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Electrochemically Induced Generation of Catalytic Species for Olefin Metathesis from Molybdenum and Tungsten Chlorides

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Abstract: The electrochemical reduction of WCl_6 or $MoCl_5$ results in the formation of stable and active olefin metathesis catalysts. Reduction of these salts in chlorinated solvents under controlled potential at a platinium cathode, with an aluminium anode, gives in situ formation of the active catalyst species. Stability is defined by the fact that the catalyst maintains good activity even after several charges of olefin have been metathesized. The rates of catalysis fall between those observed for the $WCl_6/AlLiH_4$ and the $WCl_6/EtAlCl_2/EtOH$ systems, and this new catalyst shows a very high selectivity in normal metathesis products without isomerization. The $WCl_6/e^-/Al/CH_2Cl_2$ system is also useful for metathesis of α olefins at ambient temperature, as well as for cross metathesis between α and β olefins. From an analysis of the initial byproducts and labeling experiments conducted with CD_2Cl_2, it is shown that the metallocarbene initiator arises from a reaction between the transition-metal salt and an organoaluminium compound generated in situ by an EC mechanism. An XPS comparison between electrochemically and chemically reduced systems is made, which demonstrates that under electrochemical conditions, the major function of the controlled potential is to stabilize in high oxidation state the active species responsible for the metathesis reaction, whereas with the chemically generated system, the conditions result in a further reduction of the catalyst, giving less selectivity.

Introduction

The electrochemical behavior of transition-metal salts or complexes has been the subject of many investigations, however, few studies have been devoted to the generation of catalytic species.[2] Our current interest in electrogeneration of homogeneous catalytic reduced species was initiated as a result of our observation that electroreduction of $[Fe(NO)_2Cl]_2$ produced an "$Fe(NO)_2$" specie which was highly active and selective for butadiene cyclodimerization.[3] Our success with the "$Fe(NO)_2$" system prompted us to study the generation of active moieties for metathesis of alkenes from WCl_6 and $MoCl_5$. Electroreduction of these salts at a platinium cathode under controlled potential has recently been reported to produce an active species for the metathesis of internal alkenes under mild conditions.[4]

However, many questions remain unanswered about several essential features of this catalysis. In particular, the role of the solvent (CH_2Cl_2 or $(-CH_2Cl)_2$) and of the aluminium anode (both were necessary to provide a good catalytic activity) as well as that of the cathodic controlled potential, shown to have a critical influence on the selectivity,[4] remains unexamined. In this paper, we report results related to the mechanism of generation of the active species, and evidence for a metal carbene initiated process, similar to that for olefin metathesis with conventional catalysts.[5]

Results

Electrochemical Behavior of WCl_6 and $MoCl_5$ in CH_2Cl_2. Provided that no further chemical reaction occurs, one of the most interesting aspects of the electrochemical technique is that the oxidation state of the reduced species can be stabilized at a controlled potential. Preliminary voltammetric experiments are performed to determine which oxidation-state level can be attained and the value of the corresponding half-wave potential.

In dichloromethane, with 0.1 M NBu_4PF_6 as supporting electrolyte, reduction of a 10^{-3} M solution of WCl_6 occurs at a rotating platinium electrode, exhibiting three reversible steps at +1.6, +0.3 and −1.2 V vs. a saturated aqueous calomel electrode separated from the WCl_6 solution by a junction containing a 0.1 M NBu_4PF_6 dichloromethane solution.

As shown by electrolysis results under controlled potential on these waves, these three reversible steps each give rise to the exchange of 1 faraday/mol of WCl_6. They correspond to the electrochemical reactions

$$WCl_6 + e^- \rightleftharpoons WCl_6^-$$

$$WCl_6^- + e^- \rightleftharpoons WCl_6^{2-}$$

$$WCl_6^{2-} + e^- \rightleftharpoons WCl_6^{3-}$$

Only WCl_6^{3-} is unstable in solution.

The oxidizing character of WCl_6 is evidenced by its reaction with NBu_4Cl, according to

$$WCl_6 + NBu_4Cl \rightarrow WCl_6^-NBu_4^+ + {}^1/{}_2Cl_2$$

WCl_6^- is oxidized at a platinium electrode at +1.6 V and reduced at +0.3 V. Under the conditions required for the synthesis of the metathesis catalysts, which will be shown to necessitate the use of an aluminium anode in an undivided cell, but in the presence of 0.1 M NBu_4PF_6, the coulometric reduction of WCl_6 at a platinium cathode leads again to WCl_6^-, but only 0.7 faraday/mol of WCl_6 is used to consume this salt. Under such conditions, however, as well as with numerous supporting electrolytes tested with WCl_6, no metathesis reaction occurred as soon as a trace of these salts were introduced, indicating that the active species are not stable in the presence of anions such as PF_6^-, BF_4^-, or ClO_4^-. Therefore, the electrolysis studies of the metathesis reaction were conducted in pure solvents without supporting electrolyte, at the potentials of the three reduction steps by using controlled potential. Under these conditions, the conductivity of the solution is rather low at the beginning of the reduction, but the current intensity increases very rapidly as shown in Figure 1, indicating that the cell resistance decreases, due probably to the formation of ionic species during the electrochemical process. Indeed, starting from a value lower than 10^{-6} Ω^{-1} cm^{-1} before electrolysis, the

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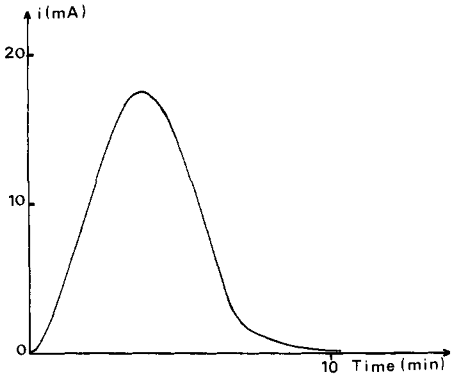

Figure 1. Intensity vs. time during electroreduction of WCl_6 in CH_2Cl_2 under controlled potential (+0.9 V vs. SCE); platinium cathode, aluminium anode.

Table I. Metathesis of 2-Pentene with Catalytic Species Obtained from Electroreduction of $MoCl_5$ and WCl_6 in Halogenated Solvents[a]

catalytic precursor	solvent	anode	E_c,[b] V	reduction[c] time, min	Q(c)	R_{to}, h^{-1} [d]
$MoCl_5$	PhCl	Al	+0.4	130	3.5	0
$MoCl_5$	o-$C_6H_5Cl_2$	Al	+0.9	105	12.7	0.8
$MoCl_5$	$(-CH_2Cl)_2$	Al	+0.9	50	2.1	16
$MoCl_5$	CH_2Cl_2	Al	+0.9	10	4.5	160
$MoCl_5$	CH_2Cl_2	Fe	+0.9	120	7.5	0
WCl_6	PhCl	Al	+0.3	140	4.8	1
WCl_6	o-$C_6H_4Cl_2$	Al	+0.9	110	3.8	11
WCl_6	$(-CH_2Cl)_2$	Al	+0.9	40	6.8	190
WCl_6	CH_2Cl_2	Al	+0.9	20	2.6	670[e]
WCl_6	CH_2Cl_2	Ti	+0.9	40	3.2	0.5
WCl_6	CH_2Cl_2	Fe	+0.9	105	6.9	0
WCl_6	CH_2Cl_2	Al		5		8.0[f]
WCl_6	$(-CH_2Cl)_2$	Al		5		5.6[f]

[a] Experimental conditions: catalyst = 0.3 mmol; solvent = 30 mL; T = 20 °C, olefin = 30 mmol, added after reduction. [b] Ec = cathodic potential, vs. SCE. [c] The electrolysis is considered to be terminated when the current has decreased to 5% of its upper value. [d] R_{to} = turnover rate; moles of 2-pentene transformed in metathesis products per hour per mole of catalyst, according to the reaction 2-pentene ⇌ 2-butenes + 3-hexenes, exclusively (the observed selectivities are very high (ca. 95–100%), and no isomerization was detected, provided the electrolysis was conducted at the first reduction level). [e] A very good stability of this system is observed, as three reloadings with 2-pentene were readily transformed with the following turnover rates: 820, 830, and 2 160 h^{-1} for 30, 30, and 60 mmol, respectively. [f] Chemical reduction by the Al foil. These reactions led to less selective reactions, as isomerization of the substrate and products occurred (10 to 20% of oligomers are also produced in these cases).

Table II. Effect of the Cathodic Potential Value on the Catalytic Behavior of Reduced Solutions of WCl_6 and $MoCl_5$ for Metathesis of 2-Pentene

catalytic precursor	cathodic potential (vs. SCE), mV	selectivity in 2-butenes and 3-hexenes, %	R_{to}, h^{-1}
WCl_6	+900	97	670
WCl_6	−100	45	600
WCl_6	−700 and −1700	0	oligomerization of the substrate
$MoCl_5$	+900	95	160
$MoCl_5$	−300	40	140
$MoCl_5$	−1100	0	oligomerization of the substrate

[a] Conditions: [M] = 10^{-2} M, [2-pentenes] = 1 M; CH_2Cl_2 = 30 mL; anode Al, cathode Pt; olefin introduced after reduction of WCl_6 or $MoCl_5$.

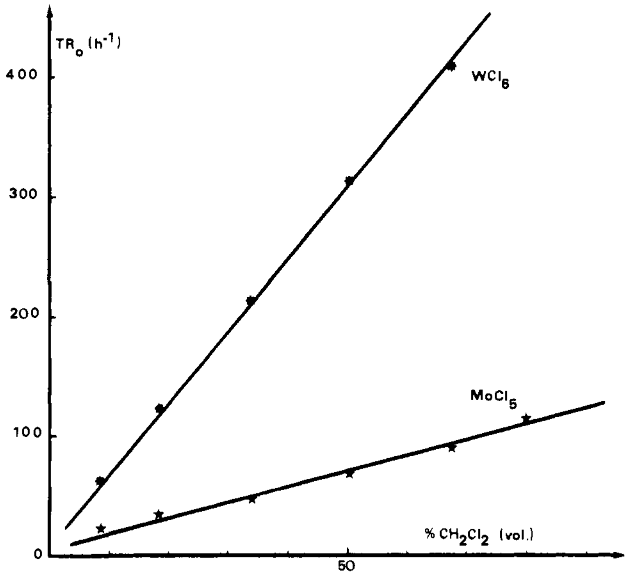

Figure 2. Turnover rates for metathesis of 2-pentene on WCl_6 and $MoCl_5$ electroreduced in different o-dichlorobenzene/dichloromethane mixtures.

conductivity of the solution increases and reaches a maximum of 2.8 × 10^{-5} Ω^{-1} cm^{-1}.

This observed conductivity led us to the assumption that our reduction potential is indeed fixed at its imposed value. The junction potentials of the reference electrode cannot be calculated but must be low enough so that, as the half-wave potentials are well separated (by at least 1.3 V), one can be sure to stabilize the oxidation state of tungsten after exhaustive electrolysis under controlled potential. In the case of $MoCl_5$, it has been impossible to obtain voltammetric curves, as this salt reacts almost immediately with the supporting electrolytes. However, without any salt one can characterize 3 half-wave potentials of reduction at +1.1, −0.3, and −1.1 V in pure CH_2Cl_2 (vs. SCE).

Effect of the Nature of the Solvent and of the Anode on the Catalytic Reaction. All catalytic experiments were conducted after electrolysis under controlled cathodic potential in halogenated solvents (all other solvents were inefficient). After exhaustive electrolysis, performed in an undivided cell on the first reduction wave level of either WCl_6 or $MoCl_5$, the olefin (2-pentene) was introduced, in which case the metathesis reaction generally occurred, as indicated in Tables I and II.

From the above results, it appears that the reaction rate strongly depends upon the nature of the solvent and of the anode, since a titanium anode is far less suitable than an aluminium one, while no catalysis could be detected with an iron anode. Some interesting features of these new electrochemical systems are that a very high selectivity to 2-butenes and 3-hexenes is obtained. In addition, no isomerization of the substrate or products is observed, and the catalytic solutions exhibit remarkably high stability (Table I) as no loss of activity was observed after four reloadings of 2-pentene. These two points contrast markedly with the general behavior of conventional metathesis catalysts, which are sometimes more reactive but much less stable and selective.

Influence of CH_2Cl_2 on the Reaction Rate. As CH_2Cl_2 seems to be the best solvent for this catalytic system, some experiments were conducted under standard conditions with an aluminium foil as the anode, at a platinium cathode, by reduction of $MoCl_5$ or WCl_6. These studies were done under controlled potential (+0.9 V vs. SCE), in different o-dichlorobenzene/dichloromethane mixtures. This aromatic solvent was chosen because its dielectric constant (ϵ_r 9.9) is practically identical with that of CH_2Cl_2 (ϵ_r 9.1), in order to avoid any difference in the cell resistance. Figure 2 summarizes the evolution of the reaction rate upon increasing the CH_2Cl_2 content in these solutions.

Two essential features can be deduced from these experiments:

(1) The most efficient reactions are those conducted at reduction potentials corresponding to only the first reduction step of WCl_6

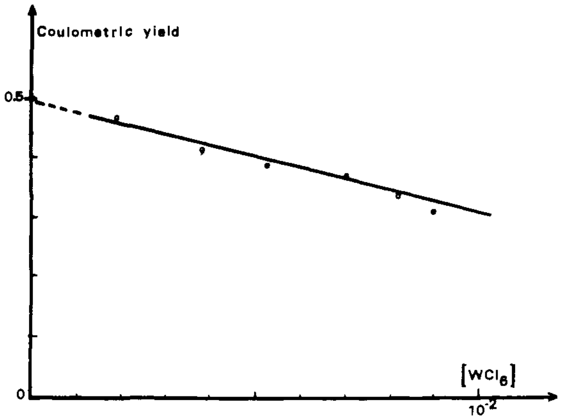

Figure 3. Determination of the coulometric yield during electroreduction of WCl_6 as a function of WCl_6 content; Al anode, Pt cathode, CH_2Cl_2 solvent (30 mL); E_c = +900 mV vs. SCE.

and $MoCl_5$. These results indicate that the active species must be in a high oxidation state. In contrast, reductions at lower potentials give rise to side reactions such as oligomerization and/or polymerization.

(2) More intriguing are the coulometric yields obtained when reduction is conducted on the first wave, where theoretically, 1 faraday/mol of transition metal should be consumed, corresponding to a $W^{VI} \rightarrow W^{V}$ or $Mo^{V} \rightarrow Mo^{IV}$ pathway. For WCl_6 as well as $MoCl_5$, one generally observes 20–30% of the theoretical reduction, which indicates that most of the starting tungsten or molybdenum salts must be either reduced by route other than the electrochemical one or transformed by a chemical reaction into other products, which are not electrochemically reducible at this high controlled-potential level.

Influence of the Tungsten Hexachloride Concentration on the Coulometric Yields during Electroreduction. As it is well-known that water-free dichloromethane is difficult to obtain, the water content of our solvent has been carefully analyzed in order to account for the amount of tungsten hexachloride chemically transformed before electrolysis during dissolution by the reaction $WCl_6 + H_2O \rightarrow WOCl_4 + 2HCl$ and hence to calculate the quantity of reducible WCl_6 after this hydrolysis has occurred. $WOCl_4$ is not reducible at 900 mV vs. SCE, so the true coulometric yields can be deduced after exhaustive electrolysis of the solutions at this potential. Thus, from a study at different WCl_6 concentrations (Figure 3), it is shown that the electrochemical yield varies regularly and reaches its upper value of 0.5 at high dilution for the theoretical $W^{VI} \rightarrow W^{V}$ step.

This result explains the lack of reproducibility during reductions and gives an interesting support for the mechanistic study of these reductions: a maximum of 50% of the starting chloride is electrochemically reduced during this process.

Metathesis of Other Internal Olefins. In the electrochemical $WCl_6/e^-/Al/CH_2Cl_2$ system, β-olefin metathesis reaction using 2-hexene or 4-nonene occurs, but with a lower activity (345 and 70 h^{-1}, respectively). This result is in accordance with previous studies on other systems[6] that have shown decreasing activity with the chain length. Again in each case the reactions proceed without isomerization.

Metathesis of α Olefins. Most catalytic systems that use WCl_6 as precursor are inefficient for metathesis of α olefins[7] and give rise to side reactions.[8] Nevertheless, at 80 °C, metathesis of α olefins takes place with WCl_6 when the reducing agent is $SnBu_4$.[9] The unusual selectivity obtained with β olefins on our electrochemical systems led us to test these new catalysts in metatheses of α olefins. As indicated in Table III, this attempt was successful: ethylene and 5-decene were produced with 1-hexene along with some polymer.

Table III. Metathesis of 1-Hexene on Different Electroreduced Systems[a]

catalytic precursor	[olefin]/[metal]	reaction time	conversion, %	R_{to}, h^{-1}	selectivity, %
WCl_6	500	1 h	58.6	360	40.3
WCl_6[b]	100	30 min	89	150	47.3
WCl_6[c]	100	3 h	20	10	24.3
$MoCl_5$	100	4 h	92	30	5.1

[a] [M] = 10^{-2} M; solvent = CH_2Cl_2 (30 mL); anode Al; cathode Pt; E_c = +900 mV/SCE. [b] Ethylene was allowed to escape. [c] Without electroreduction, by stirring the aluminum foil within 12 h before introduction of the olefin in the WCl_6/CH_2Cl_2 solution.

Table IV. Product Distribution after Cross Metathesis of 1-Pentene and 2-Pentene[a]

olefin	mol %	olefin	mol %
ethylene	8	4-octene	7.9
propene	15.7	3-heptene	15.7
1-butene	7.6	2-hexene	7.6
2-butene	6	3-hexene	6
1-pentene	0	2-pentene	18

[a] Conditions: [WCl_6] = 10^{-2} M; [1-pentene] = [2-pentenes] = 0.5 M; solvent = CH_2Cl_2 (30 mL).

Table V. Conversion and Selectivity during Consecutive Reloadings of 1-Pentene and 2-Pentene Mixtures on a WCl_6 Electroreduced Catalytic System[a]

loading	introduction time	analysis time	conversion of 2-pentene, %	selectivity, %	turnover
1	0	18	76	93	70.5
2	20	50	62	93	115
3	60	90	54	93	151

[a] Conditions: same as in Table IV. [Olefin]/[W] = 300 at the end of the experiment.

For α olefin metathesis, the best selectivities obtained were 50% with WCl_6, whereas $MoCl_5$ is essentially inactive.

Cross Metathesis between α and β Olefins. Table IV gives the product distribution for a typical reaction conducted with an equimolar mixture of 1-pentene and 2-pentene, on an electrochemically reduced WCl_6 under standard conditions but at ambient temperature after 20 min of reaction.

The selectivities obtained under these conditions are quite high (93%), and the catalyst is sufficiently stable to allow several reloadings of the olefin mixture, as indicated in Table V.

These series of experiments confirm the superiority of this system to the chemical ones, which function generally only with one loading of substrate. In the same way, 1-butene and 2-butene are readily transformed by the same catalytic system, after transfer of the solution from the electrolytic cell into an autoclave pressurized by the substrates. For an olefin/W ratio of 500, the equilibrium mixture is attained after 5 h at ambient temperature. The mixture contains ethylene (4.5%), 3-hexene (4.3%), propene (20%), 2 pentenes (20%), 1-butene (12.6%), and 2-butenes (34.4%).

Discussion

From the above data, it appears that the formation of the active species for metathesis of olefins is directly related to the CH_2Cl_2 content of the solution, and it is also noteworthy that a solvent such as $(-CH_2Cl)_2$ is also suitable for this reaction, although to a lesser extent (Table I). At this stage, from the observation that an aluminium anode is necessary to provide efficient catalytic mixtures, it seems highly probable that the Al/CH_2Cl_2 or $(-CH_2Cl)_2$ combinations have an important role in producing the catalytically active species. This assumption also must be applied

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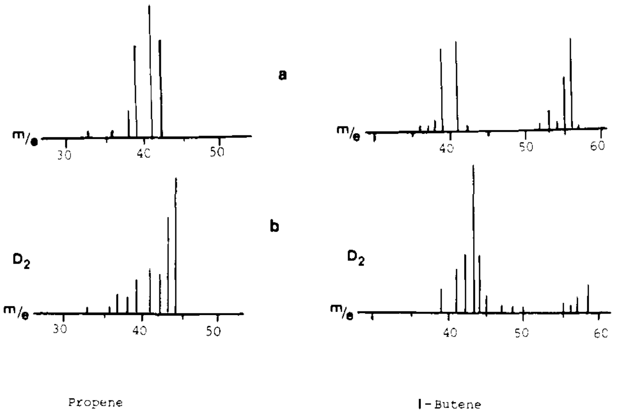


Figure 4. Mass spectra of propene (left) and 1-butene (right) during the initial step of metathesis with CH_2Cl_2 (a) and CD_2Cl_2 (b).

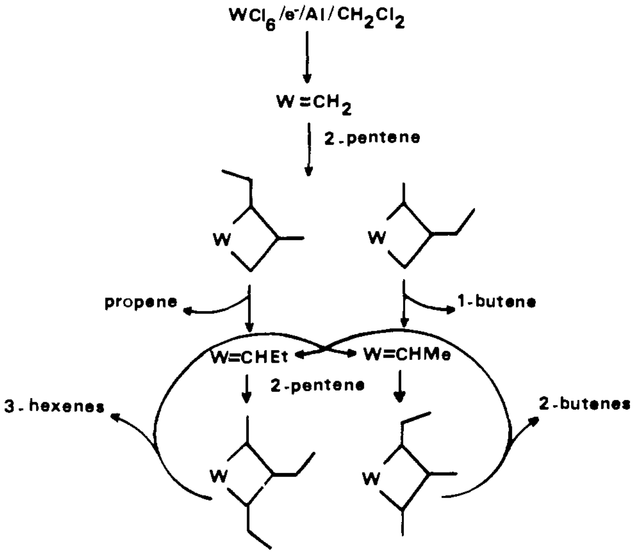
reasonably to purely chemical $WCl_6/Al/CH_2Cl_2$ or $MoCl_5/Al/CH_2Cl_2$ systems, which have been shown to give some catalytic activity, but with lower selectivities (Table I). The next section presents the mechanistic implications of this reaction.

Initial Products during Metathesis of β Olefins. Since it is now generally accepted that the propagation step of this reaction involves metallacarbene intermediates, the approach involved looking at experiments that could provide evidence for the synthesis of this kind of active species during the initiation step. For that purpose, a study of the nature of the products formed at very low conversion has already been taken as a proof for carbene formation during metathesis of 2,8-decadiene on $Mo(NO)_2(PPh_3)_2Cl_2/Me_3Al_2Cl_2$ and $WCl_6/SnBu_4$ systems;[10] this technique was even used to account for the amount of metallacarbene formed during the reduction step of the catalyst. In the same way, we have tried to make a careful analysis of the products at the early stage of the reaction. The following data show that the nature of the initial products was different when the solvent was changed from CH_2Cl_2 to $(-CH_2Cl)_2$-: With the $WCl_6/e^-/Al/CH_2Cl_2$ electroreduced system, addition of 2-pentene is followed by an intermediate production of propene and 1-butene, before the normal metathesis compounds (2-butenes and 3-hexenes) begin to appear. With 2-hexene, the same catalyst gives initially propylene and 1-pentene, whereas 1-pentene and 1-hexene are also detected with 4-nonene under the same conditions. In contrast, when $(-CH_2Cl)_2$ is used as solvent, 2-butenes and 3-hexenes are immediately formed with 2-pentene. So the question arises as to which is the source of the methylene moieties appearing only with CH_2Cl_2 as solvent. In order to prove that the methylene group arises from this solvent, experiments were conducted with CD_2Cl_2 under the same conditions. Thus, when 2-pentene was injected into a catalytic solution prepared by electroreduction of WCl_6 in CD_2Cl_2, only $CD_2CH{=}CH_3$ and $CD_2{=}CHC_2H_5$ were initially formed, as indicated in the mass spectrometry data given in Figure 4.

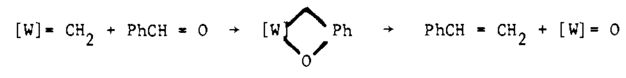
As all propene and 1-butene molecules were labeled, the methylene moieties arise from the solvent, which must take part in the formation of reactive organometallic species and yield the active initial products, through interaction with 2-pentene. According to these results, and as the production of the normal metathesis compounds 2-butenes and 3-hexenes follows the initial burst of propene and 1-butene, a mechanism in which a metallacarbene initiator and metallacyclobutanes intermediates are involved can be reasonably envisaged[5] (Scheme I).

Chemical and Spectroscopic Evidence for the Metallocarbene Complex Production. The above experiments give information about the amount of carbene formed during the electroreduction step, by careful analysis of the quantity of propylene and 1-butene evolved at the early stage of the reaction. Nevertheless, subsequent metathesis of these olefins in solution does not allow any accurate determination of these products and hence of the methylene content in the mixture, so that it was preferable to find another method giving a product, less volatile, which could not be transformed under our experimental conditions.

Scheme I



Scheme II



One possibility was to inject a carbonyl compound such as cyclohexanone, which has been shown by Tebbe to give methylenecyclohexane by interaction with the potential carbene complex $Cp_2TiCH_2AlClMe_2$.[11] Our choice was benzaldehyde, which should give styrene by a stoichiometric process similar to that involved for olefin metathesis (Scheme II).

This assumption was confirmed by further experiments where benzaldehyde was introduced just after electrolysis of WCl_6 in standard conditions, but at −20 °C. After 30 min of reaction, a maximum of 10% yield of styrene was obtained, indicating that 10% of the starting WCl_6 had been transformed to carbene complexes. This carbenic structure was finally confirmed by ^{13}C NMR spectroscopy undertaken directly on the electroreduced solution of WCl_6, in a sealed tube in $CDCl_3$ solvent: one observes a singlet whose chemical shift (299.7 ppm) is appropriate for a methylene carbene complex.

Carbene Generation Mechanism. The major problem now is to give an explanation for the carbene production mechanism. The essential features that could give some help in this context are summarized as follows: (1) The metallocarbene initiator contains a methylene group that arises from the solvent. (2) An aluminium anode is essential to obtain a good activity. (3) The selectivity strongly depends upon the cathodic potential, which is optimized at +900 mV vs. SCE, corresponding to the first reduction step $W^{VI} \rightarrow W^{V}$. (4) Under these conditions, the maximum coulometric yield accounts for only 50% of this theoretical reduction step. (5) Although the best systems are obtained by electrochemical reduction, the purely chemical $WCl_6/Al/CH_2Cl_2$ combination also gives some catalytic activity, which can be greatly improved upon treatment with CH_2Br_2.[12] However, it has to be pointed out that with these purely chemical systems, the initial activity depends upon the stirring time of aluminium and WCl_6 in CH_2Cl_2 before introduction of the olefin and that the selectivity in normal metathesis products (2-butenes and 3-hexenes) decreases, as a result of an isomerization of the substrate and

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(12) An in situ preparation of this kind of catalyst was made, initiated by CH_2Br_2 (3 mL) in CH_2Cl_2 (27 mL) with an aluminium foil and WCl_6 at ambient temperature for 12 h. This mixture gave an efficient catalytic system (R_{to} = 970 h^{-1}) for metathesis of 2-pentene but was less selective for α olefins.

Scheme III. Proposed Reaction Mechanism for the Production of Metallacarbene Species during Electroreduction of WCl_6 in the Presence of CH_2Cl_2

Cathode $$WCl_6 + e^- \rightarrow WCl_6^-$$

Anode $$WCl_6^- + Al \rightarrow AlCl + WCl_5 + e^-$$

and $$WCl_6 + \text{"Al"} \rightarrow WCl_5 + AlCl$$

$$AlCl + CH_2Cl_2 \rightarrow \underset{\text{(I)}}{Cl_2AlCH_2Cl}^{17}$$

$$WCl_6 + 2\,\text{(I)} \rightarrow CH_2 = WCl_4 + 2\,AlCl_3 + CH_2Cl_2$$

$$2WCl_5 + \text{(I)} \rightarrow CH_2 = WCl_4 + AlCl_3 + WCl_6$$

products. This behavior is confirmed by the decrease in selectivity with α olefins (Table III).

The results suggest that the electrochemical course of the reduction step follows the overall reaction sequence depicted in Scheme III. In this scheme, we believe that the cathodic reduction of WCl_6 leads first to WCl_6^-. The anodic sequence and the subsequent chemical reactions are the key steps of the carbene formation: attack of the aluminium anode by this anion gives an "AlCl" moiety, which has been shown to react with CH_2Cl_2[13] to give the organoaluminic compound I. The activated aluminium "Al" anode itself can react directly with WCl_6 and give the same "AlCl" moiety by a pure chemical reaction. The organoaluminium compound I is then supposed to react further with WCl_6 and WCl_5 to produce the metathesis initiator $Cl_4W{=}CH_2$.[14] This hypothesis is supported by recent investigations of Muetterties[15] on $WOCl_4/(CH_3)_2Mg$-based catalytic systems, in which a $CH_2{=}WOCl_2$ metathesis intermediate is proposed, as well as other recent results by Osborn[16] on addition of aluminium halides on $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Br_2$ carbene complexes.

The same scheme can be applied to the $WCl_6/e^-/Al/(-CH_2Cl)_2$ system, in which case $Cl_2AlCH_2CH_2Cl$ (I′)[17] is formed and reacts further with the tungsten salts to give a $Cl_4W{=}CHCH_3$ intermediate. In contrast with the methylene complex, this new metallacarbene initiator should not give any propene and 1-butene byproducts during metathesis of 2-pentenes: indeed, one observes an initial burst of 2-butene, followed by an equimolar production of 2-butenes and 3-hexenes. For the chemical $WCl_6/Al/CH_2Cl_2$ combination, at least in part, the same kind of catalytic activation can be envisaged reasonably, as one can suggest that the direct redox reaction

$$WCl_6 + \text{"Al"} \rightarrow WCl_5 + \text{"AlCl"}$$

occurs at the aluminium foil, and is followed by the same process as depicted in Scheme III. This kind of activation parallels the electrochemical process in concentrated WCl_6 solutions and explains the decrease of electrochemical yield with WCl_6 content. The main difference between the electrochemical and chemical system is due to the fact that the oxidation states of the catalyst are different in these two cases, owing to the electrode potential stabilization during electroreduction: as soon as the tungsten hexachloride is present in solution, reduction can occur at the imposed potential (+0.9 V vs. SCE), but the current readily stops when the reduction has occurred (Figure 1), indicating that no more reaction takes place. In particular, the high potential level avoids any further reduction of the tungsten species, which then stay in a high oxidation state, which is believed to be formally W^{VI} in the case of WCl_6 ($CH_2{=}WCl_4$) and Mo^V with $MoCl_5$ ($CH_2{=}MoCl_3$) (taking a carbene as a dianion). This assumption in confirmed by ESCA studies on the yellow solid obtained upon evaporation of the electroreduced WCl_6 solutions, which gave a W $4f_{7/2}$ binding energy of 36.85 ± 0.1 eV. This high value has to be compared to that of pure WCl_6 (37.05 ± 0.1 eV), which is, however, slightly higher. In the case of chemical systems, which are less active and selective as indicated above, the lack of selectivity can be explained by a pronounced reduction of the tungsten species, in which case a drastic effect on the metathesis reaction has already been observed, when this reduction was conducted electrochemically at low potentials (Table II).

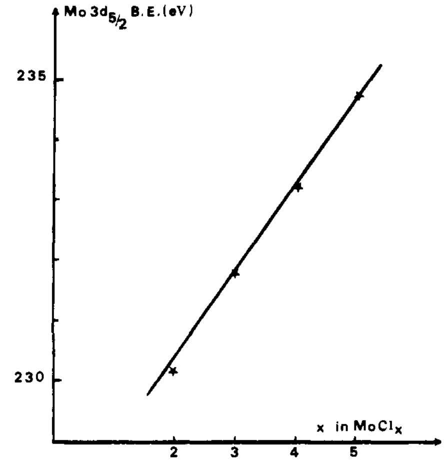

Figure 5. Binding energy of the molybdenum $3d_{5/2}$ level as a function of the apparent oxidation state of molybdenum in $MoCl_x$ complexes.

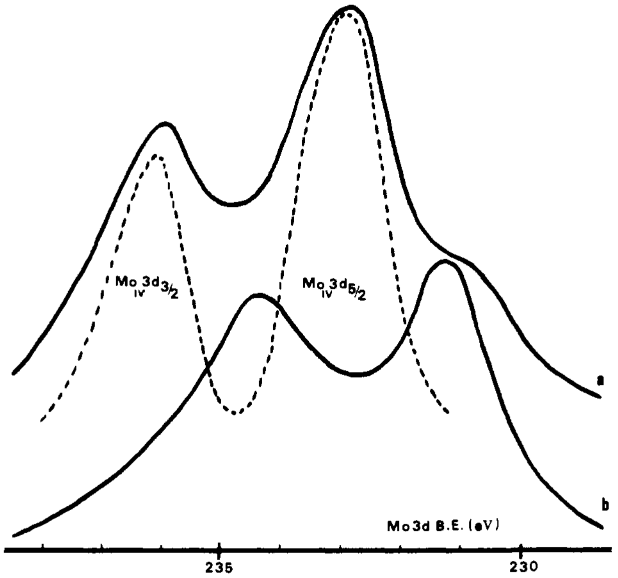

Figure 6. Comparative ESCA spectra of molybdenum-reduced complexes obtained from electroreduction (a) and chemical reduction (b) of $MoCl_5$ in CH_2Cl_2 with aluminium; the dotted line corresponds to the spectrum of $MoCl_4$.

ESCA measurements again will help us to confirm this hypothesis. For this particular study, a comparison of the electro-

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[13] E. H. Mottus and M. R. Ort, *J. Electrochem. Soc.*, **117**, 7, 885 (1970).

[14] The reaction of Cl_2AlCH_2Cl with a second "AlCl" moiety could also have been suitable to give $Cl_2AlCH_2AlCl_2$ (II), which can also react with WCl_6 to give a carbene complex, $Cl_4W{=}CH_2$. However, catalytic reactions conducted with WCl_6 chemically transformed by II have been shown to be less active and selective for metathesis of β olefins and gave no metathesis at all with α olefins. Another attractive possibility could have envisaged other organoaluminic compounds such as $ClAl(CH_2Cl)_2$ or $Al(CH_2Cl)_3$, obtained also by reaction between "AlCl" and CH_2Cl_2, which are better reducing agents and less acidic. Unless such compounds could be prepared and submitted to reaction with WCl_6, one cannot ascertain unambigously that they do not intervene in the proposed mechanism. Anyway, the yield of carbene calculated from experiments with benzaldehyde (ca. 10%) prove that side reactions may occur during this process. In particular, the presence of ethylene before introduction of the olefin can be interpreted in terms of a coupling reaction between two carbene complexes.

[15] E. L. Muetterties and E. Band, *J. Am. Chem. Soc.*, **102**, 6572 (1980).

[16] J. R. M. Kress, M. G. Wesolek, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 514 (1982).

[17] The presence of $>AlCH_2Cl$ and $>Al(-CH_2)_2Cl$ in the reduced solutions in CH_2Cl_2 and $(-CH_2Cl)_2$, respectively, has been established by decomposition studies with methanol, which gave CH_3Cl and C_2H_5Cl, respectively.

chemical and chemical behavior of the $MoCl_5/Al/CH_2Cl_2$ catalyst has been done, as a series of molybdenum chlorides was available, providing the opportunity to obtain a relationship between the $3d_{5/2}$ binding energy of the metal atom and the formal oxidation states of molybdenum in these chlorides (Figure 5).

In Figure 6 are compared the ESCA spectra of the molybdenum-based residues obtained by evaporation of two different solutions, after a typical electrochemical reduction of $MoCl_5$ for 30 min in CH_2Cl_2 with an aluminium anode (a) and a chemical reaction conducted for 30 min under the same conditions (b). Obviously, it appears from curve b that reduction to Mo^{2+} has occurred in the purely chemical systems, whereas the corresponding signal is practically nonexistant in the electrochemical system (a), which corresponds mostly to Mo^{IV}.

These last experiments provide useful information concerning one of the most important advantages of the electroreduction technique (as compared to chemical reduction), namely a stabilization of the oxidation state of the metal for catalysis. In these reactions, it appears that the high reduction potential value avoids the production of undesirable low oxidation species, which could have given side reactions such as isomerization of the substrate and products with β olefins, and polymerization in the case of α olefins.

Conclusion

As a conclusion, the results related to the metathesis of olefins over this new kind of electrochemically induced catalytic system can be rationalized in the following way.

(1) Deuterium tracer experiments, initial kinetics of the formation of the reaction products, and spectroscopic results prove that the reaction is initiated by metallocarbenes.

(2) These metallocarbene intermediates are formed by an EC mechanism, with the participation of the chlorinated solvent (CH_2Cl_2 or $(-CH_2Cl)_2$) and the aluminium anode, probably via formation of a transient organoaluminium compound.

(3) Due to electrochemical preparation at controlled potential, which limits reduction of the tungsten on molybdenum species, these new catalytic systems are highly selective for the metathesis of β olefins and show a very good stability.

(4) Under these conditions, in contrast with their chemical homologues, these $WCl_6/Al/CH_2Cl_2$ electrochemically reduced systems also catalyze metathesis of α olefins with good activity and selectivity, as well as cross metathesis between α and β olefins.

(5) The ESCA experiments suggest that these catalytic species are in a high oxidation state and are consistent with other recent results by Schrock on tantalum and niobium complexes[18] as well as earlier experiments by Osborn[16,19] and Muetterties[15] on tungsten oxo complexes.

Experimental Section

All electrochemical and catalytic work was done under nitrogen atmosphere. the solvents and reactants were purified by distillation over calcium hydride and kept under nitrogen. 2-Pentenes (95% purity) were supplied from Fluka and carefully distilled on a Nester Faust NF 51 column to eliminate 1-pentene; 1-butene and 2-butenes were commercial Air Liquide grade and used without further purification. Experimental results (yields and selectivities) were evaluated by comparing GPC chromatograms with those of standard mixtures of reactants and products (Girdel 75 FS 2 apparatus fitted with a squalane column, held at 50°C).

Apparatus and Procedure for Electroreduction and Catalysis. The apparatus used for electroreduction was a cylindrical glass undivided cell (50 mL) with a jacket through which water from a constant-temperature bath was circulated. Reductions were carried out under magnetic stirring at a cylindrical platinium grid electrode (Fisher type, 25-mm height, 20-mm diameter) under controlled potential by means of a reference electrode located very close to the working electrode, both connected to a PRT 100-1X Tacussel potentiostat and an IGC 6N Tacussel integrator. The reference electrode Hg/Hg_2Cl_2 (aqueous saturated Hg_2Cl_2) was immersed in a bridge that contained pure solvent and separated from the catalytic solution by a glass sinter. Under such conditions, water contamination of the catalytic solution was avoided within the reduction time (ca. 10–15 min). The reference electrode was removed from the apparatus before introduction of the olefin. The anode was a concentric Al cylindrical plate (99.99% purity) purchased from Johnson Matthey (30-mm height, 15-mm diameter), treated with concentrated HCl, washed with water and acetone, and dried before use. Dissolution of WCl_6 (130 mg, 0.33 mmol) in CH_2Cl_2 (30 mL) took 15 min. The electrodes were introduced into the deep red wine solution, and electrolysis was conducted until the current has lowered to 5% of its maximum value (average time 15 min). The resulting solution was orange-yellow. The three electrodes were then removed from the solution, and the olefin along with internal standard was introduced by means of a hypodermic syringe. The reaction was then followed by GPC. For cross metathesis between 1-butene and 2-butenes, the same procedure was used, but the catalytic solution was transferred after electrolysis under nitrogen into a stainless steel autoclave, which was then pressurized with the α and β olefins previously mixed in a small steel bomb in a 1/1 ratio.

^{13}C NMR Observation of the Carbene Complex. The solution of the tungsten complex obtained after electrolysis was allowed to evaporate partly, and the saturated solution was poured into an NMR tube under nitrogen at −30 °C. Purified $CDCl_3$ was then added to this orange-yellow solution, and the tube was sealed under nitrogen. The ^{13}C 50-MHz NMR spectrum was run at room temperature on a WP 200 Bruker NMR spectrometer in the ^1H noise-decoupling mode by using the following parameters: 432000 scans, spectral width 16000 Hz, pulse width 40 μs (90°), 16K point Fourier transform. Aside from the signals corresponding to CH_2Cl_2, $CDCl_3$, and the carbene complex, no other peak appeared within the 0–500-ppm range (vs. Me_4Si).

Stoichiometric Reaction with Benzaldehyde. The reduction was carried out at −20 °C for 40 min under standard conditions (208 mg of WCl_6, 0.52 mmol, 30 mL of CH_2Cl_2; E_c = +900 mV vs. SCE, aluminium anode). The electrodes were removed from the solution, and freshly distilled benzaldehyde was then added (60 mg, 0.56 mmol) with ethylbenzene as internal standard; the production of styrene was followed by GPC, which shows a maximum yield of 10% after 90 min at ambient temperature. When the reduction was conducted at 15 °C under the same conditions (20 min), styrene was produced in 9% yield after 3 h.

X-ray Photoelectron Spectra. The photoelectron spectra were obtained by using an AEI ES 200B spectrometer. The excitation source was a Mg X-Ray anode. The binding energies given conform to the C 1s binding energy (285 eV) as a reference. For the tungsten complex, the W $4f_{7/2}$ binding energy was used to analyze the chemical shift; for molybdenum, the $3d_{5/2}$ gave the binding energies of 230.1, 231.8, 233.2, and 234.65 eV for $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$, respectively, and was then used to account for the chemical shifts in the complexes.

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Registry No. WCl_6, 13283-01-7; $MoCl_5$, 10241-05-1; Al, 7429-90-5; CH_2Cl_2, 75-09-2; $Cl_4W{=}CH_2$, 85236-42-6; benzaldehyde, 100-52-7; styrene, 100-42-5; 2-pentene, 109-68-2; 1-hexene, 592-41-6; 1-pentene, 109-67-1.

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(19) J. R. M. Kress, M. J. M. Russel, M. G. Wesolek, J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 431 (1980).