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Note

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Note

SYNTHESIS AND MOLECULAR STRUCTURE OF A NOVEL ION PAIR LITHIUM COMPLEX OF A DIAZABUTADIENE

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A new lithium complex with $({}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{-dad}$ (N, N' -bis(${}^i\text{Pr}_2\text{C}_6\text{H}_3$)-1,4-diaza-1,3-butadiene) has been synthesized. The crystal structure of $\{\text{Li}_3[({}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{-dad}]_2\}\{\text{Li}(\text{THF})_4\} \cdot 0.5 \text{ Hexane}$ [triclinic, $P\bar{1}$, $a = 1.3154(2)$, $b = 1.6720(2)$ nm, $c = 1.8283(3)$ nm, $\alpha = 83.762(4)$, $\beta = 70.152(2)$, $\gamma = 68.267(2)^\circ$, $V = 3.5127(8)$ nm³, $D_c = 1.05$ g cm⁻³, $Z = 2$] is described.

Keywords: $({}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{-dad}$; Li complex; Molecular structure

INTRODUCTION

Diazabutadienes (dad) are extensively employed as coordinating ligands for the late transition metals [1], lanthanoids [2], group 4 and 5 metals [3,4]. Dad can act as either neutral or dianionic ligands in various coordination modes (from $\eta^1\text{-}N$ to $\eta^4\text{-}N_2C_2$ ($\sigma^2 \cdot \pi$)). Moreover, its N -substituents can be modified to regulate steric and electronic effects around the center metals. Usually, lithium complexes are the intermediates for synthesis of other metal complexes. Therefore, it would be useful to identify the exact structure of the lithium complexes with dad ligands. Some lithium complexes with N -alkyl-dad have been reported, such as N, N' -bis(tert-butyl)-1,4-diaza-1,3-butadiene (${}^t\text{Bu-dad}$) [2b,5] and N, N' -bis(isopropyl)-1,4-diaza-1,3-butadiene (${}^i\text{Pr-dad}$) [3a]. Herein, we report a new lithium complex coordinated

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by ($^i\text{Pr}_2\text{C}_6\text{H}_3$)₂-dad, which is different from other known dilithium complexes containing molecules of THF [2b] or Et₂O [5].

EXPERIMENTAL

Synthesis of ($^i\text{Pr}_2\text{C}_6\text{H}_3$)₂-dad

2,6-Diisopropylaniline (13.4 cm³, 71.0 mmol) was added dropwise to 40% aqueous glyoxal (5.15 g, 35.5 mmol) at room temperature with stirring. After 3 h, the resulting yellow solid was treated with 300 cm³ of Et₂O. The extract was dried over anhydrous Na₂SO₄ and concentrated to ca. 80 cm³. After filtration, 9.44 g of yellow microcrystals were obtained (yield 72.5%); m.p. 114°C; δ (C₆D₆): 8.18 (s, 2H, NCH), 7.18 (m, 6H, C₆H₃), 3.02 (sept, $J=6.5$ Hz, 4H, CHMe₂), 1.28 (d, $J=6.5$ Hz, 24H, CHMe₂); IR (KBr, cm⁻¹): 3060, 2958, 1614, 1105, 815. Calcd. for C₂₆H₂₆N₂(%): C, 82.98; H, 9.57; N, 7.45. Found: C, 82.83; H, 9.68; N, 7.34.

Synthesis of the Lithium Complex (1)

Some 200 mg of ($^i\text{Pr}_2\text{C}_6\text{H}_3$)₂-dad (0.53 mmol) in 20 cm³ of THF was treated with excess of lithium metal under argon. The solution was stirred at room temperature overnight, during which time the colour of the solution gradually changed from dark red to light red. The solvent was evaporated, and the red residue crystallized from hexane to afford 182 mg of product (62% yield), Colourless crystals suitable for X-ray diffraction were obtained from a hexane solution at -30°C. m.p. 175°C; δ (C₆D₆): 7.20 (m, 6H, C₆H₃), 5.20 (s, 2H, NCH); 3.23 (septet, $J=6.5$ Hz, CHMe₂), 1.20 (d, $J=6.5$ Hz, CHMe₂); IR (KBr, cm⁻¹): 3090, 2968, 1627, 1135, 845. Calcd. for C₇₁H₁₁₁O₄N₄Li₄(%): C, 76.59; H, 9.98; N, 5.03. Found: C, 76.31; H, 9.87; N, 5.14.

Crystallographic Study

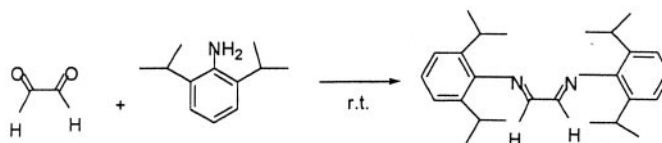
Single-crystal X-ray diffraction measurements were carried out with a Rigaku RASA-7 Quantum system equipped with an ADSC CCD detector (MoK α radiation, $\lambda=0.071067$ nm; graphite-monochromated). The structure was solved with the TEXSAN software package. Crystallographic data and experimental details for structural analyses are summarized in Table I.

TABLE I Crystallographic data and structure refinement summary

Formula	C ₇₁ H ₁₁₁ O ₄ N ₄ Li ₄	<i>V</i>	3.5127(8) nm ³
Mol wt (g/mol ⁻¹)	1112.45	<i>Z</i>	2
Crystal system	triclinic	<i>D</i> _c (g/cm)	1.05
Space group	<i>P</i> $\bar{1}$	μ (MoK α) (cm ⁻¹)	0.63
Colour of crystal	colourless	$2\theta_{\text{max}}$ (deg)	55.0
Crystal size (mm)	0.15 × 0.15 × 0.15	No. of unique rflns	15669
<i>a</i> (nm)	1.3154(2)	No. of obs. data	8568
<i>b</i> (nm)	1.6720(2)		
<i>c</i> (nm)	1.8283(3)	Residues (<i>R</i> / <i>R</i> _w)	0.083/0.088
α (deg)	83.762(4)	GOF	4.89
β (deg)	70.152(2)		
γ (deg)	68.267(2)		

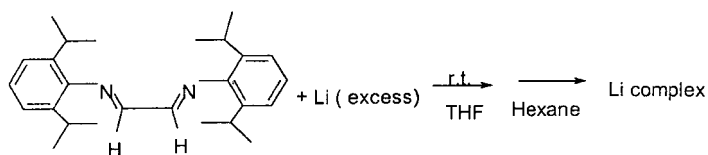
RESULTS AND DISCUSSION

The ligand was prepared by mixing of 1 equivalent of 40% glyoxal solution and 2 equivalents of 2, 6-diisopropylaniline (Scheme 1) according to the literature [6].



SCHEME 1

1 equiv. of ligand ($\text{Pr}_2\text{C}_6\text{H}_3$)₂-dad and 3 equiv. of lithium metal dissolved in THF was stirred overnight at room temperature under argon (Scheme 2). The product obtained at -30°C was an ion pair compound of composition $\{\text{Li}(\text{THF})_4\} \{\text{Li}_3[\text{Pr}_2\text{C}_6\text{H}_3\text{-NCH=CHN-Pr}_2\text{C}_6\text{H}_3]_2\} \cdot 0.5 \text{ Hexane}$. The structure was established by X-ray analysis; Fig. 1 shows the molecular structure and selected bonding parameters are listed in Table II.



SCHEME 2

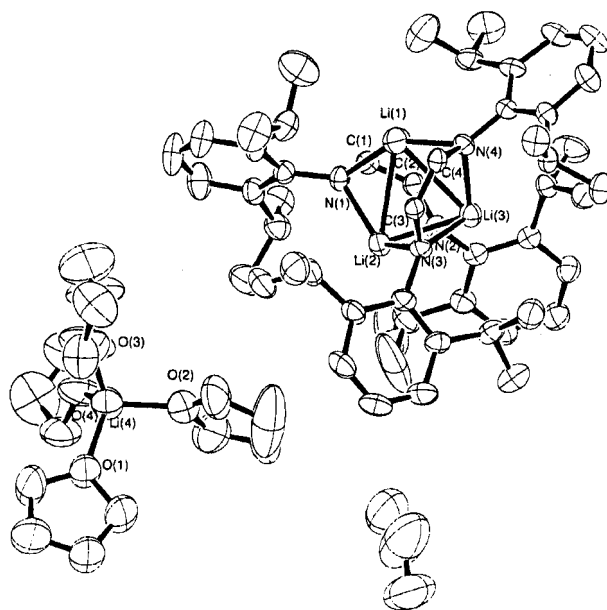


FIGURE 1 Molecular structure of the lithium complex.

TABLE II Selected bond distances (nm) and angles (deg)

Li(1)–N(1)	1.964(7)	N(1)–Li(1)–N(4)	147.7(3)
Li(1)–N(4)	1.952(7)	N(1)–Li(1)–C(1)	37.9(2)
Li(1)–C(1)	2.318(8)		
Li(2)–N(1)	2.013(6)	N(1)–Li(2)–N(3)	121.1(3)
Li(2)–N(2)	2.005(6)	N(1)–Li(2)–N(2)	91.4(2)
Li(2)–N(3)	2.065(6)	N(2)–Li(2)–N(3)	103.5(3)
Li(3)–N(2)	2.005(6)	N(2)–Li(3)–N(3)	104.2(3)
Li(3)–N(3)	2.044(6)	N(3)–Li(3)–N(4)	91.4(2)
Li(3)–N(4)	2.007(6)	Li(1)–N(1)–Li(2)	84.8(2)
Li(1)–Li(2)	2.682(8)	Li(1)–N(4)–Li(3)	84.6(3)
Li(1)–Li(3)	2.666(8)	Li(2)–N(3)–Li(3)	133.0(3)
Li(2)–Li(3)	2.459(7)	Li(2)–N(2)–Li(3)	74.8(2)
C(1)–C(2)	1.352(4)	N(2)–Li(3)–N(4)	120.3(3)
C(3)–C(4)	1.355(4)	N(3)–Li(3)–N(4)	104.2(3)
Li(4)–O(1)	1.891(9)	Li(3)–N(4)–Li(1)	84.6(3)
Li(4)–O(2)	1.915(8)	Li(1)–Li(2)–Li(3)	62.3(2)
Li(4)–O(3)	1.932(7)	Li(2)–Li(3)–Li(1)	63.0(2)
Li(4)–O(4)	1.897(8)	Li(3)–Li(1)–Li(2)	54.7(2)

Two molecules of (¹Pr₂C₆H₃)₂-dad coordinate to three lithium atoms through single Li–N bonds. In addition, a fourth lithium atom is coordinated by four oxygen atoms of THF. Two Li–N bond lengths are 0.1964(7) and 0.1952(7) nm; the other six Li–N bond lengths are slightly longer, about 0.2005(6) ~ 0.2013(6) nm. However, all Li–N bonds are shorter than those found in a related lithium complex {[Li(thf)₂]₂–[(¹Bu)NCH=CHN(¹Bu)]} (0.2176(10) and 0.2202(10) nm) [2b]. N–C bond lengths, 0.1431(4) nm for N(1)–C(1), 0.1409(4) nm for N(2)–C(2), 0.1403(4) nm for N(3)–C(3) and 0.1423(4) nm for C(4)–N(4), are larger than in the corresponding free ligand (¹Pr₂C₆H₃)₂-dad (0.1253(4) nm [7]), but are in agreement with those in enediamide ligands showing slight double-bond character [1]. C–C bond lengths of 0.1352(4) and 0.1355(4) nm are similar to those reported (0.1356(7) nm) for the lithium complex of the ¹Bu-dad ligand [2b].

Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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