

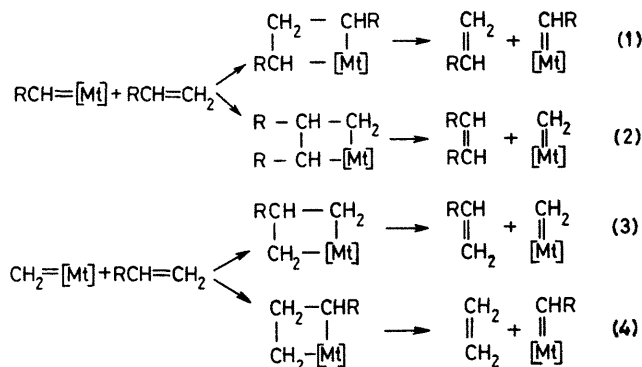
The Nature of the Preferred Chain-carrying Metallocarbene Intermediate in Metathesis Reactions Involving Alk-1-enes

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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, $\text{RCH}=[\text{Mt}]$ (where $[\text{Mt}]$ denotes the metal site with the ligands attached), are much preferred to the complexed methylene, $\text{CH}_2=[\text{Mt}]$, as chain carriers formed by the reactions of the terminal olefins, but $\text{CH}_2=[\text{Mt}]$, 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 metallocarbene chain carrier. Either the main carrier is $\text{RCH}=[\text{Mt}]$ and reaction (1) is preferred to reaction (2) or the main carrier is $\text{CH}_2=[\text{Mt}]$ 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



$[\text{Mt}]$ denotes the metal site with the ligands attached

In the cross-metathesis of cyclopentene with pent-1-ene it has been shown² that the dominant products have a nonsymmetrical structure $\text{CH}_2=[\text{CH}(\text{CH}_2)_3\text{CH}]=\text{CHCH}_2\text{CH}_2\text{CH}_3$. In such systems the propagating species may be designated $\text{PCH}=[\text{Mt}]$ and may be expected to show similar chemical behaviour to $\text{RCH}=[\text{Mt}]$. 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 $\text{CH}_2=\text{CH}-$ 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 $\text{RCH}=[\text{Mt}]$ as an electrophile, reacting with alk-1-ene according to (1), while others⁴ propose $\text{CH}_2=[\text{Mt}]$ as a nucleophile, reacting according to (3).

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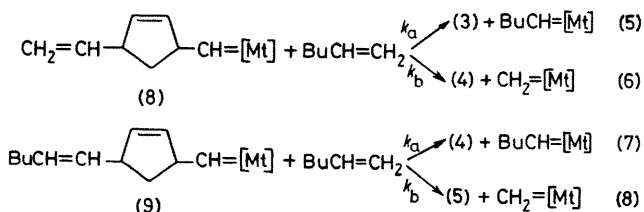
TABLE 1 Structure and relative proportions of the volatile products from the cross-metathesis of NBD and hex-1-ene^a

Product	Structure	%
(1)	$\text{CH}_2=\text{CH}_2$	2.0
(2)	$\text{BuCH}=\text{CHBu}$	0.0
(3)	$\text{CH}_2=\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CH}_2$	0.2
(4)	$\text{BuCH}=\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CH}_2$	57.0
(5)	$\text{BuCH}=\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CHBu}$	2.5
(6)	$\text{CH}_2=[\text{CH}-\text{Cyclopentene}-\text{CH}]_2\text{CH}_2$	†0.1
(7)	$\text{BuCH}=[\text{CH}-\text{Cyclopentene}-\text{CH}]_2\text{CH}_2$	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 $\text{W}(\text{Ph}_3\text{As})_2(\text{CO})_3\text{Cl}_2$ 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 glc–ms. The ¹³C n.m.r. of the heavier fraction confirmed that it contained equal proportions of $\text{BuCH}=\text{CH}-$ and $\text{CH}_2=\text{CH}-$ 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 $\text{CH}_2=[\text{Mt}]$ 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 metallocarbenes (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



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 $\text{CH}_2=[\text{Mt}]$ and $\text{BuCH}=[\text{Mt}]$, this means that if the former is correct, $\text{BuCH}=[\text{Mt}]$ and (9) would be the dominant chain carriers, while if the latter is correct $\text{CH}_2=[\text{Mt}]$ 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 $\text{CH}_2=[\text{Mt}]$ 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 $\text{CH}_2=[\text{Mt}]$ 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 $\text{CH}_2=[\text{Mt}]$ 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, $\text{BuCH}=[\text{Mt}]$, is therefore the major chain carrier.

can only be so if $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}=[\text{Mt}]$ is a major carrier in the cross-metathesis. By virtue of reaction (9) the contribution of the minor carrier $\text{CH}_2=[\text{Mt}]$ 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 $\text{CH}_2=[\text{Mt}]$ intermediates again preferentially undergo reaction (4), now with 1,7-OD.

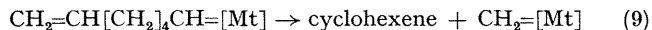
The strong electrophilicity of the methylene intermediates, now evident in metathesis, has also been inferred recently from the observation of the linear homologation of paraffins on metal films⁶ and from the Fischer-Tropsch synthesis of n-alk-1-enes on supported iron clusters.⁷ Thus, in all these transition-metal catalysed reactions the behaviour of $\text{CH}_2=[\text{Mt}]$ is in marked contrast to the reactivity of the known, relatively stable $\text{CH}_2=[\text{Mt}]$ compounds^{8,9} where

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

Reactants CP/1,7-OD	C_{13}/C_6	C_{18}/C_6	Products ^b			
			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 $\text{W}(\text{Ph}_3\text{As})_2(\text{CO})_3\text{Cl}_2$ (5.8×10^{-3} mol l⁻¹) with EtAlCl_2 (2.5×10^{-2} mol l⁻¹), or WCl_6 (1.5×10^{-2} mol l⁻¹) with SnMe_4 (1.5×10^{-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 reaction⁵ (9) may be readily



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

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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