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Lithiation of the diaminopyridine protio-ligand $MeC(2\text{-}C_5H_4N)\{CH_2N(H)Mes\}_2$ (Mes = $2,4,6\text{-}C_6H_2Me_3$)

Benjamin D. Ward,[a] Lutz H. Gade[b] and Philip Mountford[a]*

[a]Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, England, and [b]Institut für Anorganische Chemie, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Correspondence e-mail:
philip.mountford@chem.ox.ac.uk

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Key indicators

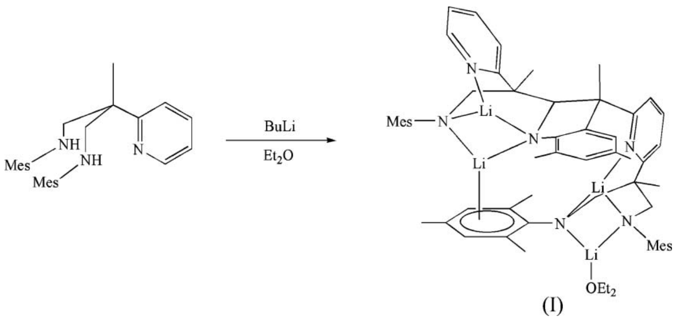
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.051
wR factor = 0.054
Data-to-parameter ratio = 7.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Reaction of the diamidopyridine protio-ligand $MeC(2\text{-}C_5H_4N)\{CH_2N(H)Mes\}_2$ (Mes = $2,4,6\text{-}C_6H_2Me_3$) with butyllithium in diethyl ether affords the compound (diethyl ether)(μ_4-2-{6-[1,3-dimethyl-3-(2-pyridyl)-1,4-bis(2,4,6-trimethylanilinio)butyl]-2-pyridyl}-2-methyl-1,3-bis(2,4,6-trimethylanilinio)propane)tetralithium(I), $[Li_4(C_{55}H_{64}N_6)(C_4H_{10}O)]$ or $Li_4[MeC(2\text{-}C_5H_4N)\{CH_2N(Mes)\}CHN(2,4,6\text{-}C_6H_2\text{-}Me_2C(Me)(2,2'\text{-}C_5H_3N)\{C(Me)\}(CH_2NMes)_2](OEt_2)$, which shows the methylation of the pyridyl *ortho*-position with a methyl group of one of the mesityl groups. The complex contains four Li atoms, each of which is chemically distinct. The tetraanionic ligand contains two protio-ligand units which are fused together into a single entity. The structure contains two disordered molecules of diethyl ether, one of which is coordinated to one of the Li atoms.

Comment

Diamidopyridine ligands of the general formula $[MeC(C_5H_4N)(CH_2NR)_2]^{2-}$ (R = silyl or aryl) have found a variety of uses in early transition metal chemistry and catalysis over the last decade (Gade & Mountford, 2001; Mehrkhodavandi *et al.*, 2000). Whereas the silylated derivatives (R = $SiMe_3$ or $SiMe_2{}^tBu$) are known as their dilithium salts (Friedrich *et al.*, 1997), the corresponding N-arylated derivatives (R = $3,5\text{-}C_6H_3Cl_2$, $4\text{-}C_6H_4Me$ or $2,4,6\text{-}C_6H_2Me_3$) have remained elusive. In attempting to prepare such complexes in our laboratories, we have consistently observed degradation products, and we report here the structural characterization of a product, (I), arising from the reaction of the mesityl protio-ligand (Mehrkhodavandi *et al.*, 2000) with butyllithium in diethyl ether.



(I)

The tetralithium complex, (I), crystallizes in space group $P\overline{1}$, and contains four Li environments which each occupy chemically different sites within the molecule. The Li atoms are arranged in two pairs, each occupying a bridging position between two amide N atoms. Each pair of Li atoms is capped at one end by a pyridyl group. At the other end, one pair of Li atoms is capped by one of the mesityl groups bonding in an η^3 mode. The second pair is capped by a molecule of diethyl ether coordinated to one of the Li centres; one of the ethyl groups of this ligand was found to be disordered over two sites. The disorder was modelled by using an occupancy of 0.5 for each atom within the ethyl group for each of the two sites.

The structure clearly does not represent a stoichiometric dimerization of the dilithium compound, since it contains an 'extra' methyl group (C29). The presence of this methyl group suggests that the structure arises from the rearrangement of three diamidopyridine units. The mechanistic details behind this rearrangement are not clear, and no other well defined product could be obtained from the reaction mixture. The structure also contains a disordered non-coordinated molecule of diethyl ether.

Experimental

The diaminopyridine protio-ligand $MeC(2\text{-}C_5H_4N)\{CH_2N(H)Mes\}_2$ (0.50 g, 1.25 mmol) was dissolved in diethyl ether (20 ml) and cooled to 195 K, followed by the dropwise addition of butyllithium (1.56 ml of a 1.6 *M* solution in hexanes, 2.50 mmol, 2 equivalents). The colourless solution immediately turned bright yellow, and the reaction was allowed to warm slowly to ambient temperature and stirred for 1 h. The reaction mixture was concentrated to 5 ml, and crystals of (I) suitable for X-ray diffraction were formed on allowing the mixture to stand overnight.

Crystal data

$[Li_4(C_{55}H_{64}N_6)(C_4H_{10}O)]$
$M_r = 911.04$
Triclinic, $P\bar{1}$
$a = 11.607$ (2) Å
$b = 14.302$ (3) Å
$c = 17.477$ (4) Å
$\alpha = 78.18$ (3)°
$\beta = 72.68$ (3)°
$\gamma = 80.31$ (3)°
$V = 2693.0$ (11) Å^3
$Z = 2$
$D_x = 1.123$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22654 reflections
$\theta = 5\text{–}28°$
$\mu = 0.07$ mm^{-1}
$T = 173$ K
Block, yellow
0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)
$T_{min} = 0.99$, $T_{max} = 0.99$
22654 measured reflections
12141 independent reflections
4760 reflections with $I > 3\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 15$
$k = -17 \rightarrow 18$
$l = 0 \rightarrow 22$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.054$
$S = 1.09$
4760 reflections
649 parameters
H-atom parameters constrained
$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/[0.516T_o(x) + 0.342T_1(x) + 0.252T_2(x)]$, where T_i are the Chebychev polynomials and $x = F_c/F_{max}$ (Prince, 1982; Watkin, 1994)
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

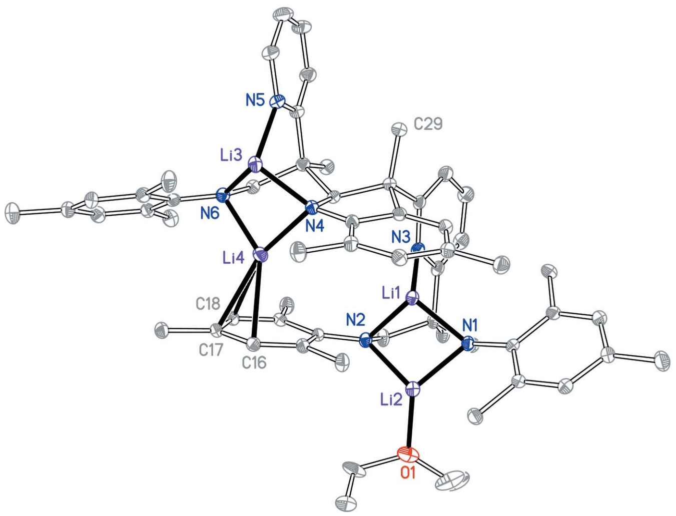


Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 25% probability level and H atoms have been omitted for clarity. The solvent of crystallization has also been omitted for clarity and only a single orientation of the disordered coordinated diethyl ether molecule is shown.

The crystal was a weak diffractor. Although sufficient data were collected, the number of data with $I > 3\sigma(I)$ was low. It is therefore inappropriate to compare bond lengths and angles with structures of higher precision, although the connectivity is thought to be reliable. The *Comment* has been written to take this into account.

The structure contains a coordinated molecule of diethyl ether, of which one ethyl group was disordered over two sites. The disorder was modelled with each C atom given 0.5 occupancy.

The asymmetric unit also contains a non-coordinated molecule of diethyl ether lying close to a centre of symmetry. Attempts were made to model this using disordered ether molecules. One model consisted of a molecule of ether interpenetrating its image in a mirror plane perpendicular to the medial axis of the molecule, *i.e.* the central region of the difference electron density phased on all the non-ether atoms was occupied by a 'split' O atom. This model needed geometric restraints and led to atoms falling on regions of relatively low electron density. Refinement of the unrestrained isotropic displacement parameters led to unacceptable values. A second model displaced the ether molecule sideways along its longest axis, so that the central region of the difference-density map now contained a disordered O and C atom. This model also needed restraints, gave a similar *R* factor to the previous model, and also gave a poor (but different) fit to the difference density. An unrestrained model gave a good fit to the density, but unacceptable distances and angles. Based on this evidence, it was felt that an atomic model was unsuitable. The disordered region was modelled using *SQUEEZE* (van der Sluis & Spek, 1990) in its advanced mode, in which the *A* and *B* parts of the structure factor are passed back to *CRYSTALS* (Betteridge *et al.*, 2003) for inclusion in F_c (rather than the term being subtracted from F_o).

H atoms associated with the aryl-methyl groups were found in a difference Fourier map. All other H atoms were placed geometrically after each cycle of refinement, with C—H distances in the range 0.96–1.1 Å. All H atoms were treated with the riding model during the refinement, with $U_{iso}(H) = 1.3U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduc-

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tion: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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