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Polyhedron 22 (2003) 843–847
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Synthesis and structures of novel bis- and tetrakis-cyclodiphosphazane compounds appended to a diol or a tetra-ol

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Received 7 October 2002; accepted 3 December 2002

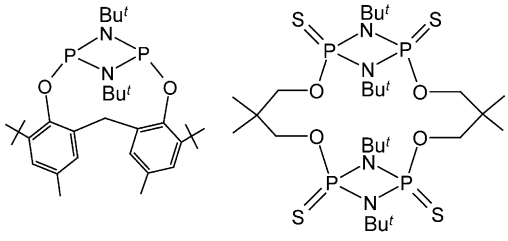
Abstract

The bis-cyclodiphosphazane compound $Et_2C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2PNH\text{-}t\text{-}Bu]_2$ (**2**) and the tetrakis–cyclodiphosphazane compound $C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2PNH\text{-}t\text{-}Bu]_4$ (**3**) have been synthesized by treating 2,2-diethyl-1,3-propanediol or pentaerythritol with 2 or 4 equiv. of $[ClP(\mu\text{-}N\text{-}t\text{-}Bu)_2P(HN\text{-}t\text{-}Bu)]$ (**1**), respectively. Compounds **2** and **3** have been characterized by X-ray crystallography and solution state NMR. Oxidative addition of *o*-chloranil to **2** and **3** yields the novel compounds $Et_2C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2P\{(HN\text{-}t\text{-}Bu)(1,2\text{-}O_2C_6Cl_4)\}]_2$ (**4**) and $C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2P\{(HN\text{-}t\text{-}Bu)(1,2\text{-}O_2C_6Cl_4)\}]_4$ (**5**) having two or four P(III)–N–P(V) centers, respectively. The ^{31}P NMR spectra of compounds **4** and **5** show characteristic doublets in the tri- and penta-coordinated regions.

Keywords: Cyclodiphosphazanes; Pentacoordinate; X-ray structures

1. Introduction

Cyclodiphosph(III)azanes, $[ClPNR]_2$, are an interesting class of heterocycles with two reactive phosphorus centers [1–6]. In their reaction with diols, triols and more functionalized reagents, the products obtained can be monomeric, dimeric or polymeric. In our previous studies on cyclodiphosphazanes, we have reported the isolation of either monomeric or dimeric products [e.g. **I** and **II**] depending on the type of the diol used [7,8]. Compound **II** has two cyclodiphosphazane units linked by a diol residue. We have also been interested in designing compounds with multiple cyclodiphosphazane units by other routes, to be used later as ligands for complexation, using similar reactions with polyfunctional amines/alcohols. For this purpose, we needed the mono substituted cyclodiphosphazanes of the type $[ClP(\mu\text{-}N\text{-}t\text{-}Bu)_2PR]$ [R = amino or alkoxo]; compounds where R = NH-*t*-Bu (**1**), F or O-2,6-Me_2–C_6H_3 represent a few examples of this type known in the literature [1,5]. Among these, the *t*-butylamino compound **1** is perhaps the easiest to prepare and has been used recently to construct novel polycyclic compounds [9]. In this paper we report the synthesis and X-ray structures of the bis-cyclodiphosphazane $Et_2C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2PNH\text{-}t\text{-}Bu]_2$ (**2**) and the tetrakis-cyclodiphosphazane $C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2PNH\text{-}t\text{-}Bu]_4$ (**3**) by reacting $[ClP(\mu\text{-}N\text{-}t\text{-}Bu)_2P(HN\text{-}t\text{-}Bu)]$ (**1**) with 2,2-diethyl-1,3-propanediol or pentaerythritol, respectively. Also reported herein are the oxidative addition reactions of **2** and **3** with *o*-chloranil to lead to the novel P(III)–N–P(V) compounds $Et_2C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2P\{(HN\text{-}t\text{-}Bu)(1,2\text{-}O_2C_6Cl_4)\}]_2$ (**4**) and $C[CH_2OP(\mu\text{-}N\text{-}t\text{-}Bu)_2P\{(HN\text{-}t\text{-}Bu)(1,2\text{-}O_2C_6Cl_4)\}]_4$ (**5**), respectively.



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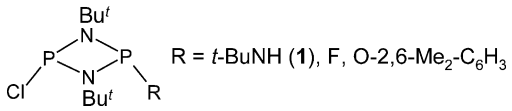
0277-5387/03/$ - see front matter
doi:10.1016/S0277-5387(02)01421-3



2. Experimental

Chemicals were procured from Aldrich–Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures [10]. All reactions, unless stated otherwise, were performed under dry nitrogen atmosphere. ^{1}H and ^{31}P{H} NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$, with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). Elemental analyses were carried out on a Perkin–Elmer 240C CHN analyzer.

2.1. Synthesis of 2

To a solution of 2,2-diethyl-1,3-propanediol (0.159 g, 1.20 mmol) and triethylamine (0.244 g, 2.41 mmol) in 5 ml of toluene was added **1** [11] (0.751 g, 2.41 mmol) in 5 ml of toluene drop-wise with stirring and the mixture stirred for 2 days at room temperature (r.t.). Upon filtration and removal of all the solvent in vacuo, a gummy residue was obtained which, on crystallization from toluene–heptane (1:1) mixture, yielded white crystals of **2** (0.71 g, 86%). M.p. 108–110 °C. IR (KBr): 3354 (w, ν(NH)), 1466 (s, $\delta(OCH_2)$), 1363 (s), 1222 (s), 1001 (s, ν(P–O)), 873 (s, ν(PNP)), 771 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.87 (t, $^3J = 7.0$ Hz, 6H, CH_2–CH_3), 1.30 (s, 54H, C(CH_3)$_3$), 1.42 (m, 4H, CH_2CH$_3$), 2.93 (d, $^2J = 8.3$ Hz, 2H, NH), 3.58 (d, $^3J = 5.5$ Hz, 4H, O–CH_2). ^{31}P NMR ($CDCl_3$): δ 116.4, 96.6. *Anal.* Calc. for $C_{31}H_{70}N_6O_2P_4$: C, 54.52; H, 10.33; N, 12.30. Found: C, 54.22; H, 10.21; N, 12.05%.

2.2. Synthesis of 3

To a mixture of tetrakis(hydroxymethyl)methane [pentaerythritol, 0.087 g, 0.64 mmol] and triethylamine (0.259 g, 2.56 mmol) in 5 ml of toluene, compound **1** [11] (0.798 g, 2.56 mmol) in 5 ml of toluene was added drop-wise with stirring and the contents stirred further for 2 days at r.t. Upon filtration and removal of all the solvent in vacuo, a gummy material was obtained which on crystallization from toluene–heptane (1:1) mixture yielded white crystals of **3** (0.67 g, 85%). M.p. 198–200 °C. IR (KBr): 3339 (w, ν(NH)), 1462 (s, $\delta(OCH_2)$), 1364 (s), 1219 (s), 1001 (s, ν(P–O)), 878 (s, ν(PNP)), 774 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 108H, C(CH_3)$_3$), 3.05 (d, $^2J \sim 10.0$ Hz, 4H, NH), 3.80 (d, $^3J = 6.0$ Hz, 8H, O–CH_2). ^{31}P NMR ($CDCl_3$): δ 117.9, 94.7. *Anal.* Calc. for $C_{53}H_{120}N_{12}O_4P_8$: C, 51.45; H, 9.77; N, 13.58. Found: C, 51.55; H, 9.80; N, 13.66%.

2.3. Synthesis of 4

To **2** (0.099 g, 0.14 mmol) in 5 ml of toluene was added tetrachloro-1,2-benzoquinone [*o*-chloranil, 0.072 g, 0.28 mmol] in 10 ml of toluene drop-wise over a period of 1 h at r.t. with continuous stirring and kept overnight undisturbed. Upon concentration (to $\sim$3 ml, by removing most of the solvent in vacuo), and addition of heptane (2 ml), compound **4** (0.15 g, 87%) precipitated out as a white solid on cooling to 0 °C. M.p. 196–198 °C. IR (KBr): 3431 (w, ν(NH)), 1467 (s, $\delta(OCH_2)$), 1221 (s), 1198 (s), 1011 (s, ν(P–O)), 895 (s, ν(PNP)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.96 (t, $^3J = 8.0$ Hz, 6H, CH_2–CH_3), 1.27 (s, 36H, N–C(CH_3)$_3$), 1.39 (s, 18H, NH–C(CH_3)$_3$), 1.48 (m, 4H, CH_2CH$_3$), 3.30 (d, $^2J =$ 15.8 Hz, 2H, NH), 3.7 (d, $^3J = 5.0$ Hz, 4H, O–CH_2). ^{31}P NMR ($CDCl_3$): δ 92.1, -40.2 (^2J(PNP) $\sim$ 20.0 Hz). *Anal.* Calc. for $C_{43}H_{70}Cl_8N_6O_6P_4$: C, 43.96; H, 6.01; N, 7.14. Found: C, 44.06; H, 6.05; N, 7.22%.

2.4. Synthesis of 5

To **3** (0.409 g, 0.33 mmol) in 5 ml of toluene was added *o*-chloranil (0.326 g, 1.33 mmol) in 10 ml of toluene drop-wise over a period of 30 min at r.t. with continuous stirring and the solution kept overnight undisturbed. Upon concentration (to 2 ml by removing most of the solvent in vacuo) and cooling to 0 °C compound **5** (0.61 g, 83%) precipitated out as a white solid. M.p. 212–214 °C. IR (KBr): 3431 (w, ν(NH)), 1467 (s, $\delta(OCH_2)$), 1221 (s), 1197 (s), 1011 (s, ν(P–O)), 899 (s, ν(PNP)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 36H, NH–C(CH_3)$_3$), δ 1.4 (s, 72H, N–C(CH_3)$_3$), 3.28 (d, $^2J = 18.0$ Hz, 4H, NH), 3.96 (d, $^3J = 6.0$ Hz, 8H, O–CH_2). ^{31}P NMR ($CDCl_3$): δ 103.6, -39.5 (^2J(PNP) $\sim$ 20.0 Hz). *Anal.* Calc. for $C_{77}H_{120}Cl_{16}N_{12}O_{12}P_8$: C, 41.64; H, 5.45; N, 7.57. Found: C, 41.75; H, 5.48; N, 7.60%.

X-ray data were collected on an Enraf–Nonius–MACH3 or X-ray diffractometer or a Bruker AXS SMART diffractometer at 293/296 K using Mo Kα ($\lambda =$ 0.71073 Å) radiation and capillary mounting. The structures were solved by direct methods [12]; all non-hydrogen atoms were refined anisotropically. For the hydrogen atoms except the NH hydrogen, the riding model was used. The crystal data are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

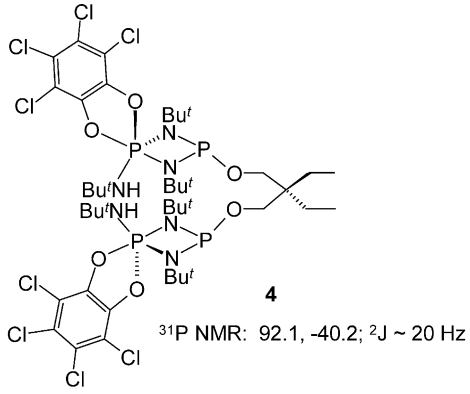
Compound **2** is synthesized by the reaction of 2,2-diethyl-1,3-propanediol with 2 mol equiv. of [ClP(μ-*N*-*t*-Bu)$_2$P(HN-*t*-Bu)] (**1**) using triethylamine as the base;

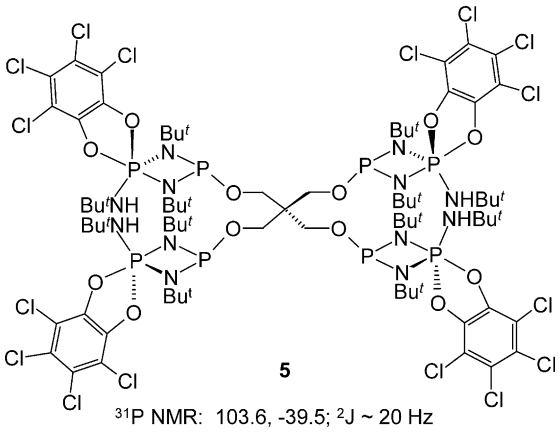
Table 1
Crystal data for **2** and **3**

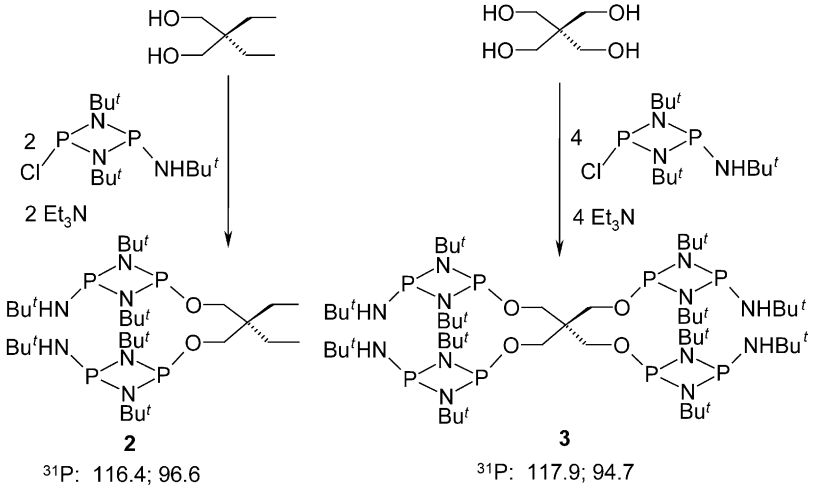
Compound	**2**	**3**
Empirical formula′	$C_{15.5}H_{35}N_3OP_2$	$C_{26.5}H_{60}N_6O_2P_4$
Formula weight	341.40	618.68
Crystal system	tetragonal	tetragonal
Space group	$P4_12_12$	$P4_32_12$
a (Å)	10.7236(3)	14.380(4)
b (Å)	10.7236(3)	14.380(4)
c (Å)	37.5546(17)	38.454(3)
α (°)	90.00	90.0
β (°)	90.00	90.0
γ (°)	90.00	90.0
V (Å^3)	4318.6(3)	7952(3)
Z	8	8
D_{calc} (g cm^{-3})	1.050	1.034
μ (mm^{-1})	0.206	0.218
$F(000)$	1496	2696
Data/restraints/parameters	3802/0/193	6968/3/367
S	1.010	1.070
Flack parameter	0.02(17)	0.6(2)
$R_1[I > 2\sigma(I)]$	0.0575	0.0672
wR_2 (all data)	0.1520	0.2217
Max/min residual electron density (e Å^{-3})	0.38/−0.29	0.34/−0.20

in a similar fashion compound **3** is prepared by the reaction of tetrakis(hydroxymethyl)methane (pentaerythritol) with 4 mole equiv. of **1** (Scheme 1). To our knowledge, compound **3** represents the first example of a molecule with four non-fused cyclodiphosphazane units. Both **2** and **3** show two signals in the ^{31}P NMR spectrum; the downfield signal is ascribable to the phosphorus connected to the –NH-*t*-Bu group.

Oxidative addition of tetrachloro-1,2-benzoquione (*o*-chloranil) to **2** or **3** leads to the novel P(III)–P(V) compounds **4** and **5**, respectively. The asymmetric stretch ν_{asym}(PNP) in **4** and **5** is observed at 896±2 cm^{-1} [cf. 874±1 cm^{-1} in **2** and **3**] in the IR spectra [13]. The ^{31}P NMR spectra of these compounds show a pair of doublets, one in the pentacoordinate region [δ(P) ~ −40] and the other in the tricoordinate region [δ(P) 92.1 for **4** and 103.6 for **5**] with a $^2J(PNP)$ value of ~20 Hz. In both the cases it can be noted that a second isomer, with *o*-chloranil addition occurring at the phosphorus connected to alcoholic oxygen, is possible. However, our previous experience suggests that J(PH) values will be higher for the pentacoordinate phosphorus compounds relative to the corresponding tricoordinate one; the higher $^2J(PNH)$ value in **5** relative to **3** suggests that oxidation has occurred at the P–NH-*t*-Bu center.







Scheme 1.

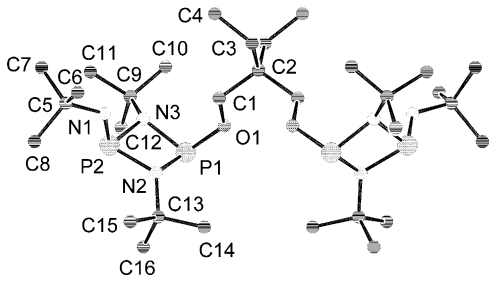


Fig. 1. Molecular structure of **2** showing all non–hydrogen atoms.

3.2. X-ray Structures of 2 and 3

The molecular structure of **2** is shown in Fig. 1; selected geometrical parameters are given in Table 2. The methyl carbons of the *t*-butyl group at N(1) are disordered, but in the figure only one of the possible orientations is shown.

The endocyclic P–N distances to a particular phosphorus atom are unequal; the longer P–N bond to one P atom is associated with the shorter bond to the second. This feature is analogous to that found in *cis*-[*t*-BuNP(O-2,6-Me_2–C_6H_3)]$_2$ [5] and is more pronounced than in *trans*-[PhNP(O-4-Me–C_6H_4)]$_2$ [14]. The endocyclic P–N distances at P(1) are shorter than those at P(2); this is expected because P(1) is connected to the exocyclic oxygen O(1) whereas P(2) is connected to the exocyclic nitrogen N(1). However, all these P–N distances are in the normal range (1.71–1.74 Å) found for analogous compounds [15]. The exocyclic P–N bond, however, is short (1.656 Å); this value is comparable to the P–N single bond in tri- and pentacoordinate phosphoranes [16–20]. The P(1)–O(1) distance of 1.629 Å is slightly shorter than that found in *cis*-[*t*-BuNP(O-2,6-Me_2–C_6H_3)]$_2$ [1.664 Å]. The ring nitrogen atoms are non-planar [sum of the angles: N(2) 347.1, N(3) 348.4°] as expected [5].

Unlike in *cis*-[*t*-BuNP(O-2,6-Me_2–C_6H_3)]$_2$, *cis*-[C_6F_5OPN-*t*-Bu]$_2$ and *trans*-[PhNP(O-4-Me–C_6H_4)]$_2$, the N_2P_2 ring in **2** is severely puckered with P(1) away from the mean plane by 0.47 Å.

Compound **3** (Fig. 2; selected geometrical parameters in Table 2) represents a unique example of a cyclophosphazane molecule bearing four cyclodiphosphazane units. The bond parameters are similar to those of **2**. The substituents on phosphorus in all the four cyclodiphosphazanes have a *cis*-disposition. The four membered N_2P_2 rings are planar to within 0.11 Å; this slight distortion is similar to that seen for *cis*-[*t*-BuNP(O-2,6-Me_2–C_6H_3)] and different from that observed for **2**.

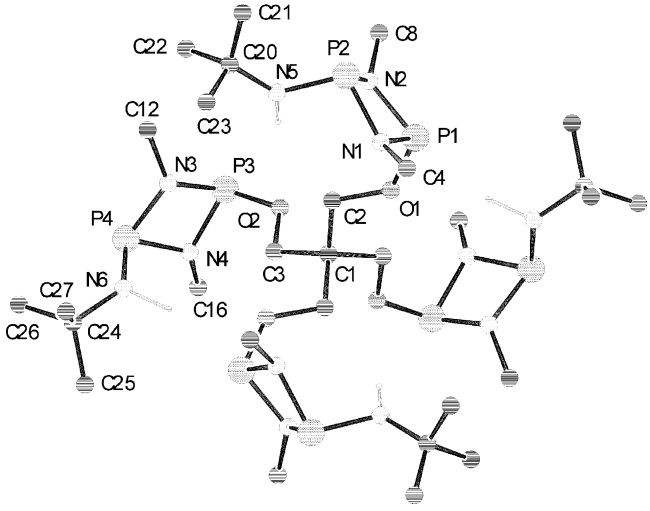


Fig. 2. Molecular structure of **3** showing all non-hydrogen atoms except the terminal carbons of the *t*-butyl group at P–N(*t*-Bu)P.

Table 2
Selected bond lengths (Å) and bond angles (°) for **2** and **3** with e.s.d.'s

Compound **2**		Compound **3**			
Bond lengths					
P(1)–O(1)	1.629(2)	P(1)–O(1)	1.611(4)	P(3)–O(2)	1.630(4)
P(1)–N(2)	1.723(3)	P(1)–N(1)	1.696(6)	P(3)–N(3)	1.706(5)
P(1)–N(3)	1.717(3)	P(1)–N(2)	1.695(6)	P(3)–N(4)	1.717(5)
P(2)–N(1)	1.656(4)	P(2)–N(1)	1.728(5)	P(4)–N(3)	1.728(5)
P(2)–N(2)	1.734(3)	P(2)–N(2)	1.735(6)	P(4)–N(4)	1.719(6)
P(2)–N(3)	1.740(3)	P(2)–N(5)	1.640(5)	P(4)–N(6)	1.657(5)
P(1)···P(2)	2.601(1)	P(1)···P(2)	2.582(3)	P(3)···P(4)	2.595(3)
Bond angles					
O(1)–P(1)–N(2)	106.4(1)	O(1)–P(1)–N(1)	106.7(3)	O(2)–P(3)–N(3)	105.6(2)
O(1)–P(1)–N(3)	107.2(1)	O(1)–P(1)–N(2)	106.8(3)	O(2)–P(3)–N(4)	107.1(2)
N(2)–P(1)–N(3)	82.0(1)	N(1)–P(1)–N(2)	81.9(3)	N(3)–P(3)–N(4)	81.3(2)
N(1)–P(2)–N(2)	104.1(1)	N(1)–P(2)–N(2)	79.8(3)	N(3)–P(4)–N(4)	80.6(2)
N(1)–P(2)–N(3)	106.2(2)	N(1)–P(2)–N(5)	104.1(3)	N(3)–P(4)–N(6)	105.9(3)
N(2)–P(2)–N(3)	81.0(1)	N(2)–P(2)–N(5)	105.2(3)	N(4)–P(4)–N(6)	105.7(3)
P(1)–N(2)–P(2)	97.6(1)	P(1)–N(1)–P(2)	97.9(3)	P(3)–N(3)–P(4)	98.2(3)
P(1)–N(3)–P(2)	97.6(1)	P(1)–N(2)–P(2)	97.6(3)	P(3)–N(4)–P(4)	98.1(3)

4. Summary

The utility of the monochloro compound [ClP(μ-*N*-*t*-Bu)$_2$P(HN-*t*-Bu)] (**1**) in constructing derivatives with multi-cyclodiphosphazane skeletons is demonstrated by the isolation and structural characterization of the novel compounds **2** and **3**. These compounds have the potential to behave as multidentate ligands towards transition metals. Compounds **2** and **3** readily react with *o*-chloranil to lead to the P(III)–P(V) species **4** and **5** in which only the P–NH-*t*-Bu end has reacted, thus showing the higher propensity of a P(III)–N end, relative to a P(III)–O end, to undergo oxidative addition.

5. Supplementary data

Supplementary data as CIF files are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition numbers CCDC 192484 and 192485.

Acknowledgements

This work was supported by the Department of Science and Technology (DST), New Delhi. P.K. thanks Council of Scientific and Industrial Research (CSIR), New Delhi for a fellowship. The National Single Crystal Diffractometer Facility at the University of Hyderabad funded by DST (New Delhi) and National University of Singapore (for the diffractometer facility) was gratefully acknowledged.

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