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Structural control of reactivity in some new cyclidene complexes

James H. Cameron *, Catherine A. Clarke, Georgina Rosair, Elinor L. Scott

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK

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Contents

Abstract

The crystal structure of a monoalkylated cyclidene complex of nickel(II) is reported. The asymmetric nature of this structure supports the results of earlier structural work in solution using NMR spectral evidence, and highlights the importance of steric control of the reactions of cyclidene molecules. The crystal structure of a new cyclidene, bearing chiral side chains, is also reported. This species shows extreme selectivity in its reactivity, refusing to alkylate with groups larger than methyl. The lack of reactivity of this cyclidene with the larger alkyl groups is ascribed to the sterically congested nature of the starting material. The structural studies show how careful choice of cyclidene substituents allows for control of the nature of the products of alkylation reactions. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclidene; macrocycle; chiral complex; reactivity control

1. Introduction

In a series of elegant papers, Busch and Alcock [1] have clearly demonstrated the fascinating chemistry of the family of macrocyclic ligands which they have termed

* Corresponding author. Fax: +44 131 451 3180; e-mail: j.h.cameron@hw.ac.uk

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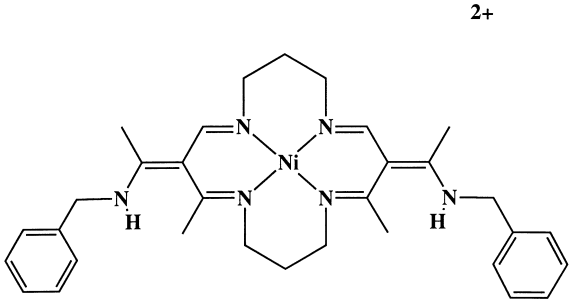
the "cyclidenes". These ligands are based upon the tetraaza macrocyclic species originally developed by Jager [2]. One of the most important features of these complexes is the ease with which the steric and electronic properties of the products may be varied by suitable choice of reagent in the general synthetic scheme [3]. For example, Busch and coworkers [4–7] have described the synthesis and characterisation of a large number of cyclidene complexes, altering the steric, electronic and structural properties in a systematic manner to show how bridged cyclidenes may participate in diverse functions such as the reversible binding of dioxygen, with either iron(II) [4] or cobalt(II) [5,6] as the metal centre, and molecular recognition, using host complexes with a specifically enlarged cavity for the inclusion of guest substrates [7].

This ability to fine tune the physical properties of the products is potentially extremely useful in terms of the utilisation of the cyclidenes in other areas of chemistry, and in recent years we have been interested in further investigation of the control of reactivity within the cyclidene family, particularly with respect to functionalisation of the ligand itself [8].

Even in the unbridged state, the cyclidenes can display remarkable behaviour.



We have shown that the complex containing two peripheral benzyl groups (**1**), Structure 1, possesses a fascinating and highly selective pattern of reactivity [9]. For example, reaction of (**1**) with methyl iodide leads to alkylation at both benzyl nitrogen atoms, but reaction with 1-bromopropane or larger homologues leads specifically to the monoalkylated products. In our earlier studies, we have investigated the reactions of complex (**1**) in some detail and, based largely on evidence from NMR spectroscopy, we were able to rationalise the results in terms of the structure adopted by the bis(benzyl) complex (Fig. 1) [10]. In this paper, we wish to report on some further examples of reactivity control in the cyclidenes and upon the crystal structures of a monoalkylated derivative of complex (**1**) and a chiral analogue of (**1**), complex (**2**).

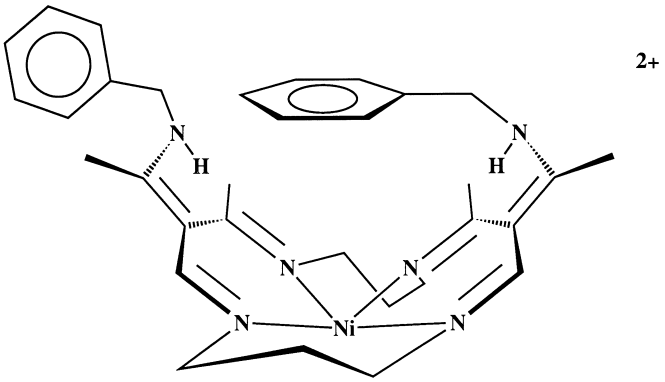


Fig. 1. Three-dimensional representation of the structure of complex (**1**) derived from NMR data.

2. Results and discussion

*2.1. Structure of the monoalkylated bis(benzyl) cyclidene (**3**)*

In our earlier studies, the inability of the bis(benzyl) functionalised cyclidene complex (**1**) to undergo alkylation at both peripheral nitrogen atoms when treated with 1-bromopropane was attributed to the asymmetric structure adopted by the parent complex [10]. Based on evidence from NMR spectroscopy, the structure of (**1**) was assigned as having one of the aromatic groups of a benzyl function "capping" a pseudo cavity located in the vicinity of one of the axial co-ordination sites of the metal ion. Although (**1**) is fluxional on the NMR time scale, with the two aromatic groups exchanging position rapidly at ca. 80 °C, steric constraints dictate that only one of the aromatic groups may occupy the capping position at any instant.

In accord with previous structural work on related molecules by Alcock et al. [11], it was envisaged that alkylation at one of the secondary nitrogen atoms of the parent complex would result in twists about the adjacent C(1)–N and C(1)–C(2) bonds (Fig. 2) in order to minimise steric repulsion between the nitrogen substituents and the methyl group located on the macrocyclic ring. The effect of these twists, allied to the increased steric crowding introduced by the new alkyl group, is to "lock" the macrocycle in such a way as to stop the fluxional exchange of aromatic groups in the capping position. "Locking" occurs because the extra bulk provided by the newly added alkyl group prevents free rotation about the C(1)–N bond due to unfavourable steric interaction with the ring methyl group. Due to the polar nature of the reaction solvent (acetonitrile), the twists occurring during alkylation prefer to place the aromatic group close to the less polar cavity, rather than the alternative possibility, with the benzene ring extended out into the solution. Moreover, in this "locked" conformation, the sterically congested nature of the system kinetically prevents reaction at the secondary nitrogen atom located at the opposite end of the molecule because steric crowding makes this nitrogen atom physically inaccessible to the approach of the alkylating agent.

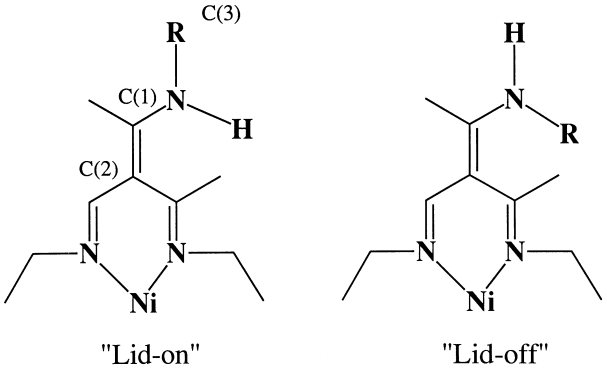


Fig. 2. Orientation of functional groups in "lid-on" and "lid-off" conformers of the cyclidenes.

This analysis, based on evidence from NMR spectroscopy, was confirmed in the present work by solution of the X-ray crystal structure of the product of the reaction between complex (**1**) and 1-bromopropane. A single crystal of the mono(propyl) functionalised complex (**3**) was grown from acetone solution and subjected to X-ray analysis. Details of the data collection and structure refinement are given in Table 1 and the bond lengths and bond angles in Table 2. A perspective view of the molecule, indicating the numbering system used, is depicted in Fig. 3.

The results of the X-ray crystallography study clearly support the structure proposed based upon the NMR evidence in that the benzyl group of the tertiary nitrogen atom is located in the "capping" position, above the metal ion, while the benzyl group on the secondary nitrogen atom is twisted away from the region of the metal centre. The steric effect on the structure of introducing the propyl group is indicated by the torsion angles around the C(1)–N and C(1)–C(2) bonds, termed ϵ and δ, respectively by Busch and coworkers in their discussion of related cyclidenes [11]. In the absence of any strain effects, the C(1), C(2), C(3) and N atoms should adopt an essentially planar structure, to maximise double bond conjugation, leading to dihedral angles of 180° and 0°, respectively. However, because there is always some strain even in the unbridged cyclidenes, for species with secondary nitrogen atoms, δ is typically in the region of 5–20° but the value for ϵ deviates only slightly from the ideal angle of 180° [11]. This produces the ligand conformation described by Busch et al. as "lid-on" (Fig. 2) [12]. As steric effects become more important, in particular upon formation of a tertiary nitrogen atom by alkylation, the C(1), C(2), C(3) and N atoms are moved out of planarity by the angle twists described above, altering the torsion angles. In complex (**3**), at the tertiary nitrogen end of the molecule, δ is found to be $-39(1)°$ and ϵ is $-17(1)°$, while at the secondary nitrogen end, δ is 21(1)° and ϵ is 178.6(8)°. These data are in accord with those for related structures, for example, a pyrazole substituted cyclidene, with tertiary nitrogen atoms at both ends of the molecule, has δ −41.8° and ϵ −26.8° and 174.7° while a cyclidene with two secondary nitrogen atoms has δ 20° and ϵ ca. 174° [11].

The value for δ of ca. 40° seems to be consistent for any cyclidene complex with tertiary nitrogen atoms since this value is also found for various examples of bridged

Table 1
Details of the data collection and structure refinement for (**3**) and (**2**)

	(**3**)	(**2**)
Crystal colour, habit	Yellow plate	Yellow block
Crystal size (mm^3)	$0.38 \times 0.22 \times 0.15$	$0.41 \times 0.15 \times 0.12$
Formula	$C_{35}H_{48}F_{12}N_6NiP_2$	$C_{34}H_{46}F_{12}N_6NiP_2$
M	901.44	887.42
System	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a (Å)	10.217(2)	11.202(3)
b (Å)	14.273(2)	15.637(6)
c (Å)	28.262(5)	22.644(6)
β (°)	96.860(10)	90.00
U ($Å^3$)	4091.9(12)	3966.4(22)
Z	4	4
D_{calc}	1.463	1.486
μ(Mo Kα) (mm^{-1})	0.641	0.660
T_{min}, T_{max}	0.726, 0.607	0.720, 0.579
$F(000)$	1864	1832
Diffractometer	Siemens P4	Siemens SMART
$\theta_{data\ collection}$ (°)	1.45–25.00	1.58–24.70
hkl Range	−1 to 12, −1 to 16, −33 to 33	−12 to 13, −15 to 18, −26 to 23
Data measured	9234	17335
Unique data	7192	6548
Reflections used	7188	6546
Weights: a, b	0.068, 11.04	0.059, 1.12
R, wR_2 (all data)	0.2253, 0.5141	0.1070, 0.1960
Observed data [$I > 2\sigma(I)$]	2972	5280
R, wR_2 (observed data)	0.0910, 0.1720	0.0811, 0.1761
S	1.200	1.725
No. of parameters	490	497
E_{max}, E_{min} (e $Å^{-3}$)	0.66, −0.43	0.58, −0.35
Flack x parameter	N/A	0.03(3)

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where $w^{-1} = [\sigma_c^2(F_o)^2 + (aP)^2 + bP]$ where $P = [0.333 \max\{F_o, 0\} + 0.667(F_o)^2]$, $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of data and p the number of parameters.

cyclidenes [13]. The value for ϵ has a greater bearing on the orientation of the nitrogen substituents. At the tertiary nitrogen end of the molecule, the torsion angle of −17° is more akin to that for a "lid-off" isomer (Fig. 2), with the N–C bond pointing into the cavity, placing the aromatic ring in the observed "capping" position. At the secondary nitrogen end of the molecule, the value of ϵ means that the second benzyl group points up and out of the region of the cavity ("lid-on" isomer). To our knowledge, this structure is the first that contains both a secondary and a tertiary nitrogen in the same cyclidene.

2.2. *Structure and physical properties of bis(α-methylbenzyl) substituted cyclidene (**2**)*

We have had an interest in the preparation and characterisation of macrocyclic species containing chiral centres as an integral part of the ligand structure [14]. In

Table 2
Selected bond lengths (Å) and angles (°) for complex (**3**)

Ni(1)–N(3)	1.870(7)	Ni(1)–N(2)	1.878(8)	Ni(1)–N(1)	1.881(7)
Ni(1)–N(4)	1.893(7)	N(1)–C(1)	1.302(11)	N(1)–C(12)	1.484(11)
N(2)–C(3)	1.298(11)	N(2)–C(4)	1.466(11)	N(3)–C(7)	1.290(10)
N(3)–C(6)	1.483(10)	N(4)–C(9)	1.293(10)	N(4)–C(10)	1.465(11)
N(5)–C(14)	1.324(11)	N(5)–C(16)	1.480(11)	N(5)–C(19)	1.485(10)
N(6)–C(26)	1.326(10)	N(6)–C(28)	1.470(10)	C(1)–C(2)	1.458(13)
C(1)–C(13)	1.500(12)	C(2)–C(3)	1.411(12)	C(2)–C(14)	1.412(13)
C(4)–C(5)	1.48(2)	C(5)–C(6)	1.42(2)	C(7)–C(8)	1.432(11)
C(8)–C(26)	1.383(11)	C(8)–C(9)	1.457(11)	C(9)–C(35)	1.519(11)
C(10)–C(11)	1.517(12)	C(11)–C(12)	1.485(13)	C(14)–C(15)	1.509(13)
C(16)–C(17)	1.533(13)	C(17)–C(18)	1.48(2)	C(19)–C(20)	1.513(10)
C(26)–C(27)	1.497(11)	C(28)–C(29)	1.519(10)		

N(3)–Ni(1)–N(2)	91.4(3)	N(3)–Ni(1)–N(1)	170.6(3)
N(2)–Ni(1)–N(1)	88.7(3)	N(3)–Ni(1)–N(4)	89.5(3)
N(2)–Ni(1)–N(4)	179.0(3)	N(1)–Ni(1)–N(4)	90.4(3)
C(1)–N(1)–C(12)	119.1(8)	C(1)–N(1)–Ni(1)	121.7(7)
C(12)–N(1)–Ni(1)	118.9(6)	C(3)–N(2)–C(4)	118.8(8)
C(3)–N(2)–Ni(1)	119.8(6)	C(4)–N(2)–Ni(1)	121.7(7)
C(7)–N(3)–C(6)	116.4(8)	C(7)–N(3)–Ni(1)	119.6(6)
C(6)–N(3)–Ni(1)	123.5(6)	C(9)–N(4)–C(10)	119.7(7)
C(9)–N(4)–Ni(1)	122.1(6)	C(10)–N(4)–Ni(1)	118.2(5)
C(14)–N(5)–C(16)	124.3(8)	C(14)–N(5)–C(19)	123.0(8)
C(16)–N(5)–C(19)	112.3(7)	C(26)–N(6)–C(28)	127.0(8)
N(1)–C(1)–C(2)	119.7(9)	N(1)–C(1)–C(13)	121.7(9)
C(2)–C(1)–C(13)	117.9(9)	C(3)–C(2)–C(14)	117.9(9)
C(3)–C(2)–C(1)	117.4(9)	C(14)–C(2)–C(1)	124.6(9)
N(2)–C(3)–C(2)	124.5(9)	N(2)–C(4)–C(5)	110.8(9)
C(6)–C(5)–C(4)	120.5(12)	C(5)–C(6)–N(3)	115.1(9)
N(3)–C(7)–C(8)	124.7(8)	C(26)–C(8)–C(7)	120.8(8)
C(26)–C(8)–C(9)	123.3(8)	C(7)–C(8)–C(9)	115.8(8)
N(4)–C(9)–C(8)	121.9(8)	N(4)–C(9)–C(35)	118.9(8)
C(8)–C(9)–C(35)	118.2(8)	N(4)–C(10)–C(11)	111.1(8)
C(12)–C(11)–C(10)	111.2(8)	N(1)–C(12)–C(11)	110.4(8)
N(5)–C(14)–C(2)	122.3(9)	N(5)–C(14)–C(15)	116.6(9)
C(2)–C(14)–C(15)	121.2(9)	N(5)–C(16)–C(17)	111.9(8)
C(18)–C(17)–C(16)	113.5(11)	N(5)–C(19)–C(20)	111.2(7)
N(6)–C(26)–C(8)	120.2(8)	N(6)–C(26)–C(27)	117.0(7)
C(8)–C(26)–C(27)	122.8(8)	N(6)–C(28)–C(29)	115.7(7)

the light of the results described above, it was of interest to investigate the effect of introducing chiral side chains into the cyclidene structure. To this end, the bis(α-methylbenzyl) functionalised cyclidene was prepared using both (R)-(+)-, and (S)-(−)-(α-methylbenzylamine). The initial plan was to investigate the possibility of chiral discrimination in the reactivity of both the (R,R) and the (S,S) diastereoisomers of the resulting cyclidenes. The desired products were prepared in good yield (ca. 75%) as yellow/orange solids using a modification of a literature procedure [10], and they were fully characterised by spectroscopy and by microanalysis. As expected,

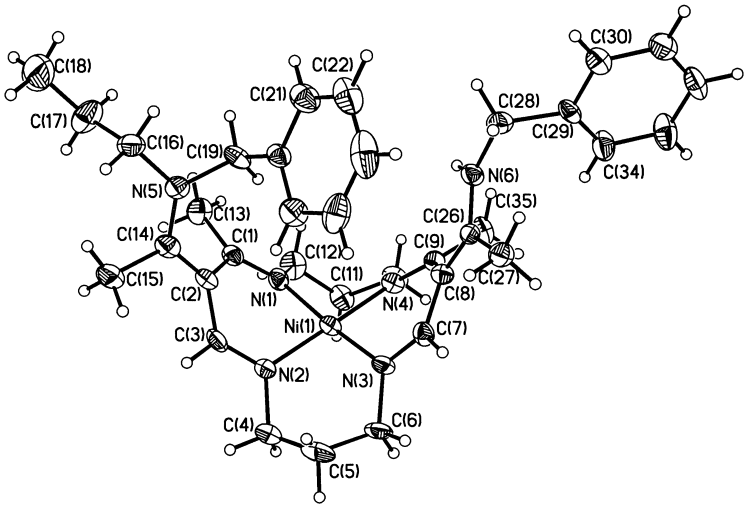


Fig. 3. Perspective view of the crystal structure of complex (**3**), indicating the numbering scheme.

the (R,R)- and (S,S)-complexes displayed identical NMR, IR and UV–visible spectroscopic properties.

In contrast to the corresponding benzyl substituted cyclidene (**1**), the ^{1}H NMR spectrum of (**2**) was indicative of a symmetric structure. For example, there is a single resonance for the protons located on the α-carbon atoms of the benzyl groups. The apparent symmetry of the structures must arise from the fluxional nature of the molecules in solution, because the X-ray structure of (**2**) shows that in the solid state it adopts an asymmetric disposition of the α-methylbenzyl groups (vide infra). At 25 °C, the signal for the α-protons takes the form of a quintet arising from coupling both to the adjacent methyl group and the secondary amino proton with, by coincidence, the same coupling constant. A broad signal for the amino protons appears at δ 7.52.

Since fluxional behaviour is well established in related cyclidene molecules [15], the ^{1}H NMR spectrum of (**2**) was investigated as a function of temperature. Progressive heating of the sample to 80 °C resulted in loss of the amino proton signal, due to the rapid exchange of the amino proton, with the α-proton signal changing to quartet fine structure. The methylene signal at δ 1.85 shifted progressively to δ ca. 2.0 and broadened.

Cooling the sample to −19 °C caused the signals assigned to the N–CH_2 groups of the parent macrocycle to broaden slightly, with the signal ascribed to the protons of the ring methyl group moving slightly down field. The signal due to the methyl group at δ 2.15 also broadened. Upon further cooling, to −39 °C, the spectrum showed signals due to the macrocyclic methylene groups as four distinct, but broad, peaks of varying intensity, while the two different types of methyl group on the parent macrocycle showed a single broad signal. We ascribe this behaviour as arising from the slowing down of the ''flexing'' of the parent macrocycle between the two

possible boat and chair conformations of the saturated six-membered metallochelate rings. As the temperature is lowered it becomes possible to distinguish separate signals for the different environments of the protons of the various CH_2 groups as this form of fluxionality is slowed down.

The ^{13}C NMR spectrum was in full accord with complex (**2**) possessing mirror symmetry and assignment was made with reference to results of earlier studies, and by use of data from both C–H correlation and nuclear Overhauser effect spectra. In keeping with results from other cyclidene systems, the UV–visible spectrum of (**2**) shows a shoulder at ca. 440 nm (ϵ ca. 620 l mol^{-1} cm^{-1}), with two more intense bands, at $\lambda_{max}=371$ and 339 nm (ϵ 29 600 and 39 200, respectively) assigned to ligand based transitions.

Crystals of the (R,R)-isomer suitable for X-ray diffraction were obtained by slow diffusion of an acetonitrile/ether solution. Details of the data collection and structure refinement are given in Table 1 and the bond lengths and bond angles in Table 3. A perspective view of the molecule, indicating the numbering scheme used, is depicted in Fig. 4. The structure is broadly similar to that of (**3**) described above in that one of the aromatic rings is turned in, to partially cap the macrocyclic unit, whilst the other ring is twisted away from the capping position. As noted above, this asymmetric structure disagrees with the findings in solution at room temperature where rapid rotation about the N–C(α) bonds on the NMR time scale leads to averaging of signals in the NMR spectra. In complex (**2**), both peripheral nitrogen atoms are secondary, and the torsion angles are found to be, for δ 22(1)° and 29(1)° and for ϵ −177(1)° and −176(1)°, in agreement with the expected ranges, as discussed above. Both chiral substituents are thus located in "lid-on" positions, again as expected, but in this molecule it is the twists about the C(α)–C(aromatic) bonds that place one group in a capping site and the other pointing out and away from the region of the metal centre.

Comparing the structures of (**3**) and (**2**), both Ni centres possess square planar geometry with the deviation of the Ni atoms from a least-squares plane containing the four coordinating N atoms being 0.080(4) and 0.062(3) Å for (**3**) and (**2**), respectively. In both (**3**) and (**2**), one of the unsaturated metallochelate rings takes up a boat conformation (Ni1, N1, C12, C11, C10, N4) and the other a chair conformation (Ni1, N2, C4, C5, C6, N3).

There are many intermolecular contacts involving the PF_6^- anions and the protons of the cation. The shortest contact in both structures involves the imine proton H6, and F8 in (**2**) [2.267(13) Å] and F10 in (**3**) [2.381(15) Å].

2.3. Reactivity of bis(α-methylbenzyl) substituted cyclidene (2)

The reactions of complex (**2**) were subjected to a detailed study, to elucidate the effect of the chiral centre on the reactivity of the complex. The standard conditions for alkylation of the cyclidenes involves the use of a strong base, generally potassium t-butoxide, to deprotonate the starting material, thus it was important to ensure that the complex did not racemise under the conditions of the alkylation experiment. Deprotonation of (**2**) in acetonitrile solution produced a deep red coloured species,

Table 3
Selected bond lengths (Å) and angles (°) for complex (**2**)

Ni(1)–N(2)	1.876(7)	Ni(1)–N(1)	1.878(6)	Ni(1)–N(3)	1.883(7)
Ni(1)–N(4)	1.905(6)	N(1)–C(1)	1.312(9)	N(1)–C(12)	1.498(9)
N(2)–C(3)	1.286(9)	N(2)–C(4)	1.469(10)	N(3)–C(7)	1.292(10)
N(3)–C(6)	1.468(10)	N(4)–C(9)	1.290(9)	N(4)–C(10)	1.483(10)
N(5)–C(14)	1.346(9)	N(5)–C(19)	1.486(9)	N(6)–C(26)	1.327(9)
N(6)–C(28)	1.494(9)	C(1)–C(2)	1.454(10)	C(1)–C(13)	1.485(10)
C(2)–C(3)	1.458(10)	C(2)–C(14)	1.373(10)	C(4)–C(5)	1.468(13)
C(5)–C(6)	1.468(14)	C(7)–C(8)	1.416(10)	C(8)–C(26)	1.422(10)
C(8)–C(9)	1.455(10)	C(9)–C(35)	1.501(10)	C(10)–C(11)	1.516(12)
C(11)–C(12)	1.493(11)	C(14)–C(15)	1.496(10)	C(18)–C(19)	1.527(11)
C(19)–C(20)	1.505(11)	C(20)–C(21)	1.378(11)	C(20)–C(25)	1.402(10)
C(21)–C(22)	1.390(13)	C(22)–C(23)	1.39(2)	C(23)–C(24)	1.37(2)
C(24)–C(25)	1.386(14)	C(26)–C(27)	1.465(10)	C(28)–C(36)	1.515(12)
C(28)–C(29)	1.533(11)	C(29)–C(30)	1.373(11)	C(29)–C(34)	1.386(11)
C(30)–C(31)	1.442(13)	C(31)–C(32)	1.337(14)	C(32)–C(33)	1.364(13)
C(33)–C(34)	1.370(12)				

N(2)–Ni(1)–N(1)	88.0(3)	N(2)–Ni(1)–N(3)	91.6(3)
N(1)–Ni(1)–N(3)	176.2(3)	N(2)–Ni(1)–N(4)	176.3(3)
N(3)–Ni(1)–N(4)	88.1(3)	N(1)–Ni(1)–N(4)	92.1(3)
C(1)–N(1)–C(12)	118.1(6)	C(1)–N(1)–Ni(1)	123.6(5)
C(12)–N(1)–Ni(1)	118.1(5)	C(3)–N(2)–C(4)	117.0(7)
C(3)–N(2)–Ni(1)	120.1(5)	C(4)–N(2)–Ni(1)	122.4(5)
C(7)–N(3)–C(6)	119.3(7)	C(7)–N(3)–Ni(1)	118.6(5)
C(6)–N(3)–Ni(1)	121.6(5)	C(9)–N(4)–C(10)	120.4(7)
C(9)–N(4)–Ni(1)	122.2(5)	C(10)–N(4)–Ni(1)	117.5(5)
C(14)–N(5)–C(19)	128.4(7)	C(26)–N(6)–C(28)	126.5(7)
N(1)–C(1)–C(2)	119.0(6)	N(1)–C(1)–C(13)	121.2(6)
C(2)–C(1)–C(13)	118.7(6)	C(3)–C(2)–C(14)	118.3(6)
C(3)–C(2)–C(1)	116.1(6)	C(14)–C(2)–C(1)	125.4(7)
N(2)–C(3)–C(2)	124.3(7)	N(2)–C(4)–C(5)	113.0(7)
C(6)–C(5)–C(4)	117.3(8)	C(5)–C(6)–N(3)	113.0(7)
N(3)–C(7)–C(8)	125.6(7)	C(26)–C(8)–C(7)	119.2(7)
C(26)–C(8)–C(9)	124.5(6)	C(7)–C(8)–C(9)	115.9(6)
N(4)–C(9)–C(8)	120.6(7)	N(4)–C(9)–C(35)	120.0(7)
C(8)–C(9)–C(35)	118.6(7)	N(4)–C(10)–C(11)	111.5(7)
C(12)–C(11)–C(10)	113.0(7)	N(1)–C(12)–C(11)	111.2(7)
N(5)–C(14)–C(2)	119.9(7)	N(5)–C(14)–C(15)	114.9(7)
C(2)–C(14)–C(15)	125.1(6)	N(5)–C(19)–C(18)	107.4(7)
C(20)–C(19)–C(18)	112.7(6)	N(5)–C(19)–C(20)	111.3(6)
N(6)–C(26)–C(8)	119.9(7)	N(6)–C(26)–C(27)	117.6(7)
C(8)–C(26)–C(27)	122.5(7)	N(6)–C(28)–C(29)	111.4(6)
C(36)–C(28)–C(29)	112.0(7)	N(6)–C(28)–C(36)	109.6(7)

which even after repeated heating at reflux over extended periods showed no change in α_D. Reprotonation resulted in isolation of the starting material with no loss of chirality.

Initially efforts were focused on reactions using racemic mixtures of alkyl halides containing a chiral centre in their structure, viz. 2-bromopentane and 2-bromooctane.

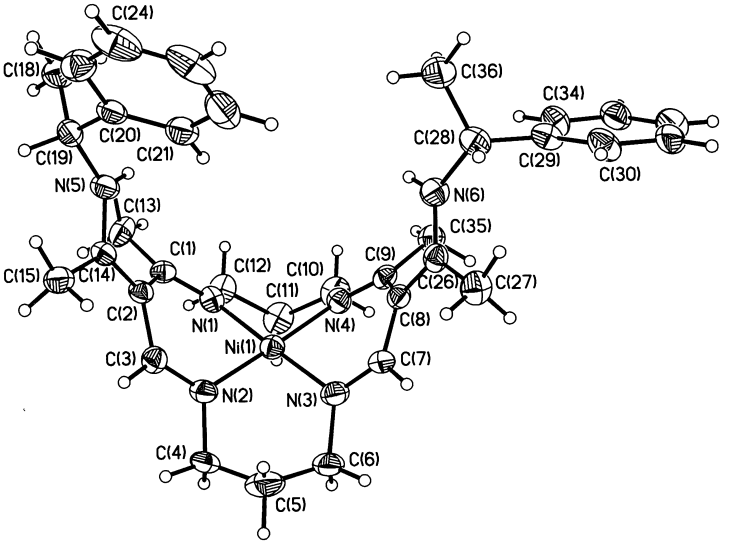


Fig. 4. Perspective view of the crystal structure of complex (**2**), indicating the numbering scheme.

In both cases, the NMR spectra of the products of the reactions gave no evidence to support the successful alkylation of (**2**), even after reaction times of several days. The failure of these alkylation reactions is attributed to the very crowded environment around the secondary nitrogen atoms of (**2**), caused by the presence of the α-methyl group. This inhibits the alkylation reaction by preventing the close approach of the alkyl halide to the nitrogen nucleophile. The severe steric constraints in the system can be seen in a space filling picture of the parent complex (Fig. 5). This explanation agrees with the interpretation of the behaviour of (**1**) described above. Whereas (**1**) becomes inactive to alkylation by relatively bulky groups once one such group has been added, (**2**) is sufficiently crowded to prevent even the first of the alkylation steps.

Thus across the range of cyclidenes we have a spectrum of behaviour in alkylation reactions. For secondary nitrogen atoms bearing small substituents (e.g. CH_3) alkylation proceeds smoothly at both nitrogen atoms. With the larger benzyl substituted species, steric control of the system limits alkylation to only one of the nitrogen atoms. Finally, in the even more bulky α-methylbenzyl species, alkylation with relatively bulky alkyl halides is completely prevented.

To probe the limit of reactivity of (**2**), it was deprotonated and reacted with methyl iodide as the least bulky alkyl group possible. In this case alkylation of (**2**) did occur, producing a product with an extremely complicated ^{1}H NMR spectrum which is difficult to interpret with a satisfactory degree of certainty. The complicated nature of the spectrum arises because the alkylated product was no longer fluxional on the NMR time scale, even when the sample was warmed to 80 °C. The alkylated product apparently exists in different conformations, leading to the multiple signals observed in the NMR spectrum. For example, the signal due to the proton on the

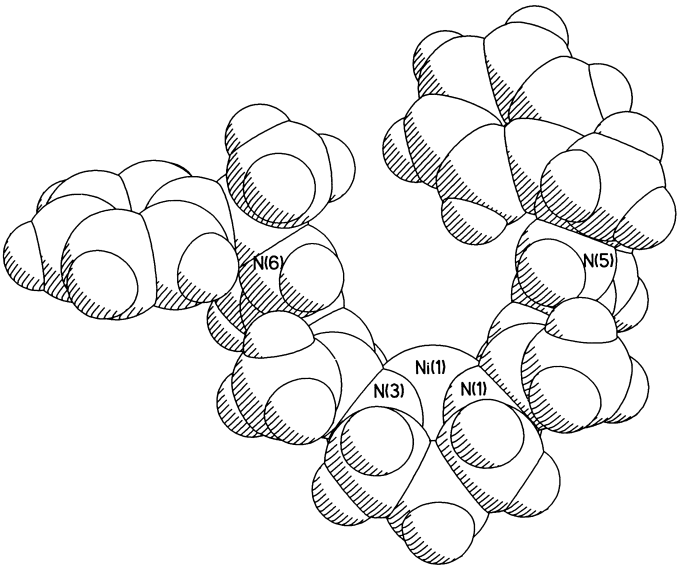


Fig. 5. Space filling picture of the structure of complex (**2**).

asymmetric carbon atom appears as three quartets of relative intensity 1:2:1, indicative of three different magnetic environments for these protons. It is possible to speculate that the various conformers arise from the relative orientation of the two aromatic groups, pointing into or out of the cavity. Unfortunately, we were unable to separate the different conformers from one another so it was not possible to identify the structures unambiguously. However, what is clear is that (**2**) can be dialkylated if a sufficiently small alkyl group is involved, and the product exists in a range of different conformations due to the kind of ''locking'' described above for derivatives of complex (**1**).

3. Experimental

All materials were reagent grade and solvents were purified and dried using standard methods. NMR spectra were recorded on a Bruker WP200 spectrometer, operating at 200.13 (^{1}H) and 50.323 MHz (^{13}C) or a Bruker WH400 spectrometer, operating at 400.13 (^{1}H) or 100.62 MHz (^{13}C). Chemical shifts are reported with respect to an external tetramethylsilane reference (positive to low field). Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer and infrared spectra as KBr discs on a Nicolet Impact 400 FTIR spectrophotometer.

3.1. Preparation of the complexes

[3,11-Bis(1-benzylaminoethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]nickel(II)bis(hexafluorophosphate), (**1**), and [3-(1-benzyl-

aminoethylidene)-11-(1-benzyl^{n}propylamino-ethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]nickel(II)bis(hexafluorophosphate), (**3**), were prepared by the literature methods [10].

*3.1.1. [3,11-(R,R)-bis(α-methylbenzylaminoethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^{4}N]nickel(II) bis(hexafluorophosphate), (**2**)*

To a solution of 3,11-bis(1-methoxyethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N]nickel(II)bis(hexafluorophosphate) (2.87 g, 4.0 mmol) in acetonitrile (100 cm^3) was added (R)-(+)-α-methylbenzylamine (1.0 g, 8.26 mmol) and the solution was heated at reflux for 1 h. The reaction mixture was reduced in volume and the product chromatographed on alumina with acetonitrile as eluent. The fast moving orange band was collected and evaporated to dryness to give the product as a yellow/orange solid. Yield 2.62 g, 74%. FAB mass spectrum, m/z 595 $[M–2PF_6]^+$. Anal. Found: C, 46.3; H, 5.13; N, 9.55. $C_{34}H_{44}N_6NiP_2F_{12}$ requires: C, 46.1; H, 4.97; N, 9.45%. The (S,S)-derivative was prepared by an identical procedure, except using (S)-(−)-α-methylbenzylamine.

*3.1.2. [3,11-(R,R)-bis(α-methylbenzylmethylaminoethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-k^{4}N]nickel(II) bis(hexafluorophosphate), (**4**)*

This complex was prepared from (**3**) using the procedure developed for alkylation of other cyclidenes [10]. Complex (**3**) (0.50 g, 0.56 mmol) dissolved in acetonitrile solution (80 cm^3) was treated with a solution of potassium t-butoxide (0.127 g, 1.13 mmol) and the mixture was heated at reflux until all of the base had reacted, by which time the solution had become deep red in colour. A large excess of methyl iodide (2.28 g, 16 mmol) was added, and the mixture was heated at reflux for 2 h. The volume of the solution was reduced in vacuo and the crude product was chromatographed twice on neutral alumina with acetonitrile as eluent. The fast moving orange band was collected and taken to dryness before resolvation in dichloromethane followed by precipitation with ether. Yield 0.31 g, 61%. Anal. Found: C, 46.7; H, 5.4; N, 8.9. $C_{36}H_{50}N_6NiP_2F_{12}\cdot CH_3OH$ requires: C, 46.9; H, 5.7; N, 8.9%.

3.2. Crystallography

Crystals of (**3**) were grown from the slow evaporation of an acetone solution and a single crystal was mounted in vacuum grease in a sealed thin-walled glass capillary. Data were collected at room temperature on a Siemens P4 diffractometer with the program XSCANS [16] using ω scans.

The unit cell parameters and orientation matrix for data collection were determined by a least-squares refinement of 27 centred reflections, with a 2θ range of 9.79–16.46°. Standard reflections were remeasured every 100 data, slight crystal decay (6.7%) was found. Data were corrected for absorption by psi scans.

Crystals of (**2**) were grown by slow diffusion of an acetonitrile/ether solution and mounted in vacuum grease in a sealed thin-walled glass capillary. Data were collected

at room temperature on a Siemens SMART CCD area detector three-circle diffractometer at Bristol University with graphite-monochromated Mo Kα radiation ($\lambda =$ 0.71069 Å). Least-squares refinement of 126 centred reflections were used to determine the unit cell parameters. Frames were collected for 30 s with 0.3° increments in ω. At the end of data collection, the first 50 frames were recollected to check for crystal decay. Data frames were integrated using the Siemens SAINT program [16].

Both structures were solved by direct and difference Fourier methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were refined anisotropically. All phenyl, ethyl and methyl H atom positions were calculated and treated as riding models. Phenyl, ethyl and methyl H atom displacement parameters were treated as riding models with U_{ij} 1.2, 1.2, and 1.5 times the bound carbon atom U_{ij}, respectively. In (**3**) one PF_6^- anion is disordered down the F(11)–P(2)–F(9) axis. There were five positions found for the remaining four fluorine atoms, each position was assigned an occupancy of 0.8. The phenyl rings in (**3**) were constrained to be rigid hexagons (C–C 1.390 Å, C–C–C 120°). The rather high R factors are a consequence of both crystals being rather small and weakly diffracting. In both cases, however, they were the best crystals that were available.

Crystallographic computing was performed using the SHELXTL [17] system version on a Pentium 90 MHz PC. Further details are given in Table 1.

Selected bond lengths and angles are given in Tables 2 and 3 for (**3**) and (**2**), respectively.

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