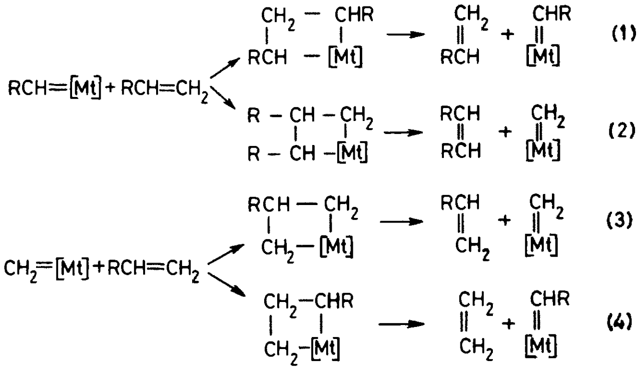
The Nature of the Preferred Chain-carrying Metallacarbene Intermediate in Metathesis Reactions Involving Alk-1-enes

By Lajos Bencze,† Kenneth J. Ivin, and John J. Rooney
(*Department of Chemistry, The Queen's University of Belfast* BT9 5AG, *N. Ireland*)

Summary The minor products from the cross-metathesis of norbornadiene (NBD) with hex-1-ene and of cyclopentene (CP) with octa-1,7-diene (1,7-OD), respectively, show that the complexed alkylidenes, RCH=[Mt] (where [Mt] denotes the metal site with the ligands attached), are much preferred to the complexed methylene, $\mathrm{CH_2}$=[Mt], as chain carriers formed by the reactions of the terminal olefins, but $\mathrm{CH_2}$=[Mt], when formed, is highly reactive towards the latter, with the strongly electrophilic methylene ligand selectively adding to the terminal olefins at the C-1 position.

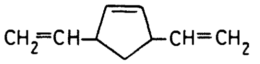
Degenerate metathesis of linear alk-1-enes can be at least one hundred times as fast as productive metathesis, depending on the catalyst used.[1] This can be interpreted in two ways, assuming a metallacarbene chain carrier. Either the main carrier is RCH=[Mt] and reaction (1) is preferred to reaction (2) or the main carrier is $\mathrm{CH_2}$=[Mt] and reaction (3) is preferred to reaction (4). It is important to note that such evidence does *not* prove that *both* $k_1 \gg k_2$ and $k_3 \gg k_4$, only that at least one of these inequalities must hold.



[Mt] denotes the metal site with the ligands attached

In the cross-metathesis of cyclopentene with pent-1-ene it has been shown[2] that the dominant products have a nonsymmetrical structure $\mathrm{CH_2[{=}CH(CH_2)_3CH{=}]_nCHC_3H_7}$. In such systems the propagating species may be designated PCH=[Mt] and may be expected to show similar chemical behaviour to RCH=[Mt]. There is no guarantee, however, that it will undergo transfer with pent-1-ene by reaction (1) in preference to reaction (2). Thus one cannot say, without further evidence, whether the $\mathrm{CH_2}$=CH– end-groups have been formed first or last in the formation of a given product molecule. This important problem has never been resolved, some authors[1,3] favour $\overset{\delta+}{\mathrm{RCH}}{=}\overset{\delta-}{[\mathrm{Mt}]}$ as an electrophile, reacting with alk-1-ene according to (1), while others[4] propose $\overset{\delta-}{\mathrm{CH_2}}{=}\overset{\delta+}{[\mathrm{Mt}]}$ as a nucleophile, reacting according to (3).

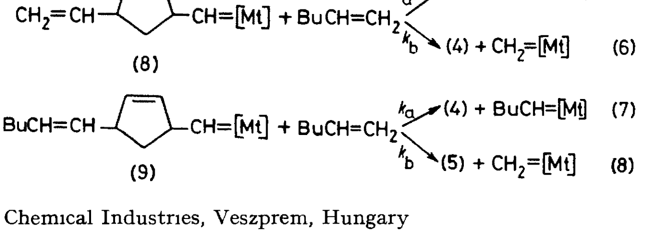
Table 1. Structure and relative proportions of the volatile products from the cross-metathesis of NBD and hex-1-ene[a]

Product	Structure	%
(1)	$\mathrm{CH_2{=}CH_2}$	2.0
(2)	BuCH=CHBu	0.0
(3)		0.2
(4)		57.0
(5)		2.5
(6)		≯0.1
(7)		38.0

[a] In a typical experiment 75 mmol of hex-1-ene and 19.8 mmol of NBD were dissolved in benzene (20 cm³) containing 0.26 mmol of $\mathrm{W(Ph_3As)_2(CO)_3Cl_2}$ and the mixture was heated under pure argon at 80—95 °C for 15 min giving 35—40% conversion of NBD. The reaction was quenched by addition of ethanol and the more volatile products isolated and analysed by g.l.c.–m.s. The ^{13}C n.m.r. of the heavier fraction confirmed that it contained equal proportions of BuCH=CH– and $\mathrm{CH_2}$=CH– end groups (Bu = n-butyl).

We report here some results for the cross-metathesis of norbornadiene (NBD) with hex-1-ene (Table 1), and cyclopentene (CP) with octa-1,7-diene (1,7-OD) (Table 2) which provide further evidence relating to this problem and also shed light on the selectivities of $\mathrm{CH_2}$=[Mt] in metathesis reactions.

As expected (Table 1) the nonsymmetrical products (**4**) and (**7**) far outweigh the symmetrical counterparts (**3**), (**5**), and (**6**), respectively, but although a little ethylene is formed, there is no sign of any dec-5-ene. The products (**3**), (**4**), and (**5**) will be formed by the reactions of metallacarbenes (**8**) and (**9**) with hex-1-ene, each in one of two ways. The structures of (**8**) and (**9**) are so similar at the reacting site that it may be assumed that the same pair of rate constants k_a and k_b applies in each case. The relative



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† Present address: Institute of Organic Chemistry, University of Chemical Industries, Veszprem, Hungary.

proportions of (**3**), (**4**), and (**5**) are consistent either with k_a/k_b 23, [**8**]/[**9**] 0·0035 or with k_a/k_b 0·0035, [**8**]/[**9**] 23. Assuming that the ratio [**8**]/[**9**] reflects the proportions of CH_2=[Mt] and BuCH=[Mt], this means that if the former is correct, BuCH=[Mt] and (**9**) would be the dominant chain carriers, while if the latter is correct CH_2=[Mt] and (**8**) would be dominant, with $k_b \gg k_a$. Also, if the nucleophilic proposal is correct $k_2 \gg k_1$ and $k_3 \gg k_4$. On this basis, (**2**) would not be expected to be absent, especially in view of significant yields of (**1**), which is formed by reaction (4). On the other hand, if [**9**] $\gg$ [**8**] and $k_a \gg k_b$, the main transfer reaction to hex-1-ene is (7) and the most likely source of any CH_2=[Mt] is reaction (8). It then follows that $k_1 \gg k_2$ and $k_4 \gg k_3$ and the occasional formation of (**1**) by the reaction (4) of $\overset{\delta+}{CH_2}=\overset{\delta-}{[Mt]}$ with hex-1-ene can be expected. The fact that the quantities of (**1**) and (**5**) are very similar may then be interpreted to mean that CH_2=[Mt] is formed almost exclusively by reaction (8) and consumed largely by (4), rather than by addition to NBD, since the % of (**3**) is very small. The substituted metallacarbene, $\overset{\delta+}{BuCH}=\overset{\delta-}{[Mt]}$, is therefore the major chain carrier.

TABLE 2. Some initial product ratios from the cross-metathesis of CP and 1,7-OD[a] at two different starting ratios.

Reactants	Products[b]					
CP/1,7-OD	C_{13}/C_6	C_{18}/C_6	C_7/C_6	C_{12}/C_6	C_{14}/C_6	C_{19}/C_6
1·0	3·0	1·4	0·35	0·2	0·06	0·04
20·0	3·6	1·8	0·2	0·12	0·05	0·06

[a] Experiments were carried out under pure argon at 22 °C using either $W(Ph_3As)_2(CO)_3Cl_2$ ($5{\cdot}8 \times 10^{-3}$ mol l^{-1}) with $EtAlCl_2$ ($2{\cdot}5 \times 10^{-2}$ mol l^{-1}), or WCl_6 ($1{\cdot}5 \times 10^{-2}$ mol l^{-1}) with $SnMe_4$ ($1{\cdot}5 \times 10^{-2}$ mol l^{-1}) solutions in benzene as catalysts. The total olefin concentration was kept at 6·54 mol l^{-1} with the CP/1,7-OD ratio ranging from 0 to 22·5. Samples were periodically withdrawn, quenched by addition of dry Al_2O_3 and analysed by g.l.c.–m.s. Product distributions are extrapolated to zero conversion, using at least five analyses in the first 10% conversion of 1,7-OD. Ethylene was found but not measured. [b] C_6 = cyclohexene; C_7 = hepta-1,6-diene; C_{12} = dodeca-1,6,11-triene; C_{13} = trideca-1,6,12-triene; C_{14} = tetradeca-1,7,13-triene; C_{18} = octadeca-1,6,11,17-tetraene; C_{19} = nonadeca-1,7,12,18-tetraene.

The data in Table 2 confirm these conclusions. Again, asymmetric cross-metathesis is dominant giving the C_{13}, C_{18}, *etc.*, series of products, but in this particular system the contribution of the known reaction[5] (9) may be readily

$$CH_2{=}CH[CH_2]_4CH{=}[Mt] \rightarrow \text{cyclohexene} + CH_2{=}[Mt] \qquad (9)$$

assessed and thus the relative importance of the C_7-metallacarbene in the overall reaction is found. Cyclohexene is a substantial *initial* product (Table 2) and this can only be so if $CH_2{=}CH(CH_2)_4\overset{\delta+}{CH}=\overset{\delta-}{[Mt]}$ is a major carrier in the cross-metathesis. By virtue of reaction (9) the contribution of the minor carrier $\overset{\delta+}{CH_2}=\overset{\delta-}{[Mt]}$ should also be considerably enhanced, and, as expected, the sequence C_7, C_{12}, *etc.*, is initially several times larger than the other minor symmetrical sequence C_{14}, C_{19}, *etc.* This is in marked contrast to the relative amounts of (**3**) and (**5**), the corresponding products in the minor sequences from the cross-metathesis of NBD and hex-1-ene (Table 1). However, the yields of the C_7, C_{12}, *etc.* series are still low in comparison to the yield of cyclohexene, indicating that the majority of CH_2=[Mt] intermediates again preferentially undergo reaction (4), now with 1,7-OD.

The strong electrophilicity of the methylene intermediates, now evident in metathesis, has also been inferred recently from the observation of the linear homologation of paraffins on metal films[6] and from the Fischer-Tropsch synthesis of n-alk-1-enes on supported iron clusters.[7] Thus, in all these transition-metal catalysed reactions the behaviour of CH_2=[Mt] is in marked contrast to the reactivity of the known, relatively stable CH_2=[Mt] compounds[8,9] where methylene acts as a nucleophile towards olefins, but does not initiate metathesis.

A corollary to our conclusions is that methylene complexes are less stable than alkylidene complexes in highly active metathesis systems.

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