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Preliminary communication

HALO-NITROSYL-CARBONYL-TUNGSTEN COMPLEXES AND THEIR TRIPHENYLPHOSPHINE DERIVATIVES AS OLEFIN METHATHESIS CATALYSTS

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Summary

The tungsten complexes $W(CO)_4(NO)X$, $W(CO)_3(NO)(PPh_3)X$ and $W(CO)_2(NO)(PPh_3)_2X$ (X = Cl, Br and I) have been shown to be effective catalysts for the metathesis of 1,7-octadiene.

The recent study of the use of $MoCl(NO)(CO)_2(PPh_3)_2$ with $EtAlCl_2$ in chlorobenzene as a homogeneous olefin metathesis catalyst [1] prompts us to report on the three series of compounds $W(CO)_4(NO)X$, $W(CO)_3(NO)(PPh_3)X$ and $W(CO)_2(NO)(PPh_3)_2X$ (X = Cl, Br and I).

All of the tungsten complexes studied showed substantially higher activities in the metathesis of 1,7-octadiene to cyclohexene and ethylene than the well known metathesis catalyst $Mo(NO)_2Cl_2(PPh_3)_2$ [2] (Table 1). The observed values for initial rate compare with results obtained by other tungsten metathesis catalysts [3]. There is a marked increase in activity if the cocatalyst/catalyst ratio (i.e. Al/W) is increased from 6/1 to 10/1 for the non-phosphine substituted compounds. The initial rate of metathesis is higher and the time to reach maximum conversion is shorter. The most active species is $W(CO)_4(NO)I$ which reaches 95% conversion within twenty minutes.

For the phosphine-substituted derivatives two observations can be made. Firstly that changing the Al/W ratio enhances the activity of only some of the complexes and, interestingly, that of the chloro derivatives is improved most. Secondly the monophosphinated derivatives are more active than the diphosphinated ones. Both points are relevant to the recent discovery of the highly active, long living catalyst $MoCl(NO)(CO)_2(PPh_3)_2$ which can be prepared from $Mo(NO)(CO)_4(AlCl_4)$ and triphenylphosphine [1]. The monosubstituted compound is not isolated from the reaction mixture. By contrast all our derivatives

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TABLE 1

METATHESIS OF 1,7-OCTADIENE AT ROOM TEMPERATURE

Catalyst	Initial rate[a]		% Conversion[c]	Time (min)
	Al/W 6/1	Al/W[b] 10/1		
$W(CO)_4(NO)Cl$	0.6	1.0	86	240
$W(CO)_4(NO)Br$	1.3	4.0	75	45
$W(CO)_4(NO)I$	0.5	13.3	95	20
$W(CO)_3(NO)(PPh_3)Cl$	1.5	10.0	63	120
$W(CO)_3(NO)(PPh_3)Br$	2.0	8.0	77	270
$W(CO)_3(NO)(PPh_3)I$	1.5	1.5	64*	120
$W(CO)_2(NO)(PPh_3)_2Cl$	0.5	3.0	70*	120
$W(CO)_2(NO)(PPh_3)_2Br$	0.7	0.5	80*	120
$W(CO)_2(NO)(PPh_3)_2I$	0.5	0.3	61*	120
$Mo(NO)_2(PPh_3)_2Cl_2$	0.1	0.2		
$W(CO)_6$	0.02			
WCl_6	0.01			

[a] moles cyclohexene/mole catalyst/minute. [b] $EtAlCl_2$ /W catalyst. [c] using Al/W at 10/1 except where an asterisk indicates Al/W at 6/1.

are obtained by direct substitution of $W(CO)_4(NO)X$ [4]. The higher activity of the monosubstituted compounds may be significant in determining the nature of the catalytic species derived from Group VI nitrosyl carbonyl halides [5].

The monophosphinated derivatives $W(CO)_3(NO)(PPh_3)X$ have been attached to functionalised polystyrene polymer beads and early results show no loss of activity caused by the change from a homogeneous to a heterogeneous system.

All reactions were carried out using W/Al/alkene ratios of either 1/6/100 or 1/10/100 in 30 cm^3 chlorobenzene at room temperature, under nitrogen. The catalyst and cocatalyst had been stirred together for ten minutes before the alkene was added. The products were analysed by GLC.

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