Reaction of Bicyclo[*n*.1.0]alkanes (*n* = 3—6) with the Olefin-metathesis Catalysts Tungsten Hexachloride–Tetraphenyltin and Tungsten Hexachloride–Ethylaluminium Dichloride

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The title reaction does not yield the products of a retro-carbene addition reaction. The main products of the reaction of bicyclo[6.1.0]nonane with these catalysts are methylenecyclo-octane and methylcyclo-octenes.

THE olefin-metathesis catalysts, phenyltungsten trichloride ($WPhCl_3$)–aluminium chloride ($AlCl_3$) and $WPhCl_3$–ethylaluminium dichloride ($AlEtCl_2$), were reported to abstract methylene from alkylcyclopropanes.[1] For example, the conversion of bicyclo[2.1.0]pentane into cyclobutene was catalysed by $WPhCl_3$–$AlEtCl_2$.[1,2]

Here we present the results of a study of the reaction of bicyclo[*n*.1.0]alkanes (*n* = 3—6) with the olefin-metathesis catalysts, tungsten hexachloride (WCl_6)–tetraphenyltin ($SnPh_4$) (A) and WCl_6–$AlEtCl_2$ (B), which suggest that the retro-carbene addition reaction is by no means general for all metathesis catalysts.

RESULTS

Reaction of Bicyclo[n.1.0]*alkanes* (n = 3–6) *with Catalysts* (*A*) *or* (*B*).—No product was observed in the reactions with bicyclo[3.1.0]hexane or bicyclo[4.1.0]heptane. Treatment of bicyclo[5.1.0]octane with (A) in benzene gave two products, (1) and (2), of molecular weight (*m*/*e*) 110 by gas chromatography–mass spectrometry (g.c.–m.s.). Treatment of bicyclo[6.1.0]nonane with (A) or (B) yielded four products, (3)—(6), of molecular weight (*m*/*e*) 124 by g.c.–m.s. Plots of the extent of conversion *vs.* reaction time and of the variations of the concentrations of reactants and products with reaction time are shown in Figures 1—4.

Identification of (3)—(6).—The relative retention times of (3)—(6) do not correspond to those of nona-1,8-diene, cyclo-octene, or cyclononene. By preparative g.c. of a fraction (b.p. 80—155 °C) of the product of reaction of bicyclo-[6.1.0]nonane, two mixtures of compounds were isolated, of (4) and (5) and of (3)—(5). From their ^1H n.m.r. spectra,

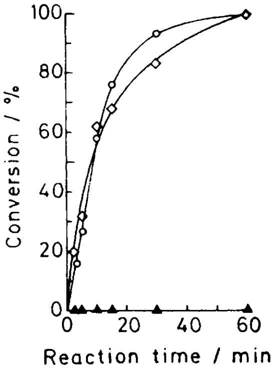


FIGURE 1 Plots of percentage conversion of bicyclo[*n*.1.0]-alkanes against time of reaction with (A). *n* = 3 or 4 (▲), 5 (◇), or 6 (○)

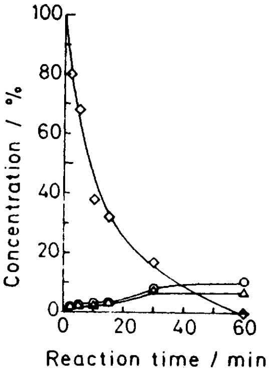


FIGURE 2 Plots of concentration against time of reaction of bicyclo[5.1.0]octane (◇) with (A). Products: (○), (1); (△), (2)

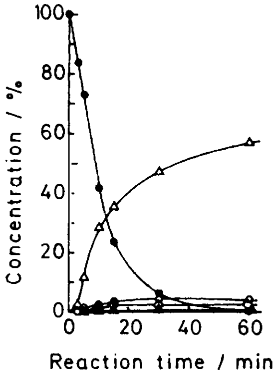


FIGURE 3 Plots as in Figure 2 for bicyclo[6.1.0]nonane (●). Products: (◇), (3); (○), (4); (△), (5); and (▲), (6)

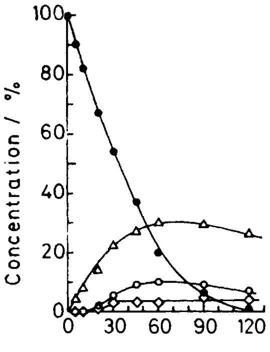


FIGURE 4 Plots as in Figure 2 for reaction of bicyclo[6.1.0]-nonane (●) with (B); WCl_6 : $AlEtCl_2$ = 1 : 2 and bicyclononane : WCl_6 = 50 : 1. Products: (◇), (3) and (6); (○), (4); and (△), (5)

the mixtures were identified as 1-methyl- and 4(or 5)-methylcyclo-octene and 1-methyl-, 3-methyl-, and 4(or 5)-methyl-cyclo-octene, respectively.

DISCUSSION

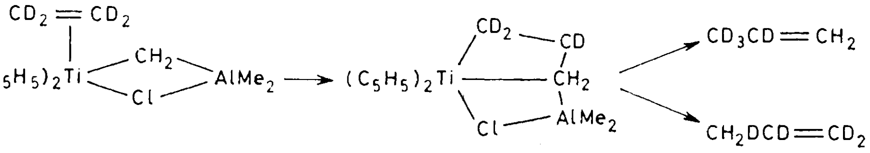
Several transition-metal complexes are known to undergo metal-insertion reactions in the carbon–carbon bonds of cyclopropane. Although the reaction of $[\{Pt(C_2H_4)Cl_2\}_2]$ with cyclopropanes gives various platinacyclobutanes,[3] with bicyclo[4.1.0]heptane the corresponding platinacyclobutane was not obtained, only a platinum complex which gives on decomposition methylenecyclohexane, 1-methylcyclohexene, and cycloheptene.[3] Similar isomerization of cyclopropanes to alkenes having the same number of carbon atoms as those in the starting material occurs in the reactions of cyclopropanes with complexes of Ir,[4] Rh,[5] or Pd.[6]

Although the decomposition of a metallacyclobutane into a metallocarbene complex and alkene is the key step in olefin metathesis, many metallacyclobutanes split in a different way. For example, the decomposition of tantalacyclobutane gives an alkene with the same number of carbon atoms as the initial trimethylene moiety.[7] Similarly, the possibility of the decomposition of a platinacyclobutane to a metallocarbene complex and alkene whose number of carbon atoms is one less than that of the initial trimethylene moiety has been eliminated,[8,9] although the rearrangements of platinacyclobutanes are best interpreted in terms of metallocarbene complex intermediates.[9] While the photochemical decomposition of some tungstenacyclobutanes gives metallocarbene complexes and alkenes whose numbers of carbon atoms are one less than that of the initial trimethylene moieties, the corresponding thermal decomposition does not give the same products.[10]

Relative retention times and g.c.–m.s. data of products (1)—(6)

Reactant	Product	Relative retention time [a]	G.c.–m.s. analysis (m/e) [b] Parent ion	Fragment ion
Bicyclo[5.1.0]octane	(1)	1.28	110(84)	95(79), 81(100), 67(80), 54(80)
	(2)	1.38	110(50)	95(36), 81(100), 67(47), 54(47)
	(3)	1.49	124	109, 96, 95, 82, 81, 68, 67, 56, 55
	(4)	1.56	124(56)	109(10), 96(52), 82(33), 81(41), 68(31), 67(41), 55(30), 54(22)
Bicyclo[6.1.0]nonane	(5)	1.64	124	109, 96, 95, 82, 81, 68, 67, 56, 54
	(6)	1.69	124	109, 96, 95, 82, 70, 69, 68, 67, 56, 55, 54

[a] Benzene, 1.0. [b] Values in parentheses are relative abundances.



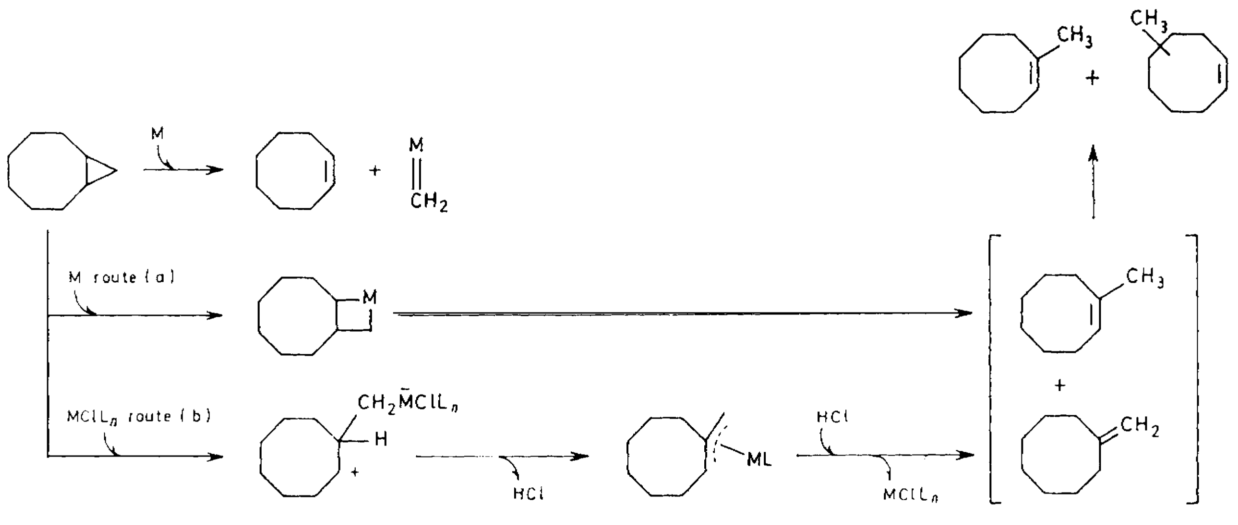
SCHEME 1

The retro-carbene addition reaction is assumed to proceed through the formation of a tungstenacyclobutane, by the reaction of cyclopropane with tungsten catalyst, followed by its decomposition into a metallocarbene complex and alkenes whose number of carbon atoms is one less than that in the initial trimethylene moiety.[1]

Bicyclo[3.1.0]hexane and bicyclo[4.1.0]heptane are found to be inert to the catalyst (A). Although treatment of bicyclo[5.1.0]octane with (A) gives two products, (1) and (2), whose molecular weight (m/e) by g.c.–m.s. corresponds to that of the starting bicycloalkane and the product of retro-carbene addition, cycloheptene, is not detected, the rapid oligomerization of cycloheptene cannot be ruled out, because the yields of (1) and (2) are low and the structure of the oligomer is not analyzed. Treatment of bicyclo[6.1.0]nonane with (A) or (B) gives four products, (3)—(6), whose molecular weight (m/e) by g.c.–m.s. is again identical with that of the starting bicycloalkane. Here, the possibility of the retro-carbene addition being the main reaction can be excluded because the sum of the yields of (3)—(6) exceeds 50% at a reaction time of 30—90 min (*ca.* 74% at 30 min).

The results of the reactions of the bicyclo[n.1.0]alkanes (n = 3, 4, or 6) are inconsistent with the reported retro-carbene addition reaction of cyclopropane.[1] The reason for this discrepancy is not clear. Lewis acids are known to stabilize metallocarbene complexes or metallacyclobutanes.[11,12] Therefore it is possible that the discrepancy is due to the stabilization of a tungsten complex, metallocarbene complex, or metallacyclobutane by the Lewis acids $AlCl_3$ or $AlEtCl_2$. However, it is noteworthy that the ethylene homologation is observed in the reaction of C_2D_4 with $[Ti(C_5H_5)_2\{CH_2(Cl)AlMe_2\}]$ where it was suggested that the metallocarbene complex and metallacyclobutane were stabilized by $AlCl_3$ (Scheme 1).[11]

The main products of the reaction of bicyclo[6.1.0]-nonane with (A) or (B) are methylenecyclo-octane and methylcyclo-octenes. The formation of methylenecyclo-octane and 1-methylcyclo-octene are not unexpected from the data reported for other transition-



SCHEME 2

metal complexes, although it is not clear whether the reaction proceeds *via* a metallocyclobutane [route (a) in Scheme 2], or an allylic intermediate [route (b)] as suggested for the reaction of the ethylene complex of Pt with bicyclo[4.1.0]heptane.[3] Double-bond migration catalyzed by transition-metal complexes is well known, and the formation of 3- and 4 (or 5)-methylcyclo-octene is not unusual.

From the experimental results described above, it is evident that the retro-carbene addition of cyclopropane catalyzed by an olefin-metathesis catalyst is not a general reaction.

EXPERIMENTAL

All of the reactions and manipulations were carried out under nitrogen or *in vacuo*. Commercial nitrogen of ultra high purity (>99.999%) was used after passing through a column of molecular sieves 5A.

The solvents were dried and distilled. Commercial cyclopentene, cyclohexene, cycloheptene, and cyclo-octene were used after drying over sieves. *trans*-Decalin (decahydronaphthalene) was distilled and stored over silica gel. Tetraphenyltin was recrystallized from n-hexane. Bicyclo[*n*.1.0]alkanes (n = 3—6) were prepared by treating cyclopentene, cyclohexene, cycloheptene, or cyclo-octene with methylene di-iodide and Zn–Cu according to a modification of the method for the preparation of norcarane.[13] Tungsten hexachloride was purified by removing the more volatile tungsten chloride oxide *in vacuo* at *ca.* 100 °C; $AlEtCl_2$ was distilled at atmospheric pressure.

The instrument used for the analytical g.c. was a Shimazuseisakusho (SS) GC-4BPTF gas chromatograph with a flame-ionization detector. The column (30 m × 0.25 mm, Goray type) was coated with Apiezon Grease L, and its temperature was kept at 100 °C or programmed from 40 to 140 °C in 10 min. *trans*-Decalin or nitrogen was used as the internal standard or the carrier gas. The preparative g.c. was carried out on a SS GC-3BT gas chromatograph with a thermal-conductivity detector. The column temperature was kept at 150 °C and hydrogen was used as the carrier gas. The column (6 m × 3 mm) was filled with Apiezon Grease L (20%) on Chromosorb W (60—80 mesh).

Proton n.m.r. spectra were obtained on a JEOL model PS-100 spectrometer and δ values were recorded relative to tetramethylsilane. Carbon-13 n.m.r. spectra were recorded in $CDCl_3$ with $SiMe_4$ as internal standard on a JNF-FT 60 spectrometer. G.c.–m.s. spectra were obtained on a Hitachi RUM-6 spectrometer, at a column temperature programmed from 40 to 140 °C in 12.5 min, using a column (6 m × 3 mm) filled with OV-1 (5%) on Uniport KS (60—80 mesh) and helium as carrier gas.

Authentic Samples.—Nona-1,8-diene was prepared by thermal decomposition of dimethyl nonanedioate at 500 °C on activated alumina in a stream of nitrogen, and purified by preparative g.c. Cyclononene was prepared from cyclo-octene *via* 9,9-dibromobicyclo[6.1.0]nonane: ^{1}H n.m.r. (neat), δ 1.50 [br s, 10 H, $(CH_2)_5$], 2.74 (m, 4 H, $CH_2CH=$), and 5.46 (m, 2 H, $CH=CH$); ^{13}C n.m.r. (neat), δ 25.014, 25.461, 25.908, and 26.151. Methylenecyclo-octane was prepared by Wittig reaction of cyclo-octanone: ^{1}H n.m.r. (neat), δ 1.56 [br s, 10 H, $(CH_2)_5$], 2.01 (br t, 4 H, $CH_2CH=$), and 4.74 (s, 2 H, $=CH_2$). 1-Methylcyclo-octene was prepared by dehydration of 1-methylcyclo-octan-1-ol (from cyclo-octanone and methylmagnesium iodide in tetrahydrofuran) with aqueous sulphuric acid (50%): ^{1}H n.m.r. (neat), δ 1.45 [br s, 8 H, $(CH_2)_4$], 1.65 (s, 3 H, CH_3), 2.08 [br m, 4 H, $CH_2CH=$ and $CH_2C(CH_3)=$], and 5.31 (br t, 1 H, $CH=$).

The relative retention times of the authentic samples were: benzene, 1.00; nona-1,8-diene, 1.28; cyclo-octene, 1.40; 1-methylcyclo-octene, 1.64; methylenecyclo-octane, 1.69; and cyclononene, 1.93.

Reaction of Bicyclo[n.1.0]*alkanes* (n = 3—6) *with* (*A*).—A mixture of $SnPh_4$ (0.208 g, 0.49 mmol) and WCl_6 (0.096 g, 0.24 mmol) in chlorobenzene (13.5 cm^3) was stirred with a magnetic stirrer at ambient temperature for 5 min and then bicyclo[3.1.0]hexane (1.0 g, 12.0 mmol) was added. Samples (*ca.* 0.1 cm^3) were removed at intervals by syringe and immediately injected into sample tubes containing water (0.1 cm^3). The organic phase was analyzed by g.c. The reactions of bicyclo[*n*.1.0]alkanes (n = 4—6) with (A) were carried out similarly except that the solvent was benzene instead of chlorobenzene.

No product was observed for bicyclo[3.1.0]hexane or bicyclo[4.1.0]heptane and the starting bicycloalkanes were recovered. Bicyclo[5.1.0]octane or bicyclo[6.1.0]nonane gave products (1) and (2), and (3)—(6), respectively. The reaction of bicyclo[6.1.0]nonane with catalyst (B) ($AlEtCl_2$ used as a 0.25 mol dm^{-3} solution in chloroform) gave a mixture of (3)—(6).

Proton N.M.R. Spectra of the Mixture of (3)—(6).—Preparative g.c. of a fraction, b.p. 80—155 °C, of the product obtained by treatment of bicyclo[6.1.0]nonane with (A) gave mixtures, of (*i*) (4) and (5) and (*ii*) (3)—(5). The ^1H n.m.r. spectra were: (*i*) (neat), δ 0.88 (d, 1.1 H, CH_3), 1.45 (br m, 7.7 H, CH_2), 1.65 (s, 1.9 H, CH_3), 1.90—2.40 [br m, 4.0 H, $C\mathit{H}_2CH=$ and $C\mathit{H}(CH_3)CH=$], 5.31 (t of m, 0.6 H, CH=), and 5.61 (t of m, 0.7 H, CH=); (*ii*) ($CDCl_3$), 0.88 (d, 1.1 H, CH_3), 1.10—1.90 [br m (including sharp signals at 1.45, 1.52, and 1.65), 8.1 H, CH_3 and CH_2], 1.90—2.40 [br m, 3.5 H, $C\mathit{H}_2CH=$ and $C\mathit{H}(CH_3)CH=$], 5.00—5.52 (m, 0.4 H, $CH_2=$), and 5.61 (t of m, 1.5 H, CH=).

The chemical shift of one of the olefinic protons in the ^1H n.m.r. spectrum of mixture (*i*) was identical with that of authentic 1-methylcyclo-octene, and the relative intensity of the resonances at δ 0.88 and 5.61 was 3 : 2. The signal at δ 1.65 corresponds to the methyl protons in 1-methylcyclo-octene: the presence of this compound was also evident from the relative retention time of product (5). The similarity in the ^1H n.m.r. spectra of mixture (*i*) and 1-methylcyclo-octene, in the range δ 1.0—2.4, indicates the presence of another isomer of methylcyclo-octene. On the basis of the proton count (1.9 H) for the signal at δ 1.65, the proton counts derived from 1-methylcyclo-octene were calculated and then subtracted from the proton counts observed to give a set of proton counts attributable to the isomer: δ 0.88 (1.1 H), 1.45 [7.7 H − (1.9 H × 8/3) = 2.6 H], 1.90—2.40 [4.0 H − (1.9 H × 4/3) = 1.5 H], and 5.61 (0.7 H). The ratio of proton counts at δ 0.88, 1.45, 1.90—2.40, and 5.61 is 1.1 : 2.6 : 1.5 : 0.7 = 3 : 7 : 4 : 2, which suggests the existence of three methyl protons (δ 0.88), four allylic protons (δ 1.90—2.40), and two olefinic protons (δ 5.61) in the isomer; the structure of 4(or 5)-methylcyclo-octene fulfils these requirements. The composition of the mixture was calculated from the ratio of proton counts at δ 0.88 (1.1 H) and 1.65 (1.9 H) giving 37% 1-methylcyclo-octene and 63% 4(or 5)-methylcyclo-octene.

In the ^1H n.m.r. spectrum of mixture (*ii*), a doublet, which is not observed for mixture (*i*), appeared in the range of the methyl protons, δ 0.98. Because the sum of the proton counts is adjusted to 16 H, the proton count of the methyl protons of 1-methylcyclo-octene is 3.0 H − 1.5 H − 1.1 H = 0.4 H, if the doublet at δ 0.98 is the signal of the methyl protons of the second isomer. The possibility that the second isomer is not an isomer of methylcyclo-octene is ruled out because of the similarity of the spectra of mixtures (*i*) and (*ii*). If the second isomer is assumed to be 5(or 4)-methylcyclo-octene, the proton counts are estimated as follows: δ 0.88 [1.5 H × (3/3) = 1.5 H], 0.98 [1.1 H × (3/3) = 1.1 H], 1.10—1.90 [1.5 H × (7/3) + 1.1 H × (7/3) + 0.4 H × (11/3) = 7.6 H], 1.90—2.40 [1.5 H × (4/3) + 1.1 H × (4/3) + 0.4 H × (4/3) = 4.0 H], and 5.00—5.61 [1.5 H × (2/3) + 1.1 H × (2/3) + 0.4 H × (1/3) = 1.8 H]. If the second isomer is 3-methylcyclo-octene, the proton counts are: δ 0.88 (1.5 H), 0.98 (1.1 H), 1.10—1.90 [1.5 H × (7/3) + 1.1 H × (8/3) + 0.4 H × (11/3) = 7.9 H], 1.90—2.40 [1.5 H × (4/3) + 1.1 H × (3/3) + 0.4 H × (4/3) = 3.6 H], and 5.00—5.61 [1.5 H × (2/3) + 1.1 H × (2/3) + 0.4 H × (1/3) = 1.8 H]. The second set of proton counts agrees well with the observed data. The composition of mixture (*ii*) estimated from the ratio of the proton counts of the methyl group is 16% 1-methylcyclo-octene, 35% 3-methylcyclo-octene, and 49% 4(or 5)-methylcyclo-octene.

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REFERENCES

[1] P. G. Gassman and J. H. Johnson, *J. Am. Chem. Soc.*, 1976, **98**, 6057; *ibid.*, 1977, **99**, 622.

[2] See also, N. Calderon, J. P. Lawrence, and E. A. Ofstead, *Adv. Organomet. Chem.*, 1979, **17**, 449.

[3] K. G. Powell and F. J. McQuillin, *Tetrahedron Lett.*, 1971, 3313; F. J. McQuillin and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 1972, 2123.

[4] (*a*) K. C. Bishop, III, *Chem. Rev.*, 1976, 461; (*b*) K. C. Bishop, III, and K. B. Wieberg, unpublished work quoted in 4*a*.

[5] K. B. Wieberg and K. C. Bishop, III, *Tetrahedron Lett.*, 1973, 2727.

[6] T. H. Johnson and Sheng-San Chen, *J. Am. Chem. Soc.*, 1979, **101**, 5277.

[7] S. J. McLain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 4558.

[8] R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Chem. Soc., Chem. Commun.*, 1976, 626.

[9] C. P. Casey, D. M. Schrock, and A. J. Shusterman, *J. Am. Chem. Soc.*, 1979, **101**, 4233.

[10] M. Ephritikhine and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1976, 926.

[11] F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.

[12] E. Verkuijlen, *Abstracts 3rd International Symposium on Metathesis*, Lyon, 10th September, 1979, p. 68.

[13] R. D. Smith and H. E. Simmons, *Org. Synth.*, 1961, **41**, 71.