Olefin Metathesis by Pyridinepentacarbonylmolybdenum

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Summary Pyridinepentacarbonylmolybdenum with ethylaluminium dichloride and tetrabutylammonium chloride constitute a catalyst system for the metathesis of terminal olefins; evidence for a co-ordinated carbene-initiated process is presented, and the nature of the co-ordinated carbene formed initially is found to be solvent dependent.

A REPORT in the patent literature claimed that the system $Mo(CO)_5(py)$–$Me_3Al_2Cl_3$–R_4NCl (py = pyridine) was an effective catalyst for the metathesis of olefins.[1] We investigated the catalytic properties of the $Mo(CO)_5(py)$–$EtAlCl_2$–$Bu^n{}_4NCl$ system and found activity toward the metathesis of terminal olefins only. These results contrast with the findings of Casey[2] and Katz,[3] whose studies on structural selectivities showed that the metathesis of terminal olefins is the least favoured reaction. Nonetheless, the $Mo(CO)_5(py)$ catalyst system did not cause metathesis of internal olefins; indeed, in an attempted cross-metathesis of hex-1-ene and hex-2-ene, the only products detected were ethylene and dec-5-ene, and hex-2-ene was recovered *in toto*.

Recent evidence on the mechanism of olefin metathesis indicates that the reaction is both initiated and propagated by co-ordinated carbenes. Where the metal catalyst does not originally contain this functional group, the initial carbene can form on the metal in at least two ways: co-ordination of the alkyl group from the co-catalyst followed by α-hydrogen abstraction,[4] or attack by the alkyl group on co-ordinated CO followed by hydrogen-for-oxygen exchange.[5] Where the co-catalyst is $\mathrm{EtAlCl_2}$, the initial, co-ordinated carbene would be either ethylidene,[4] or propylidene.[5]

TABLE. Quantities of olefins initially formed in the metathesis of octa-1,7-diene.

Solvent	Octa-1,7-diene/mmol	Mo catalyst /mmol	Propene /mmol	But-1-ene /mmol
PhCl	10	2·5	0·11	0·04
	20	2·5	0·10	0·03
	30	2·5	0·10	0·02
	10	3·75	0·15	—
	10	5·0	0·19	0·04
Heptane	10	2·5	0·0	0·46
	20	2·5	0·0	0·50
	30	2·5	0·0	0·46
	10	3·75	0·0	0·75
	10	5·0	0·0	0·97

Gas evolution studies were carried out on the catalyst system to aid in the elucidation of the nature of the initially formed carbene. When the reaction was carried out in chlorobenzene solvent using $\mathrm{Mo(CO)_5(py)}$, (2·5 mmol), $\mathrm{EtAlCl_2}$ (4 mmol), and $\mathrm{Bu^n_4NCl}$ (1·25 mmol), gas (0·6 mmol) was evolved which was identified as a 1 : 1 mixture of ethane and CO. Clearly, this is the exact mixture of gases predicted if ethylidene were the initially formed co-ordinated carbene. When heptane was employed as the solvent, the results were similar to those observed for the $\mathrm{Re(CO)_5Cl}$ system,[5] indicating that the co-ordinated propylidene is the co-ordinated carbene initially formed.

If the initiating carbene is ethylidene, then the olefin that is formed initially in the metathesis of octa-1,7-diene would be propene (not one of the metathesis products). Furthermore, the amount of propene formed should vary directly with the amount of catalyst used, but be independent of the initial amount of olefin placed in the reaction. The same argument holds for propylidene as the initiating carbene, except that the olefin formed would be but-1-ene.

The metathesis of octa-1,7-diene was carried out in the two solvent systems at ambient temperatures to minimize isomerization of the olefin (optimum temperature for metathesis is in the 50–70 °C range). The amounts of both catalyst and olefin were varied and the olefin formed initially was isolated and determined quantitatively by g.l.c. The results are shown in the Table.

Whereas the catalyst is not particularly efficient at ambient temperatures, clearly, the amount of olefin formed varies directly with the amount of catalyst, and is independent of the quantity of olefin substrate. In chlorobenzene, the trace amounts of but-1-ene formed appear to indicate that the formation of propylidene also occurs to a small extent. These results provide direct evidence that the olefin metathesis reaction is both initiated and propagated by co-ordinated carbenes, and that for this catalyst system, the formation of the initiating, co-ordinated carbene is solvent dependent.

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