Formation of a Homoleptic Unbridged Metal–Metal Bonded Isocyanide Dimer of Ruthenium(I) by Metal–Carbon Bond Cleavage in $[Ru(1\text{–}2,5\text{-}\eta\text{-}C_8H_{13})(CN\text{-xylyl})_4]PF_6$: The *X*-ray Structure Determination of $[Ru_2(CN\text{-xylyl})_{10}][BPh_4]_2$

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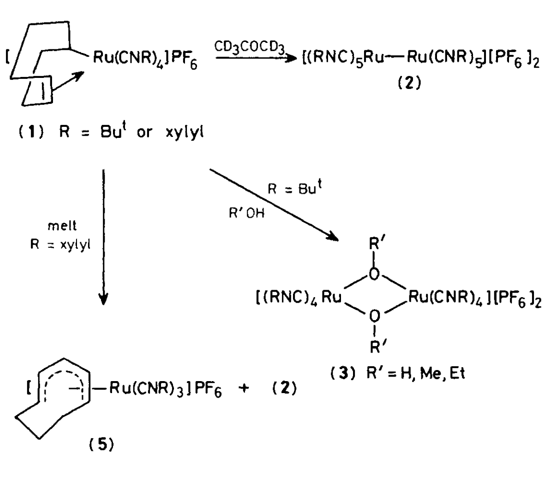
Refluxing $[Ru(1\text{–}2,5\text{-}\eta\text{-}C_8H_{13})(CN\text{-xylyl})_4]PF_6$ in $[^2H_6]$acetone gives $C_8H_{13}D$ and $[Ru_2(CN\text{-xylyl})_{10}][PF_6]_2$; an *X*-ray structure determination of $[Ru_2(CN\text{-xylyl})_{10}][BPh_4]_2$ shows the cation to be an unbridged, metal–metal bonded dimer of ruthenium(I) containing eclipsed 2,6-dimethylphenyl isocyanide ligands.

During our studies[1] on the formation and insertion reactions of $[Ru(1\text{–}2,5\text{-}\eta\text{-}C_8H_{13})(CNR)_4]PF_6$ [(**1**), R = Bu^t or 2,6-dimethylphenyl (xylyl)], we observed changes in the ^{13}C n.m.r. spectra of these complexes on prolonged standing in $[^2H_6]$acetone. We now give evidence which suggests that these changes are a result of homolytic metal–carbon bond fission[2] and, for (**1**; R = xylyl), the complex produced has been characterized as a rare example of an unbridged homoleptic dimer of the iron triad.[3]

Treatment of the hydrido complex $[RuH(cod)(NH_2NMe_2)_3]PF_6$ (cod = cyclo-octa-1,5-diene)[4] with an excess of isocyanide RNC in ethanol or acetone solution at room temperature for 10 min produced the salts (**1**) in >70% yields. The ^{13}C n.m.r. spectra of (**1**) each contain an eight-line resonance pattern (R = Bu^t: δ 95.2, 91.0, 43.2, 39.2, 29.0, 28.2, 25.0, and 21.0 in CD_2Cl_2; R = xylyl: δ 100.3, 96.5, 44.9, 40.0, 29.5, 28.3, 25.3, and 24.7 in CD_3COCD_3) characteristic of a cyclo-octenyl ring bonded 1–2,5-η to the ruthenium atom. During 4—7 days in $[^2H_6]$acetone solution or on refluxing for 24 h in this solvent these resonances are replaced by an olefinic carbon resonance at δ 132.6 corresponding to a mixture of cyclo-octene and $[^2H_1]$cyclo-octene [triplet at δ 25.5, *J*(C–D) *ca.* 20 Hz[5]] and by resonances at δ 130.6, 129.6, and 47.5. The latter resonances have not yet been assigned but possibly correspond to a substituted derivative of cyclo-octene. For (**1**; R = xylyl), the resonances at δ 129—133 are obscured by phenyl C resonances.

The oil obtained after distillation to remove the organic products produced crystals of the salt $[Ru_2(CN\text{-xylyl})_{10}][PF_6]_2$ (**2**) (10% yield) from ethanol but with (**1**; R = Bu^t) no crystalline products were obtained from the residual oil.

These results suggest[2] the formation of radical species from a homolytic fission of the Ru–C bond in (**1**) (Scheme 1) and exclude heterolysis involving traces of D_2O or D^+ impurities. The low yield of the dimer (**2**) in the decompositions may be a result of competing atom abstracting processes although similar metal carbonyl radicals have been shown to dimerize with bimolecular rate constants characteristic of diffusion controlled processes.[6] In the case of the decomposition of (**1**; R = Bu^t) it is expected that atom abstracting processes will be dominant as the ruthenium–isocyanide radical cation will be sufficiently crowded to preclude combination.[7] Evidence that interaction with solvent does occur came from decomposition reactions of (**1**; R = Bu^t) in acetone containing water or alcohols. From these solutions the dimeric complexes $[Ru_2(OX)_2(CNBu^t)_8][PF_6]_2$ (**3**; X = H, Me, or Et) were isolated in 40—50% yields.



Scheme 1. (**4**) = (**2**), $[BPh_4]_2$ salt.

Suitable crystals of (**2**) could not be obtained for *X*-ray analysis but anion exchange with $NaBPh_4$ produced $[Ru_2(CN\text{-xylyl})_{10}][BPh_4]_2$ (**4**) which formed crystals of satisfactory quality. An *X*-ray structural analysis† of (**4**) shows the cation to have a crystallographic centre of inversion, with eclipsed equatorial ligands. The Ru–Ru bond length of 3.003(1) Å is significantly longer than those of 2.886(2)—2.943(1) Å found[7—9] in other related non-bridged ruthenium(I) dimers and may be ascribed to steric repulsions between the bulky xylyl groups of the equatorial ligands.[10] Some relief of strain is obtained by the approximately parallel orientation of each pair of eclipsed xylyl groups. Calculations and inspection of models show that the non-bonded repulsions cannot be reduced by the adoption of a staggered conformation, as this would result in some extremely short C · · · C contacts. Therefore, the eclipsed conformation, although still sterically strained, represents a minimum of non-bonded contacts in the complex.

Complex (**2**) can be prepared in higher yields (27%) by refluxing (**1**; R = xylyl) in acetone with an excess of xylyl isocyanide for 24 h, but the highest yields (40%) are obtained by melting (**1**; R = xylyl) at 130 °C. The second product of this

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† *Crystal data:* $C_{138}H_{130}B_2N_{10}Ru_2$, $M = 2152.4$, monoclinic, space group $P2_1/n$, $a = 25.434(3)$, $b = 16.448(3)$, $c = 14.629(2)$ Å, $\beta = 106.41(4)°$, $U = 5870.6$ Å^3, $D_c = 1.22$ Mg m^{-3} for $Z = 2$, $F(000) = 2252$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.261 mm^{-1}. The structure was solved by conventional heavy atom methods and was refined by weighted least-squares [$w = 1/\sigma^2(F_o)$], anisotropic temperature factors for all non-H atoms, H atoms in calculated positions, C–H = 0.95 Å] to give $R = 0.0490$ and $R_w = 0.0437$ for 4232 unique reflections with $F_o \geqslant 2\sigma(F_o)$ measured on a Philips PW 1100 diffractometer.

The atomic co-ordinates for this structure 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.

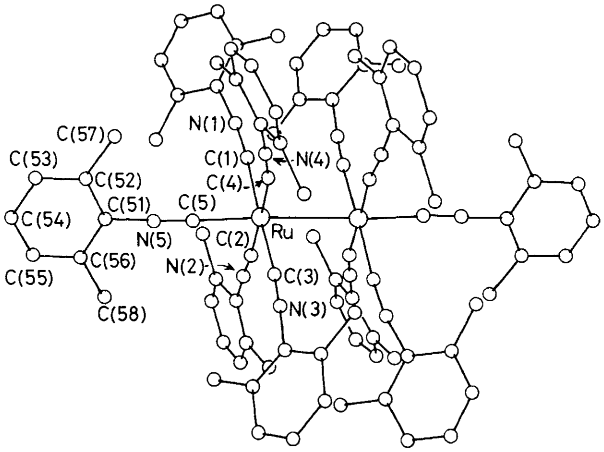

Figure 1. A perspective view of the complex cation of (**4**) showing the atom numbering scheme. The numbering of the atoms of the xylyl groups of ligands 1 to 4 follows the same pattern as that for ligand 5 [*i.e.* C(*n*1) to C(*n*8), *n* = 1—4]. Selected bond lengths (Å) and angles (°): Ru–Ru' 3.003(1), Ru–C(1) 1.994(6), Ru–C(2) 1.994(6), Ru–C(3) 1.985(6), Ru–C(4) 1.974(7), Ru–C(5) 1.966(6), C(*n*)–N(*n*) (mean) 1.166(8), N(*n*)–C(*n*1) (mean) 1.405(9); Ru'–Ru–C(1) 94.2(1), Ru'–Ru–C(2) 84.0(1), Ru'–Ru–C(3) 86.3(1), Ru'–Ru–C(4) 96.9(1), Ru'–Ru–C(5) 174.3(1).

reaction (~30%) could not be adequately purified but was inferred to be $[Ru(1\text{—}5\text{-}\eta\text{-}C_8H_{11})(CN\text{-xylyl})_3]PF_6$ (**5**) from the characteristic[11] five-line ^{13}C n.m.r. spectrum (δ 102.6, 96.6, 61.2, 27.4, and 26.5 in $CDCl_3$). Four organic products were obtained from the melt and characterized by g.c.–mass spectrometry as cyclo-octane, cyclo-octene, cyclo-octa-1,3-diene, and bicyclo[3.3.0]octane. These organic products, together with (**5**), can all be accounted for by hydrogen transfer processes[11] and olefin photoreactions[12] established in earlier systems.

Received, 13th May 1985; Com. 647

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