Fig.1 Bond Lengths and Angles

The structure was solved using the Symbolic Addition technique and all non-hydrogen atom positions located. Refinement, using block diagonal least squares and an empirical weighting scheme, proceeded smoothly and converged to an R(Fo) value of 11.5%. Phenyl hydrogen atoms were placed at calculated positions with individual isotropic thermal parameters of the atoms to which they were attached. The S - H - O hydrogen was located subsequently. Final cycles of least squares led to an R(Fo) = 7.8% and R(Fo^2) = 6.8%. Positional parameters are listed in Table 1 while bond lengths and some angles are shown in Figure 1. For clarity C - H bond lengths and angles have been omitted from the figure.

As is the case for the β-diketones, the monothio-β-diketone ring exhibits an alternation of short-long bond lengths indicative of at least partial electron localisation. The S - H - O hydrogen is located on the oxygen atom, and the whole system exists in the enolic form in a manner analogous to the β-diketones.

One of us (KET) acknowledges the tenure of an Australian Institute of Nuclear Science and Engineering Postgraduate Studentship during the course of the work.

References

1.   L.F. POWER and R.D.G. JONES, Acta Cryst., (1971), B27, 181.

2.   L.F. POWER and R.D.G. JONES, Inorg.Nucl.Chem.Letts.,(1971), 7, 35.

3.   L.F. POWER and R.D.G. JONES, Inorg.Nucl.Chem.Letts.,(1971), 7, 887.

4.   L.F. POWER, K.E. TURNER and F.H. MOORE, Inorg.Nucl.Chem.Letts.,(1972), 8, 313.

METATHESIS CATALYSTS IV [+]
COMPETITIVE CHARACTER OF METATHESIS AND ALKYLATION REACTIONS CATALYSED BY WCl$_6$ - EtAlCl$_2$

By L. Hocks [++], A.J. Hubert and Ph. Teyssié - Laboratoire de Chimie Macromoléculaire et de Catalyse Organique - Institut de Chimie - Université de Liège - SART TILMAN par 4000 Liège - Belgium.

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[2,3]; 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[4], and Höcker has reported also an interaction between benzene and WCl$_6$[5], but these authors give no indications about the mode of coordination of these aromatic molecules to tungsten.

In general, the presence of six π-electrons in the bonding π-orbitals of the aromatic molecule determine the occupation of three coordination sites; nevertheless, for complexes such as W(CO)$_5$(Ar), Stolz[6] 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

---

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[7] 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 σ-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[a].

Aromatic molecule	Alkylation[b] (%)	Metathesis[b] (%)	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, 5.10^{-5} mole; $EtAlCl_2$, 2.10^{-4} mole; 2-pentene, 10^{-2} mole. Reaction time : 1 minute.

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

References.
1) L. Hocks, A.J. Hubert, and Ph. Teyssié, Polymer Letters, in press.
2) L. Hocks, A.J. Hubert, and Ph. Teyssié, Tetrahedron Letters, 3687 (1972).
3) L. Hocks, A.J. Hubert, and Ph. Teyssié, Tetrahedron Letters, 2719 (1973).
4) H.F. Priest, W.C. Schumb, J. Am. Chem. Soc., 70, 2291 (1948).
5) H. Höcker, F.R. Jones, Makromol. Chem. 161, 251 (1972).
6) I.W. Stolz, H. Haas, R.K. Sheline, J. Am. Chem. Soc., 87, 716 (1965).
7) R.S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950).

METATHESIS REACTIONS BY IRIDIUM CATALYSTS: SYNTHESIS OF CIS-1,3-DIALKENYLCYCLOPENTANES

Renzo Rossi, Pietro Diversi, Antonio Lucherini, Lido Porri[1]
Istituto di Chimica Organica Industriale, Università di Pisa, Via Risorgimento 35
56100 Pisa, Italy

Although one of the widest scopes of the homogeneous metathesis of olefinic hydrocarbons involves the synthesis of difficulty accessible alkenes, only two reports concerning the molybdenum- or the tungsten-catalyzed synthesis of aliphatic dienes or trienes exist.[2,3] We now report the results of a synthetic and stereochemical study on the metathetical co-dimerization of norbornene 1 with aliphatic olefins, promoted by an iridium complex.

In the course of a current investigation on the catalytic activity of group VIII transition metal complexes in the metathesis reactions, we have observed that aliphatic olefins exert a marked influence on the metathetical polymerization of norbornene 1 promoted by di-μ-chlorochlorobis(cyclooctene)iridium[4]. Using aliphatic olefin/1 molar ratios higher than 1, it is possible to isolate polymeric liquid products containing terminal groups corresponding to the alkylidene moieties of the aliphatic olefin, together with metathetical co-dimers of structure 2 in amounts strongly dependent on the type of aliphatic olefin used.
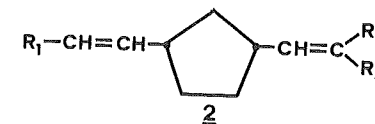
2a (R₁=R₂=Me; R₃=H) ; 2b (R₁=Me; R₂=H; R₃=Et)
2c (R₁=R₃=Et; R₂=H) ; 2d (R₁=H; R₂=R₃=Me)
2e (R₁=R₂=H; R₃=n-Pr); 2f (R₁=R₂=R₃=Me)
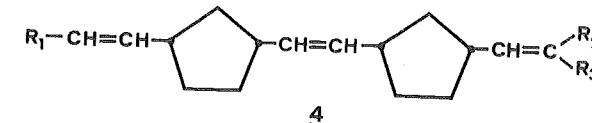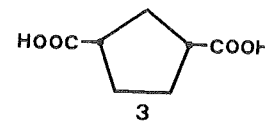
The optimal conditions in order to keep the reaction at the co-dimer level in the highest yield when vinyl, vinylidene or internal olefins are used, are reported in Table 1. The metathetical co-dimers, separated by fractional distillation from the reaction mixtures and purified by glc were identified by elemental analysis, ir, nmr and mass spectroscopy. Their structure was confirmed by degradative oxidation to cis-cyclopentane-1,3-dicarboxylic acid 3.

Reference to Table 1 indicates that the reactivity of the various aliphatic olefins em-