

Tris{2-[(2,6-dimethylphenyl)amino]-ethyl}amine

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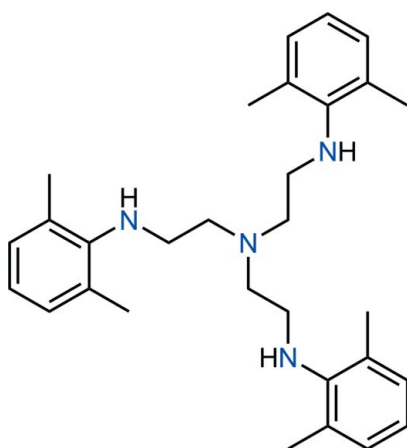
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.041; wR factor = 0.113; data-to-parameter ratio = 24.7.

The title compound, $\text{C}_{30}\text{H}_{42}\text{N}_4$, is an arylated tris(aminoethyl)-amine derivative which was obtained by reducing the corresponding tris-amide with AlH_3 . The asymmetric unit consists of one third of a C_{3v} -symmetric molecule with the tertiary N atom lying on a crystallographic threefold axis.

Related literature

For the structural parameters of arylated derivatives of tris-(aminoethyl)amine, see: Almesåker *et al.* (2009); Amoroso *et al.* (2009). For the synthesis and the structural parameters of metal complexes based on arylated derivatives of tris(aminoethyl)amine, see: Morton *et al.* (2000); Yandulov & Schrock (2005); Smythe *et al.* (2006); Reithofer *et al.* (2010); Almesåker *et al.* (2010).



Experimental

Crystal data

$\text{C}_{30}\text{H}_{42}\text{N}_4$
 $M_r = 458.68$
 Trigonal, $R\bar{3}$
 $a = 14.2880$ (7) Å
 $c = 22.3811$ (11) Å
 $V = 3956.9$ (5) Å³

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 100$ K
 $0.1 \times 0.1 \times 0.1$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2009)
 $T_{\min} = 0.680$, $T_{\max} = 0.746$

20390 measured reflections
 2695 independent reflections
 2330 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.113$
 $S = 1.06$
 2695 reflections
 109 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.42$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2430).

References

- Almesåker, A., Gamez, P., Scott, J. L., Teat, S. J., Reedijk, J. & Spiccia, L. (2010). *Eur. J. Inorg. Chem.* pp. 5394–5400.
- Almesåker, A., Scott, J. L., Spiccia, L. & Strauss, C. R. (2009). *Tetrahedron Lett.* **50**, 1847–1850.
- Amoroso, A. J., Edwards, P. G., Howard, S. T., Kariuki, B. M., Knight, J. C., Ooi, L., Malik, K. M. A., Stratford, L. & Al-Sudani, A.-R. H. (2009). *Dalton Trans.* **39**, 8356–8362.
- Bruker (2009). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Morton, C., Gillespie, K. M., Sanders, C. J. & Scott, P. (2000). *J. Organomet. Chem.* **606**, 141–146.
- Reithofer, M. R., Schrock, R. R. & Müller, P. (2010). *J. Am. Chem. Soc.* **132**, 8349–8358.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2009). SADABS. University of Göttingen, Germany.
- Smythe, N. C., Schrock, R. R., Müller, P. & Weare, W. W. (2006). *Inorg. Chem.* **45**, 9197–9205.
- Yandulov, D. V. & Schrock, R. R. (2005). *Inorg. Chem.* **44**, 1103–1117.

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Comment

Tris(aminoethyl)amine derivatives have attracted attention of chemists due to their ability to adopt a trigonal pyramidal geometry which is favourable for coordination of different metal ions in a trigonal bipyramidal environment, with one open coordination site for a small exchangeable ligand (Morton *et al.*, 2000; Yandulov *et al.*, 2005; Smythe *et al.*, 2006; Reithofer *et al.*, 2010; Almesåker *et al.*, 2010). In this report, we discuss the molecular structure of an arylated tris(aminoethyl)amine derivative which appears to be a promising ligand for obtaining high valent iron compounds.

The title compound (**1**) crystallizes in the trigonal space group $R\bar{3}$ and consists of neutral molecules (Figure 1); inter-molecular interactions include a number of van der Waals and C—H $\cdots\pi$ contacts. There are two types of the C—H $\cdots\pi$ contacts that originate from hydrogen atoms of the methyl groups pointing towards the opposite sides of the same aromatic ring; no aryl H atoms are involved. The first type of non-covalent interactions has a C10 atom acting as a donor (the C—H $\cdots\pi$ separation is 3.530 (1) Å) and results in the formation of pseudo-dimer aggregates (Figure 2) which form a three-dimensional, well defined symmetric cavity *via* the second type of C—H $\cdots\pi$ contacts and van der Waals contacts. The second type of C—H $\cdots\pi$ contacts includes C9 as a donor (the C—H $\cdots\pi$ separation is 3.641 (1) Å).

The secondary amino group is located in a *cis*-position to the tertiary N atom (N1—C1—C2—N2 torsion angle is 54.0 (1)°). The C—C, C—N bond lengths are comparable to the previously reported structures of arylated derivatives of tris(aminoethyl)amine (Almesåker *et al.*, 2009; Amoroso *et al.*, 2009).

Experimental

The title compound, (**1**), was obtained in three steps. Nitrilotriacetoanilide, (ArNC(O)CH₂)₃N, where Ar = Me₂C₆H₃, was synthesized *via* the reaction of nitrilotriacetic acid chloride and 2,6-dimethylaniline. The acid chloride was prepared *in situ*: Oxalyl chloride (10.6 ml) was added dropwise to a cooled (278 K, 5 °C) mixture of nitrilotriacetic acid (5 g, 0.03 mol, in 100 ml of DCM) with one drop of DMF as a catalyst. The mixture was stirred for 48 h at room temperature, and then the DCM and extra oxalyl chloride were removed by vacuum distillation. The crude acid chloride was dissolved in 50 ml of DCM and added dropwise to a 100 ml of DCM solution of 2,6-dimethylaniline (9.8 ml, 0.08 mol) and *N*-ethyldiisopropylamine (18.5 ml, 0.11 mol) at 263 K (−10 °C). After the addition was complete, the reaction mixture was allowed to warm up and stirred for 24 h at ambient temperature. The reaction mixture was washed with 1 N HCl (25 ml), and then with saturated NaHCO₃ (25 ml). The organic layer was dried (Na₂SO₄) and concentrated under reduced pressure. The solid was washed with water/methanol, 1/1 (v/v), filtered, and dried in an oven at 373 K (100 °C) for 2 days. Yield: 3.07 g (23%). ¹H NMR (300 MHz, dms_o-*d*₆): δ 2.16 (s, 18, Me), 3.70 (s, 6, CH₂), 7.08 (m, 9, H_p, 2H_m), 9.63 (s, 3, NH). ¹³C NMR (75 MHz, dms_o-*d*₆): δ 18.21, 57.99, 126.6, 127.74, 134.86, 135.21, 168.82.

*N*¹,*N*²,*N*³-Tris((2,6-dimethylphenyl)amino)ethyl)amine: To 200 ml of dry THF, 7.20 g (0.2 mol) of LiAlH₄ was added slowly in portions. Then the reaction mixture was cooled in an ice bath and 26 ml (0.2 mol) of chlorotrimethylsilane was

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added dropwise, followed by an addition of 3.07 g (0.006 mol) of nitrilotriacetoanilide. The reaction mixture was refluxed for 14 h (the reaction was controlled by NMR) and then cooled down to room temperature. Then 21 ml of water in 40 ml of THF was carefully added to the reaction mixture, followed by the addition of NaOH (50%, 21 ml). The reaction mixture was filtered, the precipitate was washed with THF (100 ml) and the filtrate was evaporated under reduced pressure. The solid was extracted with DCM (100 ml); the DCM solution was dried (Na_2SO_4) and concentrated. The crude product was washed with cold diethyl ether (100 ml), filtered, and dried under reduced pressure. Yield: 1.5 g (54%). Colourless crystals, which were suitable for X-ray analysis, were grown in an NMR tube from the $\text{dms}\text{-}d_6$ solution. ^1H NMR (300 MHz, $\text{dms}\text{-}d_6$): δ 2.18 (s, 18, Me), 2.64 (t, $J = 6.3$ Hz, 6, CH_2), 2.99 (td, $J = 6.3, 6$ Hz, 6, CH_2), 3.83 (t, $J = 6$ Hz, 3, NH), 6.69 (t, $J = 7.2$ Hz, 3, H_p), 6.90 (d, $J = 7.2$ Hz, 6, H_m). ^{13}C NMR (75 MHz, $\text{dms}\text{-}d_6$): δ 18.47, 45.54, 54.51, 120.8, 128.51, 146.38.

Refinement

All methyl H atoms were placed in geometrically idealized positions, allowing the initial torsion angle to be determined by a difference Fourier analysis and subsequently refined [$\text{C}-\text{H} = 0.98$ Å and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$]. Other H atoms bonded to C atoms were placed in geometrically idealized positions and included as riding atoms [$\text{C}-\text{H} = 0.95\text{--}0.99$ Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]. The position and U_{iso} value of H atom bonded to N atom were fully refined. The highest peak is located 0.75 Å from atom C2 and the deepest hole is located 1.26 Å from atom C6.

Figures

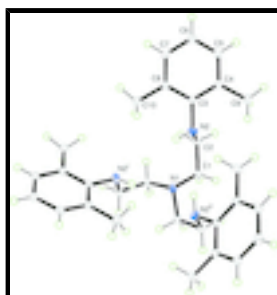


Fig. 1. A view of the title compound, with displacement ellipsoids shown at the 50% probability level. Symmetry transformations used to generate equivalent atoms: (i) $-y+1, x-y, z$; (ii) $-x+y+1, -x+1, z$.

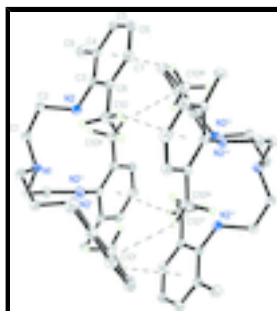


Fig. 2. A fragment of the packing diagram of the title compound, with displacement ellipsoids shown at the 50% probability level (H atoms, except H atoms attached to C10 atom, are omitted for clarity). Symmetry transformations used to generate equivalent atoms: (i) $-y+1, x-y, z$; (ii) $-x+y+1, -x+1, z$; (iii) $1/3+x-y, -1/3+x, 2/3-z$; (iv) $1/3+y, 2/3-x+y, 2/3-z$; (v) $1/3-x, 2/3-y, 2/3-z$.

Tris[2-[(2,6-dimethylphenyl)amino]ethyl]amine

Crystal data

$\text{C}_{30}\text{H}_{42}\text{N}_4$

$M_r = 458.68$

$D_x = 1.155 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Trigonal, $R\bar{3}$	Cell parameters from 9944 reflections
Hall symbol: -R 3	$\theta = 2.5\text{--}30.6^\circ$
$a = 14.2880$ (7) Å	$\mu = 0.07$ mm ⁻¹
$c = 22.3811$ (11) Å	$T = 100$ K
$V = 3956.9$ (5) Å ³	Block, colourless
$Z = 6$	$0.1 \times 0.1 \times 0.1$ mm
$F(000) = 1500$	

Data collection

Bruker Smart APEXII CCD diffractometer	2695 independent reflections
Radiation source: ImuS micro-focus sealed tube	2330 reflections with $I > 2\sigma(I)$
Icoatech ImuS multilayer optics	$R_{\text{int}} = 0.031$
Detector resolution: 8.3 pixels mm ⁻¹	$\theta_{\text{max}} = 30.6^\circ$, $\theta_{\text{min}} = 1.9^\circ$
φ and ω scans	$h = -20 \rightarrow 20$
Absorption correction: multi-scan (SADABS; ShelDRICK, 2009)	$k = -20 \rightarrow 20$
$T_{\text{min}} = 0.680$, $T_{\text{max}} = 0.746$	$l = -31 \rightarrow 31$
20390 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.113$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 4.1067P]$
2695 reflections	where $P = (F_o^2 + 2F_c^2)/3$
109 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.42$ e Å ⁻³
	$\Delta\rho_{\text{min}} = -0.18$ e Å ⁻³

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.58018 (7)	0.22760 (7)	0.11134 (4)	0.01668 (18)
H1A	0.5860	0.2233	0.0675	0.020*
H1B	0.5095	0.2218	0.1200	0.020*
C2	0.58289 (8)	0.13268 (7)	0.13995 (4)	0.01696 (18)
H2A	0.5189	0.0642	0.1271	0.020*
H2B	0.6485	0.1316	0.1268	0.020*
C3	0.58132 (7)	0.05566 (7)	0.23806 (4)	0.01446 (17)
C4	0.48468 (7)	-0.04409 (7)	0.24161 (4)	0.01604 (18)
C5	0.48377 (8)	-0.12750 (8)	0.27456 (4)	0.01872 (19)
H5	0.4192	-0.1956	0.2766	0.022*
C6	0.57519 (8)	-0.11311 (8)	0.30435 (4)	0.01925 (19)
H6	0.5732	-0.1708	0.3264	0.023*
C7	0.66954 (8)	-0.01359 (8)	0.30156 (4)	0.01794 (18)
H7	0.7318	-0.0032	0.3225	0.022*
C8	0.67430 (7)	0.07137 (7)	0.26845 (4)	0.01593 (18)
C9	0.38314 (8)	-0.06114 (8)	0.21179 (5)	0.0221 (2)
H9A	0.3838	-0.0794	0.1696	0.033*
H9B	0.3791	0.0052	0.2146	0.033*
H9C	0.3202	-0.1203	0.2316	0.033*
C10	0.77793 (8)	0.17807 (8)	0.26578 (5)	0.0238 (2)
H10A	0.8351	0.1721	0.2866	0.036*
H10B	0.7675	0.2338	0.2850	0.036*
H10C	0.7988	0.1979	0.2240	0.036*
N1	0.6667	0.3333	0.13202 (6)	0.0142 (2)
N2	0.58312 (7)	0.14184 (6)	0.20523 (4)	0.01647 (17)
H2N	0.6392 (12)	0.2043 (12)	0.2164 (6)	0.024 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0167 (4)	0.0151 (4)	0.0166 (4)	0.0067 (3)	-0.0036 (3)	-0.0003 (3)
C2	0.0202 (4)	0.0147 (4)	0.0158 (4)	0.0086 (3)	-0.0020 (3)	-0.0008 (3)
C3	0.0160 (4)	0.0149 (4)	0.0142 (4)	0.0090 (3)	-0.0006 (3)	-0.0009 (3)
C4	0.0154 (4)	0.0168 (4)	0.0159 (4)	0.0081 (3)	-0.0001 (3)	-0.0016 (3)
C5	0.0195 (4)	0.0153 (4)	0.0201 (4)	0.0077 (3)	0.0034 (3)	0.0007 (3)
C6	0.0240 (4)	0.0184 (4)	0.0196 (4)	0.0137 (4)	0.0037 (3)	0.0036 (3)
C7	0.0191 (4)	0.0216 (4)	0.0173 (4)	0.0133 (4)	-0.0003 (3)	0.0011 (3)
C8	0.0155 (4)	0.0164 (4)	0.0160 (4)	0.0081 (3)	-0.0008 (3)	-0.0007 (3)
C9	0.0149 (4)	0.0237 (5)	0.0238 (5)	0.0068 (4)	-0.0031 (3)	-0.0002 (4)
C10	0.0176 (4)	0.0201 (4)	0.0286 (5)	0.0055 (4)	-0.0063 (4)	0.0024 (4)
N1	0.0130 (3)	0.0130 (3)	0.0167 (6)	0.00651 (17)	0.000	0.000
N2	0.0204 (4)	0.0139 (3)	0.0158 (4)	0.0091 (3)	-0.0030 (3)	-0.0011 (3)

Geometric parameters (Å, °)

C1—N1	1.4686 (10)	C6—C7	1.3879 (14)
C1—C2	1.5178 (12)	C6—H6	0.9500
C1—H1A	0.9900	C7—C8	1.3946 (12)
C1—H1B	0.9900	C7—H7	0.9500
C2—N2	1.4667 (12)	C8—C10	1.5043 (13)
C2—H2A	0.9900	C9—H9A	0.9800
C2—H2B	0.9900	C9—H9B	0.9800
C3—C4	1.4059 (12)	C9—H9C	0.9800
C3—C8	1.4069 (12)	C10—H10A	0.9800
C3—N2	1.4231 (11)	C10—H10B	0.9800
C4—C5	1.3961 (13)	C10—H10C	0.9800
C4—C9	1.5020 (13)	N1—C1 ⁱ	1.4686 (10)
C5—C6	1.3872 (14)	N1—C1 ⁱⁱ	1.4686 (10)
C5—H5	0.9500	N2—H2N	0.886 (15)
N1—C1—C2	113.69 (7)	C6—C7—C8	121.01 (9)
N1—C1—H1A	108.8	C6—C7—H7	119.5
C2—C1—H1A	108.8	C8—C7—H7	119.5
N1—C1—H1B	108.8	C7—C8—C3	119.13 (8)
C2—C1—H1B	108.8	C7—C8—C10	119.87 (8)
H1A—C1—H1B	107.7	C3—C8—C10	120.99 (8)
N2—C2—C1	109.91 (7)	C4—C9—H9A	109.5
N2—C2—H2A	109.7	C4—C9—H9B	109.5
C1—C2—H2A	109.7	H9A—C9—H9B	109.5
N2—C2—H2B	109.7	C4—C9—H9C	109.5
C1—C2—H2B	109.7	H9A—C9—H9C	109.5
H2A—C2—H2B	108.2	H9B—C9—H9C	109.5
C4—C3—C8	120.33 (8)	C8—C10—H10A	109.5
C4—C3—N2	119.34 (8)	C8—C10—H10B	109.5
C8—C3—N2	120.30 (8)	H10A—C10—H10B	109.5
C5—C4—C3	118.71 (8)	C8—C10—H10C	109.5
C5—C4—C9	120.02 (8)	H10A—C10—H10C	109.5
C3—C4—C9	121.26 (8)	H10B—C10—H10C	109.5
C6—C5—C4	121.41 (9)	C1 ⁱ —N1—C1	110.54 (6)
C6—C5—H5	119.3	C1 ⁱ —N1—C1 ⁱⁱ	110.54 (6)
C4—C5—H5	119.3	C1—N1—C1 ⁱⁱ	110.54 (6)
C5—C6—C7	119.38 (9)	C3—N2—C2	116.04 (7)
C5—C6—H6	120.3	C3—N2—H2N	110.0 (9)
C7—C6—H6	120.3	C2—N2—H2N	109.3 (9)
N1—C1—C2—N2	54.02 (10)	C6—C7—C8—C10	-179.46 (9)
C8—C3—C4—C5	-1.51 (13)	C4—C3—C8—C7	0.65 (13)
N2—C3—C4—C5	-179.24 (8)	N2—C3—C8—C7	178.35 (8)
C8—C3—C4—C9	177.26 (8)	C4—C3—C8—C10	-179.19 (9)
N2—C3—C4—C9	-0.47 (13)	N2—C3—C8—C10	-1.48 (14)
C3—C4—C5—C6	1.07 (14)	C2—C1—N1—C1 ⁱ	67.79 (13)

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C9—C4—C5—C6	-177.72 (9)	C2—C1—N1—C1 ⁱⁱ	-169.49 (8)
C4—C5—C6—C7	0.25 (14)	C4—C3—N2—C2	-74.71 (11)
C5—C6—C7—C8	-1.16 (14)	C8—C3—N2—C2	107.56 (10)
C6—C7—C8—C3	0.70 (14)	C1—C2—N2—C3	177.64 (7)

Symmetry codes: (i) $-y+1, x-y, z$; (ii) $-x+y+1, -x+1, z$.

Fig. 1

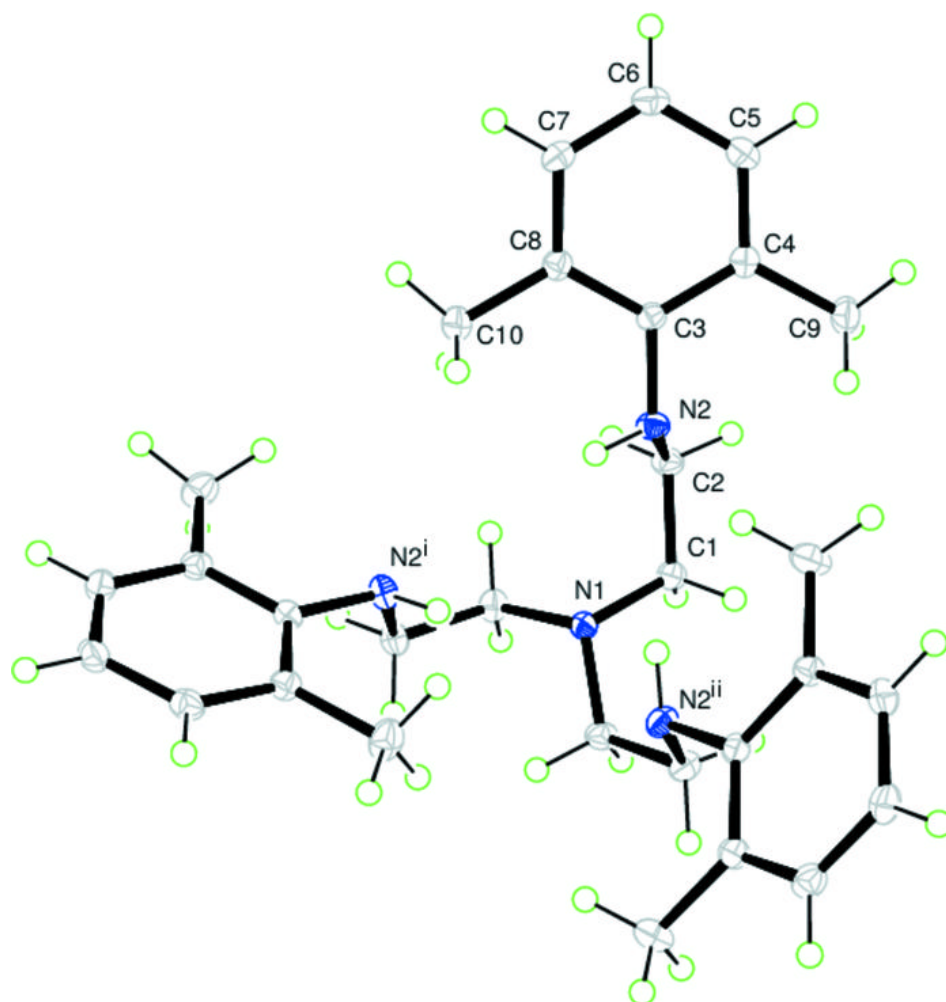


Fig. 2

