

Preliminary communication

Isonitrile-functionalized polymer supports as versatile ligands towards metal centres

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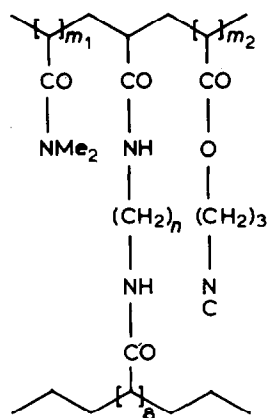
(Received January 30th, 1987)

Abstract

Novel insoluble isonitrile-bearing polymeric supports display versatile and strong ligating ability towards a variety of transition metal centres. The combination of controlled stoichiometry, elemental analysis, and IR spectroscopy gives reliable information on the nature of the molecular coordination compounds formed. The PdCl₂-containing polymers are effective catalysts for the hydrogenation of benzaldehyde and phenylacetylene under mild conditions.

The synthesis of ligand-functionalized insoluble polymeric supports suitable for producing industrially useful hybrid catalysts [1] is an attractive objective among technologically oriented scientists [2]. Disadvantages of polymer-metal complexes ($\text{P}-\text{ML}_n$) are their thermal and mechanical instability and the leaching out of metal under the plant conditions. In contrast to the large amount of information available on phosphine bearing polymeric supports [2], little is known about insoluble polymers bearing isonitrile ligands [3].

Since the discovery of a new class of copolymers carrying an isonitrile function and having general solvent and substrate compatibility [4], we have been exploring the coordination chemistry of these polymers with the aim of: (i) determining the "scope" of their metal-complexing ability; (ii) investigating the degree of metal dispersion inside the polymer beads; (iii) evaluating their thermal stability; (iv) collecting preliminary information on the resistance of the $\text{P}-\text{ML}_n$ complexes to leaching by polar solvents.



$$m_1 + m_2 + 8 = 100$$

polymer	RNC (meq/g)	<i>n</i>
M40-1	2	6
M13-8	0.5	6
P1D1	0.3	1
P3	0.49	1
P4	0.1	6
P5	0.58	1
P7	1.28	6

The type of polymeric ligand employed is depicted above.

We report here on features of Rh^{III} and Ru^{III} complexes obtained from **P7**, but all the polymers listed above react readily with the following complexes: [Ni(H₂O)₆]²⁺, [Cu(H₂O)₆]²⁺, [CuCl], [CoCl₂], [Cu(acac)₂], [PdCl₂(PPh₃)₂], [Pd(acetate)₂], [PdCl₂(PhCN)₂], RuCl₃ · 3H₂O, [RuCl₂(PPh₃)₃], [RhCl(PPh₃)₃], [Rh(acac)(CO)₂], RhCl₃ · 3H₂O, [Mo(CO)₆]. Most of these complexes are known to be catalytically active in homogeneous phase for a variety of synthetically useful reactions [5], and their efficient coordination to these polymers appears promising.

The unique analytically useful presence of isonitrile groups in the polymeric ligands makes IR spectrometry a powerful tool for determining whether coordination has occurred and for giving insight into the nature of the resulting anchored species $\text{(P)}-(\text{NC})_m-\text{ML}_n$.

The combination of elemental analysis and IR spectroscopy under controlled stoichiometric conditions (normally RNC/ML_n 1/1) permits reasonable speculation about the nature of the $\text{(P)}-(\text{NC})_m-\text{ML}_n$ complexes, account being taken of the obvious correlation of their IR data to those of the related [(RNC)_mML_n] species [6].

Some analytical data for **P7** and for its RuCl₃ and RhCl₃ complexes are shown in Table 1.

X-ray microprobe analysis of **2** shows that metal distribution is remarkably homogeneous throughout the polymer beads.

Table 1

Essential analytical data on some metal-polymer complexes

Species	$\nu(\text{NC})$ (cm ⁻¹) ^a	Metal (mol %) ^b	Metal (%) ^c
P7 (1)	2149m	—	—
$\text{(P)}-(\text{NC})_2\text{RuCl}_3(\text{H}_2\text{O})$ ^d (2)	2185s	47	7.4
	2120m		
$\text{(P)}-(\text{NC})_2\text{RhCl}_3(\text{H}_2\text{O})$ ^e (3)	2240m	45	7.1

^a Nujol mull. ^b Mol percentage of metal incorporated with respect to the initial RNC/ML_n 1/1 molar ratio. ^c Weight percentage of metal determined in the material by elemental analysis. ^d *cis*-Coordination. ^e *trans*-Coordination.

Combined TGA-DTA measurements on 1-3 reveal that the polymeric structure of these materials is stable up to 300°C and this is confirmed by monitoring the morphology of these materials by electron scanning microscopy.

The resistance of 2 and 3 to leaching by solvents was tested with dichloroethane at 100°C under argon with moderate stirring. Five consecutive leaching cycles (10 ml of dichloroethane for 100 mg material), lasting 10 h each, and with vigorous stirring, revealed that after an initial loss of ca. 12% of the metal in the first cycle, the metal percentage and the IR spectrum substantially remained unaltered.

The complex $\text{P}-(\text{NC})\text{PdCl}_2$ ($\nu(\text{NC})$ 2250 cm^{-1} ; single band in nujol mull; $\text{P} = \text{PID1}$; Pd 2.44%, theoretical for an equimolar NC/Pd ratio 3.20%) was initially tested as a catalyst for the hydrogenation of three industrially significant substrates, viz. nitrobenzene, phenylacetylene, and benzaldehyde, in methanol at 21°C and under three atmospheres of hydrogen, in a Parr apparatus. Nitrobenzene did not react, but phenylacetylene and benzaldehyde underwent complete hydrogenation after 10 h, and the products were styrene (33%) and ethylbenzene (67%) from phenylacetylene, and benzyl alcohol (81%) and some other reduction products from benzaldehyde. Work is in progress to investigate the extent of retention of the catalytic activity of the material through repeated catalytic runs, as well as the possible control of chemoselectivity in hydrogenation of phenylacetylene.

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