

Synthesis and structural characterisation of the first homoleptic organometallic nickel(III) compound

Pablo J. Alonso, Larry R. Falvello, Juan Forniés,* Antonio Martín, Babil Menjón and Gerardo Rodríguez

Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C., Pza. S. Francisco s/n, E-50009 Zaragoza, Spain

The homoleptic, square-planar, d⁷, 15-electron species [NBu₄][Ni^{III}(C₆Cl₅)₄] **2 is obtained by low-temperature oxidation of [NBu₄]₂[Ni^{II}(C₆Cl₅)₄] **1** with Cl₂.**

In the last few years the chemistry of Ni^{III} has evolved very rapidly^{1,2} partly because of its relevance to some metalloprotein systems.^{3,4} In spite of this burgeoning development, organometallic compounds of Ni^{III} are still extremely rare, the only isolated examples of this class of compounds being, to our knowledge, those reported by van Koten and coworkers.⁵ They contain a single Ni–C bond and are stabilised by using polydentate ligands. We now report on the synthesis and characterisation of the first homoleptic organometallic nickel(III) compound, which contains four non-assisted Ni–C σ bonds.

Low-temperature chlorination of the substrate [NBu₄]₂[Ni^{II}(C₆Cl₅)₄] **1**⁶ renders the complex [NBu₄][Ni^{III}(C₆Cl₅)₄] **2**, which has been isolated as a green solid in good yield.[†] Complex **2** is air- and moisture-stable but because of its rather limited thermal stability it is best formed and handled at low temperature. At room temperature it readily decomposes both in solution and in the solid state, undergoing reductive elimination of C₆Cl₅–C₆Cl₅.[‡] This observation is of particular interest because of its relevance to the nickel-mediated synthesis of biaryls, which has been shown to proceed in some instances *via* unstable aryl intermediates of Ni^{III}.⁷

The **2**–**1** couple is not only chemically but also electrochemically related by a reversible redox process at a remarkably low potential ($E_{1/2} = -0.11$ V).[§] The IR spectrum of **2** shows the absorptions corresponding to the X-sensitive mode of the C₆Cl₅ group and to the $\nu(\text{Pt}-\text{C})$ mode⁸ at higher wavenumbers than those observed for the nickel(II) parent compound (*cf.* **1**, 813 and 581 cm⁻¹; **2**, 827 and 603 cm⁻¹, respectively). This shift can be associated with the increase in the oxidation state of the metal centre in keeping with previous observations in the perchlorophenyl chemistry of palladium and platinum.^{8a,9}

The structure of the anion [Ni^{III}(C₆Cl₅)₄]⁻ as found in the dihydrate 2·2Et₂O by X-ray diffraction methods is shown in Fig. 1.[¶] The Ni atom is in an almost square-planar environment. The C₆Cl₅ groups define a helix around the metal centre with two possible orientations, Δ and Λ , both of which are present in the crystal measured (centrosymmetric space group). The mean dihedral angle formed by the C₆Cl₅ groups and the coordination plane is 63.2(3)°. The mean Ni–C_{ipso} distance [200.7(8) pm] is slightly longer than found in other pentachlorophenyl derivatives of Ni^{II} (mean value 192.2 pm).¹⁰ This seeming elongation is at variance with the expected dependence of the M–C distance on the oxidation state of M. This difference, however, must be treated with caution because it could merely be due to the recently demonstrated flexibility of bond distances.¹¹ The EPR spectrum of a powder sample of **2** is given in Fig. 2^{||} in which two features can be observed: one at *ca.* 340 mT having a parallel character and the other one at *ca.* 230 mT having a perpendicular character. This spectrum can be interpreted as due to a paramagnetic $S = 1/2$ entity in an axial symmetry including only an anisotropic electronic Zeeman interaction and can be described with the following spin-Hamiltonian $H = \mu_B$

$[g_{\perp}(S_x B_x + S_y B_y) + g_{\parallel} S_z B_z]$, where μ_B is the Bohr magneton and $g_{\parallel} = 1.92$ and $g_{\perp} = 2.84$. This would imply a low-spin (strong ligand field) situation for the 3d⁷ ion. Since the Ni^{III} centre in **2** is in a square-planar environment, the unpaired electron should be expected to occupy an a_{1g} (z²) orbital.¹² In terms of the crystal-field approximation, a second order of perturbation for such an ion would give $g_{\parallel} = g_e$ and $g_{\perp} = g_e - 6\lambda/\Delta$, where λ is the spin-orbit constant and Δ the difference in energy between the a_{1g} (z²) and e_g (xz, yz) orbitals. Since $\lambda < 0$ for Ni^{III}, the former expression predicts that $g_{\perp} > g_e$ while g_{\parallel} lies close to the free-electron value in agreement with our observation.^{**} This behaviour is in keeping with that reported for other nickel(III) species,¹³ the only remarkable feature being in our case the high g anisotropy observed.

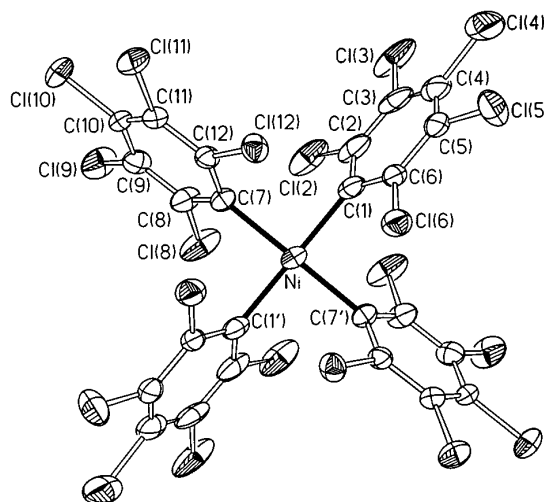


Fig. 1 Thermal ellipsoid diagram of the anion of **2**. Selected distances (pm) and angles (°): Ni–C(1) 200.1(8), Ni–C(7) 201.4(7); C(1)–Ni–C(7) 90.1(3), C(1)–Ni–C(1') 178.6(5), C(7)–Ni–C(1') 90.0(3), C(7)–Ni–C(7') 178.9(4).

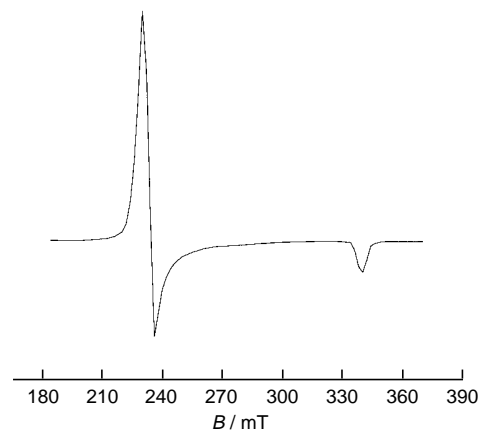


Fig. 2 EPR spectrum of a powder sample of **2** (X-band, 77.3 K)

It can be concluded that the pentachlorophenyl group is a ligand especially well suited to stabilising unusual oxidation states, at least in the platinum-group metals.^{9,14} Studies aimed at testing the reactivity of this unprecedented nickel(III) compound are in progress.

We thank the Dirección General de Enseñanza Superior (Projects PB95-0003-CO2-01 and PB95-0792) for financial support.

Footnotes

† *Experimental procedure:* to a yellowish suspension of $[\text{NBu}_4]_2[\text{Ni}^{\text{II}}(\text{C}_6\text{Cl}_5)_4]$ **1** (0.5 g, 0.32 mmol) in CH_2Cl_2 (7 cm^3) at -40°C was added Cl_2 dissolved in CCl_4 (0.18 mmol). The system changed immediately to green and, after addition of MeOH (20 cm^3) at -80°C , the resulting green solid was filtered off in a low-temperature device, subsequently washed with cold Et_2O (3×10 cm^3) and dried (2, 70% yield). Anal. Found: C 36.5, H 2.8, N 1.1; $\text{C}_{40}\text{H}_{36}\text{Cl}_{20}\text{NNi}$ requires: C 37.0, H 2.8, N 1.1%. IR(Nujol; cm^{-1}): selected absorptions associated with the C_6Cl_5 groups:⁸ 827vs (X-sensitive vibr.), 675vs, 603s [$\nu(\text{Pt}-\text{C})$] and 275m.

‡ The fate of the metal-containing fragment could not be determined so far and hence we still do not know whether this reductive elimination process takes place inter- or intra-molecularly.

§ The cyclic voltammogram of **1** at 100 mV s^{-1} scan rate in 0.1 $\text{m NBu}_4\text{PF}_6$ shows $E_{\text{pa}} = -0.055$ V and $E_{\text{pc}} = -0.168$ V vs. SCE.

¶ *Crystal data* for $2 \cdot 2\text{Et}_2\text{O} \cdot \text{C}_{48}\text{H}_{56}\text{Cl}_{20}\text{NNiO}_2$, $M = 1446.65$, monoclinic, space group C2/c (no. 15), $a = 1987.3(2)$, $b = 2167.8(1)$, $c = 1487.2(1)$ pm, $\beta = 110.026(5)^\circ$, $U = 6.031(2)$ nm^3 , $Z = 4$, $F(000) = 2940$, $D_c = 1.593$ g cm^{-3} , $\lambda(\text{Mo}-\text{K}\alpha) = 71.073$ pm, 344 parameters refined with 5300 reflections with $I > 2\sigma(I)$ to $R = 0.0736$, $R_w = 0.1577$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/365.

|| EPR data were taken on a Varian E-112 spectrometer working in the X-band. Measurements at liquid-nitrogen temperature (77.3 K) were taken using a quartz immersion Dewar. The magnetic field was measured with a Bruker ER035M gaussmeter. The diphenylpicrylhydrazyl resonance signal [$g = 2.0037(2)$] was used to determine the microwave frequencies.

** Other contributions such as charge-transfer, covalency, etc. can modify the principal g -values so as to make the crystal-field description inadequate. In fact, either positive or negative g -shifts are observed for square-planar low-spin d^7 complexes.¹²

References

- 1 A. G. Lappin and A. McAuley, *Adv. Inorg. Chem.*, 1988, **32**, 241; L. Sacconi, F. Mani and A. Bencini, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, ch. 50, p. 1; R. I. Haines and

- A. McAuley, *Coord. Chem. Rev.*, 1981, **39**, 77; K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.
- 2 K. R. Dunbar, J.-S. Sun and A. Quillevéré, *Inorg. Chem.*, 1994, **33**, 3598 and references therein.
- 3 J. J. G. Moura, M. Teixeira and I. Moura, *Pure Appl. Chem.*, 1989, **61**, 915; R. Cammack, *Adv. Inorg. Chem.*, 1988, **32**, 297; D. W. Margerum, *Pure Appl. Chem.*, 1983, **55**, 23.
- 4 C. A. Marganian, H. Vazir, N. Baidya, M. M. Olmstead and P. K. Mascharak, *J. Am. Chem. Soc.*, 1995, **117**, 1584 and references therein.
- 5 (a) 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, *J. Organomet. Chem.*, 1995, **488**, 191; (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. Murrall and A. J. Welch, *Inorg. Chem.*, 1988, **27**, 2466; (c) 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*, 1986, **5**, 322; (d) D. M. Grove, G. van Koten, R. Zoet, N. W. Murrall and A. J. Welch, *J. Am. Chem. Soc.*, 1983, **105**, 1379.
- 6 R. Usón, J. Forniés, P. Espinet, R. Navarro, F. Martínez and M. Tomás, *J. Chem. Soc., Chem. Commun.*, 1977, 789.
- 7 C. Amatore and A. Jutand, *Organometallics*, 1988, **7**, 2203; T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 7547; 1978, **100**, 1634; M. Almemark and B. Åkermark, *J. Chem. Soc., Chem. Commun.*, 1978, 66.
- 8 (a) R. Usón and J. Forniés, *Adv. Organomet. Chem.*, 1988, **28**, 219; (b) E. Maslowsky Jr., *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, 1977, p. 437; (c) J. Casabó, J. M. Coronas and J. Sales, *Inorg. Chim. Acta*, 1974, **11**, 5.
- 9 J. Forniés, B. Menjón, R. M. Sanz-Carrillo, M. Tomás, N. G. Connelly, J. G. Crossley and A. G. Orpen, *J. Am. Chem. Soc.*, 1995, **117**, 4295; R. Usón, J. Forniés, M. Tomás, B. Menjón, R. Bau, K. Sünkel and E. Kuwabara, *Organometallics*, 1986, **5**, 1576.
- 10 D. Xu, K. Miki, M. Tanaka, N. Kasai, N. Yasuoka and M. Wada, *J. Organomet. Chem.*, 1989, **371**, 267; B. Longato, B. Corain, R. Angeletti and G. Valle, *Inorg. Chim. Acta*, 1987, **130**, 243; D. Xu, K. Miki, Y. Kai, N. Kasai and M. Wada, *J. Organomet. Chem.*, 1985, **287**, 265; K. Miki, H. Taniguchi, Y. Kai, N. Kasai, K. Nishiwaki and M. Wada, *J. Chem. Soc., Chem. Commun.*, 1982, 1178.
- 11 A. Martín and A. G. Orpen, *J. Am. Chem. Soc.*, 1996, **118**, 1464.
- 12 J. A. Aramburu and M. Moreno, *J. Chem. Phys.*, 1983, **79**, 4996.
- 13 T. J. Collins, T. R. Nichols and E. S. Uffelman, *J. Am. Chem. Soc.*, 1991, **113**, 4708; H.-J. Krüger, G. Peng and R. H. Holm, *Inorg. Chem.*, 1991, **30**, 734; see also refs. 2, 5(b) and 5(d).
- 14 M. P. García, M. V. Jiménez, L. A. Oro, F. J. Lahoz, M. C. Tiripicchio and A. Tiripicchio, *Organometallics*, 1993, **12**, 4660; M. P. García, M. V. Jiménez, L. A. Oro, F. J. Lahoz, J. M. Casas and P. J. Alonso, *Organometallics*, 1993, **12**, 3257; M. P. García, M. V. Jiménez, L. A. Oro, F. J. Lahoz and P. J. Alonso, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1527.

Received, 11th November 1996; Com. 6/07668H