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Reactions of $Ru(C{\equiv}CPh)(PPh_3)_2Cp^*$ with tetracyanoethene: cycloaddition, formation of unusual η^2-CNR complexes and oligomerisation *via* bridging cyanocarbon ligands

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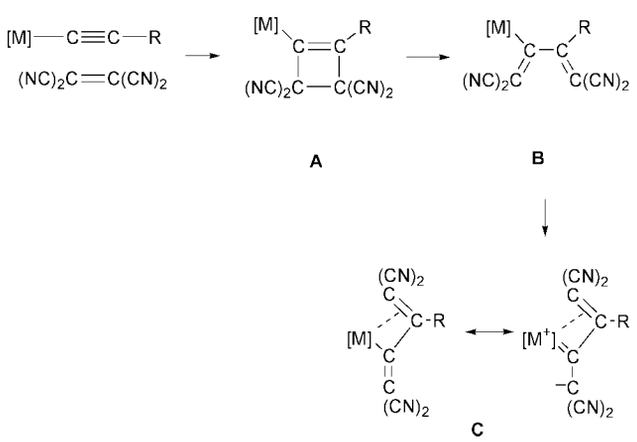
Received 12th June 2001, Accepted 3rd October 2001
First published as an Advance Article on the web 13th November 2001

Thermolysis of $Ru\{\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2\}(PPh_3)Cp^*$ (**2**), obtained from $Ru(C{\equiv}CPh)(PPh_3)_2Cp^*$ and tetracyanoethene, has given the three complexes $Ru\{\eta^1,\eta^2(C,N)\text{-}C(CN){=}C(CN)CPh{=}C(CN)(C{=}N)\}(PPh_3)Cp^*$ (**3**), $\{Ru(PPh_3)Cp^*\}\{\mu\text{-}N{:}\eta^3\text{-}NCC(CN){=}CPhC{=}C(CN)_2\}\{\mu\text{-}\eta^1{:}N\text{-}C(CN){=}C(CN)CPh{=}C(CN)_2\}\{RuCp^*\}$ (**4**) and $\{Ru[\eta^3\text{-}C(CN)_2{=}CPhC{=}C(CN)_2]Cp^*\}_3$ (**5**). All four complexes have been characterised by single-crystal X-ray structure determinations and contain isomeric forms of the $C_4(CN)_4Ph$ ligand. Unusual features of the molecular structures are (i) the presence of a side-on (η^2) CN group in **3**; (ii) formation of a second isomer of the polycyanocarbon ligand by CN migration to an adjacent carbon, in **3** and **4**; (iii) the use of one or more CN groups to bridge ruthenium centres in **4** and **5**; and (iv) the complete loss of PPh_3 ligands during the formation of the trimer **5**. Although there are three crystallographically distinct RuCp* groups in **5**, only one Cp* resonance is found in solution NMR spectra, suggesting that oligomer formation by facile CN–Ru bond breaking and making is occurring.

Introduction

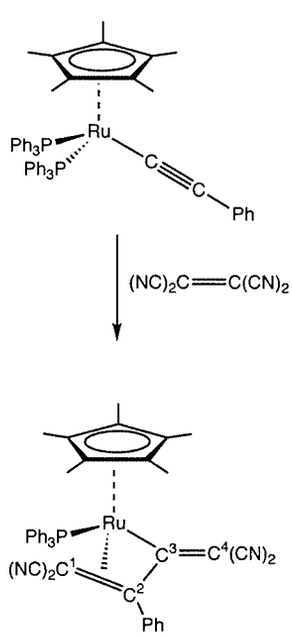
Cycloaddition of electron-deficient alkenes to transition metal σ-alkynyl complexes was first reported in 1979[1] and has been extensively investigated since then.[2,3] The initial product is a deeply coloured radical species, although this is not always observed, which fades rapidly (minutes) to the colour of the product. The first complex which has been isolated is the σ-cyclobutenyl (**A**, Scheme 1) which then undergoes a ring-opening reaction to give the buta-1,3-dien-2-yl complex **B**. Where there is a labile ligand attached to the metal centre, its loss results in the formation of the η^3-allylic species **C**. This derivative has a short M–C σ bond and is better considered as a zwitterion attached *via* an $M{=}C(sp^2)$ multiple bond. Addition of other 2e ligands may reverse the last reaction to give other complexes of type **B**.



Scheme 1

When tetracyanoethene, $C_2(CN)_4$ (tcne), is used, the resulting products are stable and do not readily enter into further reactions. In two cases, hydrolysis or methanolysis of one CN group has been reported to give chelating hydroxy- or alkoxy-imine derivatives.[2e,4] Further coordination of a second metal centre has also been observed,[5] in one case giving a macrocyclic complex containing a 10-membered ring.[6] However, apart from these, to our knowledge no further elaboration of the polycyanocarbon ligand has been reported.

Much of our earlier work was carried out with the $Ru(PPh_3)_2Cp$ fragment, where the ready loss of one PPh_3 ligand encourages the formation of complexes of type **C**. Recently, we and others have described a series of σ-alkynyls containing the $Ru(PPh_3)_2Cp^*$ fragment.[7] Many of the compounds were derived from a neutral vinylidene complex by loss of HCl in the presence of a ligand L (O_2, S_2, C_2H_4, *etc.*).[8] We now report some chemistry of the complex $Ru(C{\equiv}CPh)(PPh_3)_2Cp^*$ (**1**) with tcne and some subsequent reactions of the polycyano ligand (Schemes 2 and 3).



2

Scheme 2

DOI: 10.1039/b105131h

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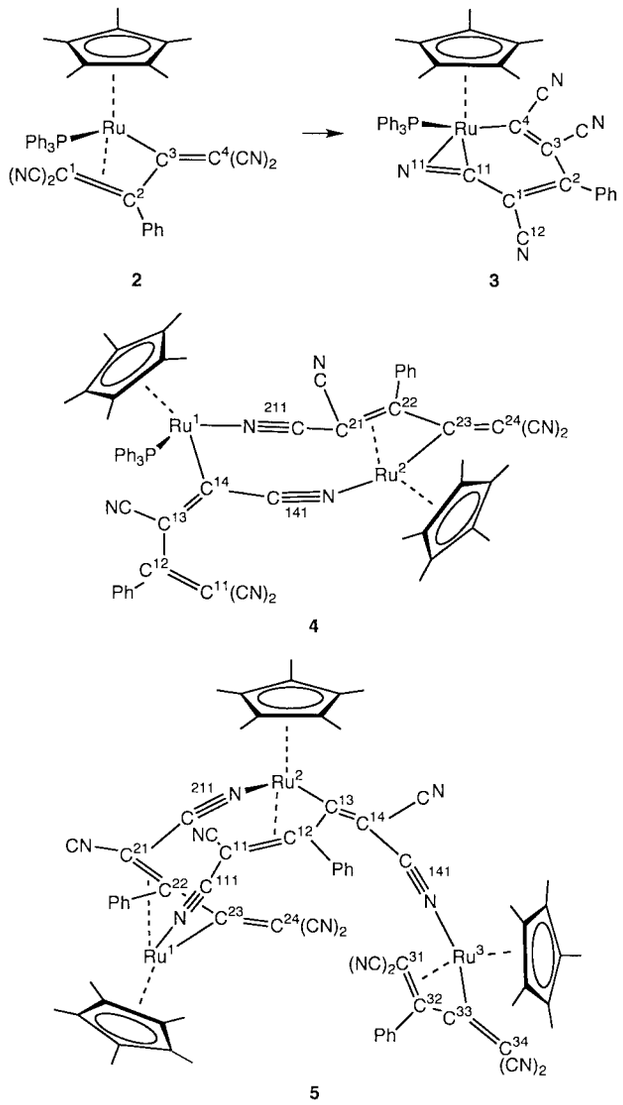


Scheme 3

Results and discussion

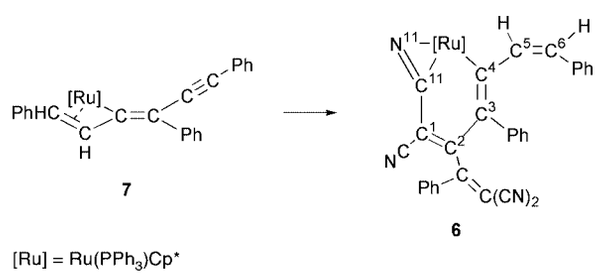
The reaction between **1** and tcne was carried out in benzene at rt for 24 h. The only detectable product is the η^3-allylic complex, Ru{η^3-C(CN)$_2$CPhC=C(CN)$_2$}(PPh$_3$)Cp* (**2**), which forms orange crystals in 73% yield. This complex was readily identified by microanalysis and spectroscopic methods. In common with earlier studies, the IR spectrum contained few characteristic bands apart from ν(CN) at 2215 cm^{-1}. The ^{1}H NMR spectrum contains a doublet for the Cp* Me groups at δ 1.35, which with the 15/20 ratio of this resonance and the Ph multiplet indicates the presence of only one PPh$_3$ ligand on the ruthenium centre. Similarly, the ES mass spectrum contains [M + H]$^+$ at *m*/*z* 729. The molecular structure of **2** was determined from a single-crystal X-ray study (see below).

Thermolysis of **2** in refluxing benzene overnight and separation by preparative t.l.c. gives three fractions. From the fastest running fraction, purple crystals of Ru{η^1,η^2(*C*,*N*)-C(CN)=C(CN)CPh=C(CN)(C=N)}(PPh$_3$)Cp* (**3**) were isolated in 16% yield. Complex **3** is an isomer of **2**, the X-ray molecular structure determination revealing two unusual features: one of the CN groups has migrated to an adjacent carbon atom, while another is η^2-bonded (side-on) to the ruthenium atom. The IR spectrum contains ν(CN) bands at 2209 and 2170 cm^{-1}. The ^{1}H NMR spectrum contains a doublet for the Cp* Me groups at δ 1.51, while in the ^{13}C NMR spectrum, these Me groups resonate as a singlet at δ 8.53; the Cp* ring carbons give a doublet at δ 101.08, however. Apart from C(3) and C(4), other carbon atoms in the polycyano ligand give rise to doublet resonances between δ 116.69 and 191.19; the latter is assigned to C(11) by analogy with the resonance at δ 235 found for [WCl(η^2-NCMe)(PMe$_3$)$_2$(bpy)]$^+$.[9] The ES mass spectrum of a solution containing NH$_4$OH gives [M + NH$_4$]$^+$and M$^+$ ions at *m*/*z* 746 and 728, respectively.

The second product, obtained in 13% yield, forms red crystals and is formulated as {Ru(PPh$_3$)Cp*}{μ-*N*:η^3-NCC(CN)=CPhC=C(CN)$_2$}{μ-η^1:*N*-C(CN)=C(CN)CPh=C(CN)$_2$}{RuCp*} (**4**) from the X-ray structure determination. The two polycyano ligands differ, one being attached to Ru(1) *via* a C–Ru σ-bond and N–Ru donor bond, the other to Ru(2) in the η^3-allylic mode and by an *N*-donor bond. Major structural details are discussed below, but in general they are similar to those found for these ligands on earlier occasions.[2] The IR spectrum contains ν(CN) bands at 2213, 2078 and 2017 cm^{-1}, while M$^+$ is found at *m*/*z* 1194.

The major product (52%) is a trimer, {Ru[η^3-C(CN)$_2$=CPhC=C(CN)$_2$]Cp*}$_3$ (**5**), as shown by the X-ray structure determination. This complex is unusual in not containing any PPh$_3$ ligands and in having the same cyanocarbon ligand with three different bonding modes, that is, a "normal" η^3 system to Ru(3), an η^3 system on Ru(1) also bridging *via* one CN to Ru(2), and the third η^3 system on Ru(2) which uses two CN groups to bridge to Ru(1) and Ru(3). Only two ν(CN) bands are found, at 2215 and 2126 cm^{-1}. The ^{1}H NMR spectrum contains only one Me resonance, at δ 1.56, suggesting that there may be some fluxional process which renders all Cp* Ru groups equivalent on the NMR time scale. However, there was no change in the NMR spectra at the lowest temperature we were able to record (218 K) when precipitation started to occur. Ready loss of a Ru{PhC$_4$(CN)$_4$} group from the [M + Na]$^+$ ion is found in the ES mass spectrum, obtained in the presence of NaOMe.

On one occasion, a small amount of a complex identified from an X-ray structure determination as Ru{η^1,η^2(*C*,*N*)-C(CH=CHPh)=CPhC[CPh=C(CN)$_2$]=C(CN)(C=N)}(PPh$_3$)-Cp* (**6**, Scheme 4) was obtained from the reaction of **1** with



[Ru] = Ru(PPh$_3$)Cp*

Scheme 4

tcne. However, it was later established that a corresponding amount of Ru{η^3-CHPh=CHC=CPh(C≡CPh)}(PPh$_3$)Cp* (**7**)[8] was present as an impurity in the sample of **1** and an independent experiment showed that **6** was formed in 51% yield in the reaction of pure **7** with tcne.[10] Compound **6** also has a side-on η^2-CN ligand, the tcne apparently adding to the non-coordinated C≡CPh group in **7**. Preparative t.l.c. separated the dark green product into two closely running bands, which each gave dark green solids after work-up. However, the spectroscopic properties (IR, NMR) of the two fractions were identical and further chromatography of each fraction gave the same two bands. X-Ray structure determinations of crystals obtained from each fraction were also identical, although it is entirely possible that the same (least soluble) isomer was obtained in each case. It is likely therefore that these two materials are isomers, either conformational or by exchange of coordinated and free CN groups.

Molecular structures

The natures of **2**, **3**, **4** and **5** were confirmed or determined from single-crystal X-ray structure determinations; the structure of **6** has been reported previously,[10] but is further discussed below. Plots of these molecules are shown in Figs. 1–4 and selected structural data are given in Tables 1 and 2.

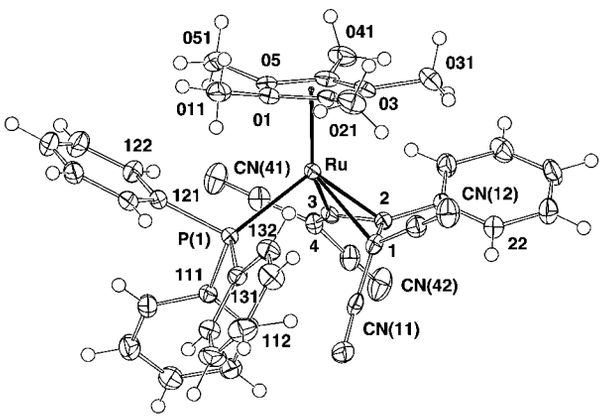


Fig. 1 Plot of a molecule of Ru{η^3-C(CN)$_2$CPhC=C(CN)$_2$}(PPh$_3$)Cp* (**2**), showing atom numbering scheme.

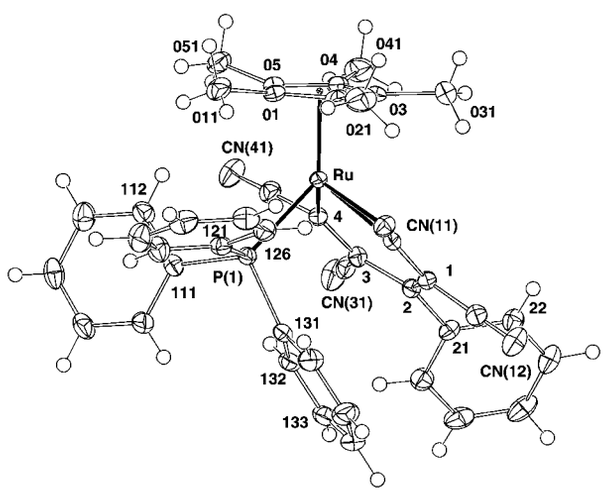


Fig. 2 Plot of a molecule of Ru{η^1,η^2(*C*,*N*)-C(CN)=C(CN)CPh=C(CN)(C–N)}(PPh$_3$)Cp* (**3**).

For **2**, **3** and **4**, common features are the Ru(PPh$_3$)Cp* groups, which have structural parameters similar to those reported earlier. Thus, the Ru–P distances range between 2.3520(7) and 2.4013(8) Å, while the average Ru–C(Cp*) separations are between 2.22(4) and 2.28(3) Å, internal precision being much better and indicative of some asymmetry in the ring–metal binding, *e.g.* in **2**, **3** or **4** where individual values range between 2.230 and 2.313(3) Å. Evidently, intramolecular steric interactions with the ring Me groups, which lie well out of the C$_5$ ring planes in some cases (up to *ca.* 0.3 Å, visibly so in some of the Figures), result in a soft attachment of the C$_5$ ring to the metal. The η^3-cyanocarbon ligands in **2**, **4** and **5** are also common, differing only in whether or not they are also attached to a second (or third) Ru centre by one of the CN groups. Bond parameters are similar to those reported in earlier examples and do not warrant detailed discussion.

The formation of the C(CN)$_2$CPhC=C(CN)$_2$ ligands by addition of tcne to the σ-phenylethynyl ligand in **1** occurs *via* the reactions that have previously been described.[2] In **3** and **4**, one of the cyanocarbon ligands has been formed by an unusual migration of a CN group to an adjacent carbon atom in the chain (Scheme 5). In **3**, chelation occurs by η^2 bonding of a CN to Ru, whereas in **4**, a CN group is N-bonded to the second Ru atom. The unusual chemistry found here, which does not occur under the same or harsher conditions with the Cp analogue, involves η^2 coordination of a CN group (in **3**) and migration of a CN group (in **3** and **4**). The presence of the strongly electron-donating Cp* group increases electron density at the Ru centre so that stabilisation of the η^2-CN arrangement by back-bonding from the metal to the CN π* orbitals can occur. This is confirmed by a lengthening of the coordinated C–N bond, as shown by comparison of C(11)–N(11) [1.212(3) Å] with the non-coordinated C(12)–N(12) group [1.142(3) Å] on the same C(1) atom, together with the bending of the C(1)–C(11)–N(11) angle by 35.4(2)° from the normal linear arrangement [*cf.* C(1)–C(12)–N(12) 176.6(2)°]. That this type of coordination occurs may be the result of steric pressures in the alternative η^2-C(1)=C(2) arrangement that would have been expected.

A possible sequence of reactions is outlined in Scheme 5. Migration of a CN group from C(4) to Ru generates a zwitterionic intermediate, represented as **D**. A related complex, Ru(CN){C(CN)C[CPh=C(CN)$_2$]PPh$_2$CH$_2$PPh$_2$}Cp*, has been described.[10] Intermediate **D** may evolve in several ways. Further

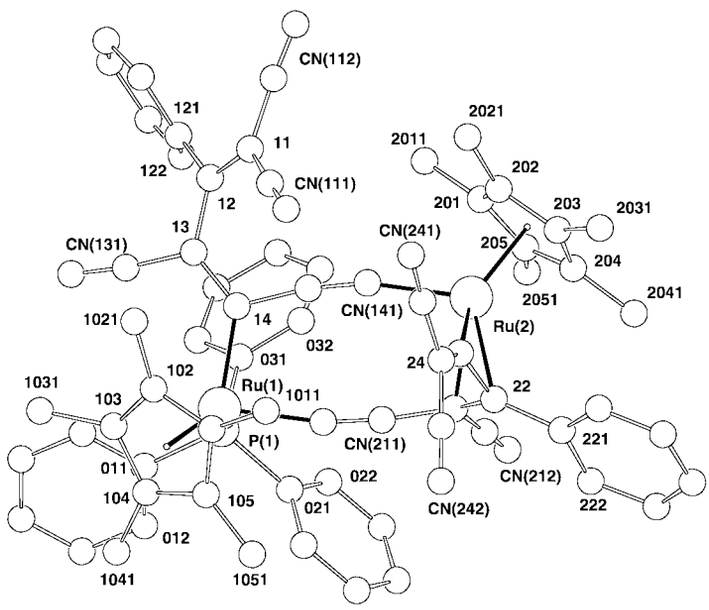
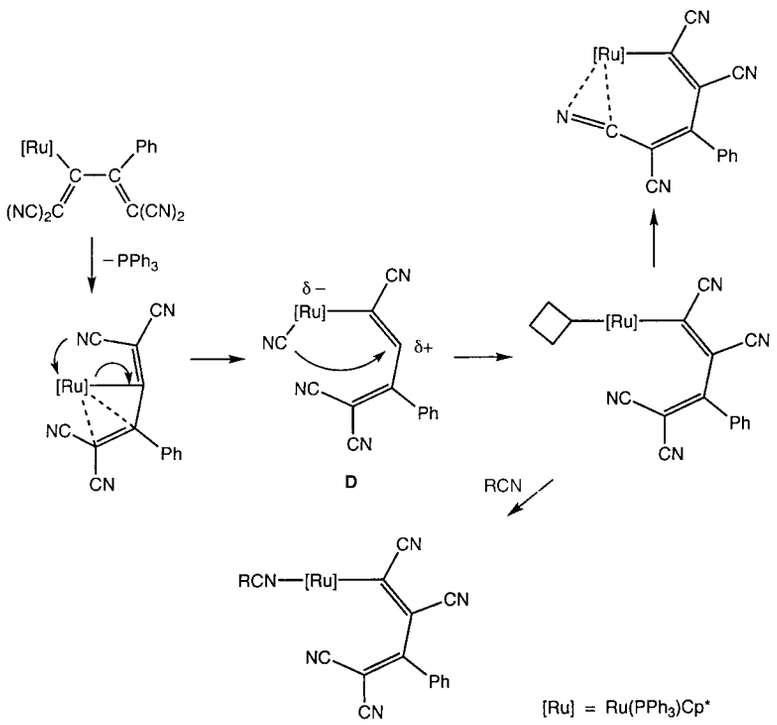


Fig. 3 Plot of a molecule of {Ru(PPh$_3$)Cp*}{μ-*N*:η^3-NCC(CN)=CPhC=C(CN)$_2$}{μ-η^1:*N*-C(CN)=C(CN)CPh=C(CN)$_2$}{RuCp*} (**4**), with H atoms omitted for clarity.



Scheme 5

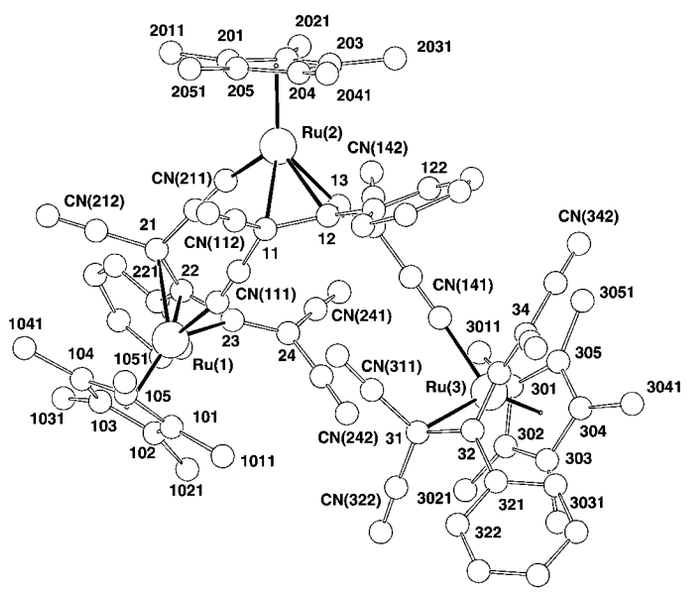


Fig. 4 Plot of a molecule of $\{Ru[\eta^3\text{-}C(CN)_2{=}CPhC{=}C(CN)_2]Cp^*\}_3$ (**5**), with H atoms omitted for clarity.

migration of the CN group to the β-carbon, C(3), of the vinyl group, results in isomerisation of the cyanocarbon ligand, as found in **3**. At the same time, a vacant coordination site on Ru is generated which, in the absence of a suitable ligand, is occupied by a CN group on C(1), bonding in the η^2 mode.

The formation of **4** occurs by addition of a second molecule of **2** (RCN in Scheme 5) to intermediate **D** *via* coordination of a CN lone-pair, with concomitant loss of PPh_3. In **4**, which contains the two isomeric forms of the cyanocarbon ligand, Ru(1) originates from **3**, while Ru(2) comes from **2**. Finally, formation of **5** occurs by trimerisation of **2**, without isomerisation, but with loss of all PPh_3 ligands. This complex contains the original cyanocarbon ligand bonding in three different modes.

Conclusions

We have demonstrated novel isomerisation reactions which are undergone by the cyanocarbon ligand formed by addition of tetracyanoethene to the phenylethynyl ligand in **1**. We suggest that the CN-migration reaction may proceed *via* a zwitterionic intermediate **D**. It is possible that attack of an alternative anionic centre or electron-rich neutral atom, may further elaborate the original cyanocarbon, as found in Ru(CN)-{C(CN)C[CPh=C(CN)$_2$]$PPh_2CH_2PPh_2$}Cp*.[10] The ready loss of a PPh_3 ligand from $Ru(PPh_3)_2Cp'$ (Cp′ = Cp or Cp*) complexes may lead to the formation of macrocyclic complexes, as found earlier,[6] or oligomeric species such as **5**, as found here. These reactions are relevant to the intramolecular oxidative addition reaction whereby NiPh(CN)(dippe) [dippe = 1,2-bis-(di-iso-propylphosphino)ethane] is formed reversibly from the η^2-nitrile complex Ni(η^2-NCPh)(dippe)[11] and may also pertain to the alkylation of molybdenum–η^2-NCMe complexes.[12]

Experimental

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen,

Table 1 Selected bond distances (Å) and angles (°) for **2**, **3** and **6**

	2	**3**	**6**[a]
Ru–P	2.4013(8)	2.3574(6)	2.3520(7)
Ru–C(Cp*)	2.230–2.313(3)	2.239–2.304(2)	2.234–2.304(3)
(av.)	2.27(4)	2.28(3)	2.27(3)
Ru–C(1)	2.210(3)		
Ru–C(2)	2.162(3)		
Ru–C(3)	1.973(3)		
Ru–C(4)		2.044(2)	2.097(3)
Ru–C(11)		2.079(2)	2.061(3)
Ru–N(11)		2.211(2)	2.208(2)
C(1)–C(2)	1.484(4)	1.369(3)	1.382(4)
C(1)–C(11)		1.436(3)	1.423(3)
C(2)–C(3)	1.425(4)	1.455(3)	1.445(4)
C(3)–C(4)	1.357(4)	1.395(3)	1.378(3)
C(4)–C(5)			1.471(4)
C(5)–C(6)			1.343(5)
C–CN (av.)	1.443(7)	1.441(9)	1.436(9)
C(11)–N(11)	1.143(4)	1.212(3)	1.215(3)
C(12)–N(12)	1.149(4)	1.142(3)	1.141(4)
C–N (av.)	1.143(7)	1.148(9)	1.139(3)
P–Ru–C(1)	90.36(8)		
P–Ru–C(3)	89.37(8)		
P–Ru–C(4)		89.63(6)	90.13(7)
P–Ru–C(11)		91.12(6)	97.40(8)
P–Ru–N(11)		85.27(5)	87.09(7)
C(1)–Ru–C(3)	71.1(1)		
C(4)–Ru–C(11)		81.01(8)	82.1(1)
C(4)–Ru–N(11)		113.02(7)	113.23(9)
C(2)–C(1)–C(11)		122.3(2)	120.1(3)
C(1)–C(2)–C(3)	114.0(2)	120.9(2)	124.7(2)
C(2)–C(3)–C(4)	134.9(2)	125.7(2)	124.4(3)
C(3)–C(4)–C(5)			117.4(3)
C(4)–C(5)–C(6)			124.2(3)
Ru–C(11)–C(1)		135.7(2)	
Ru–C(4)–C(3)		133.7(2)	
C(1)–C(11)–N(11)			145.5(3)

[a] Ref. 10.

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 t.l.c. was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thickness).

Instrumentation

IR: Perkin-Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^{1}H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. 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.[13]

Reagents

Complexes **1**[7b] and **7**[8] were prepared as previously described. tcne (Aldrich) was sublimed before use.

Reaction of Ru(C≡CPh)(PPh$_3$)$_2$Cp* with tcne. A mixture of Ru(C≡CPh)(PPh$_3$)$_2$Cp* (74 mg, 0.09 mmol) and tcne (22 mg, 0.18 mmol) in benzene (7 ml) was stirred at rt for 24 h. Removal of solvent and purification of a CH_2Cl_2 extract of the residue by preparative t.l.c. (acetone–hexane 3/7) gave a single orange band (R_f 0.4). Extraction and crystallisation (CH_2Cl_2–MeOH) gave orange crystals of Ru{η^3-C(CN)$_2$CPhC=C(CN)$_2$}(PPh$_3$)Cp* (**2**) (45.3 mg, 72.5%). Anal. Found: C, 68.45; H, 4.91; N, 7.60. Calc. for $C_{42}H_{35}N_4PRu$: C, 69.23; H, 4.80; N, 7.69%; *M*, 728. IR (CH_2Cl_2): *ν*(CN) 2215s; other bands at 1579m, 1535w, 1483m, 1437m, 1378m cm^{-1}. ^{1}H NMR: *δ* 1.35 [d, *J*(HP) 1.2 Hz, 15H, Me], 6.95–7.72 (m, 20H, Ph). ^{31}P NMR: *δ* 46.75 (s, PPh_3). ES mass spectrum (MeOH–CH_2Cl_2 + NH_3, *m*/*z*): 746, $[M + NH_4]^+$; 729, $[M + H]^+$.

Thermolysis of 2. A solution of **2** (140 mg, 0.19 mmol) in benzene (15 ml) was heated at reflux point overnight. After evaporation of benzene, the residue was dissolved in acetone and separated by preparative t.l.c. (acetone–hexane 3/7) into three fractions. Band 1 (R_f 0.51) gave purple crystals (CH_2Cl_2–MeOH) of Ru{η^1,η^2(*C*,*N*)-C(CN)=C(CN)CPh=C(CN)(C–N)}(PPh$_3$)Cp* (**3**) (23.8 mg, 16.4%). Anal. Found: C, 68.17; H, 5.08; N, 7.47. Calc. for $C_{42}H_{35}N_4PRu$·MeOH: C, 67.97; H, 5.17; N, 7.37%; *M*, 728. IR (CH_2Cl_2): *ν*(CN) 2209m, 2170m; other bands at 1605s, 1541m, 1482m, 1438m, 1378m cm^{-1}. ^{1}H NMR: *δ* 1.51 [d, *J*(HP) 1.8 Hz, 15H, Me], 7.28–7.82 (m, 20H, Ph). ^{13}C NMR: *δ* 8.53 (s, Me), 101.08 [d, *J*(CP) 2.56 Hz, Cp*], 115.72 [s, C(3)], 116.69 [d, *J*(CP) 2.56 Hz, C(31)N], 122.97 [d, *J*(CP) 3.99 Hz, C(8)N], 124.46 [d, *J*(CP) 3.16 Hz, C(3)], 128.01–130.52 (m, Ph), 136.12 [s, C(2)], 143.03 [d, *J*(CP) 2.03 Hz, C(41)N], 158.70 [d, *J*(CP) 2.86 Hz, C(4)], 191.19 [d, *J*(CP) 14.56 Hz, C(11)]. ^{31}P NMR: *δ* 44.13 (s, PPh_3). ES mass spectrum (MeOH containing NH_4OH, *m*/*z*): 746, $[M + NH_4]^+$; 728, M^+.

Band 2 (R_f 0.43) afforded {RuCp*}{μ-*N*:η^3-C[=C(CN)$_2$]-CPhC(CN)$_2$}{μ-η^1:-*N*-C(CN)=C(CN)CPh=C(CN)$_2$}{Ru(PPh$_3$)-Cp*} (**4**) (14.5 mg, 12.6%) as dark red crystals (CH_2Cl_2–MeOH). Anal. Found: C, 62.72; H, 4.58; N, 8.57. Calc. for $C_{66}H_{55}N_8PRu_2$·CH_2Cl_2: C, 62.91; H, 4.46; N, 8.78%; *M*, 1194. IR (CH_2Cl_2): *ν*(CN) 2213m, 2078w, 2017w; other bands at 1602m, 1555m, 1539w, 1434m, 1335m cm^{-1}. ^{1}H NMR: *δ* 1.41 (s, 15H, Cp*), 1.67 [d, *J*(HP) 1.5 Hz, 15H, Cp*], 6.56–7.69

Table 2 Selected bond distances (Å) and angles (°) for **4** and **5**

	4	**5**
Ru–P	2.3618(8)	
Ru(1)–C(Cp*)	2.194–2.271(2)	2.171–2.283(6)
(av.)	2.24(3)	2.22(4)
Ru(2)–C(Cp*)	2.179–2.276(3)	2.172–2.298(5)
(av.)	2.22(4)	2.23(5)
Ru(3)–C(Cp*)		2.174–2.305(5)
(av.)		2.23(6)
Ru(1)–C(14)	2.032(2)	
Ru(2)–C(11)		2.234(5)
Ru(2)–C(12)		2.159(4)
Ru(2)–C(13)		1.980(5)
Ru(2)–C(21)	2.242(2)	2.226(5) [Ru(1)]
Ru(2)–C(22)	2.163(2)	2.155(5) [Ru(1)]
Ru(2)–C(23)	1.986(3)	1.975(5) [Ru(1)]
Ru(3)–C(31)		2.198(4)
Ru(3)–C(32)		2.171(5)
Ru(3)–C(33)		1.969(5)
Ru(1)–N(11)	2.034(2) [N(211)]	2.044(4) [N(111)]
Ru(2)–N(11)	2.049(2) [N(141)]	2.074(4) [N(211)]
Ru(3)–N(141)		2.031(4)
C(11)–C(12)	1.363(6)	1.466(7)
C(11)–C(111)		1.432(7)
C(12)–C(13)	1.483(4)	1.422(7)
C(13)–C(14)	1.368(4)	1.347(7)
C(14)–C(141)	1.461(4)	1.432(7)
C(21)–C(22)	1.458(4)	1.475(7)
C(21)–C(211)	1.432(3)	1.433(7)
C(23)–C(24)	1.353(4)	1.358(7)
C(31)–C(32)		1.471(7)
C(32)–C(33)		1.429(7)
C(33)–C(34)		1.356(7)
C–CN (av.)	1.44(1)	1.436(7)
C(111)–N(111)		1.149(7)
C(141)–N(141)	1.170(3)	1.143(6)
C(211)–N(211)	1.146(3)	1.149(7)
C–N (av.)	1.142(6)	1.144(8)
P–Ru(1)–C(14)	94.31(9)	
P–Ru(1)–N(211)	86.75(7)	
C(14)–Ru(1)–N(211)	87.90(9)	
C(21)–Ru(2)–C(23)	68.6(1)	
C(11)–Ru(2)–N(211)		89.7(2)
C(13)–Ru(2)–N(211)		89.1(2)
C(21)–Ru(2)–N(141)	88.58(8)	88.4(2)[a]
C(23)–Ru(2)–N(141)	91.06(9)	91.9(2)[a]
C(31)–Ru(3)–N(141)		90.0(2)
C(33)–Ru(3)–N(141)		89.6(2)
C(12)–C(11)–C(111)		117.1(4)
C(11)–C(12)–C(13)	123.6(3)	110.2(4)
C(12)–C(13)–C(14)	127.6(3)	140.2(4)
C(13)–C(14)–C(141)	115.9(2)	122.4(5)
C(22)–C(21)–C(211)	120.4(2)	
C(21)–C(22)–C(23)	111.3(2)	
C(22)–C(23)–C(24)	132.0(2)	
C(31)–C(32)–C(33)		111.6(4)
C(32)–C(33)–C(34)		139.7(5)
Ru(1)–N(111)–C(111)		166.9(4)
Ru(2)–N(211)–C(211)	170.4(2)	164.0(4)
Ru(3)–C(141)–N(141)		177.9(4)
Ru(1)–C(14)–C(13)	132.1(2)	
Ru(1)–C(14)–C(141)	111.9(2)	
C(11)–C(111)–N(111)		174.8(5)
C(14)–C(141)–N(141)	171.2(3)	179.4(5)
C(21)–C(211)–N(211)	172.9(2)	175.6(5)

[a] Values for C(21)–Ru(1)–N(111), C(23)–Ru(1)–N(111).

(m, 25H, Ph). ^{31}P NMR: δ 43.58 (s, PPh_3). ES mass spectrum (MeOH containing NaOMe, *m*/*z*): 1217, $[M + Na]^+$; 1194, M^+; 955, $[M + Na - PPh_3]^+$.

Band 3 (R_f 0.32) gave orange crystals (acetone–hexane) of $\{Ru[\eta^3\text{-}C(CN)_2{=}CPhC{=}C(CN)_2]Cp^*\}_3$ (**5**) (46 mg, 52%). Anal. Found: C, 61.52; H, 4.40; N, 11.52. Calc. for $C_{72}H_{60}N_{12}Ru_3$: C, 61.92; H, 4.33; N, 12.03%; *M*, 1397. IR (CH_2Cl_2): ν(CN) 2215m, 2126w; other bands at 1603m, 1493w, 1449m, 1417m, 1377m cm^{-1}. ^{1}H NMR: δ 1.56 (s, 45H, Cp*), 7.37–7.57 (m, 15H, Ph). ES mass spectrum (MeOH containing NaOMe, *m*/*z*): 1420, $[M + Na]^+$; 955, $[M + Na - Ru\{PhC_4(CN)_4\}]^+$.

Reaction of Ru{η^3-CHPh=CHC=CPh(C≡CPh)}(PPh$_3$)Cp* (7) with tcne. When tcne (8 mg, 0.06 mmol) was added to a solution of Ru{η^3-CHPh=CHC=CPh(C≡CPh)}(PPh_3)Cp* (**7**) (50 mg, 0.06 mmol) in benzene (5 ml), the mixture immediately turned dark green. After 30 min at rt, no starting complex was present. Evaporation, extraction of the residue with thf and separation by preparative t.l.c. (acetone–hexane 3/7) gave two closely running deep green bands as the major product. Dark green solids were obtained after extraction (R_f 0.49, 10 mg; R_f 0.47, 19.5 mg). Both materials have identical physical properties and are probably isomers. Rechromatography of each band separately also generates two green bands. Crystal structures of products from each band were determined, but were identical, suggesting that in each case, the same isomer is preferentially crystallised. The complex was identified as Ru{η^1,η^2(*N*,*C*)-C(CH=CHPh)=CPhC[CPh=C(CN)$_2$]=C(CN)(C=N)}(PPh_3)Cp* (**6**) by X-ray crystallography. Anal. Found: C, 74.03; H, 5.18; N, 5.98. Calc. for $C_{58}H_{47}N_4P_2Ru$: C, 74.74; H, 5.08; N, 6.01%; *M*, 932. IR (CH_2Cl_2): ν(CN) 2230w, 2208s; other bands at 1597m, 1561m, 1524w, 1490s, 1371s cm^{-1}. ^{1}H NMR: δ 1.44 [d, *J*(HP) 1.4 Hz, 15H, Cp*], 3.34 [d, *J*(HH) 16 Hz, 1H, =CH], 4.41 [d, *J*(HH) 16 Hz, 1H, =CH], 5.92–7.33 (m, 30H, Ph). ^{31}P NMR: δ 48.75 (s), 50.34 (s). ES mass spectrum (CH_2Cl_2–MeOH, *m*/*z*): 934, $[M + 2H]^+$; 672, $[M + 2H - PPh_3]^+$.

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} quoted) after "empirical"/multiscan absorption correction (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-Kα radiation, $\lambda = 0.71073$ Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ 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 3.7 program system.[14] Pertinent results are given in the Figures (which show non-hydrogen atoms with 50% probability amplitude displacement envelopes and hydrogen atoms with arbitrary radii of 0.1 Å) and Tables 1–3.

Variata. *Complex* ***3****.* $(x, y, z, U_{iso})_H$ were refined. Difference map residues were modelled as methanol, seemingly hydrogen-bonded to CN(41) of the cyanocarbon ligand [N(41) ··· H,O-(x, 2 − y, z) 1.90(4), 2.915(3) Å]. C(41)–N(41) [1.158(3) Å] may be slightly elongated in consequence.

Complex ***4****.* Difference map residues were most satisfactorily modelled as two MeCN molecules, one disordered over two sets of sites, occupancies set at 0.5 after trial refinement.

Complex ***5****.* Difference map residues were modelled as three Me_2CO molecules; displacement amplitudes on the latter were high, particularly on molecule '3' which was refined with isotropic displacement parameters and constrained geometries. CCDC reference numbers 165410–165413.

See http://www.rsc.org/suppdata/dt/b1/b105131h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work was supported by the Australian Research Council. We thank Professor Brian Nicholson (University of Waikato, New Zealand) for the mass spectra. We are grateful to Johnson

Table 3 Crystal data and refinement details for **2**, **3**, **4** and **5**

Compound	**2**	**3**	**4**	**5**
Formula	$C_{42}H_{35}N_4PRu$	$C_{42}H_{35}N_4PRu{\cdot}CH_4O$	$C_{66}H_{55}N_8PRu_2{\cdot}2C_2H_3N$	$C_{72}H_{60}N_{12}Ru_3{\cdot}3C_3H_6O$
MW	727.8	759.8	1275.4	1570.8
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
a/Å	9.831(1)	10.404(1)	10.5347(6)	28.509(3)
b/Å	20.850(2)	11.359(1)	14.7397(9)	14.925(1)
c/Å	17.600(2)	15.436(2)	20.733(1)	17.749(2)
α/°		87.481(2)	89.675(1)	
β/°	92.790(2)	84.698(2)	78.178(1)	
γ/°		89.838(2)	74.698(1)	
V/Å^3	3603	1815	3035	7552
Z	4	2	2	4
D_c/g cm^{-3}	1.341	1.414	1.506	1.381
μ/cm^{-1}	5.1	5.2	5.8	6.5
Crystal size/mm	0.28 × 0.25 × 0.22	0.22 × 0.19 × 0.13	0.30 × 0.25 × 0.20	0.35 × 0.28 × 0.12
$'T'_{min,max}$	0.68, 0.83	0.74, 0.89	0.71, 0.80	0.68, 0.81
$2\theta_{max}$/°	58	58	75	75
N_{tot}	35503	18058	40562	147610
N (R_{int})	9120 (0.038)	8902 (0.024)	10667 (0.036)	19395 (0.073)
N_o	7132	7503	8875	13477
R	0.040	0.033	0.051	0.043
R_w	0.052	0.037	0.059	0.043

Matthey plc, Reading, England, for a generous loan of $RuCl_3{\cdot}xH_2O$.

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