π-Allylnickel Complexes containing Thiourea as Ligand

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π-ALLYLNICKEL complexes of the general formula π-allylNiLL'X (I) [where X = Cl,Br; I or L,L' = PR_3; L = PR_3, L' = CO; LL' = $Ph_2PCH_2{\cdot}CH_2$-PPh_2 (R = alkyl or phenyl)] have been recently reported.[1]

It has now been found that complexes of type (I) with L,L' = thiourea or alkylthiourea can easily be prepared by reaction of π-allylNiX dimer (1 mol.) and thiourea or alkylthiourea (2 mol.) in methanol at 0° in an inert atmosphere. On dilution with benzene (2–3 vol.), complexes of type (I) separate as pure, crystalline solids. In this way complexes (I), containing allyl, methylallyl, or crotyl groups, Cl, Br or I, and thiourea, di-isopropylthiourea or ethylenethiourea have been prepared.

These complexes are air-sensitive but are stable when stored in an inert atmosphere and below −10°. They crystallize as red-orange to red-violet prisms, soluble in methanol, ethanol, and generally in polar solvents, but are insoluble in benzene, hexane, and carbon tetrachloride. Their i.r. and ^1H n.m.r. spectra reveal features typical of π-allylic complexes.† They are diamagnetic and strongly dissociated in methanolic solution.

Furthermore, it has been found that π-allylNiLX complexes (II) with L = thiourea or alkylthiourea may be prepared by reaction of π-allylNiX dimer (1 mol.) and L (1 mol.) in a small volume of methanol or ethanol at 0° in an inert atmosphere. When the solutions are cooled below −40° separation of the complexes occurs, in the case of L = ethylenethiourea or di-isopropylthiourea. These π-allylic complexes are crystalline red-orange, diamagnetic solids.

Both (I) and (II) with L,L' = thiourea are efficient catalysts for the synthesis of hexadienoic esters from allylic halides, acetylene, carbon monoxide, and alcohols.[2]

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† These complexes are being investigated by *X*-ray techniques by Prof. Corradini and his co-workers at the University of Naples.

[1] D. Walter and G. Wilke, *Angew. Chem.*, 1966, **78**, 941; F. Guerrieri and G. P. Chiusoli, *Chem. Comm.*, 1967, 781; M. R. Churchill and T. A. O'Brien, *Chem. Comm.*, 1968, 246.

[2] G. P. Chiusoli and S. Merzoni, *Chimica e Industria*, 1961, **43**, 259; G. P. Chiusoli, M. Dubini, M. Ferraris, F. Guerrieri, S. Merzoni, and G. Mondelli, to be published.