Cyclopentadienyl-ruthenium and -osmium chemistry. Cleavage of Tetracyanoethylene under Mild Conditions: X-Ray Crystal Structures of [Ru{η³-C(CN)₂CPhC=C(CN)₂}(PPh₃)(η-C₅H₅)] and [Ru{C[=C(CN)₂]CPh=C(CN)₂}-(CNBuᵗ)(PPh₃)(η-C₅H₅)]
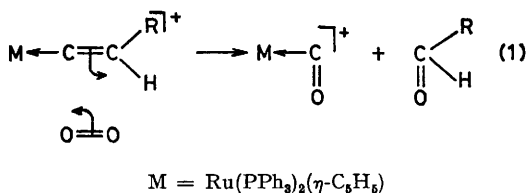
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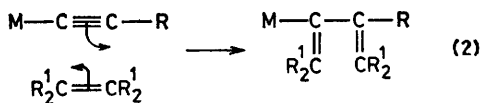(*Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia* 5001)

Summary The reaction between [Ru(C₂Ph)(PPh₃)₂(η-C₅H₅)] and C₂(CN)₄ affords [Ru{η³-C(CN)₂CPhC=C(CN)₂}-(PPh₃)(η-C₅H₅)] (2), which forms [Ru{C[=C(CN)₂]-CPh=C(CN)₂}(L)(PPh₃)(η-C₅H₅)] (5) with L = CO or CNBuᵗ; the structures of (2) and (5; L = CNBuᵗ) have been determined by X-ray crystallography.
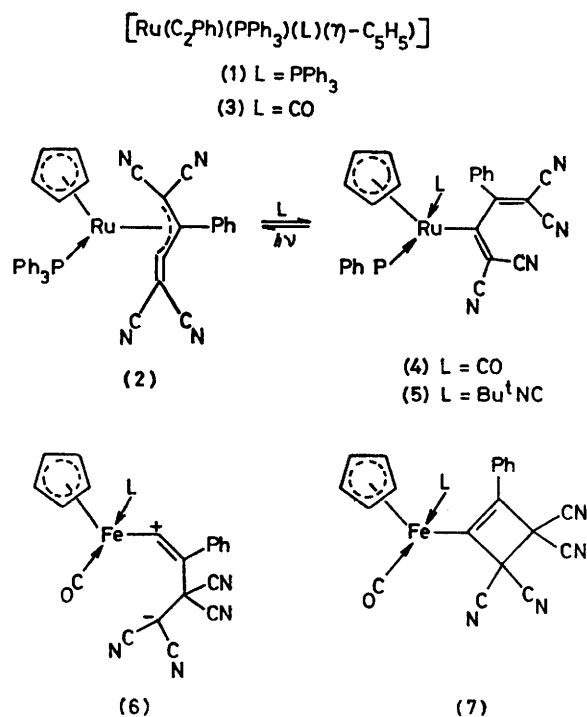
We have previously reported[1] the oxidation of vinylidene complexes to the corresponding aldehyde and metal carbonyl derivative [reaction (1)]. We now report a novel

$$M \leftarrow C \overset{R}{\underset{H}{\equiv}} C \quad \longrightarrow \quad M \leftarrow C \overset{+}{\underset{O}{\parallel}} \quad + \quad C \overset{R}{\underset{O}{\parallel}} \backslash_H \quad (1)$$

$$O \equiv O$$

$$M = Ru(PPh_3)_2(\eta\text{-}C_5H_5)$$

example of this type of reaction, which is formally related to olefin metathesis, that of a metal-substituted acetylide with an electron-deficient olefin [reaction (2)].

$$M-C \equiv C-R \quad \longrightarrow \quad M-\overset{R_2^1 C}{\underset{R_2^1 C}{\parallel}}C-\overset{R}{\underset{CR_2^1}{\parallel}}C-R \quad (2)$$

$$R_2^1 C \equiv CR_2^1$$

An intense dark green colour develops on mixing solutions of tetracyanoethylene (tcne) and [Ru(C₂Ph)(PPh₃)₂(η-C₅H₅)] (1) in benzene; the intermediate, as yet uncharacterised, gives a strong e.s.r. signal (*g ca.* 2·01). After some hours, orange crystals of a 1:1 adduct, [Ru(C₂Ph)(tcne)(PPh₃)-(η-C₅H₅)] (2) separate in 82% yield [*M⁺* at *m/e* 658 (for ¹⁰²Ru); ν(CN) 2215 m, ν(C=C) 1595 m cm⁻¹; ¹H n.m.r. δ(CDCl₃) 4·76 (s, C₅H₅) and 7·4—7·5 (m, PPh₃); ¹³C n.m.r. δ(CDCl₃) 7·3 (d, *J*cₚ 5 Hz), 84·9 (d, *J*cₚ 7 Hz), (two of three allylic C); 66·6 (s, C-4), 92·2 (s, C₅H₅), 111·0, 115·9, 118·7 and 119·0 (all s, CN), and 128·4–135·9 (m, Ph)]. A similar reaction between tcne and [Ru(C₂Ph)(CO)(PPh₃)-(η-C₅H₅)] (3) afforded [Ru(C₂Ph)(tcne)(CO) (PPh₃) (η-C₅H₅)] (4) (82%), also formed by carbonylation of (2) (100 °C; 53 bar; 17 h) [*M⁺* at *m/e* 686; ν(CN) 2200 m, ν(CO) 1941vs, ν(C=C) 1505 m cm⁻¹]. Short u.v. irradiation of (4) results in loss of CO and conversion into (2). The related complex [Ru(C₂Ph)(tcne)(CNBuᵗ)(PPh₃)(η-C₅H₅)] (5) was obtained (91%) from (2) and BuᵗNC [*M⁺* at *m/e* 741; ν(CN) 2207w, 2200w, 2193w, and 2167s; ν(C=C) 1506w cm⁻¹; ¹H n.m.r. δ(CDCl₃) 1·33 (s, Me), 4·62 (s, C₅H₅), and 7·0—7·4 (m, PPh₃); ¹³C n.m.r. δ(CDCl₃) 30·5 (s, C*Me₃*), 58·1, (s, C*Me₃*), 73·6 and

95·2 (s, C-19 and C-21), 87·0 (s, C₅H₅), 113·4, 114·1, 114·5 and 118·4 (all s, CN), 128·4—136·6 (m, PPh₃), and 178·1 (d, *J*cₚ 2 Hz, Ru*C*N)]. The formulation of (2), and the presence of three ¹³C resonances coupled to the ³¹P nucleus of the remaining PPh₃ ligand, suggested that the adduct contained

$$[Ru(C_2Ph)(PPh_3)(L)(\eta\text{-}C_5H_5)]$$

(1) L = PPh₃

(3) L = CO

(2)

(4) L = CO
(5) L = Buᵗ NC

(6)   (7)

an allylic ligand. The ready addition of 2e donor ligands to give (4) or (5) could be explained by conversion of the η³-ligand in (2) into a related η¹-ligand in these complexes. These ideas have been confirmed by single-crystal X-ray diffraction studies of complexes (2) and (5).

Crystal data: (2), C₃₂H₂₀N₄PRu, *M*ᵣ 592·6, monoclinic, space group *P*2₁/*c*, *a* = 8·870(3), *b* = 17·762(5), *c* = 19·966-(2) Å, *β* = 99·22(2)°, *U* = 3104·96 Å³, *Z* = 4, *D*c = 1·267 g cm⁻³; *F*(000) = 1888; *μ*(Mo-*K*α) = 6·08 cm⁻¹; (5) C₃₇H₂₉N₅PRu, *M*ᵣ 675·7. monoclinic, space group *P*2₁/*c*, *a* = 17·204(2), *b* = 11·349(2), *c* = 18·679(3) Å, *β* = 90·29(3)°, *U* = 3646·9 Å³; *Z* = 4, *D*c = 1·23 g cm⁻³; *F*(000) = 1972; *μ*(Mo-*K*α) = 4·60 cm⁻¹.

Both structures were solved by Patterson techniques and refined by block-matrix least squares methods using the SHELX[2] system of programmes. The hydrogen atom positions were calculated geometrically with all C-H

distances fixed at 0.965 Å. The final R-factors are: (2), $R = 4.64\%$, $R_w = 4.18\%$, $w = 1.8106/(\sigma^2 F_0 + 0.0001\ F_0{}^2)$ for 4064 independent reflexions $[I > 2.5\sigma(I); 2.5 \leqslant 2\theta \leqslant 50°$, Stoe 2-circle diffractometer]; (5), $R = 3.71\%$, $R_w = 3.69\%$, $w = 2.5186/(\sigma^2 F_0 + 0.0001\ F_0{}^2)$ for 4727 independent reflexions $[I > 2.5\sigma(I); 2.5 \leqslant 2\theta \leqslant 50°$, Stoe 2-circle diffractometer].†
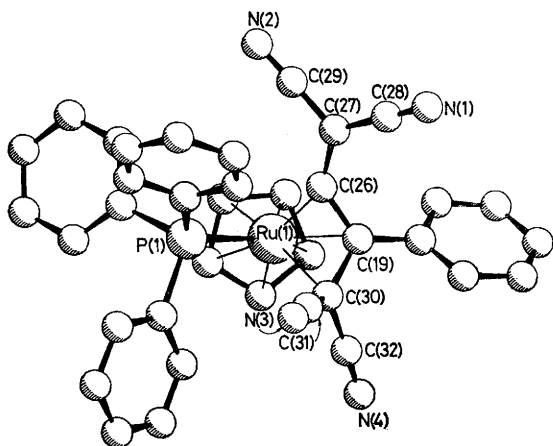

FIGURE 1. PLUTO plot (ref. 5) of [Ru{η^3-C(CN)$_2$CPhC=C(CN)$_2$}-(PPh$_3$)(η-C$_5$H$_5$)]. Selected bond lengths: Ru(1)–C(19), $2.135(4)$; Ru(1)–C(26), $1.919(5)$; Ru(1)–C(30), $2.231(4)$; C(26)–C(27), $1.383(6)$; C(19)–C(26), $1.432(7)$; C(19)–C(30), $1.476(6)$ Å.
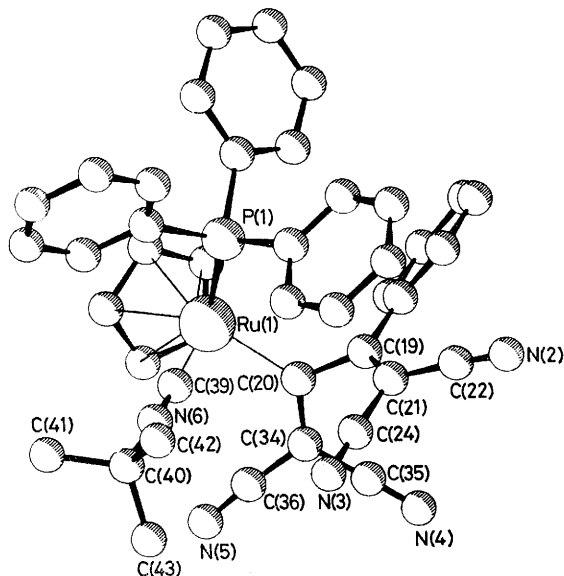

FIGURE 2. PLUTO plot (ref. 5) of [Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}-(CNBu^t)(PPh$_3$)(η-C$_5$H$_5$)]. Selected bond lengths: Ru(1)–C(20), $2.074(3)$; Ru(1)–C(39), $2.003(3)$; C(19)–C(21), $1.362(4)$; C(19)–C(20), $1.478(4)$; C(20)–C(34), $1.382(5)$ Å.

Figure 1 shows the molecular structure of (2), with significant structural parameters listed in the caption. The main feature of interest is the η^3-allylic ligand formed by addition of two dicyanomethylene fragments, one to each acetylenic carbon of the phenylacetylide ligand of (1). Figure 2 similarly shows the molecular structure of (5), from which it can be seen that the allylic ligand in (2) has been converted into the η^1-1,1,4,4-tetracyano-3-phenylbuta-1,3-dien-2-yl group by addition of the isocyanide ligand. Of some interest is the angle between the planes containing the two dicyanomethylene groups [torsion angle about C(21)–C(19)C(20)C(34), 105°], indicating that the diene fragment is considerably twisted, with consequent localisation of the two double bonds.

We note that similar reactions between tcne and [Fe(C$_2$Ph)-(CO)(L)(η-C$_5$H$_5$)] (L = CO or PPh$_3$) proceed to give complexes formulated as the dipolar intermediate (6), and the (2 + 2) cycloadduct (7); for L = PPh$_3$ these two derivatives form an equilibrium mixture.[3]

To our knowledge no previous example of cleavage of the olefinic bond of tcne on reaction with an alkyne is known; the product expected from these reactions is the (2 + 2) cycloaddition product. Several reports describe the ring-opening of cyclobutyl derivatives [(2 + 2) cycloadducts of tcne and olefins] on heating (100–180 °C), probably via radical intermediates.[4] The present reaction appears to be related to these; back-bonding into the acetylide group from the metal atom, perhaps to the extent of formation of a formally ruthenium(III) complex, may serve to facilitate the formation of the intermediate radical species, and hence cleavage of tcne under mild conditions (Scheme). The
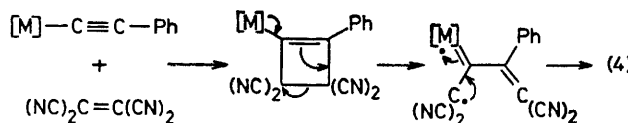
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formation of (4), rather than (2), from the reaction between (3) and tcne suggests that the latter does not first co-ordinate to the metal atom, but that attack occurs initially at the acetylide carbon; the formation of the η^3-allylic system in (2) is encouraged by the ready loss of one of the PPh$_3$ ligands, as is commonly found for Ru(PPh$_3$)$_2$(η-C$_5$H$_5$) complexes.

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† Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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