New Silicon–Nickel Complexes: Bis(substituted silyl)bipyridylnickel(II)

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Summary Two bis(substituted silyl)bipyridylnickel(II) complexes have been prepared by the reaction of diethyl(bipyridyl)nickel(II) with $HSiCl_3$ or $HSiMeCl_2$, which react with HCl and DCl to form, respectively, the corresponding hydrosilanes and deuteriosilanes.

ALTHOUGH various types of Group IVB derivatives of the transition elements have been studied,[1] only three compounds containing nickel–silicon bonds have been reported.[2,3] During our studies on hydrosilylation of olefins catalysed by nickel complexes,[4] we have isolated two complexes (**Ia**) and (**Ib**) containing nickel–silicon bonds and studied their reactions.

Diethyl(bipyridyl)nickel(II)[5] was treated with Cl_3SiH in ether at -50 to $-40°$ for 1·5 h under nitrogen. The colour of the reaction mixture changed from deep green to brown with evolution of 1 equiv of hydrogen, the only gaseous product detectable by mass spectrometry. Filtration of the reaction mixture, at *ca.* $-70°$ gave bis(trichlorosilyl)bipyridylnickel(II) (**Ia**),† an insoluble yellow-brown powder, in 85% yield. G.l.c. analysis of the filtrate showed the formation of $EtSiCl_3$ (64%). Although detection of ethane has so far been unsuccessful, the principal process of the present reaction is stoicheiometric with equation (1).

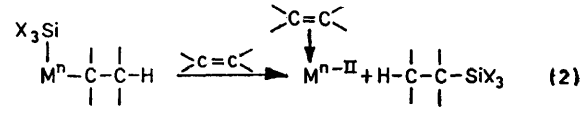
$$[NiEt_2(bipy)] + 3HSiX_3 \rightarrow [Ni(SiX_3)_2(bipy)] + EtSiX_3 + H_2 + C_2H_6 \quad (1)$$

(**I**) **a**, $X_3 = Cl_3$
b, $X_3 = MeCl_2$

Similarly, but at higher temperature (-40 to $-30°$), (**Ib**), the methyldichlorosilyl analogue of (**Ia**), was obtained. It was of similar appearance and was obtained in 84% yield, along with $EtMeSiCl_2$ (96%).

Both these new complexes are stable in an inert atmosphere but they fume and decompose spontaneously in air leaving a light green substance, possibly dichloro(bipyridyl)nickel(II). Complex (**Ia**) is insoluble in most organic solvents and decomposes immediately in protic solvents, while (**Ib**) is soluble in benzene giving a reddish solution.

Compounds (**Ia**) and (**Ib**) reacted with HCl in benzene at room temperature to give trichlorosilane [ν(Si–H) 2260 cm^{-1}] and methyldichlorosilane [ν(Si–H) 2210 cm^{-1}], respectively, along with dichloro(bipyridyl)nickel(II). With DCl, trichlorodeuteriosilane [ν(Si–D) 1645 cm^{-1}][6] was obtained from (**Ia**) and methyldichlorodeuteriosilane [ν(Si–D) 1600 cm^{-1}] from (**Ib**). These reactions show the



(2)

presence of Ni–Si bonds in (**Ia**) and (**Ib**).

The formation of $EtSiX_3$ in excellent yields in the reaction (1) may be of interest in the light of a suggested mechanism,[7] equation (2), for transition metal complex catalysed hydrosilylation of an olefin, which involves a possible intermediate with a silyl and an alkyl group attached to a transition metal atom.

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† The new compounds reported here have satisfactory analytical data.

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