Hydridic Agents as Co-catalysts in the Olefin-metathesis Reaction

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Summary Lithium aluminium hydride and sodium borohydride are extremely effective co-catalysts with tungsten(VI) chloride in the olefin-metathesis reaction.

IT has been established that alkylating agents such as ethylaluminium dichloride,[1] alkyl-lithiums (LiBu^n, LiBu^s, or LiBu^t),[2] Grignard reagents (Pr^{n}MgBr or BuMgI),[3] and tetrabutyltin[4] are necessary to produce catalytic systems from tungsten(VI) chloride or rhenium(V) chloride for the metathesis of olefins. We now report that hydridic agents such as lithium aluminium hydride and sodium borohydride also form catalytic systems for this reaction from WCl_6, and that these are comparable in activity with those derived from Grignard or alkyl-lithium reagents. Thus pent-2-ene is converted into its equilibrium mixture with but-2-ene and hex-2-ene in less than 3 h employing WCl_6 and an excess of $LiAlH_4$ (W:olefin = 1:100).†

Although this equilibration time is longer than for WCl_6–$EtAlCl_2$ systems, it can be reduced considerably by mixing the WCl_6 and $LiAlH_4$ for 2—3 h before the introduction of the olefin, the pre-mixing affording a suspension of a solid mixture in an orange-red solution. An equilibrium mixture of olefins is then produced within 15 min of the introduction of olefin even for a W:Al ratio of 1:1. This shorter interval includes an induction period, after which metathesis occurs very rapidly. The interaction of olefin with the WCl_6–$LiAlH_4$ mixture is considerably exothermic. The equilibration is still slower than when catalysed by WCl_6–$EtAlCl_2$ systems, but has the added virtue that it is not accompanied by significant alkylation of the aromatic solvent.[5]

Sodium borohydride also affords an active metathesis catalyst with WCl_6, but the system derived from lithium hydride and WCl_6 is barely catalytic and the calcium hydride–WCl_6 system is completely inactive. Lithium aluminium hydride does not produce catalytic systems with niobium(V) chloride, tantalum(V) chloride, tetrachlorobis(triphenylphosphine)tungsten(IV), or tetrachlorobis(dimethylphenylphosphine)tungsten(IV), although some catalytic activity is produced with molybdenum(V) chloride and rhenium(V) chloride.

It has been suggested[1] that WCl_6 reacts to form $EtAlCl_2$ or LiBu with, transiently, WCl_4, which interacts with the olefin to produce the catalyst. However, we find that treatment of WCl_6 with reducing agents such as zinc, magnesium, or sodium amalgam, which should produce WCl_4, does not lead to catalytically active species.

We conclude that metal alkyls and/or hydrides, which are generally interconvertible in the presence of olefins, function not only as reducing agents, but as significant components

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† All reactions in chlorobenzene; reagents mixed at ambient temperature.

of the catalyst system and should not summarily be excluded from mechanistic considerations. Also, a non-transition metal, *e.g.* aluminium, capable of binding to tungsten, perhaps through hydrogen or alkyl bridges, appears to be a constituent of the catalyst.

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