Preparation of a Silica-Bound Arenechromium-dicarbonyl-isonitrile Complex

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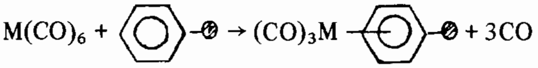
On a laboratory scale arenechromium–tricarbonyl complexes have found wide applications in organic synthesis [1] and as catalysts in hydrogenation reactions [2]. For a technical utilization of these soluble complexes, however, easier handling (*i.e.* separation and recovery) is necessary. The solution to this problem is to immobilize the soluble transition metal complex on some kind of solid support.

The method most frequently used to immobilize transition metal carbonyl complexes in general is to substitute one or more of the carbonyl ligands with a supported N- or P-donor ligand [3], (eqn. 1).

$$M(CO)_n + xL \sim O \rightarrow M(CO)_{n-x}(L \sim O)_x + xCO \quad (1)$$

For carbonyl complexes bearing ligands other than CO, *e.g.* arenechromiumtricarbonyl, the arene ligand can be used as a link to the support (eqn. 2).



(2)

This approach has been used to prepare heterogenized hydrogenation catalysts [4–6].

By the latter approach the essential catalytic properties of the metal complex are maintained upon heterogenisation [4]. One serious drawback of the catalysts prepared *via* the route of eqn. 2, however, is the problem of metal leakage and catalyst instability [4, 7]. The arene ligand probably functions as a leaving group in the catalytic cycle of the complex [8, 9]. This means that those chromiumtricarbonyl fragments formed during the reaction which do not recombine with the arene ligand will be lost from the support. In this way catalyst lifetime is substantially shortened. The approach represented by eqn. 1 is in this respect superior, since the link between the metal atom and the support is not involved in the catalytic process.

To minimize effects on the catalytic properties of the complex the exchanging ligand L should have acceptor–donor properties comparable to those of CO. Moreover the ligand L should be such that it can be bound to the support by chemical means. One type of ligand which meet such requirements to some extent are the isonitriles-RNC [10]. Recent reports have shown how isonitriles can be chemically bound to silica [11] and polystyrene [11, 12] supports. Mentzel *et al.* [12] have also shown how a wide variety of carbonyl complexes can be heterogenized *via* such supported ligands. Their attempted preparation of a polymer bound toluenechromium-dicarbonyl-isonitrile complex did not however succeed. We now report a preparative route to such polymer-bound chromium complexes.

Experimental

Infrared spectra were recorded in KBr suspensions on a PE 580B spectrometer. Photochemical reactions were carried out with an 150 W Hanau high-pressure mercury lamp with a quartz cooling jacket.

Preparation of Support

Commercially available 3-aminopropyltriethoxy silane was converted into 3-isocyanopropyl triethoxysilane according to Howell and Berry [11]. Subsequent condensation of this silane with silica (Degussa Aerosil 200) in refluxing toluene yielded the functionalized support (I).

Preparation of Immobilized Metal Complexes

All reactions with arenechromiumcarbonyl complexes were done under dry N_2.

a) Attempted Direct Substitution (Scheme 1)

4.0 g of functionalized support ($3 \cdot 10^{-4}$ mol isonitrile/g) and 0.4 g methylbenzoatechromiumtricarbonyl (Strem Chem. Inc.) in toluene/THF (50/20 ml) was irradiated for 90 minutes at room temperature. After filtration and washing with 3 X 50 ml toluene the resulting light yellow-orange silica gel was dried in a stream of N_2.

b) Indirect Substitution (Scheme 1)

This was done according to the procedure given for the preparation of thiocarbonyl complexes [13], *i.e.* 0.4 g methylbenzoatechromiumtricarbonyl in 50 ml degassed toluene and 3 ml cyclooctene (Aldrich) was irradiated for 50 minutes at room temperature. The irradiation was stopped and 4.0 g of functionalized support, carefully degassed, was added. The reaction mixture was left overnight, then filtered and finally washed (1 X 50 ml hexane, 1 X 50 ml THF, 3 X 50 ml hexane) before drying in a stream of dry N_2. This yellow silica gel was then stored in a Schlenk tube under N_2.

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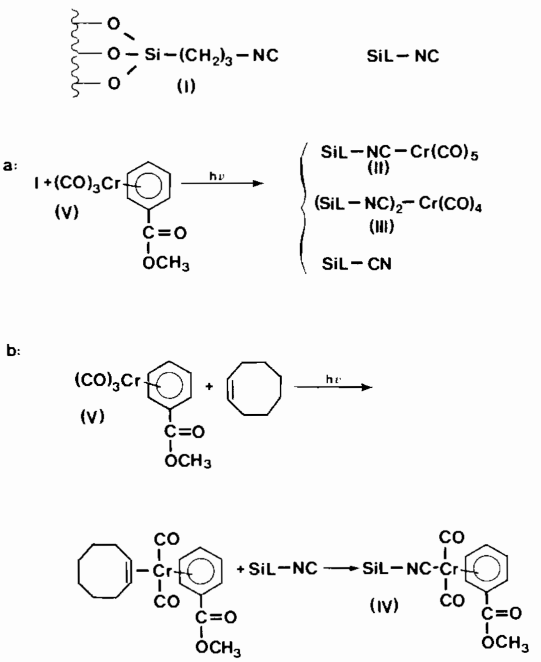

Scheme 1. Preparation of polymerbound Cr-complexes *via*: a) the direct route. b) the indirect route.

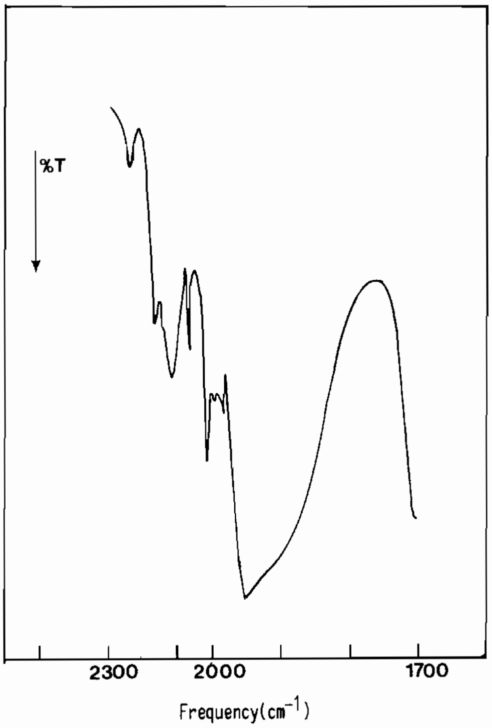

Fig. 1. Infrared spectrum of the silica gel obtained after direct substitution.

Results and Discussion

Strohmeier and Hellman [10, 14] have used the photoinitiated ligand dissociation path to substitute a CO ligand in arenechromiumtricarbonyl complexes and in this way prepared the cyclohexylisonitrile derivatives, arene $Cr(CO)_2(CNC_6H_{11})$. When applied to our silica-bonded isonitrile ligand (I) this method gave a very complex product mixture (Scheme 1a). In the infrared spectrum (Fig. 1) a large number of bands in the CO and NC stretching region can be seen.

Starting at high wavenumbers the band at 2240 cm^{-1} can be assigned to a nitrile $-(CH_2)_3-CN$ (compare butyronitrile ν(CN) 2265 cm^{-1}). Hence an isomerisation of the isonitrile to a nitrile has taken place. This effect was not observed in the study of Menzel *et al.* [12]. From the present data it cannot be concluded whether the isomerization is effected by the irradiation, or is caused by the Cr ions in the reaction medium.

Besides the isomerized isonitrile, the spectrum (Fig. 1) also suggests at least three different substitution products. The sharp peak at 2170 cm^{-1} together with the peak at 2067 cm^{-1} and the broad band at 1960 cm^{-1} suggest the formation of $Cr(CO)_5$–CN–SiL(II)($EtNCCr(CO)_5$ ν(NC) 2167 cm^{-1}, ν(CO) 2067 cm^{-1}, 1961 cm^{-1}, [15]), while the sharp peak at 2015 cm^{-1} together with the broad band at 1950 cm^{-1} and the shoulder at ~1920 cm^{-1} suggest the formation of $Cr(CO)_4(CN\text{-}SiL)_2$ (III), ($(EtCN)_2Cr(CO)_4$ ν(NC) 2162 cm^{-1}, 2128 cm^{-1}, ν(CO) 2018 cm^{-1}, 1945 cm^{-1}, 1933 cm^{-1}, 1926 cm^{-1} [15]).

The third product that the IR-spectrum gives us a hint of is the desired monosubstituted product. The rather intense band at ~2120 cm^{-1} can be assigned to ν(NC) in $CH_3O_2CC_6H_5Cr(CO)_2CN$-SIL(IV), (ν(NC) 2123 cm^{-1} in $(CO_2CH_3)_2C_6H_4$-$Cr(CO)_2CNC_6H_{11}$ [10]).

The formation of the pentacarbonyl(II) and the tetracarbonyl(III) are rather puzzling. Their formations are apparently not caused by the presence of the support, since they are formed with silica support (present study) as well as with polystyrene support (Menzel *et al.* [12]). As some amount of the monosubstituted product (IV) is observed in our experimental data (Fig. 1), it can be suggested that the radiation causes reactions that decompose the product (IV), to form the pentacarbonyl(II) and tetracarbonyl(III).

Decomposition reactions of arenechromiumdicarbonylisonitrile complexes upon prolonged irradiation have been observed before [16], but no decomposition products were identified.

To avoid the formation of undesirable side-products on the support the indirect method given in Scheme 1 was applied. As can be seen (Fig. 2)

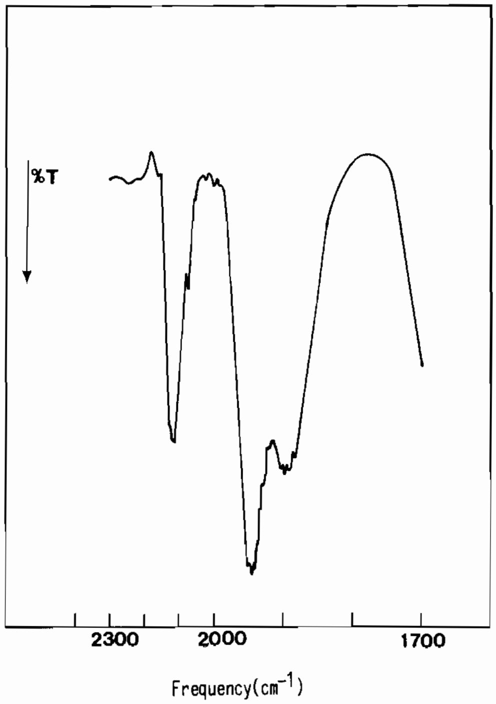

Fig. 2. Infrared spectrum of the silica gel obtained after indirect substitution.

this procedure gives a much purer product. The dominant peaks in this spectrum (*i.e.* a sharp peak at 2116 cm^{-1} and two other strong peaks at 1944 cm^{-1} and 1896 cm^{-1}) are in agreement with what has been found for other isonitrile complexes (*e.g.* $(CO_2CH_3)_2C_6H_4Cr(CO)_2C_6H_{11}NC$ $\nu(NC)$ 2123 cm^{-1}, $\nu(CO)$ 1940 cm^{-1} [10]). Hence this preparative route makes it possible to prepare a polymer bound arenechromiumdicarbonylisonitrile complex.

The rather low CO stretching frequency (1940 cm^{-1}, 50 cm^{-1} lower than that of the tricarbonyl complex (V)), indicates that the isonitrile ligand cannot fully play the π-accepting role of CO. The remaining CO-ligands have to accept more electron density from the metal ion. What consequences this might bring about on the catalytic properties are at present being studied.

Acknowledgement

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