

Trimetallic complexes containing 1,1'-Rc'(C≡C)₂ units [Rc' = ruthenocene-1,1'-diyl, Ru(η-C₅H₄-)₂]

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Abstract

Reactions between 1,1'-(Me₃SiC≡C)₂Rc' [Rc' = ruthenocene-1,1'-diyl, Ru(η-C₅H₄-)₂] and RuCl(PP)Cp' in the presence of KF gave 1,1'-(Cp(PP)RuC≡C)₂Rc' [Cp' = Cp, PP = PPh₃ **1**, P(*m*-tol)₃ **2**, dppe **3**, dppf **4**; Cp' = Cp*, PP = dppe **5**]. Compounds **1** and **2** react with tene to give two diastereomers **a/b** of the allylic (vinylcarbene) complexes **6** and **7**, while methylation of **5** gave the bis-vinylidene [1,1'-(Cp*(dppe)Ru=C=CMe)₂Rc'](BPh₄)₂ (**8**). The X-ray structures of **4**, **6b** and **8** have been determined. Cyclic voltammograms indicate that there is some electronic communication between the ruthenium end-groups through the Rc' centre.
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1. Introduction

Complexes containing redox-active transition metal end-groups linked by carbon chains have attracted much attention because of their possible use as models for molecular wires [1,2]. End-capping of the carbon chain with ferrocenyl groups has also been investigated, an early study being of the complexes Fc(C≡C)_nW(CO)₃Cp (*n* = 1–4) in which lengthening the carbon chain results in an increase in the oxidation potential of the ferrocene centre [3]. A combination of the decreased electron donor ability of the longer carbon chains and an increase in electron transfer from the ferrocene group to the chain was considered to be responsible for these features.

Several reports describing the syntheses and redox activity of bis(ferrocenylethynyl)metal derivatives have also appeared, the first examples of which were *trans*-Pt(C≡CFc)₂(PR₃)₂ [4] and *trans*-Ru(C≡CFc)₂(dppx)₂ (*x* = *m* [5–7], *e* [8]). Some polynuclear complexes, including

trans-Pt₂(μ-dppm)₂(C≡CFc)₂, [Cu₃(μ-dppm)₃(μ₃-C≡CFc)₂]⁺ [9] and *trans*-Ru₂(μ-Y-dmba)₄{(C≡C)_mFc}{(C≡C)_nFc} [Y-dmba = (MeN)₂C₆H₄Y, Y = H, OMe; *m*, *n* = 1, 2] [10] have also been studied. In most of these, medium to strong electronic coupling between the two Fc nuclei has been noted.

When the carbon chains are end-capped with a redox-active group, such as Ru(PP)Cp' [PP = (PPh₃)₂, dppe, dppf; Cp' = Cp, Cp*], and a metallocene centre (Mc = Fc, Rc), electrochemical and spectroscopic studies of the complexes McC≡CRu(PP)Cp' found there to be a considerable interaction between the two end-caps, mediated by the carbon chain [11,12]. The radical cation obtained by one-electron oxidation has some delocalised character. More recently, we described some complexes in which two metal-ethynyl substituents are bridged by the ferrocene-1,1'-diyl group and extensive electrochemical and spectroscopic (IR, UV–Vis–near IR, Mössbauer) measurements supported the conclusion that the ferrocene-1,1'-diyl moiety acts as an insulator when inserted into the C₄ chain [12]. This contrasts with the situation found for {Ru(PP)Cp'}₂(μ-C≡CC≡C) [13].

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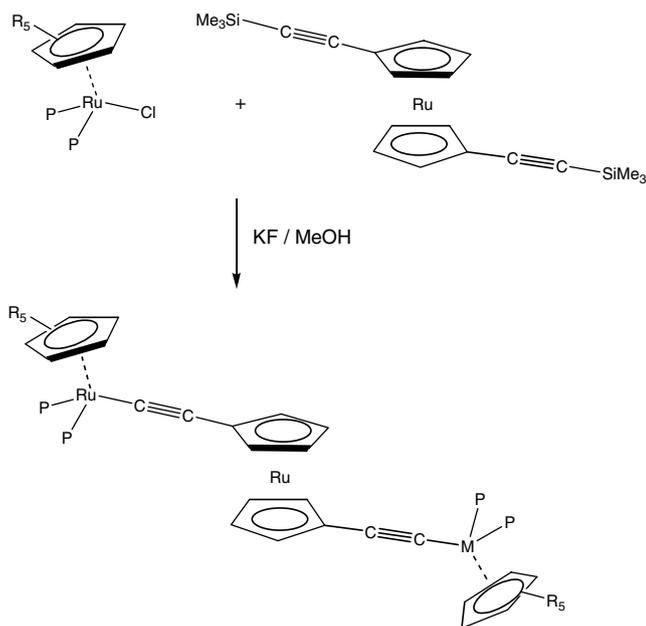
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In the case of ruthenocene complexes, Sato and coworkers [14] have found two reversible one-electron oxidation waves for complexes $RcC\equiv CRu(PP)Cp'$ [$PP = (PPh_3)_2$, $dppe$; $Cp = Cp$, Cp^*] and that the second oxidation is followed by unusual structural rearrangements leading to vinylidene or allenylidene cations. In the case of $Rc^{\#}C\equiv CRu(PPh_3)_2Cp$ [$Rc^{\#} = Cp^*Ru(\eta-C_5H_4-)$], the vinylidene cation $[Rc^{\#}CH=C=Ru(PPh_3)_2Cp]^+$ was formed after removal of one electron (the source of the proton was not identified). Similarly, complexes containing $Cp'Ru(\eta-C_5H_4C\equiv C-)$ ($Cp' = Cp$, Cp^*) and $CpRu(\eta-C_5Me_4C\equiv C-)$ ligands have been found to undergo two oxidation processes followed by a structural rearrangement [15]. It was therefore of interest to investigate derivatives with ruthenocene-1,1'-diyl groups bridging two redox-active end-groups. This paper describes the syntheses and some properties of compounds of this type.

2. Results and discussion

Several complexes containing various $-C\equiv CRu(PP)Cp'$ [$PP = (PPh_3)_2$, $dppm$, $dppe$, $dppf$; $Cp = Cp$, Cp^*] groups attached to a ruthenocene-1,1'-diyl bridge were made by the metalla-desilylation reaction described earlier [16] (Scheme 1).

Thus, reactions of $1,1'-(Me_3SiC\equiv C)_2Rc$ with $RuCl(PP)Cp'$ gave $1,1'-\{Cp(Ph_3P)_2RuC\equiv C\}_2Rc'$ (**1**; 86%), $1,1'-\{Cp([m\text{-tol}]_3P)_2RuC\equiv C\}_2Rc'$ (**2**; 86%), $1,1'-\{Cp(dppe)RuC\equiv C\}_2Rc'$ (**3**; 39%), $1,1'-\{Cp^*(dppe)_2RuC\equiv C\}_2Rc'$ (**4**; 47%), and $1,1'-\{Cp(dppf)RuC\equiv C\}_2Rc'$ (**5**; 75%), as yellow solids. The PPh_3 complex has been made



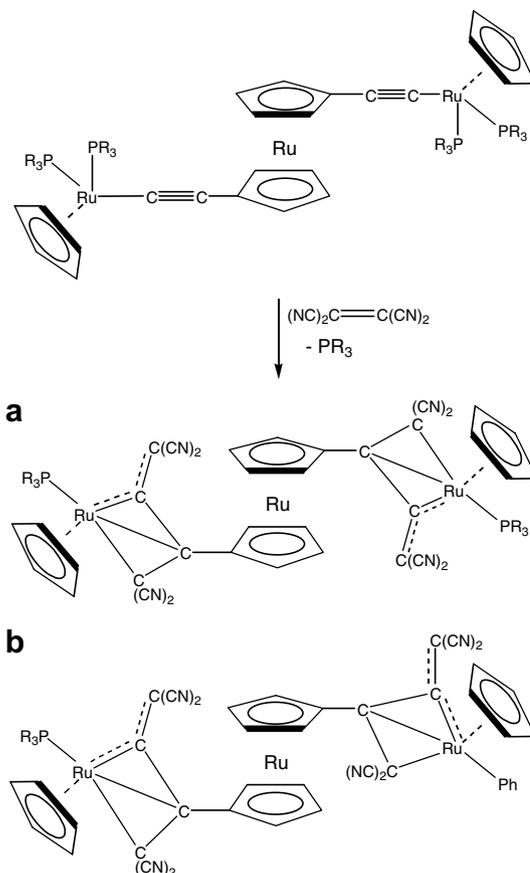
R = H, PP = $(PPh_3)_2$ **1**; $\{P(m\text{-tol})_3\}_2$ **2**; $dppe$ **3**; $dppf$ **4**
 R = Me, PP = $dppe$ **5**

Scheme 1.

previously from $HC\equiv CRc$ and $RuCl(PPh_3)_2Cp$ [14] and the identity of the present product was confirmed by comparison with the reported material. These compounds were characterised by an elemental microanalysis and by limited spectroscopic studies. Their IR spectra contained $\nu(C\equiv C)$ absorptions between 2074 and 2110 cm^{-1} and the 1H NMR spectra contained singlet resonances for the $RuCp$ groups between δ 4.36 and 4.58, or at δ 1.65 for the Cp^*Me resonance in **4**. The C_5H_4 protons gave rise to two unresolved multiplets between δ 4.09 and 4.54, and 4.38 and 5.12; in **5**, the overlap of the $Fe-$ and $Ru-C_5H_4$ signals gave four multiplets between δ 3.77 and 5.93. Electrospray mass spectra (ES MS) contained M^+ or $[M + Na]^+$ ions, together with $[Ru(PP)Cp']^+$ in some cases, as detailed in Section 4. The overall geometry of these complexes was confirmed with the single-crystal X-ray structural determination of **4** (see below).

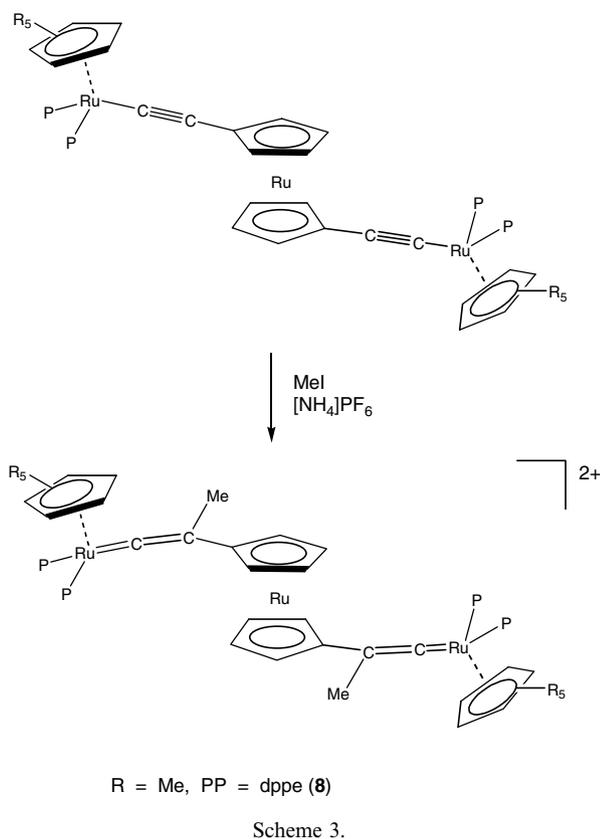
The reactions of **1** and **2** with the electron-deficient alkene $C_2(CN)_4$ (tcne) afforded orange bis-adducts, which were characterised as the dienylyls **6** (42%) and **7** (44%) (Scheme 2).

As found for the analogous ferrocene complexes [12], these were obtained as mixtures of diastereomers (63/37 for **6a/b**, 36/64 for **7a/b**), which could be converted to the



R = Ph **6**, $m\text{-tol}$ **7**

Scheme 2.



single isomers **b** by heating in refluxing benzene overnight. The ^{13}C NMR spectrum of **6b** (major isomer) contained resonances at δ 6.74, 64.65, 67.94, 74.96, 75.03, 77.33 (four singlets for the Ru–C₅H₄ groups), 85.04, 85.98, 91.85 (Ru–Cp), 110.85, 115.59, 119.29, 119.49 (four CN singlets), the phenyl multiplets between δ 128 and 134, and a downfield signal at δ 215.59 (Ru–C_z). These resonances are similar to those found for the ferrocene analogue and have been

assigned similarly. The molecular structure of **6b** has been determined and is described below.

Methylation of **4** with MeI in the presence of Na[BPh₄] resulted in formation of the bis-vinylidene complex [1,1'-{Cp*(dppe)Ru=C=CMe}₂Rc']₂(BPh₄)₂ (**8**) as a pink solid in 89% yield (Scheme 3).

This complex is characterised by ^1H NMR resonances at δ 1.52 (Cp* and Me, overlapping) and 3.63, 4.08 (C₅H₄), as well as the usual dppe CH₂ and Ph signals, and in the ^{13}C NMR spectrum by resonances at δ 10.12 and 102.49 (Cp* Me and ring C), 12.06 (Me), and the downfield C_z triplet at δ 347.08 [*J*(CP) 16.7 Hz]. Other resonances from the Rc' moiety are assigned in Section 4.

2.1. Molecular structures

Plots of single molecules of **4**, **6b** and the cation in **8** (which is isomorphous with the ferrocene analogue described earlier [12]) are shown in Figs. 1–3, with selected bond parameters collected in Table 1.

In **4**, molecule 2 of **6b**, and **8**, the molecule is disposed about a crystallographic inversion centre; in **6b**, there is a further molecule, devoid of crystallographic symmetry. The structures are similar to their ferrocene analogues and geometrical differences are limited to the expected differences which result from replacing Fe by Ru in the metallocene. Thus the Ru(PP)Cp' moieties have the usual pseudo-octahedral geometries [Ru–P, 2.268, 2.277(1) **4**; 2.376, 2.387(2) **6b**; 2.300, 2.317(1) **8**; Ru–C(cp), (av.) 2.26(2) **4**, 2.22(1) **6b**, 2.29(2) (Cp*) **8**; Ru–C(1), 2.019(5) **4**, 1.862(5) **8** Å] with C(1)–C(2) 1.220(7) in **4** and 1.322(7) Å in **8**. In the bridging Rc' group, the Ru–C distances (Δ) range between 2.17(1) and 2.20(2) Å, which may be compared with those in the ferrocene analogues [2.03–2.05 Å] and reflect the difference in atomic radii between the two metals [Fe = 1.26, Ru = 1.34 Å] [17]. Interestingly, the average Ru–C(Cp') distances in the

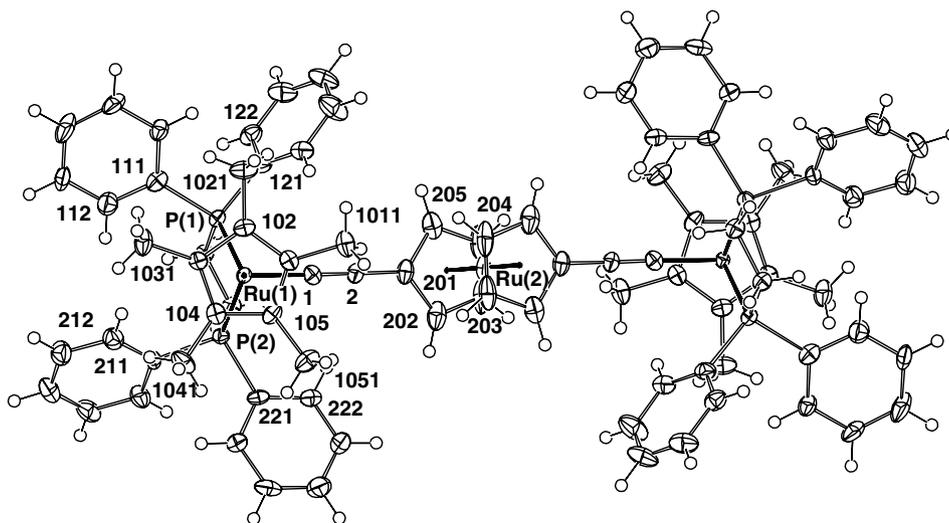


Fig. 1. Projection of an individual molecule of 1,1'-{Cp*(dppe)Ru≡C}₂Rc' **4**.

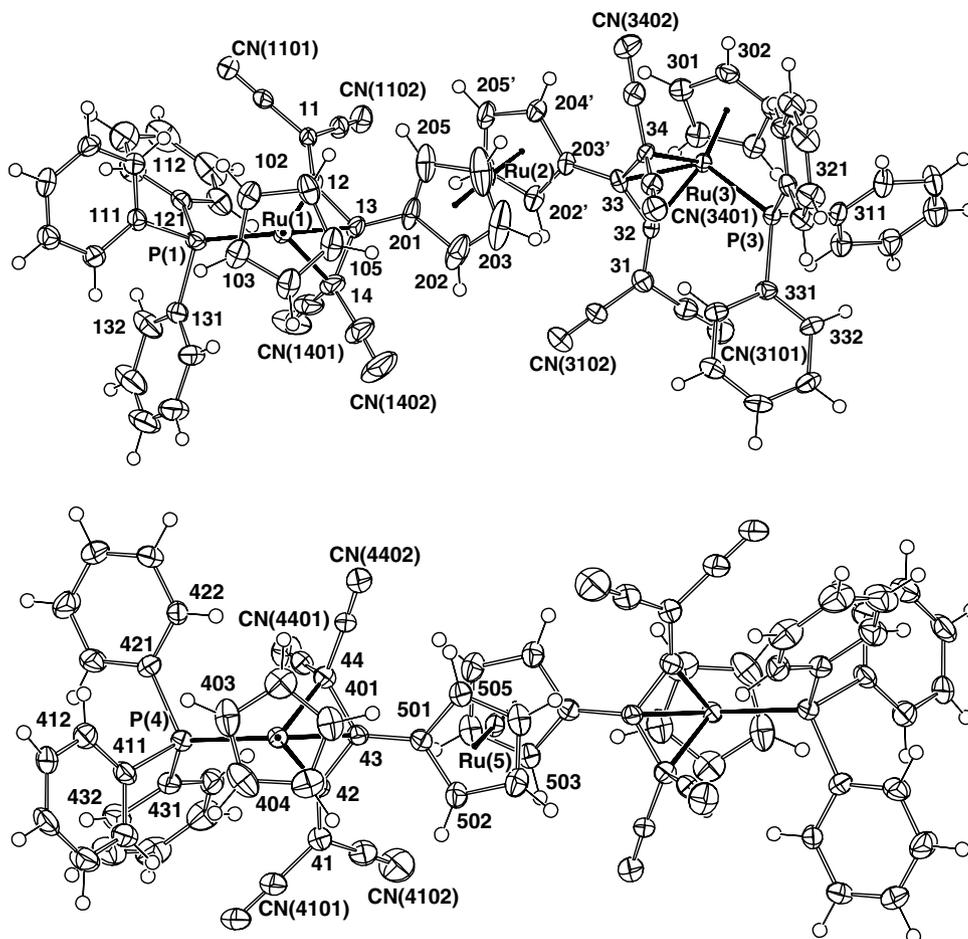


Fig. 2. Projections of the two molecules (the second centrosymmetric) of $1,1'-(\text{Cp}(\text{dppe})\text{Ru}[\eta^3\text{-C}(\text{CN})_2\text{CC}=\text{C}(\text{CN})_2])_2\text{Rc}'$ **6b**.

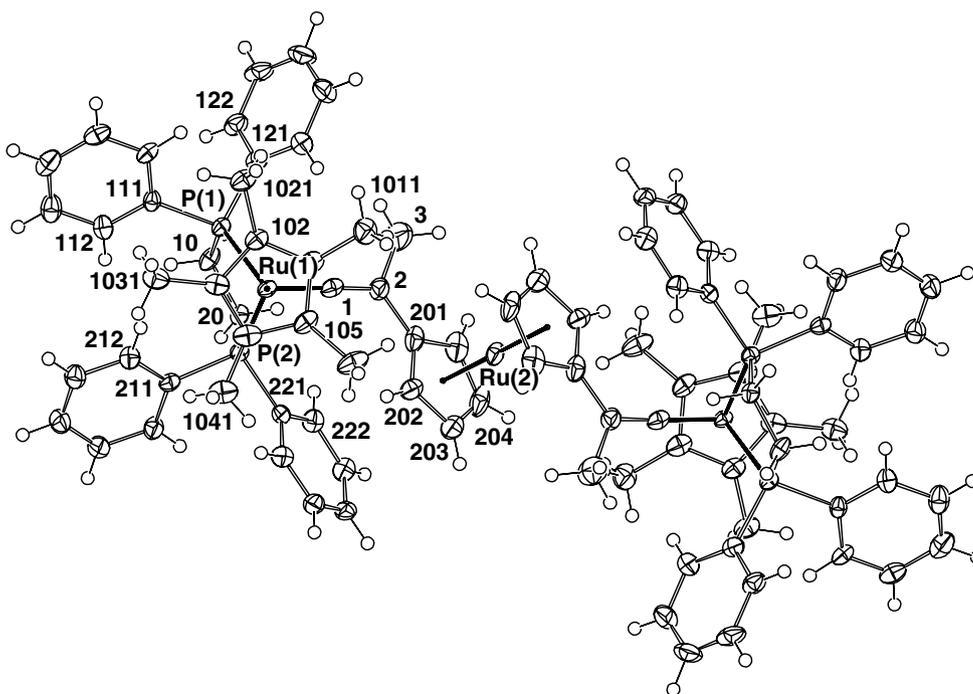


Fig. 3. Projection of the cation of $[1,1'-(\text{Cp}^*(\text{dppe})\text{Ru}=\text{C}=\text{CMe})_2\text{Rc}'](\text{BPh}_4)_2$ **8**.

Table 1
Selected bond distances (Å) and angles (°)

| Complex | 4 | 6b | 8 |
|--------------------|----------------|------------------------------------------------------|------------------|
| Bond distances (Å) | | | |
| Ru(1)–P(1) | 2.277(1) | 2.376(2), 2.387(1) 2.387(1) | 2.317(1) |
| Ru(1)–P(2) | 2.268(1) | | 2.300(1) |
| Ru(1)–C(cp) | 2.242–2.278(4) | 2.189–2.249(6), 2.197–2.248(5), 2.190–2.274(6) | 2.265–2.315(5) |
| (av.) | 2.26(2) | 2.21(3), 2.22(2), 2.22(3) | 2.29(2) |
| Ru(1)–C(1) | 2.019(5) | 1.988(5), 1.975(4), 1.981(5) [C(n2)] | 1.862(5) |
| Ru(1)–C(2) | | 2.130(5), 2.123(5), 2.117(5) [C(n3)] | |
| Ru(1)–C(3) | | 2.210(5), 2.179(4), 2.174(5) [C(n4)] | |
| C(1)–C(2) | 1.220(7) | 1.348(7), 1.353(7), 1.351(7) | 1.322(7) |
| C(2)–C(3) | | 1.439(7), 1.416(7), 1.431(7) | 1.522(9) |
| C(3)–C(4) | | 1.492(9), 1.480(7), 1.469(7) | |
| C(2)–C(201) | 1.438(7) | 1.463(9), 1.478(7), 1.467(7) ^a | 1.472(8) |
| Ru(2)–C(cp) | 2.182–2.219(6) | 2.149–2.196(5), 2.159–2.209(5) ^b | 2.161–2.190(6) |
| (av.) | 2.195(15) | 2.169(14), 2.18(2) | 2.175(11) |
| Bond angles (°) | | | |
| P(1)–Ru(1)–P(2) | 83.17(4) | | 82.15(4) |
| P(1)–Ru(1)–C(1) | 84.8(1) | | 93.0(2) |
| P(1)–Ru(1)–C(n2) | | 91.2(2), 90.6(2), 92.6(2) ^c | |
| P(1)–Ru(1)–C(n3) | | 116.2(2), 114.8(1), 117.7(1) ^c | |
| P(1)–Ru(1)–C(n4) | | 97.0(2), 96.0(1), 97.7(1) ^c | |
| P(2)–Ru(1)–C(1) | 83.9(1) | | 82.2(2) |
| Ru(1)–C(1)–C(2) | 175.3(4) | | 176.9(4) |
| Ru(1)–C(n2)–C(n1) | | 147.3(4), 145.5(4), 147.4(4) | |
| Ru(1)–C(n2)–C(n3) | | 75.0(3), 75.5(3), 74.8(3) | |
| Ru(1)–C(n3)–C(n01) | | 122.5(4), 129.1(4), 127.7(3) ^d | |
| Ru(1)–C(n4)–C(n3) | | 67.0(3), 67.9(3), 67.9(3) | |
| C(1)–C(2)–C(201) | 178.1(4) | | 123.7(5) |
| C(3)–C(2)–C(201) | | | 117.2(5) |
| C(n1)–C(n2)–C(n3) | | 137.5(4), 138.1(5), 137.3(5) | 119.0(5) |
| C(n2)–C(n3)–C(n01) | | 121.8(4), 121.8(4), 123.9(4) | [C(1)–C(2)–C(3)] |
| C(n4)–C(n3)–C(n01) | | 125.4(5), 126.1(4), 124.9(4) | |

For **6b**, C(14)–C(1401, 1302), C(31)–C(3101, 3102), C(41)–C(4101, 4102) are 1.41(1), 1.46(1); 1.445(8), 1.426(7); 1.439(8), 1.422(9) Å.

^a Values for C(13)–C(201), C(33)–C(203'), C(43)–C(501).

^b Values for Ru(2), Ru(5).

^c Values for $n = 1, 3, 4$.

^d Values for Ru(1)–C(13)–C(201), Ru(3)–C(33)–C(203'), Ru(4)–C(43)–C(501).

substituents are longer than those in the Rc' groups, probably because of increased steric hindrance caused by the phosphine ligands.

In **4** and **8**, the linear Ru–C(1)–C(2) moieties [angles at C(1,2) 175.3, 178.1(4)°] are bridged by the Rc' group and are necessarily at 180° to one another. In **6b**, the two

Table 2
Electrochemical data

| Complex [M] | E_1 | E_2 | $\Delta E_{1/2}$ | $K_C(0/+1/+2)$ | E_3 | E_4 |
|-----------------------------------------------------|-------|-------|------------------|-------------------|--------------------|--------------------|
| Ru(PPh ₃) ₂ Cp | +0.18 | +0.44 | 0.26 | 2.5×10^4 | +0.61 | +0.75 |
| Ru(dppe)Cp | +0.16 | +0.30 | 0.14 | 2.3×10^2 | +0.66 | +1.21 ^a |
| Ru(dppe)Cp* | +0.02 | +0.27 | 0.25 | 1.7×10^4 | +0.59 | +1.16 ^a |
| Ru[P(<i>m</i> -tol) ₃] ₂ Cp | +0.12 | +0.36 | 0.24 | 1.1×10^4 | +0.69 | |
| Ru(dppf)Cp | +0.27 | +0.52 | 0.25 | 1.7×10^4 | +0.77 ^b | |

Measured as 1 mM solutions in CH₂Cl₂ containing 0.5 M [NBu₄]BF₄ at 100 mV s⁻¹, referenced to internal FeCp₂/[FeCp₂]⁺ = 0.46 V.

^a Peak potential of a fully non-reversible wave.

^b Peak potential of a quasi-reversible wave.

substituents in molecule 1 form an angle of -155.8° about the C(0)–Ru–C(0') axis.

2.2. Electrochemistry

We have studied the electrochemistry of these complexes briefly, but as found for the analogous ferrocene derivatives, there is little evidence for electronic communication between the electron-rich Ru(PP)Cp' groups through the ruthenocene nucleus, insofar as no resolution of the oxidation waves of these groups was found. Generally, the previous study by Sato and coworkers showed the presence of irreversible 2–e processes, although reversible 1–e processes were found if Na[B{C₆H₃(CF₃)₂-3,5}₄] was used as supporting electrolyte [14]. Potentials for related mononuclear complexes were determined as follows: Ru(C≡CPh)(PPh₃)₂Cp, +0.05; Ru(C≡CPh)(PPh₃)₂Cp*, –0.26 (both 1–e); R_cC≡CH, +0.58 V (2–e, irrev.).

In the present study (Table 2), the expected increased ease of oxidation is found as the ligands associated with the Ru–PR₃ centre change in order of increasing electron donor power: dppf < PPh₃ < dppe < P(*m*-tol)₃, and when Cp is changed for Cp* ($E_1 + 0.16$ and $+0.02$ V, respectively). All complexes show three oxidation steps, while the PPh₃ and dppe complexes show four oxidation steps. It is likely that two of these steps are associated with the ruthenocene centre and, interestingly, all processes involve only one electron, in contrast to the 2–e oxidation found for ruthenocene itself. It has not been possible to disentangle the processes at the different centres and, while comproportionation constants, K_C , can be calculated for the species involved in E_1 and E_2 , the small values (*ca.* 10^2 – 10^4) suggest that these are somewhat localised on the Ru–PR₃ and ruthenocene centres, respectively. In the case of the dppf complex, there is no extra wave that might be associated with the dppf ligand.

3. Conclusions

Reactions between 1,1'-(Me₃SiC≡C)₂Rc' and RuCl(PP)Cp' in the presence of KF have given several complexes containing redox-active Ru(PP)Cp' centres bridged by R_c'(C≡C–)₂ ligands. Electrochemical studies revealed that, as with the analogous ferrocene derivatives, there is

essentially no electronic communication between the end-groups. Conventional reactions with tcne and with MeI gave the corresponding tetracyanobutadienyl and vinylidene complexes, respectively.

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 cm²) coated with silica gel (Merck, 0.5 mm thick).

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. Electropray mass spectra (ES MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used [18].

Electrochemical samples (1 mM) were dissolved in CH₂Cl₂ containing 0.5 M [NBu₄]BF₄ as the supporting electrolyte. Cyclic voltammograms were recorded using a PAR model 263 apparatus, with a saturated calomel electrode and ferrocene as internal calibrant (FeCp₂/[FeCp₂]⁺ = 0.46 V). The cell contained a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes. Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.3. Reagents

$\text{RuCl}(\text{PP})\text{Cp}'$ (PP = $(\text{PPh}_3)_2$, $\text{Cp}' = \text{Cp}$ [19]; PP = dppe, $\text{Cp}' = \text{Cp}^*$ [20]) were obtained as previously described; tcn (Aldrich) was sublimed before use.

4.3.1. Preparation of $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$

This compound was made in 57% yield from $1,1'$ -diacetyl ruthenocene by the same procedure as the ferrocene analogue [21]. ^1H NMR: δ 0.16 (s, 18H, SiMe_3), 4.53–4.55, 4.79–4.81 ($2 \times \text{m}$, $2 \times 2\text{H}$, C_5H_4).

4.3.2. Reactions of $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$

- (a) *With $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$.* A degassed solution of $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ (403 mg, 0.555 mmol), $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$ (108 mg, 0.251 mmol) and KF (51 mg, 0.88 mmol) in MeOH/thf (30/10 ml) was heated at reflux point for 16 h. After cooling to r.t., the resulting precipitate was collected and washed successively with MeOH, Et_2O and hexane to give pure $1,1'$ - $\{\text{Cp}(\text{PPh}_3)_2\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ (**1**) (240 mg, 58%) as a yellow solid. Anal. Calc. ($\text{C}_{96}\text{H}_{78}\text{P}_4\text{Ru}_3$): C, 69.51; H, 4.74; M, 1658. Found: C, 69.62; H, 4.81%. IR (nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2074s; other bands at 1587w, 1572w. ^1H NMR (C_6D_6): δ 4.25, 5.00 ($2 \times \text{m}$, $2 \times 4\text{H}$, C_5H_4 of Rc'), 4.42 (s, 10H, Ru–Cp), 7.00, 7.73 ($2 \times \text{m}$, 40 + 20 H, Ph). ^{31}P NMR: δ 52.2. ES MS (MeOH, m/z): 1658, M^+ ; 690, $[\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$.
- (b) *With $\text{RuCl}\{\text{P}(m\text{-tol})_3\}_2\text{Cp}$.* Similarly, from $\text{RuCl}\{\text{P}(m\text{-tol})_3\}_2\text{Cp}$ (171 mg, 0.232 mmol), $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$ (49 mg, 0.116 mmol) and KF (12 mg, 0.207 mmol) and refluxing for 18 h, was obtained $1,1'$ - $\{\text{Cp}[\text{P}(m\text{-tol})_3]_2\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ (**2**) (182 mg, 86%) as a yellow solid. Anal. Calc. ($\text{C}_{108}\text{H}_{102}\text{P}_4\text{Ru}_3$): C, 71.00; H, 5.63; M, 1827. Found: C, 70.93; H, 5.61%. IR (nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2081s; other band at 1591w. ^1H NMR (C_6D_6): δ 2.05 (s, 36H, Me), 4.54, 5.12 ($2 \times \text{m}$, $2 \times 4\text{H}$, C_5H_4 of Rc'), 4.58 (s, 10H, Ru–Cp), 6.84–7.71 (m, 48H, tol). ^{31}P NMR: δ 51.8. ES MS (MeOH, m/z): 1827, M^+ .
- (c) *With $\text{RuCl}(\text{dppe})\text{Cp}$.* Similarly, from $\text{RuCl}(\text{dppe})\text{Cp}$ (153 mg, 0.255 mmol), $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$ (54 mg, 0.126 mmol) and KF (22 mg, 0.38 mmol) in MeOH (35 ml), was obtained pure $1,1'$ - $\{\text{Cp}(\text{dppe})\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ (**3**) (70 mg, 39%) as a yellow solid. Anal. Calc. ($\text{C}_{76}\text{H}_{66}\text{P}_4\text{Ru}_3$): C, 64.90; H, 4.73; M, 1407. Found: C, 64.79; H, 4.62%. IR (nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2111m, 2093s; other bands at 1586w, 1572w. ^1H NMR (C_6D_6): δ 1.95–2.15, 2.55–2.75 ($2 \times \text{m}$, $2 \times 4\text{H}$, CH_2 of dppe), 4.09, 4.38 ($2 \times \text{m}$, $2 \times 4\text{H}$, C_5H_4 of Rc'), 6.96–6.97, 7.19–7.31, 7.99–8.04 ($3 \times \text{m}$, 12 + 20 + 8H, Ph). ^{31}P NMR: δ 86.9. ES MS (MeOH, m/z): 1430, $[\text{M} + \text{Na}]^+$.
- (d) *With $\text{RuCl}(\text{dppe})\text{Cp}^*$.* Similarly, from $\text{RuCl}(\text{dppe})\text{Cp}^*$ (289 mg, 0.431 mmol), $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$ (77 mg, 0.18 mmol) and KF (27 mg, 0.47 mmol) in

MeOH (35 ml) pure $1,1'$ - $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ (**4**) (130 mg, 47%) was isolated as a yellow crystalline solid. Anal. Calc. ($\text{C}_{86}\text{H}_{86}\text{P}_4\text{Ru}_3$): C, 66.78; H, 5.60; M, 1547. Found: C, 66.70; H, 5.64%. IR (nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2099w, 2077s; other bands at 1585w, 1572w. ^1H NMR (C_6D_6): δ 1.65 (s, 30H, Cp^*), 1.80–2.00, 2.60–2.80 ($2 \times \text{m}$, $2 \times 4\text{H}$, CH_2 of dppe), 4.48, 4.75 ($2 \times \text{m}$, $2 \times 4\text{H}$, C_5H_4 of Rc'), 7.06–7.33, 7.92–8.01 ($2 \times \text{m}$, 32 + 8H, Ph). ^{31}P NMR: δ 80.8. ES MS (MeOH, m/z): 1547, M^+ ; 914, $[\text{M} + \text{H} - \text{Ru}(\text{dppe})\text{Cp}^*]^+$.

- (e) *With $\text{RuCl}(\text{dppf})\text{Cp}$.* A degassed solution of $\text{RuCl}(\text{dppf})\text{Cp}$ (143 mg, 0.176 mmol), $1,1'-(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{Rc}'$ (41 mg, 0.095 mmol) and KF (22 mg, 0.38 mmol) in MeOH (35 ml) was heated at reflux point for 24 h. After cooling to r.t., the resulting precipitate was collected and washed with MeOH and hexane to give pure $1,1'$ - $\{\text{Cp}(\text{dppf})\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ (**5**) (113 mg, 75%) as a bright yellow solid. Anal. Calc. ($\text{C}_{92}\text{H}_{74}\text{Fe}_2\text{P}_4\text{Ru}_3$): C, 64.30; H, 4.34; M, 1718. Found: C, 63.98; H, 4.42%. IR (nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2105w, 2084s; other bands at 1585w, 1571w. ^1H NMR (C_6D_6): δ 3.77, 4.29, 4.61, 5.93 ($4 \times \text{m}$, 4 + 8 + 4 + 4 H, Ru– C_5H_4), 4.36 (s, 10H, Ru–Cp), 5.23 (m, 4H, Fe– C_5H_4), 7.53, 8.18 ($2 \times \text{m}$, 10 + 8H, Ph) The remaining 22 Ph protons are under the C_6H_6 peak at δ 7.16. ^{31}P NMR: δ 56.1. ES MS (MeOH, m/z): 1718, M^+ .

4.3.3. Reaction between $1,1'$ - $\{\text{Cp}(\text{PPh}_3)_2\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ and tcn

Tetracyanoethene (17 mg, 0.13 mmol) was added to a stirred suspension of $1,1'$ - $\{\text{Cp}(\text{PPh}_3)_2\text{RuC}\equiv\text{C}\}_2\text{Rc}'$ (93 mg, 0.56 mmol) in dry CH_2Cl_2 (20 ml) and the mixture was stirred for 2 d. Removal of solvent under vacuum and purification of the residue by preparative t.l.c. (acetone– CH_2Cl_2 1/99) afforded a mixture of diastereomers (63 a/37 b) of the bis-adduct **6** (33 mg, 42%) as an orange solid. Conversion of **6b** to **6a** was achieved by heating a solution in refluxing benzene overnight. Anal. Calc. ($\text{C}_{72}\text{H}_{48}\text{N}_8\text{P}_2\text{Ru}_3$): C, 62.20; H, 3.48; N, 8.06; M, 1390. Found: C, 62.21; H, 3.39; N, 8.09%. IR (nujol, cm^{-1}): $\nu(\text{CN})$ 2214s; other band at 1616m. ES MS (MeOH, m/z): 1413, $[\text{M} + \text{Na}]^+$. NMR data: Minor isomer **6a**: ^1H NMR: δ 4.61 (s, 10H, Ru–Cp), 5.12, 5.16, 5.34, 6.01 ($4 \times \text{m}$, $4 \times 2\text{H}$, C_5H_4), 7.35–7.53 (m, 30H, Ph). ^{13}C NMR: δ 7.00 (d, J 6.0 Hz), 64.59 (d, J 2.3 Hz), 70.32, 72.36, 75.36, 77.20 ($4 \times \text{s}$, C_5H_4), 84.50 (d, J 8.3 Hz), 86.11, 91.85 (Ru–Cp), 111.03 (d, J 2.5 Hz, CN), 115.56, 119.18, 119.39 ($3 \times \text{s}$, CN), 128.47–128.62, 131.25, 134.20–134.34 ($3 \times \text{m}$, Ph), 216.47 (d, J 13.4 Hz). ^{31}P NMR: δ 40.5. Major isomer **6b**: ^1H NMR: δ 4.59 (s, Ru–Cp), 5.17, 5.18, 5.27, 5.84 ($4 \times \text{m}$, $4 \times 2\text{H}$, C_5H_4), 7.35–7.53 (m, 30H, Ph). ^{13}C NMR: δ 6.74 (d, J 5.1 Hz), 64.65 (d, J 2.3 Hz), 67.94, 74.66, 75.03, 77.33 ($4 \times \text{s}$, C_5H_4), 85.04 (d, J 8.3 Hz), 85.98, 91.85 (Ru–Cp), 110.85 (d, J 2.7 Hz), 115.59,

Table 3
Crystal data and refinement details

| Complex | 4 | 6b | 8 |
|-------------------------------------------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| Formula | C ₈₆ H ₈₆ P ₄ Ru ₃ · 2C ₄ H ₈ O | C ₇₂ H ₄₈ N ₈ P ₂ Ru ₃ · 1.33CH ₂ Cl ₂ | C ₈₈ H ₉₂ P ₄ Ru ₃ ²⁺ · 2C ₂₄ H ₂₀ B ⁻ |
| MW | 1691.05 | 1503.67 | 2215.39 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> (Å) | 12.027(3) | 12.102(1) | 16.243(2) |
| <i>b</i> (Å) | 12.106(3) | 16.019(1) | 18.275(2) |
| <i>c</i> (Å) | 15.637(4) | 24.952(2) | 18.655(2) |
| α (°) | 72.100(4) | 76.698(2) | |
| β (°) | 67.750(4) | 89.976(2) | 100.115(2) |
| γ (°) | 89.977(4) | 88.308(2) | |
| <i>V</i> (Å ³) | 1987 | 4706 | 5451 |
| ρ_c (g cm ⁻³) | 1.41 ₃ | 1.59 ₂ | 1.34 ₉ |
| <i>Z</i> | 1 | 3 | 2 |
| 2 θ_{\max} (°) | 58 | 60 | 53 |
| μ (Mo K α) (mm ⁻¹) | 0.69 | 0.93 | 0.52 |
| <i>T</i> _{min/max} | | 0.85 | 0.91 |
| Crystal dimensions (mm ³) | 0.12 × 0.12 × 0.04 | 0.24 × 0.08 × 0.07 | 0.38 × 0.17 × 0.13 |
| <i>N</i> _{tot} | 18152 | 72613 | 40785 |
| <i>N</i> (<i>R</i> _{int}) | 9342 (0.038) | 26997 (0.043) | 11060 (0.098) |
| <i>N</i> _o | 7424 | 19904 | 8019 |
| <i>R</i> | 0.067 | 0.060 | 0.054 |
| <i>R</i> _w (<i>n</i> _w) | 0.14 (20) | 0.12 (62) | 0.12 (7.2) |

119.29, 119.49 (3 × s, CN), 128.47–128.62, 131.25, 134.20–134.34 (3 × m, Ph), 215.59 (d, *J* 13.4 Hz). ³¹P NMR: δ 40.5.

4.3.4. Reaction between 1,1'-{Cp[P(*m*-tol)₃]₂RuC≡C}₂Rc' and tcne

The reaction was carried out as for the PPh₃ complex, using 1,1'-{Cp[P(*m*-tol)₃]₂RuC≡C}₂Rc' (100 mg, 0.055 mmol) and tcne (17 mg, 0.137 mmol) to give **7** as a 36/64 mixture of diastereomers as an orange solid (36 mg, 44%). Anal. Calc. (C₇₈H₆₀N₈P₂Ru₃): C, 65.23; H, 3.91; N, 7.25; *M*, 1475. Found: C, 65.23; H, 3.98; N, 7.28%. IR (nujol, cm⁻¹): ν (CN) 2213s; other band at 1614m. ES MS (MeOH + NaOMe, *m/z*): 1498, [M + Na]⁺. NMR data: Minor isomer **7a**: ¹H NMR: δ 2.44 (s, 36H, Me), 4.63 (s, 10H, Ru–Cp), 5.23, 5.32, 5.92 (3 × m, 4 + 2 + 2H, C₅H₄), 7.18–7.41 (m, 48H, tol). ³¹P NMR: δ 39.5. Major isomer **7b**: ¹H NMR: δ 1.30 (s, 36H, Me), 4.65 (s, Ru–Cp), 5.08, 5.23, 5.39, 6.09 (4 × m, 4 × 2H, C₅H₄), 7.18–7.41 (m, 48H, tol). ³¹P NMR: δ 39.4.

4.3.5. Methylation of 1,1'-{Cp*(*dppe*)RuC≡C}₂Rc'

Iodomethane (10 drops, excess) was added to a solution of 1,1'-{Cp*(*dppe*)RuC≡C}₂Rc' (56 mg, 0.036 mmol) and Na[BPh₄] (50 mg, 0.15 mmol) in thf (20 ml) and the mixture was heated at reflux point for 16 h. After cooling, solvent was removed under vacuum and the residue was purified by column chromatography (acetone–CH₂Cl₂ 1/4) to give 1,1'-{[Cp*(*dppe*)RuCMe=C=]₂Rc'}(BPh₄)₂ (**8**) (71 mg, 89%) as a pink solid. Anal. Calc. (C₁₃₆H₁₃₂B₂P₄Ru₃): C, 73.74; H, 6.01; *M* (cation), 1578. Found: C, 73.74; H, 6.09%. IR (nujol, cm⁻¹): 1648m, 1616w, 1580w. ¹H NMR (C₆D₆): δ 1.52 (br s, 36H, Cp* + Me), 2.00–2.50, (br m, 8H, CH₂ of *dppe*), 3.63, 4.08 (2 × m, 2 × 4H, C₅H₄ of Rc'), 6.72–6.93, 7.13–7.48 (2 × m, 32 + 48H, Ph). ¹³C NMR: δ

10.12 (C₅Me₅), 12.06 (Me), 69.83, 70.30 (2 × s, Ru–C₅H₄), 77.21 (Rc' *ipso*), 102.48, 115.46, 125.37–125.40, 127.12–127.21, 128.43–128.50, 131.9–131.74, 132.56–133.18, 134.18–134.94, 136.20 (6 × m, Ph), 163.17–165.14 (m), 347.08 [t, *J*(CP) 16.7 Hz, C_x]. ³¹P NMR: δ 74.7. ES MS (MeOH, *m/z*): 789, M²⁺.

4.3.6. Structure determinations

Full spheres of diffraction data were measured at ca. 153 K using a Bruker AXS 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 σ (*F*) being used in the full-matrix least squares refinements. All data were measured using monochromatic Mo K α radiation, λ = 0.71073 Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H being included, constrained at estimates. Conventional residuals *R*, *R*_w on *F*² are quoted [weights: ($\sigma^2(F^2) + n_w F^2$)⁻¹]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [22].

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 3.

4.4. Variata

4. Displacement parameters on the solvent molecules were high, O being tentatively assigned from the refinement behaviour.

6b. One of the chloroform molecules was modelled as disordered over a pair of sites, occupancies refining to 0.650(8) and complement.

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Appendix A. Supplementary material

CCDC 619541, 619542 and 619543 contain the supplementary crystallographic data for the compounds **4**, **6** and **8**. This material can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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