A novel enantiopure proline-based organonickel(III) halide monocation with a pentadentate C, N₂, O₂-bonded bis(*ortho*-chelating) aryldiamine ligand ☆

Lucia A. van de Kuil [a,b], Yvonne S.J. Veldhuizen [b], David M. Grove [a], Jan W. Zwikker [b],
Leonardus W. Jenneskens [b], Wiendelt Drenth [b], Wilberth J.J. Smeets [c], Anthony L. Spek [c],
Gerard van Koten [a,*]

[a] *Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b] *Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[c] *Bijvoet Centre for Biomolecular Research, Laboratory of Crystal and Structural Chemistry, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands*

Abstract

An attempt was made to use the enantiopure arylnickel(II) complex [Ni(L*-N, C, N)Br], **1**, (L* is the monoanionic ligand, 2,6-bis[(2-(S)-2-isopropoxycarbonyl-1-pyrrolidinyl)methyl]phenyl) as a catalyst for the Kharasch addition reaction of CCl_4 to alkenes which led instead to a new ionic arylnickel(III) complex [Ni(L*)Cl]₂[NiCl₄] (= [**2-Cl**]₂[NiCl₄]. An X-ray diffraction study of this complex revealed the presence of two identical monocations [**2-Cl**]⁺ that have octahedrally coordinated Ni(III) centres and a single dianionic $NiCl_4^{2-}$ unit. The octahedral ligand sphere of cation [**2-Cl**]⁺ is best described as tetragonally compressed, with the meridional coordination comprising N₂, O₂ donative bonding from the two N atoms of the pyrollidine groups and two carbonyl O atoms of the ester groups of L*, the mutually *trans* apical sites are occupied by a Cl atom and the C atom of the Ni–C_{aryl} bond; i.e. the monoanionic organic ligand L* binds as a monoanionic C, N₂, O₂ pentadentate system. Spectroscopic data for [**2-Cl**]⁺ are presented and compared with those for the square-planar arylnickel(II) complex **1**, in which the oxygen donor atoms of the ester groups of L* are not coordinated and the ligand thus acts as a C, N₂ terdentate system.

Keywords: Nickel; Diamine; Proline; Crystal structure

1. Introduction

A few years ago we reported the synthesis and characterization of unique organometallic nickel(III) aryldiamine species [Ni{C₆H₃(CH₂NMe₂)₂-2,6}X₂] (X = Cl, Br, I) in which the coordination sphere of nickel consists of two nitrogen donor atoms, two halides, and a direct Ni–C_{aryl} σ bond [1]. In these species the Ni(III) oxidation state is stabilized by the special coordination properties of the monoanionic terdentate ligand C₆H₃(CH₂NMe₂)₂-2,6. These air-stable square-

pyramidal aryldiamine Ni(III) species can be formed from the corresponding aryldiamine nickel(II) halide species [Ni{C₆H₃(CH₂NMe₂)₂-2,6}X] either by chemical single-electron transfer oxidation with electrophiles (see Eq. 1) or by electrochemical oxidation.
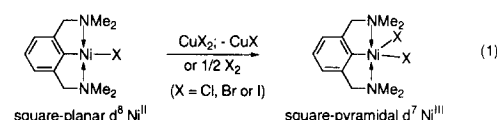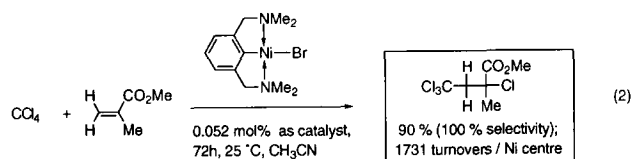

We subjected this unusual organometallic Ni(II)/Ni(III) system to a number of spectroscopic and chemico-physical investigations, and recognized that the Ni(III) centre had some properties that could be of significance for researchers working on the elucidation of the active site in nickel hydrogenases [2]. Furthermore, organonickel(II) complexes of this type (see Eq.

☆ Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday for his fine contributions to the field of inorganic chemistry.

* Corresponding author.

1) are excellent homogeneous catalysts for the Kharasch addition reaction, i.e. the 1:1 addition of polyhalogenated compounds to terminal alkenes, a typical example of which is shown in Eq. 2 [3].

$$CCl_4 + \underset{H}{\overset{H}{\rangle}}\!=\!\underset{Me}{\overset{CO_2Me}{\langle}} \xrightarrow[\substack{0.052 \text{ mol\% as catalyst,} \\ 72h, 25\,^\circ C, CH_3CN}]{} \underset{H}{\overset{H}{\underset{Me}{Cl_3C\!-\!\!\!-\!\!\!-\!Cl}}} \quad (2)$$

90 % (100 % selectivity); 1731 turnovers / Ni centre

Recent investigations into the mechanism of this reaction with organonickel(II) complexes [Ni{C$_6$H$_3$-(CH$_2$NMe$_2$)$_2$-2,6}X] and derivatives as catalysts, have shown that formation of Ni(III) intermediates plays an important role [4]. In our study of the factors influencing the catalytic activity of such complexes we modified the aryl ring (introduction of electron-withdrawing/releasing *para*-substituents) [5] and varied the N donor atom substituents [3b]. With respect to the latter we recently showed that it is possible to incorporate proline groups, in which the nitrogen centres are stereogenic, so affording complexes that could be potential enantioselective catalysts [6]. With one of these enantiopure proline-based organonickel complexes we have now encountered an unexpected reaction with CCl$_4$ that affords a novel octahedral arylnickel(III) complex cation in which there is a pentadentate C, N$_2$, O$_2$, binding ligand system.

2. Experimental details

2.1. General

The organonickel(II) complex [Ni(L*-N, C, N)Br], 1, was synthesized by a published procedure [6]. All other reagents were commercially available and used after appropriate purification. Solvents were dried and freshly distilled under nitrogen before use. Manipulations of air-sensitive nickel complexes were carried out under nitrogen using Schlenk techniques. Solution UV/VIS spectra were recorded on a Varian Cary 1. Fourier Transform IR spectra were recorded on Mattson Galaxy Series FTIR 5000 spectrometer. GLC analyses were performed with a Varian 3400 Gaschromatograph (column: CP Sil5 (0.31 mm × 30 m); injector temperature: 250°C; detector temperature: 250°C; temperature programme: 105°C, 3 min, 20°C min^{-1}, 245°C, 5 min.) equipped with a FID and internal integrator. Reaction products were identified variously by GC/MS, NMR spectroscopy and GLC, and also by comparison with authentic samples. ESR spectra were recorded, both in CH$_2$Cl$_2$ and as powders in KBr on a JEOL RE 2X ESR spectrometer at −196°C, at the Department of Inorganic Chemistry, University of Lei-

den, under the supervision of Prof. Dr. J. Reedijk. Elemental analyses were carried out by Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr, Germany.

2.2. Synthesis of [2-Cl]$_2$[NiCl$_4$]

To a mixture of styrene (23.0 ml, 0.2 mol) and CCl$_4$ (80 ml, 0.83 mol) in CH$_2$Cl$_2$ (100 ml) was added a solution of the organonickel(II) complex 1 (1.0 g, 1.8 mmol) in CH$_2$Cl$_2$ (10 ml). Within a few minutes the colour changed from orange to green. After 30 min the volatiles were removed in vacuo and the residue dissolved in CH$_2$Cl$_2$. Hexane was added to the green CH$_2$Cl$_2$ solution and a green solid separated. It was isolated by filtration and dried in vacuo, affording the product as a green powder (0.52 g; 71% yield). Further purification was carried out by crystallization by diffusion of hexane into a solution of the product in CH$_2$Cl$_2$ to afford very dark green crystals (0.28 g; 38% yield).

The same experimental conditions, but in the absence of the alkene, also gives [2-Cl]$_2$[NiCl$_4$] but the extent of incorporation of Br in place of Cl in the product is significantly higher.

Selected IR data for [2-Cl]$_2$[NiCl$_4$] (CH$_2$Cl$_2$, cm^{-1}): 3100–3030 (aryl CH), 3000–2840 (saturated CH), 1653 (C=O), 1096 (C–O). UV/VIS spectrum of [2-Cl]$_2$[NiCl$_4$] (CH$_2$Cl$_2$): 227 nm ($\epsilon = 1.2 \times 10^4$ l mol^{-1} cm^{-1}), 265 nm ($\epsilon = 1.6 \times 10^4$ l mol^{-1} cm^{-1}) and two bands with low intensity at 620 nm and 705 nm. Elemental analysis data for [2-Cl]$_2$[NiCl$_4$]: Calc. for C$_{48}$H$_{70}$BrCl$_5$N$_4$Ni$_3$O$_8$: C, 45.60; H, 5.58; N, 4.43; Br, 6.32; Cl, 14.02. Found: C, 45.51; H, 5.65; N, 4.30; Br, 6.27; Cl, 14.32%.

2.3. X-ray crystallographic analysis of [2-Cl]$_2$[NiCl$_4$]

Crystal data: C$_{24}$H$_{35}$ClN$_2$NiO$_4$ · 0.5 NiCl$_4$, M_w = 609.94, $Z = 4$, orthorhombic space group $P2_12_12_1$ (non-standard $P2_12_12$, # 18), $a = 9.9427(10)$ Å, $b = 12.7754(10)$ Å, $c = 21.3924(10)$ Å. X-ray data were collected for a greenish, plate-shaped crystal glued on top of a glass fibre on an ENRAF-NONIUS CAD4T/ rotating anode system (Mo Kα, 295 K, 9 kW, θ_{max} = 27.5°, $\Delta\omega = 0.68 + 0.35 \, tg\theta°$). A total of 4555 reflections were scanned, corrected for Lp and absorption (DIFABS) [7] and a linear decay of 4%, and averaged in a unique set of 4365 reflections. The structure was solved by Patterson techniques (SHELXS-86/PATT) [8] and refined on F by full-matrix least-squares (SHELX-76) [9] to a final $R = 0.042$, $wR = 0.039$. Hydrogen atoms were accounted for at calculated positions and refined with one common U_{iso}. Excursions in the final difference map were within the range $-0.45 < \Delta\rho < 0.37$ e Å^{-3}. A slight disorder involving the positions of C9 and C18 (ring pucker) was not pursued. The final data are for the absolute structure giving the lowest R

Table 1
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for complex [2-Cl]$_2$[NiCl$_4$]

Atom	x	y	z	U_{eq} [Å^2]
Ni(1)	0.22219(7)	0.22147(6)	0.23954(3)	0.0326(2)
Cl(1)	0.00079(16)	0.17493(14)	0.23904(9)	0.0573(6)
O(1)	0.2023(4)	0.3554(3)	0.18744(18)	0.0400(14)
O(2)	0.2674(5)	0.4217(3)	0.09664(18)	0.0490(14)
O(3)	0.2589(4)	0.0952(3)	0.29707(17)	0.0380(14)
O(4)	0.2554(5)	0.0522(3)	0.39814(18)	0.0473(14)
N(1)	0.2805(5)	0.1546(3)	0.1545(2)	0.0337(14)
N(2)	0.2241(5)	0.3065(3)	0.3221(2)	0.0337(16)
C(1)	0.4092(5)	0.2514(4)	0.2429(3)	0.0323(17)
C(2)	0.4519(6)	0.3219(4)	0.2859(3)	0.0370(19)
C(3)	0.5899(6)	0.3364(5)	0.2930(3)	0.0423(19)
C(4)	0.6764(6)	0.2817(5)	0.2543(3)	0.0430(19)
C(5)	0.6311(6)	0.2126(5)	0.2091(3)	0.044(2)
C(6)	0.4912(6)	0.1944(4)	0.2031(3)	0.0350(17)
C(7)	0.4228(6)	0.1183(5)	0.1626(3)	0.039(2)
C(8)	0.1946(7)	0.0660(5)	0.1302(3)	0.048(2)
C(9)	0.1041(10)	0.1116(7)	0.0843(5)	0.114(5)
C(10)	0.1614(8)	0.2065(5)	0.0599(3)	0.060(3)
C(11)	0.2713(7)	0.2389(4)	0.1053(3)	0.0373(17)
C(12)	0.2445(6)	0.3436(4)	0.1347(3)	0.036(2)
C(13)	0.2641(18)	0.5301(4)	0.1213(3)	0.054(3)
C(14)	0.2289(12)	0.5981(6)	0.0674(4)	0.090(4)
C(15)	0.3960(9)	0.5520(7)	0.1501(5)	0.088(4)
C(16)	0.3414(6)	0.3798(5)	0.3196(3)	0.041(2)
C(17)	0.0965(7)	0.3675(5)	0.3358(3)	0.048(2)
C(18)	0.0354(10)	0.3158(9)	0.3886(5)	0.138(5)
C(19)	0.1245(8)	0.2492(6)	0.4203(3)	0.066(3)
C(20)	0.2427(6)	0.2308(4)	0.3758(3)	0.0393(19)
C(21)	0.2515(6)	0.1194(5)	0.2520(3)	0.0363(19)
C(22)	0.2572(8)	−0.0613(5)	0.3826(3)	0.055(3)
C(23)	0.3284(12)	−0.1135(6)	0.4368(4)	0.090(4)
C(24)	0.1195(10)	−0.0961(7)	0.3722(5)	0.098(4)
Ni(2)	0.59512(13)	0	0	0.0489(4)
Cl(2)	0.7340(2)	0.08365(13)	0.06591(8)	0.0593(6)
Cl(3)	0.4574(2)	0.12870(17)	−0.03746(9)	0.0702(7)

$U_{eq} = 1/3$ of the trace of the orthogonalized U.

factor. The final values of the refined parameters are given in Table 1. The molecular geometry along with the adopted numbering scheme is shown in Fig. 1 and
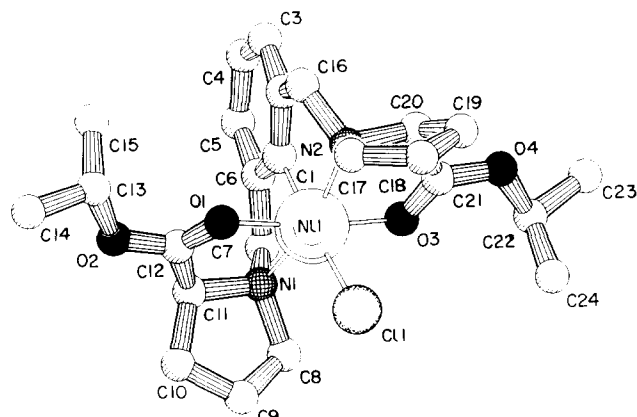

Fig. 1. PLUTON drawing of one aryldiamine nickel(III) complex mono-cation of [2-Cl]$_2$[NiCl$_4$] with the adopted numbering scheme. For clarity hydrogen atoms and the NiCl$_4^{2-}$ anion are not shown.

relevant bond distances and angles are given in Table 2. Geometry calculations were carried out with PLATON [10].

Tables of hydrogen atom coordinates and thermal parameters and a complete lists of bond lengths and

Table 2
Bond distances (Å) and bond angles (degrees) for [2-Cl]$_2$[NiCl$_4$]

Bond Distances (Å)			
Ni(1)–Cl(1)	2.2802(18)	C(1)–C(2)	1.356(8)
Ni(1)–O(1)	2.052(4)	C(1)–C(6)	1.386(8)
Ni(1)–O(3)	2.063(4)	C(2)–C(3)	1.393(8)
Ni(1)–N(1)	2.092(4)	C(2)–C(16)	1.508(9)
Ni(1)–N(2)	2.074(4)	C(3)–C(4)	1.383(9)
Ni(1)–C(1)	1.900(5)	C(4)–C(5)	1.385(9)
O(1)–C(12)	1.213(7)	C(5)–C(6)	1.416(8)
O(2)–C(12)	1.308(7)	C(6)–C(7)	1.469(9)
O(2)–C(13)	1.482(7)	C(8)–C(9)	1.454(12)
O(3)–C(21)	1.218(7)	C(10)–C(11)	1.519(10)
O(4)–C(21)	1.309(7)	C(11)–C(12)	1.502(8)
O(4)–C(22)	1.488(7)	C(13)–C(14)	1.485(10)
N(1)–C(7)	1.499(8)	C(13)–C(15)	1.475(12)
N(1)–C(8)	1.510(8)	C(17)–C(18)	1.443(13)
N(1)–C(11)	1.509(7)	C(18)–C(19)	1.403(13)
N(2)–C(16)	1.497(8)	C(19)–C(20)	1.531(10)
N(2)–C(17)	1.517(8)	C(20)–C(21)	1.514(8)
N(2)–C(20)	1.513(7)	C(22)–C(23)	1.513(11)
Bond Angles (Degrees)			
Cl(1)–Ni(1)–O(1)	97.00(12)	C(1)–C(2)–C(16)	115.0(5)
Cl(1)–Ni(1)–O(3)	88.25(12)	C(3)–C(2)–C(16)	126.9(5)
Cl(1)–Ni(1)–N(1)	99.03(14)	C(2)–C(3)–C(4)	118.7(6)
Cl(1)–Ni(1)–N(2)	98.59(15)	C(3)–C(4)–C(5)	122.5(6)
Cl(1)–Ni(1)–C(1)	176.02(17)	C(4)–C(5)–C(6)	119.2(6)
O(1)–Ni(1)–O(3)	173.73(15)	C(1)–C(6)–C(5)	115.8(5)
O(1)–Ni(1)–N(1)	83.96(15)	C(1)–C(6)–C(7)	116.0(5)
O(1)–Ni(1)–N(2)	91.53(16)	C(5)–C(6)–C(7)	128.1(5)
O(1)–Ni(1)–C(1)	87.0(2)	N(1)–C(7)–C(6)	107.5(5)
O(3)–Ni(1)–N(1)	98.64(15)	N(1)–C(8)–C(9)	106.4(6)
O(3)–Ni(1)–N(2)	84.27(15)	C(8)–C(9)–C(10)	109.7(8)
O(3)–Ni(1)–C(1)	87.8(2)	C(9)–C(10)–C(11)	106.4(6)
N(1)–Ni(1)–N(2)	162.21(19)	N(1)–C(11)–C(10)	107.2(5)
N(1)–Ni(1)–C(1)	81.0(2)	N(1)–C(11)–C(12)	110.8(5)
N(2)–Ni(1)–C(1)	81.6(2)	C(10)–C(11)–C(12)	112.5(5)
Ni(1)–O(1)–C(12)	111.6(3)	O(1)–C(12)–O(2)	123.0(5)
C(12)–O(2)–C(13)	119.2(5)	O(1)–C(12)–C(11)	124.2(5)
Ni(1)–O(3)–C(21)	111.4(4)	O(2)–C(12)–C(11)	112.8(5)
C(21)–O(4)–C(22)	118.1(5)	O(2)–C(13)–C(14)	106.0(5)
Ni(1)–N(1)–C(7)	106.7(3)	O(2)–C(13)–C(15)	107.8(6)
Ni(1)–N(1)–C(8)	116.7(4)	C(14)–C(13)–C(15)	114.9(7)
Ni(1)–N(1)–C(11)	107.4(3)	N(2)–C(16)–C(2)	106.1(5)
C(7)–N(1)–C(8)	110.0(4)	N(2)–C(17)–C(18)	105.6(6)
C(7)–N(1)–C(11)	111.0(5)	C(17)–C(18)–C(19)	113.0(8)
C(8)–N(1)–C(11)	105.1(4)	C(18)–C(19)–C(20)	106.1(6)
Ni(1)–N(2)–C(16)	107.7(3)	N(2)–C(20)–C(19)	106.3(5)
Ni(1)–N(2)–C(17)	115.2(4)	N(2)–C(20)–C(21)	110.6(5)
Ni(1)–N(2)–C(20)	108.2(3)	C(19)–C(20)–C(21)	113.4(5)
C(16)–N(2)–C(17)	109.7(4)	O(3)–C(21)–O(4)	124.0(6)
C(16)–N(2)–C(20)	109.4(4)	O(3)–C(21)–C(20)	124.6(6)
C(17)–N(2)–C(20)	106.5(4)	O(4)–C(21)–C(20)	111.4(5)
Ni(1)–C(1)–C(2)	117.8(4)	O(4)–C(22)–C(23)	105.3(5)
Ni(1)–C(1)–C(6)	116.5(4)	O(4)–C(22)–C(24)	108.7(6)
C(2)–C(1)–C(6)	125.6(5)	C(23)–C(22)–C(24)	115.0(7)
C(1)–C(2)–C(3)	118.1(5)		

angles have been deposited at the Cambridge Crystallographic Data Centre.

2.4. Synthesis of [2-Br]₂[CuBr₄]

To a stirred suspension of the organonickel(II) complex **1** (0.19 g, 0.34 mmol) in acetone (30 ml) at room temperature was added a little more than one equivalent of $CuBr_2$ (0.092 g, 0.41 mmol). The solution darkened quickly, and after 15 min all volatiles were removed in vacuo. The dark solid was washed with a little THF and the residue extracted with CH_2Cl_2 (30 ml). The extract was filtered and evaporated to dryness to give the crude product which was recrystallized by slow evaporation from a CH_2Cl_2/pentane solution to give black crystals; 0.1 g (48% yield).

One crystal was subject to a single crystal X-ray diffraction study. Preliminary refinement (R value of 15%) shows the [2-Br]⁺ cation to have a geometry essentially like the cation in [2-Cl]₂[NiCl₄]. However, apparent disorder in the [CuBr₄] dianion and the rather low quality of the dataset, probably because of twinning, precluded further refinement [11].

Elemental microanalysis data for [2-Br]₂[CuBr₄] from the bulk material is more consistent with [2-Br]₂ 0.3 [CuBr₄] 1.4 [Br₃]; Calc. for $C_{48}H_{70}Br_{7.4}Cu_{0.3}N_4O_8$: C, 36.99; H, 4.53; N, 3.59; Br, 37.93. Found: C, 36.50; H, 4.60; N, 3.34; Br, 37.46%: cf [2-Br]₂ [CuBr₄]; Calc. for $C_{48}H_{70}Br_6Cu_1N_4Ni_2O_8$: C, 38.66; H, 4.73; N, 3.76; Br, 32.35%. Selected IR data for [2-Br]₂[CuBr₄] (KBr, cm⁻¹): 1650 (C=O), 1102 (C–O).

3. Results and discussion

We have previously employed the monoanionic aryldiamine ligand 2,6-bis[(2-(S)-2-isopropoxycarbonyl-1-pyrrolidinyl)methyl]phenyl (=L*) for the preparation of the enantiopure square-planar arylnickel(II) complex [Ni(L*-N, C, N)Br] **1**; this is one of several complexes we have explored as potential chiral catalysts for the enantioselective Kharasch addition reaction [6].

Surprisingly, when [Ni(L*-N, C, N)Br] was added as the catalyst to a mixture of styrene and CCl_4 the colour changed rapidly from orange to green. Analysis of the resulting mixture showed that the 1:1 Kharasch addition reaction had not occurred to a significant extent, and two 1:1 adducts, viz. $PhC(Cl)HCH_2CCl_3$ and $PhC(Br)HCH_2CCl_3$, were present only in small amounts (less than 1% conversion of the styrene substrate; see Experimental details). The presence of bromine in the latter adduct indicated that bromo complex **1** participated in the product formation. Besides these organic materials it was also possible to isolate a green inorganic product from the mixture, and this was obtained as dark-green crystals by diffusion of
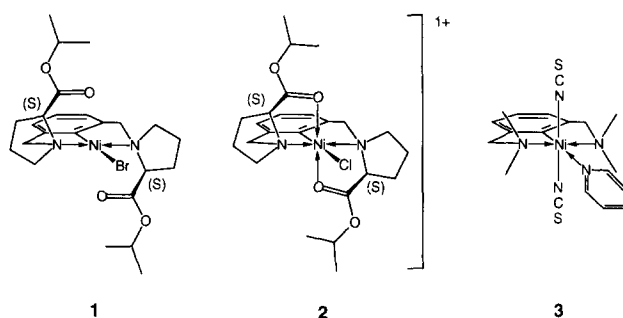

Fig. 2. Schematic drawings of (a) the neutral square planar aryldiamine nickel(II) complex **1** with non-coordinating proline ester O-donor atoms (S,S diastereoisomer); (b) the six-coordinate monocation [2-Cl]⁺ of the nickel(III) complex [2-Cl]₂[NiCl₄]; (c) the neutral six-coordinate Ni(III) complex[Ni{C₆H₃(CH₂NMe₂)₂-2,6}(NCS)₂-(C₅H₅N)], **3**.

hexane into its solution in CH_2Cl_2. This new complex was air-stable and soluble in CH_2Cl_2 and polar solvents such as acetonitrile and alcohols. The complex seemed likely to be a d⁷ Ni(III) species, because we could not detect any signals from it in ¹H NMR spectroscopy and its colour was reminiscent of that of Ni(III) metal ions coordinated by {C₆H₃(CH₂NMe₂)₂-2,6} [1]. Although initial elemental microanalysis data (C, H, N) clearly proved that the aryldiamine ligand L* was present in this complex, we were unable to suggest a reasonable mononuclear structure. Thus a single-crystal structure X-ray diffraction study was undertaken, and showed the product to be an unusual ionic species [Ni(L*)Cl]₂[NiCl₄] (= [2-Cl]₂[NiCl₄]).

3.1. X-ray characterization of [2-Cl]₂[NiCl₄]

The crystal structure of [2-Cl]₂[NiCl₄] consists of four (symmetry-related) units of an arylnickel(III) chloride complex monocation [Ni(L*)Cl]⁺, as depicted in Fig. 1, and two dianions, $[Ni^{II}Cl_4]^{2-}$, located on a two-fold axis in the orthorhombic unit cell. Each monocation [2-Cl]⁺ comprises a nickel(III) centre bonded solely to the substituted aryldiamine ligand that is acting as pentadentate C, N₂, O₂-donor and a single halide atom so that the metal is octahedrally coordinated, i.e. $[Ni(L*-C,N_2,O_2)Cl]^+$. In detail the Ni(III) coordination sphere may be seen as tetragonally compressed, with two *trans* nitrogen donor atoms (N1, N2) and two *trans* oxygen atoms (O1, O2) of the carbonyl bonds of the ester groups in the meridional plane and a C_{aryl} atom (C1), and one halide substituent (C11) occupying the mutually *trans* apical sites. The bonding of oxygen atoms to the metal centre results in a lengthening of the C–O bond from 1.179(8) Å in the parent organonickel(II) complex **1** (in which these C=O bonds are not coordinated [6]) to 1.213(7) Å and 1.218(7) Å in this nickel(III) cation, [2-Cl]⁺. Furthermore, in [2-Cl]⁺ the Ni–N bonds of 2.092(4) and

2.074(4) and the Ni–C$_{aryl}$ σ bond (1.900(5) Å) are significantly longer than those in the nickel(II) complex **1** (see Table 3); these lengths in **[2-Cl]$^+$** are however somewhat less than those in the neutral six-coordinate Ni(III) complex [Ni{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(NCS)$_2$-(C$_5$H$_5$N)], **3** (see Table 3) [12]. The one dianionic unit of NiCl$_4^{2-}$ is not involved in any short intermolecular contacts with the accompanying two complex cations of **[2-Cl]$^+$** and it has a slightly distorted tetrahedral structure (Ni–Cl = 2.244(2) Å and 2.285(2) Å), as is not uncommon for this anion [13].

3.2. Analytical and spectroscopic characterization of [2-Cl]$_2$[NiCl$_4$]

Although the X-ray study only revealed the presence of chlorine in **[2-Cl]$_2$[NiCl$_4$]**, elemental analysis of the bulk product showed some bromine to be present (originating from the starting arylnickel(II) bromo complex **1**), the ratio Cl:Br being 5:1 (see Experimental details). When this was taken into account, the elemental microanalysis data were consistent with the ionic structure found by X-ray analysis.

FTIR spectroscopy of the aryl nickel(III) complex **[2-Cl]$_2$[NiCl$_4$]** in CH$_2$Cl$_2$ shows the C=O stretching frequency for the cation **[2-Cl]$^+$** at 1653 cm^{-1}, consistent with the carbonyl group being coordinated to nickel(III); both the aryl bromide 2,6-bis[2-(S)-2-isopropoxycarbonyl-1-pyrrolidinyl)methyl]bromobenzene and the parent organonickel(II) complex **1** show a C=O stretching frequency at 1725 cm^{-1} (see Fig. 3) that can be ascribed to a free uncoordinated carbonyl group.

Although the solid state FTIR spectrum of **1** (in KBr) shows a single band in the C=O region at 1738 cm^{-1} in solution an additional, less intense, band at 1638 cm^{-1} was found, but the identity of the species with a coordinating carbonyl group that generates this band has not yet been elucidated; owing to the low redox potential of complexes such as **1**, small amounts of Ni(III) species could be present as a result of inadvertent oxidation.

Complex **[2-Cl]$_2$[NiCl$_4$]** gives green solutions with most solvents, but when it is dissolved in alcohols the solutions are orange. However, after evaporation of the
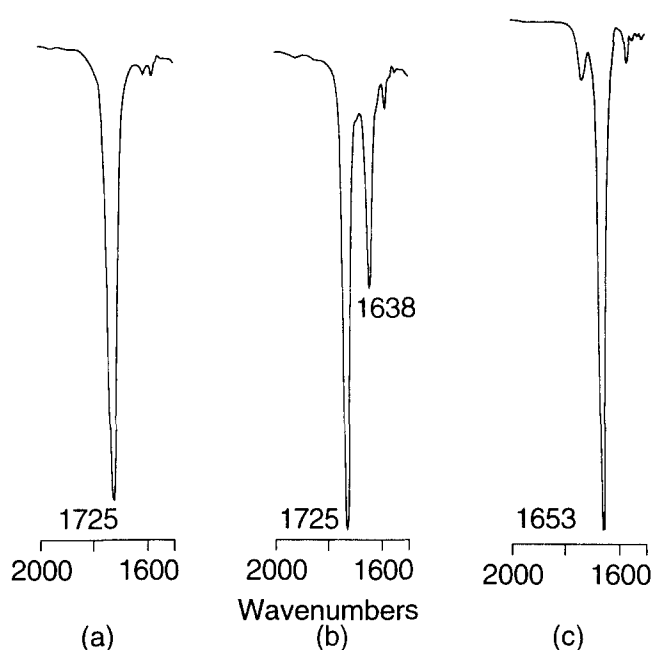

Fig. 3. The C=O region of the solution IR spectra (CH$_2$Cl$_2$) of (a) the parent aryldiamine bromide 2,6-bis[2-(S)-2-isopropoxycarbonyl-1-pyrrolidinyl)methyl]bromobenzene; (b) the arylnickel(II) complex **1**; and (c) the new organonickel(III) complex **[2-Cl]$_2$[NiCl$_4$]**.

alcoholic solvent the green complex is recovered unchanged, i.e. a reversible process occurs. Our present view is that, rather than coordination of the alcohol itself to metal, it is more likely that the C=O group of the ester function becomes involved in H-bridge bonding with the solvent. UV/VIS studies showed that in methanol the concentration dependency of the extinction coefficients of the absorption bands do not follow Beer's law.

The ESR spectra of d^7 Ni(III) complexes can be very instructive, although true organometallic Ni(III) species with a well-defined stereochemistry are still rare. Those with five-coordinate nickel centres, which we investigated earlier [1], have some relevance to the determination of the ligand sphere of the Ni(III) sites involved in nickel hydrogenases [2]. The ESR spectrum of the six-coordinated nickel complex **[2-Cl]$_2$[NiCl$_4$]** has been recorded for a powder (mixed with KBr) in the solid state at 77 K (Fig. 4). Although the resonance lines in this spectrum, Fig. 4, are quite broad (greater than 50 G), the principal component resulting from the monocationic octahedral Ni(III) species **[2-Cl]$^+$**, affords an axial spectrum with g_z of 2.32, and g_x and g_y of ca. 2.10. In this description the x–y plane is the meridional plane containing the two N donor atoms and two O donor atoms of the organic ligand L* and the z axis is C$_{aryl}$–(Ni)–Cl. The g values for this cation are similar to those for [Ni{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(NCS)$_2$(C$_5$H$_5$N)], **3**, (g_z = 2.26, $g_x \sim g_y$ = 2.10 [12]) and are consistent with a low-spin d^7 Ni(III) species in

Table 3
Comparison of selected bond lengths (in Å) of the arylnickel(II) complex [Ni{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}Br], **1**, and arylnickel(III) complexes [2-Cl]$_2$[NiCl$_4$] and [Ni{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(NCS)$_2$-(C$_5$H$_5$N)], **3**

	1; Ni(II)	[2-Cl]$^+$; Ni(III)	3; Ni(III)
Ni–N1	1.984(4)	2.092(4)	2.207(6)
Ni–N2	1.984(4)	2.074(4)	2.207(6)
Ni–C1	1.816(5)	1.900(5)	1.900(9)
Ni–X [a]	2.4071(10) [b]	2.2802(18) [c]	2.057(8) [d]

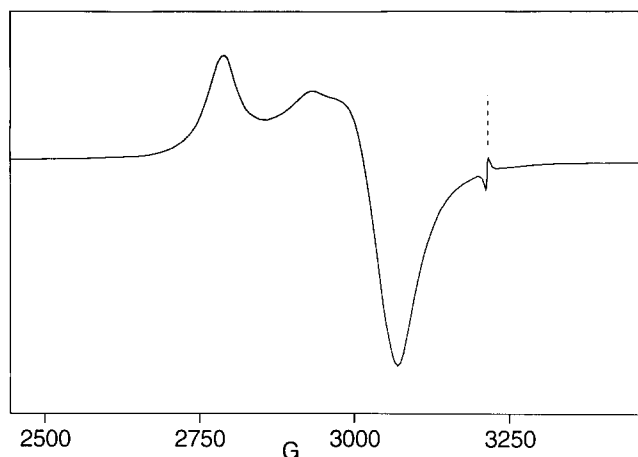[a] Ligand *trans* to Cl. [b] X = Br. [c] X = Cl. [d] X = N of pyridine.

Fig. 4. 9.12 GHz X-band ESR powder spectrum of [2-Cl]$_2$[NiCl$_4$] at 77 K in KBr with g = 2.0036 indicated by a dashed line.

which the unpaired spin seems to be in the d$_{x^2-y^2}$ orbital [14]. Paramagnetic [NiCl$_4$]$^{2-}$ has a Jahn-Teller distorted tetrahedral geometry, and as a consequence the two unpaired spins of the Ni(II) centre do not give rise to an ESR spectrum [15].

3.3. Mechanism of formation of [2-Cl]$_2$[NiCl$_4$]; Synthesis of [2-Br]$_2$[CuBr$_4$]

A number of separate experiments were carried out to help elucidate the way in which the new organonickel(III) cation [2-Cl]$^+$ is formed from CCl$_4$, styrene, and Ni(II) complex 1 in what was intended to be a catalytic system.

First, it was found that the presence of styrene is unnecessary; i.e., the oxidation reaction involves solely CCl$_4$ and 1; the presence of styrene does however, improve the purity of the product [2-Cl]$_2$[NiCl$_4$] in that it serves to remove some bromine (by inclusion in the 1:1 Kharasch addition product).

Secondly, CuBr$_2$ was tried as oxidant, not only to determine the generality of the reaction but also to remove the problem of having two different halides present in the starting materials. This reaction of CuBr$_2$ with 1 (see Experimental details) affords the bromide-containing analogue of [2-Cl]$^+$, i.e., [2-Br]$^+$, in fair yield though, unexpectedly, as revealed by a single crystal X-ray diffraction study, now with [CuBr$_4$]$^{2-}$ rather than [NiCl$_4$]$^{2-}$ as the counter anion. This result clearly demonstrates that the arylnickel(II) cation [2-X]$^+$ (X = Cl, Br) is readily formed, and that a variety of (di)anions may be appropriate for obtaining crystalline materials. The elemental microanalysis of the bulk material from this experiment with CuBr$_2$ showed that the [2-Br]$^+$ cation is accompanied by anions with a large percentage of bromide, and it is possible that both [CuBr$_4$]$^{2-}$ and [Br$_3$] counteranions are present. The spectroscopic data for [2-Br]$^+$ (FTIR and ESR)

are very similar to those for [2-Cl][NiCl$_4$], and in particular the ESR spectrum shows no hyperfine coupling to bromine; i.e. the unpaired electron is not likely to be in an orbital associated with the C–(Ni)–Br vector. This result provides further support for the orbital arrangement assignment suggested for [2-Cl][NiCl$_4$] above.

Finally, consideration of the mass-balance of the formation of [2-Cl][NiCl$_4$] tells us that at least one third of the arylNi(II) starting complex 1 is consumed in the production of the inorganic [NiCl$_4$]$^{2-}$, and our interest turned to the fate of the aryl ligand. In order to examine the other product(s) of the reaction, experiments were carried out with 1 and CCl$_4$ in which 1 was present in more than the usual catalytic quantity, and from such a reaction mixture it was possible to isolate a colourless organic material. Although its characterization is not complete, the spectroscopic evidence obtained so far indicates that it comes from a C–C cross-coupling reaction involving the carbon atom of the former Ni–C$_{aryl}$ bond of the L* aryldiamine ligand system with a C–Cl-containing organic species. For example, IR analysis shows the presence of (i) an uncoordinated C=O group (1735 cm^{-1}), (ii) a C–H stretch band (3000–2900 cm^{-1}), and (iii) a band around 700–800 cm^{-1} that could be a C–Cl stretching frequency. ^{1}H and ^{13}C NMR spectroscopy show the presence of an isopropyl unit. The cross-coupling reaction that generated this organic material would also be responsible for the eventual formation of the [NiCl$_4$]$^{2-}$ unit.

4. Conclusions

The molecular structure of [2-Cl]$_2$[NiCl$_4$] demonstrates the potential of the monoanionic terdentate ligand system with two tertiary amine substituents, [C$_6$H$_3$(CH$_2$NRR')$_2$-2,6]$^-$, to stabilize higher oxidation states of a complexed metal centre without cleavage of the M–C σ bond. The coordination sphere of Ni(III) in this species is noteworthy; the C, N$_2$, O$_2$ cavity stabilizes an octahedral monocation and this parallels C, N_2, N_2' coordination encountered earlier in copper chemistry [1]. This pentadentate ligand coordination mode is relevant to the current interest in unusual Ni(III) coordination spheres, not only as models for nickel hydrogenases but also as materials for EXAFS and the study of catalytically active surfaces [2].

Acknowledgements

References

[1] (a) D.M. Grove, G. van Koten, R. Zoet, N.W. Murrall and A.J. Welch, J. Am. Chem. Soc., 105 (1983) 1379; (b) D.M. Grove, G. van Koten, P. Mul, R. Zoet, J.G.M. van der Linden, J. Legters, J.E.J. Schmitz, N.W. Murall and A.J. Welch, Inorg. Chem., 27 (1988) 2466.

[2] (a) S.P.J. Albracht, J.W. van der Zwaan and R.D. Fontijn, Biochim. Biophys. Acta, 766 (1984) 245; (b) P.A. Lindahl, N. Kojima, R.P. Hausinger, J.A. Fox, B.K. Teo, C.T. Walsh and W.H Orme-Johnson, J. Am. Chem. Soc., 106 (1984) 3062; (c) I. Okura, Coord. Chem. Rev., 68 (1985) 53; (d) J.M. Corker, J. Evans, W. Levason, M.D. Spicer and P. Andrews, Inorg. Chem., 30 (1991) 331; (d) M. Zimmer, G. Schulte, X. Luo and R.H. Crabtree, Angew. Chem., Int. Edn. Engl., 30 (1991) 193.

[3] (a) D.M. Grove, G. van Koten and A.H.M. Verschuuren, J. Mol. Catal., 45 (1988) 169; (b) D.M. Grove, A.H.M. Verschuuren, G. van Koten and J.A.J.M. van Beek, J. Organomet. Chem., 372 (1989) C1.

[4] L.A. van de Kuil, P.M.F.C. Groot, J.-P. van Rijswijk, D.M. Grove, J.W. Zwikker, L.W. Jenneskens, W. Drenth and G. van Koten, J. Am. Chem. Soc., accepted for publication (1994).

[5] L.A. van de Kuil, H. Luitjes, D.M. Grove, J.W. Zwikker, J.G.M. van der Linden, A.M. Roelofson, L.W. Jenneskens, W. Drenth and G. van Koten, Organometallics, 13 (1994) 468.

[6] L.A. van de Kuil, Y.S.J. Veldhuizen, D.M. Grove, J.W. Zwikker, L.W. Jenneskens, W. Drenth, W.J.J. Smeets, A.L. Spek and G. van Koten, Recl. Trav. Chim. Pays-Bas, 113 (1994) 267.

[7] N. Walker and D. Stuart, Acta Cryst., A 39 (1983) 158.

[8] G.M. Sheldrick, SHELXS86 Program for crystal structure determination, University of Göttingen, FRG, 1986.

[9] G.M. Sheldrick, SHELX76, Crystal structure analysis package, University of Cambridge, England, 1976.

[10] A.L. Spek, Acta Cryst., A 46 (1990) C34.

[11] A. Fernandia Bartolome, D.M. Grove, N. Veldman, A.L. Spek and G. van Koten, unpublished results.

[12] D.M. Grove, G. van Koten, W.P. Mul, A.A.H. van der Zeijden, J. Terheijden, M.C. Zoutberg and C.H. Stam, Organometallics, 5 (1986) 322.

[13] J.A. Albanese, D.A. Staley, A.L. Rheingold and J.L. Burmeister, Acta Cryst., C45, (1989) 1128, and references cited therein.

[14] (a) A. Bencini, L. Fabbrizzi and A. Poggi, Inorg. Chem., 20 (1981) 2544; (b) S.A. Jacobs and D.W. Margerum, Inorg. Chem., 23 (1984) 1195.

[15] A. Bencini and D. Gatteschi, ESR spectra of metal complexes of the first transition series in low-symmetry environments, in A.G. Melson and B.N. Figgis (eds.), Transition Metal Chemistry, A series of Advances, Vol. 8, Marcel Dekker, New York and Basel, 1982, Ch. 1, p. 118.

[16] G.M. Kapteijn, I.C.M. Wehman-Ooyevaar, D.M. Grove, W.J.J. Smeets, A.L. Spek and G. van Koten, Angew. Chem., Int. Edn. Engl., 32 (1993) 72.