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POLYMER-SUPPORTED 2,2′-DIPYRIDYLMETHANE: SYNTHESIS AND FORMATION OF TRANSITION METAL COMPLEXES

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Summary

The chelating ligand 2,2′-dipyridylmethane can be anchored to styrene-divinylbenzene polymers by reaction of the anion of 2,2′-dipyridylmethanol with chloromethylated or chloroacetylated resins under mild conditions. A number of transition metal complexes of the polymeric ligand have been prepared. Alkenes and alkynes are readily hydrogenated with the $Pd(OAc)_2$ complex of the polymeric ligand as catalyst.

Introduction

The synthesis of polymer-supported transition metal complexes and their use in catalytic reactions has received much attention [1]. Such polymeric catalysts offer the advantage of being easily separated after reaction, and they can often be recovered and reused. In addition, increases in stability [2], activity [3,4] and selectivity [2,5] are often observed compared with those of the homogeneous analogues. One serious drawback often encountered with polymeric catalysts is the leakage of metal from the polymer into solution, resulting in a decreased activity of the catalyst [6]. This problem can, however, often be eliminated by using chelating ligands [1c,7].

Various transition metal complexes of polymeric chelating ligands, mainly phosphines, have been prepared and used in catalytic reactions [1,7], but further methods of anchoring such ligands to polymers are desirable. In order that a homogeneous resin should be obtained the ligand should be attached to the polymer, preferably in one step, by a clean reaction giving only small amounts of by-products [8].

An attractive type of ligand is a dipyridine (**1**). Bipyridine itself (**1a**) has previously been attached to styrene-divinylbenzene resins by reaction of lithiated polystyrene with bipyridine [9]. Transition metal complexes of this ligand have been prepared and their catalytic properties investigated [9,10].

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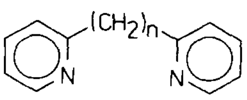

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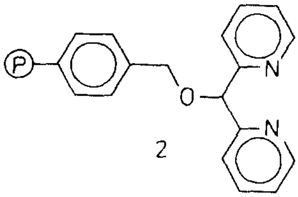

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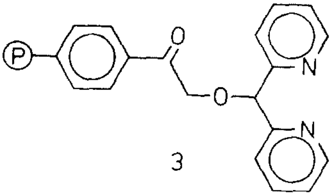

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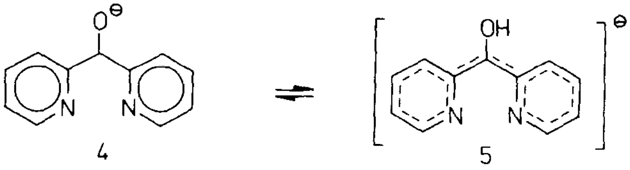

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Dipyridylmethane (**1b**) also forms complexes with a variety of metals [11]. These six-membered ring chelates are somewhat less stable than their five-membered ring analogues, but considerably more stable than metal complexes of the higher homologues. We describe below the anchoring of dipyridylmethane to polystyrene resin under mild conditions, and the formation of transition metal complexes from the bound ligand.

Results and discussion

Preparation of polymer-bound dipyridylmethane

Polymer **2** was prepared by reaction of chloromethylated polystyrene-2% divinylbenzene with the anion of 2,2′-dipyridylmethanol at ambient temperature in tetrahydrofuran (THF). Polymeric dipyridylmethane prepared from a resin with 2.6 mmol of chloromethyl groups per gram contained, according to elemental analysis, 2.73% nitrogen, which corresponds to 0.97 mmol of ligand per gram of resin (i.e. approximately one dipyridylmethyl group for every seven phenyl residues) and a yield of 42%. After reaction 58% of the chloromethyl groups remained unchanged, indicating that no cross-linkage of the resin occurred during the substitution. A more heavily substituted resin, containing one ligand group per 3.6 phenyl residues, was obtained by starting with a chloromethylated polymer originally containing 5 mmol of chloromethyl groups per gram of resin.

The same ligand could also be attached in low yield under the same conditions to chloroacetylated resins [12], to give polymers of structure **3**. Starting with a 2% cross-linked resin containing 11.68% chlorine, a polymer with 0.31 mmol of ligand per gram resin (10% yield) was obtained. A considerable amount (28%) of the chlorine was lost in the reaction, probably due to cross-linkage of the resin. A 12% cross-linked gel with 3.14% chlorine was essentially inert to substitution, whereas a resin with 0.38 mmol of ligand per gram was obtained (19% yield, 81% chlorine unchanged) from a macroporous styrene-divinylbenzene polymer (XAD-4).

When treated with base, 2,2'-dipyridylmethanol forms an anion which can exist in the tautomeric forms **4** and **5**. Consequently, on addition of an alkyl halide, products resulting from both O- and C-alkylation can be expected. Reaction of the anion with ethyl bromide, however, resulted in the formation of only O-alkylated product [13]. It is therefore also assumed that alkylation with the sterically crowded polymeric halide affords only the O-alkylated products **2** and **3** and not their C-alkylkated isomers.

Preparation of metal complexes

Transition metal complexes of polymeric dipyridylmethane were prepared by reaction of resin **2** with the appropriate metal salt, usually in THF. In poorly swelling solvents like ethanol, essentially no metal was adsorbed by the polymer.

The amount of metal incorporated was determined by elemental analysis. The ligand to metal ratios of the complexes varied with the different metals (Table 1). Palladium(II) chloride, palladium(II) acetate and nickel(II) bromide formed 1/1 complexes of ligand and metal, while iron(III) chloride and copper(II) acetate gave complexes with higher and lower ratios, respectively. Cobalt(II) bromide gave a complex which according to elemental analysis had a N/Co/Br ratio of 2/1/3 [14]. The structure of this complex, however, requires further investigation.

The uptake of $FeCl_3$ by polymer **2** was followed spectrophotometrically by observing the decrease in absorption at 405 nm of a 20 mM solution of $FeCl_3$ in THF in contact with **2** [9]. It was found that one equivalent of Fe^{III} was incorporated within less than 30 min ($t_{1/2} < 5$ min).

Essentially no metal salts were incorporated into polymer **2** from an acidic aqueous solution of $CuSO_4$ due to the poor swelling ability of this polymer in water. A macroporous resin with structure **3** [15], however, incorporated 0.28 mmol of Cu^{II} per gram at pH 2.5 and 0.22 mmol at pH 2 from 50 mM solutions of $CuSO_4$ in

TABLE 1

AMOUNTS OF METAL SALTS ADSORBED BY POLYMER 2

Metal compound	Quantity bound mmol/g resin [a]	Ligand/metal ratio [a]
$FeCl_3$ [b]	0.73	1.27
$NiBr_2 \cdot 3H_2O$ [b]	0.85	1.05
$PdCl_2 \cdot 2PhCN$ [b]	0.95	0.98
$Pd(OAc)_2$ [c]	0.98	1.02
$Cu(OAc)_2 \cdot H_2O$ [b]	1.4	0.59

[a] Determined by elemental analysis. [b] In tetrahydrofuran. [c] In toluene.

H_2SO_4. From a mixture of 10 ml of an aqueous solution 2 m*M* in each Cu^{II}, Co^{II}, Cd^{II}, Ni^{II} and Zn^{II}, 69% Cu^{II}, 0% Co^{II}, 11% Cd^{II}, 8% Ni^{II} and 41% Zn^{II} were incorporated in 0.5 g of the same polymer at pH 2.6, whereas from another aqueous solution of a mixture of metal salts (2 m*M* in each) 40% Cu^{II}, 0% Co^{II}, 3% Ni^{II}, 8% Zn^{II} and 12% Fe^{III} were adsorbed at pH 2 [16].

Hydrogenations with polymer-bound palladium(II) acetate

The catalytic activity of the palladium(II) acetate complex of **2** is very similar to that of (poly(styryl)bipyridyl)palladium(II) acetate [9]. Alkenes and alkynes are readily hydrogenated at ambient temperature and one atmosphere of hydrogen, whereas aromatic rings and nitro groups remain unchanged under these conditions.

The hydrogenation of 2-methyl-3-butyn-2-ol proceeded at a nearly constant rate of hydrogen uptake until two equivalents of hydrogen were consumed. With a catalyst containing 0.069 mmol of palladium and 10 mmol of substrate in 10 ml of tetrahydrofuran ca. 8 h were required for complete reduction. In the reduction of 4-octyne, however, the rate of hydrogen uptake became considerably slower (0.7 ml/min compared to 1.4 ml/min) when one equivalent of hydrogen had been consumed. After the consumption of 0.5 equivalents of hydrogen, a ca. 1/1 mixture of 4-octyne and *cis*-4-octene [17] was isolated. When all the 4-octyne had been consumed, double bond isomerization of the 4-octene was observed (by ^1H NMR) to occur.

In the hydrogenation of 1-octene, considerable isomerization to 2-octene (which is more resistant to reduction) occurred, and the rate of hydrogen consumption was therefore non-linear. When the reaction was interrupted before reduction was complete, no 1-octene could be detected in the reaction mixture.

Both double bonds of *N,N*-diethyl-*trans*-2,7-octadienylamine were reduced within 4.5 h at ambient temperature and one atmosphere of hydrogen in the presence of 3% catalyst. The rate of hydrogen consumption was considerably higher in the initial part of the reaction. Some double bond isomerization took place; after the uptake of ca. 0.6 equivalents of hydrogen, the reaction mixture consisted of an ca. 2.5/1/5 mixture of *N,N*-diethyl-2,7-octadienylamine, *N,N*-diethyl-2,6-octadienylamine and *N,N*-diethyl-2-octenylamine, as indicated by ^1H NMR spectroscopy.

The catalyst can be reused at least three times without any loss in activity. In the first run, a short induction period was always observed, probably due to reduction of palladium(II) to palladium(0), which has to precede hydrogenation.

Experimental section

Merrifield resins were purchased from Fluka, the styrene-divinylbenzene polymers SX-2 and SX-12 were from Bio-Rad. The macroporous resin XAD-4 was a generous gift from the Rohm & Haas company. Tetrahydrofuran (THF) was distilled from benzophenone ketyl before use. Di-2-pyridylmethanol was made as a white crystalline solid (m.p. 54–56°C) by published procedures from 2-lithiopyridine and 2-pyridyl aldehyde [18] or by reduction of di-2-pyridyl ketone [19] (obtained from Fluka).

NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a JEOL JNM-PMX instrument at 60 MHz and on a Bruker WP 200 instrument at 200 MHz. Spectrophotometric measurements were made on a Beckman model G 2400 spectrometer. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany and by Mikro Kemi AB, Uppsala, Sweden.

Chloroacetylation of crosslinked polystyrene

The appropriate polymer (SX-2, SX-12 or XAD-4) (10 g) was added in portions to a mixture of chloroacetyl chloride (12.60 g, 112.5 mmol) and $AlCl_3$ (20 g, 150 mmol) in CS_2 (60 ml) at 0°C and the mixture was shaken at ambient temperature for 44 h. After hydrolysis with ice-methanol, the polymer was washed with H_2O, CH_3COOH and MeOH and dried in vacuo at 70°C to give chloroacetylated SX-2, SX-12 and XAD-4 polymers with 3.3, 0.89 and 2.1 mmol chlorine per gram resin, respectively.

Preparation of polymeric dipyridylmethane

Dipyridylmethane (5.58 g, 30 mmol) in THF (20 ml) was added to a suspension of NaH (720 mg, 30 mmol) in THF (10 ml) under nitrogen to give a deep blue solution [20]. After stirring for 30 min, 7.8 ml (7.8 mmol) of the solution was added to the chloromethylated polymer containing 2.6 mmol Cl/g (3 g, 7.8 mmol) suspended in THF (20 ml). After 18 h at ambient temperature the polymer was filtered off, washed with THF, H_2O and MeOH, and finally dried in vacuo at 60°C to afford polymer **2** in 42% yield. The chloromethylated resin containing 5 mmol Cl/g was treated in the same way with one equivalent of the anion, to give **2** (42%).

Polymers **3** were prepared analogously from chloroacetylated SX-2 and XAD-4 in yields of 10 and 19%, respectively.

Preparation of metal complexes of 2

The appropriate metal compound ($FeCl_3$, $CoBr_2 \cdot H_2O$, $NiBr_2 \cdot 3H_2O$, $PdCl_2 \cdot 2PhCN$, $Cu(OAc)_2 \cdot H_2O$) (0.5 mmol) was added to polymer **2** (200 mg, 0.19 mmol) in THF (25 ml) at ambient temperature under nitrogen. After ca. 20 h the complexes were filtered off, washed with THF and dried in vacuo at 60°C.

The $Pd(OAc)_2$ complex of **2** was similarily prepared in toluene.

Hydrogenation of alkenes and alkynes

General procedure. The $Pd(OAc)_2$ complex of **2** (74 mg, 0.065 mmol) was suspended in THF (10 ml) and the system was purged with hydrogen. The appropriate alkene or alkyne (10 mmol) was added and stirring of the mixture was commenced. The hydrogen consumption was monitored using a gas burette. After reaction the catalyst was filtered off and the solvent evaporated under reduced pressure. The products were identified by NMR spectroscopy and by comparison with authentic samples.

Hydrogenation of N,N-diethyl-2,7-octadienylamine

The reduction was performed as described above using the $Pd(OAc)_2$ complex of **2** (15 mg, 0.014 mmol) and *N*,*N*-diethyl-2,7-octadienylamine [21] (80 mg, 0.44 mmol) in THF (2.5 ml).

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References and Notes

1 (a) F.R. Hartley and P.N. Vezey, Adv. Organomet. Chem., 15 (1977) 189; (b) Y. Chauvin, D. Commereuc and F. Dawans, Prog. Polym. Sci., 5 (1977) 95; (c) P. Hodge and D.C. Sherrington, Polymer-supported Reactions in Organic Synthesis, Wiley, Chichester, New York, Brisbane, Toronto, 1980; (d) N.K. Mathur, C.K. Narang and R.E. Williams, Polymers as Aids in Organic Chemistry, Academic Press: New York, London, Toronto, Sydney, San Francisco, 1980.

2 B.M. Trost and E. Keinan, J. Amer. Chem. Soc., 100 (1978) 7779.

3 R.H. Grubbs, C. Gibbons, L.C. Kroll, W.D. Bonds, Jr. and C.H. Brubaker, Jr., J. Amer. Chem. Soc., 96 (1974) 2373.

4 C.U. Pittman, Jr. and Q. Ng, J. Organomet. Chem., 153 (1978) 85.

5 T. Antonsson and C. Moberg, Organometallics, in press.

6 C.U. Pittman, Jr., S.K. Wuu and S.E. Jacobson, J. Catal., 44 (1976) 87.

7 F. Ciardelli, G. Braca, C. Carlini, G. Sbrana and G. Valentini, J. Mol. Catal., 14 (1982) 1.

8 A. Warshawsky, A. Deshe, G. Rossey and A. Patchornik, React. Polym., Ion Exch., Sorbents, 2 (1984) 301.

9 R.J. Card and D.C. Neckers, Inorg. Chem., 17 (1978) 2345.

10 (a) R.J. Card and D.C. Neckers, J. Org. Chem., 43 (1978) 2958; (b) R.J. Card, C.E. Liesner and D.C. Neckers, J. Org. Chem., 44 (1979) 1095; (c) R.S. Drago, E.D. Nyberg and A.G. El A'mma, Inorg. Chem., 20 (1981) 2461; (d) A. Modelli, F. Scagnolari, G. Innorta, A. Foffani and S. Torroni, J. Mol. Catal., 24 (1984) 361.

11 H. Bühler and G. Anderegg, Chimia, 24 (1970) 433.

12 W.O. Kenyon and G.P. Waugh, J. Polym., Sci., 32 (1958) 83.

13 No signals attributable to the C-alkylated isomer (independently synthesized from 2,2'-dipyridyl ketone and ethylmagnesium bromide) could be observed in the ^{1}H NMR spectrum of the crude product.

14 The Co/Br ratio may indicate that Co^{II}, possibly during manipulations in air, is oxidized to Co^{III}, which is known to occur readily in the presence of nitrogen donors: F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley; New York, Chichester, Brisbane, Toronto, Singapore, 1980.

15 Prepared from the macroporous styrene-divinylbenzene polymer Bonopore®, which was a generous gift from Bofors Nobel Kemi AB.

16 Values determined by atomic absorption spectroscopy.

17 The configuration of the double bond was determined by ^{13}C NMR: J.W. de Haan and L.J.M. van de Ven, Org. Magn. Res., 5 (1973) 147.

18 H.C. Beyerman and J.S. Bontekoe, Rec. Trav. Chim., 74 (1955) 1395.

19 J. Murphy and J.W. Bunting, Org. Prep. and Proc. Int., 3 (1971) 255.

20 The blue colour is probably due to the presence of an anion radical. Cf: V.G. Ermolaeva, I.S. Musatova and M.N. Shchukina, Zh. Obshch. Khim., 33 (1963) 825 (J. Gen. Chem. USSR, 33 (1963) 811) and M.N. Shchukina, V.G. Ermolaeva and A.E. Kalmanson, Dokl. Akad. Nauk. SSSR, 158 (1964) 436 (Acad. Sci. USSR, Proc., Chem. Sect., 158 (1964) 931). A considerable peak broadening was observed in the ^{13}C NMR spectrum of the sodium alcoholate of 2,2'-dipyridylmethanol under N_2 in THF, in accord with this assumption.

21 B. Åkermark, G. Åkermark, C. Moberg, C. Björklund and K. Siirala-Hansén, J. Organomet. Chem., 164 (1979) 97.