Synthesis and Characterisation of Neutral and Cationic 2,7-Dimethyloctadienediylruthenium(IV) Complexes. X-Ray Crystal Structure of *cis*-Bis(acetonitrile)chloro[(1,2,3,6,7,8-η)-2,7-dimethylocta-2,6-diene-1,8-diyl]ruthenium(IV) Tetrafluoroborate†

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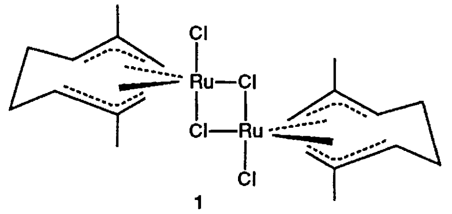
Reactions of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **1** with the ligands (L) $P(OMe)_3$, Bu^tNC or Pr^iNC in chloroform solution give the complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ **2–4**. Treatment of these complexes with $Ag[BF_4]$ and additional free ligand in acetone solution gives the salts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})ClL_2][BF_4]$ **5–7**. The reaction of **1** with $Ag[BF_4]$ in acetonitrile solution yields $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NCMe)_2][BF_4]$ **8** which slowly converts in solution into an alternative stereoisomer **9**. The structures proposed for **2–9** all feature an approximate trigonal-bipyramidal co-ordination at ruthenium, occupation of two equatorial sites by the $\eta^3:\eta^3$-2,7-dimethyloctadienediyl ligand, and a local C_2-symmetry configuration for the octadienediyl chain. In **2–4** it is the two-electron ligand that occupies the third equatorial site with both chlorides axial. In **5–7** the chloride occupies the third equatorial site and both the two-electron ligands are axial. For the two acetonitrile-containing stereoisomers, the chloride is axial in **8** and equatorial in **9**. An equilibrium $\mathbf{8} \rightleftharpoons \mathbf{9}$ exists in acetonitrile solution with $K_{298} = 30 \pm 5$, $k_{298}(\text{forward}) = (7.6 \pm 0.6) \times 10^{-6}\ s^{-1}$, $\Delta H^{\ddagger} = 123 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 68 \pm 9$ J K^{-1} mol^{-1}, as determined by ^1H NMR spectroscopy and sampling techniques. The structure of **8** has been confirmed by X-ray diffraction: space group $P\bar{1}$ with $a = 7.80(1)$, $b = 15.69(1)$, $c = 7.63(1)$ Å, $\alpha = 96.5(1)$, $\beta = 87.1(1)$, $\gamma = 96.9(1)^\circ$ and $Z = 2$. The structure was refined to $R = 0.082$ for 1766 unique reflections.

Complexes containing an $\eta^3:\eta^3$-octadienediyl ligand are known for a range of transition metals,[1] and in certain systems have been recognised as reactive intermediates in transition-metal-catalysed diene dimerisations, oligomerisations and telomerisations.[2] The stable 2,7-dimethyloctadienediylruthenium(IV) complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **1**, however, appears to be a suitable precursor to explore the possibility of an octadienediyl chain acting as a spectator ligand. For example, the structurally related $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ complexes have been widely used to develop the co-ordination chemistry of $Ru(\eta^6$-arene) fragments.[3]

The synthesis of complex **1** and the recognition of its dimeric nature were first reported by Allegra and co-workers[4] in 1965. The co-ordination geometry about the ruthenium atoms approximates to trigonal bipyramidal.[5] Although neutral monomeric adducts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ [L = CO, PPh_3, PF_3, $PF_2(NMe_2)$, $PCl_2(CF_3)$ or $P(OCH_2)_3CPh$] were described by Nixon and co-workers[6] in 1974, further derivatives of **1** have not been prepared.

In recent articles we have discussed the nature of complex **1** in solutions of various organic solvents, identified an equilibrium between the diastereoisomeric *meso* and *rac* forms, and have shown that a synthetically useful labilisation of the octadienediyl ligand may be promoted by chloride ion removal.[7,8] We now report that substitution of chloride by two-electron ligands in the monomeric adducts of **1** with $P(OMe)_3$, Bu^tNC, Pr^iNC and MeCN is achieved using silver(I) tetrafluoroborate. Monocations of formula $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})ClL_2]^+$ have thus been synthesised, and are the first examples of cationic transition-metal complexes containing a chelating $\eta^3:\eta^3$-octadienediyl ligand.



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Experimental

Microanalyses were carried out by Ilse Beetz Microanalytisches Laboratorium, Kronach, West Germany. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, NMR spectra on Bruker WH-360 (^1H, 360; ^{13}C, 90.55 MHz) and AC-200 (^1H, 200; ^{31}P, 81.01 MHz) FT spectrometers. Chemical shifts are reported in ppm downfield from $SiMe_4$ (^1H and ^{13}C) and from 85% H_3PO_4 (^{31}P). Conductivity measurements were made on *ca.* 10^{-3} mol dm^{-3} solutions at 20 °C using a Metrohm 660 conductometer. Commercial reagents were used and $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ was prepared by our modified synthesis of the original preparation.[7] All solvents were dried, distilled and deoxygenated prior to use, and all manipulations were routinely carried out under nitrogen using standard Schlenk techniques.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Preparation and Characterisation of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ *and* $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})ClL_2][BF_4]$ *Complexes*.—Proton and ^{13}C NMR data for complexes **2**–**9** are summarised in Tables 1 and 2 respectively.

Dichloro[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*](*trimethyl phosphite*)*ruthenium*(IV) **2**. Trimethyl phosphite (0.175 cm^3, 1.48 mmol) was added to a solution of complex **1** (0.400 g, 0.65 mmol) in chloroform (30 cm^3) and the mixture was stirred at room temperature for 1 h. Filtration, partial evaporation of the solution, addition of hexane and cooling, gave orange crystals of complex **2** (0.47 g, 84%), m.p. 109 °C (Found: C, 36.0; H, 5.9; P, 7.1. $C_{13}H_{25}Cl_2O_3PRu$ requires C, 36.1; H, 5.8; P, 7.2%). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 131.6(s).

(tert-*Butyl isocyanide*)*dichloro*[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*]*ruthenium*(IV) **3**. As for complex **2**, but replacing $P(OMe)_3$ by Bu^tNC (0.165 cm^3, 1.46 mmol), gave orange crystals of complex **3** (0.45 g, 88%), m.p. 123 °C (Found: C, 46.2; H, 6.3. $C_{15}H_{25}Cl_2NRu$ requires C, 46.1; H, 6.4%); ν_{max}(CN) 2192 cm^{-1} ($CHCl_3$).

Dichloro[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*](*isopropyl isocyanide*)*ruthenium*(IV) **4**. As for **2**, but replacing $P(OMe)_3$ by Pr^iNC (0.135 cm^3, 1.48 mmol), gave orange crystals of complex **4** (0.44 g, 90%), m.p. 131 °C (Found: C, 44.7; H, 6.2; N, 3.8. $C_{14}H_{23}Cl_2NRu$ requires C, 44.6; H, 6.1; N, 3.7%); ν_{max}(CN) 2198 cm^{-1} ($CHCl_3$).

Chloro[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*]*bis*(*trimethyl phosphite*)*ruthenium*(IV) *tetrafluoroborate* **5**. A solution of complex **2** (0.30 g, 0.69 mmol) in acetone (20 cm^3) was treated with a solution of $Ag[BF_4]$ (0.135 g, 0.69 mmol) in acetone (10 cm^3), and the mixture was stirred for 1 h at room temperature. One mol equivalent of AgCl was precipitated and was removed by filtration through a short bed (1 cm) of Celite. Trimethyl phosphite (0.095 cm^3, 0.81 mmol) was added to the filtrate and stirring continued for 1 h. Partial solvent evaporation, addition of diethyl ether and cooling, gave pale yellow microcrystals of complex **5** (0.34 g, 81%), m.p. 107 °C (Found: C, 31.8; H, 5.8; Cl, 5.9; P, 10.2. $C_{16}H_{34}BClF_4O_6P_2Ru$ requires C, 31.6; H, 5.6; Cl, 5.8; P, 10.2%). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 101.0(s). Conductivity: Λ_M(MeCN): 129 S cm^2 mol^{-1}.

Bis(tert-*Butyl isocyanide*)*chloro*[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*]*ruthenium*(IV) *tetrafluoroborate* **6**. As for **5**, but replacing mol equivalents of **2** by **3** (0.27 g, 0.69 mmol) and of $P(OMe)_3$ by Bu^tNC (0.090 cm^3, 0.80 mmol), gave cream microcrystals of complex **6** (0.31 g, 85%), m.p. 175 °C (decomp.) (Found: C, 45.6; H, 6.9; Cl, 6.6; N, 5.4. $C_{20}H_{34}BClF_4N_2Ru$ requires C, 45.7; H, 6.5; Cl, 6.7; N, 5.3%); ν_{max}(CN) 2208w and 2177s cm^{-1} ($CHCl_3$). Conductivity: Λ_M(MeCN): 121 S cm^2 mol^{-1}.

Chloro[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*]*bis*(*isopropyl isocyanide*)*ruthenium*(IV) *tetrafluoroborate* **7**. As for **5**, but replacing mol equivalents of **2** by **4** (0.26 g, 0.69 mmol) and of $P(OMe)_3$ by Pr^iNC (0.075 cm^3, 0.82 mmol), gave pale yellow microcrystals of complex **7** (0.29 g, 84%), m.p. 134 °C (Found: C, 43.4; H, 6.2; N, 5.6. $C_{18}H_{30}BClF_4N_2Ru$ requires C, 43.4; H, 6.1; N, 5.6%); ν_{max}(CN) 2213w and 2185s cm^{-1} ($CHCl_3$). Conductivity: Λ_M(MeCN): 125 S cm^2 mol^{-1}.

cis-*Bis*(*acetonitrile*)*chloro*[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*]*ruthenium*(IV) *tetrafluoroborate* **8**. Complex **1** (0.51 g, 0.83 mmol) was dissolved in acetonitrile (20 cm^3) and a solution of $Ag[BF_4]$ (0.322 g, 1.65 mmol) in acetonitrile (10 cm^3) was added. The mixture was stirred at room temperature for 80 min, then filtered through a short bed (1 cm) of Celite to remove the precipitate of AgCl. The solution was partially evaporated without heating, and sufficient diethyl ether added to induce, on trituration, the formation of orange-yellow microcrystals of complex **8** (0.65 g, 89%), m.p. 182 °C (decomp.) (Found: C, 38.2; H, 5.0; N, 7.0. $C_{14}H_{22}BClF_4N_2Ru$ requires C, 38.1; H, 5.0; N, 6.3%); ν_{max}(CN) 2321m and 2295m cm^{-1} (Nujol). Conductivity: Λ_M(MeCN): 130 S cm^2 mol^{-1}.

trans-*Bis*(*acetonitrile*)*chloro*[(1,2,3,6,7,8-η)-2,7-*dimethylocta*-2,6-*diene*-1,8-*diyl*]*ruthenium*(IV) *tetrafluoroborate* **9**. A solution of complex **8** (0.40 g, 0.91 mmol) in acetonitrile (30 cm^3) was stirred for 48 h at 40 °C. Partial solvent evaporation, addition of diethyl ether and cooling gave lime-yellow microcrystals of **9** (0.355 g, 89%), m.p. 188 °C (decomp.) (Found: C, 38.3; H, 5.1; N, 7.0. $C_{14}H_{22}BClF_4N_2Ru$ requires C, 38.1; H, 5.0; N, 6.3%); ν_{max}(CN) 2322w and 2304w cm^{-1} (Nujol). Conductivity: Λ_M(MeCN): 132 S cm^2 mol^{-1}.

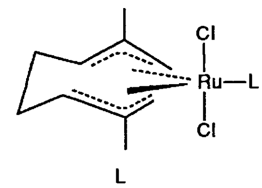
X-Ray Structure Determination of Complex **8**.—Single crystals of complex **8** were obtained from acetonitrile–diethyl ether solution.

Crystal data. $C_{14}H_{22}BClF_4N_2Ru$, $M = 441.7$, triclinic, space group $P\bar{1}$, $a = 7.80(1)$, $b = 15.69(1)$, $c = 7.63(1)$ Å, $\alpha = 96.5(1)$, $\beta = 87.1(1)$, $\gamma = 96.9(1)°$, $U = 920.4$ Å^3, $Z = 2$, $D_c = 1.594$ g cm^{-3}, $F(000) = 444.0$, λ(Mo-Kα) = 0.7107 Å, $\mu = 8.88$ cm^{-1}, $T = 290$ K. Pale yellow prisms showing {100}, {010}, {001}, elongated along *a*.

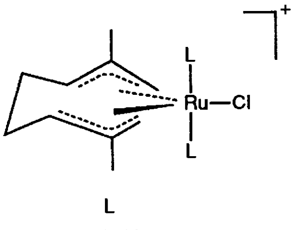
Unit-cell dimensions were initially determined from Weissenberg photographs (Cu-Kα 1.542 Å) and refined from setting angles of 20 reflections in the range $10 < 2\theta < 40$ on a STADI-2 two-circle diffractometer (graphite-monochromatised Mo-Kα). This diffractometer was also used for measurement of intensities from a crystal 0.3 × 0.08 × 0.12 mm for the layers $hk0$ to $hk7$, h −8 to +8, k −16 to +16, and from a second crystal 0.36 × 0.08 × 0.12 mm for the layers $0kl$ to $2kl$, k −16 to +16, l −8 to +8. Maximum $\sin\theta/\lambda = 0.55$, variable ω scan 2θ′ fixed, stationary background count, standard measured every 20 reflections. A total of 2685 reflections were measured, 2372 unique with $R_{int} = 0.02$ after absorption corrections (maximum, minimum transmission factors 0.93, 0.83 and 0.93, 0.90). 1766 Reflections for which $I > 3\sigma(I)$ were used in the refinement. Atomic scattering factors were taken from the tables for ruthenium,[9] and for the other atoms.[10] SHELX 76 programs were used throughout.[11] The Patterson method was used to locate the ruthenium atom, and the remaining non-H atoms were found through Fourier difference mapping. Full-matrix least-squares refinement based on F of positions, and with anisotropic thermal parameters for all non-H atoms, was carried out. The H atoms were included in the refinement in idealised positions [d(C–H) = 1.08 Å]. Separate common isotropic thermal parameters were refined for CH, CH_2 and CH_3 hydrogen atoms. A total of 219 parameters were refined until $\Delta/\sigma < 0.07$, and the largest features on the final Fourier difference map were +1.12 to −1.23 e Å^{-3} in the vicinity of the Ru atom. The refinement converged with $R = 0.082$, $R' = 0.096$, $s = 3.55$ and $w = 10.8/[\sigma^2(F) + 0.000\,21\,F^2]$. The final fractional coordinates for the non-H atoms are presented in Table 3, along with their estimated standard deviations (e.s.d.s). The cation with atomic labelling is shown in Fig. 1, and selected bond distances and bond angles are given in Table 4.

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

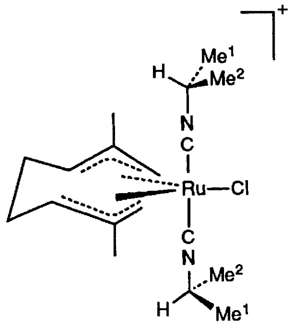
Kinetics of the Isomerisation **8** $\rightleftharpoons$ **9**.—The isomerisation of complex **8** was followed in CD_3CN and $(CD_3)_2CO$ solutions by ^1H NMR spectroscopy using sampling techniques. The spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-1000 temperature-control unit. Samples were kept either in a thermostatted bath and transferred to the probe at regular intervals, or were kept in the thermostatted probe for the entire duration of each kinetic run. Temperatures (constant to ±0.3 °C) were measured before and after each run, using a 100 Ω platinum resistance attached to a Hewlett-Packard 2802A digital thermometer. The substitution technique was used to measure temperatures directly within the probe.[12] In general, each kinetic run consisted of at least 10 spectra collected at regular intervals over 2–3 half-lives, with a further spectrum of the system at equilibrium. The relative abundances of complexes **8** and **9** at each sampling were



L
2 P(OMe)$_3$
3 Bu^{t}NC
4 Pr^{i}NC



L
5 P(OMe)$_3$
6 Bu^{t}NC
7 Pr^{i}NC



evaluated by integration of the characteristic singlets assigned to the allyl protons at the termini of the octadienediyl ligands (*e.g.* in CD_3CN: δ 5.15, 4.91, 4.32 and 4.04 for **8**; δ 4.77 and 3.95 for **9**). For each run plots of ln [(% **8**) − (% **8** at equilibrium)] *vs.* time were linear and the negative slopes gave the sum of the rate constants for the forward and reverse reactions of the equilibrium $\mathbf{8} \rightleftharpoons \mathbf{9}$. The observed values of k(forward) from each plot were: (i) in CD_3CN solution, 4.8×10^{-6} (295.7), 4.5×10^{-5} (309.1), 1.7×10^{-4} (317.0), 4.9×10^{-4} (324.8) and 1.3×10^{-3} s^{-1} (332.5 K); (ii) in $(CD_3)_2CO$ solution, 1.5×10^{-5} (295.7), 1.6×10^{-4} (309.1), 4.7×10^{-4} (317.0) and 1.2×10^{-3} s^{-1} (324.8 K). Least-squares fitting of these results by the Eyring equation gave the k_{298} values and the activation parameters reported in the main text.

Results and Discussion

Neutral $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ *Complexes.*—Treatment of chloroform solutions of complex **1** with 2 mol equivalents of the ligands P(OMe)$_3$, Bu^{t}NC or Pr^{i}NC resulted in formation of the monomeric adducts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$, [L = P(OMe)$_3$, **2**; Bu^{t}NC, **3**; Pr^{i}NC, **4**], in high yields (>80%). The solution ^{1}H and ^{13}C NMR spectra of these compounds are summarised in Tables 1 and 2 respectively, and are all temperature invariant (200–320 K). The two allyl moieties of the 2,7-dimethyloctadienediyl ligand are clearly chemically equivalent, and the spectra are fully consistent with the illustrated structures proposed for **2**–**4**.

The approximate trigonal-bipyramidal co-ordination about ruthenium, the occupation of two equatorial co-ordination sites by the $\eta^3:\eta^3$-2,7-dimethyloctadienediyl ligand, and the local C_2-symmetry configuration of the octadienediyl chain have previously been observed crystallographically in the structures of the *meso* form of **1** and of the related monomer $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(PF_3)]$.[5,13] Comparable structures for a range of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ complexes have also been proposed,[6] although for L = MeCN and NMe$_2$CHO (O-bound) the existence of an alternative stereoisomer with L in an axial site has been demonstrated.[7] As a consequence of the C_2-symmetry configuration of the octadienediyl chain, complexes **2**–**4** are racemic mixtures of enantiomers.

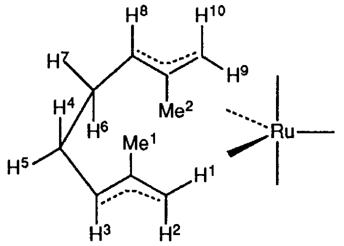
Cationic $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})ClL_2]^+$ *Complexes.*—Treatment of acetone solutions of complexes **2**–**4** with 1 mol equivalent of silver(I) tetrafluoroborate resulted in the quantitative precipitation of silver(I) chloride which was removed by filtration. Upon addition of P(OMe)$_3$, Bu^{t}NC or Pr^{i}NC, respectively, to the solutions, the salts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})ClL_2][BF_4]$ [L = P(OMe)$_3$, **5**; Bu^{t}NC, **6**; or Pr^{i}NC, **7**] were isolated in high yields (>80%) on work-up. Their molar conductivities in acetonitrile solution are all in the range Λ_M = 120–130 S cm^2 mol^{-1} and confirm that the salts are 1:1 electrolytes.[14] The solution ^{1}H and ^{13}C NMR spectra are summarised in Tables 1 and 2, respectively, and are all temperature invariant (200–320 K). They show in each case a chemical equivalence of the two allyl moieties of the 2,7-dimethyloctadienediyl ligand and of the two two-electron ligands. Structures of C_2 symmetry for the cations are therefore proposed, with the two two-electron ligands occupying both axial sites as shown.

Additional evidence in support of these structures is provided by the NMR resonances from the isopropyl groups of complex **7**. The four isopropyl methyl groups resonate as two overlapping doublets at δ 1.46 and 1.44 [^3J(HH) = 6.6 Hz] in the ^{1}H NMR spectrum, although the two Pr^{i}NC ligands are chemically equivalent. Irradiation of the unique septet at δ 4.26, which is the resonance from the central CH group protons of the Pr^{i}NC ligands, collapses the doublets to two singlets. Further, in the ^{13}C-{^{1}H} NMR spectrum the four iso-propyl methyl groups are resolved into two singlets at δ 22.8 and 22.7. These observations confirm the retention of the C_2-symmetry configuration of the $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})]$ fragment since this configuration renders the methyl groups of each Pr^{i}NC ligand diastereotopic, as shown. The failure to resolve separate NMR resonances from the diastereotopic methyl groups of the equatorial Pr^{i}NC ligand in complex **4** can be attributed to the isopropyl group being more remote from the chiral centre than those of **7**. The observation that the ^{1}H NMR resonance from the methyl groups of the phosphites of **5** appears as a virtual triplet [J(PH) = 4.9 Hz] is consistent with a *trans* disposition of the two two-electron ligands.

Treatment of an acetonitrile solution of complex **1** with 2 mol equivalents of silver(I) tetrafluoroborate precipitated silver(I) chloride and led, upon work-up of the solution, to a high yield (89%) of orange-yellow microcrystals of formula $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NCMe)_2][BF_4]$ **8**. A more stable lime-yellow isomer of **8**, complex **9**, was subsequently isolated in high yield (89%) from an acetonitrile solution of **8** that had been stirred at 40 °C for 48 h. The molar conductivities of **8** and **9** in acetonitrile solution are Λ_M = 130 and 132 S cm^2 mol^{-1}, respectively, confirming that they are 1:1 electrolytes.[14] The solution ^{1}H and ^{13}C NMR spectra of complexes **8** and **9** are quite distinct, and are summarised in Tables 1 and 2. For **9**, the spectra indicate chemical equivalence of the two allyl groups of the 2,7-dimethyloctadienediyl ligand and of the two acetonitrile ligands. A C_2-symmetry structure for the cation of **9**, analogous to the structures of the cations in **5**–**7**, is therefore proposed. For **8**, the spectra show that the two allyl groups and the two acetonitrile ligands are both inequivalent. The cation of **8** must therefore possess a molecular structure of low symmetry, and a single-crystal X-ray diffraction study was undertaken.

Crystal Structure of Complex **8**.—The molecular structure of

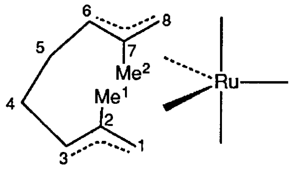
Table 1 Proton NMR data for 2,7-dimethyloctadienediylruthenium(IV) complexes



Complex^{a}	Proton assignment^{b} H^{1}, H^{9} and H^{2}, H^{10c}	H^{3} and H^{8d}	H^{4}, H^{6} and H^{5}, H^{7d}	Me^{1} and Me^{2c}	L
[Ru($C_{10}H_{16}$)Cl_2L]					
2 L = P(OMe)$_3$	4.60,^{e} 3.39^{f}	5.15	3.54, 2.67	2.18^{g}	3.87^{h}
3 L = Bu^{t}NC	4.56, 3.56	5.10	3.49, 2.68	2.22	1.61^{i}
4 L = Pr^{i}NC	4.60, 3.57	5.11	3.50, 2.70	2.23	4.31,^{j} 1.56^{k}
[Ru($C_{10}H_{16}$)ClL$_2$][BF$_4$]					
5 L = P(OMe)$_3$	4.02,^{l} 3.60^{m}	4.13	2.8–2.4	2.39	3.95^{n}
6 L = Bu^{t}NC	4.07, 3.68	5.02	3.20, 2.68	2.64	1.52^{i}
7 L = Pr^{i}NC	4.10, 3.77	5.10	3.22, 2.66	2.65	4.26,^{j} 1.46,^{o} 1.44^{o}
8 L = MeCN^{p}	5.15, 4.91, 4.32, 4.04	5.03, 4.90	3.17,^{q} 2.51^{q}	2.32, 2.31	2.49,^{r} 2.33^{r}
9 L = MeCN^{p}	4.77, 3.95	4.79	3.25, 2.61	2.34	2.33^{r}

[a] In $CDCl_3$ solution at room temperature unless otherwise stated. [b] Chemical shifts in δ. Relative integrations are all consistent with assignment. [c] Singlets. [d] Multiplets. [e] Doublet, J(PH) = 8.6 Hz. [f] Doublet, J(PH) = 3.4 Hz. [g] Doublet, J(PH) = 0.8 Hz. [h] Doublet, J(PH) = 10.3 Hz. [i] Singlet. [j] Septet, ^{3}J = 6.6 Hz, Me$_2$C*H*NC. [k] Doublet, *Me*$_2$CHNC. [l] Triplet, J(PH) = 3.5 Hz. [m] Triplet, J(PH) = 6.6 Hz. [n] Triplet, J(PH) = 4.9 Hz. [o] Doublets, ^{3}J = 6.6 Hz, inequivalent methyls of Pr^{i}NC. [p] In CD_3CN solution. [q] Complex multiplets consistent with four inequivalent protons. [r] Singlets, MeCN, in solutions prepared and recorded at 253 K.

Table 2 Carbon-13 NMR data for 2,7-dimethyloctadienediylruthenium(IV) complexes



Complex^{a}	C^{1}, C^{8b}	C^{2}, C^{7c}	C^{3}, 6^{6d}	C^{4}, C^{5e}	Me^{1}, Me^{2f}	L
[Ru($C_{10}H_{16}$)Cl_2L]						
2	61.3	124.7	110.7^{g}	37.1	20.9	54.4^{h}
3	63.2	125.3	108.4	37.8	20.8	143.5,^{i} 58.7,^{j} 30.6^{k}
4	63.3	125.4	108.5	37.9	20.9	143.8,^{l} 49.8,^{m} 23.5^{n}
[Ru($C_{10}H_{16}$)ClL$_2$][BF$_4$]						
5	70.3	113.9	85.1	32.3	19.1	57.2^{h}
6	73.1	121.2	94.2	38.6	20.4	140.6,^{i} 59.2,^{j} 30.1^{k}
7	73.1	121.5	94.0	38.5	20.4	140.6,^{l} 49.9,^{m} 22.8,^{o}, 22.7^{o}
8^{p}	78.0, 74.7	132.0, 130.2	103.1, 96.7	37.8, 36.8	21.0, 19.9	133.0,^{q} 129.2,^{q} 4.2,^{r} 3.9^{r}
9^{s}	80.6	127.5	99.2	38.5	19.9	128.1,^{q} 4.2^{r}

[a] In $CDCl_3$ solution at room temperature unless otherwise stated. Chemical shifts in δ. [b] All triplets, J(CH) = 160–164 Hz. [c] All singlets. [d] All doublets, J(CH) = 159–164 Hz. [e] All triplets, J(CH) = 128–132 Hz. [f] All quartets, J(CH) = 128–131 Hz. [g] J(PC) = 15 Hz. [h] Quartet, J(CH) = 147 Hz. [i] Singlet Bu^{t}N*C*, [j] Singlet, Me$_3$*C*NC. [k] Quartet, J(CH) = 127 Hz, *Me*$_3$CNC. [l] Singlet, Pr^{i}N*C*. [m] Doublet, J(CH) = 146 Hz, Me$_2$*C*HNC. [n] Quartet, J(CH) = 130 Hz, *Me*$_2$CHNC. [o] Quartets, J(CH) = 130 Hz, inequivalent methyls of Pr^{i}NC. [p] In $(CD_3)_2CO$ solution at 220 K. [q] Quartet, J(CH) = 11 Hz, Me*C*N. [r] Quartet, J(CH) = 138 Hz, *Me*CN. [s] In $(CD_3)_2CO$ solution.

the cation of complex **8** with the hydrogen atoms omitted is shown in Fig. 1. The final positional parameters of the non-hydrogen atoms are given in Table 3, and selected bond lengths and angles with e.s.d.s in Table 4. The allyl groups of the 2,7-dimethyloctadienediyl ligand are both η^3-bound to the ruthenium atom with Ru–C distances in the range 2.233(15)–2.314(15) Å. The dihedral angles between an allyl plane [C(1)C(2)C(3) or C(6)C(7)C(8)] and the plane defined by the ruthenium atom and the outer allyl carbon atoms [C(1)C(3)Ru or C(6)C(8)Ru] are 110.5 and 113.8°, respectively. These values together with the C–C distances (1.41 Å mean) and the internal C–C–C angles (116° mean) within the allyl groups are all within the ranges typical of transition-metal η^3-allyl co-ordination.[15] The methyl substituents C(9) and C(10) both deviate from their respective allyl plane and bend slightly towards the ruthenium atom by 4.2 and 4.7° for the C(2)–C(9) and C(7)–C(10) vectors, respectively.

The co-ordination geometry about ruthenium can be described by considering the allyl groups as monodentate ligands bound to the ruthenium atom through their centres of mass [D(1) for C(1)C(2)C(3) and D(2) for C(6)C(7)C(8)]. It is then a distorted trigonal bipyramid (*TBPY*) with D(1), D(2)

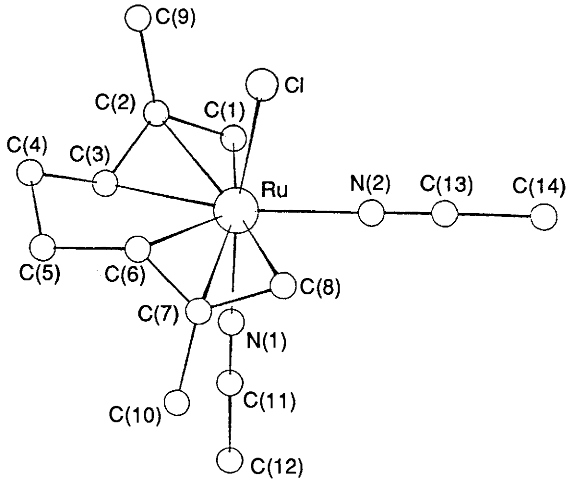


Fig. 1 Molecular structure of the cation in compound **8**

Table 3 Fractional atomic coordinates (× 10^4) for compound **8**

Atom	*x*	*y*	*z*
Ru	1832.4(17)	2022.2(8)	3829.1(18)
Cl	2193(6)	607(3)	2343(6)
N(1)	1739(17)	3199(9)	5322(17)
N(2)	3156(15)	1661(8)	5881(18)
C(1)	−481(19)	1572(11)	5495(20)
C(2)	−1032(18)	1519(8)	3789(23)
C(3)	−766(16)	2288(11)	2959(18)
C(4)	−918(23)	2354(12)	1045(24)
C(5)	742(22)	2862(11)	414(22)
C(6)	2187(22)	2450(11)	1098(22)
C(7)	3610(20)	2893(11)	2073(21)
C(8)	4567(19)	2361(12)	2908(24)
C(9)	−1807(21)	662(10)	2851(25)
C(10)	3909(24)	3861(11)	2404(24)
C(11)	1729(20)	3820(12)	6204(21)
C(12)	1748(26)	4654(10)	7260(25)
C(13)	4027(21)	1435(9)	6840(23)
C(14)	5200(20)	1154(11)	8120(22)
B	3135(30)	6224(15)	2453(36)
F(1)	2373(19)	5741(10)	1144(19)
F(2)	2771(25)	7023(9)	2576(25)
F(3)	2642(29)	5948(11)	3988(21)
F(4)	4809(19)	6243(14)	2252(28)

Table 4 Selected bond lengths (Å) and angles (°) for compound **8***

Ru–Cl	2.417(4)	C(1)–C(2)	1.38(2)
Ru–N(1)	2.064(14)	C(2)–C(3)	1.41(2)
Ru–N(2)	2.085(14)	C(2)–C(9)	1.52(2)
Ru–C(1)	2.244(15)	C(3)–C(4)	1.49(2)
Ru–C(2)	2.279(13)	C(4)–C(5)	1.52(2)
Ru–C(3)	2.264(12)	C(5)–C(6)	1.51(2)
Ru–C(6)	2.255(15)	C(6)–C(7)	1.43(2)
Ru–C(7)	2.314(15)	C(7)–C(8)	1.41(2)
Ru–C(8)	2.233(15)	C(7)–C(10)	1.50(2)
Ru–D(1)	2.014	N(1)–C(11)	1.12(2)
Ru–D(2)	2.014	N(2)–C(13)	1.14(2)
Cl–Ru–N(1)	172.8(4)	D(2)–Ru–Cl	90.1
Cl–Ru–N(2)	86.0(4)	D(2)–Ru–N(1)	91.3
N(1)–Ru–N(2)	87.0(5)	D(2)–Ru–N(2)	111.9
C(1)–Ru–C(3)	63.6(5)	C(1)–C(2)–C(3)	117(1)
C(6)–Ru–C(8)	64.5(6)	C(2)–C(3)–C(4)	126(2)
D(1)–Ru–D(2)	133.5	C(3)–C(4)–C(5)	107(1)
D(1)–Ru–Cl	94.6	C(4)–C(5)–C(6)	105(1)
D(1)–Ru–N(1)	89.5	C(5)–C(6)–C(7)	126(2)
D(1)–Ru–N(2)	114.6	C(6)–C(7)–C(8)	115(2)

* D(1) and D(2) are the centres of mass of the atoms C(1), C(2), C(3) and C(6), C(7), C(8), respectively.

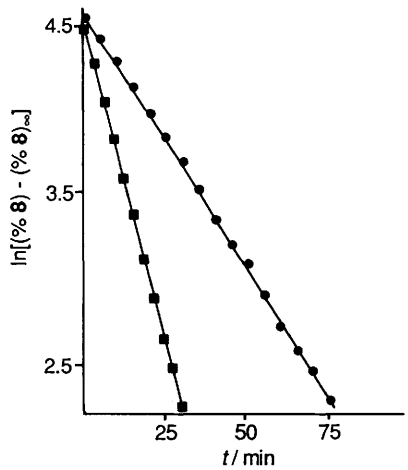
and N(2) in the equatorial sites and Cl and N(1) in the axial sites. The ruthenium atom lies 0.020 Å out of the equatorial plane defined by D(1)D(2)N(2) on the same side as the chlorine atom. The largest angular deviation from an idealised *TBPY* co-ordination is the D(1)–Ru–D(2) angle of 133.5°, which is the effective bite angle of the $\eta^3:\eta^3$-2,7-dimethyloctadienediyl ligand. The two acetonitrile ligands are both linear with Ru–N–C and N–C–C angles > 170°, and although the equatorial Ru–N(2) distance [2.085(14) Å] is slightly longer than the axial Ru–N(1) distance [2.064(14) Å] the difference is not statistically significant ($< 2\sigma$).

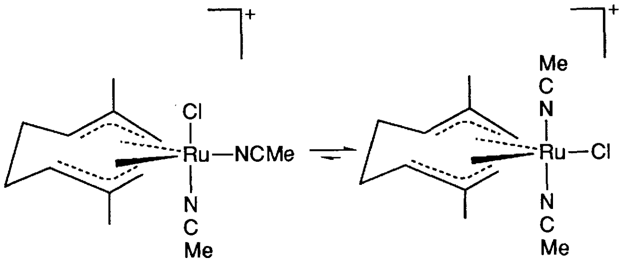
The main configurational features of the $\eta^3:\eta^3$-2,7-dimethyloctadienediyl ligand are *syn* substitution of both allyl groups by the ethylene chain, and an approximate local C_2 symmetry. They are therefore qualitatively similar to those previously established for complex **1**,[5] and to those proposed for **2**–**7**. A quantitative comparison of the Ru($\eta^3:\eta^3$-$C_{10}H_{16}$) fragments common to **1** and **8**, however, reveals two noteworthy differences: (*i*) the bite angle of the organic ligand, D(1)–Ru–D(2) as defined above, is greater in **8** (133.5°) than in **1** (118.5°); (*ii*) the Ru–C (central allyl) distances are significantly longer in **8** (mean 2.30 Å) than in **1** (mean 2.235 Å), with $\sigma \sim 0.02$ Å, although the Ru–C (outer allyl) distances are similar (mean 2.25 for **8**, 2.25 Å for **1**). These differences are reflected in major variations in the three central torsion angles for the two octadienediyl chains, and relevant torsion angles for **8**, with corresponding values for **1** in parentheses, are: C(1)–C(2)–C(3)–C(4) +166.9 (+171.9), C(2)–C(3)–C(4)–C(5) −128.2 (−62.3), C(3)–C(4)–C(5)–C(6) +48.7 (−27.3), C(4)–C(5)–C(6)–C(7) −129.0 (−65.8) and C(5)–C(6)–C(7)–C(8) +166.1 (+173.0°). Although the origin of these differences is unclear, their existence demonstrates that there remains a degree of flexibility in the bonding requirements of an $\eta^3:\eta^3$-octadienediyl chain even within the constraints of a configuration involving *syn* substitution of the allyl groups and a local C_2 symmetry.

Formation and Stereoisomerisation of Complex **8**.—Upon dissolution of complex **1** in acetonitrile we have previously established that solvolysis occurs to give initially an equatorial solvate [Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)Cl_2(NCMe)] similar in structure to **2**–**4**. Rapid isomerisation to an axial solvate then occurs, and an equilibrium is established between the equatorially and axially solvated stereoisomers. Thermodynamic and kinetic parameters for this equilibrium were reported: $K_{298} = 11$, $\Delta H^\ominus = -19 \pm 1$ kJ mol^{-1}, k_{298}(forward) = $(4.6 \pm 0.9) \times 10^{-2}$ s^{-1}; $\Delta H^\ddagger = 98 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = 57 \pm 15$ J K^{-1} mol^{-1}.[7]

The kinetic product of the reaction of an acetonitrile solution of complex **1** with silver(I) tetrafluoroborate is now known to be **8**. For the two neutral acetonitrile solvates, however, nothing is known regarding their relative reactivities toward silver(I) ion, and hence there is insufficient information to deduce the reasons for the regioselective formation of **8**.

The stereoisomerisation of complex **8** to **9** has been followed by ^1H NMR spectroscopy in CD_3CN and $(CD_3)_2CO$ solutions, as described in the Experimental section. The isomerisation does not proceed to completion in either solvent, and a value for the equilibrium constant of $K_{298} = 30 \pm 5$ was estimated. Accurate measurements of the temperature dependence of *K* were not feasible. Representative plots of ln[(% **8**) − (% **8** at equilibrium)] *vs.* time for over three half-lives of the isomerisation at 324.8 K, in CD_3CN and $(CD_3)_2CO$ solutions, are shown in Fig. 2. Similar plots were obtained at other temperatures within the range 295–335 K. Their linearity demonstrates first-order behaviour in the concentrations of **8**





8 **9**

Fig. 2 First-order plots of the stereoisomerisation of complex **8** in acetonitrile(●) and acetone (■) solutions at 324.8 K

and **9**, and the negative slope of the plots gives the sum of the rate constants for the forward and reverse isomerisations. Eyring plots of the observed rate constants for the formation of complex **9** from **8** yielded the following activation parameters: (*i*) in CD_3CN solution, $k_{298} = (7.6 \pm 0.6) \times 10^{-6}\ s^{-1}$, $\Delta H^{\ddagger} = 123 \pm 3\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = 68 \pm 9\ J\ K^{-1}\ mol^{-1}$; (*ii*) in $(CD_3)_2CO$ solution, $k_{298} = (2.4 \pm 0.4) \times 10^{-5}\ s^{-1}$, $\Delta H^{\ddagger} = 118 \pm 8\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = 63 \pm 25\ J\ K^{-1}\ mol^{-1}$. The results suggest that the stereoisomerisation of **8** follows a similar pathway in the two solvents, with the difference in rates due either to differing solvation effects or to a slight retardation of the reaction by free acetonitrile. Compared to the related stereoisomerisation of the neutral equatorial solvate $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NCMe)]$,[7] the rate of isomerisation of **8** in acetonitrile solution is slower by a factor of more than 5×10^3, and we believe this is due chiefly to stronger Ru–N interactions in the cationic species. Evidence that the mechanism of the stereoisomerisation involves acetonitrile dissociation will be presented in a future article where the kinetics of the acetonitrile solvent exchanges in complexes **8**, **9** and a related dication will be discussed.

Conclusions

The salts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})ClL_2][BF_4]$ [L = $P(OMe)_3$, Bu^tNC, Pr^iNC or MeCN] are produced in high yields by reaction of the neutral complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ with silver(I) tetrafluoroborate and free ligand L, and their existence suggests that a more extensive co-ordination chemistry based on the $Ru^{IV}(\eta^3:\eta^3\text{-}C_{10}H_{16})$ fragment may be accessible. Such complexes are representative of a potentially larger class of $[Ru^{IV}(\eta^3\text{-allyl})_2]$ derivatives, but unfortunately there is no known synthetic route to complexes containing such moieties where the allyl groups are mutually independent. Hence, it is not at present possible to assess the degree to which the complexes described here are stabilised by the presence of the ethylene chain linking the allyl groups.

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