Preparation of $[Ru(\eta^6-C_6Me_6)Cl(C\equiv CPh)(RNC)]$ (R = C_8H_9 or $C_6H_2Me_3$-2,4,6) and its Reaction with Tetracyanoethylene. Crystal Structures of $[Ru(\eta^6-C_6Me_6)Cl\{C[=C(CN)_2]CPh=C(CN)_2\}(C_8H_9NC)]$ and *cis*-$[RuCl_2(C_8H_9NC)_2]$†

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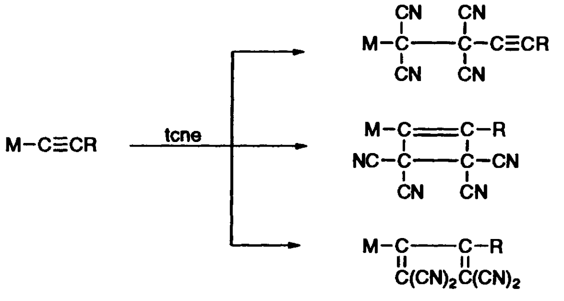
Reaction of $[Ru(\eta^6-C_6Me_6)Cl_2(RNC)]$ with phenylacetylene in the presence of potassium hydroxide in methanol gave the corresponding acetylide complex $[Ru(\eta^6-C_6Me_6)Cl(C\equiv CPh)(RNC)]$ (R = C_8H_9 **1a** or 2,4,6-$Me_3C_6H_2$ **1b**). Compound **1a** reacted with triphenylphosphine at reflux in toluene to give $[Ru(\eta^6-C_6Me_6)Cl(C\equiv CPh)(PPh_3)]$ **2** and $[RuCl(C\equiv CPh)(C_8H_9NC)(PPh_3)]$ **3**. When **1a** was treated with tetracyanoethylene (tcne) at room temperature $[Ru(\eta^6-C_6Me_6)Cl\{C[=C(CN)_2]CPh=C(CN)_2\}(C_8H_9NC)]$ **4** was obtained. The structure was confirmed by an X-ray analysis: space group *Pbca*, *a* = 20.128(4), *b* = 17.821(6), *c* = 17.407(9) Å, and *Z* = 8. The molecule contains a ligand resulting from α,β addition of $C(CN)_2$ fragments to the acetylide group. Reaction of **2** with tcne gave $[Ru(\eta^6-C_6Me_6)Cl\{C(CN)_2CPhC=C(CN)_2\}]$ **5** which has lost the terminal isocyanide in **4**. Preparation and X-ray analysis of square-planar *cis*-$[RuCl_2(C_8H_9NC)_2]$ were also carried out: space group $P\bar{1}$, *a* = 10.573(3), *b* = 10.865(3), *c* = 8.244(2) Å, α = 99.66(2), β = 93.37(2), γ = 85.85(3)° and *Z* = 2. The structure consists of a pair of molcules of *cis* configuration with a centrosymmetry, but there is no interaction between the ruthenium atoms.

The insertion reactions of small molecules such as carbon monoxide and isocyanide into the M–C(sp^3) bond of transition-metal complexes are widespread, but there are relatively few examples of those into M–C(sp^2) and M–C(sp) bonds.[2] Three characteristic modes (Scheme 1) have been observed in the reactions of metal acetylide M–C≡CR with the electrophilic tetracyanoethylene (tcne) molecule: (*i*) it has been reported to insert into M–C≡CR bonds of palladium(II) and platinum(II);[3,4] (*ii*) when treated with $[Ni(\eta-C_5H_5)(PPh_3)(C\equiv CPh)]$,[5] $[Fe(\eta-C_5H_5)(CO)_2(C\equiv CPh)]$[6] and $[W(\eta-C_5H_5)(CO)_3(C\equiv CPh)]$[7] a (2 + 2) addition to the acetylide groups occurred to give a cyclobutene metal complex; (*iii*) α,β addition of dicyanomethylene fragments derived from cleavage of the double bond of tcne to the acetylide group, as observed in cyclopentadienyl complexes of W, Ru and Fe as well as in square-planar platinum complexes.[8]

This paper describes the preparation and reactions of areneruthenium(II) acetylide complexes containing isocyanide.

Experimental

All chemicals were of the best commercial grade. Dichloromethane was distilled over CaH_2. Isocyanide,[9] *trans*-$[RuCl_2(C_8H_9NC)_4]$[10] (C_8H_9 = 2,6-xylyl) and $[Ru(\eta^6-C_6Me_6)Cl_2(RNC)]$[11] were prepared according to the literature methods. Infrared spectra were measured on a JASCO A-100 spectrometer, electronic spectra with a Ubest-30 spectrometer, and ^1H NMR spectra on JEOL JNW GX400 and Bruker AC250 spectrometers.



Scheme 1 Reaction modes of tcne with metal acetylides

Preparation of $[Ru(\eta^6-C_6Me_6)Cl(C\equiv CPh)(C_8H_9NC)]\cdot 0.25CH_2Cl_2$ **1a**.—To a mixture of $[Ru(\eta^6-C_6Me_6)Cl_2(C_8H_9NC)]$ (0.20 g, 0.42 mmol) and phenylacetylene (0.5 cm^3, 4.9 mmol) in methanol (15 cm^3) was added a solution of potassium hydroxide (0.42 mmol) in methanol (4.2 cm^3) at room temperature. After 4 h, yellow solids precipitated. These were filtered off and recrystallized from CH_2Cl_2–hexane to give yellow crystals of complex **1a** (0.097 mg, 43%). IR(Nujol) 2110 (N≡C) and 2091 cm^{-1} (C≡C); UV/VIS (CH_2Cl_2) λ_{max} (log ε) 279 nm (4.44); ^1H NMR($CDCl_3$): δ 2.21 (s, 18 H, C_6Me_6), 2.48 (s, 6 H, *o*-Me), 5.27 (s, CH_2Cl_2) and 6.9–7.4 (m, 8 H, Ph) (Found: C, 63.60; H, 5.80; N, 2.45. Calc. for $C_{29.25}H_{32.5}Cl_{1.5}NRu$: C, 63.60; H, 5.95; N, 2.45%).

The complex $[Ru(\eta^6-C_6Me_6)Cl(C\equiv CPh)(2,4,6-Me_3C_6H_2NC)]\cdot 0.25CH_2Cl_2$ **1b** (34%) was obtained similarly. IR(Nujol) 2104 (N≡C) and 2085 (C≡C) cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max} (log ε) 279 nm (4.44); ^1H NMR ($CDCl_3$): δ 2.23 (2, 18 H, C_6Me_6), 2.26 (s, 3 H, *p*-Me), 2.44 (s, 6 H, *o*-Me), 5.27 (CH_2Cl_2) and 6.7–7.4 (m, 7 H, Ph) (Found: C, 64.15; H, 6.40; N, 2.30. Calc. for $C_{30.25}H_{34.5}Cl_{1.5}NRu$: C, 64.75; H, 6.15; N, 2.45%).

Reactions of Complex **1a**.—*With* PPh_3. A solution of complex **1a** (0.20 g, 0.38 mmol) and PPh_3 (0.50 g, 1.9 mmol) in toluene (30 cm^3) was heated at reflux for 24 h. Upon completion

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† Studies on Interaction of Isocyanide with Transition-metal Complexes. Part 41.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

of the reaction the solvent was removed *in vacuo* and the residue chromatographed on alumina. After elution of triphenylphosphine by use of benzene, elution with CH_2Cl_2 gave a yellow-orange solution. Removal of the solvent and recrystallization of the residue from CH_2Cl_2–hexane gave orange yellow crystals of $[Ru(\eta^6\text{-}C_6Me_6)Cl(C{\equiv}CPh)(PPh_3)]$ **2** (0.10 g, 41%) containing $0.25CH_2Cl_2$, and white crystals of $[RuCl(C{\equiv}CPh)(C_8H_9NC)(PPh_3)]$ **3** were obtained in a 48% yield (0.098 g) from the mother-liquor. Compound **2**: IR(Nujol) 2089 cm^{-1} (C≡C); UV/VIS (CH_2Cl_2) λ_{max} (log ε) 290 nm (4.27); ^1H NMR($CDCl_3$): δ 1.80 (s, 18 H, C_6Me_6), 5.27 (s, CH_2Cl_2) and 7.0–8.3 (m, 20 H, Ph); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 16.08 (C_6Me_6), 18.4 (2,6-Me), 115.5 (*C*Ph), 125.3 (RuC), 126–135 (m, Ph) and 158.2 (N≡C) (Found: C, 67.40; H, 5.30. Calc. for $C_{38.25}H_{56.5}Cl_{1.5}PRu$: C, 67.20; H, 5.65%). Compound **3**: IR(Nujol) 2139 (N≡C) and 2092 cm^{-1} (C≡C); UV/VIS (CH_2Cl_2) λ_{max}(log ε) 335 (sh) (3.24) and 278 nm (4.37); ^1H NMR($CDCl_3$): δ 1.83 (s, 6 H, Me), 6.2–8.2 (m, 23 H, Ph) (Found: C, 66.85; H, 5.05; N, 2.80. Calc. for $C_{35}H_{29}ClNPRu$: C, 66.60; H, 4.60; N, 2.20%).

With tcne. A mixture of complex **1a** (0.20 g, 0.30 mmol) and tcne (0.10 g, 0.78 mmol) in benzene (30 cm^3) was stirred at room temperature. After 1 h the solvent was reduced in volume to *ca.* 5 cm^3 *in vacuo*, and hexane was added to give reddish brown solids. Recrystallization from benzene–hexane gave reddish brown crystals of $[Ru(\eta^6\text{-}C_6Me_6)Cl\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(C_8H_9NC)]$ **4** (0.096 mg, 40%). IR(Nujol) 2233, 2222 (C≡N), 2135 (N≡C) and 1547 cm^{-1} (C=C); UV/VIS (CH_2Cl_2) λ_{max}(log ε) 313 (sh) (4.12) and 258 nm (4.49); NMR ($CDCl_3$): ^1H, δ 1.89 (s, 18 H, C_6Me_6), 2.45 (s, 6 H, Me) and 7.1–7.6 (m, 8 H, Ph); ^{13}C, δ 16.0 (C_6*Me_6*), 19.5 (*o*-Me), 80.1 [*C*$(CN)_2$], 92.9 [*C*$(CN)_2$], 105.0 (*C_6*Me_6), 112.5, 112.6, 113.2, 117.6 (C≡N) 127.7–136.1 (aromatic), 155 (N≡C), 177.6 (*C*Ph) and 223.8 (RuC) (Found: C, 63.30; H, 4.85; N, 10.50. Calc. for $C_{35}H_{32}ClN_5Ru$: C, 63.75; H, 4.90; N, 10.60%).

Reaction of Complex **2** *with* tcne.—A solution of complex **2** (0.20 g, 0.30 mmol) and tcne (0.10 g, 0.78 mmol) in benzene (30 cm^3) was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the residue chromatographed on alumina. Elution with tetrahydrofuran (thf) gave a brown solution. Removal of the solvent and recrystallization of the residue from thf–hexane gave brown crystals of $[Ru(\eta^6\text{-}C_6Me_6)Cl\{C(CN)_2CPhC{=}C(CN)_2\}]$ **5** (0.44 mg, 28%). IR (Nujol) 2220 (C≡N) and 1537 cm^{-1} (C=C); UV/VIS (CH_2Cl_2) λ_{max}(log ε) 385 (sh) (3.84) 307 (415) and 263 (sh) nm (4.22); ^1H NMR ($CDCl_3$): δ 1.77 (s, 18 H, C_6Me_6) and 7.3–8.0 (m, 5 H, Ph) (Found: C, 59.35; H, 4.55; N, 10.30. Calc. for $C_{26}H_{28}ClN_4Ru$: C, 59.15; H, 4.40; N, 10.60%).

Reaction of Complex **5** *with Xylyl Isocyanide.*—A solution of complex **5** (0.019 g, 0.036 mmol) and xylyl isocyanide (0.024 g, 0.18 mmol) in thf (15 cm^3) was refluxed for 5 h. Removal of the solvent and recrystallization of the residue from CH_2Cl_2–hexane gave **4**.

Thermal Reaction of trans-$[RuCl_2(C_8H_9NC)_4]$.—The complex $[RuCl_2(C_8H_9NC)_4]$ (0.20 g, 0.29 mmol) was charged in a sealed tube and heated at *ca.* 170 °C for 4 h. After cessation of the reaction the residue was crystallized from a CH_2Cl_2–hexane mixture to give very pale yellow crystals of *cis*-$[RuCl_2(C_8H_9NC)_2]$ **6** (0.11 mg, 0.25 mmol); IR (Nujol) 2203 and 2136 cm^{-1} (N≡C); ^1H NMR ($CDCl_3$) δ 2.51 (s, 2 *o*-Me) and 7.0–8.0 (m, 6 H, Ph) (Found: C, 49.55; H, 4.25; N, 6.75. Calc. for $C_{18}H_{18}Cl_2N_2Ru$: C, 49.80; H, 4.20; N, 6.45%).

X-Ray Crystallographic Studies.—Suitable crystals of complexes **4** and **6** for X-ray analysis were obtained by recrystallization from CH_2Cl_2–Et_2O. The crystal of **4** was orthorhombic with systematic extinction (0*kl*, $k = 2n$; *h*0*l*, $l = 2n$; *hk*0, $h = 2n$) and that of **6** triclinic, consistent with the space groups *Pbca* (no. 61) and $P\bar{1}$ (no. 2), respectively.

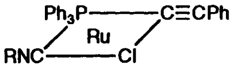
Crystal data. $C_{35}H_{32}ClN_5Ru$ **4**, $M = 659.2$, $a = 20.128(4)$, $b = 17.821(6)$, $c = 17.407(9)$ Å, $U = 6244(6)$ Å, $Z = 8$, $D_c = 1.402$ g cm^{-3} and $F(000) = 2704$. $C_{18}H_{18}ClN_2Ru$, $M = 434.3$, $a = 10.574(3)$, $b = 10.865(3)$, $c = 8.244(2)$ Å, $\alpha = 99.66(2)$, $\beta = 93.37(2)$, $\gamma = 85.85(3)°$, $U = 930.1(9)$ Å^3, $Z = 2$, $D_c = 1.551$ g cm^{-3} and $F(000) = 436$.

Data collections were carried out on a Rigaku AFC5S four-circle automated diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) with $3 < 2\theta < 50$ for **4** and $3 < 2\theta < 55°$ for **6** and the ω–2θ scan technique with scan rates of 16 for **4** and 8 ° min^{-1} for **6**. Three standard reflections were monitored every 150 and showed no systematic decrease in intensity. Totals of 3999 for **4** and 4271 for **6** reflections were measured of which 2452 having $I > 3\sigma(I_o)$ and 2851 having $I > 4.0\sigma(I_o)$ respectively were used in the calculations. Intensities were corrected for Lorentz-polarization effects. The linear absorption coefficients were 6.1 for **4** and 11.2 cm^{-1} for **6**, and absorption corrections were made by the φ-scan method. The structures were determined by direct methods. The non-hydrogen atoms were located in successive Fourier-difference syntheses and the hydrogen atoms were placed at the ideal positions with C–H 0.95 Å. The non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods, but the hydrogen atoms were not refined. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ values were 0.051 and 0.042 for **4** and 0.034 and 0.029 for **6** [$w = 1/\sigma^2(F_o)$], respectively. The final Fourier-difference maps showed residual peaks at less than 0.7 for **4** and 0.6 e Å^{-3} for **6**. Atomic scattering factors were taken from ref. 12. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all atoms.[13] The calculations were carried out using the TEXSAN crystallographic software package.[14] Atomic coordinates of **4** and **6** are listed in Tables 1 and 2.

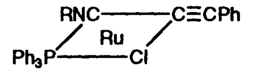
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

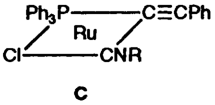
Preparation and Reactions of Acetylide Complexes.—When a suspension of $[Ru(\eta^6\text{-}C_6Me_6)Cl_2(RNC)]$ [R = 2,6-$Me_2C_6H_3$ (C_8H_9) or 2,4,6-$Me_3C_6H_2$] and phenylacetylene was treated with potassium hydroxide in methanol after 4 h at room temperature a yellow solid deposited, formulated as $[Ru(\eta^6\text{-}C_6Me_6)Cl(C{\equiv}CPh)(RNC)]{\cdot}0.25CH_2Cl_2$ (R = C_8H_9 **1a** or $C_6H_2Me_3$-2,4,6 **1b**). The infrared spectrum of **1** showed two bands at *ca.* 2100 cm^{-1} due to C≡N and C≡C triple bonds. The ^1H NMR spectrum showed the presence of isocyanide and acetylide groups. When compound **1a** was refluxed in toluene in the presence of triphenylphosphine two compounds were obtained, formulated as $[Ru(\eta^6\text{-}C_6Me_6)Cl(C{\equiv}CPh)(PPh_3)]{\cdot}0.25CH_2Cl_2$ **2** (known) and $[RuCl(C{\equiv}CPh)(C_8H_9NC)(PPh_3)]$ **3**. Compound **3** is a rare co-ordinatively unsaturated complex (14 electrons). Its infrared spectrum showed sharp bands at 2139 and 2092 cm^{-1} due to ν(C≡N) and ν(C≡C) stretching frequencies. The ^1H NMR spectrum showed a singlet at δ 1.83 assignable to *o*-methyl groups. Three structures for **3** were considered (R = C_8H_9). At present the compound is assumed to be **A** or **B** based on an analogy to the structure of



A



B



C

Table 1 Positional coordinates of complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.927 56(3)	0.159 51(4)	0.193 33(4)	C(22)	0.883 7(5)	0.261 9(5)	0.138 7(6)
Cl	0.989 1(1)	0.044 7(1)	0.179 2(2)	C(23)	0.918 3(6)	0.226 6(5)	0.077 0(5)
N(1)	0.935 2(4)	0.125 3(4)	0.366 5(4)	C(24)	0.984 0(6)	0.205 1(5)	0.089 0(6)
N(2)	0.767 8(4)	0.223 1(5)	0.330 0(5)	C(25)	1.018 8(5)	0.226 5(6)	0.157 8(8)
N(3)	0.678 9(4)	0.029 0(5)	0.222 1(4)	C(26)	0.986 1(6)	0.266 4(7)	0.213 2(6)
N(4)	0.840 7(4)	−0.158 2(5)	0.090 0(5)	C(31)	0.884 0(6)	0.333 0(6)	0.263 1(6)
N(5)	0.864 3(4)	−0.062 7(5)	0.313 0(5)	C(32)	0.810 9(5)	0.280 6(6)	0.126 4(7)
C(1)	0.929 2(5)	0.138 4(4)	0.302 7(5)	C(33)	0.886 5(6)	0.214 7(6)	0.000 0(5)
C(2)	0.783 0(5)	0.113 0(5)	0.233 0(5)	C(34)	1.020 4(7)	0.165 4(8)	0.026 7(7)
C(3)	0.839 6(4)	0.100 0(4)	0.192 6(5)	C(35)	1.091 1(5)	0.207 1(8)	0.165(1)
C(4)	0.836 3(4)	0.033 6(5)	0.141 5(5)	C(36)	1.021 9(7)	0.296 0(7)	0.282 1(7)
C(5)	0.844 7(4)	−0.035 8(6)	0.169 0(5)	C(41)	0.775 8(4)	0.175 6(6)	0.286 3(6)
C(11)	0.947 8(5)	0.107 2(5)	0.444 7(5)	C(42)	0.724 3(5)	0.066 1(6)	0.226 8(5)
C(12)	0.895 6(6)	0.083 5(5)	0.489 0(6)	C(43)	0.843 3(5)	−0.102 9(6)	0.123 2(6)
C(13)	0.910 5(7)	0.063 1(7)	0.564 9(7)	C(44)	0.856 4(4)	−0.049 1(5)	0.250 4(6)
C(14)	0.973 0(8)	0.068 8(7)	0.592 0(7)	C(51)	0.823 6(4)	0.045 3(5)	0.057 0(5)
C(15)	1.025 0(6)	0.092 3(6)	0.545 1(7)	C(52)	0.767 9(4)	0.086 7(6)	0.033 9(5)
C(16)	1.013 0(6)	0.113 8(6)	0.469 9(6)	C(53)	0.753 8(5)	0.096 3(6)	−0.043 1(5)
C(17)	1.067 2(6)	0.136 8(6)	0.418 2(6)	C(54)	0.795 5(6)	0.063 7(6)	−0.097 0(5)
C(18)	0.827 6(6)	0.078 8(6)	0.459 0(6)	C(55)	0.850 4(5)	0.024 0(6)	−0.075 7(6)
C(21)	0.917 8(6)	0.284 5(5)	0.205 6(5)	C(56)	0.864 7(5)	0.014 6(6)	0.001 6(6)

Table 2 Positional coordinates for complex **6**

Atom	*x*	*y*	*z*
Ru	0.0103(1)	0.0121(1)	0.7546(2)
Cl(1)	−0.0624(1)	−0.1821(1)	0.6488(2)
Cl(2)	0.2046(1)	−0.0710(1)	0.8413(2)
N(1)	0.1179(3)	0.2686(3)	0.8674(4)
N(2)	−0.2513(3)	0.1295(3)	0.6581(4)
C(1)	0.0745(4)	0.1750(4)	0.8332(5)
C(2)	−0.1519(4)	0.0859(4)	0.6898(5)
C(11)	0.1744(4)	0.3831(3)	0.9128(5)
C(12)	0.1171(4)	0.4852(3)	0.8456(5)
C(13)	0.1727(6)	0.5980(4)	0.8910(6)
C(14)	0.2806(6)	0.6069(5)	0.9943(7)
C(15)	0.3343(5)	0.5043(5)	1.0570(6)
C(16)	0.2823(4)	0.3889(4)	1.0181(5)
C(17)	0.3383(7)	0.2747(6)	1.0852(8)
C(18)	0.0007(6)	0.4714(5)	0.7309(7)
C(21)	−0.3757(4)	0.1751(4)	0.6273(5)
C(22)	−0.4739(4)	0.1143(4)	0.6805(5)
C(23)	−0.5955(4)	0.1611(5)	0.6471(6)
C(24)	−0.6191(5)	0.2626(5)	0.5676(6)
C(25)	−0.5195(5)	0.3205(4)	0.5190(6)
C(26)	−0.3947(4)	0.2782(4)	0.5450(5)
C(27)	−0.2855(6)	0.3406(5)	0.4918(9)
C(28)	−0.4459(6)	0.0052(5)	0.7712(7)

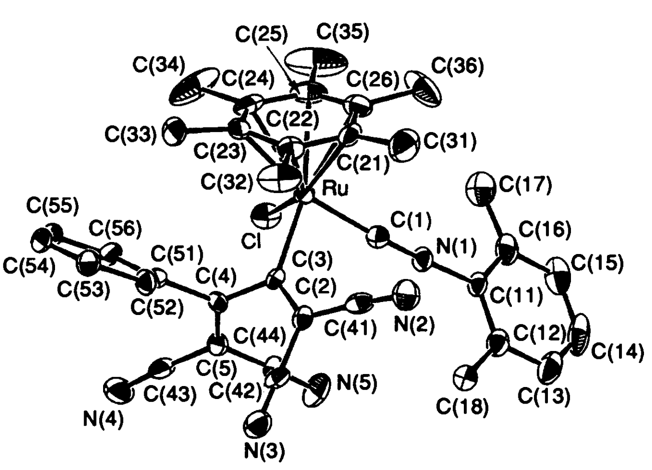


Fig. 1 Molecular structure of complex **4**

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Complex **4**

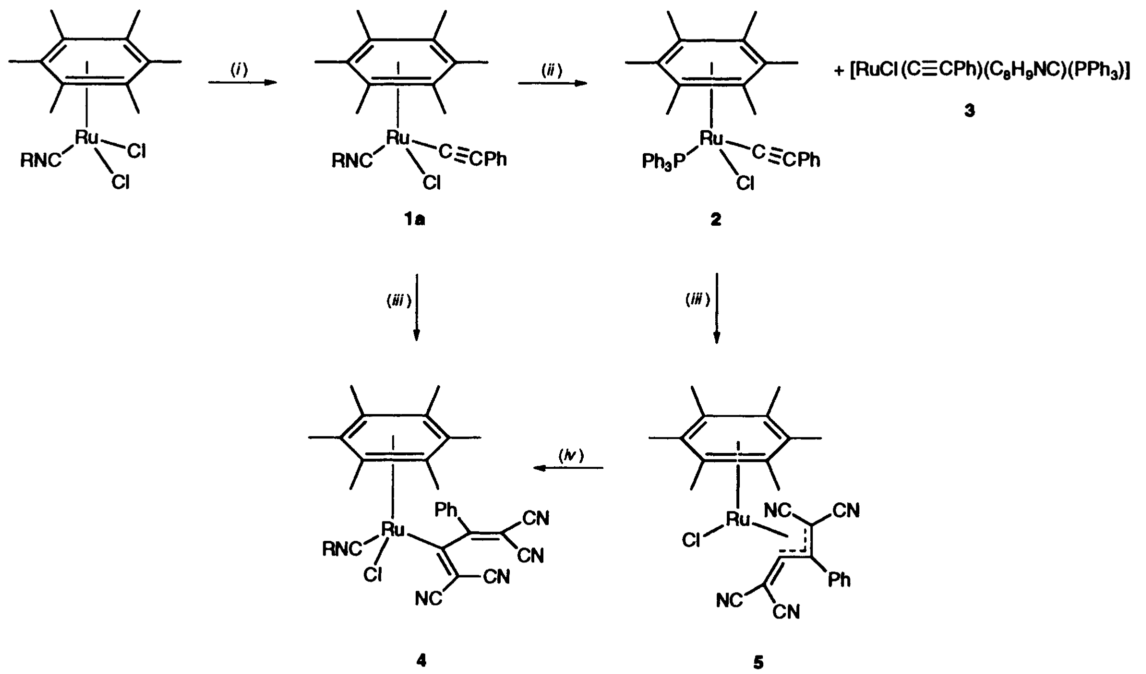
Ru–Cl	2.404(3)	Ru–C(26)	2.278(1)
Ru–C(1)	1.941(9)	N(1)–C(11)	1.42(1)
Ru–C(3)	2.064(8)	C(1)–N(1)	1.14(1)
Ru–C(21)	2.246(9)	C–N (mean)	1.138
Ru–C(22)	2.24(1)	C(2)–C(3)	1.36(1)
Ru–C(23)	2.359(9)	C(3)–C(4)	1.48(1)
Ru–C(24)	2.29(1)	C(4)–C(5)	1.34(1)
Ru–C(25)	2.28(1)		
Cl–Ru–C(1)	85.8(3)	Cl–Ru–C(3)	90.2(2)
C(1)–Ru–C(3)	85.5(4)	Ru–C(1)–N(1)	175(1)
C(1)–N(1)–C(11)	175(1)	Ru–C(3)–C(2)	128.9(7)
Ru–C(3)–C(4)	116.9(6)	C(2)–C(3)–C(4)	114.2(8)
C(3)–C(4)–C(5)	121.2(8)	C–C–N (mean)	177.3
C(3)–C(2)–C(41)	123.0(9)	C(3)–C(2)–C(42)	123.0(9)
C(41)–C(2)–C(42)	114.0(9)	C(4)–C(5)–C(43)	124.6(9)
C(4)–C(5)–C(44)	121.4(9)	C(43)–C(5)–C(44)	114.0(9)

(*b*) Complex **6**

Ru–Cl(1)	2.312(1)	C(1)–N(1)	1.131(4)
Ru–Cl(2)	2.308(1)	C(2)–N(2)	1.156(5)
Ru–C(1)	1.936(4)	N(1)–C(11)	1.404(5)
Ru–C(2)	1.925(4)	N(2)–C(21)	1.395(5)
Cl(1)–Ru–Cl(2)	92.25(5)	Cl(1)–Ru–C(1)	177.3(1)
Cl(1)–Ru–C(2)	88.4(1)	Cl(2)–Ru–C(1)	86.7(1)
Cl(2)–Ru–C(2)	177.9(1)	C(1)–Ru–C(2)	91.8(2)
Ru–C(1)–N(1)	174.1(4)	C(1)–N(1)–C(11)	178.4(4)
Ru–C(2)–N(2)	176.7(4)	C(2)–N(2)–C(21)	175.1(4)

cis-[$RuCl_2(C_8H_9NC)_2$] which was obtained by thermal decomposition of *trans*-[$RuCl_2(C_8H_9NC)_4$] (see above). The detailed structure must await an X-ray analysis, but suitable crystals have not yet been obtained.

Reaction of the acetylide complex **1a** with tcne in benzene gave reddish brown crystals in 40% yield, formulated as [Ru(η^6-C_6Me_6)Cl{C[=C(CN)$_2$]CPh=C(CN)$_2$}(C_8H_9NC)] **4**. The infrared spectrum showed four characteristic bands at 2233, 2222, 2135 and 1547 cm^{-1}. The first two bands are assignable to ν(C≡N) of tcne and the second two to ν(N≡C) of isocyanide and ν(C=C). The ^{1}H NMR spectrum showed two singlets due to methyl groups at δ 1.89 and 2.45 in intensity ratio 3:1, assignable to arene and isocyanide groups. The structure was confirmed by an X-ray analysis (Fig. 1). Selected bond distances and angles are shown in Table 3. The ruthenium is co-ordinated



Scheme 2 Reactions of [Ru(η^6-C_6Me_6)Cl(C≡CPh)(C_8H_9NC)], R = C_8H_9. (*i*) PhC≡CH, KOH-MeOH; (*ii*) PPh_3; (*iii*) tcne; (*iv*) RNC

by hexamethylbenzene [mean Ru–C 2.281(10) Å], chloride [Ru–Cl 2.404(3) Å], and isocyanide [Ru–C(1) 1.941(9) Å] ligands and the 1,1,4,4-tetracyano-3-phenylbuta-1,3-dien-2-yl group [Ru–C(3) 2.064(8) Å] formed by addition of two dicyanomethylene fragments to each acetylenic carbon of the phenylacetylide ligand of **1**. Similar types of compounds have been observed for Ru, Fe and W.[7] The bond angles and distances were not significantly different from usual values. Compound **4** was recovered when treated with carbon monoxide (50 kg cm^{-2}) at room temperature or heated with xylyl isocyanide in toluene.

Reaction of complex **2** with tcne was similar except that elimination of triphenylphosphine occurred to give brown crystals of **5** [Ru(η^6-C_6Me_6)Cl{$C(CN)_2CPhC{=}C(CN)_2$}], consistent with loss of isocyanide from **4**. The infrared spectrum showed two bands at 2220 (C≡N) and 1537 cm^{-1} (C=C). The ^1H NMR spectrum showed the methyl protons of the η^6-arene group at δ 1.77. When compound **5** was treated with PPh_3 the starting materials were recovered, whereas the reaction with xylyl isocyanide generated **4**. From these results the molecule is assumed to have a structure in which the $C(CN)_2CPh{=}C(CN)_2$ moiety acts in a κ*N*,η^3-co-ordination mode, as depicted in Scheme 2. This type of complex has been noted previously.[7] A possible path for this reaction consists of a (2π + 2π) addition between triple and double bonds, and then electron transfer and cleavage of a carbon–carbon bond to give the final complex **4**. In the triphenylphosphine complex the steric bulk of the phosphine ligand might accelerate its elimination to give the κ*N*,η^3 complex **5**.

Preparation and Structure of cis-[$RuCl_2(C_8H_9NC)_2$] **6**.— Heating *trans*-[$RuCl_2(C_8H_9NC)_4$] at *ca.* 170 °C for 4.0 h gave a very pale yellow compound **6**, formulated as [$RuCl_2(C_8H_9NC)_2$]. The infrared spectrum showed two N≡C stretching frequencies, suggesting a *cis* structure. An X-ray analysis showed a pair of *cis*-$RuCl_2(C_8H_9NC)_2$ molecules with a centre of symmetry at (000). The molecular structure and crystal packing are shown in Fig. 2. Selected bond distances and angles are presented in Table 3. The Ru–Ru bond distances are 4.118(1) (−*x*, −*y*, 2 − *z*) and 4.155(1) Å (−*x*, −*y*, 1 − *z*), indicating no interaction. The shortest intermolecular distance is C(17) ··· C(28) (−*x*, −*y*, 2 − *z*) 3.535(8) Å.

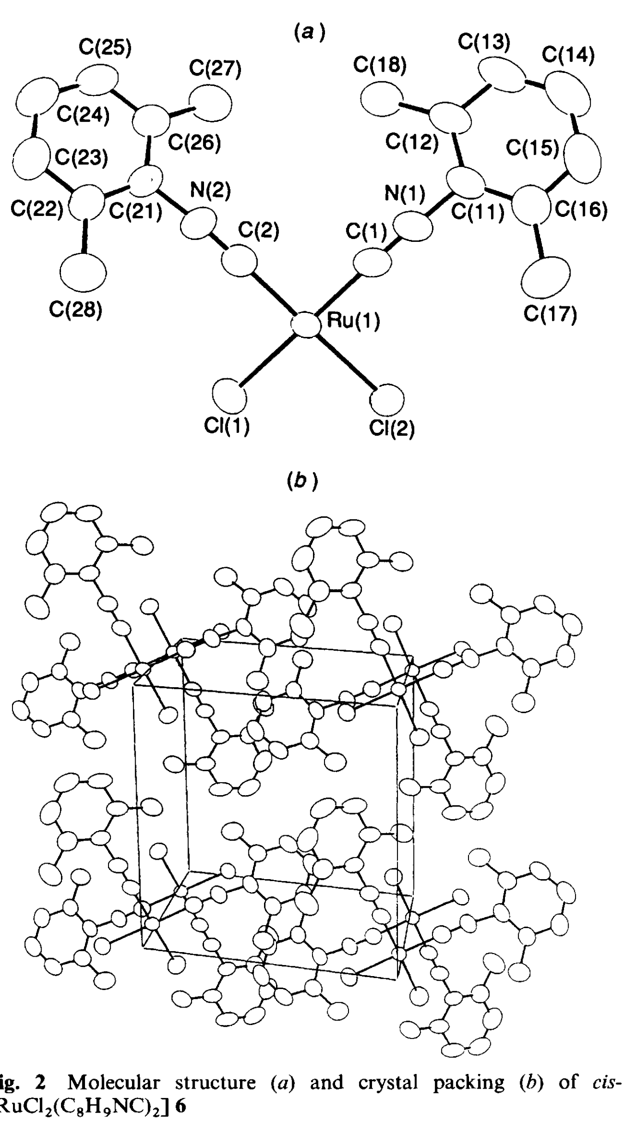


Fig. 2 Molecular structure (*a*) and crystal packing (*b*) of *cis*-[$RuCl_2(C_8H_9NC)_2$] **6**

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