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# SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $[Li(C_4H_8O)_4][Ni(2,4,6-Me_3C_6H_2)_3]$

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Abstract—The tetrahydrofuran-solvated lithium salt of the ato anion  $[Ni(mes)_3]^-$  (mes = mesityl, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) was obtained as a crystalline solid from the interaction of NiCl<sub>2</sub>(dme), (dme = 2,2'-dimethoxyethane) and mesityl lithium in Et<sub>2</sub>O–C<sub>4</sub>H<sub>8</sub>O. The blue compound 1 is unstable above  $ca - 10^{\circ}$ C and the X-ray crystal structure was determined at low temperature. The metal centre was found to exhibit an unusual T-shaped coordination geometry, which can be explained in terms of CH<sub>3</sub>… Ni agostic interactions at the fourth site of a formally square-planar Ni<sup>II</sup> centre. Reactions of 1 with donor ligands produced Ni(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)<sub>4</sub>, Ni(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> and Ni(mes)<sub>2</sub>(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>). Crown copyright © 1996 Published by Elsevier Science Ltd

Homoleptic nickel aryls or arylate anions excepting fluoro or chloro arenes are rather poorly characterized.<sup>1</sup> The interaction of NiBr, and mesMgBr in THF gave a red-brown unstable solution said to contain Ni(mes), on the basis of some reactions;<sup>2</sup> other preparations have been reported and  $Ni(mes)_2$  was said to be green (ref. 1b, Table IV). Some lithium ato complexes are said to be fairly stable:  $Li_2[NiR_4](THF)_4$ , <sup>3a</sup> R = Ph, Me, C = CPh;  $Li_{2}[Ni\{2,6-(MeO)_{2}C_{6}H_{4}\}_{4}] \cdot (THF)_{3};^{3b} Li_{2}[Ni\{2,2' C_6H_4OC_6H_2$  (THF)<sub>4</sub>;<sup>3c</sup> Li<sub>2</sub>[NiPh<sub>2</sub>(phenanthrene)]  $(THF)_4$ .<sup>3d</sup> Li<sub>2</sub>[Ni(C<sub>4</sub>H<sub>8</sub>)<sub>2</sub>]Et<sub>2</sub>O,<sup>3e</sup> while a partial structure of  $[{Ni_2Ph_4(N_2)}Li_4(Et_2O)_2(LiPh)]_2$  was reported.<sup>3e</sup> The only well-defined structure is that recently determined for the thermally stable but airsensitive aminomethyl compound [Li(OEt<sub>2</sub>)<sub>2</sub>][Ni  $(H_2CNC_5H_{10})_4$ ], which was found to have a planar NiC<sub>4</sub> unit.<sup>4</sup>

## **RESULTS AND DISCUSSION**

The complex  $[\text{Li}(\text{THF})_4][\text{Ni}(\text{mes})_3]$  has now been obtained as deep blue-purple crystals from the interaction of NiCl<sub>2</sub>(dme) and Li(mes) in THF-Et<sub>2</sub>O. The compound is very air-sensitive and is stable only below  $ca - 10^{\circ}$ C; decomposition gives unreactive insoluble material. The crystals can be kept at  $-78^{\circ}$ C under argon for several weeks. In THF the X-band EPR spectrum shows a broad signal at g = 1.999.

Blue crystals of a dme adduct can also be obtained when the synthesis is carried out in dme. The structure of 1 is shown in Fig. 1 while bond lengths and angles are given in Table 1.

The Ni<sup>II</sup> centre exhibits an unusual T-shaped planar geometry, with the three mesityl rings twisted out of the plane. Two C—Ni—C angles are close to 100°, C(10)—Ni—C(20) 101.9(2) and C(20)—Ni—C(30) 99.0(2)°, whilst C(10)—Ni— C(30) has a value of 159.2(2)°. The Ni—C distances are slightly different; with that to the unique

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Fig. 1. The structure of the anion  $[Ni(mes)_3]^-$ .

Table 1. Selected bond lengths (Å) and angles (°) for [Ni(mes)<sub>3</sub>]<sup>-</sup>[Li(thf)<sub>4</sub>]<sup>+</sup> (1) with estimated standard deviations in parentheses

Ni - C(10)	1.932(6)	C(10) - Ni - C(20)	101 9(2)
Ni-C(20)	1.838(5)	C(10) $-Ni$ $-C(30)$	159.2(2)
NiC(30)	1.903(6)	C(20) - Ni - C(30)	99.0(2)
$Ni \cdots H(18A)$	2.17(1)	O(1)-Li-O(2)	107.1(6)
$Ni \cdots H(32A)$	2.13(1)	O(1)-Li-O(3)	112.9(6)
LiO(1)	1.921(10)	O(1)LiO(4)	108.4(6)
LiO(2)	1.916(13)	O(2)—-Li— $O(3)$	111.4(6)
LiO(3)	1.885(12)	O(2)—Li— $O(4)$	106.3(6)
LiO(4)	1.915(12)	O(3)Li-O(4)	110.4(6)

aryl carbon at 1.838(5) and the others at 1.903(6) and 1.932(6) Å. These distances are all less than those in the anion  $[Ni(CH_2NC_5H_{10})_4]^{2-4}$  which are 2.023(4) and 2.032(4) Å. The plane of the mesityl ring [C(20)-C(28)] is at an angle of 70.8° to the coordination plane defined by Ni, C(10), C(20) and C(30), whilst the other two make angles of 30.5°, C(10)-C(18), and 38.4°, C(30)-C(38). These smaller values relate to the fact that the Ni centre has two short contacts to C(18) [2.88 Å] and C(32) [2.89 Å], which we consider to be attractive, arising from interactions between the Ni atom and the close methyls. Two short contacts are identified between the Ni and the two experimentally located hydrogen atoms, H(18A) (2.17 Å) and H(32A) (2.13 Å). This structure is simply interpreted in terms of agostic hydrogen interactions with an empty orbital of the Ni<sup>II</sup> square-planar sigma set, consistent with the 14e count at the metal. The Li<sup>+</sup> cation exhibits distorted tetrahedral geometry with the O—Li<sup>+</sup>—O angles ranging from 106.3(6) to 112.9(6)°. The Li<sup>+</sup>—O distances lie in the range 1.885(12)–1.921(10) Å, the variation presumably reflecting the severe disorder exhibited by the four THF molecules.

The interaction of 1 in the minimum amount of THF at  $-78^{\circ}$ C with excess 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC followed by warming to  $-10^{\circ}$ C and re-cooling gave

orange crystals of Ni[CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>]<sub>4</sub> as the only isolable nickel species; it was characterized by <sup>1</sup>H NMR spectra (C<sub>6</sub>D<sub>6</sub>,  $\delta$ 2.36s, 6H, *o*-MeAr;  $\delta$ 6.74m, 3H, Ar) and analysis. Although tetraisocyanides are well established <sup>5</sup> this compound appears to be new.

A similar reaction with the chelate phosphine  $Ph_2PCH_2CH_2PPh_2$  (dppe) gave only Ni(dppe)<sub>2</sub><sup>6</sup> [<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) :  $\delta$ 2.09s, br, 4H *CH*<sub>2</sub>-P, 7.47–6.94m, br, 20H, Ar. <sup>31</sup>P  $\delta$ 44.8 versus H<sub>3</sub>PO<sub>4</sub>].

Using  $Me_2NCH_2CH_2NMe_2$  (tmeda) at  $-60^{\circ}C$ blue crystals were obtained, but on work-up at room temperature Ni(mes)<sub>2</sub>(tmeda) was isolated : this compound also appears to be new. Phosphine complexes such as Ni(mes)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> which is unstable in solution at  $-30^{\circ}C$ , are known.<sup>7</sup>

The attempted protonation of **1** with HBF<sub>4</sub> · Et<sub>2</sub>O at  $-78^{\circ}$ C gave only a black decomposition product, in contrast to the reaction of [Li(THF)<sub>4</sub>][Co (mes)<sub>3</sub>] at  $-30^{\circ}$ C which gave [Co(mes)( $\mu$ -mes)<sub>2</sub>]<sub>2</sub>.<sup>8</sup>

## **EXPERIMENTAL**

The general techniques and instrumentation are as described previously.<sup>9</sup> All reactions were carried out under purified argon. Chemicals were from Aldrich and Avocado. NiCl<sub>2</sub>(dme)<sup>10a</sup> and Li(mes)  $Et_2O^{10b}$  were made as referenced.

#### Synthesis of 1

To a suspension of NiCl<sub>2</sub>(dme) (0.2 g, 0.91 mmol) in THF (5 cm<sup>3</sup>) and Et<sub>2</sub>O (15 cm<sup>3</sup>) at  $-78^{\circ}$ C was added a suspension of Li(mes)  $\cdot$  Et<sub>2</sub>O (0.73 g, 3.65 mmol) in Et<sub>2</sub>O (20 cm<sup>3</sup>). On warming slowly to  $-10^{\circ}$ C the reaction mixture became dark blue; after stirring for 1 h at  $-10^{\circ}$ C the mixture was cooled to  $-78^{\circ}$ C and stored for *ca* 12 h to give deep blue–purple crystals, some of X-ray quality in *ca* 80–85% yield.

Attempts to get reliable microanalyses were unsuccessful.

### X-ray crystallography

The X-ray data for compound 1 were collected at 120 K on a crystal of dimensions  $0.36 \times 0.15 \times 0.12$ mm, rapidly selected from a cold sample and mounted on the diffractometer using the oil-drop method. A FAST-TV area detector diffractometer with Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å) was employed, as previously described.<sup>11</sup> The structure was solved via the direct method procedures of SHELXS-86<sup>12</sup> and refined by full-matrix least-squares on  $F_{o}^2$ , using the program SHELXL-93.<sup>13</sup> All unique data used were corrected for Lorentz and polarization factors. The

data set was corrected for absorption using the program DIFABS,<sup>14</sup> with maximum and minimum correction factors of 0.785 and 1.190, respectively. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the anion were included in idealized positions, with those on the methyl groups containing H(18A) and H(32A), which form close interactions with the Ni<sup>II</sup> centre, oriented according to electron-density map indications. The solvate molecules within the lattice exhibit severe positional disorder and we presume that this contributes to the poor quality of the crystal and the resulting data. Accordingly the THF hydrogen atoms were ignored in the refinement. The crystal data and refinement details are summarized below :  $[Ni(C_{27}H_{33})]^{-}[Li(O_4C_{16}H_{32})]^+,$  $M_r = 711.6$ , monoclinic, cell dimensions a = 35.030(8), b = 15.727(9) and c = 17.031(6) Å,  $\beta = 117.22(4)^{\circ}$ , V = 8344(6) Å<sup>3</sup>, space group C2/c,  $\mu_{\text{Mo-}K_{\alpha}} = 0.502 \text{ mm}^{-1}, Z = 8, D_c = 1.133 \text{ Mg m}^{-3},$ F(000) 3088. 16,486 reflections were measured producing 6312 unique data ( $R_{int} = 0.0912$ ); 440 parameters were refined; goodness-of-fit (S) on  $F^2 = 0.908$ . The final R indices for  $[I > 2\sigma(I)]$  are  $R_1 = 0.0741$  and  $wR_2 = 0.1769$ , and for all data,  $R_1 = 0.1323$  and w $R_2 = 0.2014$ . The largest residual peak and hole in the difference map were 1.023 and -0.409 e Å<sup>-3</sup>, respectively.

Definition of terms used are:

$$S = [\Sigma(w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2},$$
  

$$R_1 = \Sigma[(F_o - F_c)] / \Sigma F_o,$$
  

$$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2},$$
  

$$w = 1 / [\sigma^2 (F_o^2) - (xP)^2 + gP],$$
  

$$P = [\max(F_o^2) + 2(F_c^2)] / 3,$$

where n = number of reflections and p = total number of parameters, x = 0.0969 and q = 0.

Additional material available from the Cambridge Crystallographic Data Centre comprises fractional atomic coordinates, thermal parameters and remaining bond lengths and angles.

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