

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

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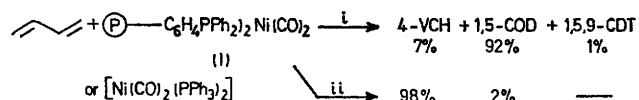
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**Summary** Polystyrene-divinylbenzene resin-anchored  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  has been used selectively to oligomerize butadiene to either 4-vinylcyclohexene or cyclo-octa-1,5-diene, and anchored  $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$  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.<sup>1</sup> Cyclo-oligomerization of butadiene by  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  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%).<sup>2,3</sup> The product distribution could be varied by using carbon monoxide or phosphites.<sup>2</sup>

We now report that butadiene was selectively converted into 4-VCH (98%) using either  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  or its resin-anchored form, (I) (styrene-1% divinylbenzene 1.33% P, P:Ni = 2:1) in the presence of CO (10 lb in<sup>2</sup>) 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  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  under these con-

ditions 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).

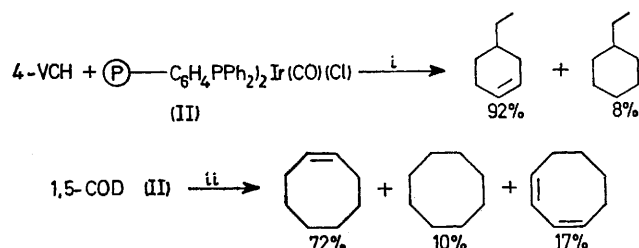


SCHEME 1. i, tri-*o*-tolyl phosphite; 115 °C, C<sub>6</sub>H<sub>6</sub>; ii, CO (10 lb in<sup>2</sup>), 115 °C, THF or C<sub>6</sub>H<sub>6</sub>.

Commercial styrene-divinylbenzene (Bio Rad Labs, SX-1 or SX-2 resins, 200–400 mesh) was brominated (dark) using Br<sub>2</sub>-FeBr<sub>3</sub> and then treated with excess of LiPPh<sub>2</sub> or NaPPh<sub>2</sub> in THF to provide a series of resins with 0.7–4.0% P.<sup>1,4</sup> The metal complexes were anchored by simple phosphine exchange with multiple anchoring to the polymer prevailing.<sup>1,5</sup>

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  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  in place of (Ia) and

the rate was 3 times that with (Ia). At the maximum molar turnover ( $>1300$ ) the  $\nu(\text{CO})$  i.r. bands had disappeared. The activity was determined in a fixed-bed operation. The catalyst (Ia) was deactivated on recycling.

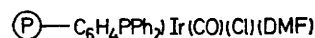


SCHEME 2. i,  $\text{C}_6\text{H}_6$ ,  $80^\circ\text{C}$ ,  $\text{H}_2$  (100 lb in<sup>2</sup>), 1.75 h; ii,  $\text{H}_2$  (100 lb in<sup>2</sup>),  $90^\circ\text{C}$ , DMF, 2 h.

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  $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$  used homogeneously (benzene;  $80^\circ\text{C}$ ; 100 lb in<sup>2</sup>  $\text{H}_2$ ). After one cycle, the hydrogenation rate using (II) increased to 1.5 times the rate using the homogeneous catalyst at  $80^\circ\text{C}$ . On a third recycle at  $70^\circ\text{C}$ , the rate using (II) was 6 times that of the homogeneous reaction at  $70^\circ\text{C}$ . This suggests an  $\text{Ir}(\text{H}_2)$  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  $70^\circ\text{C}$ . Both (II) and Vaska's complex lose their selectivity at higher  $\text{H}_2$  pressures and long reaction times (complete formation of ethylcyclohexane at  $100^\circ\text{C}$ ; 300 lb in<sup>2</sup>  $\text{H}_2$ ; 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  $[\text{Ir}(\text{CO})(\text{X})(\text{PPh}_3)_2]$  and Rh catalysts.<sup>6</sup>  $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$  catalysed the hydrogenation of cyclohexa-1,3- and -1,4-diene to cyclohexene in dimethylacetamide.<sup>7</sup> Thus 1,5-COD was hydrogenated over resin (II) in DMF ( $90^\circ\text{C}$ ; 100 lb in<sup>2</sup>  $\text{H}_2$ ; 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<sup>8</sup>). After the first recycle, the rate using (II) was 3 times that using  $[\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2]$  homogeneously ( $90^\circ\text{C}$ ; 100 lb in<sup>2</sup>). The bright yellow (II) becomes a dark green solid upon repeated recycling. An i.r. band at  $2060\text{ cm}^{-1}$  in addition to  $\nu(\text{CO})$  at  $1950\text{ cm}^{-1}$  of (II) indicated the presence of CO *trans* to Ir-co-ordinated DMF, in accord with the expected *trans* effect<sup>9</sup> and the following structure.



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