

Polymer-supported 2,2'-dipyridylmethane: catalytic activity of transition metal complexes in hydrogenations and oligomerizations

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Abstract

The palladium(II) acetate complex of the chelating ligand 2,2'-dipyridylmethane supported on polystyrene-2% divinylbenzene is an efficient catalyst for hydrogenation of alkenes and alkynes. Cyclopentadiene can be reduced with high selectivity to cyclopentene, but no selectivity is observed for the non-conjugated diene 1,5-cyclooctadiene. In the hydrogenation of 3-methylcyclohex-2-en-1-ol only small amounts of ketone are formed as a by-product, in contrast to the reaction catalysed by palladium on charcoal. Nickel(II) complexes of the same ligand catalyze the trimerization of butadiene to 1,5,9-cyclododecatrienes.

Introduction

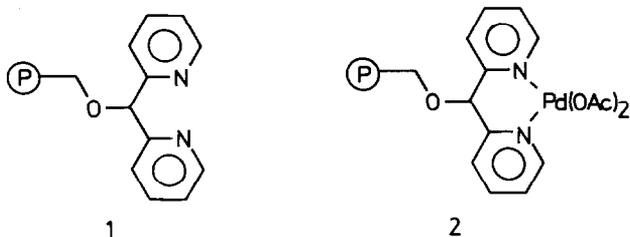
Heterogenized transition metal catalysts are currently the subject of great interest, and polymeric analogues of many different kinds of homogeneous catalysts now exist [1]. In spite of extensive studies, details of the nature of the catalytically active species in many cases are still unknown.

Research in this area has mainly dealt with phosphine-containing ligands, and relatively few studies [2] have been carried out on nitrogen-functionalized polymers. Recently we found [3] that 2,2'-dipyridylmethanol can be anchored to chloromethylated styrene-divinylbenzene resins and that various metal complexes of this polymeric ligand can be prepared. The ligand may act as a bidentate nitrogen donor or as a tridentate donor with a weak metal–oxygen interaction, in the same way as the hydrate [4] and the 1,3-dioxolane [5] of dipyridyl ketone. We have now investigated the catalytic activity of the palladium acetate complex of this polymeric ligand in hydrogenations of alkenes and alkynes, and the use of nickel(II) complexes in the trimerization of butadiene.

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Results and discussion

Polymer **1** was prepared as previously described [3] by reaction of chloromethylated polystyrene-2% divinylbenzene with 2,2'-dipyridylmethanol, which in turn was obtained either by reaction of 2-lithiopyridine with pyridine-2-carbaldehyde or by reduction of commercially available dipyridyl ketone. The polymer was analyzed by solid phase-magic angle spinning ^{13}C NMR spectroscopy, and showed resonances



for the non-aromatic carbon atoms at δ ca. 68 and 100 ppm. Transition metal complexes of the polymeric ligand were prepared by reaction of the polymer with the appropriate metal salt [3].

Palladium-catalyzed hydrogenations of alkenes and alkynes

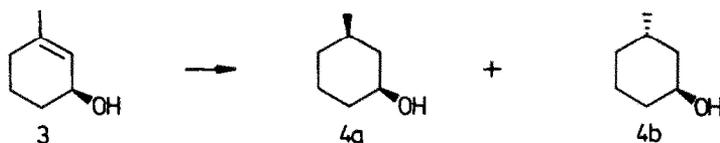
The palladium acetate complex of **1**, complex **2**, is a catalyst precursor for the hydrogenation of alkenes and alkynes at ambient temperature and pressure, but not for aromatic rings and nitro groups under these conditions. Alkynes are reduced selectively in the presence of alkenes but it is difficult to stop the reduction at the alkene stage because the rates of reduction of the two steps are usually quite similar [3].

The rate of reduction is strongly influenced by the polarity of the solvent. For example, in the case of 2-methyl-3-butyn-2-ol, if the rate of hydrogenation in acetonitrile is taken as 1 (0.41 ml/min using 1 mmol of substrate and 1.4% catalyst), the relative rates for hydrogenations in methanol, THF, methylene chloride, and toluene are 0.6, 0.5, 0.3 and 0.2, respectively, despite the higher tendency of the last three to swell the polymer.

In the hydrogenation of cyclopentadiene almost complete reduction to the monoene took place before formation of the saturated compound started, although the rates of reduction of the two steps were equal. The maximum yield of cyclopentene, 85%, together with 3% of cyclopentane, was obtained at 90% conversion. Palladium on charcoal has been reported to give an 88.4% yield of cyclopentene at total conversion, and this was improved to 93.2% by the addition of a 75-fold molar excess of the disodium salt of *N*-benzyliminodiacetic acid [6]. Higher selectivities for cyclopentene have been obtained using colloidal palladium supported on resins containing iminodiacetic acid moieties attached to a styrene-divinylbenzene copolymer (97.1% at 100% conversion) [6] or to poly(*N*-vinyl-2-pyrrolidone) (98.7% at total conversion) [7].

Hydrogenation of the non-conjugated diene 1,5-cyclooctadiene with **2** as catalyst gave a mixture of cyclooctene and cyclooctane. During the hydrogenation an isomer, which was indicated by GLC probably to be 1,3-cyclooctadiene, was formed which then disappeared. At 75% conversion, 3% of this isomer was obtained, together with 51% of cyclooctene and 21% of cyclooctane.

We have also studied the stereochemistry of hydrogenation of olefins containing two diastereotopic faces. Hydrogenation of racemic 3-methylcyclohex-2-en-1-ol (**3**) with **2** in methanol gave a quantitative yield (GLC) of *cis*- and *trans*-3-methylcyclohexan-1-ol (**4a** and **4b**) in a ratio of 3.8/1, whereas only a 50% yield of an equal

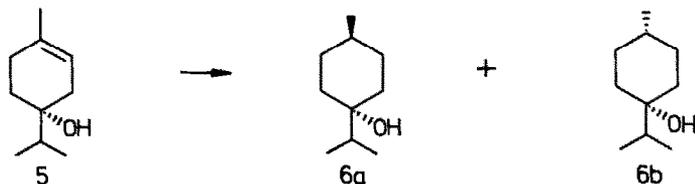


mixture of **4a** and **4b** together with several other products was obtained when palladium on charcoal was used as a catalyst [8 *]. The most abundant of these was 3-methylcyclohexanone (35%), which could be expected to form since rearrangement of allylic alcohols is commonly observed with palladium catalysts on various supports [9]. Palladium on charcoal was, though, more active than **2**, as it required 2 h for complete conversion (1 mmol substrate, 2% Pd) compared to 12 h for **2**.

In methylene chloride the reduction of compound **3** using catalyst **2** was slower and resulted in a somewhat lower ratio, 3.0/1, of **4a** and **4b** and, in addition, 6% of 3-methylcyclohexanone. Under these conditions palladium on charcoal yielded 3-methylcyclohexanone (75%) as the main product and only 24% of **4a** and **4b**.

A catalyst prepared analogously to **2** from chloromethylated Bonopore, a macroporous divinylbenzene polymer, turned out to be less reactive but gave essentially the same product pattern as catalyst **2** in methanol, whereas a catalyst prepared by precipitation of palladium on Bonopore [10] gave a complex reaction mixture.

Reduction of *R*-terpinen-4-ol (**5**) in methanol using **2** as a catalyst gave a 1/3.8 mixture of the isomers **6a** and **6b** in a total yield of 97% and in methylene chloride a



1/1.0 mixture of the same compounds in 44% yield together with unreacted starting material. Palladium on charcoal was also in this case considerably more active (requiring 55 min for the reduction of 1 mmol of substrate using 1.4% catalyst in methanol compared to 25 h for **2**) but had a lower product selectivity. In both methanol and methylene chloride at least three unidentified compounds were formed (according to GLC) in addition to compounds **6a** and **6b** (62% yield in both solvents), which were formed in ratios of 1/4.0 and 1/1.2 in methanol and methylene chloride, respectively, i.e. similar to the ratios observed using **2** as a catalyst. These results indicate that with catalyst **2**, even in aprotic solvents, no such chelate control of the stereochemistry exists as has been observed with homogeneous cationic rhodium(I) and iridium(I) complexes [11]. While the latter complexes favour attack of hydrogen from the face containing the hydroxy group, attack of hydrogen from the less hindered side is preferred with our catalyst.

* This and other references marked with asterisks indicate notes occurring in the list of references.

There is a certain ambiguity about the oxidation state of palladium in polymer-bound hydrogenation catalysts. Catalysts prepared from palladium(II) bound to phosphinated polymers have been assumed to contain palladium(II) [12], while at least partial reduction to the zerovalent state has been shown to occur for catalysts prepared from palladium(II) bound to polymeric bipyridine [13].

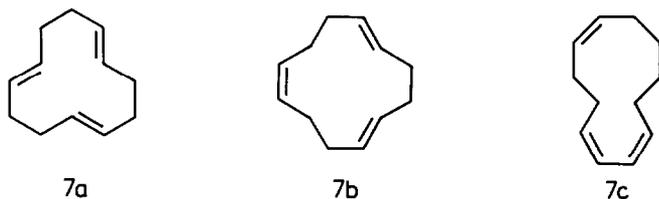
In hydrogenations with **2** an induction period was always observed when fresh catalysts were used, probably due to the reduction of palladium(II) to palladium(0) prior to reaction. During the hydrogenations the catalysts darkened which indicated the presence of palladium(0) in the form of metallic palladium. In order to verify this assumption a used catalyst was investigated by ESCA.

The ESCA spectrum of **2** has the Pd $d_{5/2}$ band at 338.1 eV, confirming that the metal is in a divalent state. A sample of the used catalyst showed a considerable broadening of this band which indicated the presence of a mixture of divalent and zerovalent palladium in a roughly 1/1 ratio [14].

Serious drawbacks often encountered with polymer catalysts include leakage of metal ions from the polymer into solution and loss of supported ligands [2]. From data available it is not possible to conclude whether any loss of ligand from **2** takes place during hydrogenation, since when a polymer with a slight excess of palladium containing 3.08% N and 15.80% Pd, corresponding to a N/Pd molar ratio of 1.48/1 was used, a polymer with 3.26% N and 16.45% Pd (corresponding to a N/Pd molar ratio of 1.51/1) was recovered after the reduction. Complete reduction of palladium(II) to palladium(0), resulting in complete loss of acetate ligands, would in the absence of palladium leakage give a polymer containing 3.74% nitrogen. The increased nitrogen/palladium ratio indicates a slight leakage of palladium.

Nickel-catalyzed trimerization of butadiene

It is well known that zerovalent naked nickel catalysts cyclotrimerize butadiene to a mixture of *trans,trans,trans*-, *trans,trans,cis*- and *trans,cis,cis*-cyclododecatriene (**7a-c**) [15]. The catalysts are usually prepared either by reduction of a



nickel salt in the presence of butadiene or from preformed zerovalent nickel compounds [16].

We have found that a useful catalyst for the trimerization of butadiene can be prepared from the nickel chloride or nickel acetate complex of **1** and triethylaluminum. The results obtained with this catalyst in toluene were very similar to those obtained from previously used catalysts. The total yield of cyclododecatrienes increased from 9 to 70% when the temperature was raised from 40 to 70°C, but a further increase in temperature had no effect on the yield (Table 1). In addition to the cyclotrimers compounds, which according to GLC probably are dimers of butadiene, were formed in ca. 3–4% yields. The proportion of the *trans,cis,cis*-isomer increased with increasing temperature at the expense of the all-*trans* isomer, but

Table 1

Trimerization of butadiene (ca. 30 mmol) in toluene (5 ml) in the presence of triethyl aluminium (0.4 mmol) and (a) the nickel acetate complex of **1** (0.1 mmol Ni) or (b) nickel acetate (0.1 mmol)

Temperature (°C)		Time (h)	Yields (%) of			Total yield (%)
			7a	7b	7c	
40	a	20	87	7	7	9
70	a	21	80	7	13	46
80	a	20	71	9	20	48
80	a	42	71	9	20	58
80	a	64	73	8	18	70
90	a	23	73	11	16	58
80	b	15	79	8	13	52
80	b	20	76	8	16	64

the isomer ratio did not change with time. When THF was used as a solvent in place of toluene, the total yield of cyclotrimers was only 9% even at 70 °C.

During the cyclotrimerizations the reaction solutions turned deep red, indicating leakage of metal ions from the polymer into solution. Furthermore, the expected increase in selectivity for the all-*trans* isomer in the presence of pyridine ligands [16] was not observed, but rather a slight decrease in both selectivity and activity, as shown by the results obtained from reactions in the absence of **1** (Table 1). These observations suggest that the polymeric complex is dissociated prior to reaction.

Nickel(0) anchored on linear polyvinylpyridine has previously been used for the trimerization of butadiene [17]. In this case, however, it was claimed that the catalytic reaction occurs while the metal is coordinated to the polymer, since nickel complexes of 20% cross-linked polyvinylpyridine were shown to be catalytically inactive.

Experimental

NMR spectra were recorded on a Bruker WP-200 spectrometer in CDCl₃ with TMS as internal standard. GLC analyses were carried out on a Varian 3700 chromatograph fitted with a SE-30 capillary column (24 m), or on a Pye Unicam chromatograph fitted with an OV-101 (30 m) capillary column. All elemental analyses were performed by Analytical Laboratories, Engelskirchen, West Germany.

THF was distilled from benzophenone ketyl and CH₂Cl₂ from CaCl₂ before use. Pro Analsi grade MeOH was purchased from Riedel de Haen and used as received. 3-Methylcyclohex-2-ene-1-ol was purchased from Aldrich. Unfunctionalized Bonopore and Bonopore containing metallic palladium were generous gifts from Nobel Chemicals AB, and 4-terpinen-4-ol was kindly provided by Firminich AG.

General procedure for the hydrogenations

A typical hydrogenation procedure is as follows: The reaction flask containing the catalyst (2 mol%) and 5 ml of solvent was purged three times with hydrogen, the substrate (1 mmol) was then added through a septum, and the mixture was stirred under 1 atm of hydrogen at room temperature. The hydrogen consumption was

monitored with a gas burette and aliquots were removed during the reaction and analyzed on a capillary GLC. At the end of the reaction the catalyst was filtered off and the solvent was evaporated. The crude products were analyzed by GLC and by ^1H NMR spectroscopy.

Hydrogenation of 3-methylcyclohex-2-en-1-ol

The reaction mixtures were analyzed on capillary GLC with a SE-30 column. The two diastereomers of 3-methylcyclohexanol could not be separated, on a SE-30 nor an OV-101 column. The diastereomeric ratios were thus determined by ^1H NMR by determining the integrals of the carbinol protons (δ 3.45 and 3.97 ppm for *cis* and *trans*, respectively). The NMR spectrum of 3-methylcyclohexanol was in good agreement with the data previously published [18].

The ^1H NMR spectrum of 3-methylcyclohexanone was identical with that of a sample prepared by CrO_3 -pyridine oxidation of 3-methylcyclohexanol. The IR spectrum showed a C=O band at 1700 cm^{-1} .

Hydrogenation of (–)-terpinen-4-ol

The *cis/trans* ratio of the reaction mixture was measured by capillary GLC with an SE-30 column. The NMR spectrum was in agreement with data previously published [19].

Hydrogenation of cyclopentadiene

The reaction mixture was analyzed by capillary GLC with an OV-101 column. Cyclopentadiene, cyclopentane and cyclopentene were identified by simultaneous injection of reference samples.

Hydrogenation of cyclooctadiene

The reaction mixture was analyzed by capillary GLC with a SE-30 column. Cyclooctadiene, cyclooctene, and cyclooctane were identified by simultaneous injection of reference samples.

Oligomerization of butadiene

Butadiene was condensed into a Fisher and Porter glass autoclave containing 108 mg of the $\text{Ni}(\text{acac})_2$ complex of polymer 1 (0.1 mmol) or 26 mg of $\text{Ni}(\text{acac})_2$ (0.1 mmol) under a nitrogen at -78°C , and 5 ml of solvent (toluene or THF) and 0.20 ml of Et_3Al were then added at -78°C . The mixture was stirred without cooling for 30 minutes, then at the temperatures and times indicated in Table 1. The mixture was diluted with petroleum ether and filtered through Celite, and after a few days additional precipitates were filtered off. The product mixtures were analyzed by GLC with n-dodecane as an internal standard.

Acknowledgements

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