Reaction of Bis(trichlorosilyl)bipyridylnickel(II) with Diphenylacetylene

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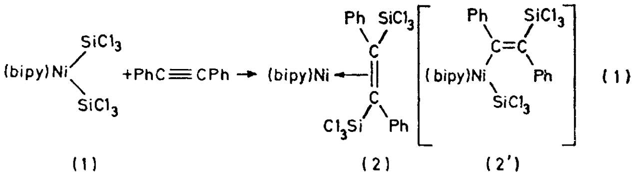
Summary A violet complex, possibly [*trans*-α,α′-bis-trichlorosilyl)stilbene]bipyridylnickel(0), was obtained from the reaction of bis(trichlorosilyl)bipyridylnickel(II) with diphenylacetylene, and converted into *trans*-α,α′-bis(trimethylsilyl)stilbene by methylation.

The reaction of transition-metal hydrides and alkyls with acetylenic compounds has been extensively investigated,[1] but few reactions leading to the formation of transition metal–olefin complexes are known.[1e] We now report the first example of the transfer of silyl groups in a silicon–nickel complex from nickel to acetylenic carbon atoms, forming a disilylolefin–nickel(0) complex.

To a mixture of bis(trichlorosilyl)bipyridylnickel(II) (**1**)[2] (1 part) and diphenylacetylene (2·5 parts) was added benzene at room temperature in an atmosphere of nitrogen. After 30 min the colour changed from brown to purple. After 3 h, filtration of the reaction mixture gave a violet powdery product (**2**)† (65% yield), decomposing at 194—196° in a sealed tube. The i.r. spectrum (KBr) showed no peaks in the range of 1500—1650 cm^{-1} other than those displayed by the starting material (**1**).



(1) (2) (2′) (1)

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† Satisfactory analytical data were obtained.

‡ The possibility of (**2′**) as an alternative structure was suggested by a referee.

Although an alternative structure (**2′**) is possible,‡ the chemical behaviour of the product supports the suggested structure (**2**).

Treatment of the reaction product with methylmagnesium bromide afforded, after decomposition with dilute hydrochloric acid, *trans*-α,α′-bis(trimethylsilyl)stilbene,[3] m.p. 115—116°, as the sole product (55% yield). No *cis*-isomer[4] was detected. This is consistent with the *trans*-configuration of the olefin ligand attached to the nickel atom.

The action of dry hydrogen chloride (room temperature, 2 h) on the product of reaction (1) gave, after filtration of the reaction mixture, dichloro(bipyridyl)nickel(II) in quantitative yield. Examination of the filtrate by i.r. spectroscopy showed the complete absence of trichlorosilane which should be formed if the structure is (**2′**). Methylation of the filtrate afforded 1,2-bis(trimethylsilyl)-1,2-diphenylethane,[3] m.p. 152—153·5° (18% yield) and a minor unidentified product. No α-trimethylsilylstilbene was produced.

The olefin complex (**2**) is unstable in air and the solution is air-sensitive; it is slightly soluble in benzene but insoluble in ether. Compound (**2**) is almost inert to the action of an excess of triphenylphosphine or trichlorosilane in ether or benzene even under reflux conditions. The strength of the nickel–olefin bond may be attributed to the presence of electron-accepting trichlorosilyl groups and also phenyl groups on olefinic carbon atoms.

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