Ruthenium-mediated cyclodimerisation of buta-1,3-diene

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Treatment of solvated Ru^{2+} ions in acetone solution with a large excess of buta-1,3-diene results in the formation of the unusual cyclooctatriene/cyclooctadienyl complex $[Ru(\eta^6\text{-}C_8H_{10})(1\text{-}3:5\text{-}6\text{-}\eta\text{-}C_8H_{11})]^+$ 1 derived from the cyclodimerisation and dehydrogenation of two pairs of butadiene molecules at the metal centre.

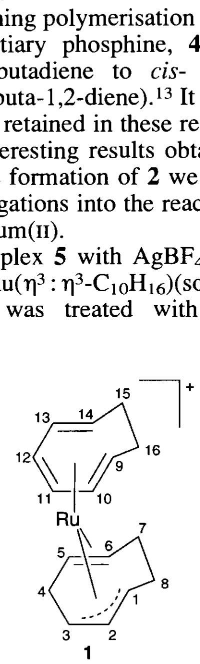
The metal-mediated oligomerisation and polymerisation of alkenes such as buta-1,3-diene and its derivatives is a process of considerable importance both from the perspective of formation of new cyclic alkenes and in the synthesis of polymers with useful mechanical properties.[1–4] Reaction of the cyclododecatriene (cdt) complex $[Ni(\eta^2:\eta^2:\eta^2\text{-}C_{12}H_{18})]$ **2** (or any other source of 'naked' nickel) with butadiene at 20 °C results in the formation of free cdt in proportion to the amount of butadiene added.[1] At −40 °C the intermediate bis(allyl)nickel(II) species $[Ni(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})]$ **3** may be isolated. Addition of butadiene in the presence of donors such as PPh_3 or tris(2-biphenyl)phosphite allows only two butadiene molecules to coordinate to the metal centre, which couple to give cyclooctadiene with up to 95% selectivity.[1]

Treatment of ruthenium trichloride hydrate with buta-1,3-diene in refluxing 2-ethoxyethanol results in trimerisation of butadiene to give the bis(allyl)ruthenium(IV) compound $[Ru(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})Cl_2]$ **4**.[5,6] Unlike **3**, **4** is stable and does not release free cdt under comparable conditions. Similarly, reaction of '$RuCl_3{\cdot}xH_2O$' with isoprene (2-methylbutadiene) in ethanol at 70 °C[7] results in the ruthenium(IV) complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **5**, arising from dimerisation of the diene.

Both **4** and **5** have an extensive chemistry[8,9] and have been examined as catalysts for a number of alkene polymerisations, notably the ring-opening polymerisation of norbornene.[10–12] In the presence of tertiary phosphine, **4** and **5** catalyse the polymerisation of butadiene to *cis*- and *trans*-poly(buta-1,4-diene) and poly(buta-1,2-diene).[13] It is unclear whether the bis(allyl) ligands are retained in these reactions.

In view of the interesting results obtained from the use of 'naked' nickel in the formation of **2** we now report the initial results of our investigations into the reaction of buta-1,3-diene with 'naked' ruthenium(II).

Treatment of complex **5** with $AgBF_4$ in acetone gives the labile complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(solv)_3][BF_4]_2$.[9,14] This solvated precursor was treated with a large excess of buta-1,3-diene in acetone in a sealed vessel at *ca.* 80 °C for 12 h resulting in the deposition of a yellow precipitate analysing for $C_{16}H_{21}RuBF_4$ (**1**) in 56% yield (FABMS, *m/z* 315, $C_{16}H_{21}Ru^+$). The ionic nature of the product was confirmed by anion metathesis with $NaBPh_4$. At room temperature in both $(CD_3)_2CO$ and CD_3NO_2 solution the ^1H NMR spectrum was broad, as were four resonances in the high-field region of the $^{13}C\{^1H\}$ spectrum. Sharp spectra† were obtained at −90 °C in $(CD_3)_2CO$ and +80 °C in CD_3NO_2. Surprisingly, given the structures of **4** and **5**, examination of the proton-coupled ^{13}C NMR spectrum at +70 °C gave no evidence for terminal alkenic or allylic functionalities.



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Homonuclear ^1H NMR decoupling experiments revealed the presence of two independent hydrocarbon ligands attached to the metal centre, suggesting a structure involving two different eight-membered carbocyclic rings, *viz.* $[Ru(\eta^6\text{-}C_8H_{10})(\eta^5\text{-}C_8H_{11})]BF_4$. Comparison with data on cyclooctatriene (cot) and cyclooctadienyl species in the literature[4,15] confirmed this formulation and revealed the cyclooctadienyl ligand to be in the 1-3:5-6-η form. Surprisingly, the ^1H NMR spectrum of **1**, recorded at −90 °C, exhibits an extremely high field signal at δ −0.90 suggestive of an agostic interaction, although no reduced $^1J_{CH}$ was observed in the ^{13}C NMR spectrum of the complex. Decoupling experiments indicated that this signal was associated with the cyclooctatriene ligand and it seems likely that the unusual chemical shift of this signal is associated with the conformation of the cot moiety, which may result in an *exo* proton of one of the $-CH_2-$ groups being situated within the shielding region of the alkenic functionalities. High-field resonances have been observed in related cot species {[Ru(cot)(cod)][16] (cod = cycloocta-1,5-diene), δ 0.90, $[RuH(cot)(cod)]BF_4$, δ 0.37[17] and $[Ru(cot)(\eta^4\text{-}C_5H_8)]$[18], δ 0.78, although the chemical shift in the present example is extreme. On warming the sample this resonance moves to lower field such that at +80 °C in CD_3NO_2 it occurs at δ +0.31 suggesting that the fluxionality of the molecule is connected with a conformational change of the methylene groups. This suggestion is supported by the broadness of four of the resonances assigned to methylene groups in the room-temperature $^{13}C\{^1H\}$ NMR spectrum. Interestingly, the only resonances in the ^1H NMR spectra which remain *unchanged* with temperature are those corresponding to the protons at C^5 on the cyclooctadienyl ligand, consistent with the sharp methylene signal at δ 20.8 in the room-temperature $^{13}C\{^1H\}$ NMR spectrum. This region is a long way from the flexible portions of the molecule and might be expected to be relatively unaffected by any conformational inversion. The possibility of different conformations for the cot ligand has been suggested previously.[17]

Complex **1** proved difficult to crystallise, but its formulation was finally confirmed by a single-crystal X-ray structure determination.‡ Unfortunately the molecule was found to crystallise in the acentric orthorhombic space group $Cmc2_1$ and both the cation and tetrafluoroborate anion were severely disordered across the crystallographic mirror plane, resulting in a poor refinement. The disorder was modelled successfully, however, and a view of the molecule is presented in Fig. 1. As anticipated, the 1-3:5-6-η-C_8H_{11} ligand is bound in a similar

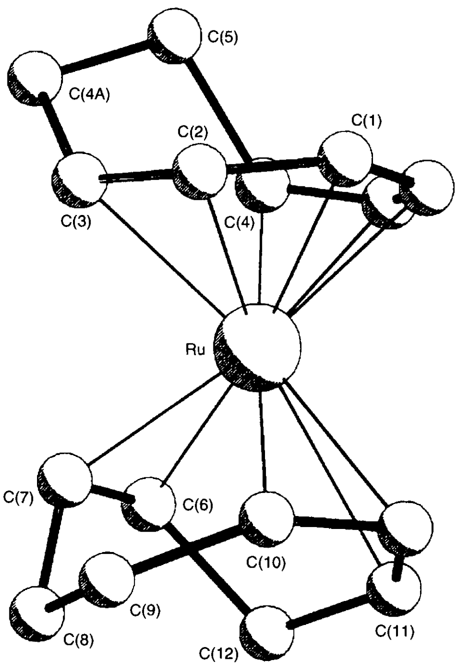

Fig. 1 X-Ray crystal structure of the cation in **1** showing the atom labelling scheme adopted

fashion to that observed crystallographically in [Ru(η^6-$C_6H_5BX_3$)(1-3 : 5-6-η-C_8H_{11})] (X = Ph **6a**, F **6b**).[19] In particular the Ru–C(11) bond length is long, 2.56(3) Å, compared with values of *ca.* 2.2 Å to the remaining carbon atoms, indicating the allylic functionality in the cyclooctadienyl ligand to be asymmetrically bound. This phenomenon was noted for **6a**, though not for **6b**.[19]

The mechanism of formation of complex **1** may well involve the intramolecular cyclisation of two pairs of butadiene ligands which should result in an intermediate with two cyclooctadiene ligands. The mechanism by which this species dehydrogenates in order to form cot and cyclooctadienyl moieties is unclear, but may involve hydrido intermediates. Similar dehydrogenations have been observed for cod in [Ru(cod)(N_2H_4)$_4$][BPh_4]$_2$[19] and for cyclohexadiene in the formation of [{Ru(η^6-C_6H_6)Cl(μ-Cl)}$_2$].[20]

In summary, the use of the readily prepared intermediate **5** provides a simple new route into cyclooctatriene chemistry of ruthenium(II). In addition, new insight has been gained into the mechanism of alkene oligomerisation and dehydrogenation at transition-metal centres. While the goal of cyclotetramerisation of butadiene has not yet been realised in this system, the simultaneous coordination of four butadiene units offers scope for the formation of other interesting hydrocarbon species.

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Footnotes

† ^1H NMR data [−90 °C, $(CD_3)_2CO$, 400 MHz, J_{HH}/Hz]: δ 6.64 (t, 1 H, *J* 6.2, H^{10}), 6.56 (d, 1 H, *J* 10.0, H^{14}), 6.10 (m, 2 H, H^{11}, H^{13}), 5.82 (t, 1 H, *J* 8.3, H^{12}), 5.68 (dd, 1 H, *J* 6.1, 8.7, H^6), 4.69 (pseudo q, 1 H, H^9), 4.37 (pseudo q, 1 H, H^1), 3.98 (m, 1 H, H^3), 3.85 (t, 1 H, *J* 6.9, H^2), 3.43 (pseudo q, 1 H, H^5), 3.16 (m, 1 H, *endo*-H^{15}), 3.06 (m, 1 H, H^4), 2.71 (m, 3 H, *exo*-H^{15}, $H^{4'}$, *endo*-H^7), 2.48 (dd, 1 H, *J* 6.2, 14.5, *exo*-H^7), 1.68 (m, 1 H, H^8), 1.43 (m, 1 H, $H^{8'}$), 1.24 (m, 1 H, *endo*-H^{16}), −0.90 (pseudo q, 1 H, *exo*-H^{16}). ^{13}C NMR data [70 °C, (CD_3NO_2), 100.6 MHz, $^1J_{CH}$/Hz]: δ 101.6 (d, *J* 166), 100.5 (d, *J* 168), 98.2 (d, *J* 169), 97.3 (d, *J* 161), 96.9 (d, *J* 164), 96.0 (d, *J* 162), 95.5 (d, *J* 168), 89.2 (d, *J* 163), 80.9 (d, *J* 158), 46.0 (d, *J* 165), 42.1 (d, *J* 166), 37.2 (t, *J* 133), 35.8 (t, *J* 133), 29.3 (t, *J* 131), 28.6 (t, *J* 131), 20.8 (t, *J* 135).

‡ *Crystal data* for $C_{16}H_{21}BF_4Ru$ **1**: M_w 401.21, pale yellow plate, orthorhombic, space group *Cmc*2$_1$, a = 10.5695(6), b = 13.3274(6), c = 10.5234(6) Å, U = 1482.37(14) Å^3, Z = 4, D_c = 1.80 g cm^{-3}, μ = 10.93 cm^{-1}. Of 2836 reflections collected on a Siemens SMART diffractometer (Mo-Kα, λ = 0.71073 Å, 2θ 5–47° at −100 °C) 1020 were independent and were used in the refinement according to the SHELXL-93 method. Data were corrected for Lorentz, polarisation and absorption effects (pseudo ψ-scan method). The structure was solved using the direct methods option of SHELXS-86 and refined using alternating least-squares and difference Fourier techniques. Both cation and anion were found to be disordered across a crystallographic mirror plane and were modelled using 50% occupancy for C(4), C(4A), C(7–9), C(11–12) as well as atoms situated on the mirror plane and fluorine atoms. Hydrogen atoms were not included because of the difficulty in predicting their positions. Final refinement converged to wR_2 = 0.216 which corresponds to a conventional R factor, R_1, based upon 991 data with $I > 2\sigma(I)$ of 0.088. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/128.

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