36%) as dark red crystals (CH₂Cl₂/pentane). Anal. Found: C, 51.30; H, 2.25. Calcd $(C_{41}H_{22}Co_3F_5O_7P_2)$: C, 51.28; H, 2.31; M, 960. IR (Nujol, cm⁻¹): *v*(CC) 2122 w, *v*(CO) 2062 s, 2015 s, 1976 (sh). ¹H NMR (CDCl₃): δ 3.49, 4.24 (2 m, 2 × 1H, CH₂), 7.18–7.73 (m, 20H, Ph). ¹³C NMR: δ 29.6 (s, CH₂), 72.2 (s, C=C), 128.7–132.4 (m, Ph + C₆F₅). ¹⁹F NMR: δ –139.8 (m, 2F, *o*-F), –158.4 [t, *J*(FF) = 21 Hz, 1F, *p*-F], -165.5 (m, 2F, *m*-F). ³¹P NMR: δ 34.7 (s, br, dppm). ES-MS (MeOH + NaOMe, m/z): 982, $[M + Na]^+$; 960, M^+ .

(c) $FcC \equiv CC_6F_5$ (7). A mixture of $Au(C \equiv CC_6F_5)(PPh_3)$ (60 mg, 0.09 mmol), IC=CFc (30 mg, 0.09 mmol), Pd(PPh₃)₄ (15 mg, 0.01 mmol) and CuI (5 mg, 0.02 mmol) in thf (10 ml) was stirred at r.t. for 2 h. The solvent was then removed and the residue purified by preparative t.l.c. using acetone-hexane (3:7, v/v) as eluent. The major fraction was collected as a bright orange band containing FcC=CC=CC₆F₅ (7) (19 mg, 50%). Anal. Calcd (C₂₀H₉F₅Fe): C, 60.04; H, 2.27; *M*, 400. Found: C, 59.96; H, 2.15. IR (Nujol, cm⁻¹): v(CC) 2220 m. ¹H NMR (C₆D₆): δ 4.29, 4.58 (2 × m, 9H, Cp + C₅H₄). ¹³C NMR: δ 62.1, 69.5, 86.9, 99.6 (4 s, C≡C), 70.4, 70.8, 72.9 (3 s, C₅H₄), 132.3–137.5 (m, Ph). ¹⁹F NMR: δ –137.7 (m, 2F, *o*-F), –153.9 [t, *J*(FF) = 21 Hz, 1F, *p*-F], -163.8 (m, 2F, m-F). ES-MS (MeOH, m/z): 400, M⁺. A minor band containing FcC=CC=CFc (7 mg, 20%) was also obtained and identified by comparison with an authentic sample and from the ES-MS (m/z 418).

Derivatives of 1,4-(Me₃SiC≡C)₂C₆F₄

(a) 1,4-{Cp(Ph₃P)₂Ru(C=C)}₂C₆F₄ (8). A mixture of 1,4-(Me₃SiC=C)₂C₆F₄ (24 mg, 0.07 mmol), RuCl(PPh₃)₂Cp (100 mg, 0.14 mol) and KF (8 mg, 0.15 mmol) in thf (5 ml) and MeOH (20 ml) was heated under reflux for 5 h. The resulting yellow precipitate was collected and washed with MeOH followed by hexane to give 1,4-{CpRu(PPh₃)₂(C=C)}₂C₆F₄ (8) (66 mg, 60%). Anal. Calcd (C₉₂H₇₀P₄Ru₂F₄): C, 70.04; H, 4.47; *M*, 1578. Found: C, 70.09; H, 4.47. IR (Nujol, cm⁻¹): *v*(CC) 2073 m, 2039 m. ¹H NMR (C₆D₆): δ 4.86 (s, 5H, Cp), 6.94–7.75 (m, 30H, Ph). ¹³C NMR (CDCl₃): δ 93.5 (s, Cp), 127.6–137.3 (m, Ph). ¹⁹F NMR (C₆D₆): δ –147.0 (s, C₆F₄). ³¹P NMR (C₆D₆): δ 51.7 (s, PPh₃). ES-MS (MeCN, *m/z*): 1578, M⁺; 731, [Ru(NCMe)(PPh₃)₂Cp]⁺; 691, [Ru(PPh₃)₂Cp]⁺.

(b) 1,4-{Cp(dppe)Ru(C=C)}₂C₆F₄ (9). As for 8, 1,4-(Me₃SiC=C)₂C₆F₄ (28 mg, 0.08 mmol), RuCl(dppe)Cp (100 mg, 0.17 mmol) and KF (9 mg, 0.16 mmol) in thf (5 ml) and MeOH (20 ml) gave yellow 1,4-{Cp(dppe)Ru(C=C)}₂C₆F₄ (9) (28 mg, 26%). Anal. Calcd (C₇₂H₅₈P₄Ru₂F₄.CHCl₃): C, 60.69; H, 4.12; *M* (unsolvated), 1326. Found: C, 60.92; H, 4.11. IR (Nujol, cm⁻¹): v(CC) 2072 m, 2037 m. ¹H NMR (C₆D₆): δ 2.07, 2.70 (2 m, 2 × 2H, CH₂CH₂), 4.71 (s, 5H, Cp), 6.91–7.99 (m, 20H, Ph). ¹³C NMR (CDCl₃): δ 32.2 (m, CH₂CH₂), 88.4 (s, Cp), 126.0– 133.8 (m, Ph). ¹⁹F NMR (C₆D₆): δ –147.8 (s, C₆F₄). ³¹P NMR (C₆D₆): δ 86.7 (s, dppe). ES-MS (MeCN, *m/z*): 1326, M⁺; 605, [Ru(NCMe)(dppe)Cp]⁺; 565, [Ru(dppe)Cp]⁺.

(c) 1,4-{Cp*(dppe)Ru(C=C)}_2C_6F_4 (10). Similarly, from 1,4-(Me₃SiC=C)₂C₆F₄ (26 mg, 0.07 mmol), RuCl(dppe)Cp* (100 mg, 0.15 mmol) and KF (8 mg, 0.15 mmol) in thf (5 ml) and MeOH (20 ml) was obtained yellow 1,4-{Cp*(dppe)Ru(C=C)}_2C_6F_4 (10) (65 mg, 63%). Anal. Calcd ($C_{82}H_{78}F_4P_4Ru_2$): C, 67.20; H, 5.36; *M*, 1466. Found: C, 67.21; H, 5.40. IR (Nujol, cm⁻¹): *v*(CC) 2063 m, 2032 m. ¹H NMR (C₆D₆): δ 1.68 (s, 15H, Cp*), 1.99, 2.88 (2 m, 2 × 2H, CH₂CH₂), 7.03–7.95 (m, 20H, Ph). ¹³C NMR (CDCl₃): δ 10.7 (s, C₅*Me*₅), 30.1 (m, CH₂CH₂), 93.7 (s, *C*₅Me₅), 95.9 (s, br, RuC), 127.9–147.8 (m, Ph). ¹⁹F NMR (C₆D₆): δ –148.0 (s, C₆F₄). ³¹P NMR (C₆D₆): δ 80.9 (s, dppe). ES-MS (MeCN, *m/z*): 1467, [M + H]⁺; 675, [Ru(NCMe)(dppe)RuCp^{*}]⁺; 635, [Ru(dppe)Cp^{*}]⁺.

Derivatives of 1,4-(Me₃SiC≡C)₂C₆H₄

(a) 1,4-{Cp(dppe)Ru(C=C)}₂C₆H₄ (12). A mixture of 1,4-(Me₃SiC=C)₂C₆H₄ (50 mg, 0.19 mmol), RuCl(dppe)Cp (222 mg, 0.37 mol) and KF (21 mg, 0.37 mmol) in MeOH (30 ml) was heated under reflux for 16 h. The yellow precipitate was collected and washed with MeOH, Et₂O and hexane to give 1,4-{Cp(dppe)Ru(C=C)}₂C₆H₄ (12) (69 mg, 30%). Anal. Calcd (C₇₂H₆₂P₄Ru₂): C, 69.00; H, 4.99; *M*, 1254. Found: C, 68.98; H, 5.06. IR (Nujol, cm⁻¹): *v*(CC) 2072 m, 2044 (sh). ¹H NMR (C₆D₆): δ 1.96, 2.54 (2 m, 2 × 2H, CH₂CH₂), 4.26 (s, 10H, Cp), 6.75– 7.97 (m, 44H, Ph and C₆H₄). ³¹P NMR: δ 87.0 (s, dppe). ES-MS (MeOH + NaOMe, *m/z*): 1277, [M + Na]⁺; 1255, [M + H]⁺.

(b) 1,4-{Cp*(dppe)Ru(C=C)}₂C₆H₄ (13). A suspension of RuCl(dppe)Cp* (500 mg, 0.747 mmol), $1,4-(Me_3SiC=C)_2C_6H_4$ (99 mg, 0.374 mmol), and KF (100 mg, 1.72 mmol) in methanol (40 ml) was heated at reflux for 1 h under a nitrogen atmosphere. The yellow precipitate formed was collected and washed with MeOH and hexane and dried to give 13 as a yellow powder (390 mg, 0.280 mmol, 75%). Anal. Calcd (C₇₈H₈₂P₄Ru₂): C, 69.53; H, 6.09; M, 1346. Found: C, 69.17; H, 5.84. IR (Nujol, cm⁻¹): v(C=C) 2067 m, 2046(sh). ¹H NMR (C₆D₆): δ 1.63 (s, 30H, Cp*); 1.85 (m, 4H, CH₂); 2.66 (m, 4H, CH₂); 7.02 (m, 16H, meta and para CH dppe), 7.10 (s, 4H, CH C₆H₄), 7.12 (m, 8H, meta CH dppe), 7.19 (m, 8H, ortho CH dppe), 7.89 (m, 8H, ortho CH dppe). ¹H NMR (CDCl₃): δ 1.54 (s, 30H, Cp*); 2.05 (m, 4H, CH₂); 2.70 (m, 4H, CH₂); 6.55 (s, 4H, C₆H₄), 7.19 (m, 8H, CH dppe), 7.26 (m, 8H, CH dppe), 7.33 (m, 16H, CH dppe), 7.89 (m, 8H, ortho CH dppe). ³¹P NMR (C₆D₆): δ 82.1 (s, dppe). ³¹P NMR (CDCl₃): δ 82.0 (s, dppe). ¹³C NMR (C₆D₆): 10.4 (s, C₅Me₅), 29.8 (m, CH₂), 92.6 (s, C_5Me_5), 111.5 (s, C= CC_6H_4), 129.1, 128.9 ($C_{p,p'}$); 130.4 (CH in C₆H₄); 133.7, 134.2 (dds, *J*_{CP/CCP} ~ 5 Hz, C_{o,o'}); 137.6, 139.7 (m, $C_{i,i'}$). The $C_{m,m'}$ dppe peak is assumed to be hidden by the C₆D₆ peak. The low intensity resonances corresponding to Ru–C and one unique C of C₆H₄ were not observed. ES-MS (MeOH + NaOMe, m/z): 1369, $[M + Na]^+$.

Structure determinations

Full spheres of CCD area-detector diffraction data were measured. N_{tot} reflections were merged to N unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinements on F^2 . All data were measured using monochromatic Mo- $K\alpha$ radiation, $\lambda = 0.7107_3$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})_H being included following a riding model. Residuals R, R_w on F^2 are quoted. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system.⁴⁷ Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Tables 1 and 2.

Variata

1. The solvent molecule (benzene) was modelled as disordered over two sets of sites, occupancy 0.5.

2. x_{abs} refined to -0.07(5); refinement on |F|.

6. Refinement was carried out using the SHELXL 97 program.⁴⁸

Computations

All DFT computations were carried out with the Gaussian 03 package.⁴⁹ The model geometries **1-H**, **1-F**, **8-F** and **11-H** discussed here were optimised at the B3LYP/3–21G* level of theory,⁵⁰ to reduce computational effort, with no symmetry constraints. Test calculations carried out with a larger basis set gave similar results, in a manner similar to that reported elsewhere.⁹ MOs and frequencies were computed on these optimised geometries at the same level of theory. All geometries were identified as minima (no imaginary frequencies). The barriers in the rotations between the aryl group and the Ru(PH₃)₂Cp groups in **1-H** and **1-F** were estimated by fixing the dihedral angles P1–Ru–C1–C2 at 15° intervals (see Fig. 1 for numbering scheme).

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References

- 1 G. M. Brooke, J. Fluorine Chem., 1997, 86, 1.
- 2 R. D. Chambers, F. G. Drakesmith and W. K. R. Musgrave, J. Chem. Soc., 1965, 5045.
- 3 (a) R. D. Chambers, *Fluorine in Organic Chemistry*, Wiley: New York, 1973, ch. 9.II, p. 274; (b) G. Sandford, *Philos. Trans. R. Soc. London*, *Ser. A*, 2000, **358**, 455.
- 4 (a) M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, 1966, 1837; (b) M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, 1968, **80**, 835, (*Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 747).
- 5 (a) O. M. Abu Salah and M. I. Bruce, J. Chem. Soc., Dalton Trans., 1975, 2311; (b) M. I. Bruce and R. C. Wallis, Aust. J. Chem., 1979, 32, 1471.
- 6 (a) M. I. Bruce, G. A. Koutsantonis, M. J. Liddell and B. K. Nicholson, J. Organomet. Chem., 1987, **321**, 217; (b) M. I. Bruce, M. G. Humphrey and M. J. Liddell, J. Organomet. Chem., 1987, **321**, 91; (c) M. I.

Bruce, M. G. Humphrey, G. A. Koutsantonis and M. J. Liddell, *J. Organomet. Chem.*, 1987, **326**, 247; (*d*) M. I. Bruce and M. G. Humphrey, *Aust. J. Chem.*, 1989, **42**, 1067.

- 7 (a) F. Paul, J.-Y. Mevellec and C. Lapinte, J. Chem. Soc., Dalton Trans., 2002, 1783; (b) K. Costuas, F. Paul, L. Toupet, J.-F. Halet and C. Lapinte, Organometallics, 2004, 23, 2053; (c) F. Paul, L. Toupet, J.-Y. Thépot, K. Costuas, J.-F. Halet and C. Lapinte, Organometallics, 2005, 24, 5464; (d) F. Paul, G. da Costa, A. Bondon, N. Gauthier, S. Sinbandhit, L. Toupet, K. Costuas, J.-F. Halet and C. Lapinte, Organometallics, 2007, 26, 874.
- 8 F. Paul, B. G. Ellis, M. I. Bruce, L. Toupet, T. Roisnel, K. Costuas, J.-F. Halet and C. Lapinte, *Organometallics*, 2006, 25, 649.
- 9 M. A. Fox, R. L. Roberts, W. M. Khairul, F. Hartl and P. J. Low, J. Organomet. Chem., 2007, 692, 3277.
- (a) M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best and G. A. Heath, J. Am. Chem. Soc., 2000, **122**, 1949; (b) M. I. Bruce, B. D. Kelly, B. W. Skelton and A. H. White, J. Organomet. Chem., 2000, **604**, 150; (c) M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, M. E. Smith, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans., 1999, 3719; (d) M. I. Bruce, B. G. Ellis, P. J. Low, B. W. Skelton and A. H. White, Organometallics, 2003, **22**, 3184; (e) M. I. Bruce, K. Costuas, T. Davin, B. G. Ellis, J.-F. Halet, C. Lapinte, P. J. Low, M. E. Smith, B. W. Skelton, L. Toupet and A. H. White, Organometallics, 2005, **24**, 3864.
- 11 F. Coat, P. Thominot and C. Lapinte, J. Organomet. Chem., 2001, 629, 39.
- 12 (a) M. I. Bruce, M. Ke and P. J. Low, *Chem. Commun.*, 1996, 2405; (b) M. I. Bruce, M. Ke, P. J. Low, B. W. Skelton and A. H. White, *Organometallics*, 1998, **17**, 3539.
- 13 R. Denis, T. Weyland, F. Paul and C. Lapinte, J. Organomet. Chem., 1997, 545–546, 615.
- 14 (a) R. Dembinski, T. Lis, S. Szafert, C. L. Mayne, T. Bartik and J. A. Gladysz, J. Organomet. Chem., 1999, 578, 229; (b) Q. Zheng and J. A. Gladysz, J. Am. Chem. Soc., 2005, 127, 10508.
- 15 (a) A. B. Antonova, M. I. Bruce, B. G. Ellis, M. Gaudio, P. A. Humphrey, M. Jevric, G. Melino, B. K. Nicholson, G. J. Perkins, B. W. Skelton, B. Stapleton, A. H. White and N. N. Zaitseva, *Chem. Commun.*, 2004, 960; (b) A. B. Antonova, M. I. Bruce, P. A. Humphrey, M. Gaudio, B. K. Nicholson, N. Scoleri, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Organomet. Chem.*, 2006, **691**, 4694; (c) M. I. Bruce, M. E. Smith, N. N. Zaitseva, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2003, **670**, 170; (d) M. I. Bruce, B. W. Skelton, A. H. White, A. H. White and N. N. Zaitseva, *J. Organomet. Chem.*, 2003, **683**, 398.
- 16 (a) T. X. Neenan and G. M. Whitesides, J. Org. Chem., 1988, 53, 2489; (b) P. Nguyen, Z. Yuan, L. Agocs, G. Lesley and T. B. Marder, Inorg. Chim. Acta, 1994, 220, 289.
- 17 P. Bladon, D. W. A. Sharp and J. M. Winfield, *Spectrochim. Acta*, 1964, 20, 1033.
- 18 M. I. Bruce, J. Chem. Soc. A, 1968, 1459.
- 19 P. G. Pringle and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1983, 889.
- 20 M. J. Irwin, G. Jia, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1996, **15**, 5321.
- 21 G. Eglinton and W. McCrae, Adv. Org. Chem., 1963, 4, 225.
- 22 M. S. Khan, M. R. A. Al-Mandhury, M. K. Al-Suti, T. C. Corcoran, Y. Al-Mahrooqi, J. P. Attfield, N. Feeder, W. I. F. David, K. Shankland, R. H. Friend, A. Köhler, E. A. Marseglia, E. Tedesco, C. C. Tang, P. R. Raithby, J. C. Collings, K. P. Roscoe, A. S. Batsanov, L. M. Stimson and T. B. Marder, *New J. Chem.*, 2003, **27**, 140.
- 23 (a) J. M. Wisner, T. J. Bartczak and J. A. Ibers, *Inorg. Chim. Acta*, 1985, **100**, 115; (b) M. I. Bruce, M. G. Humphrey and M. R. Snow, *J. Organomet. Chem.*, 1986, **314**, 213.
- 24 M. I. Bruce, M. G. Humphrey, M. R. Snow and E. R. T. Tiekink, J. Organomet. Chem., 1986, 314, 213.
- 25 (a) A. J. Downard, B. H. Robinson and J. Simpson, *Organometallics*, 1986, **5**, 1122; (b) A. J. Downard, B. H. Robinson and J. Simpson, *J. Organomet. Chem.*, 1993, **447**, 281.
- 26 M. I. Bruce, B. G. Ellis, M. Gaudio, C. Lapinte, G. Melino, F. Paul, B. W. Skelton, M. E. Smith, L. Toupet and A. H. White, *Dalton Trans.*, 2004, 1601.
- 27 G. Balavoine, J. Collin, J.-J. Bonnet and G. Lavigne, J. Organomet. Chem., 1985, 280, 429.
- 28 D. N. Duffy, M. M. Kassis and A. D. Rae, Acta Crystallogr., Sect. C, 1991, 47, 2054.
- 29 (a) F.-E. Hong, Y.-L. Huang, Y.-C. Chang, K.-M. Chu and Y.-T. Tsai, *Appl. Organomet. Chem.*, 2003, **17**, 458; (b) F.-E. Hong, Y.-C. Lai, Y.-J. Ho and Y.-C. Chang, *J. Organomet. Chem.*, 2003, **688**, 161.

- 30 (a) M. I. Bruce, K. A. Kramarczuk, G. J. Perkins, B. W. Skelton, A. H. White and N. N. Zaitseva, J. Cluster Sci., 2004, 15, 119; (b) M. I. Bruce, P. A. Humphrey, G. Melino, B. W. Skelton, A. H. White and N. N. Zaitseva, Inorg. Chim. Acta, 2005, 358, 1453; (c) M. I. Bruce, K. A. Kramarczuk, N. N. Zaitseva, B. W. Skelton and A. H. White, J. Organomet. Chem., 2005, 690, 1549; (d) M. I. Bruce, N. N. Zaitseva, P. J. Low, B. W. Skelton and A. H. White, J. Organomet. Chem., 2006, 691, 4273; (e) M. I. Bruce, M. L. Cole, M. Gaudio, B. W. Skelton and A. H. White, J. Organomet. Chem., 2006, 691, 4203;
- 31 C. Bitcon and M. W. Whiteley, J. Organomet. Chem., 1987, 336, 385.
- 32 I. R. Whittall, M. P. Ciuentes, M. G. Humphrey, B. Luther-Davis, M. Samoc, S. Houbrechts, A. Persoons, G. A. Heath and D. C. R. Hockless, *J. Organomet. Chem.*, **549**, 127.
- 33 T. Weyland, C. Lapinte, G. Frapper, M. J. Calhorda, J.-F. Halet and L. Toupet, *Organometallics*, 1997, 16, 2024.
- 34 A. Klein, O. Lavastre and J. Fiedler, Organometallics, 2006, 25, 635.
- 35 (a) S. E. Bailey, J. I. Zink and S. F. Nelson, J. Am. Chem. Soc., 2003, 125, 5939; (b) P. K. Sudeep, P. V. James, K. G. Thomas and P. V. Kamat, J. Phys. Chem. A, 2006, 110, 5642.
- 36 S. I. Ghazala, F. Paul, L. Toupet, T. Roisnel, P. Hapiot and C. Lapinte, J. Am. Chem. Soc., 2006, 128, 2463.
- 37 C. Creutz, Prog. Inorg. Chem., 1980, 30, 1.
- 38 (a) M. D. Ward and J. A. McCleverty, J. Chem. Soc., Dalton Trans., 2002, 275; (b) W. Kaim and G. K. Lahiri, Angew. Chem., Int. Ed., 2007, 46, 1778.
- 39 W. Henderson, J. S. McIndoe, B. K. Nicholson and P. J. Dyson, J. Chem. Soc., Dalton Trans., 1998, 519.
- 40 M. I. Bruce, B. C. Hall, P. J. Low, B. W. Skelton and A. H. White, J. Organomet. Chem., 1999, **592**, 74.
- 41 A. G. Alonso and L. B. Reventós, J. Organomet. Chem., 1988, 338, 249.
- 42 M. I. Bruce, C. Hameister, A. G. Swincer and R. C. Wallis, *Inorg. Synth.*, 1990, 28, 270.

- 43 F. J. Lalor, T. J. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez and B. Ruhl, J. Chem. Soc., Dalton Trans., 1995, 1709.
- 44 D. R. Coulson, Inorg. Synth., 1990, 28, 107.
- 45 M. I. Bruce, M. E. Smith, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1999, **52**, 431.
- 46 M. I. Bruce, E. Horn, J. G. Matisons and M. R. Snow, Aust. J. Chem., 1984, 37, 1163.
- 47 S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, (eds), *The XTAL* 3.7 System, University of Western Australia, 2000.
- 48 G. M. Sheldrick, SHELXL97: A Program for Crystal Structure Refinement, University of Gottingen, 1997.
- 49 Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- 50 (a) A. D. Becke, J. Chem. Phys., 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, **37**, 785; (c) G. A. Petersson and M. A. Al-Laham, J. Chem. Phys., 1991, **94**, 6081; (d) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, J. Chem. Phys., 1988, **89**, 2193.