# Ruthenium Complex-catalysed Dimerization of Norbornadiene to Pentacyclotetradecadiene

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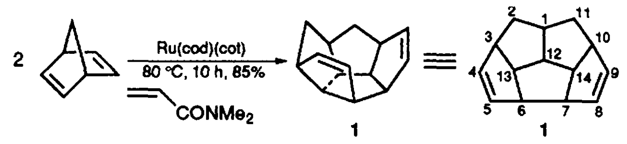
[Ru(cod)(cot)] catalyses an unusual dimerization of norbornadiene to give pentacyclo[$5.4.2^{1,7}.1^{3,6}.0^{10,13}.0^{12,14}$]tetradeca-4,8-diene in high yield (85%) with high selectivity, the structure of which is established by X-ray analysis of its brominated derivative, pentacyclo[$5.4.2^{1,7}.1^{3,6}.0^{10,13}.0^{12,14}$]-4,5,8,9-tetrabromotetradecane, to have five five-membered rings as a result of multi-carbon–carbon bond activation.

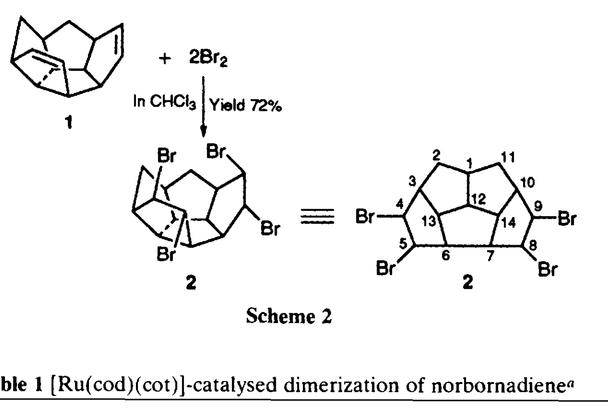
Activation of carbon–carbon bonds by ruthenium complexes under mild conditions has received much attention.[1,2] We now report the dimerization of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) to pentacyclotetradecadiene, catalysed by Ru(cycloocta-1,5-diene)(cycloocta-1,3,5-triene) [Ru(cod)(cot)], Scheme 1. This reaction should involve multi-carbon–carbon bond activation.

[Ru(cod)(cot)][3,4] (0.031 g, 0.10 mmol), norbornadiene (0.46 g, 5.0 mmol), *N,N*-dimethylacrylamide (0.10 ml, 1.0 mmol), *N*-methylpiperidine (0.30 ml) were placed in a heavy-walled glass ampoule under an argon atmosphere. The mixture was stirred at 80 °C for 10 h. Double Kugelrohr distillation of the reaction mixture gave 0.39g (yield 85%) of pentacyclo[$5.4.2^{1,7}.1^{3,6}.0^{10,13}.0^{12,14}$]tetradeca-4,8-diene **1** as colourless crystals.

The yield of the product **1** was very sensitive to reaction conditions, see Table 1. The presence of *N,N*-dimethylacrylamide was crucial. Acrylamide may work as a key ligand controlling the electronic conditions of the ruthenium complex. Above 80 °C, acrylamide dimerized and the dimer was found to contaminate the product **1**. Below 80 °C the reaction was very slow, and at room temp. did not occur. Under the present reaction conditions, a palladium complex such as $Pd(PPh_3)_4$ or a rhodium complex such as $RhCl(PPh_3)_3$ showed no catalytic activity.



Scheme 1



Scheme 2

The structure of **1** was inferred from analytical and spectral data† [IR, mass, $^1H$ (300 MHz) and $^{13}C$ NMR, $^1H$–$^1H$ COSY, $^1H$–$^{13}C$ COSY and DEPT] and confirmed by an X-ray analysis‡ of the brominated derivative **2**. Compound **1** reacted with 2 mol of $Br_2$ in $CHCl_3$ at room temp. to give **2**,§ Scheme

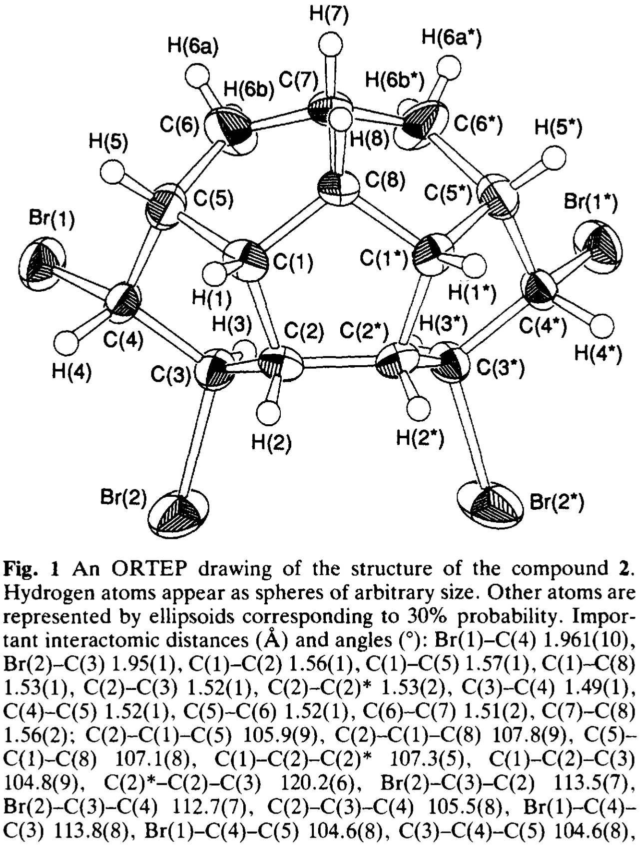


**Fig. 1** An ORTEP drawing of the structure of the compound **2**. Hydrogen atoms appear as spheres of arbitrary size. Other atoms are represented by ellipsoids corresponding to 30% probability. Important interactomic distances (Å) and angles (°): Br(1)–C(4) 1.961(10), Br(2)–C(3) 1.95(1), C(1)–C(2) 1.56(1), C(1)–C(5) 1.57(1), C(1)–C(8) 1.53(1), C(2)–C(3) 1.52(1), C(2)–C(2)* 1.53(2), C(3)–C(4) 1.49(1), C(4)–C(5) 1.52(1), C(5)–C(6) 1.52(1), C(6)–C(7) 1.51(2), C(7)–C(8) 1.56(2); C(2)–C(1)–C(5) 105.9(9), C(2)–C(1)–C(8) 107.8(9), C(5)–C(1)–C(8) 107.1(8), C(1)–C(2)–C(2)* 107.3(5), C(1)–C(2)–C(3) 104.8(9), C(2)*–C(2)–C(3) 120.2(6), Br(2)–C(3)–C(2) 113.5(7), Br(2)–C(3)–C(4) 112.7(7), C(2)–C(3)–C(4) 105.5(8), Br(1)–C(4)–C(3) 113.8(8), Br(1)–C(4)–C(5) 104.6(8), C(3)–C(4)–C(5) 104.6(8), C(1)–C(5)–C(4) 100.7(8), C(1)–C(5)–C(6) 105.0(8), C(4)–C(5)–C(6) 116(1), C(5)–C(6)–C(7) 109(1), C(6)–C(7)–C(6)* 111(1), C(6)–C(7)–C(8) 107.3(8), C(1)–C(8)–C(1)* 107(1), C(1)–C(8)–C(7) 106.8(8).

Table 1 [Ru(cod)(cot)]-catalysed dimerization of norbornadiene[a]

| Run | Norbornadiene /mmol | *N*-methyl-piperidine /mmol | *N,N*-dimethyl-acrylamide /mmol | *T*/°C | *t*/h | Yield of **1** (%) |
|---|---|---|---|---|---|---|
| 1 | 5.0 | 2.5 | 1.0 | 80 | 10 | 85 |
| 2 | 5.0 | 2.5 | 1.0 | 70 | 20 | 57 |
| 3 | 5.0 | 2.5 | 2.5 | 25 | 11 | Trace |
| 4 | 2.5 | 2.5 | 0.25 | 80 | 8 | 30 |
| 5 | 2.5 | 2.5 | 0 | 80 | 8 | 0 |
| 6[b] | 5.0 | 0 | 7.5 | 80 | 4 | 84 |

[a] [Ru(cod)(cot)] 0.1 mmol. [b] Dimers of *N,N*-dimethylacrylamide are also formed.

2, crystals of which separated trom the $CHCl_3$ solution. Analytical data showed that four bromine atoms were introduced and all spectral data showed that only the olefinic carbons in **1** were brominated. The molecular structure of **2** is shown in Fig. 1. The bromination reaction involved a *trans* addition and only one isomer was isolated. The bromine atoms at C-5 and C-8 were *exo* oriented avoiding steric hindrance.

The X-ray result confirmed the inferred structure; the product **1** has a plane of symmetry ($C_s$) and has five five-membered rings. The structure cannot be constructed to result from a simple dimerization. The mechanism of the formation of **1** from norbornadiene catalysed by a ruthenium complex is very interesting, though it is not clear at the present time how it occurs. It is obvious that this reaction involves repeated activation of one or more carbon–carbon bonds. Various dimerizations of norbornadiene catalysed by metal complexes such as iron,[5] cobalt,[6] nickel,[7] rhodium,[8] and molybdenum[9] complexes have been reported. The present dimerization of norbornadiene, however, is quite different. It seems that the structure of norbornadiene could have initially decomposed to smaller molecules such as $C_5$ and $C_2$ moieties.¶ Further carbon–carbon activation and reconstruction of the skeleton could subsequently take place. Compound **1** may be used as an unusual monomer and a precursor for the synthesis of cage compounds such as dodecahedrane.[10]

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## Footnotes

† *Data* for **1**: mp 102–104 °C; IR (KBr) ν/cm$^{-1}$: 3043, 2934, 2902, 1451, 1349, 848, 723; $^1$H NMR (270 MHz, $CDCl_3$) δ 1.43 (dt, 2H, *J* 13.2 and 5.4 Hz), 1.75 (dt, 2H, *J* 13.2 and 8.4 Hz), 2.57 (qt, 1H, *J* 8.8 Hz and 5.9 Hz), 2.89 (m, 1H), 3.05 (m, 2H), 3.35 (m, 4H), 5.34 (d, 2H, *J* 5.6 Hz), 5.51 (dd, 2H, *J* 5.6 and 2.2 Hz); $^{13}$C NMR ($CDCl_3$) δ 36.8 ($CH_2$ × 2), 48.2 (*C*H), 52.2 (*C*H × 2), 55.5 (*C*H), 56.6 (*C*H × 2), 58.0 (*C*H × 2), 129.9 (*C*H= × 2), 134.5 (*C*H= × 2); MS (*m/z*) 184 (M$^+$). Compound **1** is air sensitive. Both the carbon and hydrogen content decreased in 1 h.

‡ Crystals of **2** belong to the orthorhombic space group *Pnma* with $a$ = 14.183(4), $b$ = 16.477(4), $c$ = 6.387(4) Å, $V$ = 1492(1) Å$^3$, $D_c$ = 2.242 g cm$^{-3}$, and $Z$ = 4. Data were collected at 18 °C, and the structure was solved by direct methods and refined to $R = 0.045$, $R_w = 0.034$ for 729 reflections with $I > 3.00\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The reaction procedure is as follows. To a chloroform solution (1 ml) of the product **1** (0.18 g, 1 mmol), stirred magnetically in a 20 ml flask, was added dropwise a solution of bromine (0.48 g, 3.00 mmol) in chloroform (3.00 ml) until the liquid stayed brown. After stirring for 30 min, white crystals precipitated out from the reaction mixture. The crystals were collected by filtration and were washed with cold $CHCl_3$ and dried *in vacuo* to give 0.36 g (72%) of colourless crystals.

*Data* for **2**: mp 232–234 °C; IR (KBr) ν/cm$^{-1}$: 2963, 2939, 1456, 1312, 1285, 1229, 1202, 1183, 1165, 762, 743, 708; $^1$H NMR (270 MHz, $CDCl_3$) δ 1.59 (dt, 2H, *J* 15.0 and 7.0 Hz), 2.20 (dt, 2H, *J* 15.0 and 9.9 Hz), 2.71 (qt, 1H, *J* 9.9 and 7.0 Hz), 2.90 (m, 2H), 3.18 (m, 4H), 3.25 (m, 1H), 4.24 (dm, 2H, *J* 9.9 Hz), 4.38 (dd, 2H, *J* 9.9 and 6.2 Hz); $^{13}$C NMR ($CDCl_3$) δ 37.5 ($CH_2$ × 2), 45.5 (CH), 52.4 (CH × 2), 54.6 (CHBr × 2), 55.5 (CH × 2), 57.4 (CH × 2), 59.3 (CH), 61.1 (CHBr × 2).

¶ Decomposition of norbornadiene into $C_5$ and $C_2$ moieties catalysed by a ruthenium complex was observed in the reaction of norbornadiene with terminal acetylenes. T. Mitsudo, H. Naruse, T. Kondo and Y. Watanabe, unpublished results.

## References

1 R. Carreno, B. Chaudret, D. Labroue and S. Sabo-Etienne, *Organometallics*, 1993, **12**, 13.
2 K. Masuda, H. Ohkita, S. Kurumatani and K. Itoh, *Organometallics*, 1993, **12**, 2221.
3 (*a*) P. Pertici, G. Vitulli and L. Porri, *J. Chem. Soc., Chem. Commun.*, 1975, 846; *Inorg. Synth.*, 1983, **22**, 178; (*b*) K. Itoh, H. Nagashima, T. Ohshima and H. Nishiyama, *J. Organomet. Chem.*, 1984, **272**, 179.
4 For a review: T. Mitsudo, Y. Hori and Y. Watanabe, *J. Organomet. Chem.*, 1987, **334**, 157.
5 (*a*) P. W. Jolly, F. G. A. Stone and K. Mackenzie, *J. Chem. Soc.*, 1965, 6416; (*b*) A. P. Marchand and B. R. Hayes, *Tetrahedron Lett.*, 1977, 1027; (*c*) A. P. Marchand and A. D. Earlywine, *J. Org. Chem.*, 1984, **49**, 1660.
6 (*a*) H. Kanai, Y. Watabe and T. Nakayama, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1277; (*b*) M. Ennis and A. R. Manning, *J. Organomet. Chem.*, 1976, **116**, C31; 1979, **166**, C18.
7 D. R. Arnold, D. J. Treckor and E. B. Whipple, *J. Am. Chem. Soc.*, 1965, **87**, 2596.
8 N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier and I. C. Paul, *J. Am. Chem. Soc.*, 1972, **94**, 5546.
9 T. J. Chow, Y.-S. Chao and L.-K. Liu, *J. Am. Chem. Soc.*, 1987, **109**, 797.
10 P. E. Eaton and R. H. Mueller, *J. Am. Chem. Soc.*, 1972, **94**, 1014.