

Carbene Complexes of the Group VI Metals as Olefin Disproportionation Catalysts

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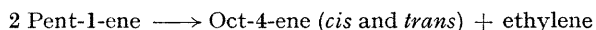
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Summary Group VI metal carbene complexes of the type $\text{NR}_4[\text{M}(\text{CO})_5\text{COR}']$ can be activated with alkylaluminum halides to give catalysts which disproportionate not only non-terminal olefins but also terminal olefins.

SOLUBLE catalyst systems for olefin disproportionation derived from WCl_6^{1-3} and from $[\text{Ph}_3\text{P}]_2\text{MoCl}_2(\text{NO})_2^{4,5}$ have been reported. The catalysts described herein not only contain different ligands but also specify the use of low-valent Group VI metal carbene complexes. In contrast to the systems derived from WCl_6 in which only non-terminal olefins were satisfactory reactants, these complex carbene catalysts will effect the disproportionation of terminal olefins at a high rate.

The ionic carbene complexes can be easily prepared⁶ and belong to the general type $\text{NR}_4[\text{M}(\text{CO})_5\text{COR}']$ where $\text{R}' = \text{Me}$ or Ph . Treatment of these complexes (which are not catalytically active by themselves) with alkylaluminum dichlorides or alkylaluminum sesquichlorides in chlorobenzene leads to brown solutions which are active catalysts for olefin disproportionation at ambient temperature.

The test reaction carried out was the disproportionation of pent-1-ene:



In a typical disproportionation reaction (Table), to the carbene complex (0.5 mmol) in chlorobenzene (10 ml) was added pent-1-ene (10 ml). The reaction was started by activation with methylaluminum dichloride (5 ml; 1 M) in chlorobenzene at ambient temperature. The reaction was followed by measuring the amount of ethylene formed and was terminated after 4 h and the volatile liquid reaction products were analysed by g.l.c. Although no exact rate

studies were carried out the evolution of ethylene was used to distinguish very active catalysts from less active ones.

TABLE

Disproportionation of pent-1-ene at ambient temperature

Transition metal carbene complex $\text{NBu}^n_4[\text{M}(\text{Co})_5\text{COR}']$	Wt. % C_8 olefins (solvent-free)	
M	R'	
Mo	Me	45
Mo	Ph	62
W	Me	16
W	Ph	45

The order of reactivity for the disproportionation of pent-1-ene is clearly $\text{Mo} > \text{W}$ and $\text{Ph} > \text{Me}$. Lower rates are observed if the Bu^n_4N^+ cation is replaced by Me_4N^+ or Li^+ . Similarly other olefins were disproportionated *e.g.*, 4-methylpent-1-ene and pent-2-ene. The disproportionation of octa-1,7-diene gave cyclohexene and ethylene in 29% yield and 99% selectivity.

The use of neutral carbenes⁶⁻⁸ of the type $\text{W}(\text{CO})_5(\text{COMe})\text{Et}$ and $\text{W}(\text{CO})_5[\text{CNMe}_2]\text{Me}$ was briefly investigated. Using the same reaction conditions as in the Table there was only a trace of disproportionation. However when 0.25 mmol NBu^n_4Cl was added to the above catalyst system the conversion into octenes increased to 98% and 75% (by weight), respectively.

Our data demonstrate for the first time that carbonyl-containing Group VI metal complexes can be activated for the homogeneous disproportionation of olefins at low temperatures.

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