Preparation of Polymer-supported Isonitrile Complexes

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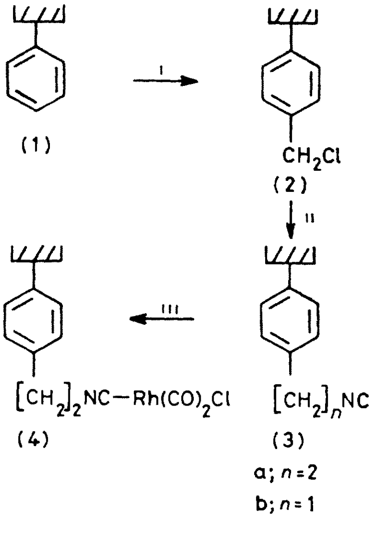
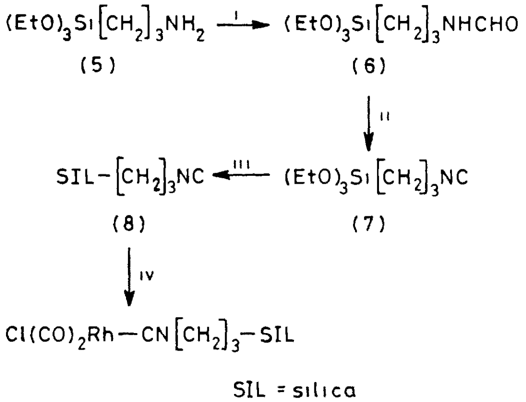
Summary The preparation of isonitrile ligands bound to polystyrene and silica supports is reported, these ligands react with $[Rh(CO)_2Cl]_2$ to yield $[Rh(CO)_2Cl(pol\text{–}NC)]$ complexes (pol = polymeric support)

There is currently some interest in the preparation and heterogeneous catalytic activity of transition metal complexes of ligands chemically bound to polymeric supports, primarily those based on polystyrene or silica substrates [1] Concurrently, there has been an increasing interest in the chemistry of low-valent transition metals complexed to isonitrile ligands In particular, the recent syntheses of binary mono- and poly-metallic isonitrile complexes may be noted, several of which are known to have interesting catalytic properties [2–4] We report here the preparation of isonitrile ligands chemically bound to polystyrene and silica supports and their reaction with $[Rh(CO)_2Cl]_2$

Polystyrene (**1**) (Eastman-Kodak, 200—400 mesh, cross-linked with 2% divinylbenzene) was chloromethylated[5] (Scheme 1) to yield (**2**) in which approximately 20% of the rings were functionalized On reaction of (**2**) with $LiCH_2NC$[6] in tetrahydrofuran at −78 °C, essentially complete halogen substitution was achieved to yield the isonitrile ligand (**3a**) (ν_{CN} 2162 cm^{-1}, KBr disc) Attempts to prepare (**3b**) by reaction of brominated polystyrene[7] with $LiCH_2NC$ resulted in only partial halogen substitution Rapid reaction of (**3a**) with an excess of $[Rh(CO)_2Cl]_2$ occurred in toluene at room temperature to yield a red solid exhibiting vibrational bands (KBr disc) at ν_{CN} 2208 and ν_{CO} 2092 and 2009 cm^{-1} By comparison with the known spectrum[8] of $[Rh(CO)_2Cl(CNBu^t)]$ (ν_{CN} 2223 cm^{-1} and ν_{CO} 2101 and 2033 cm^{-1}, $CHCl_3$ solution), the complex may be formulated as $Rh(CO)_2Cl(pol\text{–}NC)$ (pol = polymer support) (**4**) Microanalyses and a residual i r band at 2155 cm^{-1} indicate that, under these conditions, about 1 in 1·6 of the isonitrile ligands is complexed Even in the presence of a large molar excess of (**3a**) only the $[Rh(CO)_2Cl(pol\text{–}NC)]$ complex is observed This is in contrast to the reaction with non-bound isonitriles which, in the presence of an excess of the ligand, yields the $[Rh(CNR)_4]Cl$ derivative [8]



Scheme 1 *Reagents* i, $ClCH_2OMe\text{–}SnCl_4$, 25 °C, ii, $LiCH_2NC$ in tetrahydrofuran, −78 °C, iii, $[Rh(CO)_2Cl]_2$ in toluene, 25 °C



Scheme 2 *Reagents* i, HCO_2Et, reflux, ii, $PPh_3\text{–}CCl_4\text{–}NEt_3$ in dichloroethane, 65 °C, iii, SiO_2, toluene–H_2O, reflux, iv, $[Rh(CO)_2Cl]_2$ in toluene, 25 °C

Conversion of commercially available 3-aminopropyltriethoxysilane (**5**) into the formamide (**6**)[9] (Scheme 2), followed by dehydration[10] yields the isonitrile (**7**) which on condensation with silica (Degussa Aerosil 200) in refluxing toluene–H_2O yields (**8**) (ν_{CN} 2160 cm^{-1}, pressed disc)

Reaction of (**8**) with an excess of $[Rh(CO)_2Cl]_2$ in toluene yields a greyish solid exhibiting i r bands (pressed disc) at ν_{CN} 2200, ν_{CO} 2099 and 2035 cm^{-1}, consistent again with a formulation as the $[Rh(CO)_2Cl(pol–NC)]$ complex (**9**)

Preliminary experiments show that metals other than rhodium may be complexed and that metal clusters may be supported as their monosubstituted isonitrile complexes

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