Olefin Metathesis by Halogenopentacarbonylrhenium–Dichloroethylaluminium Catalysts: Evidence for a Co-ordinated Carbene-initiated Reaction

By Michael F. Farona* and William S. Greenlee
(*Department of Chemistry, The University of Akron, Akron, Ohio* 44325)

Summary A mixture of rhenium pentacarbonyl chloride or bromide and ethylaluminium dichloride is a long-lived, active, homogeneous catalyst for the metathesis of terminal and internal olefins; evidence for a propyl carbene-initiated reaction, based on analysis of the product mixture, is presented.

Whereas most active homogeneous catalyst systems for olefin metathesis are based on compounds of the Group VIb metals, a few compounds of rhenium have been reported to be active. High oxidation-state rhenium compounds in systems such as $[ReCl_5]$-Bu_4Sn,[1] $[ReCl_5]$-Et_3Al,[2] $[ReCl_4(PPh_3)_2]$-$EtAlCl_2$,[3] and $[ReOX_3(PPh_3)_2]$ (X = Cl or Br)[3] have been reported to be active, but the oxidation states of the catalytically active Re species were not determined. One system of low oxidation-state rhenium has been employed in a carbonyl compound with a metal–metal bond to a Group VIb metal.[4] We report that $[Re(CO)_5X]$ (X = Cl or Br) with cocatalyst $EtAlCl_2$ is active in promoting olefin metathesis.

A solution containing $[Re(CO)_5X]$ (0·5 mmol) and $EtAlCl_2$ (4·0 mmol) in 10 ml of chlorobenzene is active for the metathesis of straight-chain olefins (terminal or internal) at 90 °C (see Table). Small amounts of products arising from isomerisation and polymerisation were also observed.

This catalyst system is unique in that it shows high stability and can be recycled for several days in contrast to the Group VIb systems which lose considerable activity after 1—8 h. Thus, if the active catalyst, employed for several hours at 90 °C is cooled to room temperature, it becomes inactive; heating to 90 °C reactivates the system. The process may be repeated for about 5 days before loss of activity is noticeable.

Recent evidence on the mechanistic aspects of other metathesis catalysts indicates that the disproportionation of olefins occurs *via* a co-ordinated carbene.[5] In the system $[Re(CO)_5Cl]$-$EtAlCl_2$, such a carbene could not arise *via* initial co-ordination of an ethyl group since no ethane or CO evolution is observed. However, the formation of $MeCH_2CH{=}Re$ groups *via* initial attack of an ethyl group on CO and subsequent elimination of oxygen might be detectable by analysis of the initial products of a metathesis reaction. Fully consistent with this, the metathesis of octa-1,7-diene over a catalyst containing 2·2 mmol of the rhenium complex yielded, after 3 min 1·5 mmol of but-1-ene, as well as the expected metathesis products. The reaction of oct-4-ene with a catalyst containing 2·5 mmol of the rhenium complex yielded, initially, 2·7 mmol of hept-3-ene. The but-1-ene and hept-3-ene are unique to their particular reactions, and careful product analysis showed that they could not have been produced by a combination of isomerisation and metathesis.

Table. Metathesis of some olefins in $[Re(CO)_5Cl_2\ EtAlCl]^-$.

Olefin	Primary products	Conversion /%	Selectivity toward indicated olefin /%	Reaction time /min
Hex-1-ene	Dec-5-ene + Ethylene	96	Dec-5-ene, 70	20
Octa-1,7-diene	Cyclohexene + Ethylene	100	Cyclohexene, 100	15
trans-Non-4-ene	Oct-4-ene + Dec-5-ene	50	Oct-4-ene, 50	45
Propene	But-2-ene + Ethylene	40	Ethylene, 50	90
cis-Pent-2-ene	Hex-3-ene + But-2-ene	80	Hex-3-ene, 50	25

Clearly, the best explanation for these data is that a co-ordinated propene carbene is the initiator of metathesis, although we cannot yet account for its formation in detail.

We are grateful to the Goodyear Tire and Rubber Co., Akron, Ohio, for use of their g.c.–m.s. apparatus.

(*Received*, 12*th May* 1975; *Com.* 535.)

---

[1] J. A. Moulijn and C. Boelhouwer, *Chem. Comm.*, 1971, 1170.

[2] Y. Uchida, M. Hidai, and T. Tatsumi, *Bull. Chem. Soc. Japan*, 1972, **45**, 1158.

[3] E. T. Kittleman and E. A. Zeuch, Fr. P. 1,561,025; *Chem. Abs.*, 1970, **72**, 31193f.

[4] W. R. Kroll and G. Doyle, *J. Catalysis*, 1972, **24**, 356.

[5] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1974, **96**, 7808; T. J. Katz and J. McGinnis, *ibid.*, 1975, **97**, 1592; E. L. Muetterties, *Inorg. Chem.*, 1975, **14**, 951.