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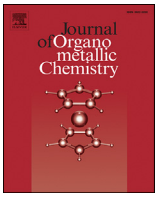

Some cyclic ligands obtained from reactions of polycyanocarbon–metal complexes

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Dedicated to our friend and colleague Claude Lapinte on his 65th birthday, in recognition of his extensive contributions to organo-iron chemistry.

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ABSTRACT

Several complexes containing Ru(dppe)Cp* fragments attached to heterocyclic ligands were obtained from polycyanocarbons. Reactions of Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* with LiC≡CSiMe$_3$ and LiOCH=CH$_2$ gave binuclear {[Ru(dppe)Cp*]C≡C–*c*-C=C(C≡CSiMe$_3$)N(H···OH$_2$)CC=C(CN)}$_2$(N=N) **2** and Ru{*c*-C=CHC[=C(CN)$_2$]CH=CHO}(dppe)Cp* **4** [together with known Ru{C≡CCMe=C(CN)$_2$}(dppe)Cp* **3**], respectively, while lithiation of Ru(C≡CC≡CH)(dppe)Cp* and subsequent reaction with TCNE afforded Ru{C≡C–*c*-C=C(CN)C(O)NH[=C(CN)$_2$]}(dppe)Cp* **6** and Ru{C≡C–*c*-C=CHC[=C(CN)$_2$]NHCMe=N}(dppe)Cp* **7**, as well as known {Ru(dppe)Cp*}$_2${μ-C≡CC[=C(CN)$_2$]C[=C(CN)$_2$]C≡C} **5**. A second product from the earlier described reaction between TCNE and Ru(C≡CC≡CI)(dppe)Cp* was identified as Ru{C≡C–*c*-CC(CN)C(CN)=C(NH$_2$)C(CN)$_2$}(dppe)Cp* **9**. X-ray determined structures of **2**, **4**, **6**, **7** and **9** are reported together with plausible routes by which they may be formed.

1. Introduction

The reactions of tetracyanoethene [(NC)$_2$C=C(CN)$_2$, TCNE] with alkynyl- and poly-ynyl-transition metal complexes have been studied for many years [1]. Characteristic of these is cycloaddition to an alkynyl–metal complex to give a zwitterionic intermediate **B** (possibly formed from an initially formed radical cation–anion salt [{L$_n$M}–CC–R]$^{+\bullet}$[TCNE]$^{-\bullet}$ **A**), which rapidly evolves via a [2 + 2]-cycloaddition reaction to the tetracyanocyclobutenyl derivative **C**, which in turn undergoes a more or less ready ring-opening (retro-cycloaddition) to form a η^1-tetracyanobuta-1,3-dienyl complex **D** (Scheme 1). A further reaction occurs if a weakly bound 2-e donor ligand is present on the metal centre, which can be displaced with formation of the analogous η^3-tetracyanobutadienyl complexes **E**. An interesting structural feature of structure **E** is the presence of a short Ru–C bond, consistent with some degree of multiple bonding character. This feature has been examined in more detail using DFT calculations [2].

An alternative reaction path which has been detailed recently involves the reactions of strongly nucleophilic ethynyl-metal complexes, such as Ru(C≡CH)(dppe)Cp*, which react with TCNE to give tricyanovinylethynyl complexes **F** by substitution of one CN group of the TCNE molecule (Scheme 1) [3]. The CN group in **F** that is *gem* to the ML$_n$ group is readily displaced by other nucleophiles, while addition of other M′L′$_m$ fragments to the CN group *trans* to ML$_n$ can also occur. Protonation of the C≡C triple bond affords a vinylidene derivative which is easily deprotonated.

In the chemistry of TCNE itself, formation of cyclic systems occurs readily, either by double displacement of CN groups, e.g., with ethylene glycol, or by attack on one or more of the CN groups themselves [4]. Much of this chemistry was uncovered during the early comprehensive studies of the reactions of TCNE and has been reviewed [5,6]. More fundamental have been the studies of hydrogen cyanide, which is a potent source of heterocyclic

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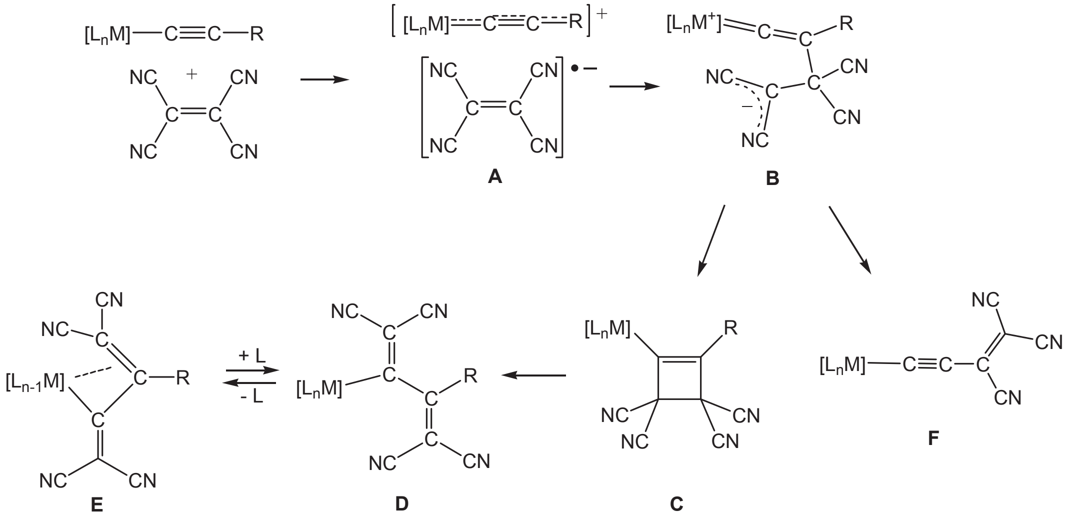
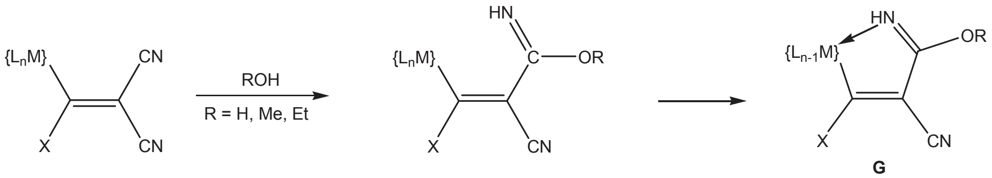


Scheme 1. [2 + 2]-Cycloaddition of TCNE to alkynyl–metal complexes. For **F**, [ML$_n$] = Ru(PPh$_3$)$_2$Cp, Os(PPh$_3$)$_2$Cp, Ru(dppe)Cp*.



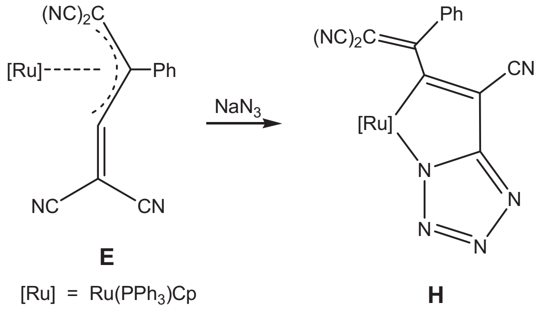
L$_n$M = Mo(CO)$_3$Cp, X = Cl, CN; L$_n$M = W(CO)$_3$Cp, X = CFc=C(CN)$_2$

Scheme 2. Hydrolysis of tricyanovinyl ligands to imido chelates.

compounds [7]. This topic has also been surveyed by Donald and Webster [8], who have emphasised the chemistry of HCN trimers, including aminomalononitrile, diaminomaleonitrile (DAMN) and the oxidation product of the latter, diiminosuccinonitrile (DISN). Conversions of DAMN to imidazoles or pyrazines predominate, while several other *N*-heterocyclic systems can be obtained from HCN.

However, reports of further transformations of polycyanocarbon ligands in their metal complexes are relatively rare. Ready hydrolysis or alcoholysis of a CN group may afford chelate imido complexes **G**, such as Mo{NH=C(OR)CX=C(CN)}(CO)$_2$Cp (R = H, Me, Et), from Mo{CX=C(CN)$_2$}(CO)$_3$Cp (X = Cl, CN) with ROH, or W{NH=C(OMe)C(CN)=CCFc=C(CN)$_2$}(CO)$_2$Cp, from W{η^1-C[=C(CN)$_2$]CFc=C(CN)$_2$}(CO)$_3$Cp and MeOH (Scheme 2) [9,10].

More recently, we described cycloaddition of azide to a CN group of the tetracyanobutadienyl ligand in **E** to give bicyclic systems such as Ru{C[CPh=C(CN)$_2$]=C(CN)CN$_4$}(PPh$_3$)Cp **H** (Scheme 3) [2].



Scheme 3. Cycloaddition of azide to an η^3-tetracyanobutadienyl–ruthenium complex.

In the course of further studies of the chemistry of TCNE with alkynyl–metal complexes and related compounds, we have discovered several products which contain new cyclic ligands. X-ray structural studies of some of these complexes and plausible routes by which they may be formed form the subject of this account.

2. Results and discussion

2.1. Reactions of Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp*

2.1.1. With LiC≡CSiMe$_3$

As mentioned above, reactions of the tricyanovinyl complex Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* **1** with nucleophiles, such as Nu = H$^-$, R$^-$, OR$^-$, NR$_2^-$ or PR$_2^-$, result in displacement of a second CN group, *gem* to the metal centre, to give Ru{C≡CCNu=C(CN)$_2$}(dppe)Cp* **3** [3]. In extending these reactions to unsaturated carbon nucleophiles, we have examined the reactions between **1** and several lithiated alkynes. Most of these have given unresolved mixtures of products, there being so far only one well-characterised replacement of CN by an alkynyl group, namely from the reaction with Ru(C≡CC≡CLi)(dppe)Cp*, which afforded the binuclear complex {Cp*(dppe)Ru}{μ-C≡CC[=C(CN)$_2$]C≡CC≡C}{Ru(dppe)Cp*} [11]. In contrast, the related reaction with LiC≡CSiMe$_3$ at room temperature afforded as the major product the dark green symmetrical azo dimer {[Ru(dppe)Cp*]C≡C–*c*-C=C(C≡CSiMe$_3$)N(H···OH$_2$)C(N=...)=(CN)}$_2$ **2** (Chart 1) which was identified by a single-crystal X-ray diffraction study. Chart 1 illustrates the structures of complexes whose structures have been determined crystallographically during this work.

Fig. 1 is a plot of a centrosymmetric binuclear molecule of **2**; selected bond parameters of all structures described herein are

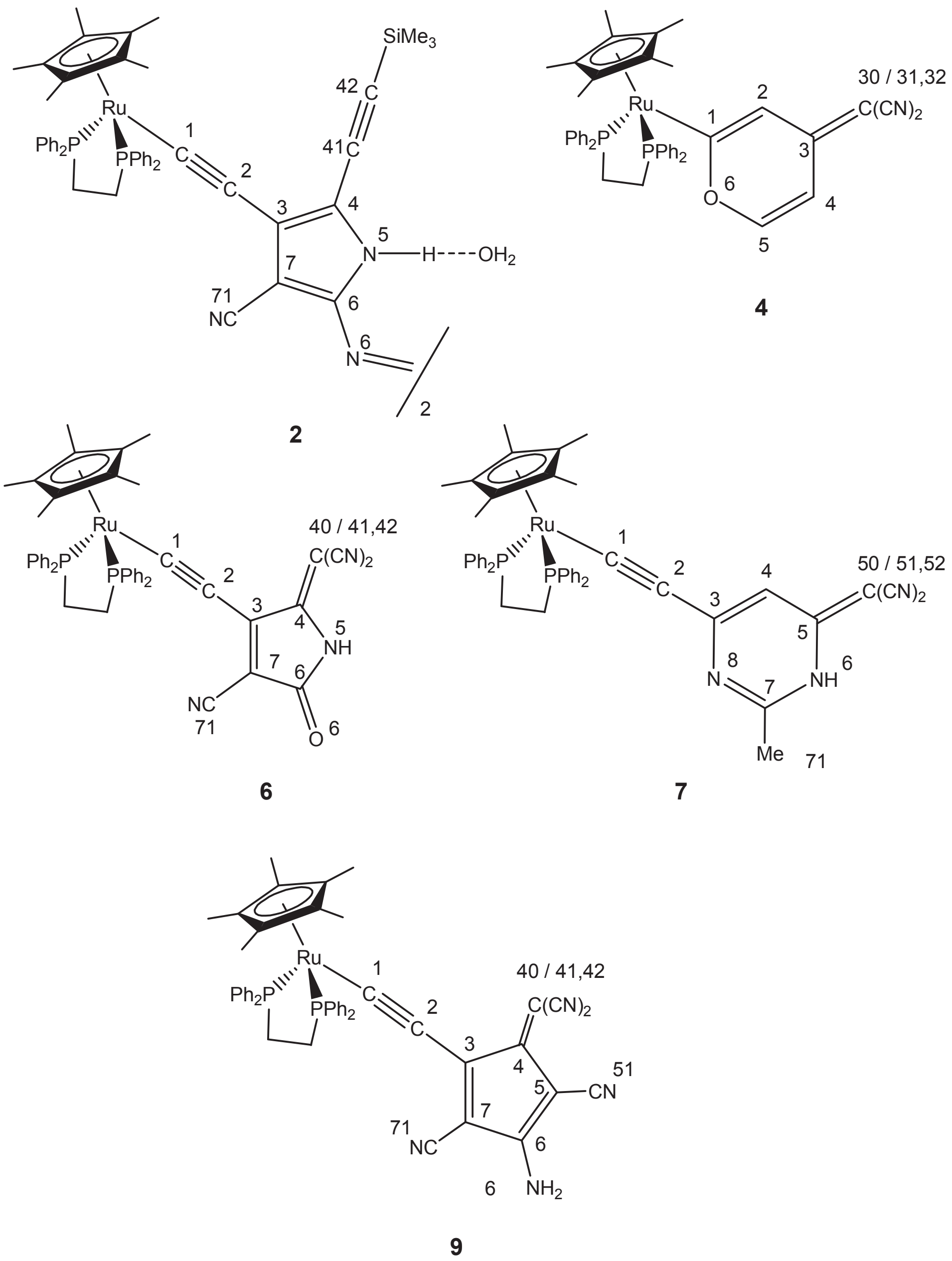


Chart 1. Partial atom-numbering schemes for organic ligands in complexes **2**, **4**, **6**, **7** and **9**, whose crystallographically-determined structures are reported herein.

included in the respective Figure captions. The familiar Cp*(dppe)Ru—C≡C— moiety is present in all molecules which have been structurally characterised in this work. In the five structures described below, the near octahedral Ru(dppe)Cp* fragment is characterised by normal bond parameters for Ru—P(1,2) [2.262–2.302(2) Å] and Ru—C(cp) [2.248–2.271 Å], with P(1)—Ru—P(2) [81.66–84.10(4)°] and P(1,2)—Ru—C(1) [81.6–92.65(7)°]. For **2**, this group has Ru(1)—C(1) and C(1)—C(2) 1.996(5) and 1.198(7) Å, respectively, cf. similar values for Ru—C 2.025(2), C≡C 1.202(3) Å in **1** [3]. It is attached by C(2) to atom C(3) of a pyrrole ring (crystallographic numbering). The heterocycle also carries trimethylsilylethynyl [at C(4)] and cyano [at C(7)] substituents. Short separations between atoms C(3)—C(4) and C(6)—C(7) [1.403(7), 1.395(7) Å, respectively] are consistent with localised C=C double bonds. The pyrrole NH group is hydrogen-bonded to a water molecule [N(5)—H···O(1) 2.845(8) Å], and two pyrrole nuclei are joined through an azo group [N(6)=N(6′), 1.303(8) Å] at C(6).

Spectroscopic data for **2** are in accord with the solid-state structure. The IR spectrum contains ν(CN) (2218 cm^{-1}), ν(C≡C) [2050 with 1971 (sh) cm^{-1}], ν(N=N) (1464 cm^{-1}) and ν(C=C) bands (1421 and 1377 cm^{-1}). The ^{1}H and ^{13}C NMR spectra contain the expected signals for the metal—ligand fragment, together with resonances at δ_H 0.23, δ_C 0.44 for the $SiMe_3$ groups. The ES-MS contained $[M + H]^+$ at m/z 1718 and $[Ru(dppe)Cp^*]^+$ at m/z 635; while no elemental microanalyses have been obtained (the compound is relatively unstable and rapidly turns brown), the dimeric formulation is confirmed by HR-MS on $[M + H]^+$ (found m/z 1718.344, calcd 1718.442). However, the water molecule attached to NH(5) could not be detected in the mass spectrum.

A plausible mechanism for this unusual reaction is given in Scheme 4. Attack by $LiC{\equiv}CSiMe_3$ at the CN attached to C(3) of **1**, followed by intramolecular attack at the *cis* CN on C(4) gives the anion {Cp*(dppe)Ru}{*c*-C=C(CN)C(=N⁻) N=C(C≡CSiMe₃)} **I**. Protonation of **I** (from either an excess of $HC{\equiv}CSiMe_3$ or THF solvent) forms the diazafulvene **J**, which would be a potent electrophile. A significant driving force may be the formation of the aromatic pyrrole in **J**. Addition of a further equiv. of anion **I** at N(5) of the imine and subsequent tautomerisation would generate the diazo compound. Subsequent protonation (either from its surroundings or upon work-up) gives **2**.

2.1.2. With $LiOCH{=}CH_2$ (a decomposition product formed by reaction between LiBu and THF)

While the reaction of $LiC{\equiv}CC{\equiv}CLi$, formed by double desilylation of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ with LiBu in THF, with **1** does not proceed at −78 °C, two major products were isolated from a reaction carried out at room temperature. These were identified as the known orange $Ru\{C{\equiv}CCMe{=}C(CN)_2\}(dppe)Cp^*$ **3** (R = Me)[3] (24%) and yellow $Ru\{c\text{-}C{=}CHC[{=}C(CN)_2]CH{=}CHO\}(dppe)Cp^*$ **4** (17%). The same products were also formed in the absence of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, suggesting that it was $LiOCH{=}CH_2$ (formed by elimination of ethene from THF in the presence of LiBu [12–14]) which reacted with **1**. The structures of both compounds were determined by single-crystal X-ray diffraction studies, that of **3** matching the previously determined structure [3c]. The formation of the methyl adduct **3** (R = Me) was initially surprising as LiBu rather than LiMe was used for desilylation $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$. However, all the experimental data confirmed the identity as **3** (R = Me) rather than the *n*-butyl analogue **3** (R = Bu) [3].

The molecule of **4** (Fig. 2) contains a 4-(dicyanomethylene)pyran-2-yl ligand coordinated to the Ru(dppe)Cp* fragment via the Ru–C(1) bond [2.038(2) Å]. Within the planar six-membered ring, short C(1)–C(2) [1.387(3) Å] and C(4)–C(5) [1.328(3) Å] separations confirm the locations of C=C double bonds; the exocyclic C(3)–C(30) bond [1.401(3) Å] is similar to the first of these. The differing bonds from O(6) to C(1) [1.396(3) Å] and to C(5) [1.347(3) Å] suggest that there is a degree of electron delocalisation onto the C(4)–C(5)–O(6) fragment, perhaps indicating a degree of charge separation (zwitter-ion). However, the normal Ru–C(1) bond length [2.038(1) Å] indicates that there is no significant charge donation from the Ru centre.

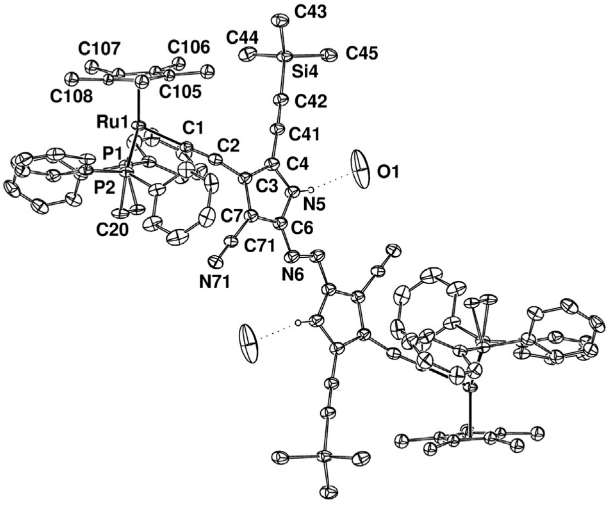
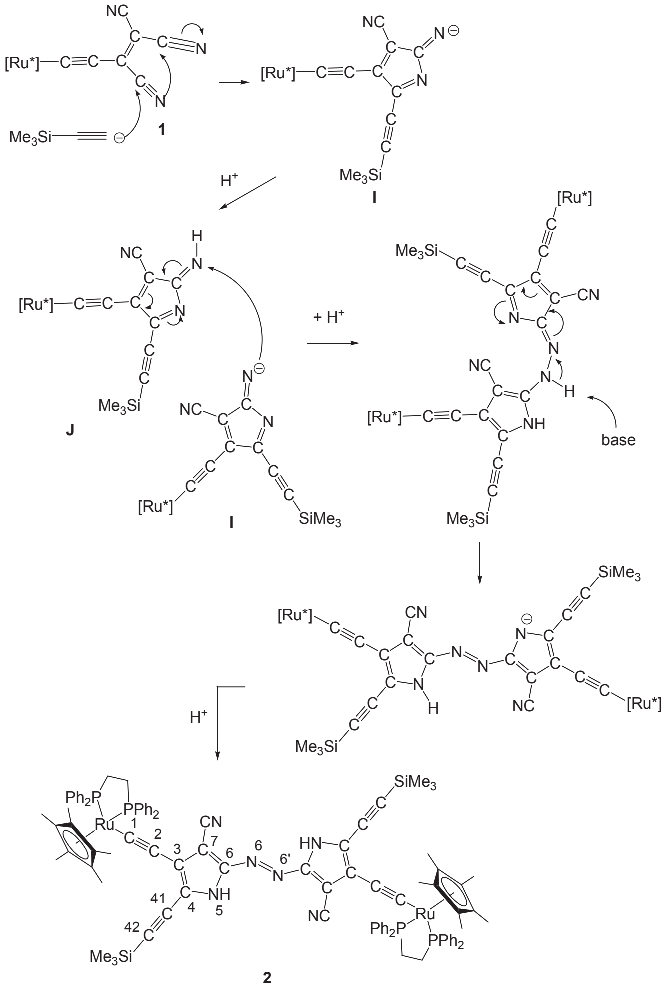


Fig. 1. Plot of a molecule of $\{[Ru(dppe)Cp^*]C{\equiv}C\text{–}c\text{-}C{=}C(C{\equiv}CSiMe_3)N(H\cdots OH_2)C(N{=}\ldots){=}(CN)\}_2$ **2**. One component of the disordered atoms and hydrogen atoms [except those on N(5,5′)] have been omitted. Selected bond parameters: Ru–C(1) 1.996(5), C(1)–C(2) 1.198(7), C(2)–C(3) 1.428(7), C(3)–C(4) 1.403(7), C(3)–C(7) 1.424(7), C(4)–N(5) 1.374(6), C(4)–C(41) 1.408(7), C(41)–C(42) 1.206(7), C(42)–Si(4) 1.845(5), N(5)–C(6) 1.353(6), C(6)–N(6) 1.369(7), C(6)–C(7) 1.395(7), N(6)–N(6′) 1.303(8) Å. Ru–C(1)–C(2) 177.3(4), C(1)–C(2)–C(3) 164.3(5), C(2)–C(3)–C(4) 126.4(5), C(2)–C(3)–C(7) 127.0(5), C(3)–C(4)–N(5) 108.1(4), C(3)–C(4)–C(41) 130.1(5), C(4)–N(5)–C(6) 110.1(4), N(5)–C(6)–C(7) 108.2(4), N(5)–C(6)–N(6) 126.6(5), N(6)–C(6)–C(7) 125.0(5), C(3)–C(7)–C(6) 107.5(4), C(6)–N(6)–N(6′) 112.0(5), C(4)–C(41)–C(42) 175.7(6), C(41)–C(42)–Si(4) 174.2(5)°.



Scheme 4. A plausible mechanism for the formation of $\{[Ru(dppe)Cp^*]C{\equiv}C\text{–}c\text{-}C{=}C(C{\equiv}CSiMe_3)N(H\cdots OH_2)C(N{=}\ldots){=}(CN)\}_2$ **2**. [Ru*] = Ru(dppe)Cp*.

Spectroscopic data of **4** are generally in accord with its solid-state structure, with the exception of the unusually downfield singlet in the ^{31}P NMR at δ_P 93.6 [which may be compared to the usual value for $Ru(C{\equiv}CR)(dppe)Cp^*$ of δ_P ca 80]. This feature may indicate a partial zwitter-ionic structure for **4**, with some positive charge on the metal centre (see three resonance structures shown). The IR spectrum has ν(CN) [2194, 2170 cm^{-1}] and ν(C=C) bands [1620, 1476, 1453, 1436 cm^{-1}], but no ν(C≡C) absorption. The ^{1}H NMR spectrum shows three =CH resonances at δ_H 5.85(dd), 6.33(d) and 6.54(s, br). The ^{13}C NMR spectrum contains two CN singlets [δ_C 119.17, 119.63] with other carbons of the heterocyclic ring at δ_C 107.94, 124.19, 148.70 and 153.53. A peak at δ_C 217.04, broadened by coupling to phosphorus, is assigned to Ru–C. The dppe singlet in the ^{31}P NMR spectrum is at δ 93.6, somewhat downfield from the usual value for δ_P at ca 80 usually found for $Ru(C{\equiv}CR)(dppe)Cp^*$ complexes. The ES-MS contained M$^+$ and $[Ru(dppe)Cp^*]^+$ at *m*/*z* 778 and 635, respectively.

Possible routes for the formation of **3** and **4** (Scheme 5) involve deprotonation (metallation) of solvent THF with the organolithium reagent, which is a well-known reaction pathway, often occurring to the detriment of intended syntheses run in this solvent [12–14]. Ether cleavage, following deprotonation at C_α to give either $LiOCH_2CH_2CH{=}CH_2$ [15], or ethene and $LiOCH{=}CH_2$ (the lithiated

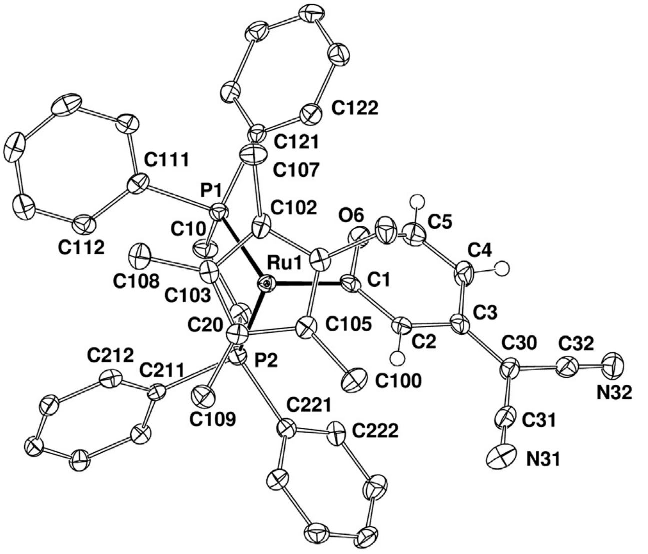


Fig. 2. Plot of a molecule Ru{*c*-C=CHC[=C(CN)$_2$]CH=CHO}(dppe)Cp* **4**. Some hydrogen atoms have been omitted for clarity. Selected bond parameters: Ru–C(1) 2.038(2), C(1)–C(2) 1.387(3), C(1)–O(6) 1.396(3), C(2)–C(3) 1.416(3), C(3)–C(4) 1.429(3), C(3)–C(30) 1.401(3), C(30)–C(31,32) 1.419, 1.422(4), C(4)–C(5) 1.328(3), C(5)–O(6) 1.347(3) Å. Ru–C(1)–C(2) 126.2(2), Ru–C(1)–O(6) 118.9(2), C(2)–C(1)–O(6) 114.9(2), C(1)–C(2)–C(3) 124.9(2), C(1)–O(6)–C(5) 121.3(2), C(2)–C(3)–C(4) 115.5(2), C(2)–C(3)–C(30) 122.9(2), C(3)–C(4)–C(5) 118.9(2), C(4)–C(5)–O(6) 124.5(2), C(4)–C(3)–C(30) 121.6(2)°.

enol of MeCHO) [16], followed by retro-[3 + 2]-cycloaddition, are the commonly observed routes. In some instances, the *O*-nucleophile may ketonise to the *C*-nucleophile, LiCH$_2$CHO, which is more reactive and hence less stable.

Here, attack of LiCH$_2$CHO (alkyllithiums are more reactive than alkoxides with **1** [3]) on **1** produces an intermediate aldehyde Ru{C≡CC(CH$_2$CHO)=C(CN)$_2$}(dppe)Cp* **K** which then reacts further to give the two reaction products **3** (R = Me) and **4**, as shown. Analysis (^{31}P NMR) of the reaction mixture before work-up showed a resonance at δ_P 81.6 corresponding to **3** (R = Me) but not the downfield singlet at δ_P 93.6 found for **4**. There was no trace of the butyl Ru{C≡CCBu=C(CN)$_2$}(dppe)Cp* **3** (R = Bu) which implies all the LiBu had reacted with the THF. Further attack on aldehyde **K** by LiOCH=CH$_2$ [pathway (i)] and β-cleavage of the resulting allylic alkoxide with elimination of propane-1,3-dial gives a γ-methylene intermediate **L** in which the negative charge is stabilised on the C(CN)$_2$ group. Protonation then forms **3** (R = Me) [3].

In a competitive reaction [pathway (ii)], protonation of **K** to the vinylidene **M** is followed by enolisation to vinyl alcohol **M**. This evolves via rapid intramolecular attack on C(1) by the oxygen to form the six-membered pyrylium cation **N** (possibly the source of a strong singlet at δ_P 81.9 in the reaction mixture), and subsequent deprotonation to give the neutral product **4**. Overall, this resembles the well-known reaction of alcohols with vinylidenes [Ru(=C=CH$_2$)(PP)Cp]PF$_6$ [where PP = (PPh$_3$)$_2$ or dppe] to give the analogous alkoxycarbene complexes, which in the case of HC≡C(CH$_2$)$_n$OH (n = 2, 3) undergo intramolecular cyclisations to give the cyclic carbenes [17]. In this case, the cyclisation is driven by the thermodynamically preferred formation of the pyrylium species **4**.

2.2. Reaction between Ru(C≡CC≡CLi)(dppe)Cp and TCNE*

Lithiation of Ru(C≡CC≡CH)(dppe)Cp* with LiBu affords the presumed intermediate Ru(C≡CC≡CLi)(dppe)Cp* [18] which reacts at −78 °C with one equivalent of TCNE in THF with an immediate change in colour from yellow to dark green (Scheme 6). After purification, known {Ru(dppe)Cp*}$_2${μ-C≡CC[=C(CN)$_2$]C[=C(CN)$_2$]C≡C} **5** was isolated as the major product in 32% yield [19]. This compound was characterised by the usual spectroscopic methods (specifically, IR ν(CN) bands at 2208 and 2075 cm^{-1}, an AB quartet in the ^{31}P NMR spectrum at δ 81.3, 79.9 [both d, ^3J(PP) = 13 Hz] and [M + Na]$^+$ at m/z 1493 in the ES-MS of a solution in MeOH containing NaOMe).

Two other compounds were isolated from this reaction: blue Ru{C≡C–*c*-C=C(CN)C(O)NHC[=C(CN)$_2$]}(dppe)Cp* **6** (20%) and bright orange Ru{C≡C–*c*-C=CHC[=C(CN)$_2$]NHCMe=N}(dppe)Cp* **7** (16%). Single crystals of both complexes suitable for X-ray studies were grown from CH$_2$Cl$_2$/hexane and Figs. 3 and 4 show molecular projections of **6** and **7**, respectively. Elemental microanalyses are in accord with the solid-state structure of **6**, while high resolution MS measurements confirm [M + Na]$^+$ for **6**, and [M − Me]$^+$ for **7**.

In **6**, the organic ligand is a substituted methylene–pyrrolone attached to the metal centre by an Ru–C(1) single bond [1.964(11) Å]. The C(1)–C(2) separation of 1.22(1) Å and angles Ru–C(1)–C(2) and C(1)–C(2)–C(3), both close to linear at 175.2(8) and 166.9(12)°, respectively, are consistent with the presence of a C≡C triple bond between atoms C(1) and C(2). Atom C(2) is attached to the cyclic C$_4$N portion of the ligand by a C–C single bond [C(2)–C(3) 1.43(2) Å], with atoms C(3)–C(4)–N(5)–C(6)–C(7) forming part of a cyano(dicyanomethylene)pyrrolone heterocycle, with double bonds located between atoms C(4)–C(40), C(3)–C(7) [1.38(2), 1.43(2) Å] and C(6)–O(6) [1.26(2) Å]. Some charge delocalisation is suggested by separations between atoms C(4)–N(5) [1.32(1) Å] and C(7)–C(71) [1.34(2) Å], which are both significantly shorter than single bonds. Internal angles in the C$_4$N ring range between 106 and 110(1)°.

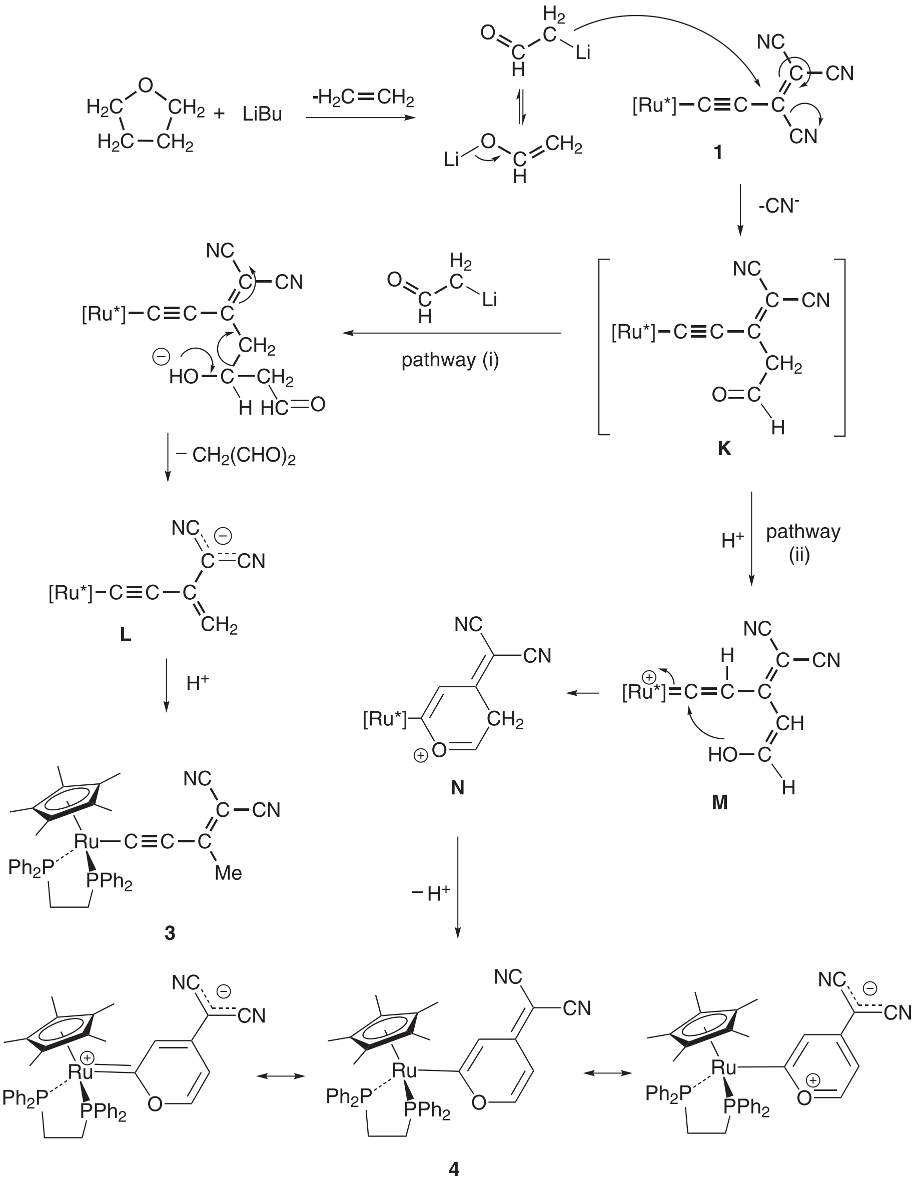
In **7** (Fig. 4), the Ru–C(1)–C(2)–C(3) separations [1.963(3), 1.232(4), 1.387(4) Å] and angles at C(1) and C(2) [178.3(2), 168.3(3)°] are again consistent with the presence of the Ru–C≡C– fragment, which is attached to a C$_4$N$_2$ ring at C(3) (crystallographic numbering). The ring geometry, with multiple bonds between C(3)–C(4) [1.282(4) Å], N(8)–C(7) [1.377(5) Å] and C(5)–C(50) [1.396(4) Å], is consistent with its formulation as a substituted dihydropyrimidine, containing a dicyanomethylene group in the 4-position.

In both molecules, short Ru–C(1) bonds, together with the long C(5)–C(50) bond in **7**, suggest that there is significant charge transfer from the electron-rich Ru centre through the conjugated links to the =C(CN)$_2$ moiety, which stabilises negative charge.

Spectroscopic features of **6** and **7** are consistent with the solid-state structures. For **6**, these include IR bands assigned to ν(NH), ν(CN) (broad), ν(C≡C), ν(CO) and ν(C=C) at 3058, 2212, 1954, 1716 and 1603 cm^{-1}, respectively, and the usual NMR signature for the Ru(dppe)Cp* moiety, including a singlet in the ^{31}P NMR spectrum at δ 72.9 (dppe). The HR ES-MS contains [M + Na]$^+$ at m/z 851.1624 (calcd 851.1626). The IR spectrum of **7** contained ν(NH), ν(CN), ν(C≡C) and ν(C=C) bands at 3060, 2204, 2024 and 1644 cm^{-1}, respectively. Besides the usual resonances for the Ru(dppe)Cp* group, the ^{1}H NMR spectrum contains three singlets at δ 1.26 (Me), 2.17 (CH) and 4.19 (NH). A high resolution ES-MS of **7** confirmed the formulation of [M + H]$^+$ at m/z 817.211 (calcd. 817.216).

We have considered possible routes for the formation of these three complexes in the reaction between TCNE and the lithiated diynyl complex. A possible route to **6**, shown in Scheme 7, involves partial hydrolysis of the tetracyanobutadienyl **O** derived from Ru(C≡CC≡CH)(dppe)Cp* and TCNE, with one CN group being converted to an amide (cf. Scheme 2 above). Subsequent intramolecular attack would generate dihydrolactam **P**. As there is no obvious oxidant in the reaction mixture (except for TCNE itself), it is proposed that loss of a proton from **P** generates the intermediate pyrrole **Q**, which by loss of hydride in a Cannizzaro-like process then affords **6**.

It is known that TCNE reacts with {Cp*(dppe)Ru}$_2${μ-(C≡C)$_3$} to give **5** (above) [19], but clearly the question remains as to how the


Scheme 5. Postulated mechanisms for the formation of **3** (R = Me) and **4**. [Ru*] = Ru(dppe)Cp*.

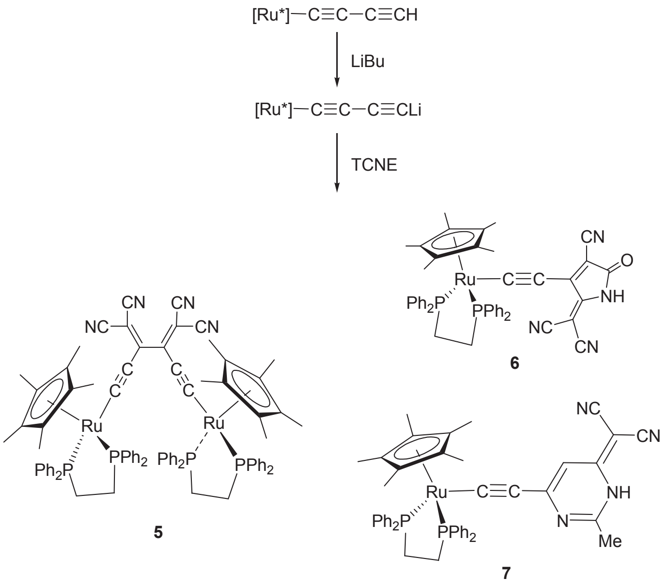
triynyl complex is generated in a reaction where the initial ruthenium reagent is Ru(C≡CC≡CH)(dppe)Cp*. A possible route to **5** might involve the hydride generated in forming **6** triggering a reductive dimerisation of Ru(C≡CC≡CH)(dppe)Cp* to give {[Cp*(dppe)Ru]C≡CC=CH$_2$}$_2$. Electrocyclic formation of the cyclobutene, followed by loss of ethene, could then give {Cp*(dppe)Ru}(C≡C)$_3${(Rudppe)Cp*} which reacts with TCNE to give the observed **5**. However, the route to **7** is not so obvious. While [2 + 2]-cycloaddition of TCNE to either the proto- or lithio-butadiynyl–ruthenium complex and subsequent ring-opening is an attractive possibility, it is not clear how the =C(CN)$_2$ group attached to C(3) in the resulting product might have further reacted/rearranged to afford the observed –N=CMe–NH– portion of the ring. Further work is necessary to clarify these interesting rearrangements.

2.3. Reaction between TCNE and Ru(C≡CC≡CI)(dppe)Cp*

The major product from the reaction between TCNE and Ru(C≡CC≡CI)(dppe)Cp* has previously been described: the deep purple complex Ru{C≡CC=C(CN)$_2$CI=C(CN)$_2$}(dppe)Cp* **8** is obtained in 46% yield (Scheme 8) [20]. A second, pink, product, isolated in only 10% yield, has now been identified as the tetracyano(amino)cyclopentadienyl complex Ru{C≡C–*c*-C=C(CN)C(NH$_2$)=C(CN)C(CN)$_2$}(dppe)Cp* **9** by a single-crystal X-ray structure determination.

As can be seen from the plot of a molecule of **9** in Fig. 5, the usual Cp*(dppe)Ru–C≡C– group is attached to a penta-substituted cyclopentadienyl ligand at C(3) (crystallographic numbering) with C(2)–C(3) 1.367(5) Å. Within the C$_5$ ring, C=C double bonds occur between C(3)–C(7) and C(5)–C(6) [1.376(5), 1.383(5) Å, respectively]. Atom C(4) is displaced from the C(3)–C(7)–C(6)–C(5) plane by 0.028(8) Å. Substituents on the C$_5$ ring comprise the NH$_2$ group [C(6)–N(6) 1.319(5) Å] and four CN groups, one each on C(5) and C(7) and two on C(4).

Although there is no strongly electron-withdrawing =C(CN)$_2$ group to accommodate charge in **9**, the dimensions of the Ru–C(1)–C(2)–C(3) moiety again suggest that some charge transfer from the Ru centre to the polycyano ligand occurs, the short Ru–C(1) bond [1.936(4) Å], long C(1)–C(2) [1.234(5) Å] and short C(2)–C(3) [1.367(5) Å] bonds suggesting some delocalisation, with the



Scheme 6. Reaction of lithiated Ru(C≡CC≡CH)(dppe)Cp* with TCNE to give **5**, **6** and **7**. [Ru*] = Ru(dppe)Cp*.

negative charge residing within the C(3)–C(7)–CN fragment [cf. the short C(3)–C(7) bond, 1.376(5) Å].

Spectroscopic data are consistent with the solid-state structure. The IR spectrum contains ν(NH) [3453 (br) cm^{-1}], ν(CN) [2200w (sh), 2185m cm^{-1}], ν(C≡C) [1984s cm^{-1}] and ν(C=C) bands [1654w, 1575w, 1507m cm^{-1}]. In addition to the usual Ru(dppe)Cp* resonances, the ^{1}H and ^{13}C NMR spectra contained resonances for NH$_2$ (δ_H 5.10), CN (δ_C 110.53, 114.46, 114.70) and ring C atoms (δ_C 123.87, 162.59). The ES-MS contained ions at *m*/*z* 1496 and 862, assigned to [M + Na + Ru(dppe)Cp*]$^+$ and [M + Na]$^+$, respectively, with an HR-MS measurement on the latter confirming its overall formulation.

This complex is unusual in having a highly substituted C$_5$ ring. A plausible route (Scheme 9) involves initial addition of TCNE to the lithiated butadiynyl ligand in **R** (an intermediate in the formation of **8**, and also possibly formed by lithiation of **8**), which replaces a CN group in a second molecule of TCNE to give **S**. Addition of water to this potent Michael acceptor, during the reaction or work-up, forms the five-membered ring in **T**, from which loss of carbonyl cyanide OC(CN)$_2$ then generates the observed product **9**.

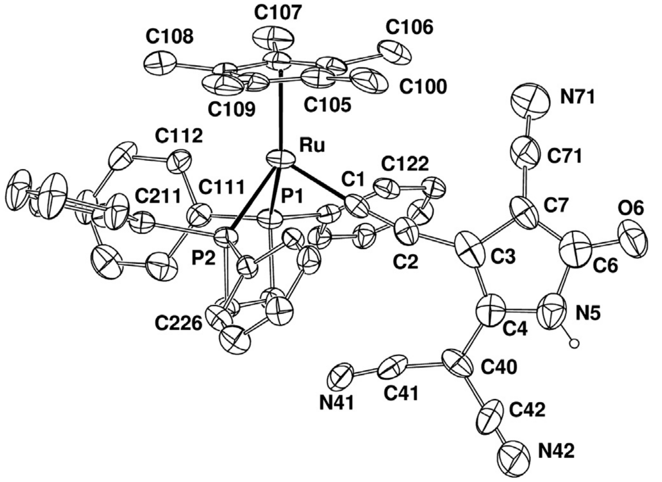


Fig. 3. Plot of a molecule of Ru{C≡C–*c*-C=C(CN)C(O)NHC[=C(CN)$_2$]}(dppe)Cp* **6**. Hydrogen atoms have been omitted for clarity. Selected bond parameters: Ru–C(1) 1.964(11), C(1)–C(2) 1.22(1), C(2)–C(3) 1.43(2), C(3)–C(4) 1.42(2), C(3)–C(7) 1.43(2), C(4)–N(5) 1.32(1), C(4)–C(40) 1.38(2), N(5)–C(6) 1.48(2), C(6)–C(7) 1.38(2), C(6)–O(6) 1.26(2), C(40)–C(41,42) 1.41, 1.40(2) Å. Ru–C(1)–C(2) 175.2(8), C(1)–C(2)–C(3) 166.9(12), C(2)–C(3)–C(4) 124.8(12), C(2,4)–C(3)–C(7) 129, 106(2), C(3)–C(4)–N(5) 110(1), C(3)–C(4)–C(40) 130(2), N(5)–C(4)–C(40) 120(2), C(4)–N(5)–C(6) 109(1), N(5)–C(6)–O(6) 122(2), N(5)–C(6)–C(7) 106(2), C(7)–C(6)–O(6) 133(2), C(3)–C(7)–C(6) 109(2), C(6)–C(7)–C(71) 125(2)°.

This reaction may be related to the earlier described formation of Ru{=C=C$_5$(CN)$_3$[=C(CN)$_2$]$_2$}(dppe)Cp* in the reactions of Ag–C≡CC≡C–[Ru*] or (Ph$_3$P)Au–C≡CC≡C–[Ru*] with TCNE [21]. The proposed route to the cyclic product involves attack of a silver–tetracyanobutadienyl on TCNE, followed by an intramolecular 5-*exo-trig* cyclisation and elimination of AgCN.

3. Conclusions

The chemistry described above has given an indication of a range of intramolecular cyclisation reactions which may occur with polycyanocarbon ligands on an electron-rich ruthenium centre. While the precise mechanisms of the transformations noted here may not presently be known (although we have endeavoured to present plausible routes), there is scope for considerable further studies, which will be reported in due course.

This chemistry has developed from further investigation of the reactions of the tricyanovinyl(ethynyl)ruthenium complex Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* **1** which have been described in detail elsewhere [3]. In devising possible routes to the various complexes described above, we have had recourse to the following types of reactions:

(i) Attack of Me$_3$SiC≡C$^-$ on CN(3) of **1** rather than on C(3);
(ii) Hydrolysis of a CN group to C(O)NH$_2$, possibly by water adsorbed on the TLC matrix during work-up;
(iii) Several intramolecular cyclisation reactions following either (i), (ii) or replacement of CN(3) by other nucleophiles.

As mentioned above in the discussions of the molecular structures, the various bond parameters support some charge transfer

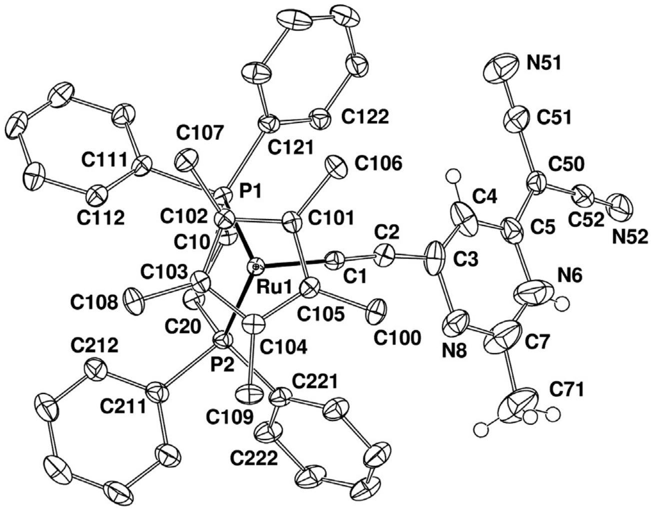
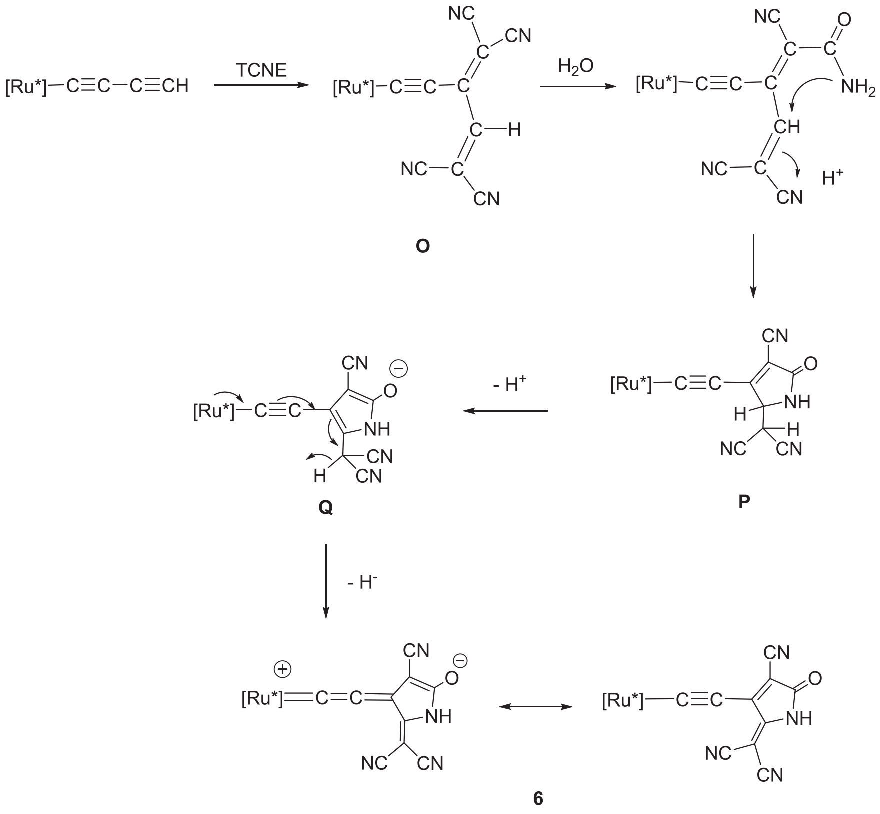
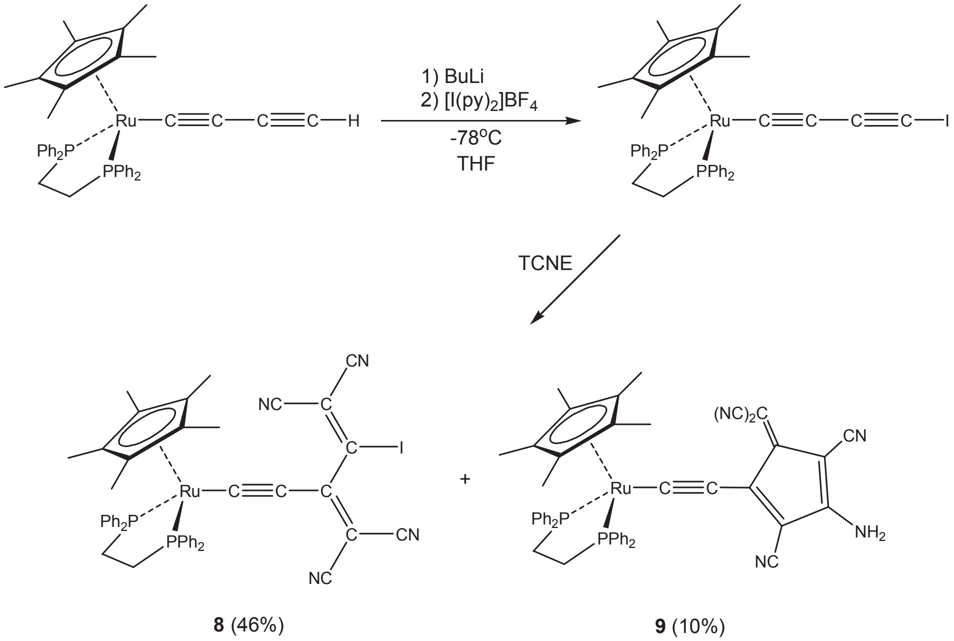


Fig. 4. Plot of a molecule of Ru{C≡C–*c*-C=CHC[=C(CN)$_2$]NHCMe=N}(dppe)Cp* **7**. Some hydrogen atoms have been omitted for clarity. Selected bond parameters: Ru–C(1) 1.963(3), C(1)–C(2) 1.232(4), C(2)–C(3) 1.387(4), C(3)–N(8) 1.456(4), C(3)–C(4) 1.282(4), N(8)–C(7) 1.377(5), C(7)–N(6) 1.472(6), C(7)–C(71) 1.486(6), N(6)–C(5) 1.414(5), C(4)–C(5) 1.433(5), C(5)–C(50) 1.396(4), C(50)–C(51,52) 1.418, 1.430(4) Å. Ru–C(1)–C(2) 178.3(2), C(1)–C(2)–C(3) 168.3(3), C(2, 4)–C(3)–N(8) 109.3, 114.7(3), C(2)–C(3)–C(4) 135.9(4), C(3)–N(8)–C(7) 118.4(3), N(6)–C(7)–N(8) 127.0(4), N(8)–C(7)–C(71) 110.1(4), N(6)–C(7)–C(71) 122.9(4), C(5)–N(6)–C(7) 110.6(4), N(6)–C(5)–C(4) 119.8(3), N(6)–C(5)–C(50) 118.2(3), C(3)–C(4)–C(5) 129.3(4), N(8)–C(3)–C(4) 114.7(3)°.



Scheme 7. Proposed mechanism for the formation of **6**. [Ru*] = Ru(dppe)Cp*.



Scheme 8. Reaction of TCNE with lithiated Ru(C≡CC≡CH)(dppe)Cp*.

from the electron-rich Ru centre to the polycyano ligand, it being readily accommodated on the $=C(CN)_2$ groups, or more dispersed around the CN-substituted ring. This is a common feature of complexes of this type and in other cases, the polarisation results in solvatochromism [3c]. More detailed studies are warranted, particularly to refine the degree of charge transfer and its potential in the field of opto-electronics.

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

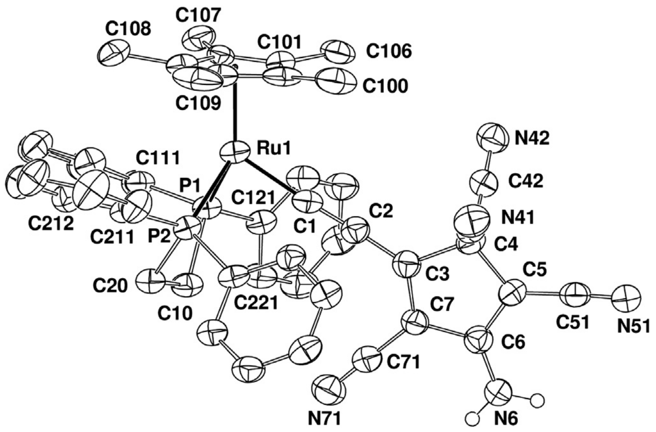


Fig. 5. Plot of a molecule of Ru{C≡C–*c*-C=C(CN)C(NH_2)=C(CN)C($CN)_2$}(dppe)Cp* **9**. Hydrogen atoms and one set of atoms of the disordered Cp* ring have been omitted for clarity. Ru–C(1) 1.936(4), C(1)–C(2) 1.234(5), C(2)–C(3) 1.367(5), C(3)–C(4) 1.554(6), C(3)–C(7) 1.376(5), C(4)–C(5) 1.507(5), C(5)–C(6) 1.383(5), C(5)–C(51) 1.405(6), C(6)–C(7) 1.453(5), C(6)–N(6) 1.319(5) Å. Ru–C(1)–C(2) 176.0(3), C(1)–C(2)–C(3) 177.2(4), C(2)–C(3)–C(4) 123.0(3), C(2)–C(3)–C(7) 130.9(4), C(3)–C(4)–C(5) 103.8(3), C(4)–C(5)–C(6) 109.5(3), C(5)–C(6)–C(7) 108.4(3), C(3)–C(7)–C(6) 112.2(3), C(4)–C(3)–C(7) 106.1(3), C(5)–C(6)–N(6) 127.9(4), C(7)–C(6)–N(6) 123.7(4)°.

nitrogen 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 on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_2 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 Gemini 2000 instrument (^1H at 300.145 MHz, ^{13}C at 75.479 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 ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH, with added NaOMe to aid ionisation [22]. 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. Elemental analyses were by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

4.3. Reagents

Ru(C≡CC≡CH)(dppe)Cp* [23] and Ru{C≡CC(CN)=C($CN)_2$}(dppe)Cp* [5] were made by the cited methods. TCNE was a commercial sample.

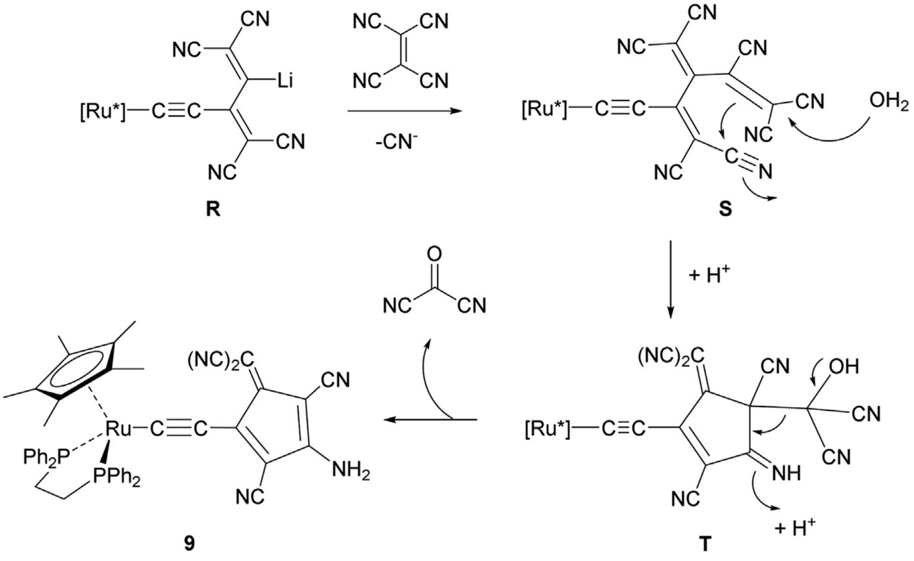
4.4. Reactions of Ru{C≡CC(CN)=C($CN)_2$}(dppe)Cp* 1

4.4.1. With LiC≡CSiMe$_3$

LiBu (0.13 ml of 1.5 M solution in hexane, 0.197 mmol) was added to a stirred solution of HC≡CSiMe_3 (0.037 ml, 0.262 mmol) in THF (8 ml) at −78 °C. After warming to r.t. for 1 h, Ru{C≡CC(CN)=C($CN)_2$}(dppe)Cp* **1** (100 mg, 0.131 mmol) was added to the solution. After 3.5 h solvent was removed and the residue was purified by preparative TLC (acetone-hexane, 3/7) to give a green band ($R_f = 0.61$) containing {[Ru(dppe)Cp*]C≡C–*c*-C=C(C≡CSiMe_3)N(H···OH_2)C(N=…)=(CN)}$_2$ **2** (16 mg, 15%). X-ray quality crystals were grown from C_6H_6–MeOH. Anal. Calcd ($C_{96}H_{98}N_6P_4Ru_2Si_2$): *M*, 1718. IR (nujol, cm^{-1}): *ν*(C≡N) 2219w, 2142w, *ν*(C≡C) 2050s, 1971w (sh), *ν*(N=N) 1464vs, *ν*(C=C) 1546w, 1421m, 1377s. ^1H NMR (C_6D_6): *δ* 0.23 (s, 18H, SiMe_3); 1.75 (s, 30H, Cp*), 2.18, 3.25 (2× m, 8H, 4× CH_2, dppe), 3.64 (s, 2H, NH), 7.01–7.43 (m, 40H, Ph). ^{13}C NMR (C_6D_6): *δ* 0.44 (s, SiMe_3), 10.99 (s, C_5*Me*$_5$), 29.83–30.40 (m, dppe), 93.79 (s, *C*$_5$Me$_5$), 126.01–137.24 (m, Ph). ^{31}P NMR (C_6D_6): *δ* 82.2 [s, 4P, 2× Ru(dppe)]. ES-MS (MeOH, *m*/*z*): 1718, M^+; 635, [Ru(dppe)Cp*]$^+$; HR-MS: $[M + H]^+$ 1718.344 (calcd 1718.442).

4.4.2. With LiOCH=CH$_2$ (a decomposition product formed by reaction of THF with BuLi)

To a stirred solution of Me_3SiC≡CC≡CSiMe_3 (13 mg, 0.066 mmol) in THF (6 ml) was added of LiBu (0.061 ml of 2.15 M solution in hexane, 0.131 mmol) at −78 °C. This was allowed to warm to r.t. at which point the solution turned from colourless to a golden-yellow colour, which faded back to colourless after about 3 h. After 5 h, Ru{C≡CC(CN)=C($CN)_2$}(dppe)Cp* **1** (34 mg, 0.045 mmol) was added and the mixture slowly turned from purple to yellow–brown. After 17 h, solvent was removed and the residue



Scheme 9. Possible mechanism for the formation of **9**. [Ru*] = Ru(dppe)Cp*.

Table 1
Crystal data and refinement details for **2**, **4**, **6**, **7**, **9**.

Complex	**2**	**4**	**6**	**7**	**9**
CCDC #	887533	705436	887534	887535	887536
Formula	$C_{96}H_{98}N_6P_4Ru_2Si_2\cdot 2H_2O$	$C_{44}H_{42}N_2OP_2Ru$	$C_{46}H_{40}N_4OP_2Ru\cdot 0.386CH_2Cl_2$	$C_{46}H_{44}N_4P_2Ru\cdot 0.30CH_2Cl_2$	$C_{47}H_{41}N_5P_2Ru$
MW	1754.04	777.81	860.61	841.09	838.86
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1$	$P4/n$	$P2_1/n$	$P\bar{1}$
a/Å	9.1099(1)	12.4183(2)	27.107(2)	12.0547(10)	11.7031(11)
b/Å	19.9990(5)	10.4022(2)	27.107(2)	20.0027(4)	11.9711(10)
c/Å	24.6501(5)	14.2891(2)	11.727(5)	16.9280(10)	16.2496(10)
α/deg.					79.336(6)
β/deg.	96.403(2)	98.860(2)		101.042(8)	87.205(6)
γ/deg.					67.758(8)
V/Å^3	4463.0(2)	1823.81(5)	8617(4)	4006.2(4)	2070.2(3)
ρ_c (g cm^{-3})	1.305	1.416	1.327	1.394	1.346
Z	2	2	8	4	2
$2\theta_{max}$/deg.	135	64	50	62	55
μ(Mo-$K\alpha$)/mm^{-1}	4.07 [Cu-$K\alpha$]	0.56	0.53	0.55	0.50
$T_{min/max}$	0.72	0.94	0.98/1.03	0.94	0.81
Crystal dimensions/mm^3	0.27 × 0.06 × 0.05	0.39 × 0.11 × 0.05	0.26 × 0.07 × 0.05	0.37 × 0.25 × 0.15	0.27 × 0.14 × 0.12
Reflections collected	55,036	27,774	35,352	64,047	17,407
Unique reflections (R_{int})	7959 (0.051)	11,439 (0.038)	7576 (0.092)	12,760 (0.035)	8604 (0.070)
Reflections ($I > 2\sigma(I)$)	5535	8485	3152	9510	6226
$R1$ ($I > 2\sigma(I)$)	0.055	0.033	0.090	0.045	0.061
$wR2$ (all data)	0.161	0.061	0.239	0.123	0.159

was purified by preparative TLC (acetone-hexane, 3/7). Two major bands were collected: orange (R_f = 0.46) containing Ru{C≡CCMe=C(CN)$_2$}(dppe)Cp* **3** (R = Me) (8 mg, 24%) [3] and yellow (R_f = 0.38) containing Ru{*c*-C=CHC[=C(CN)$_2$]CH=CHO}(dppe)Cp* **4** (6 mg, 17%) as a bright yellow solid. X-ray quality crystals were grown from CH$_2$Cl$_2$/hexane. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡N) 2194m, 2170w, ν(C=C) 1620s, 1476m, 1453s, 1436w. ^{1}H NMR (CDCl$_3$): δ 1.45 (s, 15H, Cp*), 2.48, 2.74 (2× m, 2× CH$_2$, dppe), 5.85 [dd, J(HH) = 5.6, 2.3 Hz, 1H, H], 6.33 [d, J(HH) = 5.6 Hz, 1H, H], 6.54 (s, 1H, H), 7.13–7.38 (m, 20H, Ph). ^{13}C NMR (CDCl$_3$): δ 10.16 (s, C$_5$*Me*$_5$), 28.66–31.16 (m, dppe), 95.61 (s, *C*$_5$Me$_5$), 107.94, 124.19, 148.70, 153.53 (4× s, C), 119.17, 119.63 (2× s, CN), 127.94–137.92 (m, Ph), 217.04 (m, Ru–C). ^{31}P NMR (CDCl$_3$): δ 93.6 [s, 2P, Ru(dppe)]. ES-MS (MeOH, m/z): 778, M$^+$ (calcd $C_{44}H_{42}N_2OP_2Ru$, 778); 635, [Ru(dppe)Cp*]$^+$; HR-MS: [M + H]$^+$ 779.201 (calcd 779.189); [M + Na]$^+$ 801.184 (801.171).

4.5. *Reactions of TCNE*

4.5.1. *With Ru(C≡CC≡CLi)(dppe)Cp**

A solution of Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.07 mmol) in THF (5 ml) was treated with LiBu (70 μL, 1.5 M solution in hexanes) and stirred for 30 min at −78 °C. TCNE (9 mg, 0.07 mmol) was added and the mixture was stirred at −78 °C for 30 min and then at r.t. for 4 h. Solvent was removed and the residue was dissolved in minimum amount of CH$_2$Cl$_2$ and purified by preparative TLC. Three bands separated with CH$_2$Cl$_2$ as eluant. Band 1 (red, R_f = 0.33) contained {Ru(dppe)Cp*}$_2${μ-C≡CC[=C(CN)$_2$]C[=C(CN)$_2$]C≡C} **5** (35 mg, 32%). Anal. Calcd. ($C_{82}H_{80}N_4P_4Ru_2$): C, 68.65; H, 5.35; N, 3.81. Found: C, 68.71; H, 5.79; N, 3.72. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2208w, 2075w; ν(C≡C) 1967 (sh), 1866m. ^{1}H NMR (CDCl$_3$): δ 1.51 [t, ^4J(HP) = 2 Hz, 30H, Cp*], 1.98, 2.44 (2× m, 2× 4H, CH$_2$P), 6.77–7.71 (m, 40H, Ph). ^{31}P NMR (CDCl$_3$): δ 79.9, 81.3 [AB q, ^3J(PP) = 13 Hz, dppe]. ES-MS (m/z): 1493, [M + Na]$^+$; 635, [Ru(dppe)Cp*]$^+$.

Band 2 (blue, R_f = 0.27) afforded Ru{C≡C–*c*-C=C(CN)C(O)NHC[=C(CN)$_2$]}-(dppe)Cp* **6** (10 mg, 20%). Single crystals suitable for X-ray studies were grown from CH$_2$Cl$_2$/hexane. Anal. Calcd. ($C_{46}H_{40}N_4OP_2Ru$): C, 66.65; H, 4.87; N, 6.76. Found: C, 66.54; H, 5.44; N, 6.44. IR (CH$_2$Cl$_2$, cm^{-1}): ν(NH) 3058w; ν(CN) 2212w, ν(C≡C) 1954m, ν(CO) 1716m, ν(C=C) 1603w. ^{1}H NMR (CDCl$_3$): δ 1.68 (s, 15H, Cp*), 1.76–1.83, 2.68–2.74 (2× m, 4H, CH$_2$CH$_2$), 7.23–7.62 (m, 20H, Ph). ^{31}P NMR (CDCl$_3$): δ 72.9 (s, dppe). ES-MS (MeOH + NaOMe, m/z): 659, [C$_2$Ru(dppe)Cp*]$^+$; 635, [Ru(dppe)Cp*]$^+$. High resolution MS (m/z): 851.1624, [M + Na]$^+$ (calcd for $C_{46}H_{40}N_4NaOP_2Ru$ 851.1618).

Band 3 (orange, R_f = 0.23) contained Ru{C≡C–*c*-C=CHC[=C(CN)$_2$]NHCMe=N}(dppe)Cp* **7** (8 mg, 16%). Single crystals suitable for X-ray studies were grown from CH$_2$Cl$_2$/hexane. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CH) 2926m, ν(CN) 2204m, ν(C≡C) 2024m; ν(C=C) 1644 (w); ν(NH) 1529 (w). ^{1}H NMR (CDCl$_3$): δ 1.26 (s, H, Me), 1.54 (s, 15H, Cp*), 2.17 (s, 3H, CH), 2.13–2.18, 2.27–2.31 (2× m, 2× 2H, CH$_2$CH$_2$), 4.19 (s, H, NH), 7.07–7.63 (m, 20H, Ph). ^{31}P NMR (CDCl$_3$): δ 79.7 (s, dppe). ES-MS (MeOH, m/z): 816, [M]$^+$; 635, [Ru(dppe)Cp*]$^+$. High resolution MS (m/z): 817.211, [M − Me]$^+$ (calcd for $C_{45}H_{41}N_4OP_2Ru$, 817.180).

4.5.2. *With Ru(C≡CC≡CI)(dppe)Cp** **8**

To a solution of Ru(C≡CC≡CH)(dppe)Cp* (156 mg, 0.23 mmol) in THF (10 ml) at −78 °C was added LiBu (0.10 ml, 2.5 M in hexanes, 0.25 mmol) and stirred for 5 min. [I(py)$_2$]BF$_4$ (88 mg, 0.24 mmol) was then added and the mixture was stirred 20 min to give a solution containing Ru(C≡CC≡CI)(dppe)Cp* **8**. TCNE (33 mg, 0.26 mmol) was added at −78 °C and the vessel allowed to warm to r.t. Solvent was removed and the residue purified by preparative TLC (1% acetone/dichloromethane) to afford dark purple Ru{C≡CC=C(CN)$_2$CI=C(CN)$_2$}(dppe)Cp* (99 mg, 46%) [20] and pink Ru{C≡C–*c*-C=C(CN)C(NH$_2$)=C(CN)C(CN)$_2$}(dppe)Cp* **9** (20 mg, 10%). X-ray quality crystals were grown from CH$_2$Cl$_2$/hexane. Anal. Calcd ($C_{47}H_{41}N_5P_2Ru$): C, 67.29; H, 4.93; N, 8.35; *M*, 839. Found: C, 66.67; H, 4.88; N, 8.16. IR (Nujol, cm^{-1}): ν(NH) 3453 (br), ν(CN) 2200w (sh), 2185m, ν(C≡C) 1984s, ν(C=C) 1654w, 1575w, 1507m. ^{1}H NMR (CDCl$_3$): δ 1.61 (s, 15H, Cp*), 2.36, 2.95 (2× m, 2× CH$_2$, dppe), 5.10 (s, 2H, NH$_2$), 7.15–7.58 (m, 20H, Ph). ^{13}C NMR (CDCl$_3$): δ 10.01 (C$_5$*Me*$_5$), 29.69 (m, PCH$_2$), 96.90 (s, *C*$_5$Me$_5$), 110.53, 114.46, 114.70 (3× s, CN), 123.87, 162.59 (2× s, C) 127.91–134.90 (m, Ph). ^{31}P NMR (CDCl$_3$): δ 81.2 (s, dppe). ES-MS (MeOH + NaOMe, m/z): 1496, [M + Na + Ru(dppe)Cp*]$^+$; 862, [M + Na]$^+$; 635, [Ru(dppe)Cp*]$^+$. HR-MS: [M + Na]$^+$, 862.183 (calcd 862.177).

4.6. *Structure determinations*

Crystallographic data for the structures were collected at 100(2) K on CCD diffractometers fitted with Mo-Kα radiation,

$\lambda = 0.71073$ Å (Cu-Kα, $\lambda = 1.54184$ Å, for **2**). Following multi-scan absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97 [24]. Anisotropic displacement parameters were employed for the non-hydrogen atoms. All H-atoms were added at calculated positions and refined by use of riding models with isotropic displacement parameters based on those of the parent atom. Pertinent results are given in the Figures, which show non-hydrogen atoms with 50% probability amplitude displacement envelopes, and in Table 1.

For the crystal structure of **2**, the atoms of the Cp* ring and those of one Ph ring (22n) are both disordered over two sets of sites, each with occupancies constrained to 0.5 after trial refinement. For **6**, the solvent was modelled as a dichloromethane molecule with a refined occupancy of 0.386(15). For **7**, the site occupancy of the dichloromethane solvent molecule refined to 0.297(3) with geometries restrained to ideal values. For **9**, the Cp* ring was modelled as being disordered over two sets of sites with occupancies refined to 0.725(4) and its complement.

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Appendix A. Supplementary material

CCDC 887533 (**2**), 705436 (**4**), 887534 (**6**), 887535 (**7**) and 887536 (**9**) 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.

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