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Syntheses and molecular structures of some polyfluoroaryldiynyl–ruthenium complexes

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ABSTRACT

Lithiated Ru(C≡CC≡CH)(dppe)Cp* reacts with polyfluoroaromatic compounds C_6F_5X (X = F, OMe, CN, NO_2) and $C_{10}F_8$ to give novel polyfluoroaryldiynyls end-capped with the Ru(dppe)Cp* group. Addition of tcne to Ru(C≡CC≡CC_6F_5)(dppe)Cp* afforded the butadienynyl Ru{C≡CC[=$C(CN)_2$]$C(C_6F_5)$=C$(CN)_2$}(dppe)Cp*, while protonation with HBF_4·OEt_2 resulted in cycloaddition to give [1,3-{Cp*(dppe)RuC≡C}$_2${μ-$C_4H(C_6F_5)_2$}]BF_4. XRD molecular structures of complexes with X = F, CN, OMe and the $C_{10}F_7$ derivative are reported.

1. Introduction

A variety of methods is available for the synthesis of diynyl–metal complexes L_nM–C≡CC≡CR [1]. In general, these depend upon the availability of the parent diyne HC≡CC≡CR or its group 14 derivatives, Me_3EC≡CC≡CR (E = Si, Sn). Most reported examples involve diynes with R = Me, Bu^t, Ph or $SiMe_3$, but contemporary interest in poly-ynyl-metal complexes as potential components in molecular scale electronic devices (wires, switches, amplifiers) [2–7] suggests that routes to compounds bearing other functional groups would be useful. The parent diynes often have limited stability or are difficult to access. However, one potential route which has been little explored is the metallation of a parent diynyl complex L_nMC≡CC≡CH to give lithio- or magnesio-derivatives, which can then be further elaborated. There are presently relatively few examples of this type of reaction in the literature. The tungsten diynyl W(C≡CC≡CH)$(CO)_3$Cp reacts with LiN$(SiMe_3)_2$ to give a derivative which reacted with $SiClMe_3$ or $PClPh_2$ to give W(C≡CC≡C$SiMe_3$)$(CO)_3$Cp and W{C≡CC≡CP(O)Ph_2}$(CO)_3$Cp, respectively [8]. Later examples include the lithiation of Re(C≡CC≡CH)(PPh_3)(NO)Cp* to give Re(C≡CC≡CLi)(PPh_3)(NO)Cp*, which was then cuprated with CuI or Cu(OBu^t) and coupled with IC≡C$SiMe_3$ or BrC≡C$SiEt_3$ to give Re(C≡CC≡CC≡CSiR_3)(PPh_3)(NO)Cp* (R = Me, Et, respectively) [9]; the copper complex has been isolated [10]. Reactions of Re(C≡CC≡CLi)(PPh_3)(NO)Cp* with various metal carbonyls have given unsaturated carbene complexes {Cp*(Ph_3P)(NO)Re}C≡CC≡CC(OMe)=$\{ML_n\}$ [ML_n = $Fe(CO)_4$, $Mn(CO)_2(\eta$-$C_5X_5)$ (X_5 = HCl_4, Cl_5, Br_5)] [11].

We have found that metallation of diynyl–ruthenium complexes with organolithium reagents produces synthetically useful intermediates of the type Ru(C≡CC≡CLi)(PP)Cp′ [PP = $(PPh_3)_2$, dppe; Cp′ = Cp, Cp*]. For example, addition of LiBu to Ru(C≡CC≡CH)(dppe)Cp* in thf solution at −78 °C, followed by warming to r.t. to complete the reaction, and cooling again to −78 °C before adding an electrophile, has proved to be a useful route into complexes which are otherwise accessible with difficulty. The reaction of the diynyl-lithium with 1,2-dichlorohexafluorocyclopentene results in displacement of one Cl to give Ru(C≡CC≡CC_5F_6Cl-2)(dppe)Cp* [12].

There is currently some interest in fluorinated aryldi- and polyynes, both from the viewpoint of their solid-state properties [13–17] and the non-linear optical properties of fluorinated polydiynes [18]. However, there are relatively few polyfluoroaromatic diynes known [19,20] and they are not readily employed in the synthesis of polyfluoroaryl-substituted diynyl complexes. Syntheses are generally based upon coupling of C_6F_5I with HC≡C$SiMe_3$, followed by desilylation and Cu(I)-catalysed oxidative coupling to form the diyne, which can then be further elaborated by conventional nucleophilic substitution reactions [19–21].

Polyfluoroaromatic compounds, exemplified by hexafluorobenzene, are characterised by their susceptibility to nucleophilic attack, in complete contrast to benzene itself [22]. Mono- and

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di-substitution of ring fluorines by alkynyl groups using LiC≡CPh was first reported in 1967 [23]. This paper describes the syntheses and characterisation of several diynyl–ruthenium complexes Ru(C≡CC≡CAr$_F$)(dppe)Cp*, with Ar$_F$ = C_6F_5, C_6F_4OMe-*p*, C_6F_4CN-*p*, $C_6F_5NO_2$-*p* and $C_{10}F_7$-2, and some reactions of the first of these.

2. Results and discussion

In general, the ruthenium diynyl complex was lithiated at −78 °C and added to a solution of the polyfluoroaromatic compound, also at −78 °C. After several hours reaction, the product mixture was worked up after warming to r.t., separation by preparative t.l.c. providing the fluoroaromatic complexes. From these reactions were obtained Ru(C≡CC≡CAr$_F$)(dppe)Cp* (Ar$_F$ = C_6F_5 (**1**), C_6F_4OMe-*p* (**2**), C_6F_4CN-*p* (**3**), $C_6F_5NO_2$-*p* (**4**) and $C_{10}F_7$-2 (**5**); Scheme 1) in moderate to good yields as yellow to yellow–orange solids, apparently stable in air indefinitely. Identification of the products was by elemental microanalyses and from their spectroscopic properties. The ES-MS contained molecular ions, together with the fragment ion [Ru(dppe)Cp*]$^+$ (*m*/*z* 635). In all cases, the Ru(dppe)Cp* moiety was also identified by its characteristic NMR signals at δ_H ca 1.55 (Cp*), 2.35 and 3.35 (CH_2 of dppe) and Ph multiplets at δ_H ca 7.5.

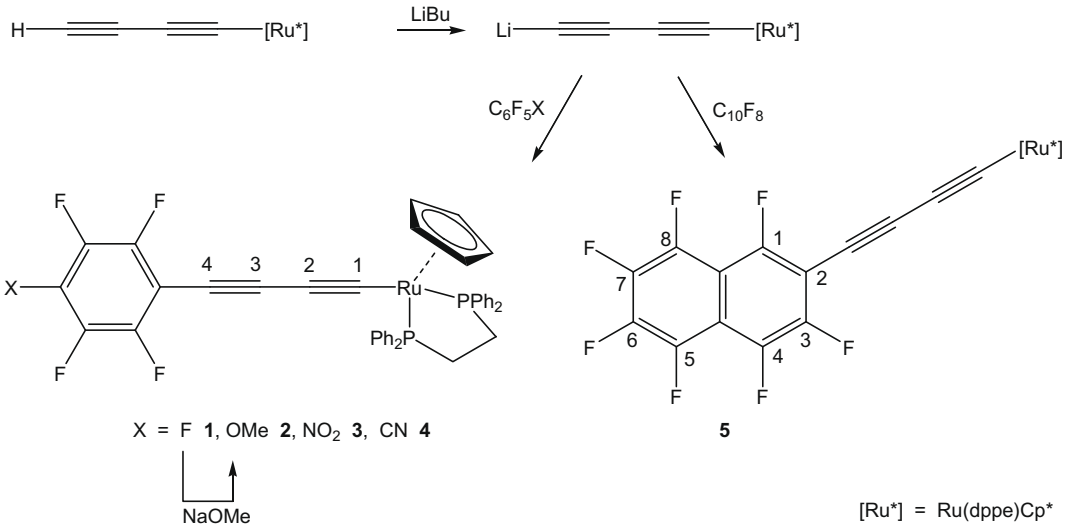
The ^{13}C NMR spectra contained resonances at δ_C ca 10 and ca 94 (Cp*) and aromatic signals between δ_C 125 and 135. In some cases, the carbon chain nuclei were detected. Atom C_1 resonates at δ_C 126.5 for **1** and **5**, containing unsubstituted C_6F_5 or $C_{10}F_7$ groups, but upfield at δ_C ca 100 for **2**–**4**. The resonance of atom C_2 is found at δ_C 99.2 (for **1**) or between 92.5 and 95.9 for **2**–**5**. The resonance for C_3 is between δ_C 89.4 and 90.0 (**1**, **3**–**5**) but at δ_C 75.5 for **2**, while C_4 resonates at δ_C 53.3–59.5 (**1**–**3**) and 75.5, 76.3 (for **4**, **5**). At present, there is no rationale for these observed differences.

The ^{19}F NMR spectrum of the C_6F_5 complex **1** contained three signals at δ_F −149.1, −161.7 and −166.6 (relative intensities 2/1/2), assigned to the *o*-, *p*- and *m*-F atoms, respectively. These are in positions similar to those found in a host of C_6F_5 compounds studied some decades ago [24]. The *p*-F nuclei give rise to triplets [*J*(FF) ca 20 Hz] by coupling with the two *m*-F nuclei; in some cases, further broadening of the components of the triplet suggests a smaller unresolved coupling to the *o*-F nuclei. Signals for the *o*- and *m*-F atoms are multi-line resonances of the AA′XX′ system, which were not sufficiently resolved for assignment of the coupling constants in these spectra. The C_6F_4X-*p* (X = OMe, CN, NO_2) compounds **2**–**4** contained only two equal intensity signals for the *o*- and *m*-F nuclei, again the components of AA′XX′ spin systems. Assignments are based upon the relative constancy of the resonances of fluorines adjacent to the dinyl group at δ_F ca 140. A NOESY experiment enabled a tentative assignment of the five resonances observed for **5**, based on the XRD structural determination of this complex as the expected 2-naphthyl isomer. The two fluorines adjacent to the diynyl group resonate at δ_F −150.2 and −151.3; resonances at δ_F −161.0 and −163 each have relative intensity 2 and are assigned to F(4,5) and F(6,7), respectively.

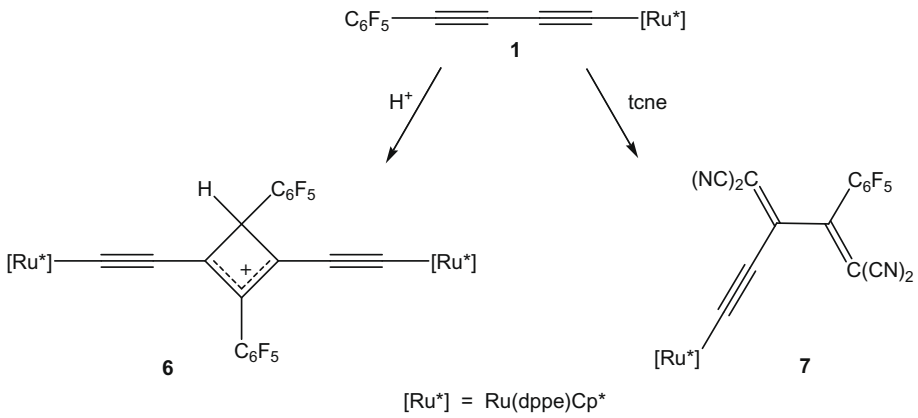
Introduction of the metalladiynyl group does not perturb the usual substitution reactivity of the fluoroaromatic group, further reaction of **1** with NaOMe providing an alternative route to **2** in 60% yield. The fluoroaromatic group also does not change the usual diynyl reactivity. Protonation of **1** gives the binuclear cyclobutenylidinium cation in **6** (Scheme 2) by addition of a putative highly reactive butatrienylidene intermediate to unreacted diynyl. For **6**, two sets of ^{19}F resonances are found, consistent with the structure containing two different C_6F_5 groups. Although this type of reaction has been often found between alkynyl and vinylidene complexes [25–30], there is only one earlier report describing the reaction for diynyl complexes [31].

The electron-deficient alkene tcne reacts with **1** to give the tetracyanobutadienyl complex **7**, formed by [2 + 2]-cycloaddition of the cyanoalkene to the outer C≡C triple bond, followed by ring-opening (Scheme 2). Spectroscopic properties of **7** include the presence of [M+Na]$^+$ in the ES-MS obtained from solutions containing NaOMe, and resonances at δ_C 154.01, 139.14, 92.81 and 78.91 for the four carbons of the C_4 chain. Several examples of this type of reaction have been described previously [32].

Electrochemical studies (Table 1) showed that the electron-withdrawing polyfluoroaromatic substituent results in an increase in the oxidation potential of **1** to +0.56 V when compared with that of Ru(C≡CC≡CPh)(dppe)Cp* (+0.44 V), as anticipated when the more electron-withdrawing C_6F_5 group replaces Ph. Substitution of the *para*-F atom in **1** with OMe results in a reduction of the oxidation potential, two processes occurring here. Irreversible reduction of the NO_2 group in **3** occurs at −1.45 V, while addition of two electrons to the tcne adduct **7** gives anionic species which are stabilized by delocalization of charge onto the =C(CN)$_2$ groups. Only **2** and **7** show fully reversible oxidation processes, others being partially reversible under the conditions used.



Scheme 1. Syntheses of polyfluoroaromatic diynyl–ruthenium complexes (numbering system for NMR assignments shown).



Scheme 2. Reactions of Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* with electrophiles.

Table 1
Some electrochemical data for Ru(C≡CC≡CAr$_F$)(dppe)Cp* and derivatives.

ArF	Redox potentials/V versus SCE
C_6F_5 (**1**)	+0.56[a]
C_6F_4OMe-*p* (**2**)	+0.17[a], +0.34[a]
$C_6F_4NO_2$-*p* (**3**)	−1.45[c], +0.30[a], +0.58[a]
C_6F_4CN-*p* (**4**)	+0.50[b]
$C_{10}F_7$-2 (**5**)	+0.51[a]
C_6F_5-tcne adduct (**7**)	−0.89[a], −0.52[a], +0.86[b]

All processes diffusion controlled.
Conditions: solutions (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).
[a] Partially reversible.
[b] Fully reversible.
[c] Irreversible.

2.1. Molecular structures

Figs. 1 and 2 depict single molecules of complexes **1**, **2**, **3** and **4**, selected structural data being collected in Table 2. All contain the familiar Ru(dppe)Cp* group, with parameters differing little from many other complexes containing this group, with Ru–P 2.264(1)–2.2824(6) and Ru–C(cp) 2.09(2)–2.37(3) Å and the angles P(1)–Ru–P(2) 80.09(3)–83.47(4) and P(1,2)–Ru–C(1) 79.8(1)–91.2(1)°, and having the usual pseudo-octahedral geometry.

The diynyl group is attached to Ru via C(1) [Ru–C(1) range 1.958(2)–1.993(4) Å], with alternating short and long C–C bonds along the chain [C(1)–C(2) 1.179(5)–1.231(2), C(2)–C(3) 1.361(2)–1.401(6), C(3)–C(4) 1.192(6)–1.212(2), C(4)–C(41) 1.416(2)–1.499(10) Å]. The structures confirm the expected *para* substitution of the fluorinated ring, or the 2-substitution of the naphthyl group. The ring C–F bond lengths are remarkably consistent [(non-disordered) C(4n)–F(4n) 1.314–1.354(3), av.1.34(1) Å]. In the C_6 ring of **3**, there is an appreciable quinonoid contribution [1.341, 1.366(2), cf. 1.390–1.404(2) Å], while in the naphthalene skeleton of **4**, the usual Kekulé form persists [four bonds (α–β) 1.344–1.366(4), others 1.407–1.451(4) Å]. In **4**, inversion-related naphthyl groups stack up the centre of the cell along *a*.

3. Conclusions

Reactions of lithiated Ru(C≡CC≡CH)(dppe)Cp* with polyfluoroaromatic compounds results in substitution of F *para* to the substituent, providing a useful route into polyfluoroaryl–diynyl–ruthenium complexes. Protonation of Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* afforded the corresponding binuclear cyclobutenylidinium cation, while tcne adds to the C≡C triple bond away from the metal, both reactions indicating that the diynyl function is not significantly affected by the presence of the fluorinated group.

4. Experimental

4.1. 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).

4.2. Instruments

IR spectra were obtained using a Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 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). Unless otherwise stated, samples were dissolved in $CDCl_3$ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C NMR spectra, external H_3PO_4 for ^{31}P NMR spectra, and $CFCl_3$ for ^{19}F NMR spectra (referenced to internal C_6F_6 at δ_F −164.9). Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH which, unless otherwise stated, contained NaOMe as an aid to ionisation [33]. 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. Elemental analyses were by the Campbell Microanalytical Centre, University of Otao, Dunedin, New Zealand.

4.3. Reagents

The compound Ru(C≡CC≡CH)(dppe)Cp* [34] was prepared by the cited method. Polyfluoroaromatics were samples supplied by Imperial Smelting Co., Avonmouth.

4.3.1. Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* (**1**)

A solution of Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.07 mmol) in THF (10 mL) was treated with BuLi (91 μL, 1.6 M solution in hexane, 0.145 mmol) and stirred at −78 °C for 30 min. C_6F_6 (17 μL, 0.14 mmol) was then added and the reaction was stirred at −78 °C for 1 h before being allowed to warm to r.t. over 3 h.

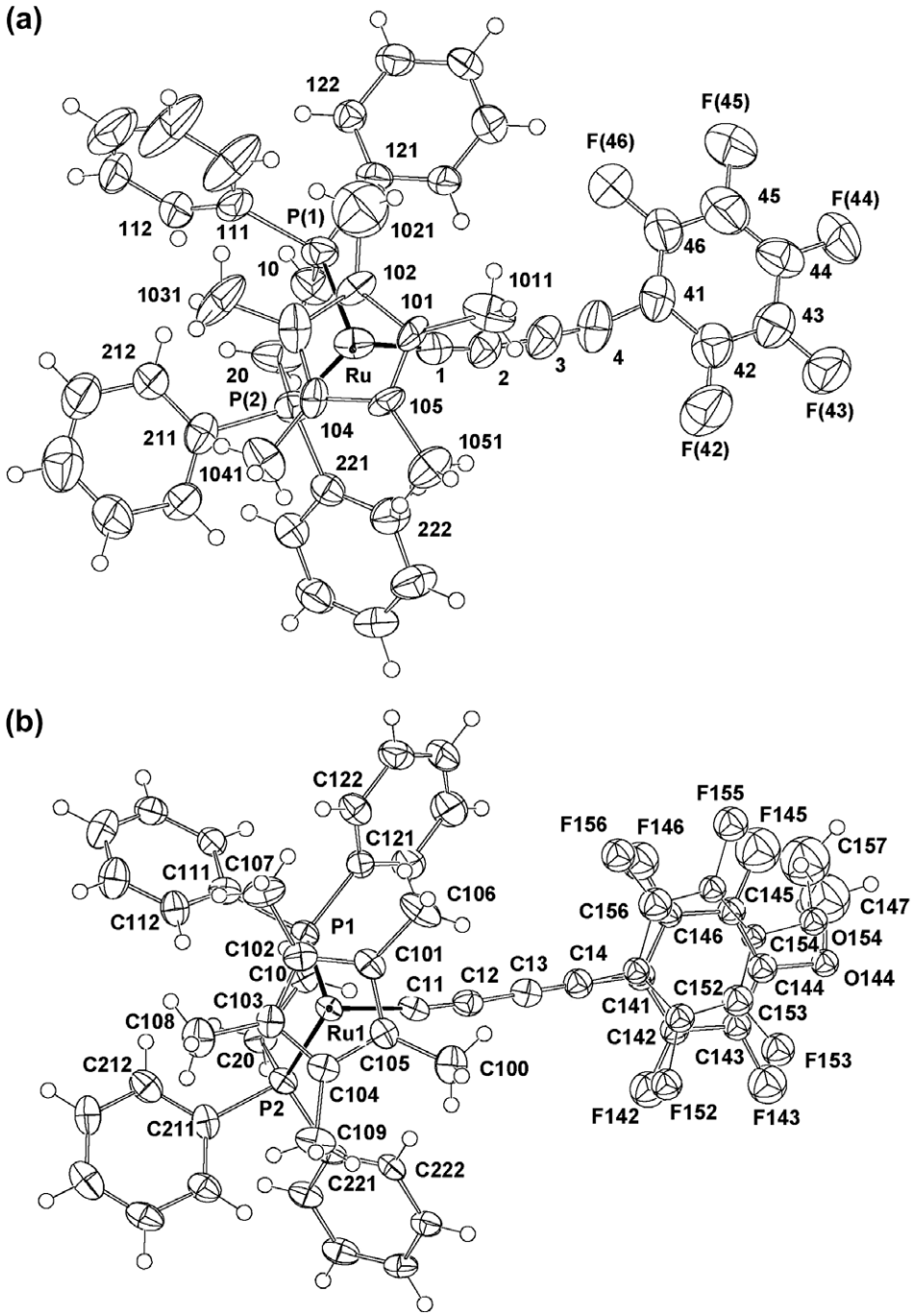


Fig. 1. Plots of molecules of (a) Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* (**1**) (major component) and (b) Ru(C≡CC≡CC$_6$F$_4$OMe-*p*)(dppe)Cp* (**2**).

Solvent was then removed to give a residue which was dissolved in hexane (90 mL) and the solution was filtered via cannula and evaporated to dryness to give Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* **1** as an orange powder (50 mg, 80%). Alternatively, the hexane extract was chromatographed (basic Al_2O_3 column; hexane-CH_2Cl_2-NEt_3, 16/3/1) to give a bright yellow fraction containing pure **1**. Single crystals suitable for X-ray studies were grown from CH_2Cl_2/hexane. *Anal.* Calc. ($C_{46}H_{39}F_5P_2Ru$): C, 64.93; H, 4.62; *M*, 850. Found: C, 64.72; H, 4.90%. IR/cm^{-1}: *ν*(C≡C) 2151m, 2005m; *ν*(CF) 1513m, 1488m, 1434m, 1376m, 1261m, 1093m, 1060m, 981m, 805m, 741m, 693m. ^{1}H NMR (C_6D_6): *δ* 7.42–7.01 (m, 20H, Ph); 2.47, 1.79 (2m, 2 × 2H, PCH_2); 1.56 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): *δ* 134.48–127.75 (m, Ph); 126.48 (s, C_1); 99.23 (s, C_2); 93.80 [t, ^2J(CP) 2 Hz, C_5Me_5]; 89.37 (s, C_3); 53.27 (s, C_4); 29.85 (m, CH_2CH_2); 10.05 (s, C_5Me_5). ^{19}F NMR (C_6D_6): *δ* −149.1 (m, 2F, *o*-F); −161.7 [t, ^3J(FF) = 22 Hz, 1F, *p*-F]; −166.6 (m, 2F, *m*-F). ^{31}P NMR (C_6D_6): *δ* 80.8 (s, dppe). ES-MS (positive ion, MeOH, *m/z*): 1702, $[2M]^+$; 851, M^+; 635, $[Ru(dppe)Cp^*]^+$.

4.3.2. Ru(C≡CC≡CC$_6$F$_4$OMe-*p*)(dppe)Cp* (**2**)

(a) Similarly, the reaction of Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.07 mmol) with ^{n}BuLi (91 μL, 1.6 M solution in hexane, 0.145 mmol), followed by addition of C_6F_5OMe (21 μL, 0.14 mmol) afforded Ru(C≡CC≡CC$_6$F$_4$OMe-*p*)(dppe)Cp* **2** as an orange powder (38 mg, 60%).

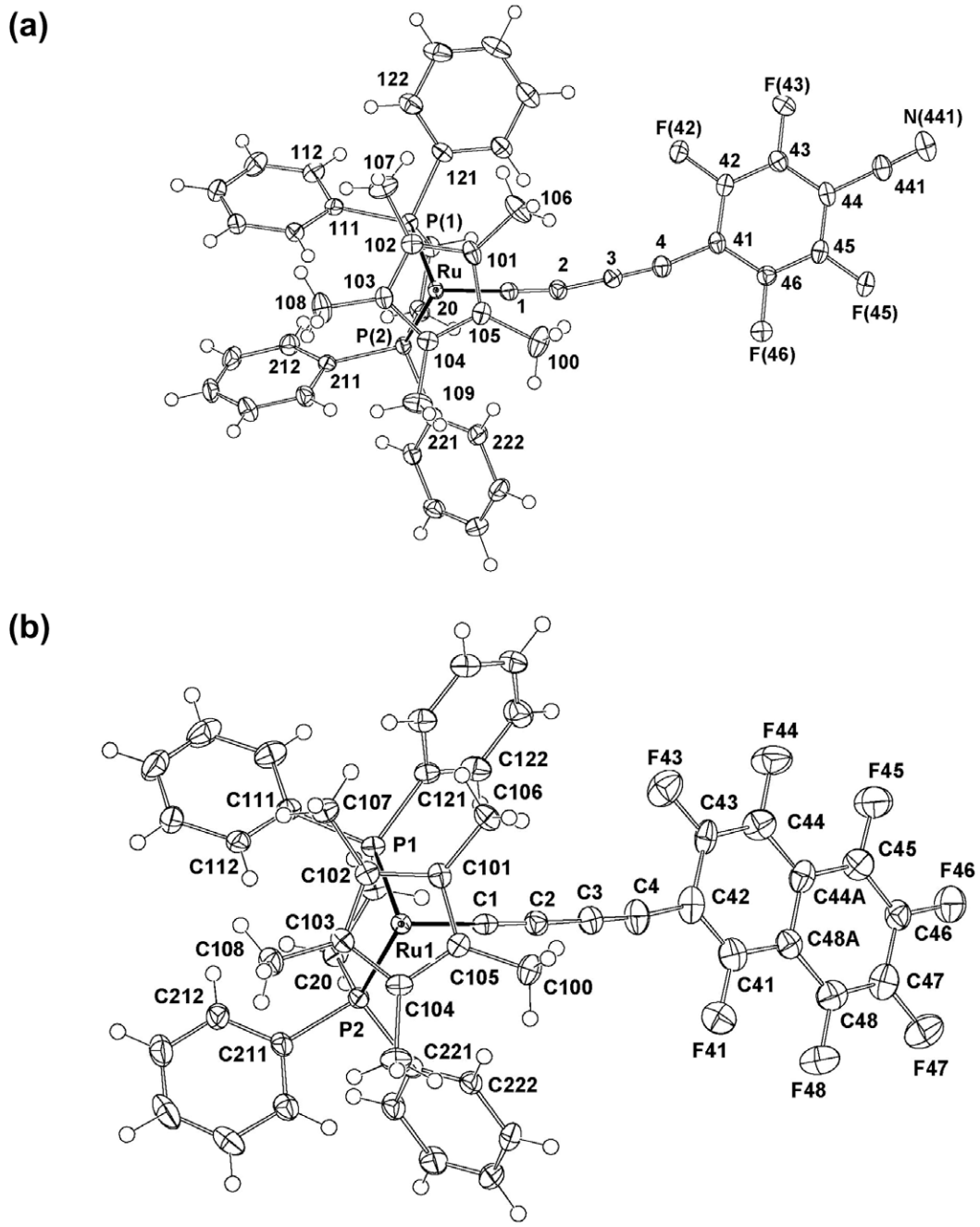


Fig. 2. Plots of molecules of (a) Ru(C≡CC≡CC$_6$F$_4$CN-*p*)(dppe)Cp* (**3**) and (b) Ru(C≡CC≡CC$_{10}$F$_7$-2)(dppe)Cp* (**4**).

(b) Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* (31 mg, 0.04 mmol) was dissolved in thf (10 mL) and NaOMe (1.2 mg in 2 mL of MeOH, 0.05 mmol) was added. The solution was stirred at r.t. for 16 h. The solvent was removed and the residue was dissolved in hexane (60 mL) and then evaporated to dryness to afford **2** as an orange powder (27 mg, 87%). Single crystals suitable for X-ray studies were grown from CH_2Cl_2/hexane. *Anal.* Calc. for $C_{47}H_{42}F_4OP_2Ru$: C, 65.42; H, 4.91; *M*, 862. Found: C, 65.39; H, 5.03%. IR/cm^{-1}: *ν*(C≡C) 2149m, 2005m; *ν*(CO) 1711m; *ν*(CF) 1573m, 1501m, 1480m, 1434m, 1377m, 1263m, 1095m, 1026m, 804m, 742m, 698m. ^{1}H NMR (C_6D_6): *δ* 7.37–7.02 (m, 20H, Ph); 3.30 (s, 3H, OCH_3); 2.46–1.77 (2m, 2 × 2H, PCH_2); 1.54 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): *δ* 136.78–127.64 (m, Ph); 100.28 (s, C_1); 93.71 (s, C_5Me_5); 92.54 (s, C_2); 89.95 (s, C_3); 74.00 (s, OCH_3); 53.26 (s, C_4); 29.87 (m, CH_2CH_2); 10.08 (s, C_5Me_5). ^{19}F NMR (C_6D_6): *δ* −142.5 (m, 2F); −161.6 (m, 2F). ^{31}P NMR (C_6D_6): *δ* 80.8 (s, dppe). ES-MS (+ve ion, MeOH, *m/z*): 862, M$^+$; 885, [M+Na]$^+$; 635, [Ru(dppe)Cp*]$^+$.

4.3.3. Ru(C≡CC≡CC$_6$F$_4$NO$_2$-p)(dppe)Cp (**3**)*

Similarly, from Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.07 mmol) and $C_6F_5NO_2$ (30 μL, 0.14 mmol) was obtained Ru(C≡CC≡CC$_6$F$_4$-NO$_2$-*p*)(dppe)Cp* **3** as a purple powder (52 mg, 80%). *Anal.* Calc. for $C_{46}H_{39}F_4NO_2P_2Ru$: C, 63.01; H, 4.48; N, 1.60; *M*, 878. Found: C, 63.07; H, 4.52, N, 1.63%. IR/cm^{-1}: *ν*(C≡C) 2126m, 1998m; *ν*(NO) 1634m; *ν*(CF) 1556m, 1504m, 1455m, 1435m, 1259m, 1016m, 802m, 767m, 697m. ^{1}H NMR (C_6D_6): *δ* 7.42–7.04 (m, 20H, Ph); 2.35, 1.83 (2m, 2 × 2H, PCH_2); 1.56 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): *δ* 133.77–126.44 (m, Ph); 100.25 (s, C_1); 94.26 [t,

Table 2
Selected bond parameters.

Bond	**1**	**2** (mols 1; 2)	**3**	**4**
Bond distances (Å)				
Ru–P(1)	2.2797(10)	2.269(1); 2.264(1)	2.2656(6)	2.2689(6)
Ru–P(2)	2.2712(10)	2.281(1); 2.276(1)	2.2754(9)	2.2824(6)
Ru–C(cp)	2.09–2.33(2); 2.24–2.37(3)	2.241–2.278(4), 2.223–2.266(4)	2.229–2.290(2)	2.232–2.272(2)
(av.)	2.20(13); 2.29(6)	2.26; 2.25(2)	2.27(3)	2.256(16)
Ru–C(1)	1.993(4)	1.991(4); 1.976(4)	1.958(2)	1.976(2)
C(1)–C(2)	1.179(5)	1.226(5); 1.219(6)	1.231(2)	1.209(3)
C(2)–C(3)	1.402(6)	1.373(6); 1.370(7)	1.361(2)	1.373(3)
C(3)–C(4)	1.197(5)	1.206(5); 1.192(6)	1.212(2)	1.199(3)
C(4)–C(41)	1.431(9); 1.44(2)	1.499(10); 1.495(11)	1.416(2)	1.421(3)
C(4*n*)–F(4*n*)	1.309–1.344(10) [< >1.335(16)]; 1.31(2)–1.386(14) [< >1.35(3)]	1.291–1.379(9), 1.335–1.388(10); 1.257–1.408(12), 1.200–1.408(10) [< >1.34(4), 1.36(2); 1.36(7), 1.34(10)]	1.340–1.345(2) [< >1.342(2)]	1.314–1.354(3) [< >1.338(14)]
Bond angles (°)				
P(1)–Ru–P(2)	83.30(4)	83.47(4); 83.20(4)	80.09(3)	83.32(2)
P(1)–Ru–C(1)	83.9(1)	79.8(1); 83.2(1)	86.07(5)	80.53(6)
P(2)–Ru–C(1)	86.8(1)	91.2(1); 87.2(1)	85.71(6)	87.13(6)
Ru–C(1)–C(2)	174.9(3)	173.8(3); 174.5(4)	171.9(1)	178.7(2)
C(1)–C(2)–C(3)	171.2(4)	176.1(4); 173.6(5)	168.1(2)	174.3(2)
C(2)–C(3)–C(4)	178.5(5)	179.7(5); 177.8(6)	178.2(2)	178.2(3)
C(3)–C(4)–C(41)	166.9(6); 175.0(8)	175.7(6); 163.5(7)	167.4(2)	173.5(3)

For **1**: values are given for the two disordered components.
For **2**: C(44)–O(44) 1.421(7), 1.387(10) Å.
For **3**: C(44)–C(441) 1.434(2), C(441)–N(441) 1.141(2) Å; C(44)–C(441)–N(441) 178.2(2)°.

^2J(CP) 2 Hz, C_5Me_5]; 94.40 (s, C_2); 89.38 (s, C_3); 76.28 (s, C_4); 31.89 (m, CH_2CH_2); 10.22 (s, C_5Me_5). ^{19}F NMR (C_6D_6): δ −140.3 (m, 2F); −151.9 (m, 2F). ^{31}P NMR (C_6D_6): δ 80.4 (s, dppe). ES-MS (positive ion, MeOH + NaOMe, *m/z*): 901, $[M+Na]^+$; 878, M^+; 635, $[Ru(dppe)Cp^*]^+$.

4.3.4. Ru(C≡CC≡CC$_6$F$_4$CN-p)(dppe)Cp* (**4**)

Similarly, the reaction of Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.07 mmol) with BuLi (0.17 mL, 0.86 M solution in hexane, 0.145 mmol) and C_6F_5CN (19 μL, 0.14 mmol) gave Ru(C≡CC≡CC$_6$F$_4$CN-*p*)(dppe)Cp* **4** as an orange powder (58 mg, 90%). Single crystals suitable for X-ray studies were grown from benzene/hexane. *Anal.* Calc. for $C_{47}H_{39}F_4NP_2Ru$: C, 65.80; H, 4.59; N, 1.63; M, 857. Found: C, 65.70; H, 4.61, N, 1.63%. IR/cm^{-1}: *ν*(CN) 2214m; *ν*(C≡C) 2128m, 1995m; *ν*(CF) 1634m, 1486m, 1435m, 1380m, 1264m, 1095m, 978m, 803m, 743m, 698m. ^{1}H NMR (C_6D_6): δ 7.27–7.06 (m, 20H, Ph); 2.53, 1.98 (2m, 2 × 2H, PCH_2); 1.53 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): δ 133.68–127.63 (m, Ph); 99.39 (s, C_1); 94.75 (s, C_2); 94.25 (s, C_5Me_5); 75.49 (s, C_3); 59.48 (s, C_4); 31.95 (m, CH_2CH_2); 10.01 (s, C_5Me_5). ^{19}F NMR (C_6D_6): δ −138.7 (m, 2F); −139.3 (m, 2F). ^{31}P NMR (C_6D_6): δ 80.2 (s, dppe). ES-MS (positive ion, MeOH, *m/z*): 858, $[M+H]^+$; 635, $[Ru(dppe)Cp^*]^+$.

4.3.5. Ru(C≡CC≡CC$_{10}$F$_7$-2)(dppe)Cp* (**5**)

Similarly, from Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.07 mmol) and $C_{10}F_8$ (22 mg, 0.07 mmol) was obtained Ru(C≡CC≡CC$_{10}$F$_7$-2)(dppe)Cp* **5** as an orange powder (24 mg, 35%). *Anal.* Calc. for $C_{50}H_{39}F_7P_2Ru$: C, 64.17; H, 4.20. Found: C, 64.19; H, 4.19%. IR cm^{-1}/: *ν*(C≡C) 2138m, 2008m; *ν*(CF) 1651m, 1574m, 1470m, 1455m, 1403m, 1263m, 1197m, 1095m, 1026m, 949m, 805m, 744m, 697m. ^{1}H NMR (C_6D_6): δ 7.54–6.89 (m, 20H, Ph); 2.62, 1.78 (2m, 2 × 2H, PCH_2CH_2P); 1.56 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): δ 133.94–127.75 (m, Ph); 126.56 (s, C_1); 95.93 (s, C_2); 94.06 [t, ^2J(CP) 2 Hz, C_5Me_5]; 89.49 (s, C_3); 75.48 (s, C_4); 30.25 (m, CH_2CH_2); 10.17 (s, C_5Me_5). ^{19}F NMR (C_6D_6): δ −150.2 [t, ^3J(FF) = 19 Hz, 1F], −151.3 [t, ^3J(FF) = 20 Hz, 1F], −157.3 [dt, ^3J(FF) = 18 Hz, ^4J(FF) = 8 Hz, 1F], −161.0 [dt, ^3J(FF) = 18 Hz, $^4J_{(FF)}$ = 58 Hz, 1F], −163.0 [dt, ^3J(FF) = 18 Hz, ^4J(FF) = 65 Hz, 1F]. ^{31}P NMR (C_6D_6): δ 80.7 (s, dppe). ES-MS (+ve ion, MeOH, *m/z*): 937, M^+; 969, $[M+MeOH]^+$; 635, $[Ru(dppe)Cp^*]^+$.

4.3.6. [1,3-{Cp*(dppe)RuC≡C}$_2${μ-C$_4$H(C$_6$F$_5$)$_2$-2,4}]BF$_4$ (**6**)

To a solution of Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* (31 mg, 0.04 mmol) in THF (15 mL) was added $HBF_4{\cdot}OEt_2$ (6 μL, 0.04 mmol) and the mixture was stirred at r.t. for 16 h. The solvent was removed and the blue residue was dissolved in minimum amount of CH_2Cl_2 and was added to hexane with rapid stirring. The resulting precipitate was collected on a sintered funnel and washed with hexane to afford [1,3-{Cp*(dppe)RuC≡C}$_2${μ-C$_4$H(C$_6$F$_5$)$_2$-2,4}]BF$_4$ **6** as a bright blue powder (23 mg, 84%). *Anal.* Calc. ($C_{92}H_{79}BF_{14}P_4Ru_2$): C, 61.73; H, 4.45; *M* (cation), 1699. Found: C, 61.50; H, 4.38%. IR/cm^{-1}: *ν*(CH) 2924m, *ν*(C≡C) 1965m, 1897m; *ν*(CF) 1573m, 1500m, 1435m, 1397m, 1264m, 1158m, 1089m, 876m, 746m, 697m. ^{1}H NMR (C_6D_6): δ 7.42–6.89 (m, 40H, Ph); 2.14, 2.11 (2m, 2 × 4H, PCH_2); 2.02 (s, 1H, H); 1.70 (s, 30H, Cp*). ^{13}C NMR ($CDCl_3$): δ 320.72 (s, C_1); 201.55 (s, C_2); 132.59–127.36 (m, Ph); 116.7 (s, C_3); 102.07 (s, C_4); 97.77 (s, C_5Me_5); 29.37 (m, CH_2CH_2); 9.27 (s, C_5Me_5). ^{19}F NMR ($CDCl_3$): δ -158.1 (m, 2F, *m*-F); −164.0 (m, 2F, *m*-F); −176.9 [t, ^3J(FF) = 22 Hz, 1F, *p*-F]; −172.3 [t, ^3J(FF) = 22 Hz, 1F, *p*-F]; −184.0 (m, 2F, *o*-F); −185.5 (m, 2F, *o*-F). ^{31}P NMR (C_6D_6): δ 81.0 (s, dppe). ES-MS (MeOH, *m/z*): 1700, $[M-H]^+$; 635, $[Ru(dppe)Cp^*]^+$.

4.3.7. Ru{C≡CC[=C(CN)$_2$]C(C$_6$F$_5$)=C(CN)$_2$}(dppe)Cp* (**7**)

To a suspension of Ru(C≡CC≡CC$_6$F$_5$)(dppe)Cp* (31 mg, 0.04 mmol) in benzene (15 mL) was added TCNE (5 mg, 0.04 mmol) resulting in an immediate colour change from yellow to green. The mixture was stirred at r.t for 7 h. The solvent was removed and the residue was extracted in minimum CH_2Cl_2 and purified by preparative t.l.c. plates using 1:1 CH_2Cl_2/Et_2O as eluant to give a green band containing Ru{C≡CC[=C(CN)$_2$]C(C$_6$F$_5$)=C(CN)$_2$}(dppe)Cp* **7** (41 mg, 97%). *Anal.* Calc. for $C_{52}H_{39}F_5N_4P_2Ru$: C, 63.79; H, 4.02; N, 5.73. Found: C, 63.43; H, 4.51; N, 5.41%. IR/cm^{-1}): *ν*(CN) 2211m; *ν*(C≡C) 1964m; *ν*(CF) 1573m, 1521m, 1455m, 1262m, 1096m, 966m, 802m, 743m, 697m. ^{1}H NMR ($CDCl_3$): δ 7.45–7.15 (m, 20H, Ph); 2.78, 2.23 (2m, 2 × 2H, PCH_2); 1.53 (s, 15H, Cp*). ^{13}C NMR ($CDCl_3$): δ 154.01 (s, C_1); 139.14 (s, C_2); 132.88–128.29 (m, Ph); 116.53, 116.33 (2 × s, 2 × CN); 111.30, 110.62 (2 × s, 2 × CN); 92.81 (s, C_3); 97.37 [t, ^2J(CP) 2 Hz, C_5Me_5]; 78.91 (s, C_4); 29.99 (m, CH_2CH_2); 9.95 (s, C_5Me_5). ^{19}F NMR ($CDCl_3$): δ −159.8 (m, 2F, *m*-F); −168.9 [t, ^3J(FF) = 22 Hz, 1F,

Table 3
Crystal data and refinement details.

Complex	1	2	3	4
Formula	$C_{46}H_{39}F_5P_2Ru$	$C_{47}H_{42}F_4OP_2Ru$	$C_{47}H_{39}F_4NP_2Ru.C_6H_6$	$C_{50}H_{39}F_7P_2Ru$
MW	849.83	861.82	934.91	935.82
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	29.275(2)	11.653(1)	13.011(3)	10.0040(3)
b (Å)	15.0289(10)	12.314(1)	13.059(3)	12.4220(5)
c (Å)	22.2046(10)	29.680(5)	15.493(2)	18.1524(6)
α (°)		100.29(1)	106.22(1)	85.737(3)
β (°)	127.934(8)	93.22(1)	91.64(3)	79.806(3)
γ (°)		105.582(7)	119.58(2)	69.074(3)
V (Å^3)	7705	4012	2154	2074
ρ_c	1.465	1.427	1.441	1.499
Z	8	4	2	2
μ (Mo Kα) (mm^{-1})	0.55	0.53	0.49	0.52
$T_{min/max}$	0.89	0.97	0.97	0.72
Crystal dimensions (mm^3)	0.32 × 0.10 × 0.07	0.32 × 0.21 × 0.08	0.28 × 0.15 × 0.14	0.23 × 0.14 × 0.065
$2\theta_{max}$ (°)	57	63	63	69
N_{tot}	43789	123031	67484	43907
N (R_{int})	8963 (0.071)	25526 (0.074)	13861 (0.040)	16507 (0.048)
N_o	4018	10374	10029	9601
R_1	0.044	0.060	0.031	0.045
wR_2 (a)	0.100 (0.049)	0.166 (0.078)	0.074 (0.040)	0.096 (0.042)

p-F]; −179.8 (m, 2F, *o*-F). ^{31}P NMR ($CDCl_3$): δ 81.1 (s, dppe). ES-MS (MeOH+NaOMe, *m/z*): 1001, $[M+Na]^+$; 635, $[Ru(dppe)Cp^*]^+$.

4.4. Structure determinations

Full spheres of diffraction data were measured at ca 100 K using a CCD area-detector instrument. 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 considered "observed". All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å. In the full-matrix least squares refinements on F^2, anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included following a riding model. Neutral atom complex scattering factors were used; computation used the SHELXL 97 program [35] [weights: $(\sigma^2(F^2) + (aP)^2)^{-1}$ $(P = (F_o^2 + 2F_c^2)/3)$]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement envelopes and hydrogen atoms with arbitrary radii of 0.1 Å, as well as numbering schemes) and in Tables 2 and 3).

4.5. Variata

1. All aromatic substituents (including Cp*) were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement for the Cp* component, 0.757(3) and complement for the pendants of P(1) and 0.685(3) and complement for the pendants of P(2) and the fluoroaromatic group.

2. In both molecules of the asymmetric unit, the C_6F_4O and CH_3 groups were modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement. The disorder detracts from the definition of the OMe groups and their assignment rests on the chemistry.

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Appendix A. Supplementary material

CCDC 687428, 687429, 687430, 687431 contain the supplementary crystallographic data for this paper. 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.2010.03.017.

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