Reactivity Patterns of Charged Delocalized Six-membered Chelate Rings; *N*-Alkylation, Deacylation, and Protonation

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Summary Reactivity patterns paralleling those found for transition metal corrole complexes are reported for a nickel(II) 15-membered macrocyclic complex containing charged delocalized six-membered chelate rings; *N*-alkylation of the nitrogen donor atoms as well as deacylation and reversible protonation of the *meso*-carbon atoms of such rings have been observed, and the resultant *N*-alkyl groups are reactive, being solvolysed in nucleophilic solvents.

The reactive sites in macrocyclic polypyrrolic ligands and their transition-metal complexes include the nitrogen and *meso*-carbon atoms.[1] We report here several reactions of the nickel(II) complex (I)[2]† and related species which suggest that the distinctive reactivity patterns found in the above-mentioned systems are common to charged delocalized six-membered chelate rings.

The neutral nickel complex (I) undergoes several reactions known to occur with transition-metal porphyrin and corrole complexes including *N*-alkylation[1a,b] and *meso*-carbon protonation[1b,d] (see Scheme).

Treatment of solutions of (I) in dry $CHCl_2$ with methyl fluorosulphonate, followed by removal of solvent and addition of MeOH and $LiClO_4$ gives yellow crystals of (II)

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† Satisfactory elemental analyses were obtained for all complexes.

($>$90%), a 2 : 1 electrolyte in MeCN. The *N*-methyl n.m.r. resonances occur as a singlet at τ 5·80, requiring that the methyl groups be symmetrically located, *i.e.*, on the two identical nitrogen atoms of either the five- or six-membered saturated ring. The latter possibility is more likely from steric requirements.‡

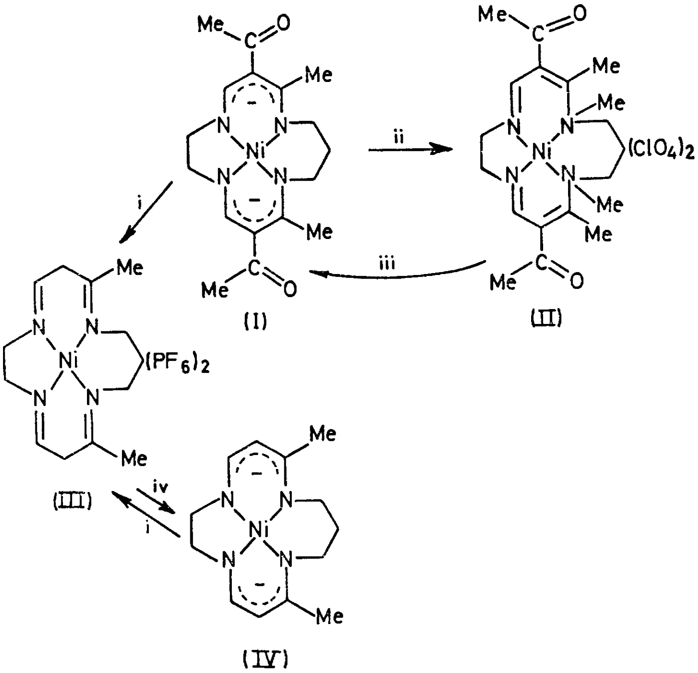
Aqueous slurries of (I) react with mineral acids to produce amber solutions from which (III) ($>$90%), a 2 : 1 electrolyte in MeCN, can be isolated. Key features of the n.m.r. spectrum of this material, from which the acetyl groups have been displaced (in contrast to its fourteen-membered analogue which undergoes reversible protonation)[3] are the absence of acetyl methyl resonances and the presence at τ 5·60 of signals due to the CH$_2$ groups generated at the site of the carbonyl substituents.

Solutions of (III) in MeCN can in turn be reversibly deprotonated to give (IV) ($>$ 90%). The structure of this complex was established by n.m.r. spectroscopy. The protons on the six-membered unsaturated chelate rings now couple (*J ca.* 5 Hz) to give two doublets at τ 5·48 and 3·53 in CDCl$_3$.

Thus, in complex (I), as found for transition-metal–corrole complexes,[1a,b] charged delocalized six-membered chelate rings are subject to electrophilic attack at both the nitrogen and *meso*-carbon. Alkylation produces the *N*-alkyl species (II), while protonation gives (III).

The resultant *N*-alkyl groups are, as expected, susceptible to nucleophilic displacement, as determined spectrophotometrically. Solutions of (II) (10^{-5} M in aqueous MeCN) revert to (I), the reaction being essentially complete ($>$ 95%) in 24 h at room temperature.§ At higher concentrations of (II), however, the product is (III). As implied, (I) is subject to protonation at the *meso*-carbon atom with the acetyl groups rapidly undergoing nucleophilic displacement, as shown by the isolation of (III).

The reversible protonation (III) $\rightleftharpoons$ (IV) is not unexpected, in view of reports of such reactions for macrocyclic complexes possessing one charged delocalized six-membered ring.[4] Ready alkylation of nitrogen donor atoms in such rings to yield reactive *N*-alkyl groups is uncommon, and we are aware of no similar reactions involving macrocyclic complexes lacking pyrrole nitrogen donor atoms.



Scheme. *Reagents:* i, H$^+$; ii, MeSO$_3$F–CH$_2$Cl$_2$; iii, aqueous MeCN; iv, NaOEt–MeCN.

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‡ Dr. P. W. R. Corfield has initiated *X*-ray studies on the crystal structure of (II).

§ Methanol, generated from the hydrolysis of (I) was detected by g.l.c.

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