Selective Catalytic Oligomerizations and Hydrogenations Using Polymer-anchored Complexes of Nickel and Iridium

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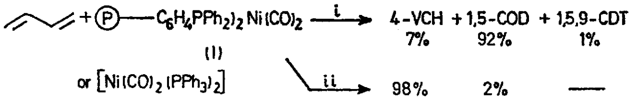
Summary Polystyrene–divinylbenene resin-anchored $[Ni(CO)_2(PPh_3)_2]$ has been used selectively to oligomerize butadiene to either 4-vinylcyclohexene or cycloocta-1,5-diene, and anchored $[Ir(Cl)(CO)(PPh_3)_2]$ selectively catalyses the hydrogenation of cyclo-octa-1,5-diene to cyclo-octene; the activity of these catalysts in some cases surpasses that of their homogeneous counterparts under identical conditions.

Anchoring homogeneous catalysts on to resins to give a fixed-bed catalyst which has the selectivity of the original homogeneous species is receiving increased attention.[1] Cyclo-oligomerization of butadiene by $[Ni(CO)_2(PPh_3)_2]$ gives 4-vinylcyclohexene (4-VCH; 30%), cyclo-octa-1,5-diene (1,5-COD; 60%), and cyclododeca-1,5,9-triene (1,5,9-CDT; 10%).[2,3] The product distribution could be varied by using carbon monoxide or phosphites.[2]

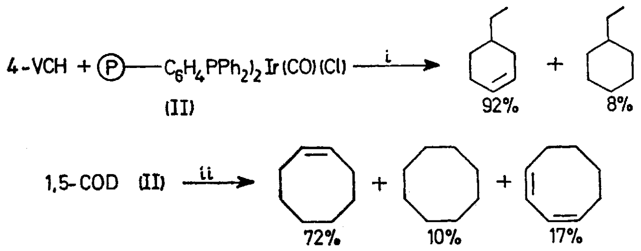
We now report that butadiene was selectively converted into 4-VCH (98%) using either $[Ni(CO)_2(PPh_3)_2]$ or its resin-anchored form, (I) (styrene–1% divinylbenzene 1·33% P, P:Ni = 2:1) in the presence of CO (10 lb in^2) in tetrahydrofuran (THF) or benzene at 115 °C (Scheme 1). CO slows the oligomerization. The rate using (I) was *ca.* 30% of the rate using $[Ni(CO)_2(PPh_3)_2]$ under these conditions in benzene, presumably owing to diffusion limitations. In multiple runs (4 recycles) the molar turnover with (I) was >2000 in benzene and *ca.* 1000 in THF, which caused leaching of Ni from (I) which was slowed using a 2% divinylbenzene resin (Ia) (1·75% P, P:Ni = 2:1).



Scheme 1. i, tri-*o*-tolyl phosphite; 115 °C, C_6H_6; ii, CO (10 lb in^2), 115 °C, THF or C_6H_6.

Commercial styrene–divinylbenzene (Bio Rad Labs, SX-1 or SX-2 resins, 200—400 mesh) was brominated (dark) using Br_2–$FeBr_3$ and then treated with excess of $LiPPh_2$ or $NaPPh_2$ in THF to provide a series of resins with 0·7—4·0% P.[1,4] The metal complexes were anchored by simple phosphine exchange with multiple anchoring to the polymer prevailing.[1,5]

Butadiene was also converted selectively (92%) into 1,5-COD using (Ia) with a 4 mol. excess of tri-*o*-tolyl phosphite in benzene (Scheme 1). The product distribution was identical using $[Ni(CO)_2(PPh_3)_2]$ in place of (Ia) and the rate was 3 times that with (Ia). At the maximum molar turnover (>1300) the ν(CO) i.r. bands had disappeared. The activity was determined in a fixed-bed operation. The catalyst (Ia) was deactivated on recycling.



Scheme 2. i, C_6H_6, 80 °C, H_2 (100 lb in^2), 1·75 h; ii, H_2 (100 lb in^2), 90 °C, DMF, 2 h.

Anchored Vaska's complex (II) selectively catalysed the hydrogenation of 4-VCH to 4-ethylcyclohexene (92%) and 1,5-COD to cyclo-octene (72%) under the conditions in Scheme 2. Resin (II) (1% divinylbenzene, 1·25% P, P : Ir = 7 : 1) at first catalysed this reaction at a rate of 0·6 that of $[Ir(CO)(Cl)(PPh_3)_2$ used homogeneously (benzene; 80 °C; 100 lb in^2 H_2). After one cycle, the hydrogenation rate using (II) increased to 1·5 times the rate using the homogeneous catalyst at 80 °C. On a third recycle at 70 °C, the rate using (II) was 6 times that of the homogeneous reaction at 70 °C. This suggests an $Ir(H_2)$ intermediate is formed which is stabilized in the matrix relative to its homogeneous counterpart. Setting aside (II) for 1 week after the third recycle resulted in a rate, on the fourth recycle, only twice that of the homogeneous rate at 70 °C. Both (II) and Vaska's complex lose their selectivity at higher H_2 pressures and long reaction times (complete formation of ethylcyclohexane at 100 °C; 300 lb in^2 H_2; 24 h). Catalyst (II) was repeatedly recycled without loss of activity or selectivity.

Co-ordinating solvents, i.e. dimethylformamide (DMF), are known to enhance catalytic hydrogenation activity with the $[Ir(CO)(X)(PPh_3)_2]$ and Rh catalysts.[6] $[Ir(Cl)(CO)(PPh_3)_2]$ catalysed the hydrogenation of cyclohexa-1,3- and -1,4-diene to cyclohexene in dimethylacetamide.[7] Thus 1,5-COD was hydrogenated over resin (II) in DMF (90 °C; 100 lb in^2 H_2; 2 h) to give 70—80% cyclo-octene. Resin (II) was repeatedly recycled without loss of activity (molar turnover > 4000). Cyclo-octa-1,3-diene was isolated as an intermediate in each case (conjugated dienes were previously observed in related reductions[8]). After the first recycle, the rate using (II) was 3 times that using $[Ir(CO)(Cl)(PPh_3)_2]$ homogeneously (90 °C; 100 lb in^2). The bright yellow (II) becomes a dark green solid upon repeated recycling. An i.r. band at 2060 cm^{-1} in addition to ν(CO) at 1950 cm^{-1} of (II) indicated the presence of CO *trans* to Ir-co-ordinated DMF, in accord with the expected *trans* effect[9] and the following structure.

Ⓟ—$C_6H_4PPh_2$)Ir(CO)(Cl)(DMF)

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