

Reactions of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{L}_2)\text{Cp}^*$ ($\text{L}_2 = \text{dppm}, \text{dppe}$) with tetracyanoethene: cycloaddition, formation of monodentate dppm and dppmO complexes and migration of CN to ruthenium

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Abstract

The reaction of $\text{C}_2(\text{CN})_4$ with $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ in THF has given the anticipated tetracyanobuta-1,3-dien-2-yl complex $\text{Ru}\{\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm})\text{Cp}^*$ (**3**). In benzene, η^3 -cyano-enyl complexes $\text{Ru}\{\eta^3\text{-C}[\text{C}(\text{CN})_2]\text{CPhCC}(\text{CN})_2\}(\text{L})\text{Cp}^*$ ($\text{L} = \text{dppm-}P$ (**4**) or dppmO (**5**)) are formed, the latter by adventitious oxidation. On warming, complex **3** rearranges to the cyanoruthenium-ylid complex $\text{Ru}(\text{CN})\{\text{C}(\text{CN})=\text{C}[\text{CPh}=\text{C}(\text{CN})_2]\text{PPh}_2\text{CH}_2\text{PPh}_2\}\text{Cp}^*$ (**6**). A possible reaction sequence, involving a zwitterionic intermediate such as $\text{Ru}(\delta^-)(\text{CN})\{\text{C}(\text{CN})\text{C}(\delta^+)\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm-}P)\text{Cp}^*$ **D**, is discussed. Only the η^1 -dienyl complex **7** is obtained from $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$ and TCNE. © 2002 Published by Elsevier Science B.V.

Keywords: Ruthenium; Alkynyl; Cycloaddition; TCNE

1. Introduction

Reactions of transition metal σ -alkynyl complexes with electron-deficient cyanocarbon alkenes afford σ -cyclobutenyl (**A**, Scheme 1), σ -butadienyl (**B**) or η^3 -allylic complexes (**C**), according to the nature of the metal centre and its associated ligands [1]. Many studies of this chemistry have been carried out using the $\text{Ru}(\text{PR}_3)_2\text{Cp}$ system: if the two tertiary phosphines are present as a chelating diphosphine, then the last stage of the transformation of the adducts is precluded [1b]. Further reactions of the cyanocarbon ligand are rare, apparently being limited to hydrolysis or alcoholysis to give hydroxy- or alkoxy-imine ligands [2], or addition of a second ML_n group to one of the CN groups, sometimes with the formation of macrocyclic complexes [3].

We have recently described reactions of complexes containing the more electron-rich $\text{Ru}(\text{PPh}_3)_2\text{Cp}^*$ fragment, in which ready loss of one or both PPh_3 ligands occurs [4]. Isomerisation of the initial polycyanocarbon

ligand by CN migration is also found, while the electron-rich ruthenium centre allows coordination of a CN group in the η^2 mode. This paper describes a series of products which we have obtained from similar reactions of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PP})\text{Cp}^*$ ($\text{PP} = \text{dppm}$ **1**, dppe **2**), in which the dppm ligand (but not dppe) becomes monodentate and enters into further reaction with the cyanocarbon. Part of this work has been communicated previously [5].

2. Results

The complex $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ (**1**) was made in 80% yield by reaction of $\text{RuCl}(\text{dppm})\text{Cp}^*$ with $\text{HC}\equiv\text{CPh}$, using NaOEt in EtOH as the base. It was identified by elemental microanalysis and spectroscopically. The IR spectrum contains a strong $\nu(\text{C}\equiv\text{C})$ band at 2072 cm^{-1} and the $^1\text{H-NMR}$ spectrum contains a Cp^* triplet at δ 2.01 (by long-range coupling to phosphorus) with the dppm CH_2 and Ph resonances at δ 4.37 and between 6.94 and 7.83, respectively. The dppe analogue **2** has been described before [6].

The reaction between **1** and tetracyanoethene, $\text{C}_2(\text{CN})_4$ (TCNE), when carried out in a polar solvent

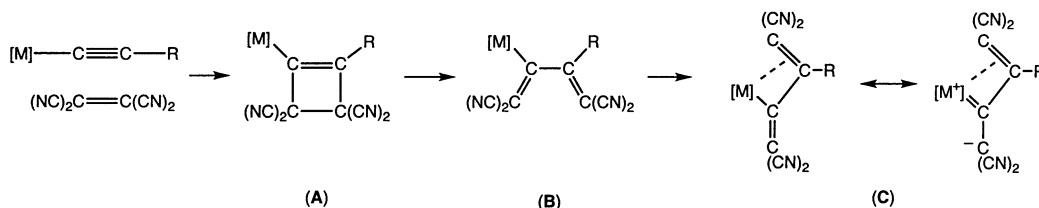
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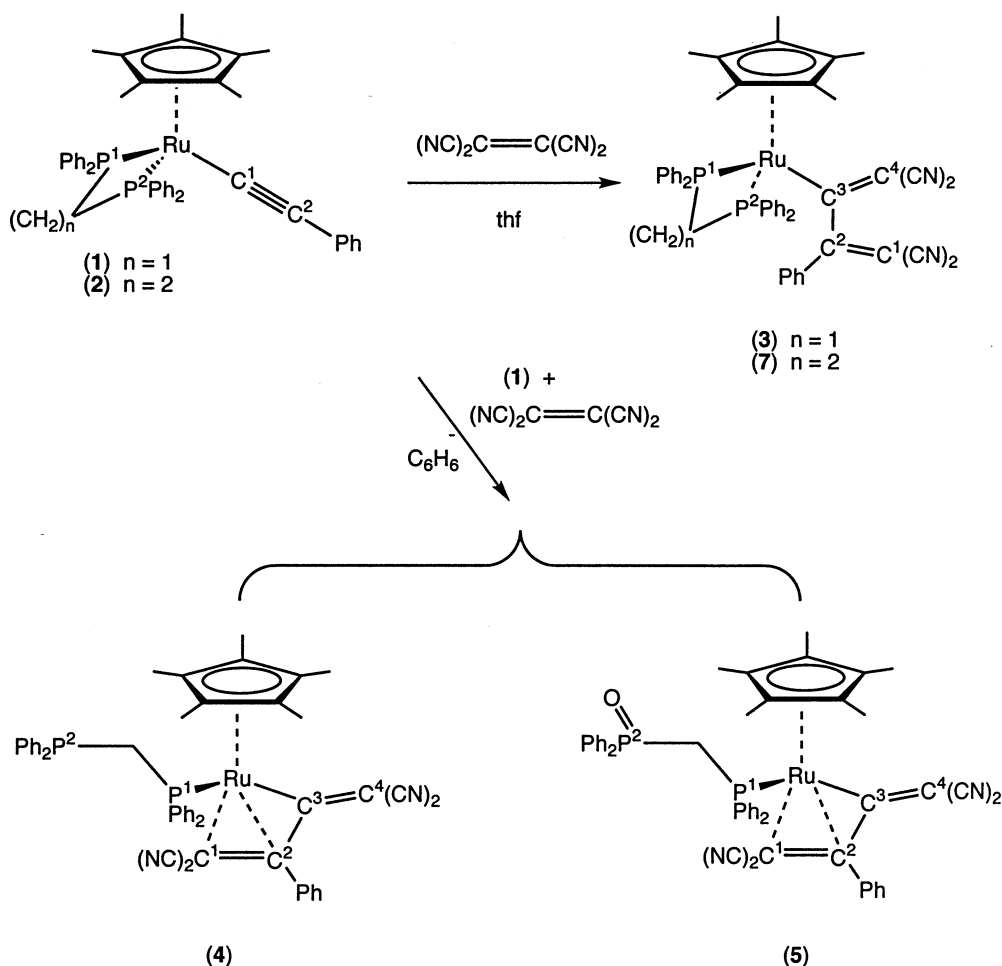
such as THF, gives a product mixture from which the anticipated butadienyl derivative $\text{Ru}\{\text{C}[\text{CPh}=\text{C}(\text{CN})_2]=\text{C}(\text{CN})_2\}(\text{dppm})\text{Cp}^*$ (**3**, Scheme 2) could be isolated as dark red crystals in 20% yield. The structure has been confirmed by a single-crystal X-ray determination (see below) and spectroscopic data are consistent with the solid state structure. The IR spectrum contains $\nu(\text{CN})$ at 2217 cm^{-1} and the electrospray (ES) mass spectrum of a solution containing NaOMe contains $[\text{M} + \text{Na}]^+$, $[\text{M} + \text{H}]^+$ and $[\text{M} - \text{CN}]^+$ ions. During purification by preparative TLC, we noticed that the second band changed colour, and in solution the change occurs too rapidly to allow the NMR spectrum to be obtained.

Eventually repeated TLC enabled pure samples of complexes **5** and **6** (see below) to be obtained, in 31 and 8% yields, respectively. The latter complex is also formed when solid **3** or its solutions are left standing in air or when **3** is adsorbed on silica gel.

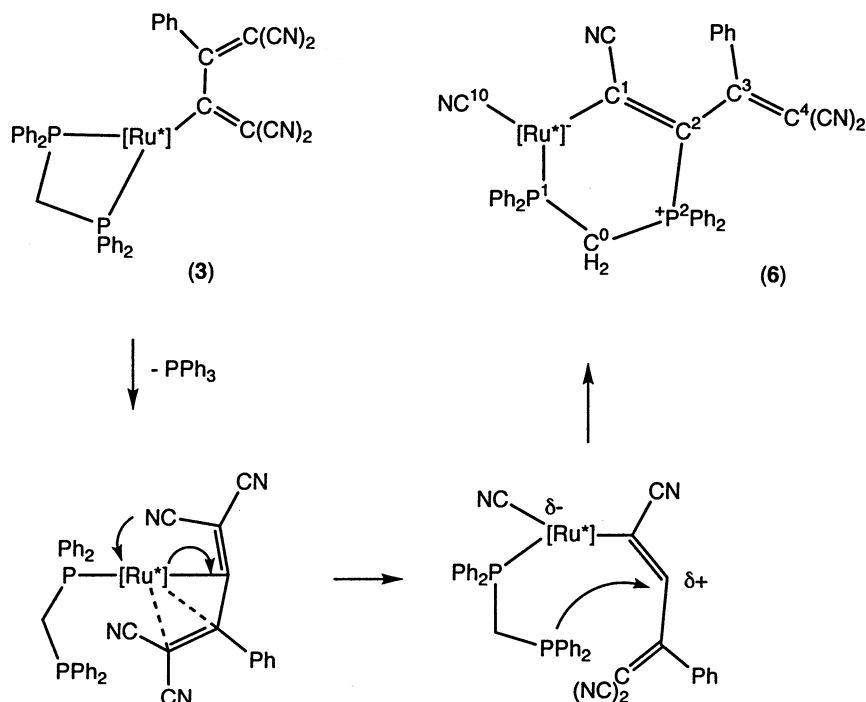
If the reaction between **1** and TCNE is carried out in benzene, two orange complexes identified as $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm-}P)\text{Cp}^*$ (**4**, 42%), containing monodentate dppm, and $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppmO})\text{Cp}^*$ (**5**, 2.2%), containing the mono-oxidised ligand $\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (dppmO), were isolated and identified by X-ray structure determinations. Complex **4** was also obtained from the reaction in THF



Scheme 1.



Scheme 2.



Scheme 3.

in 31% yield. The IR spectra of **4** and **5** contain $\nu(\text{CN})$ at 2217 and 2216 cm^{-1} , respectively, while that of **4** has $\nu(\text{PO})$ at 1200 cm^{-1} . The Me resonance is a doublet at δ 1.26 for **4**, indicating coupling to only one of the two ^{31}P nuclei, while for **5**, a singlet is found at δ 1.48. The dppm-CH₂ multiplets are at δ 3.26 (for **4**) and 3.38, 3.51 (for **5**). The ^{31}P -NMR spectra are informative, with two doublets at δ -18.5 and 39.1 for the free and coordinated PPh₂ groups in **4**, and at δ 26.0 and 41.9 for the P=O and P-Ru nuclei in **5**. The ES mass spectra contain $[\text{M} + \text{H}]^+$ and $[\text{M} - \text{dppm}]^+$ or $[\text{M} - \text{dppmO}]^+$ ions.

The smaller bite angle of the dppm ligand results in ring strain which is eased by ready dissociation of one of the P atoms from the ruthenium centre. This allows the cyanocarbon ligand to take up the familiar η^3 -allylic form, with its short Ru-C(2) distance which corresponds to a carbenic form or zwitterion. The monodentate dppm is air-sensitive, some of **4** being converted to **5** by addition of oxygen to the uncoordinated P atom to give the phosphine oxide.

As mentioned, complex **3** is very reactive, changing to purple during chromatography, upon standing in solution (CH_2Cl_2) or in the solid state in air. We found that the same product was formed, together with some intractable decomposition product, by heating **4** in refluxing benzene for 36 h. It could be isolated in 73% yield by preparative TLC as dark red crystals. These were shown to be the cyanoruthenium complex $\text{Ru}(\text{CN})\{\text{C}(\text{CN})=\text{C}[\text{CPh}=\text{C}(\text{CN})_2]\text{PPh}_2\text{CH}_2\text{PPh}_2\}\text{Cp}^*$ (**6**, Scheme 3), the structure of which has been reported

earlier [5]. The IR spectrum contains three $\nu(\text{CN})$ bands at 2218, 2157 and 2070 cm^{-1} , while the ES mass spectrum shows $[\text{M} + \text{H}]^+$ and $[\text{M} - \text{CN}]^+$ ions at m/z 851 and 824, respectively. The Me groups appear as a doublet at δ 1.60 in the ^1H -NMR spectrum and the CH₂ multiplets are unusually well separated at δ 3.24 and 5.40. A plethora of peaks in the ^{13}C -NMR spectrum includes those for the Cp* group at δ 9.42 and 99.90, the CH₂ group as a double doublet at δ 30.09, and three equal intensity singlets for the CN groups at δ 114.87, 116.14, 122.58. The carbon chain gives rise to singlets at δ 125.33 and 126.43 [C(3) and C(4), not assigned individually], that for C(2) being within the Ph multiplet between δ 127.92 and 135.85. The Ru-bonded C(1) and CN carbons are considerably deshielded at δ 153.22 and 179.96, respectively, and exhibit CP couplings of 18.86 and 19.16 Hz, respectively.

We have studied the effect of increasing the bite angle of the chelating diphosphine by examining similar reactions of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$ (**2**). The reaction of TCNE with **2** in THF gives the expected butadienyl derivative $\text{Ru}\{\text{C}[\text{CPh}=\text{C}(\text{CN})_2]=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ (**7**), which is stable in solution, no doubt a result of the increased stability of the five-membered chelate Ru(dppe) system. The identity of **7** was also confirmed by an X-ray structure determination: the ES mass spectrum has M^+ at m/z 865. The IR spectrum contained $\nu(\text{CN})$ bands at 2206 and 2198 cm^{-1} , while the ^1H -NMR spectrum has resonances for the Me groups at δ 0.96 and multiplets for the dppe-CH₂ groups at δ 2.00, 2.34 and 2.76. The ^{31}P -NMR spectrum contains only a doublet at δ 48.47.

2.1. Molecular structures

Plots of single molecules of **1**, **3–5** and **7** are shown

in Figs. 1–5, with selected bond parameters collected in Table 1. While **1** is a benzene hemi-solvate, the others were all modelled as variously solvated with

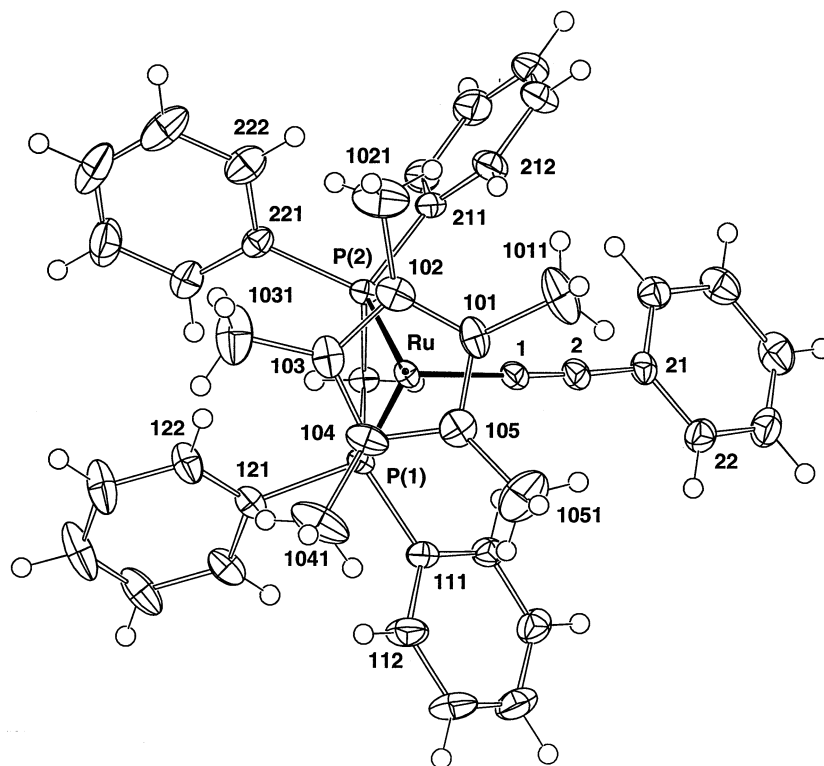


Fig. 1. Plot of a molecule of Ru(C≡CPh)(dppm)Cp* (**1**), showing atom numbering scheme.

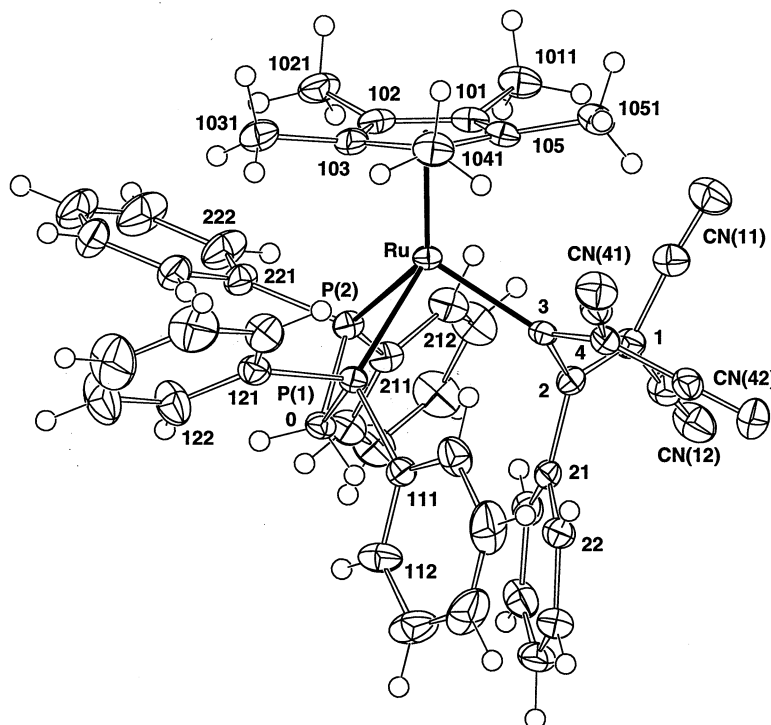


Fig. 2. Plot of a molecule of Ru{C[=C(CN)₂]CPh=C(CN)₂} (dppm)Cp* (**3**) showing atom numbering scheme.

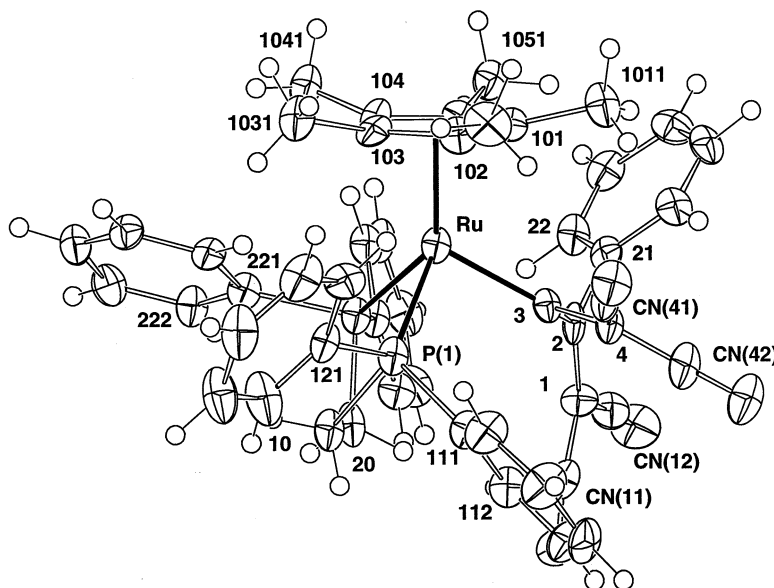


Fig. 3. Plot of a molecule of $\text{Ru}\{\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ (**7**) showing atom numbering scheme.

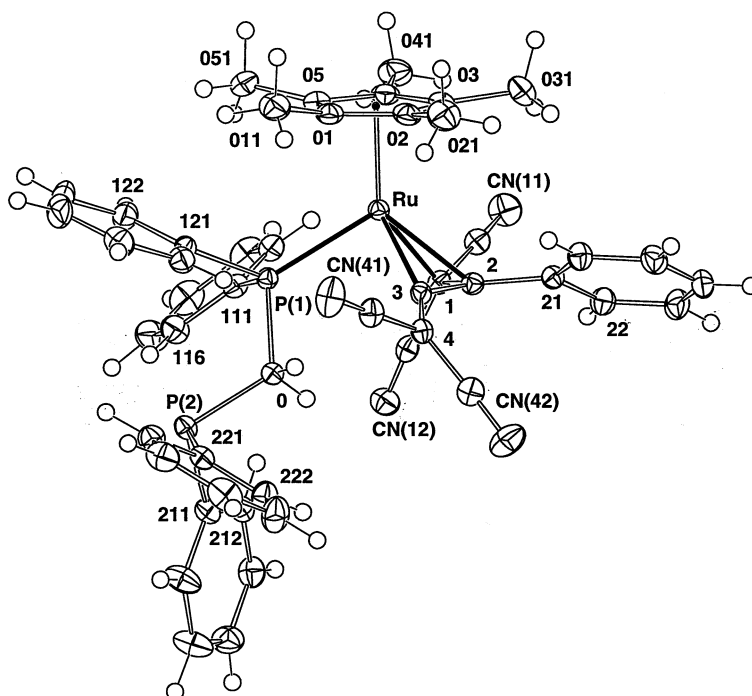


Fig. 4. Plot of a molecule of $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPhC}=\text{C}(\text{CN})_2\}(\text{dppm-}P)\text{Cp}^*$ (**4**) showing atom numbering scheme.

dichloromethane. Common to all are the Cp^* groups, which have average $\text{Ru}-\text{C}(\text{Cp}^*)$ distances between 2.25 and 2.30 Å, the ranges of individual values being between 2.214(2) and 2.326(2) Å. Comparison of the $\text{Ru}-\text{P}$ distances in **3** and **7** show the smaller bite angle of the dppm ligand [71.28(3) vs. 81.90(9) for dppe] has no effect on the $\text{Ru}-\text{P}$ distances [2.32(2) vs. 2.341(3) Å]. The increased ring strain in **3** is accommodated around the RuPCP ring, all intraring angles being noticeably smaller than those found in **7**.

The $\text{Ru}-\text{C}(\text{sp})$ distance in **1** [2.017(2) Å] is identical with that found in $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$, while the $\text{C}\equiv\text{C}$ separations are also experimentally the same [1.217(3) and 1.204(5) Å, respectively] [7]. The $\text{Ru}-\text{C}(\text{sp}^2)$ distances in **3** and **7** [2.106(2), 2.090(9) Å] are ca. 0.09 Å longer than the $\text{Ru}-\text{C}(\text{sp})$ separations, as expected. Average $\text{C}-\text{CN}$ and $\text{C}-\text{N}$ distances in all complexes are constant, at 1.44 and 1.14 Å, respectively.

In **4** and **5**, conversion of the butadienyl into the

η^3 -allylic ligand has occurred, with the dppm in **4** becoming monodentate. The cyanocarbon ligand has almost equal C–C distances within the coordinated C_3 unit, although the Ru–C distances are significantly different. The ' π -bonded' C(1)–C(2) fragments in **4** [5] are 2.206(2) [2.218(2)] and 2.175(2) Å [2.158(2) Å] distant from the metal, while the short Ru–C(3) distances (1.985(2) [1.983(2) Å]) are consistent with a degree of multiple bonding which can be rationalised in terms of a contribution from the zwitterionic form (C, Scheme 1).

Oxidation of the non-coordinated phosphorus centre in **6** has little effect on the molecular structure. Complexes **4** and **5** differ only by addition of an oxygen atom to P(2) in the latter [P(2)–O 1.489(1) Å]. Other distances and angles in the two complexes are similar except for the shortening of P(2)–C(0) in **5** [1.879(2) in **4** vs. 1.834(2) Å in **5**].

3. Discussion

While similar complexes containing Cp ligands have been found not to undergo further reaction, the same is not true for the Cp* derivatives. We have surmised that this increased reactivity is due to the increased electron density at the ruthenium centre, which in other examples has allowed the formation of η^2 -CN groups, as well as encouraging isomerisation by CN group migration [5]. We have previously suggested that a possible route to the cyano-ruthenium complexes might be migration of a CN group from a dicyanomethylene frag-

ment to the metal [5]. Concomitant cleavage of a Ru–C bond then generates an electron-deficient centre at C(2), as in **D** (Scheme 3). Isomerisation of the cyanocarbon occurs by migration of the CN group from the metal to C(2), the resulting vacant co-ordination site then being filled by an electron-donor ligand, such as an η^2 -CN group or a CN group from a second molecule of complex. A third type of reaction is that proposed here, whereby the free arm of the dppm ligand (as found in **4**) intramolecularly attacks C(2) to give ylid complex **6**, the cyano group remaining attached to the metal centre.

The smaller bite angle of the dppm ligand results in some degree of ring strain which is relieved by ready dissociation of one of the P atoms from the ruthenium centre. This allows the cyanocarbon ligand to take up the familiar η^3 -allylic form, with its short Ru–C(3) distance which corresponds to a carbenic form or zwitterion. Complex **4** with monodentate dppm is air-sensitive, being converted to the analogous dppmO derivative **5** on standing in air, by addition of oxygen to the uncoordinated phosphorus atom.

4. Conclusions

We have shown that the reactivity of σ -bonded cyanocarbon ligands is considerably enhanced when Cp is replaced by the more strongly electron-donating Cp* ligand. While not surprising, the resulting chemistry has revealed novel examples of C(sp²)–CN bond cleavage,

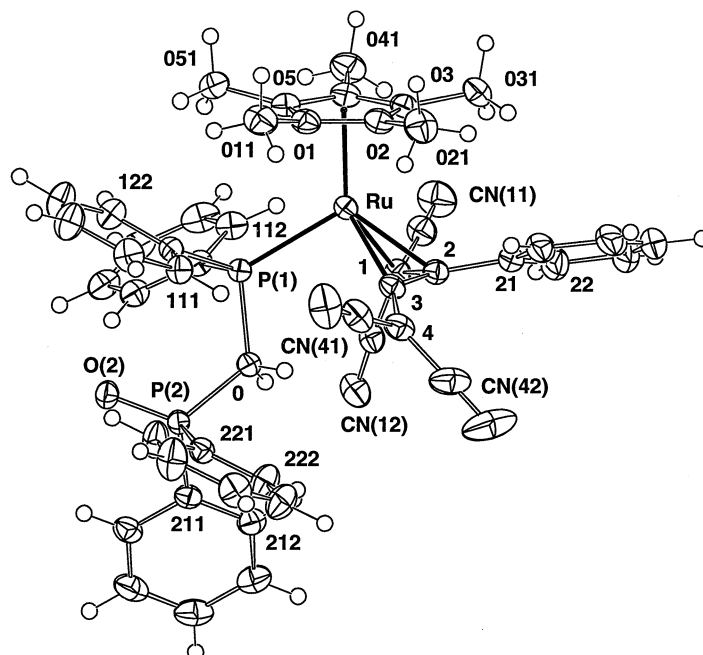


Fig. 5. Plot of a molecule of $Ru\{\eta^3-C(CN)_2CPhC=C(CN)_2\}(dppmO)Cp^*$ (**5**) showing atom numbering scheme.

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**, **3–5** and **7**

	1	3	4	5	7
<i>Bond lengths</i>					
Ru–P(1)	2.2679(8)	2.3356(7)	2.3939(6)	2.3935(6)	2.379(3)
Ru–P(2)	2.2735(6)	2.3071(6)	—	—	2.303(2)
Ru–C(Cp*)	2.220(4)–2.272(6)	2.255(3)–2.300(2)	2.214–2.308(2)	2.214–2.326(2)	2.23–2.32(1)
(av.)	2.25(2)	2.28(3)	2.26(4)	2.26(5)	2.30(4)
Ru–C(100)	1.89 ₂	1.91 ₈	1.89 ₉	1.90 ₅	1.93 ₇
Ru–C(1)	2.017(2)	—	2.206(2)	2.218(2)	—
Ru–C(2)	—	—	2.175(2)	2.158(2)	—
Ru–C(3)	—	2.106(2)	1.985(2)	1.983(2)	2.090(9)
C(1)–C(2)	1.217(3)	1.364(3)	1.473(2)	1.479(2)	1.37(1)
C(2)–C(3)	—	1.490(3)	1.427(2)	1.432(3)	1.51(1)
C(2)–C(21)	1.436(3)	1.491(4)	1.491(3)	1.489(3)	1.46(2)
C(3)–C(4)	—	1.377(3)	1.362(2)	1.360(3)	1.39(1)
C(1,4)–CN (range)	—	1.438–1.443(4)	1.433–1.455(2)	1.434–1.450(3)	1.42–1.47(1)
P(1)–C(0)	1.855(2)	1.845(2)	1.844(2)	1.851(2)	1.81(1) [C(10)]
P(2)–C(0)	1.850(3)	1.840(3)	1.879(2)	1.834(2)	1.865(9) [C(20)]
<i>Bond angles</i>					
C(100)–Ru–P(1)	137. ₈	133. ₆	120. ₅	119. ₆	130. ₃
C(100)–Ru–P(2)	139. ₃	125. ₅	—	—	126. ₄
C(100)–Ru–C(1)	—	—	132. ₆	133. ₃	—
C(100)–Ru–C(2)	—	—	129. ₆	127. ₂	—
C(100)–Ru–C(3)	—	123. ₁	135. ₅	133. ₉	120. ₁
P(1)–Ru–P(2)	71.28(3)	70.97(2)	—	—	81.90(9)
P(1)–Ru–C(1)	81.53(9)	—	92.38(5)	93.37(5)	—
P(1)–Ru–C(2)	—	—	109.91(5)	113.15(6)	—
P(1)–Ru–C(3)	—	89.27(7)	89.27(5)	91.45(6)	91.8(3)
P(2)–Ru–C(1)	80.04(7)	—	—	—	—
P(2)–Ru–C(3)	—	99.99(6)	—	—	95.3(3)
C(1)–Ru–C(3)	—	—	70.80(6)	70.20(8)	—
Ru–P(1)–C(0)	96.2(1)	95.61(8)	114.21(6)	114.12(6)	108.8(3) [C(20)]
Ru–P(2)–C(0)	96.11(7)	96.72(7)	—	—	109.6(3) [C(10)]
P(1)–C(0)–P(2)	91.2(1)	94.0(1)	119.7(1)	124.2(1)	—
Ru–C(1)–C(2)	175.2(2)	—	69.2(1)	68.1(1)	—
Ru–C(3)–C(4)	—	—	—	—	125.4(7)
C(1)–C(2)–C(3)	—	120.7(2)	114.1(1)	112.7(2)	127(1)
C(2)–C(3)–C(4)	—	110.7(2)	133.6(2)	133.4(2)	110.4(8)
C(21)–C(2)–C(1)	174.7(2)	117.9(2)	123.6(1)	124.3(2)	116.2(9)
C(21)–C(2)–C(3)	—	120.6(2)	122.3(1)	123.0(2)	116.7(9)
<i>Torsion/dihedral angles</i>					
C(1)–C(2)–C(3)–C(4)	—	–79.9(3)	141.5(2)	136.6(2)	–76(1)

In **1**, Cp* parameters refer to the major component; for all compounds C(100) is the Cp* ring centroid. Additional data: For **5**: P(2)–O(2) 1.489(1) Å; C(0)–P(2)–O(92) 117.61(9)°. For **7**: C(10)–C(20) 1.53(1) Å; P(1)–C(10)–C(20) 110.8(6), P(2)–C(20)–C(10) 108.0(7)°.

which may be related to the recently reported conversion (by an intramolecular oxidative addition reaction) of Ni(η^2 -NCPh)(dippe) to Ni(CN)(Ph)(dippe) [8]. With PPh₃ complexes, facile loss of one phosphorus ligand allows its replacement by an N-bonded cyanocarbon from a second molecule of complex. In the case of dppm, in contrast, the free phosphorus is tethered by the CH₂ group and is able to attack a positively-charged carbon of the alkenyl ligand to give **7**. The reactions described above and earlier provide a route for modifying cyanocarbon ligands attached to electron-rich transition metals.

5. Experimental

5.1. General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF254, 0.5 mm thickness).

5.1.1. Instrumentation

IR: Perkin–Elmer 1720X FTIR. NMR: Bruker CXP300 or ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Unless otherwise stated, spectra were recorded using solutions in CDCl_3 in 5 mm sample tubes. ES mass spectra: Finnegan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [9].

5.1.2. Reagents

The complexes $\text{RuCl}(\text{dppm})\text{Cp}^*$ [4] and $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$ [6] were obtained as previously described. TCNE (Aldrich) was sublimed before use.

5.1.3. Preparation of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ (**1**)

A solution of $\text{RuCl}(\text{dppm})\text{Cp}^*$ (140 mg, 0.2 mmol) and $\text{HC}\equiv\text{CPh}$ (65 mg, 0.6 mmol) in EtOH (15 ml) was heated at reflux point for 2 h. After cooling to room temperature (r.t.), a solution of NaOEt [from sodium (40 mg-atom) in EtOH (1 ml)] was added dropwise to the reaction mixture. Cooling in an ice-bath for 10 min resulted in deposition of a yellow precipitate, which was filtered and washed with cold EtOH to give $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ (**1**) (120 mg, 80%) as yellow crystals (benzene–hexane). Anal. Found: C, 70.83; H, 5.75. Calc. for $\text{C}_{43}\text{H}_{42}\text{P}_2\text{Ru}$: C, 71.55; H, 5.87%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2072s cm^{-1} . ^1H -NMR (C_6D_6): δ 2.01 [t, $^4J(\text{HP})$ 1.8, 15H, Cp^*], 4.37 (m, 2H, CH_2), 6.94–7.83 (m, 25H, Ph). ^{31}P -NMR (C_6D_6): δ 18.21 (s, dppm).

5.1.4. Reactions between $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ and

TCNE. (a) In THF

A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ (290 mg, 0.4 mmol) and TCNE (154 mg, 1.2 mmol) in THF (25 ml) was stirred overnight at r.t. After evaporation of solvent, the residue was extracted with CH_2Cl_2 and separated by preparative TLC (acetone–hexane 3/7) into two fractions.

The orange band (R_f 0.49) contained **5** (104.3 mg, 31%). A cherry-red band (R_f 0.40) gave dark red crystals (CH_2Cl_2 –MeOH) of $\text{Ru}\{\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm})\text{Cp}^*$ (**3**) (67.4 mg, 20%). IR (nujol): $\nu(\text{CN})$ 2217m, 2194m; other bands at 1575m, 1539m, 1471m, 1434s cm^{-1} . ES mass spectrum (MeOH containing NaOMe, m/z): 873, $[\text{M} + \text{Na}]^+$; 851, $[\text{M} + \text{H}]^+$; 824, $[\text{M} - \text{CN}]^+$.

During development, the second band above gradually developed dark purple steaks, which was further purified to give a dark purple band (R_f 0.17) which contained

$\text{Ru}(\text{CN})\{\text{C}(\text{CN})\text{C}[\text{CPh}=\text{C}(\text{CN})_2]\text{PPh}_2\text{CH}_2\text{PPh}_2\}\text{Cp}^*$ (**6**) (27.2 mg, 8%). Complex **6** is formed when solutions of **3** in CH_2Cl_2 are left to stand, when **3** is adsorbed on silica gel, or when solid **3** is kept in air (the latter process is accompanied by some decomposition).

5.1.5. (b) In benzene

TCNE (60 mg, 0.48 mmol) was added to a solution of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppm})\text{Cp}^*$ (170 mg, 0.24 mmol) in benzene (10 ml). After stirring overnight at r.t., the mixture had become dark brown with a black precipitate. The latter was filtered off, the filtrate was evaporated and the residue dissolved in CH_2Cl_2 and separated by preparative TLC (acetone–hexane 3/7) into two fractions.

Band 1 (R_f 0.49) gave orange crystals (CH_2Cl_2) of $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm-}P)\text{Cp}^*$ (**4**) (85 mg, 42.5%). Anal. Found: C, 68.80; H, 5.16; N, 6.75. Calc. for $\text{C}_{49}\text{H}_{42}\text{N}_4\text{P}_2\text{Ru}$: C, 69.25; H, 4.98; N, 6.59%; M , 850. IR (CH_2Cl_2): $\nu(\text{CN})$ 2217s; other bands at 1589m, 1572s, 1482m, 1434s, 1379m cm^{-1} . ^1H -NMR (CDCl_3): δ 1.26 [d, $^4J(\text{HP})$ 1.0, 15H, Cp^*], 3.26 (m, 2H, PCH_2), 6.99–8.19 (m, 25H, Ph). ^{31}P -NMR (CDCl_3): δ –18.50 [d, $J(\text{PP})$ 30.6, PPh_2], 39.11 [d, $J(\text{PP})$ 30.6, Ru– PPh_2]. ES mass spectrum (MeOH, m/z): 850, M^+ ; 466, $[\text{M} - \text{dppm}]^+$.

Band 2 (R_f 0.09) afforded orange crystals (CH_2Cl_2 –MeOH) of $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppmO})\text{Cp}^*$ (**5**) (4.5 mg, 2.2%). Found: C, 66.86; H, 4.88; N, 6.19. Calc. for $\text{C}_{49}\text{H}_{42}\text{N}_4\text{OP}_2\text{Ru}$: C, 67.89; H, 4.84; N, 6.47%; M , 866. IR (CH_2Cl_2): $\nu(\text{CN})$ 2216s, $\nu(\text{PO})$ 1200m; other bands at 1605m, 1571s, 1492m, 1437s, 1379m cm^{-1} . ^1H -NMR (CDCl_3): δ 1.48 (s, 15H, Cp^*), 3.38, 3.51 ($2 \times$ s, CH_2), 7.16–7.47 (m, 25H, Ph). ^{31}P -NMR (CDCl_3): δ 26.03 [d, $J(\text{PP})$ 31.9, $\text{P}(\text{O})$], 41.9 [d, $J(\text{PP})$ 31.9, Ru–P]. ES mass spectrum (MeOH containing NaOMe, m/z): 889, $[\text{M} + \text{Na}]^+$; 867, $[\text{M} + \text{H}]^+$; 466, $[\text{M} - \text{dppmO}]^+$.

5.1.6. Thermolysis of

$\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm-}P)\text{Cp}^*$ (**4**)

Only one product is formed if $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppm-}P)\text{Cp}^*$ (**4**) (75 mg, 0.09 mmol) is heated in refluxing benzene (7 ml) for 36 h. Purification by preparative TLC gave a dark purple band (R_f 0.17) which afforded dark red crystals (benzene–hexane) of $\text{Ru}(\text{CN})\{\text{C}(\text{CN})\text{C}[\text{CPh}=\text{C}(\text{CN})_2]\text{PPh}_2\text{CH}_2\text{PPh}_2\}\text{Cp}^*$ (**6**) (55 mg, 73%). Anal. Found: C, 68.06; H, 5.15; N, 6.03. Calc. for $\text{C}_{49}\text{H}_{42}\text{N}_4\text{P}_2\text{Ru}$: C, 69.25; H, 4.98; N, 6.59%; M , 850. IR (CH_2Cl_2): $\nu(\text{CN})$ 2218m, 2157w, 2070m; other bands at 1601s, 1478m, 1436s, 1302w cm^{-1} . ^1H -NMR (CDCl_3): δ 1.60 [d, $^4J(\text{HP})$ 1.6, 15H, Cp^*], 3.24, 5.40 ($2 \times$ m, $2 \times$ 1H, CH_2), 6.64–7.76 (m, 25H, Ph). ^{13}C -NMR (CDCl_3): δ 9.42 (s, Me), 30.09 [dd, $J(\text{CP})$ 48, 37, CH_2], 99.90 (s, Cp^*), 114.87 [s, C(5)N], 116.14 [s, C(6)N], 122.58 [s, C(8)N], 125.33 [s, C(3)], 126.43 [s, C(4)], 127.92–135.85 (m, Ph + C(2)], 153.22 [d, $J(\text{CP})$ 18.86, C(1)], 179.96 [d, $J(\text{CP})$ 19.16, C(7)N]. ^{31}P -NMR (CDCl_3): δ 13.87 (s, P–C), 58.61 (s, Ru–P). ES mass spectrum (MeOH, m/z): 851, $[\text{M} + \text{H}]^+$; 824, $[\text{M} - \text{CN}]^+$; 621, $[\text{Ru}(\text{dppm})\text{Cp}^*]^+$.

5.1.7. Reaction of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$ (**2**) with TCNE

A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$ (100 mg, 0.136 mmol) and TCNE (52 mg, 0.406 mmol) in THF (10 ml) was stirred at r.t. for 4 h when all starting ruthenium complex had been consumed. Removal of THF, extraction of the residue with CH_2Cl_2 and separation by preparative TLC (acetone–hexane 3/7) gave a bright yellow baseline, which could not be investigated further, and a red band (R_f 0.38). The latter afforded dark red crystals (CH_2Cl_2 –MeOH) of $\text{Ru}\{\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ (**7**) (60.3 mg, 51%). Found: C, 66.39; H, 5.02; N, 6.03. Calc. for $\text{C}_{50}\text{H}_{44}\text{N}_4\text{P}_2\text{Ru}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 66.88; H, 4.97; N, 6.18%; M , 865. IR (CH_2Cl_2): $\nu(\text{CN})$ 2206m, 2198m; other bands at 1606w, 1518m, 1486m, 1434s cm^{-1} . ^1H -NMR (CDCl_3): δ 0.96 (s, 15H, Cp^*), 2.00 (m, 2H, CH_2), 2.34, 2.76 ($2 \times$ m, $2 \times$ 1H, CH_2), 6.10–7.87 (m, 25H, Ph). ^{31}P -NMR (CDCl_3): δ 48.47 [d, $J(\text{PP})$ 13, PPh_2], 77.30 [d, $J(\text{PP})$ 13, PPh_2]. ES mass spectrum (CH_2Cl_2 –MeOH, m/z): 865, M^+ .

Complex **7** slowly decomposes in air to give purple and green solids.

5.2. Structure determinations

Full spheres of diffraction data were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{total} reflections were merged to N unique (R_{int} quoted) after ‘empirical’ multiscan absorption correc-

tion with proprietary software, N_o with $F > 4\sigma(F)$ being used in the full-matrix least-squares refinement. All data were measured using monochromatic Mo– $\text{K}\alpha$ radiation, $\lambda = 0.71073$ Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, (x , y , z , $U_{\text{iso}})_\text{H}$ being constrained at estimated values. Conventional residuals R , R_w on $|F|$ are given [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.4 program system [10]. 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 Tables 1 and 2, individual variations, difficulties, etc., being noted.

5.2.1. Variata

1. The Cp^* ligand is rotationally disordered about the Ru-centroid axis, major and minor components refining to occupancies $x = 0.718(3)$, $1 - x$, with the methyl substituents of the minor component quasi-symmetrically disposed between those of the major component, which is depicted in Fig. 1.

2. Difference map residues were modelled in terms of a pair of 0.25 weighted CH_2Cl_2 moieties disposed about a crystallographic 2-axis.

4. All hydrogen atoms were refined in (x , y , z , U_{iso}).

5. Difference map residues were modelled in terms of a pair of CH_2Cl_2 moieties, occupancies refining to 0.371(2), 0.265(2).

Table 2
Crystal data and refinement details for **1**, **3–5** and **7**

Compound	1	3	4	5	7
Empirical formula	$\text{C}_{43}\text{H}_{42}\text{P}_2\text{Ru}\cdot 0.5\text{C}_6\text{H}_6$	$\text{C}_{49}\text{H}_{42}\text{N}_4\text{P}_2\text{Ru}\cdot 0.5\text{CH}_2\text{Cl}_2$	$\text{C}_{49}\text{H}_{42}\text{N}_4\text{P}_2\text{Ru}\cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{49}\text{H}_{42}\text{N}_4\text{OP}_2\text{Ru}\cdot 0.64\text{CH}_2\text{Cl}_2$	$\text{C}_{50}\text{H}_{44}\text{N}_4\text{P}_2\text{Ru}\cdot 0.5\text{CH}_2\text{Cl}_2$
Formula weight	760.9	892.4	934.9	920.3	906.4
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$ (C_{2h}^6 , No. 15)	$C2/c$	$P\bar{1}$ (C_1^1 , No. 2)	$P\bar{1}$	$C2/c$
a (Å)	31.560(1)	36.101(2)	11.845(2)	10.068(1)	34.392(5)
b (Å)	16.5455(8)	12.8567(8)	11.935(2)	15.242(2)	11.391(1)
c (Å)	17.2744(8)	19.546(2)	17.677(3)	15.535(2)	22.572(2)
α (°)			94.017(2)	96.438(2)	
β (°)	121.548(1)	107.054(2)	108.986(2)	99.673(2)	107.004(3)
γ (°)			105.567(2)	106.123(2)	
V (Å ³)	7687	8673	2242	2226	8456
Z	8	8	2	2	8
D_{calc} (g cm ^{−3})	1.31 ₅	1.36 ₇	1.38 ₅	1.37 ₃	1.42 ₄
μ (cm ^{−1})	5.2	5.4	5.8	5.4	5.5
Crystal size (mm)	$0.37 \times 0.14 \times 0.08$	$0.35 \times 0.14 \times 0.12$	$0.45 \times 0.38 \times 0.32$	$0.45 \times 0.45 \times 0.16$	$0.15 \times 0.12 \times 0.10$
$T_{\text{max/min}}$	0.73, 0.86	0.70, 0.83	0.77, 0.87	0.72, 0.80	0.59, 0.84
$2\theta_{\text{max}}$ (°)	75	75	58	58	50
N_{tot}	79862	76313	21979	21273	25116
N_r (R_{int})	20178 (0.068)	21492 (0.069)	10873 (0.018)	10582 (0.013)	7431 (0.012)
N_o	11287	11969	9391	9526	4173
R	0.046	0.049	0.028	0.031	0.069
R_w	0.048	0.050	0.035	0.039	0.077
$ \Delta\rho_{\text{max}} $ (e Å ³)	1.6(1)	1.9(1)	0.58(4)	0.96(3)	2.9(3)

6. Supplementary material

Crystallographic data for the structure determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 174607–174611 for compounds **1**, **3**, **4**, **5** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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