

Carbene complexes

XXIV *. Preparation and characterization of two enetetramine-derived carbenerhodium(I) chloride complexes $\text{RhCl}(\text{L}^{\text{R}})_3$ and $[\text{RhCl}(\text{COD})\text{L}^{\text{R}}]$ ($\text{L}^{\text{R}} = \text{dCN}(\text{Me})\text{Cu}(\text{CH})_4\text{CNMe-}o$) and the preparation and X-ray structures of the enetetramine L_2^{R} and its salt $[\text{L}_2^{\text{R}}][\text{BF}_4]_2$ **

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(Received January 4, 1994)

Abstract

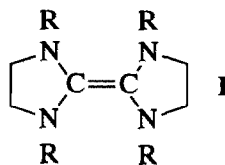
The enetetramine [$o\text{-C}_6\text{H}_4(\text{N}(\text{Me})_2\text{C})_2$] (abbreviated as L_2^{B}) (**1**) has been obtained either from *N,N'*-dimethyl-*o*-phenylenediamine and $\text{CH}(\text{OMe})_2\text{NMe}_2$ or from [$o\text{-C}_6\text{H}_4(\text{N}(\text{Me})_2\text{C})\text{I}$] and NaH. Treatment of **1** with $\text{Ag}[\text{BF}_4]$ yielded the salt $[\text{L}_2^{\text{R}}][\text{BF}_4]_2$ (**2**). Use of L_2^{B} and $[\text{Rh}(\mu\text{-Cl})(\text{COD})_2]$ in appropriate stoichiometry gave the carbenerhodium(I) chlorides $[\text{RhCl}(\text{COD})\text{L}^{\text{R}}]$ and $\text{RhCl}(\text{L}^{\text{R}})_3$; ^{103}Rh NMR chemical shifts for **3** and **4** have been recorded. Crystal structure determinations were carried out on compounds **1** and **2**. The most notable features are the differences between **1** and **2** with respect to (i) the C–C bond length [1.344(4) Å (**1**) and 1.462(13) Å (**2**)], (ii) the adjacent endocyclic N–C bond length [1.428(8) Å (**1**) and 1.331(4) Å (**2**)], (iii) the torsion angle about the central C–C bond [21° (**1**) and 72° (**2**)] and (iv) the closer approach of the nitrogen environment to trigonal planar in **2** than in **1**.

Key words: Rhodium; Carbene; Crystal structure; Enetetramine

1. Introduction

In the preceding paper in this series [1], the preparation, characterization and structures of some enetetramine-derived carbenemetal(I) chloride complexes were described. The parent enetetramine was **I** or **II**.

We now describe additional chemistry based on the use of a new enetetramine of formula **1**.



$\text{R} = \text{CH}_2\text{Ph}$ **Ia** (abbreviated as $\text{L}_2^{\text{CH}_2\text{Ph}}$)

$\text{R} = \text{Et}$ **Ib** (abbreviated as L_2^{Et})

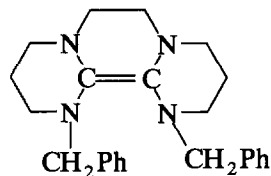
$\text{R} = \text{Me}$ **Ic** (abbreviated as L_2^{Me})

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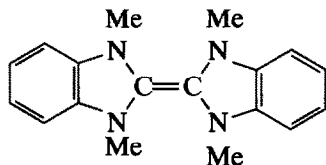
* For Part XXIII, see ref. 1. No reprints available.

** Dedicated to Professor Hans Bock on the occasion of his 65th birthday.

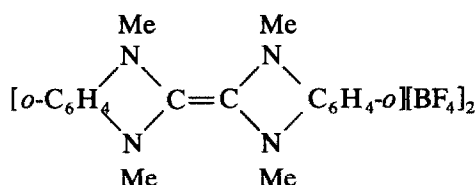
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II [abbreviated as $L_2^{(323)CH_2Ph}$]



1 (abbreviated as L_2^R)



2 (abbreviated as $[L_2^R][BF_4]_2$)

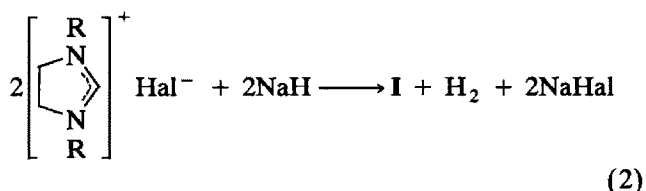
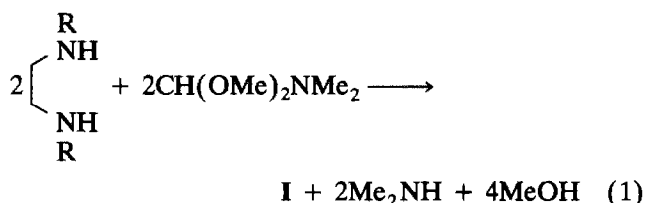
Various further reactions of compound 1 have been carried out which do not involve the formation of carbenometal complexes. Of particular interest, as described in Sections 2 and 3, is its oxidation to the dication salt 2. The structures of 1 and 2 have been determined by single-crystal X-ray diffraction studies.

The reducing ability of an enetetramine such as I has long been recognized; thus, we have used compounds Ia, Ib or $C_2(NMe_2)_4$ (III) as a powerful reducing reagent in an organometallic context. For example, treatment of a compound MR_3Cl or $M'R_2Cl$ ($R = CH(SiMe_3)_2$, $M = Ge$ or Sn [2], $M' = P$ or As [3]), GeR_3Cl ($R = C_6H_3Me_3-2,6$ or $C_6H_2Me_3-2,4,6$) [4] or $Ge[N(SiMe_3)_2]_3 Cl$ [5] in toluene with one of these reagents under photolytic conditions yielded the corresponding persistent metal-centred radical MR_3 or $M'R_2$. Because compounds such as I are soluble in hydrocarbons and the coproduct (*e.g.* $[I]Cl_2$), being a salt, is insoluble, such a reaction is particularly conve-

nient and indeed an enetetramine under these conditions is more effective than, for example, Na/K alloy. A further feature which shows that a compound such as I or III is a powerful reducing agent is its first ionization potential of *ca.* 6 eV (*cf.* Na, 5.1 eV) as measured by He(I) photoelectron spectroscopy [6] (see also refs. 7 and 8).

The literature on electron-rich carbene-metal complexes derived from an enetetramine or an immonium salt has been reviewed [9]. Such complexes have the formula $[M(CXY)L_n]$, L_n representing the sum of all other ligands apart from one electron-rich carbene CXY within the inner coordination sphere of the metal. In general, at least one of the Groups X or Y attached to the carbene-carbon atom was nitrogen-centred.

We have recently described two general methods for the synthesis of enetetramines based on either one of the reactions illustrated for compounds I by eq. (1) or (2) [11].



X-Ray structures have been reported previously for the crystalline compounds Ia [11], Id (I, $R = Ph$) [10], II [11] and III [12] and gas electron diffraction data are available for III [12,13].

Cations based on such an enetetramine have long been known, but only one example has been characterized by X-ray diffraction (by Bock and co-workers) namely the salt $[III]X_2$ ($X = Cl$ or Br [14] or $[PF_6]^-$ [15]). In solution, the cation was shown by 1H NMR

TABLE 1. Yields, colours, melting points and analytical data for compounds 1-4

Compound ^a	Yield (%)	Colour	M.p. (°C)	Analysis [found (calc.) (%)]		
				C	H	N
L_2^R (1)	55 ^b , 90 ^c	White	160	73.5 (74.0)	7.03 (6.85)	18.6 (19.2)
$[L_2^R][BF_4]_2$ (2)	100	White	> 289	46.9 (46.4)	4.12 (4.29)	12.1 (12.0)
$[RhCl(COD)(L^R)]$ (3)	100	Yellow	178-180	50.9 (51.9)	5.65 (5.60)	7.24 (7.12)
$RhCl(L^R)_3$ (4)	100	Yellow	283-285	58.4 (56.2)	5.78 (5.20)	14.8 (14.6)

^a $L^R = [o-C_6H_4(N(Me)_2)_2C]_2$.

^b Method 2.1.

^c Method 2.2.

spectroscopy to have inequivalent methyl groups, consistent with $[\text{III}]^{2+}$ (unlike its neutral precursor **III**), lacking an inversion centre, as corroborated also by the presence of two $\nu(\text{CN}_2)$ IR bands at 1667 and 1672 cm^{-1} .

2. Experimental details

2.1. Synthesis of bis(1,3-dimethylbenzimidazolidin-2-ylidene) (**1**) from a diamine

An equimolar mixture of *N,N'*-dimethyl-1,2-diaminobenzene (3.0 cm^3 , 22.1 mmol) and *N,N*-dimethylformamide dimethylacetal (3.2 cm^3 , 24.2 mmol) was heated at 90°C for 3 h and then at 140°C under distillation conditions in an argon atmosphere, dimethylamine and methanol being distilled off. Volatiles were removed from the residue *in vacuo* and the oily residue was crystallized from toluene-*n*-hexane (1.2:1). Orange crystals of the title compound **1** (1.60 g, 50%) were obtained, m.p. 158–160°C. Analytical and spectroscopic data are summarized in Tables 1 and 2, respectively.

2.2. Synthesis of the bis(1,3-dimethylimidazolidin-2-ylidene) (**1**) from the 1,3-dimethylbenzimidazolium iodide [*o*- $\text{C}_6\text{H}_4\{\text{N}(\text{Me})\}_2\text{C}\}\text{I}$

An equimolar mixture of the imidazolium iodide (10.09 g, 34.8 mmol) and sodium hydride (1.259 g, 52.2 mmol) in tetrahydrofuran (100 cm^3) was stirred for 3 h at room temperature and then for a further 1 h at 50°C. The solvent was removed *in vacuo* and the residue was extracted with hot toluene (50 cm^3) and

the extract filtered hot. The yellow filtrate was concentrated (to ca. 20 cm^3), *n*-hexane (20 cm^3) was added and the solution was cooled to –30°C to yield the crystalline orange compound **1** (90%), m.p. 158–160°C. Analytical and spectroscopic data are given in Tables 1 and 2, respectively.

2.3. Synthesis of the salt **2**, the bis(tetrafluoroborate) of the dication **1**

Silver tetrafluoroborate (1.0 g, 5.13 mmol) in tetrahydrofuran (25 cm^3) was added to the enetetramine **1** (0.64 g, 2.19 mmol) at ambient temperature. A grey-cream precipitate formed instantly, and a silver mirror was deposited on the walls of the Schlenk tube. Solvent was removed *in vacuo* and the residue was crystallized from acetonitrile/diethyl ether (4:1). Cream crystals of **2** (100%) were obtained, which did not melt below 290°C. Analytical and spectroscopic data are given in Tables 1 and 2, respectively.

2.4. Synthesis of the carbenerhodium(I) chloride **3**

Dimeric (cycloocta-1,5-diene)rhodium(I) chloride (0.85 g, 1.71 mmol) was added to the enetetramine **1** (0.50 g, 1.71 mmol) in toluene (25 cm^3) and the mixture was heated under reflux for 30 min. Removal of toluene left a residue of the yellow carbene complex **3** in quantitative yield, and this was recrystallized from toluene, m.p. 178–180°C. Analytical and spectroscopic data are given in Tables 1 and 2, respectively.

2.5. Synthesis of the tris(carbene)rhodium(I) chloride (**4**)

In a similar fashion to that described in Section 2.4, heating under reflux of a mixture of the enetetramine **1** with three equivalents of (cycloocta-1,5-diene)rhodium(I) chloride for 2 h and a similar work-up afforded in quantitative yield the yellow title complex **4**, m.p. 283–285°C. Analytical and spectroscopic data are given in Tables 1 and 2, respectively.

2.6. X-Ray structure determination of $L_2^R(\mathbf{1})$ and $[L_2^R][BF_4]_2$ (**2**)

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo- K_α radiation and crystals sealed in capillaries. Cell dimensions were calculated from the setting angles for 25 reflections with $9 < \theta < 13^\circ$. Intensities for reflections with $2 < \theta < 25^\circ$ were measured by an $\omega - 2\theta$ scan. Corrections were made for Lorentz and polarization effects but not for absorption. There was no crystal decay as measured by two standard reflections. For **1** the origin in the **b** direction was defined by fixing the *y* coordinate of N(1). Positions of non-hydrogen atoms were derived by direct methods using SHELXS-86 and refined with anisotropic thermal parameters by full-matrix least-

TABLE 2. Selected NMR spectroscopic data for compounds 1–4^a

Com- pound	¹ H NMR		¹³ C(¹ H) NMR			δ [¹⁰³ Rh(¹ H)]
	δ (Me)	δ (C ₆ H ₄)	δ (Me)	δ (C ₆ H ₄)	δ (C _{carb})	
1	2.68	6.44–6.78	36.0	108.6 121.0 143.0	124.0	–
2	4.20	7.90–8.20	34.0	114.6 128.8 133.5	130.5	–
3	4.29	7.3m	34.65	100.2 122.3 135.2	195.9 ^b	642 ^c
4	3.57	7.5m	35.1	111.0 124.8 134.9	179.9 ^d	2874 ^c

^a Spectra were run at ambient temperature in (CD₃)₂SO (**2**) or in CDCl₃ using a Bruker AMX-500 spectrometer for ¹³C at 125.8 MHz and for ¹⁰³Rh at 15.81 MHz.

^b ¹*J* (¹³C–¹⁰³Rh) = 50 Hz.

^c Relative to –3.16 MHz.

^d ¹*J* (¹³C–¹⁰³Rh) = 33.1 Hz.

TABLE 3. Crystal structure details for L_2^R (1) and $[L_2^R][BF_4]_2$ (2)

	1	2
Formula	$C_{18}H_{20}N_4$	$C_{18}H_{20}B_2F_8N_4$
M	292.4	466.0
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$ (No. 4)	$Pnma$ (No. 53)
a (Å)	8.150(1)	23.508(4)
b (Å)	7.934(3)	11.224(3)
c (Å)	12.277(4)	7.881(3)
β ($^\circ$)	93.34(2)	90
U (Å ³)	792.5	2079.3
Z	2	4
D_{calc}	1.23	1.49
$F(000)$	312	952
μ (cm ⁻¹)	0.7	1.3
Crystal size (mm ³)	0.3 × 0.3 × 0.2	0.35 × 0.4 × 0.2
Total number of reflections	1613	2136
Unique reflections	1516	2136
R_{int}	0.02	–
Observed reflections ($I > 2\sigma(I)$)	1181	941
R	0.042	0.090
R'	0.047	0.106
S	1.5	4.4
Number of parameters	278	203
(Δ/σ) max	0.2	0.3
$\Delta\rho_{max}$ (e Å ⁻³)	0.16	0.75
$\Delta\rho_{min}$ (e Å ⁻³)	–0.30	–0.66

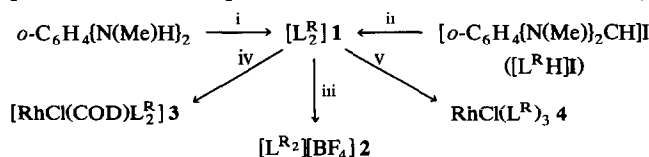
squares. In both cases hydrogen atoms were located and their positions refined but for 1 their isotropic thermal parameters were also refined, whereas for 2 these were fixed at $U_{iso} = 1.3U_{eq}$ for the parent atom. Further details are given in Table 3. Hydrogen atom positions, anisotropic thermal parameters and structure factor listings are available from P.B.H.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of the enetetramine 1, its dicationic salt 2 and the derived carbenerhodium complexes 3 and 4

The synthesis of the complexes 1–4 is summarized in Scheme 1. Yields, colours, melting points and analytical results are listed in Table 1 and spectroscopic data in Table 2.

Each of the procedures used for preparing compounds 1–4 has a precedent (see Section 1). However,



Scheme 1. Reagents and conditions: (i) $CH(OMe)_2NMe_2$, PhMe, 110°C; (ii) NaH, THF, 20°C; (iii) $Ag[BF_4]$, THF, 20°C; (iv) $\frac{1}{2}[(Rh(\mu-Cl)(COD))_2]$, PhMe, 110°C; (v) $\frac{1}{2}(Rh(\mu-Cl)(COD))_2$, PhMe, 110°C.

the isolation of the compounds in a crystalline form suitable for X-ray diffraction is noteworthy.

The enetetramine L_2^R (1) showed weak IR absorption at 1725 cm⁻¹ which is assigned to $\nu(C=C)$, significantly higher than the 1650 cm⁻¹ found for $L_2^{(323)CH_2Ph}$ (II) [11]. The EI mass spectrum for 1 (like that of the salt 2) showed the parent molecular monocation in high intensity at $m/e = 292$, and two successive fragment ions from loss of 1Me or 2Me radicals. The NMR spectral data (Table 2) for 1 are unexceptional; C_{carb} refers to the central olefinic carbon atoms. For comparison, it is noted that $\delta(^{13}C_{carb})$ in II is at 140.7 ppm.

For the cation of $[L_2^R][BF_4]_2$ (2) a $\nu(C=C)$ IR band was not identified, and the assignment (Table 2) for $\delta(^{13}C_{carb})$ must be regarded as tentative.

The value of $\delta[^{13}C\{^1H\}]$ in carbene–metal complexes is usually around 210 ± 20 [9]. For $[RhCl(L^{CH_2Ph})_3]$, $[RhCl(L^{Et})_3]$ and $[(RhCl(COD))_2(\mu-L^{(323)CH_2Ph})]$ it was found to be δ 223.4 and 221.9 (*trans* to Cl⁻), 222.4 and 218.7 (*trans* to Cl⁻) and 207.0, respectively, $^1J(^{13}C-^{103}Rh)$ being 42.5 and 64.7 (*trans* to Cl⁻), 41.4 and 64.4 (*trans* to Cl⁻) and 46.4 Hz, respectively [1]. The corresponding data for 3 are therefore unexceptional. For 4, however, only a single $^{13}C_{carb}$ signal was observed, at δ 179.9 with $J(^{13}C-^{103}Rh) = 33.1$ Hz. This suggests that in solution 4 is dissociated, probably to $[Rh(L^R)_3]Cl$.

For the carbenerhodium(I) complexes 3 and 4 the recording of ^{103}Rh NMR spectra is noteworthy. It has been observed in a recent review that chemical shifts for rhodium(I) complexes fall in the range $\delta - 1224$ to 2344 relative to $\Xi 3.16$ MHz [16], and so the value of δ 2874 for $RhCl(L^R)_3$ is of interest; the significant difference from the literature data may support the suggestion made above that in solution the complex is dissociated. For rhodium complexes chemical shifts are dominated by the paramagnetic term and the range of such shifts is particularly dependent on the HOMO–LUMO gap, which is especially small for an atom such as ^{103}Rh with a partially filled d-shell [16].

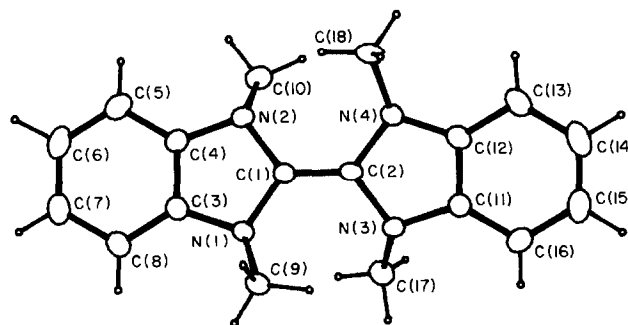


Fig. 1. X-Ray structure and atom labelling for $[o-C_6H_4(N(Me))_2Cl]_2Cl$ (1).

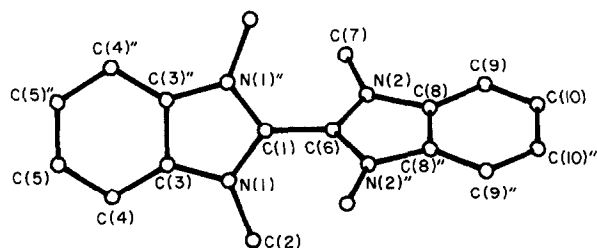
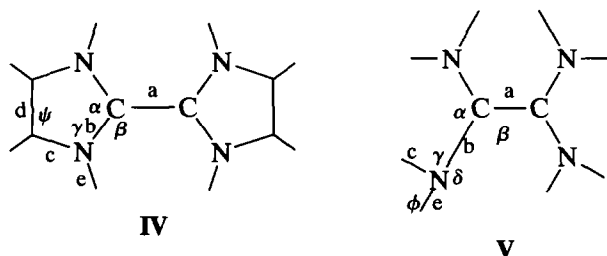


Fig. 2. X-Ray structure and atom labelling for the cation of $[(o\text{-C}_6\text{H}_4(\text{N}(\text{Me})_2)_2\text{C})_2]\text{BF}_4$ (**2**).

3.2. Molecular structures of the crystalline complexes 1 and 2

The X-ray structures of the two compounds are illustrated in Figs. 1 (**1**) and 2 (**2**). Selected bond lengths and angles with standard deviations are given in Tables 4 (**1**) and 5 (**2**) and atomic coordinates in Tables 6 (**1**) and 7 (**2**).



The more important geometric parameters of the crystalline compounds **1** and **2** are summarized in Table 8, together with comparative data for $\text{C}_2(\text{NMe}_2)_4$ (**III**) and its dication $[\text{III}]^{2+}$.

TABLE 4. Average dimensions and root mean square deviations in crystalline L_2^{R} (**1**) and the dication in $[\text{L}_2^{\text{R}}]\text{BF}_4$ (**2**) (see IV) and in $\text{C}_2(\text{NMe}_2)_4$ (**III**) [12] and the dication in $[\text{III}]\text{Br}_2$ [14] (see V)

Bonds (Å) or angles (°)	L_2^{R} (1)	$[\text{L}_2^{\text{R}}]^{2+}$ ^a	III ^b	$[\text{III}]^{2+}$ ^b
a	1.344(4)	1.462(13)	1.350(2)	1.512(2)
b	1.428(8)	1.331(4)	1.418(3)	1.315(2)
c	1.407(9)	1.385(4)	1.444(1)	1.469
d	1.392(4)	1.385(5)	—	—
e	1.463(10)	1.462(7)	1.439(3)	1.469
α	108.2(10)	110.3(13)	119.9(1)	126.1
β	125.9(9)	124.9(6)	124.6(1)	—
γ	106.6(10)	108.0(10)	119.4(1)	—
δ	119.9(24)	126.7(6)	118.4(2)	—
ϕ	117.7(19)	125.2(2)	115.2(2)	114.5
ψ	109.1(6)	106.8(2)	—	—
Torsion angle (°) about central C—C (a)	21	72	28.3	76 ^c
Sum of angles at N	344.2	359.9	352/353	360

^a See IV.

^b See V.

^c 72° in $[\text{III}]\text{PF}_6$ [15].

TABLE 5. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[o\text{-C}_6\text{H}_4(\text{N}(\text{Me})_2)_2\text{C}]_2$ (**1**)

(a) Bonds			
N(1)—C(1)	1.438(4)	N(1)—C(3)	1.413(4)
N(1)—C(9)	1.474(4)	N(2)—C(1)	1.431(4)
N(2)—C(4)	1.416(4)	N(2)—C(10)	1.462(4)
N(3)—C(2)	1.425(4)	N(3)—C(11)	1.407(4)
N(3)—C(17)	1.452(5)	N(4)—C(2)	1.418(4)
N(4)—C(12)	1.397(4)	N(4)—C(18)	1.457(5)
C(1)—C(2)	1.344(4)	C(3)—C(4)	1.388(4)
C(3)—C(8)	1.384(4)	C(4)—C(5)	1.377(4)
C(5)—C(6)	1.390(5)	C(6)—C(7)	1.371(5)
C(7)—C(8)	1.402(5)	C(11)—C(12)	1.396(5)
C(11)—C(16)	1.380(4)	C(12)—C(13)	1.374(5)
C(13)—C(14)	1.392(5)	C(14)—C(15)	1.369(7)
C(15)—C(16)	1.383(5)		
(b) Angles			
C(1)—N(1)—C(3)	105.4(2)	C(1)—N(1)—C(9)	118.4(2)
C(3)—N(1)—C(9)	116.4(2)	C(1)—N(2)—C(4)	105.7(2)
C(1)—N(2)—C(10)	117.1(3)	C(4)—N(2)—C(10)	115.2(2)
C(2)—N(3)—C(11)	107.4(3)	C(2)—N(3)—C(17)	120.8(3)
C(11)—N(3)—C(17)	119.7(3)	C(2)—N(4)—C(12)	107.9(3)
C(2)—N(4)—C(18)	123.3(3)	C(12)—N(4)—C(18)	119.3(3)
N(1)—C(1)—N(2)	109.2(2)	N(1)—C(1)—C(2)	125.8(3)
N(2)—C(1)—C(2)	125.0(3)	N(3)—C(2)—N(4)	107.2(2)
N(3)—C(2)—C(1)	125.5(3)	N(4)—C(2)—C(1)	127.3(3)
N(1)—C(3)—C(4)	109.9(2)	N(1)—C(3)—C(8)	128.9(3)
C(4)—C(3)—C(8)	121.2(3)	N(2)—C(4)—C(3)	109.4(2)
N(2)—C(4)—C(5)	129.8(3)	C(3)—C(4)—C(5)	120.8(3)
C(4)—C(5)—C(6)	118.4(3)	C(5)—C(6)—C(7)	121.0(3)
C(6)—C(7)—C(8)	121.0(3)	C(3)—C(8)—C(7)	117.5(3)
N(3)—C(11)—C(12)	108.5(3)	N(3)—C(11)—C(16)	130.2(3)
C(12)—C(11)—C(16)	121.4(3)	N(4)—C(12)—C(11)	108.6(3)
N(4)—C(12)—C(13)	131.1(3)	C(11)—C(12)—C(13)	120.3(3)
C(12)—C(13)—C(14)	118.1(4)	C(13)—C(14)—C(15)	121.3(4)
C(14)—C(15)—C(16)	121.1(3)	C(11)—C(16)—C(15)	117.7(4)

Molecules of **1** have no imposed crystallographic symmetry. At each end of the molecule the fused six- or five-membered ring unit is essentially planar, but the methyl substituents are bent out of plane on opposite sides of the fused rings so that the geometry at N is pyramidal, with average sum of angles at N of 344.2°. In addition, the two ends of the molecule are twisted with respect to each other by a rotation of 21° about the central C—C bond. These two distortions presumably reduce the steric strain between the adjacent methyl groups. The central C—C bond has a length, 1.344(4) Å, typical of an isolated double bond, and the bonds from N to these central C atoms average 1.428(8) Å indicating that there is only a small amount of conjugation with the central double bond.

The cations of **2** have a crystallographic twofold rotation axis coincident with the C=C double bond. At each end of the molecule the fused ring system is planar and the methyl substituents are coplanar with the rings so that the geometry at the N atoms is planar with average sum of angles at N of 359.9°. The two

TABLE 6. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [(*o*-C₆H₄{N(Me)}₂C)₂] (2)

(a) Bonds			
F(1)–B(1)	1.353(9)	F(2)–B(1)	1.337(10)
F(3)–B(2)	1.320(8)	F(4)–B(2)	1.254(11)
N(1)–C(1)	1.333(7)	N(1)–C(2)	1.468(9)
N(1)–C(3)	1.381(8)	N(2)–C(6)	1.328(7)
N(2)–C(7)	1.455(9)	N(2)–C(8)	1.388(8)
C(1)–C(6)	1.462(13)	C(3)–C(4)	1.399(9)
C(4)–C(5)	1.378(10)	C(8)–C(9)	1.397(10)
C(9)–C(10)	1.358(10)	C(3)–C(3) ^y	1.380(9)
C(5)–C(5) ^y	1.379(11)	C(8)–C(8) ^y	1.389(8)
C(10)–C(10) ^y	1.394(10)		
(b) Angles			
C(1)–N(1)–C(2)	126.1(6)	C(1)–N(1)–C(3)	108.9(5)
C(2)–N(1)–C(3)	125.0(5)	C(6)–N(2)–C(7)	127.2(6)
C(6)–N(2)–C(8)	107.4(5)	C(7)–N(2)–C(8)	125.3(5)
N(1)–C(1)–C(6)	125.5(4)	N(1)–C(3)–C(4)	131.6(6)
C(3)–C(4)–C(5)	115.9(7)	N(2)–C(6)–C(1)	124.3(4)
N(2)–C(8)–C(9)	130.6(6)	C(8)–C(9)–C(10)	114.1(6)
F(1)–B(1)–F(2)	108.3(3)	F(3)–B(2)–F(4)	109.2(5)
F(1)–B(1)–F(3)	122.6(9)	F(1)–B(1)–F(2) ^y	110.3(4)
F(2)–B(1)–F(2) ^y	107.0(9)	F(3)–B(2)–F(3) ^y	118.3(9)
F(3)–B(2)–F(4) ^y	105.4(5)	F(4)–B(2)–F(4) ^y	109(1)
N(1)–C(1)–N(1) ^y	109.0(7)	N(1)–C(3)–C(3) ^y	106.6(5)
C(4)–C(3)–C(3) ^y	121.7(6)	C(4)–C(5)–C(5) ^y	122.3(7)
N(2)–C(6)–N(2) ^y	111.5(7)	N(2)–C(8)–C(8) ^y	106.9(6)
C(9)–C(8)–C(8) ^y	122.5(6)	C(9)–C(10)–C(10) ^y	123.4(6)

The symmetry element is ^y 0.5 – x, – y, z and ^y x, 0.5 – y, 0.5 – z.

ends of the dication are twisted with respect to each other by a rotation of 72° about the central C–C bond, which has a length 1.462(13) Å, indicative of a single

TABLE 7. Atomic coordinates (× 10⁴) for [*o*-C₆H₄{N(Me)}₂C]₂ (1)

Atom	x	y	z	U _{eq} ^a
N(1)	9164(3)	4191	5523(2)	45(1)
N(2)	7057(3)	2674(4)	6289(2)	47(1)
N(3)	11127(3)	3929(4)	7688(2)	49(1)
N(4)	9432(3)	1819(4)	8216(2)	50(1)
C(1)	8708(3)	3270(4)	6468(2)	44(1)
C(2)	9661(3)	3023(4)	7384(2)	43(1)
C(3)	7837(4)	3984(4)	4742(2)	46(1)
C(4)	6581(3)	3090(4)	5194(2)	49(2)
C(5)	5162(4)	2701(5)	4582(3)	63(2)
C(6)	5000(4)	3265(5)	3509(3)	71(2)
C(7)	6228(5)	4169(5)	3063(3)	67(2)
C(8)	7681(4)	4561(5)	3677(3)	57(2)
C(9)	10824(4)	3932(5)	5135(3)	56(2)
C(10)	5885(4)	3153(5)	7092(3)	63(2)
C(11)	11836(4)	3172(5)	8639(2)	49(2)
C(12)	10822(4)	1853(5)	8937(2)	52(2)
C(13)	11267(5)	859(5)	9822(3)	69(2)
C(14)	12740(5)	1218(6)	10407(3)	84(2)
C(15)	13699(4)	2553(7)	10135(3)	77(2)
C(16)	13270(4)	3556(5)	9242(3)	63(2)
C(17)	11198(5)	5746(5)	7562(3)	68(2)
C(18)	8556(5)	236(5)	8026(3)	67(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_i tensor.

TABLE 8. Atomic coordinates (× 10⁴) for [(*o*-C₆H₄{N(Me)}₂C)₂] [BF₄]₂ (2)

Atom	x	y	z	U _{eq} ^a
F(1)	2689(2)	921(5)	1827(6)	100(4)
F(2)	2925(3)	– 356(6)	– 135(9)	162(5)
F(3)	597(2)	1781(5)	1491(8)	108(4)
F(4)	0(4)	1891(9)	3465(11)	344(8)
N(1)	5625(2)	1538(4)	2360(7)	41(3)
N(2)	6894(2)	2935(5)	1253(7)	42(3)
C(1)	5955(4)	2500	2500	39(5)
C(2)	5822(3)	311(6)	2090(11)	68(5)
C(3)	5062(3)	1888(6)	2420(9)	44(3)
C(4)	4556(3)	1237(7)	2305(10)	57(4)
C(5)	4061(3)	1889(7)	2402(12)	70(5)
C(6)	6576(4)	2500	2500	40(5)
C(7)	6698(3)	3421(8)	– 355(10)	65(5)
C(8)	7459(3)	2768(6)	1706(7)	42(4)
C(9)	7961(3)	3043(7)	837(9)	54(4)
C(10)	8443(3)	2752(8)	1691(9)	61(5)
B(1)	2500	0	874(15)	47(7)
B(2)	309(5)	2500	2500	62(8)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_i tensor.

bond between two sp²-hybridized C atoms. Within the five-membered ring the bond lengths indicate a delocalized bonding, the N to central C atoms averaging 1.331(4) Å and the other endocyclic N–C bond and the C–C bond both averaging 1.385(5) Å. The N–C (methyl) bonds average 1.462(7) Å, the same as those in the olefin.

The central C–C bond lengths (a in Table 4) of 1.344(4) Å in **1** may be compared with those of 1.319(8) Å in L₂^{CH₂Ph} (**Ia**) [11], 1.372(6) in L₂^{Ph} (**Id**) [10], 1.329(5) Å in L₂^{(323)CH₂Ph} [11], 1.387(11) Å in gaseous L₂^{Me} [13] and 1.351(2) in C₂(NMe₂)₄ (**III**) [12]. The N–CH₃ bond (e in Table 4) of 1.463(10) Å in **1** is essentially identical with the 1.465(6) Å in gaseous L₂^{Me} [13]. The torsion angle about the central C–C bond of 21° in **1** compares with that of 53.5(8)° in gaseous L₂^{Me} [13] and 28.3° in crystalline **III** [12]. Comparable data relating to the nitrogen environment of enetetramines show a significant degree of pyramidity except for L₂^{Ph}. Thus, the sum of the angles at the four nitrogen atoms ranges from 329.5 to 332.1° in L₂^{CH₂Ph} (**Ia**) [11], and a similar pyramidal nitrogen geometry was found in both gaseous L₂^{Me} [13] and crystalline L₂^{(323)CH₂Ph} [11], but for L₂^{Ph} the angles at nitrogen varied from 354.1 to 358.1° [10].

Acknowledgements

We are grateful to İnönü University for providing study leave (and costs of consumables) for H.K., and the SERC for support.

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