Unique Stable Organometallic Nickel(III) Complexes: Syntheses and the Molecular Structure of Ni[C6H3(CH2NMe2)2-*o*,*o*']I2

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There are several reports of stable paramagnetic organo transition-metal species in which there is a direct metal–carbon interaction.[1] However, the metals of the nickel triad are poorly represented, and those examples known for nickel almost invariably contain cyclopentadienyl, carbaborane, cyano, or CO moieties.[2,3] We now report the preparation of a unique series of organometallic Ni(III) complexes of general formula Ni[C6H3(CH2NMe2)2-*o*,*o*']X2 (**1a–c**, X = Cl, Br, I), in which the square-pyramidal metal coordination sphere comprises two halo atoms (one apical), two N donor atoms, and most importantly a direct Ni–C σ bond to an aryl function.

The reaction of diamagnetic square-planar Ni[C6H3-(CH2NMe2)2-*o*,*o*']X **2a–c**,[4] X = Cl, Br, I, with an appropriate reagent (CuCl2, CuBr2, I2) affords the new complexes **1a–c** in high yield[5] (eq 1). These almost black solid paramagnetic[6] complexes
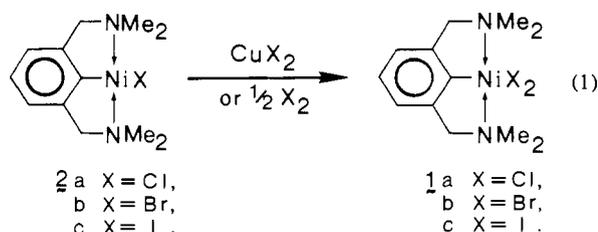
are air-stable and are reasonably soluble in CH2Cl2 and sparingly soluble in toluene to afford brown-yellow, green, and red-violet solutions for **1a**, **1b**, and **1c**, respectively.[7] The ESR spectrum (X band) of each of these monomeric complexes at room temperature shows a single broad absorption signal[8] (lacking hyperfine

(1) A fairly recent review covering this subject is given in the following: Lappert, M. F.; Lednor, P. *Adv. Organomet. Chem.* **1976**, *14*, 345–399.
(2) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77–119.
(3) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87–147.
(4) The syntheses and characterization of these and related complexes will be the subject of a forthcoming publication.
(5) Complex **1b** has also been isolated in low yield from the reaction of **2b** with either Br2 or *N*-bromosuccinimide. The copper halide reactions were carried out in acetone, whereas benzene was used for the syntheses of **1c**.
(6) An NMR method was used to measure the paramagnetism, and this gave a value of one unpaired electron per molecule at room temperature in CH2Cl2: Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Löliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.
(7) The UV–visible spectra of these solutions show several absorption maxima between 300 and 750 nm with ε values in the range 200–2000 L mol⁻¹ cm⁻¹.
(8) For ESR data, complexes **1a–c** are assumed to have a principal pseudo-*C*2 axis colinear with the Ni apical halide bond. ⟨*g*⟩ values for **1a–c** at room temperature are ca. 2.19, 2.17, and 2.14 respectively.

Figure 1. ESR spectrum of **1a** at −140 °C in a toluene glass.[20]
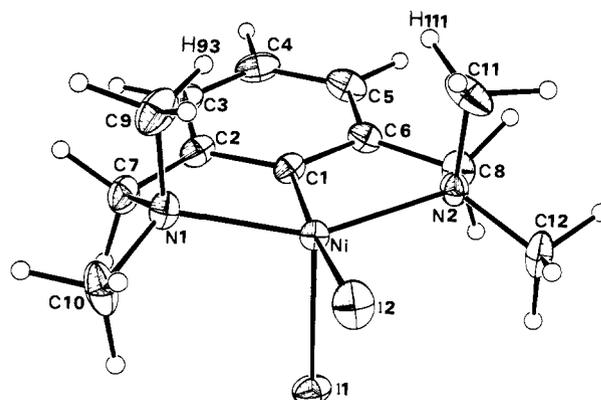
Figure 2. ORTEP drawing of Ni[C6H3(CH2NMe2)2-*o*,*o*']I2 (**1c**). Some relevant bond lengths (Å) and angles (deg) are as follows: Ni–I1, 2.613 (1); Ni–I2, 2.627; Ni–N1, 2.050 (4); Ni–N2, 2.038 (4); Ni–C1, 1.898 (5); N1–Ni–N2, 152.0 (2); C1–Ni–I2, 168.8 (2); I1–Ni–I2, 103.0 (1); I1–Ni–C1, 88.2 (2); I2–Ni–N1, 95.6 (1); N1–Ni–C1, 81.9 (2); I1–Ni–N1, 102.0 (1).

structure) which at ~−140 °C (toluene glass) becomes an orthorhombic signal with three distinct *g* values. As an example, that of the chloro derivative **1a** is shown in Figure 1 ($g_\parallel$ = 2.020, $g_\perp$ = 2.190, $g_\perp'$ = 2.366), and here only the $g_\parallel$ tensor shows hyperfine coupling consistent with coupling of the electron to a single Cl atom; *A* = 28 G. The diiodo and dibromo analogues give comparable signals with the hyperfine coupling on the $g_\parallel$ tensor being approximately 140 and 150 G, respectively. However, these latter spectra possess hyperfine structure on the $g_\perp$ tensor also, and second-order hyperfine interactions are present since the hyperfine components of the parallel and perpendicular regions are not separated.[9] These data taken together with the absence of ¹⁴N coupling suggest that the unpaired electron does not lie in an orbital in the plane of the coordinated [C6H3-(CH2NMe2)2-*o*,*o*'] skeleton but is probably localized in a unique metal–halogen orbital. To definitively establish the nature of these complexes, an X-ray crystallographic study has been carried out on **1c** (X = I).

Some crystal data for **1c** are as follows: C12H19I2N2Ni, monoclinic, space group *P*2₁/*c*, with *a* = 13.9696 (9) Å, *b* = 7.8683 (9) Å, *c* = 15.0510 (17) Å, β = 108.769 (7)°, *U* = 1566.4 Å³, *Z* = 4, *D*c = 1.28 g cm⁻³, *F*(000) = 956 electrons, μ(Mo Kᾱ) = 48.6 cm⁻¹. A total of 3968 symmetry-independent reflections, from a crystal of dimensions 0.25 × 0.30 × 0.50 mm, were re-

(9) Although Cl has two isotopes with *I* = ³/₂, it was not possible to detect their individual lines. However, Br with two isotopes (both *I* = ³/₂) exhibits much larger spin–spin couplings, and resolution of the separate lines is to be anticipated. This together with the second-order complications makes extraction of accurate data for **1b** and **1c** nontrivial, and further work, including measurement of Q-band spectra, is in progress.

corded (θ–2θ scans at 291 K) to θ_{max} = 28° (graphite-monochromated Mo K$\bar{\alpha}$ X-radiation, $\bar{\lambda}$ 0.71069 Å) on an Enraf-Nonius CAD4 diffractometer and were corrected empirically for absorption. The structure was solved by Patterson (Ni and I atoms) and difference Fourier techniques and refined by full-matrix least squares (SHELX[10]) to an R value of 0.0499, with a weighted index R_w (= $\sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$) of 0.0603 (w^{-1} = $\sigma^2(F_o)$ + 0.0076F_o^2) for 3365 reflections with $F_o \geq 2.0\sigma(F_o)$). In the final stages of refinement, hydrogen atomic positions were idealized and all non-hydrogen atoms were allowed anisotropic thermal motion.[11]

Figure 2 shows the molecular structure of **1c** together with some important molecular parameters. The geometry at Ni is best described as square pyramidal (SP) with the Ni atom displaced ca. 0.34 Å out of the basal plane[12] toward the apical atom I1 although there is a significant distortion from an ideal SP geometry toward trigonal bypyramidal (TBP, C1 and I2 axial). As far as we are aware compound **1c** represents the first known example of a true organonickel(III) species. Ni–C1 is 1.898 (5) Å, and the average Ni–N bond is 2.044 (4) Å, these bond lengths in **1c** being consistently ca. 0.07 Å longer than equivalent distances[13] in the four-coordinate Ni(II) complex Ni[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o*]OC(O)H. However, the significance of this observation is difficult to assess since both the oxidation state of the metal and its coordination number change between these species in ways that would be expected to alter bond lengths in opposite senses. From the average Ni–I distance of 2.62 Å an approximate covalent radius for five-coordinate Ni(III) of ca. 1.3 Å may be estimated and compared with the value of ca. 1.2 Å calculated from the non-Jahn–Teller-elongated Ni–Br bonds of NiBr$_3$(PPhMe$_2$)$_2$.[14]

The crystallographic study now provides a rationalization of the ESR results that can be seen to be consistent with a Ni(III) low-spin d^7 system [(e)^4(b$_2$)^2(a$_1$)^1] in which the unpaired electron is in an orbital of d$_{z^2}$ symmetry, i.e., the orbital containing the apical halide.[15] Moreover, EHMO calculations[11] indicate that the unpaired electron resides primarily in a molecular orbital that is antibonding between Ni d$_{z^2}$ and I1 p$_z$. The stability of these neutral 17-electron species is interesting since dimerization could theoretically provide an 18-electron configuration. It is too early to say whether the stability of the monomeric unit is steric or electronic in origin, but it should be noted that the proximal methyl functions (C9)H$_3$ and (C11)H$_3$, which stand axially to the two five-membered mirror-plane-related $\overline{\text{NiCCCN}}$ rings, serve to protect the vacant coordination site trans to I1.[16]

The formation of the five-coordinate d^7 **1a–c** from the d^8 species **2** can be considered as a ligand-transfer oxidation reaction, and cyclovoltametric measurements show that an electrochemically irreversible single-electron oxidation of d^8 **2b** to d^7 **1b** occurs at +0.38 V.[17] The existence of the SP Pt(II) complex Pt[C$_6$H$_3$-(CH$_2$NMe$_2$)$_2$-*o,o*](RNC(H)NR)HgClBr (R = *p*-tolyl)[18] suggests that the path of the oxidation reaction of the SP Ni(II) complexes **2a** and **2b** with CuX$_2$ may involve a heterobimetallic intermediate having a related structure. Noteworthy is the fact that the

carbanionic terdentate ligand used in these studies also assists the oxidation of other metal centers. The Pt(IV) complexes Pt-[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o*]X$_3$ may be prepared in a way similar to **1a–c** from appropriate Pt(II) materials.[19] Further studies on the properties of these Ni(III) and Pt(IV) species as well as the ability of the terdentate ligand to stabilize higher oxidation states are in progress.

(19) Terheijden, J.; van Koten, G.; Ubbels, H. J. C., manuscript in preparation.

(20) The small features observable at approximately 2915, 3270, and 3410 G are assignable to another Ni(III) complex, Ni[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o*]BrCl, which has been separately synthesized and characterized. Its presence was due to a contamination of a sample of **2a** by **2b**.

Formation of a σ-Bonded Aryliron Complex in the Reaction of Arylhydrazines with Hemoglobin and Myoglobin[1]

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Phenylhydrazine inactivates hemoglobin in vivo and triggers its precipitation in the form of Heinz bodies.[2] Myoglobin is similarly disabled by phenylhydrazine even though it does not precipitate from solution.[3] Stoichiometric studies establish that six molecules of phenylhydrazine are consumed and five molecules of benzene are formed per heme in these reactions. The sixth phenyl residue is found incorporated into *N*-phenylprotoporphyrin IX when the hemoproteins are denatured aerobically in the presence of acid, but only heme is recovered if denaturation occurs in the absence of oxygen.[3] We have proposed that the phenyl group in the inactivated hemoprotein is σ-bonded to the heme iron but undergoes an oxidative shift to the heme nitrogen as the protein denatures. This proposal is supported by a model for the iron–nitrogen shift,[4] although the available data do not definitively rule out either a phenyldiazene–iron complex[5] or a reversible *N*-phenylheme complex.[4b] We unambiguously demonstrate here that

(10) Sheldrick, G. M., University of Cambridge, **1976.**

(11) Full data and other details will be published elsewhere (N.W.M. and A.J.W.).

(12) Defined by the atoms C1, N1, N2, and I2.

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(14) Stalik, J. K.; Ibers, J. A. *Inorg. Chem.* **1970,** *9,* 453–458.

(15) These conclusions are in line with those of other workers involved with Ni(III) complexes and in particular the published data for [NiBr(1,4,8,11-tetraazacyclotetradecane)]$^{2+}$ bear close comparison. Desideri, A.; Raynoor, J. B.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1977,** 2051–2054.

(16) The shortest mutual contact is H(93)···H(111) at 2.93 Å.

(17) Referenced to the standard H$_2$ electrode. The potential was measured at +0.24 V in acetone by using 0.1 M Bu$_4$NBr as base electrolyte with Pt electrodes referred to an Ag/AgCl (0.1 M LiCl in acetone) reference electrode. See: Bond, A. M.; Hendrickson, A. F.; Martin, R. L. *J. Am. Chem. Soc.* **1973,** *95,* 1449–1456.

(18) In this complex the heterobimetallic interaction is donative from Pt(II) to Hg(II) but nevertheless results in a similar terdentate ligand conformation and metal coordination geometry as that found in **1c**: van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1982,** *1,* 1366.

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(4) (a) Ortiz de Montellano, P. R.; Kunze, K. L.; Augusto, O. *J. Am. Chem. Soc.* **1982,** *104,* 3545–3546. (b) Mansuy, D.; Battioni, J.-P.; Dupre, D.; Sartori, E.; Chottard, G. *J. Am. Chem. Soc.* **1982,** *104,* 6159–6161.

(5) (a) Itano, H. A. *Proc. Natl. Acad. Sci. U.S.A.* **1970,** *67,* 485–492. (b) Itano, H. A.; Hirota, K.; Vedvick, T. S. *Ibid.* **1977,** *74,* 2556–2560. (c) Mansuy, D.; Battioni, P.; Mahy, J. P.; Gillet, G. *Biochem. Biophys. Res. Commun.* **1982,** *106,* 30–36.