Reaction of $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)$ with tetracyanoethene: macrocycle formation by intermolecular CN coordination

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Reactions between $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)$ and $C_2(CN)_4$ result in addition of the cyanocarbon to one of the C≡C triple bonds and formation of the allylic complex $Ru\{\eta^3\text{-}C(CN)_2C[C{\equiv}C\{Ru(PPh_3)_2Cp\}]C{=}C(CN)_2\}(PPh_3)Cp$ (**2**). In solution, **2** is in equilibrium with its dimer **3**, the X-ray crystal structure of which has been determined. In **3**, a ten-membered macrocyclic ring is present, being formed by displacement of the coordinated double bond in one molecule of **2** by a CN group from a second molecule.

Previously we have described the synthesis, characterisation and structure of the diruthenium C_4 complex $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)$ (**1**).[1,2] Electrochemical studies of **1** and the related PMe_3 derivative revealed an unprecedented series of four one-electron oxidation steps to form the cations $[\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)]^{n+}$ (n = 1–4).[2] In view of theoretical studies that indicated that the electrons removed during the oxidations come from HOMOs somewhat removed from the main orbital manifest,[3] we were interested to examine some chemistry of this complex *in vitro*. A characteristic reaction of transition metal alkynyl compounds is their cycloaddition to electron-deficient olefins, such as tetracyanoethene [$C_2(CN)_4$, tcne] and 1,1-dicyano-2,2-bis(trifluoromethyl)ethene, as has been described elsewhere.[4–12] This paper describes the reaction of **1** with $C_2(CN)_4$, together with the molecular structure of a macrocyclic dimer of the initially formed product of this reaction.

Results and Discussion

Reaction of tetracyanoethene with $\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$ (1)

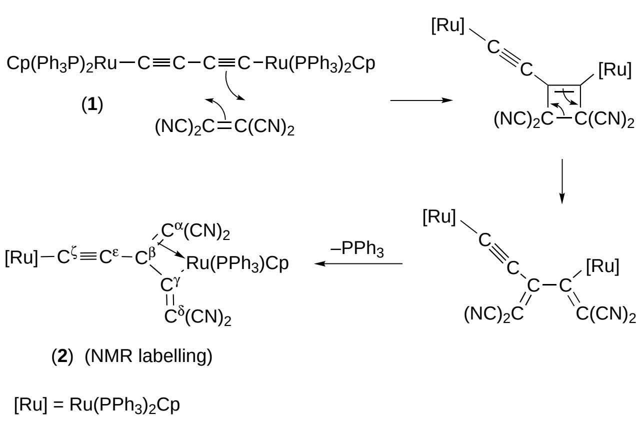
Addition of one equivalent of tcne to **1** in CH_2Cl_2 at room temperature resulted in rapid changes in colour from orange through deep green to blood-red over a period of five minutes. Similar dramatic colour changes accompany reactions of tcne with other transition metal alkynyl complexes.[4,5] After this time the reaction appeared to be complete, as judged by ^1H NMR spectroscopy, and the allylic complex $Ru\{\eta^3\text{-}C(CN)_2C[C{\equiv}C\{Ru(PPh_3)_2Cp\}]C{=}C(CN)_2\}(PPh_3)Cp$ (**2**) could be isolated as a dark-red powder by precipitation with hexane.

The spectral properties of **2** are similar to those reported for related compounds derived from $Ru(C{\equiv}CR)(PPh_3)_2Cp$ (R = Ph, Me).[5] The ^1H NMR spectrum contained resonances assigned to two non-equivalent Cp ligands at δ 4.51 and 4.39; integration of the PPh_3 signal confirmed that only three PPh_3 ligands were present, as expected for the allylic formulation. The ^{13}C NMR spectrum contained the usual signals for the PPh_3 and Cp ligands, and resonances characteristic of the four carbons of the allylic fragment were found at δ 224.7, 81.58, 60.21 and 14.09 and assigned to C_γ, C_α, C_δ and C_β, respectively.[6] The ES MS spectrum obtained in the presence of NaOMe gave an intense $[M + Na]^+$ ion at m/z 1318. The IR spectrum contained a strong ν(CN) band at 2210 cm^{-1}, a strong ν(C=C) band at 1585 cm^{-1} and a very intense absorption at 1933 cm^{-1}. The position and intensity of the latter more closely resembles the ν(C=C=C) bands of allenylidene complexes than a ν(C≡C) absorption of metal acetylide complexes.

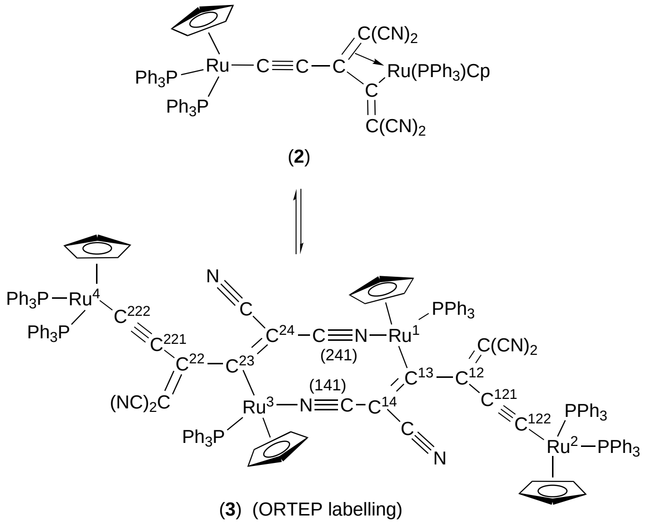
Initial cycloaddition of tcne to one of the C≡C triple bonds in **1** is followed by ring-opening to give a 1,1,4,4-tetracyanobuta-1,3-diene containing $Ru(PPh_3)_2Cp$ and $C{\equiv}C\{Ru(PPh_3)_2Cp\}$ substituents on the 2 and 3 carbons, respectively (Scheme 1). In this reaction, cleavage of tcne into two dicyanomethylene groups occurs; the electron-withdrawing cyano groups are conjugated with the C≡C triple bond. Displacement of one of the PPh_3 ligands on the butadienyl ruthenium by chelation of the C=C double bond furthest from the metal completes formation of **2**. We have previously commented on the short Ru—C σ bond present in related complexes, which is consistent with some multiple bonding character and delocalisation over the ligand.[9,11]

Dimerisation of 2

In solution, **2** exists in equilibrium with a yellow tetranuclear compound characterised as $\{Ru[C\{{=}C(CN)_2\}C\{C{\equiv}C[Ru(PPh_3)_2Cp]\}C(CN)_2](PPh_3)Cp\}_2$ (**3**) (Scheme 2), which was first detected by ^1H NMR spectroscopy in an aged solution of **2**. Attempts to purify **2** by preparative TLC on silica gel also resulted in conversion of the complex to **3**: a pure sample of the latter complex was obtained after recrystallisation. The IR spectrum of **3** was very similar to that of **2**, and strong ν(CN) and ν(C≡C) bands were observed at 2202 and 1976 cm^{-1}, respectively, and two very weak bands in the ν(C=C) region were observed at 1586 and 1571 cm^{-1}. The ^1H NMR spectrum of **3** contained two resonances for the Cp



Scheme 1



Scheme 2

ligands at δ 4.59 and 4.26. Integration of the Ph resonances revealed that 1.5 PPh_3 ligands per Ru atom were present, *i.e.* no further dissociation of PPh_3 ligands from **2** had occurred. The ^{13}C NMR spectrum contained only resonances associated with the Cp (two singlets at δ 87.09 and 81.59), CN (three sharp singlets at δ 118.06, 115.23 and 113.27) and PPh_3 ligands; the resonances of the skeletal carbon atoms of the cyanocarbon ligand were not observed. The dimeric compound was cleaved under the conditions of the FAB MS experiment, and the base peak at *m*/*z* 1296 was assigned to the $[M/2]^+$ ion, from which fragment ions at *m*/*z* 1034 and 772 were formed by loss of one and two PPh_3 ligands, respectively.

As these spectral data were not unambiguous, a single crystal X-ray study of **3** was undertaken. A plot of a molecule of **3** is shown in Fig. 1 and selected bond parameters are collected in Table 1. As can be seen from the figure, the molecule has been formed by displacement of the C=C double bond coordinated to ruthenium in **2** by one the CN groups of a second molecule of **2**. This process generates a puckered ten-membered ring. Although the precision of the determination is not sufficient to distinguish between C and N atoms, they may be assigned from the chemistry, which requires that N(141, 241) are coordinated to Ru(3) and Ru(1), respectively. Within the ring, angles at Ru are 89 and 94(1)° and the CN groups are experimentally linear [Ru—N—C: 178 and 177(3)°; NCC: 171 and 175(4)°].

Table 1 Selected bond parameters (in Å and °) for $\{Ru[C\{=C(CN)_2\}C\{C\equiv C[Ru(PPh_3)_2Cp]\}C(CN)_2](PPh_3)Cp\}_2$ (**3**)

Ru(1)—P(11)	2.32(1)	Ru(1)—C(13)	2.11(4)
Ru(2)—P(21)	2.31(1)	Ru(1)—N(241)	1.98(3)
Ru(2)—P(22)	2.31(1)	Ru(2)—C(122)	1.93(3)
Ru(3)—P(31)	2.31(1)	Ru(3)—C(23)	2.07(3)
Ru(4)—P(41)	2.28(1)	Ru(3)—N(141)	2.04(3)
Ru(4)—P(42)	2.30(1)	Ru(4)—C(222)	1.86(4)
C(13)—Ru(1)—N(241)	89(1)	N(141)—Ru(3)—C(23)	94(1)
Ru(1)—C(13)—C(14)	132(4)	Ru(3)—C(23)—C(24)	119(2)
C(13)—C(14)—C(141)	123(4)	C(23)—C(24)—C(241)	131(3)
C(14)—C(141)—N(141)	175(4)	C(24)—C(241)—N(241)	171(4)
C(141)—N(141)—Ru(3)	178(3)	C(241)—N(241)—Ru(1)	177(3)
Ru(2)—C(122)—C(121)	165(3)	Ru(4)—C(222)—C(221)	161(3)

The N(4) atoms of the $C(CN)_2$ groups attached to the carbons nearest the metal become coordinated to Ru(1, 3) in the dimer **3**. Of the two C≡C triple bonds in the precursor complex **1**, one remains unchanged [C(121, 221)—C(122, 222)]. The Ru(2, 4) atoms remain attached to two PPh_3 ligands each, while only one such ligand is present on the Ru(1, 3) atoms [Ru—P: 2.28–2.32(1) Å]. Short Ru—C bonds are found to C(122, 222) [Ru—C: 1.93 and 1.86(3) Å], while the Ru—N bonds are 1.98 and 2.04(3) Å.

Interconversion of 2 and 3

The equilibration between **2** and **3** was conveniently monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum of a freshly prepared solution of **2** in $CDCl_3$ was recorded at intervals over a period of three days, after which time equilibirum had been reached. The resulting solution contained *ca.* 10% **3**, as estimated from the integration of the Cp resonances. Similarly, a solution of **3** reached the same equilibrium point with **2** after *ca.* 7 days.

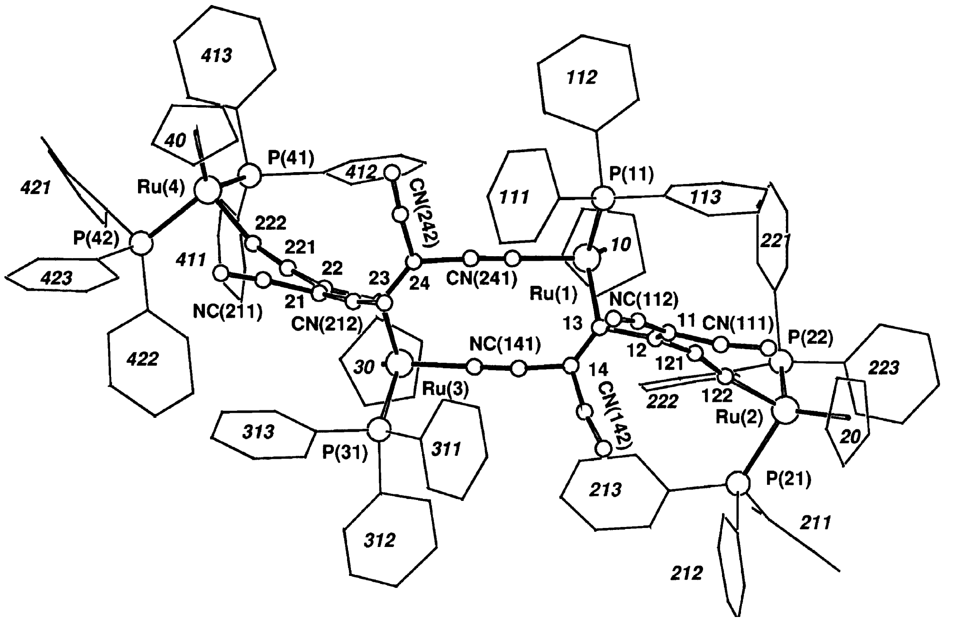


Fig. 1 Molecular projection of $\{Ru[C\{=C(CN)_2\}C\{C\equiv C[Ru(PPh_3)_2Cp]\}C(CN)_2](PPh_3)Cp\}_2$ (**3**) normal to the plane of the central macrocycle. For clarity, hydrogen atoms are omitted and Cp and phenyl rings are shown with stick bonds. Labelling of the rings is shown in 2- (Cp) or 3-digit (Ph) italics; other carbon atoms are shown with bold numerals

Conclusions

Reaction of the diruthenium-diyndiyl complex **1** with tcne proceeds as anticipated to give the allylic complex **2**, as found in several related alkynyl derivatives. In solution, however, association of two molecules of **2** occurs by displacement of the coordinated C=C double bond by a CN group of a second molecule, with formation of the ten-membered macrocyclic dimer **3**. In solution at room temperature, these two complexes are in equilibrium, **2** being favoured in $CDCl_3$. The formation of **3** has precedent to some degree in the preparation of related nitrile complexes, such as $\{Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)Cp\}_2\{\mu\text{-}(NC)_2C{=}C(CF_3)_2\}$.[12]

Experimental

General

Reaction conditions and starting materials. All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried, distilled and degassed before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

$\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)$ was prepared by the literature method.[1] Tetracyanoethene (Aldrich) was sublimed before use.

Instrumentation. IR: Perkin–Elmer 1700X FT-IR; 683 double beam, NaCl optics. NMR: Bruker ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV). ES MS: The samples were dissolved in acetonitrile–water (1 : 1), unless otherwise indicated, and injected into a 10 ml injection loop attached to a VG Platform II mass spectrometer. Nitrogen was used as the drying and nebulising gas. Samples were examined over a range of cone voltages (20–90 V) to find the best conditions. Addition of NaOMe afforded better spectra.[13]

Preparations

$Ru\{\eta^3\text{-}C(CN)_2C[C\equiv C\{Ru(PPh_3)_2Cp\}]C{=}C(CN)_2\}(PPh_3)Cp$ (2). A solution of $\{Cp(PPh_3)_2Ru\}_2(\mu\text{-}C_4)$ (200 mg, 0.14 mmol) in THF (20 ml) was treated with tcne (20 mg, 0.15 mmol). The orange solution rapidly turned deep green, then deep red within a few minutes. After stirring for 15 min the solvent was removed *in vacuo*. The residue was triturated with hexane to give $Ru\{\eta^3\text{-}C(CN)_2C[C\equiv C\{Ru(PPh_3)_2Cp\}]C{=}C(CN)_2\}(PPh_3)Cp$ (**2**) (150 mg, 69%) as a brick-red powder. Anal. found: C, 68.51; H, 4.24; N, 4.32. Calcd for $C_{74}H_{55}N_4P_3Ru_2$: C, 68.62; H, 4.25; N, 4.32%. IR (nujol): ν(CN) 2210 m, ν(C≡C) 1993 s, ν(C=C) 1585 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50–7.20 (60H, m, Ph), 4.55, 4.43 (2 × 5H, 2 × s, 2 × Cp). ^{13}C NMR ($CDCl_3$): δ 224.7 (d, $J_{CP} = 60$ Hz, C_γ), 138.69–127.56 (m, Ph), 119.86, 119.76 (2 × s, 2 × CN), 112.26 (br, C_ζ), 106.34 (br, C_ε), 91.43, 87.09 (2 × s, 2 × Cp), 81.58 (d, $J_{CP} = 6$ Hz, C_α), 60.21 (s, C_δ), 14.09 (br, C_β). ES MS (*m*/*z*): 1318, $[M + Na]^+$.

Preparation of $\{Ru[C\{=C(CN)_2\}C\{C\equiv C[Ru(PPh_3)_2Cp]\}C(CN)_2](PPh_3)Cp\}_2$ (3). Attempts to purify **2** by preparative TLC (light petroleum–acetone, 55 : 45) resulted in the development of two bands. The top red band contained **2** (identified by IR and ^1H NMR spectroscopy). The second band contained yellow $\{Ru[C\{=C(CN)_2\}C\{C\equiv C[Ru(PPh_3)_2Cp]\}C(CN)_2](PPh_3)Cp\}_2$ (**3**), purified by crystallisation (CH_2Cl_2–MeOH). Anal. found: C, 68.59; H, 4.18; N, 4.37. Calcd for $C_{148}H_{110}N_8P_6Ru_4$: C, 68.51; H, 4.24; N, 4.32%. IR (nujol): ν(CN) 2202 m, ν(C≡C) 1976 s, ν(C=C) 1586, 1571 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.61–6.87 (45H, m, Ph), 4.59, 4.26 (2 × 5H, 2 × s, 2 × Cp). ^{13}C NMR ($CDCl_3$): δ 139.9–127.4 (m, Ph), 118.06, 115.23, 113.27 (3 × s, 3 × CN), 87.10, 81.59 (2 × s, 2 × Cp). FAB MS (*m*/*z*): 1296, $[M/2]^+$; 1034, $[M/2 - PPh_3]^+$; 772, $[M/2 - 2PPh_3]^+$; 691, $[Ru(PPh_3)_2Cp]^+$.

Crystallography

A unique data set was measured at *ca.* 295 K to $2\theta_{max} = 50°$ using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-Kα radiation, λ 0.7107_3 Å); 26 480 independent reflections were obtained, 5069 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R and R' on $|F|$ are 0.104 and 0.116, respectively, with the statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system[14] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables.

Crystal and refinement data. $\{Ru[C\{=C(CN)_2\}C\{C\equiv C[Ru(PPh_3)_2Cp]\}C(CN)_2](PPh_3)Cp\}_2 \cdot 2.75CH_2Cl_2$ (**3**) $\equiv C_{148}H_{110}N_8P_6Ru_4 \cdot 2.75CH_2Cl_2$, $M = 2824.3$. Monoclinic, space group $P2_1/n$, $a = 23.347(9)$, $b = 26.060(12)$, $c = 25.697(17)$ Å, $\beta = 98.67(4)°$, $U = 15456$ Å^3, $Z = 4$, $\rho_c = 1.214$ g cm^{-3}, $F(000) = 5808$. Crystal dimensions 0.40 × 0.05 × 0.40 mm, μ(Mo-Kα) = 5.9 cm^{-1}, A^*(min, max) = 1.04, 1.33.

Abnormal features/variations in procedure. Weak data, from a thin flake, and a very large structure would support meaningful anisotropic thermal parameter refinement for Ru and P only. Difference map residues were modelled as dichloromethane of solvation, site occupancies were constrained at 0.5 or 0.25 after trial refinement, with geometries also being constrained; solvent 'thermal motion' was also very high.

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