

A Novel Quinquedentate N₅ Macrocyclic containing a Pendant Amino Group

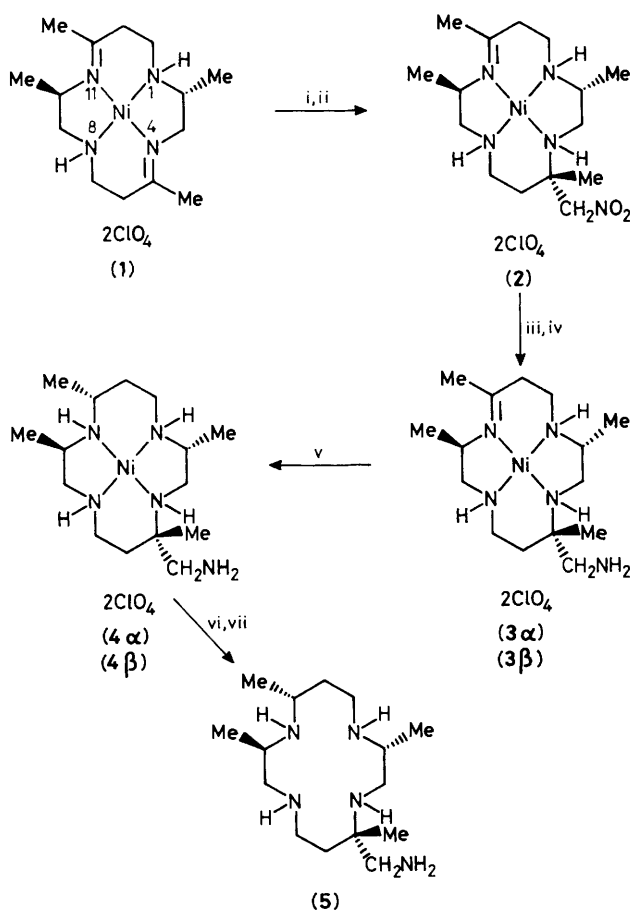
Bohdan Korybut-Daszkiwicz

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw 01-224, Poland

The addition of the monoanion of nitromethane to the C=N group of [Ni(*C-rac-N-meso*-2,5,10,12-tetra-methyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)](ClO₄)₂ (**1**) followed by reduction gives the nickel(II) complex (**4**), containing the pendant -CH₂NH₂ group; the free ligand (**5**) may be obtained by treating the nickel complex with dry HCl gas in acetonitrile solution.

The preparation of pendant arm macrocycles has attracted considerable attention in recent years.¹ House² has reported the preparation and crystal structure of a quinquedentate N₄O ligand prepared by dioxygen oxidation of *trans*-(*RSSR*)-[CoCl₂(tet a)]ClO₄.[†] In this reaction oxidation of one of the *gem*-dimethyl substituents to a co-ordinated -CH₂OH group occurs. The present communication describes the preparation of a C-functionalised cyclam derivative with a -CH₂NH₂ side chain.

The ligand synthesis is summarised in Scheme 1. Addition of Et₃N to a nitromethane solution of the nickel(II) complex [Ni(2,5,10,12-Me₄[14]4,11-dieneN₄)](ClO₄)₂[‡] (**1**)³ leads to



Scheme 1. Reagents: i, MeNO₂, Et₃N; ii, HClO₄; iii, Zn, HCl; iv, NaOH; v, NaBH₄; vi, HCl, MeCN; vii, NaOH.

[†] (2,5,10,12-Me₄[14]4,11-dieneN₄) = *C-rac-N-meso*-2,5,10,12-tetra-methyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene; tet a = *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane.

addition of -CH₂NO₂ to the less hindered -C=N group of (**1**) to give the sparingly soluble paramagnetic monoperochlorate salt of (**2**). The paramagnetic product was then protonated with perchloric acid in methanol-nitromethane (9:1) solution giving the yellow diamagnetic diperochlorate (**2**).

Reduction of the nitro group with zinc powder and hydrochloric acid gave two paramagnetic *N*-isomeric 5-aminomethyl derivatives (**3α**)·H₂O and (**3β**)·2H₂O. Further reduction with sodium borohydride in methanol solution reduced the remaining C=N double bond, yielding the paramagnetic, *N*-isomeric complexes (**4α**)·H₂O and (**4β**)·2H₂O. Demetallation of (**4α**) and (**4β**) in acetonitrile saturated with dry hydrogen chloride gave the same free ligand (**5**) (m.p. 120 °C).

All 5-aminomethyl derivatives (**3**) and (**4**)[‡] were also isolated in the form of their protonated diamagnetic triperchlorates, which were precipitated with benzene from nitromethane solutions acidified with perchloric acid.

Compounds (**2**)–(**5**) as well as the triperchlorate salts gave satisfactory analytical data and were characterised by the i.r., u.v., and visible spectra. The ¹³C and ¹H n.m.r. spectra (Table 1) of the diamagnetic triperchlorates are also consistent with the structures (**2**)–(**5**).

We have found that the addition of nitromethane to the C=N bonds in other readily accessible nickel(II) complexes of

Table 1. ¹H N.m.r. data of compounds (**1**)–(**5**).^a

Compound	Solvent	=CCMe	>CHMe	NCH ₂ CMe
(1) [ClO ₄] ₂	CD ₃ NO ₂	2.36s (3),	1.38d (3),	
		2.23s (3)	1.22d (3)	
(2) [ClO ₄] ₂	CD ₃ NO ₂	2.28s (3)	1.41d (3),	1.45s (3) ^c
			1.21d (3)	
(3α) [ClO ₄] ₃		2.37s (3)	1.47d (3),	1.50s (3)
(3β) [ClO ₄] ₃		2.36s (3)	1.43d (3),	1.53s (3)
			1.27d (3)	
(4α) [ClO ₄] ₃	CD ₃ NO ₂ + CD ₃ OD + HClO ₄		2.00d ^b (3),	1.50s (3)
			1.22d (3),	
(4β) [ClO ₄] ₃			1.17d (3)	
			1.62d (3),	1.40s (3)
			1.17d ^b (3),	
			1.17d (3)	
(5)	CDCl ₃		1.05d (3),	1.07s (3)
			1.04d (6)	

^a 60 MHz, δ relative to SiMe₄; relative intensities in parentheses.

^b Singlet when NaBD₄ was used for reduction of the double bond.

^c NCH₂CMe at 5.39d (1) and 6.11d (1).

[‡] The relative C- and N-configurations in complexes (**3**) and (**4**) established on the basis of ¹H n.m.r. spectra^{3,4} is as follows: (**3α**), (1*RS*,2*RS*,4*RS*,5*SR*,8*RS*,10*RS*); (**3β**), (1*SR*,2*RS*,4*RS*,5*SR*,8*RS*,10*RS*); (**4α**), (1*RS*,2*RS*,4*RS*,5*SR*,8*RS*,10*RS*,11*RS*,12*RS*); (**4β**), (1*SR*,2*RS*,4*RS*,5*SR*,8*RS*,10*RS*,11*SR*,12*RS*).

unsaturated cyclam derivatives^{3,4} proceeds with equal ease to give macrocycles carrying a pendant arm.

This work was supported by the Polish Academy of Sciences.

Received, 25th September 1984; Com. 1364

References

- 1 T. A. Kaden, *Top. Curr. Chem.*, 1984, **121**, 157.
 - 2 D. A. House, M. Harnett, W. T. Robinson, and M. C. Couldwell, *J. Chem. Soc., Chem. Commun.*, 1984, 979.
 - 3 R. A. Koliński, B. Korybut-Daszkiewicz, Z. Kubaj, and J. Mroziński, *Inorg. Chim. Acta*, 1982, **57**, 269.
 - 4 R. A. Koliński and B. Korybut-Daszkiewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.
-