Alkylation of Nickel(II) Corrole Ambident Anions

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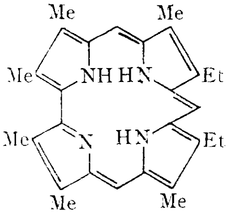
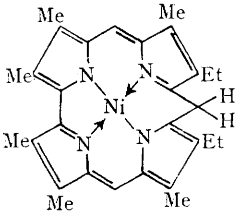
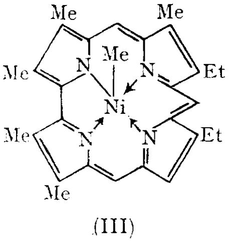
WE have shown[1] that corroles (I) readily form nickel(II) complexes in which one of the imine hydrogens of the original corrole is transferred to carbon. This 'extra' hydrogen atom causes a break in the conjugated system with consequent loss of aromatic character in the nickel corrole as revealed by the visible spectrum.[1] In this respect the nickel corroles resemble cyclopentadiene where removal of the 'extra' hydrogen atom by the action of base yields the aromatic anion; the same behaviour was observed with the paramagnetic nickel corrole, provisionally formulated as (II). Methylation of this ambident anion gave a derivative $C_{30}H_{34}N_4Ni$, the n.m.r. spectrum of which contained a singlet at τ 12·65 corresponding to the 'extra' methyl group which, by analogy with the corresponding signals of methylcobalt(III) porphins,[2] is clearly located on the nickel atom. Methylation of the nickel corrole anion had therefore occurred at the metal and none of the corresponding *C*-alkylated products were obtained. Elemental analysis and the i.r. spectrum indicated the absence of any water or alcohol ligands and the diamagnetic methylnickel complex is therefore formulated as a resonance hybrid of (III) and (IV). The canonical form (III) emphasises the presence of nickel(II) but contains a non-aromatic 16π-electron conjugated system whereas the nickel(IV) formulation (IV) has an aromatic 18π-electron system.



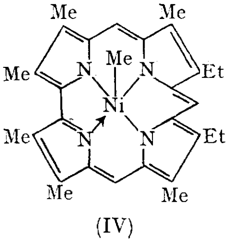
(I)



(II)



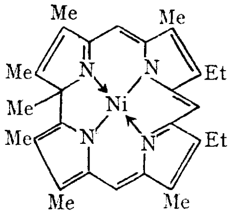
(III)



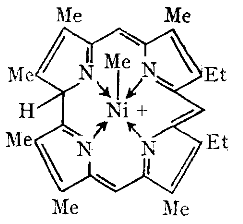
(IV)

Analogous nickel(II)-ethyl and -n-propyl derivatives were also prepared. Although five-co-ordinate nickel complexes are well known,[3] we are not aware of other stable five-co-ordinate nickel(II)-alkyl derivatives. Protonation of (III) with trifluoroacetic acid caused a marked colour change from red to green accompanied by a dramatic shift of the n.m.r. signals. The nickel-methyl signal moved downfield and was obscured by the ligand C—Me signals at about τ 7·6, and the *meso*-proton signals moved upfield from τ 0·6 to 2·5 (2H) and 2·6 (1H). The spectrum showed the absence of any saturated alkyl signals and indicated that angular protonation had occurred. The electronic spectrum of the protonated form closely resembled that of a nickel 1-methyltetradehydrocorrin[4] (V), and one structure consistent with these observations is (VI) in which a break in the aromatic conjugated sytem and the positive charge on the complex cause deshielding of the nickel-methyl protons. The protonation is reversible and treatment of (VI) with base regenerates (III).

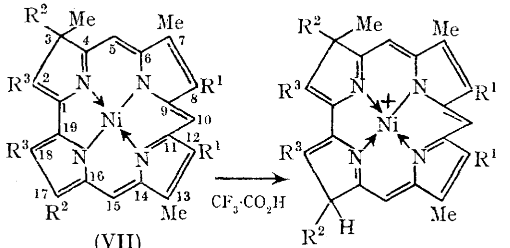
When the nickel-methyl derivative (III) was heated for 90 min. in chlorobenzene solution under



(V)



(VI) $O_2C{\cdot}CF_3$



(VII)

(VIII) $O_2C{\cdot}CF_3$

reflux in an atmosphere of nitrogen, a mixture of products was obtained, from which the main component (30%) proved to be the nickel 3,3-dimethylcorrole (VII; R^1 = Et; R^2 = R^3 = Me). This was confirmed by examination of the similar product (VII; R^1 = R^3 = Me; R^2 = Et), derived from nickel 3,17-diethyl-2,7,8,12,13,18,-hexamethylcorrole, in which an n.m.r. triplet at τ 9·78 indicated the presence of the methyl of an ethyl group attached to saturated carbon. These nickel 3,3-dialkylcorroles could arise by an intermolecular process or an intramolecular sigmatropic route and evidence on this point is being sought. Nickel 3,3-dialkylcorroles have been obtained from the action of heat on the corresponding nickel 2-alkyl-1-methyltetradehydrocorrins[5] (V).

In another series the nickel corrole (II) was converted to its anion which was treated with allyl bromide. Two neutral products were obtained, neither of which was the nickel-allyl derivative. One of these (35%) has proved to be a nickel *gem*-allyl-methylcorrole whereas the other product is a *meso*-di-allyl derivative which is still under investigation. It is possible that the nickel-allyl derivative is an intermediate in the reaction and that the observed products are formed by intramolecular sigmatropic rearrangements.

Protonation of the nickel 3,3-dialkylcorroles with trifluoroacetic acid occurs at C-17 giving a charged species (VIII) and causing a colour change from green to blue. Protonation creates a further chiral centre and examination of the 100 Mc. n.m.r. spectrum of (VIII; R^1 = R^3 = Me; R^2 = Et) indicates that the existing centre of chirality at C-3 has some influence on the protonation since there is a slight preponderence (6 : 5) of protonation from one face of the molecule.

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[2] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc.* (*C*), 1968, 881.

[3] E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 245.

[4] D. A. Clarke, R. Grigg, R. L. N. Harris, A. W. Johnson, I. T. Kay, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1967, 1648.

[5] R. Grigg, A. W. Johnson, and K. Shelton, *J. Chem. Soc.* (*C*), 1968, 1291; R. Grigg, A. W. Johnson, K. Richardson, and K. Shelton, *Chem. Comm.*, 1967, 1192. Later work has shown that the products, originally formulated as nickel 2,2-dialkylcorroles, should be represented as 3.3-dialkyl derivatives.