Metal Complexes with Macromolecular Ligands Containing the Isocyano Group

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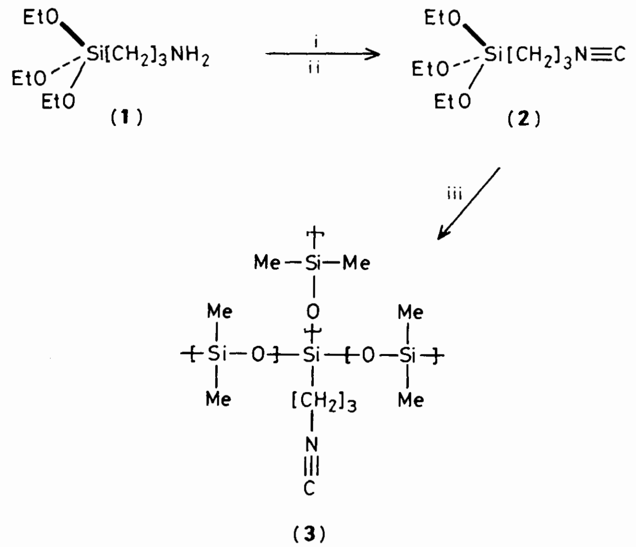
Reaction of Cr, Mo, W, or V vapours with an isocyano-functionalised polysiloxane (**3**) gives the polymer-encapsulated $M(CNR)_6$ complexes as shown by fluid matrix i.r. and u.v.–visible spectroscopic studies.

The wide range of structural forms adopted by the metal carbonyl complexes, at both a monometallic and cluster level, has been reflected in recent years by species containing the isoelectronic isocyano ligand.[1] However, while the bonding characteristics of the RNC ligand have been studied extensively, an additional feature of such molecules[2] has been largely neglected; namely, that in possessing a substituent R on the isocyano group there is the potential for synthesis of metal complexes, exhibiting a well defined microstructure, but encapsulated within a macromolecular environment. In this communication we report that the reaction of an isocyano-derivatised polysiloxane with group 5a and 6a metal



Scheme 1. *Reagents:* i and ii, see ref. 2a; iii, $Me_2Si(OEt)_2$, aqueous NaOH, stir overnight at room temperature under N_2.

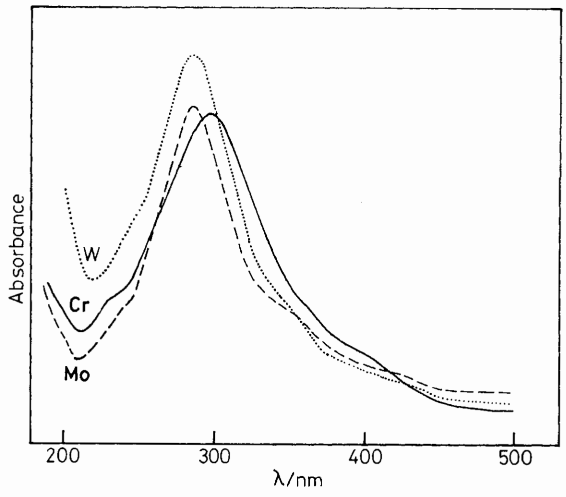


Figure 1. U.v.–visible absorption spectra obtained after the deposition of metal vapours into a thin film of (**3**) at ~220 K: (a), Cr; (b), Mo; (c), W.

vapours affords novel polymer-based binary metal–isocyanide complexes.

The isocyano-polysiloxane (**3**) was prepared (Scheme 1) by stirring (**2**), synthesised from the corresponding amine (**1**),[2] with $Me_2Si(OEt)_2$ (in the molar ratio 1 : 17) in the presence of aqueous NaOH. The product was purified to give a clear oil from which any unchanged starting material and low molecular weight product could be sublimed at 10^{-2} Torr. This afforded (**3**) as a colourless, viscous fluid (M_w 1500, by g.p.c.) characterised by ^1H and ^{13}C n.m.r. and i.r. spectroscopy† as containing approximately 3.5 $-N{\equiv}C$ functional groups per macromolecule.

The reactions of (**3**) with Cr, Mo, W, and V vapours were studied using a metal vapour–matrix isolation spectroscopic apparatus[3] with *in situ* monitoring of product formation by i.r. and u.v.–visible spectroscopy. Deposition of Cr vapour into the polymer film at ~220 K resulted in a decrease in the intensity of the i.r. band at 2145 cm^{-1} due to $\tilde{\nu}(C{\equiv}N)$ in (**3**), and the appearance of a broad asymmetric band at ~1950 cm^{-1} assigned to a terminal isocyanide ligand complexed to chromium. On cooling the film to 77 K the spectrum sharpened revealing a band at 2010 cm^{-1} with two broader, overlapping bands at 1975 and 1950 cm^{-1}, consistent with formation of a $Cr(CNR)_6$ complex in which distortion from the idealised O_h symmetry results in the splitting of the triply degenerate i.r.-active vibration into the corresponding A and E modes. On exposure to air, these bands decrease in intensity and a new band appears at 2085 cm^{-1} assigned to the $[Cr(CNR)_6]^+$ cation. These observations are in good agreement with previous studies for chromium complexes of small-molecule isocyanide ligands.[4—6] The identity of the $Cr(CNR)_6$ complex for the macromolecular ligand (**3**) was confirmed by its electronic spectrum (Figure 1a). The existence of an intense band at 298 nm, with a low intensity–high energy shoulder at 232 nm and two low intensity–low energy shoulders at 350 and 400 nm compares well with the spectrum for $Cr(CO)_6$, and similarly may be assigned to a metal-to-ligand charge transfer ($^1A_{1g}$–$^1T_{1u}$) transition and d–d transitions respectively.[7,8] Differences between Figure 1(a) and the electronic spectrum of $Cr(CNPh)_6$[4] may be explained by M.O. calculations[9] for the non-co-ordinated RNC molecule which show that the degenerate π^* orbitals in alkyl isocyanides (and CO) become non-degenerate in the case of an aryl isocyanide owing to the influence of the π orbitals on the arene ring.

Mo or W vapours also reacted with a thin film of the isocyano-polymer (**3**) at ~220 K to give products whose i.r. spectra were in accord with an $M(CNR)_6$ assignment; bands occur at 2010 and 1960br. cm^{-1} for Mo and 2010 and 1945br. cm^{-1} for W. The electronic spectra of these complexes (Figure 1b and c) were very similar to that of $Cr(CNR)_6$ (Figure 1a) and to the spectra of their carbonyl counterparts.[7]

No zerovalent binary isocyanide complexes of V are known currently, although $[V(CNR)_6]^{2+}$ has been defined structurally.[10] The reaction of V vapour with polymer (**3**) resulted in a product whose i.r. spectrum contained new bands at 2112 and 2056 cm^{-1} indicative of terminal isocyanide ligands. The u.v.–visible spectrum consisted of two broad overlapping bands at 322 and 350 nm with shoulders at 242/265 and 450/560 nm. Comparison of the electronic spectrum with that for $V(CO)_6$[11] points to an assignment to the novel $V(CNR)_6$ complex, both spectra exhibiting a pronounced broadening compared with the Cr analogues which has been attributed previously[11] to a dynamic Jahn–Teller distortion for the carbonyl complex. While the existence of $V_2(CO)_{12}$ has been suggested,[12] we find no evidence for the isocyanide counterpart in the present studies.

Finally, the presence of the propyl group between the isocyano function and the polymer backbone is expected to impart sufficient flexibility to permit the polysiloxane chain to wrap around each metal centre, although, with only 3—4 isocyano groups per macromolecule, no single chain can complete the co-ordination sphere. Further studies are now in progress to investigate the extent of inter- *vs.* intra-chain binding in these complexes and to extend our studies with

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† (**3**): ^{13}C n.m.r. ($CDCl_3$), δ 156.0 ($-N{\equiv}C$), 58.15 ($MeCH_2O$), 43.85 (J_{CN} 6.1 Hz, $CH_2N{\equiv}C$), 23.42 (CH_2), 18.28 ($MeCH_2O$), 10.96, 9.77, and 8.64 (CH_2Si), and 0.94 and −1.12 (MeSi); ^1H n.m.r. ($CDCl_3$), δ 3.70 (q, $MeCH_2O$), 3.34 (m, $CH_2N{\equiv}C$), 1.72 (m, CH_2), δ 1.18 (t, $MeCH_2O$), 0.66 (m, CH_2Si), and 0.10, 0.07, and 0.06 (3 × s, MeSi); i.r. (thin film): $\tilde{\nu}(C{\equiv}N)$ 2145 cm^{-1}.

macromolecular ligands, such as (**3**), to other transition metals.

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