Journal of Organometallic Chemistry, 87 (1975) C4—C6
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A MECHANISM FOR ACTIVATION OF THE PRECURSOR COMPLEX IN THE METATHESIS OF OLEFINS WITH THE CATALYTIC SYSTEM $W(CO)_5L,C_2H_5AlCl_2,O_2$

J.L. BIHOU, J.M. BASSET* and R. MUTIN

Institut de Recherches sur la Catalyse, 39 Bd du 11 novembre 1918, 69626 Villeurbanne (France)

(Received December 30th, 1974)

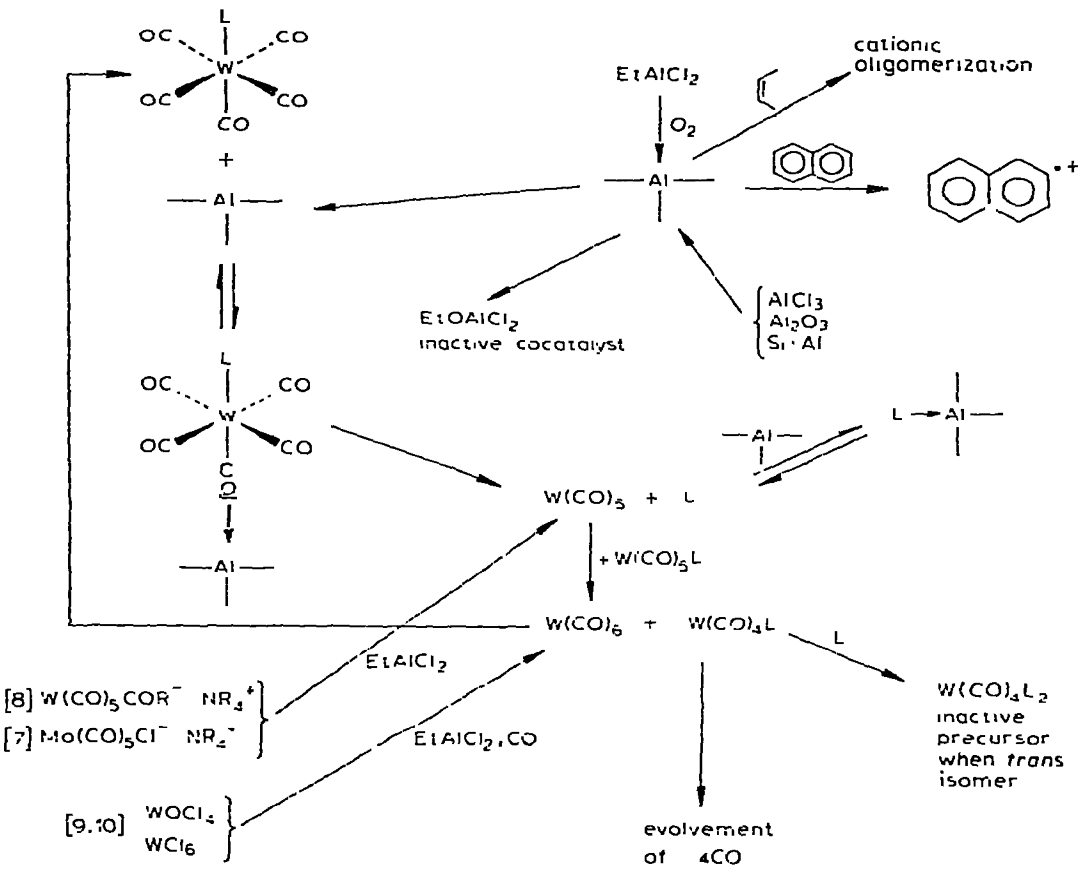
Summary

In the catalyst mixture $W(CO)_5L,C_2H_5AlCl_2,O_2$ the organoaluminium compound acts as a Lewis acid to promote formation of an active zerovalent tungsten species.

Since the first report on homogeneous metathesis of olefins by Calderon et al. [1] a great variety of precursor complexes associated with many kinds of cocatalysts have been shown to be active in this reaction [2].

We now propose a mechanism (Scheme 1) for the initial steps of activation of a zero valent precursor complex of tungsten of the type $W(CO)_5L$ where L is CO, a phosphine or a phosphite, after confirming some of the intermediates by spectroscopic studies and chemical analysis.

Olefin metathesis is possible with the precursor complexes $W(CO)_5L$ (L = CO, PPh_3, P-n-Bu_3, $P(OPh)_3$) when they are associated with $C_2H_5AlCl_2$ and molecular oxygen [3]. Each component is necessary for catalytic activity and O_2 has a strong promoting effect; thus after introduction of O_2 into $W(CO)_5L + C_2H_5AlCl_2$ + olefin, the thermodynamic equilibrium is reached in a few minutes with *cis*-2-pentene at 25°C whereas in the absence of oxygen, only 5% conversion occurs in about 22 hours. We have established that the effect of O_2 is to increase the Lewis acidity of the alkylaluminium compound [4]: it is an intermediate compound ($Al\leqq$) produced during the oxydation of $EtAlCl_2$ to $Et{-}OAlCl_2$ which is responsible for this enhanced Lewis acidity. $Al\leqq$ also catalyses cationic oligomerization of olefins [4], and also with naphthalene gives the corresponding radical cation naphthalene $^{+\cdot}$ [4]. In the absence of any base or metal carbonyl capable of acid—base complexation, $Al\leqq$ reacts further with O_2 to give $C_2H_5{-}O{-}AlCl_2$ which was found to be inactive as a cocatalyst with $W(CO)_5L$ in olefin metathesis [3]. The presence of O_2 is unnecessary if one uses $AlCl_3$ as cocatalyst with



SCHEME 1

$W(CO)_5L$: in this case thermodynamic equilibrium for metathesis of *cis*-2-pentene is reached in 5 minutes at room temperature.

In contrast to $C_2H_5AlCl_2$ alone, $Al\leqslant$ gives an adduct with $W(CO)_5L$ and this adduct has been identified by IR spectroscopy for L = PPh_3 [3], P-n-Bu_3 and $P(OPh)_3$. The aluminium atom is probably bound to the terminal oxygen of the carbonyl group *trans* to the ligand L. For such adducts, the ν(CO) vibration of the carbonyl group complexed to $Al\leqslant$ appears at about 1667 cm^{-1}, whereas the ν(CO) vibrations corresponding to the E mode appear at 1993, 1998 and 2011 cm^{-1} for L = P-n-Bu_3, PPh_3 [3] and $P(OPh)_3$, respectively. This acid–base complexation leads to considerable increase in the back-donation (d_π–p_π) of tungsten d electrons into π^* orbitals of the CO group complexed to $Al\leqslant$ and a decrease of the (d_π–p_π) or (d_π–d_π) back-donation to the other carbonyl groups of the square plane (shift of 61 ± 2 cm^{-1} of the E mode towards higher wave numbers), and to the ligand L. The adducts are in equilibrium with the starting complex and the Lewis acid, since they are observed for Al/W ratios higher than ca. 7 for L = PPh_3. Destruction of the adduct by butanol as soon as it is formed reforms the starting complex $W(CO)_5L$.

The adducts are not very stable and decompose in a few minutes at room temperature into $W(CO)_6$ (characterized by IR spectroscopy and chemical analysis for L = $P\text{-}n\text{-}Bu_3$, PPh_3 and $P(OPh)_3$) and carbon monoxide. $W(CO)_5$ is necessarily an intermediate in this decomposition which involves the loss of the ligand L, probably complexed to the Lewis acid $\mathrm{Al}\leqslant$ in excess in the medium. When the concentration of $W(CO)_6$ is maximum and equal to about ½ of that of $W(CO)_5L$, approximately two molecules of CO per starting complex are evolved. This suggests either the formation of a highly unsaturated zerovalent tungsten or a further reaction of a subcarbonyl complex with the organoaluminium compound.

In the case of L = CO the adduct could not be identified by IR spectroscopy. This is probably due to the low basicity of the carbonyl groups which leads to a low concentration of the adduct. However, decomposition of $W(CO)_6$ into carbon monoxide and a tungsten subcarbonyl was observed, but with a much slower rate than with L = PPh_3, $P(OPh)_3$ or $P\text{-}n\text{-}Bu_3$.

Formation of $W(CO)_4L$ has not been confirmed spectroscopically, but the destruction of the (phosphine → $\mathrm{Al}\leqslant$) complexation by butanol in the course of the decomposition of the adduct compound, with liberation of the phosphine PPh_3, produced $W(CO)_4(PPh_3)_2$ (*cis* and *trans*), which was identified by chemical analysis, and IR spectroscopy.

With $AlCl_3$ instead of $C_2H_5AlCl_2 + O_2$, the adduct was not identified, probably because the low solubility of $AlCl_3$ leads to a low ratio Al/W. However, a fast decomposition of the starting complex $W(CO)_5L$ into $W(CO)_6$ + CO + unidentified W compound was observed with L = $P(OPh)_3$ and PPh_3.

Our results indicate that the role of the organoaluminium compound is that of a Lewis acid, at least for the initial step of activation of $W(CO)_5L$. We have no experimental evidence so far to show at which stage of the decomposition the olefins become coordinated: ($LW(CO)_4$, W).

The mechanism we propose for formation of a zerovalent active tungsten species also explains results obtained with other precursor complexes. Starting from the zerovalent molybdenum complex $Mo(CO)_5Cl^-NR_4^+$ associated with $C_2H_5AlCl_2$, Doyle [7] isolated $Mo(CO)_6$ and concluded that the active molybdenum species is zerovalent molybdenum, the role of the alkylaluminium compound being only that of a Lewis acid. Bencze [9] found that CO had a promoting effect on olefin metathesis with the catalytic components WCl_6, $C_2H_5AlCl_2$. He also found [9] that $WOCl_4$ (or WCl_6) can be reduced to zerovalent tungsten by $C_2H_5AlCl_2$ in the presence of carbon monoxide with formation of $W(CO)_6$. Finally Lewandos and Pettit [5, 6] found that toluene—$W(CO)_3$ is active on its own in olefin metathesis by loss of the toluene ligand and of at least one CO group.

References

1 N. Calderon, H.Y. Chen and K.W. Scott, Tetrahedron Lett., (1967) 3327.
2 W.B. Hughes, Organometal. Chem. Syn., 1 (1972) 341.
3 J.M. Basset, R. Mutin, H. Praliaud, G. Couduner and Y. Trambouze, J. Catalysis, 34 (1974) 196.
4 J.M. Basset, H. Praliaud, G. Coudurier, Y. Ben Taarit and R. Mutin, J. Organometal. Chem., 74 (1974) 167.
5 G.S. Lewandos and R. Pettit, Tetrahedron Lett., (1967) 789.
6 G.S. Lewandos and R. Pettit, Tetrahedron Lett., (1971) 780.
7 G. Doyle, J. Catalysis, 30 (1973) 118.
8 W.R. Kroll and G. Doyle, Chem. Commun., (1971) 839.
9 L. Bencze and L. Markó, J. Organometal. Chem., 28 (1971) 271.
10 L. Bencze, J. Organometal. Chem., 37 (1972) C37.