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Alkene metathesis catalysed by $[WBr_2(CO)_2(diene)]/AlCl_2Et$

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Abstract

$[WBr_2(CO)_2(diene)]/AlCl_2Et$ mixtures promote metathesis of *cis*-2-pentene to give 2-butene and 3-hexene. For diene = norbornadiene the reaction is catalytic, and is accompanied by *cis* to *trans* isomerisation of the 2-pentene, whereas for diene = 1,5-cyclooctadiene or cyclooctatetraene the metathesis is essentially stoicheiometric. The same complexes catalyze the metathesis of *trans*-2-pentene to give 2-butene and 3-hexene, but at approximately twice the rate observed for the *cis*-alkene. $[WBr_2(CO)_2(diene)]/AlCl_2Et$ mixtures also catalyse the metathesis of 1,7-octadiene to give cyclohexene and ethene. The intermediacy of metal carbene derivatives in such reactions is supported by the reactions of $[WBr_2(CO)_2(norbornadiene)]$ with alkylating agents $SiMe_4$ and MeMgBr which give methane, whereas $[WBr_2(CO)_2$-(norbornadiene)] and $AlCl_2Et$ in the absence of alkenes gave virtually stoicheiometric amounts of ethane.

Introduction

The generally accepted mechanism for metal-promoted alkene metathesis involves metal-carbene initiators and metallacyclobutane intermediates [1]. The source of the carbene ligand is not always known with certainty but in reactions involving metal halides and aluminium alkyl cocatalysts a widely accepted route involves hydrogen transfer (carbon → metal) in an intermediate alkyl metal [2]. A prerequisite for α or β hydride transfer is a vacant coordination site on the metal centre. Recently we reported the synthesis and some of the chemistry of coordinatively unsaturated alkene complexes $[WBr_2(CO)_2(diene)]$ (diene = norbornadiene, (NBD) (**1a**), 1,5-cyclooctadiene (COD) (**1b**), or cyclooctatetraene (COT (**1c**)) [3]. The seven-coordinate W^{II} complex $[WCl_2(CO)_2(PPh_3)_3]$ in conjunction with $AlCl_2Et$

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has previously been shown to function as a catalyst for metathesis of *cis*-2-pentene [4]. Complexes of this type are known to undergo ligand dissociation in solution to give six-coordinate species related to **1** [5]. It was therefore of interest to investigate the potential of the diene complexes **1** as metathesis catalysts in view of the ready availability of a coordination site at the metal and we now report the results of our initial studies.

Results and discussion

Metathesis of *cis*-2-pentene was investigated with three related complexes $[WBr_2(CO)_2(diene)]$ (**1**) (diene = norbornadiene, 1,5-cyclooctadiene or cyclooctatetraene) as catalysts with, in each case, $AlCl_2Et$ is co-catalyst. The results, which are summarised in Table 1, illustrate that metathesis occurs in benzene at 65 °C to give the expected products 2-butene (*cis* + *trans*) and 3-hexene (*cis* + *trans*) in addition to small quantities of ethane. Appreciable catalytic activity was observed only with the norbornadiene complex (the other reactions are essentially stoichiometric) although even in this case the reaction is sluggish under these conditions. The metathesis is also accompanied by *cis* → *trans* isomerisation of the 2-pentene, a well known phenomenon in this type of reaction [1,6,7]. Metathesis of *trans*-2-pentene was also studied under the same conditions as that of the *cis*-isomer and again catalytic activity was observed only with the norbornadiene complex, although a more efficient reaction was found (see Table 2). The metathesis of 1,7-octadiene in the presence of $[WBr_2(CO)_2(NBD)]/AlCl_2Et$ in benzene at 65 °C was also carried out, and after 3 h the products were cyclohexene (28%), ethene (29%), and small quantities of ethane (See Table 3). Again significant catalytic activity was observed only with the norbornadiene complex.

These data are all readily interpreted in terms of a one carbene exchange mechanism which is now well established [1]. The formation of a carbene initiator can occur in several different way with $[WBr_2(CO)_2(diene)]$ as catalyst and $AlCl_2Et$ as co-catalyst. Since control experiments established that metathesis does not occur in the absence of the $AlCl_2Et$ co-catalyst, we can eliminate a hydrogen shift process analogous to that proposed for the ring opening polymerisation of norbornene with $[WCl_2(CO)_3(AsPh_3)_3]$ [8]. Two mechanisms involving both catalyst components are therefore plausible on the basis of results of previous studies. The first, proposed by Muetterties [2], involves metathetical replacement of the halide ligands by ethyl groups, as shown in Scheme 1, to give an intermediate bis-alkyl complex **2**. Since there is a vacant coordination site on the metal, α-hydride transfer can readily occur

Table 1 [a]

$$cis\text{-2-pentene} \xrightarrow[AlEtCl_2]{[WBr_2(CO)_2(diene)]} \text{2-butene} + \text{3-hexene}$$

Diene	2-Butene (%)	3-Hexene (%)	*trans*-2-Pentene (%)	*cis*-2-Pentene (%)
NBD	16.75	17.00	25.74	40.1
COD	5.1	5.1	21.1	68.2
COT	4.9	4.9	20.1	67.3

[a] Conditions: solvent C_6H_6, temperature 65 °C, time 3 h.

Table 2 [a]

$$\textit{trans}\text{-2-pentene} \xrightarrow[\text{AlEtCl}_2]{[\text{WBr}_2(\text{CO})_2(\text{diene})]} \text{2-butene} + \text{3-hexene}$$

Diene	2-Butene (%)	3-Hexene (%)	*trans*-2-Pentene (%)
NBD	30.0	30.2	39.3
COD	3.3	4.0	90.5
COT	3.5	3.7	90.3

[a] Conditions: solvent C_6H_6, temperature 65 ° C, time 3 h.

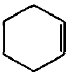
to give a carbene derivative **3**. This subsequently undergoes reductive elimination of ethane to generate the coordinatively unsaturated derivative **4** which can act as the initiator. An alternative process is conceivable in view of the presence of carbonyl ligands, since Farona has demonstrated the possibility of carbene formation via initial coordination of a carbonyl oxygen to the alkylaluminium [9]. In the present case this would lead ultimately to the formation of a carbene initiator and ethene. However, available evidence favours the mechanism in Scheme 1, since traces of ethane rather than ethene were detected in all of the reactions reported here.

Other evidence for carbene formation was also sought. For example in the absence of alkenes the 1/2 reaction of complex **1a** with $AlCl_2Et$ in benzene at 65 ° C gives ethane in 88% yield, in keeping with the above proposal. Similar reactions of **1a** with $SnMe_4$ and MeMgBr gave high yields (89 and 91%, respectively) of methane, which is consistent with the formation and subsequent reaction of a bis-methyl complex to give a methylene derivative. Reactions of **1b** and **1c** with $SnMe_4$ similarly resulted in methane formation. Interestingly the reaction of $[MoCl_3(PR_3)(thf)_2]$ with Me_2Mg and 1,5-cyclooctadiene affords $[MoMe_2(PR_3)_2(cod)]$ ($PR_3 = PMe_3$ or PMe_2Ph) in low yields, whereas attempts to isolate cyclooctatetraene and norbornadiene analogues were unsuccessful [10]. Moreover the cyclooctadiene complexes were observed to decompose readily above 60 ° C in solution.

Metathesis of *cis*-2-pentene with **1a** and $SnMe_4$ or MeMgCl as co-catalysts were also carried out, but a variety of unidentified products were obtained in addition to small quantities of 2-butene and 3-hexene. This finding parallels previous observations in metathesis reactions where the use of $AlCl_2Me$ rather than $AlCl_2Et$ as co-catalyst was found to lead to extensive side reactions, including alkene polymerisation [9].

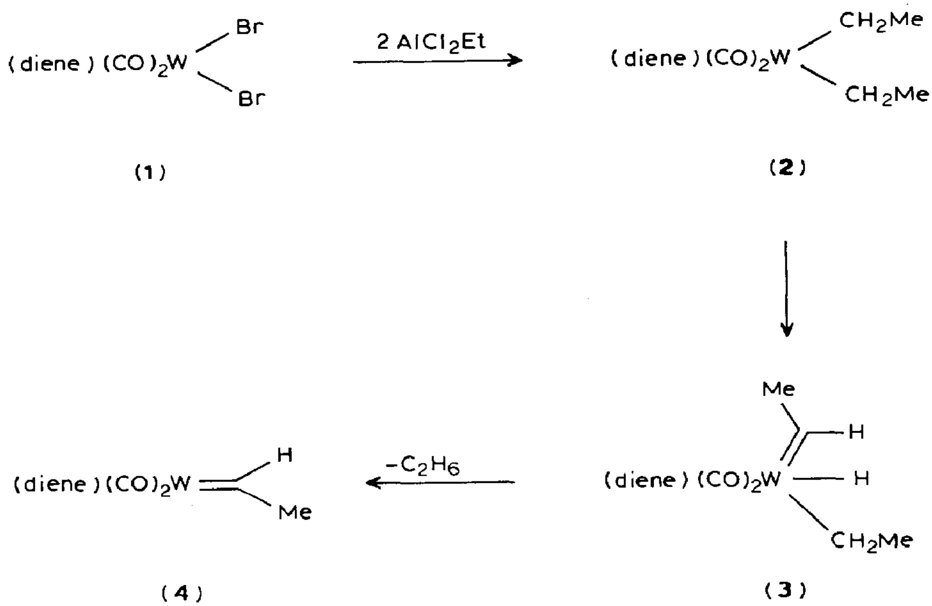
Table 3 [a]

$$\text{1,7-octadiene} \xrightarrow{[\text{WBr}_2(\text{CO})_2(\text{diene})]} C_2H_4 +$$



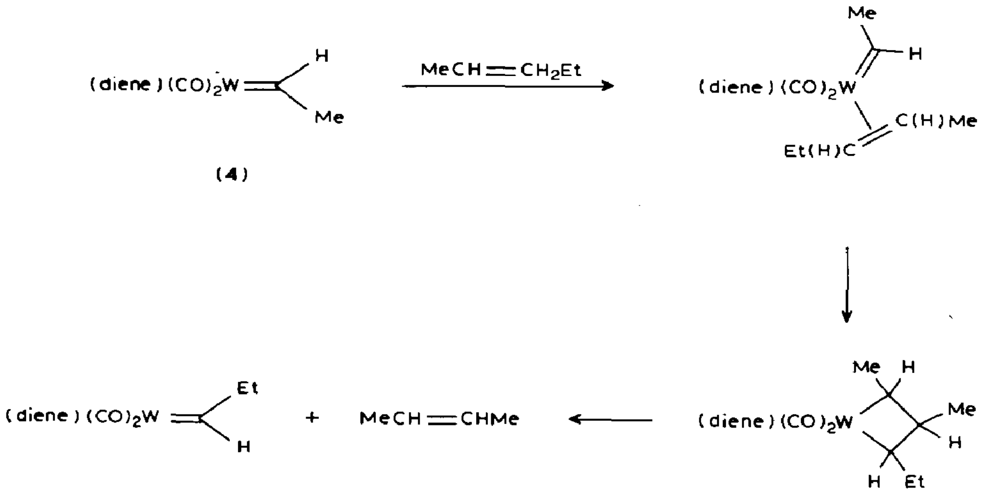
Diene	Ethene (%)	Cyclohexene (%)
NBD	57	56
COD	1.95	2.09
COT	1.89	1.95

[a] Conditions: solvent C_6H_6, temperature 65 ° C, time 3 h.



Scheme 1

On the assumption that Scheme 1 accurately depicts formation of the initiator, metathesis of *cis*-2-pentene probably proceeds as shown in Scheme 2. Since the initiator is assumed to contain the M=CHCH$_3$ grouping, the initially formed alkene products 2-butene and 3-hexene will be the same as those produced in the later stages of metathesis. In accord with this, no traces of other alkene products apart from *trans*-2-pentene were detected. However we do note that metathesis of 1,7-octadiene using the same initiator should produce propene in small quantities as the first formed alkene [9]. Since small quantities of ethane are produced in this reaction



Scheme 2

the same carbene initiator is implied, and we can only assume that the GC conditions employed were insufficient to detect the small quantities of propene which are generated.

Finally we draw attention to the effect of the diene on the catalytic activity of complexes $[WBr_2(CO)(diene)]$. In all the cases studied catalytic activity was observed only with the norbornadiene complex, and although $[WBr_2(CO)_2(diene)]$ (diene = COD or COT) did promote metathesis the reactions were essentially stoicheiometric. This suggests that the initiator **4** is formed in each case but is consumed or decomposes as the reaction proceeds. A plausible explanation is suggested by our previous studies of complexes **1**, and in particular their reactions with Lewis bases [3]. Simple adducts $[WBr_2(CO)L_2(diene)]$ are formed when the diene is NBD, but the COD and COT complexes in contrast undergo diene substitution. We attributed this to the greater coordinating ability of NBD which results from the relief of strain associated with changes in bond angles on coordination. Conceivably diene dissociation also occurs during metathesis reactions with the cyclooctadiene and cyclooctatetraene complexes but not with $[WBr_2(CO)_2(NBD)]$.

Experimental

Benzene was refluxed over sodium and distilled under nitrogen before use. Reactions were carried out by standard techniques in a sealed thermostatted glass vessel (45 cm^3). GLC analyses were carried out with a Varian 6000 Chromatograph fitted with a 9 m column (10 wt-% 1,2,3-tris(2-cyanoethoxy)propene on Chromosorb PAW). GC analysis of methane and ethane was carried out on a 3 m Porapak Q column using a Carlo Erba Fractovap C connected to a Hewlett–Packard 3380A integrator. Complexes $[WBr_2(CO)(diene)]$ were made by previously reported methods [3]. $AlCl_2Et$ was obtained from Aldrich as a 1.8 *M* solution, and diluted with toluene to 0.1 *M* before use. Solutions of $SnMe_4$ and MeMgCl (3.0 *M* in THF diluted to 0.1 *M*) were obtained similarly.

Reaction of $[WBr_2(CO)_2(NBD)]$ with $SnMe_4$

The complex (200 mg, 0.42 mmol) was dissolved in benzene (10 cm^3) and 188 mg (1.05 mmol) of $SnMe_4$ were added. The stirred mixture was kept at 65 °C for 3 h. GC gas analysis revealed the formation of methane 0.33 mmol (89% based on the tungsten complex).

Use of $[WBr_2(CO)_2(COT)]$ and $[WBr_2(CO)_2(COD)]$ with $SnMe_4$ similarly gave 0.33 mmol (80%) and 0.34 mmol (81%) of methane respectively.

Reaction of $[WBr_2(CO)_2(NBD)]$ with MeMgBr

The complex (200 mg, 0.42 mmol) was dissolved in benzene (10 cm^3) and MeMgBr in THF (1.05 mmol) was added. After 3 h stirring at room temperature GLC analysis revealed the formation of methane (0.38 mmol, 91%).

Reaction of $[WBr_2(CO)_2(NBD)]$ with $AlCl_2Et$

A mixture of 200 mg (0.42 mmol) of the complex and $AlCl_2Et$ (1.05 mmol) was kept at 65 °C for 3 h to give ethane (0.37 mmol, 88%).

Alkene metathesis reactions

These were all carried out as described below for metathesis of *cis*-2-pentene with

$[WBr_2(CO)_2(NBD)]/AlCl_2Et$ as catalyst. The results are shown in Tables 1–3.

A mixture of 100 mg (0.21 mmol) of $[WBr_2(CO)_2(NBD)]$, 330 mg (4.7 mmol) of *cis*-2-pentene, 10 cm^3 of benzene, and $AlCl_2Et$ (0.63 mmol) was placed in the glass reactor which was then sealed and kept at 65 ° C for 3 h. After being cooled to room temperature the mixture was analysed by GLC, which revealed the formation of 2-butene (16.75%), 3 hexene (17%), *trans*-2-pentene (25.75%) and ethane (0.19 mmol, 90% based on the tungsten complex).

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