

METATHESIS CATALYSTS IV (+)

COMPETITIVE CHARACTER OF METATHESIS AND ALKYLATION REACTIONS CATALYSED

BY  $WCl_6 - EtAlCl_2$

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The olefins metathesis catalyst  $WCl_6 - EtAlCl_2$ , in an aromatic solvent, can promote both metathesis and alkylation reactions. The relative importance of these two reactions depends strongly on the molar ratios olefin/benzene and olefin/catalysts<sup>2,3</sup>); from these results, we have proposed a competitive coordination of benzene and olefin on the same active catalyst center, i.e. the coordination of two olefinic molecules promoting the metathesis reaction and the coordination of both benzene and olefin leading to alkylation.

The coordination of aromatics on  $WF_6$  has been observed since 1948 by Priest<sup>4</sup>), and Höcker has reported also an interaction between benzene and  $WCl_6$ <sup>5</sup>), but these authors give no indications about the mode of coordination of these aromatic molecules to tungsten.

In general, the presence of six  $\pi$ -electrons in the bonding  $\pi$ -orbitals of the aromatic molecule determine the occupation of three coordination sites; nevertheless, for complexes such as  $W(CO)_5(Ar)$ , Stolz<sup>6</sup>) has proposed a monodentate coordination of aromatics on tungsten : such a coordination mode could explain very well the behaviour and structure of our active catalytic center.

Moreover, this competitive coordination of aromatics and olefin is strongly supported by the practical absence of alkylation reaction with 1,5-cyclooctadiene in benzene under every conditions, since this molecule has a favourable spatial arrangement to act as a bidentate ligand occupying both vacant coordination positions.

In this paper, we report the crucial importance of the electron donor power of the aromatic ligand on the course of both metathesis and alkylation reactions. We have indeed observed that the extent of the alkylation reaction increases steadily with the degree of substitution of the ring by methyl groups along the series : benzene, toluene, xylene and mesitylene; on the opposite, ortho-dichlorobenzene is not alkylated at all by the olefin in the presence of this metathesis catalyst. Such an effect indicates again the formation of

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(+) For part III, see reference 1).

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molecular complexes between the aromatics (electron donor) and tungsten (electron acceptor), and this is further supported by the relationship between the ionisation potential of the donor<sup>7)</sup> and the importance of the alkylation/metathesis ratio, as expressed in Table I.

The structure of this complex is not precisely known as yet, but we can propose the following reaction steps to explain this catalytic alkylation of the aromatic molecule by an olefin :

- 1° reversible formation of a molecular complex between tungsten and an aromatic molecule, competing with an olefin for the same coordination position;
- 2° alkylation of the aromatic ligand by an olefin coordinated on a vicinal position of the same tungsten atom; this reaction would be governed by the intermediate formation of a  $\sigma$ -complex between the carbenium ion (ex-olefin) and the aromatic molecule, as supported by the different behaviour of the more basic metaxylene with respect to paraxylene (see Table I).

This particular problem is now under investigation, as well as the structure of the molecular complex between aromatics and tungsten.

Table I

Yields of metathesis and alkylation reactions for different aromatic hydrocarbons<sup>a)</sup>.

Aromatic molecule	Alkylation <sup>b)</sup> (%)	Metathesis <sup>b)</sup> (%)	Ionisation potential (eV)
Benzene	10	90	9,24
Toluene	33	67	8,92
Para-xylene	48	52	8,3
Meta-xylene	68	32	8,3
Mesitylene	92	8	8,1

a) Olefin used : 2-pentene. Conditions = aromatics,  $10^{-2}$  mole;  $WCl_6$ ,  $5 \cdot 10^{-5}$  mole;  $EtAlCl_2$ ,  $2 \cdot 10^{-4}$  mole; 2-pentene,  $10^{-2}$  mole. Reaction time : 1 minute.

b) Relative yields are calculated as in paper (3).

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