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The synthesis and structural characterisation of the first phosphavinyl–Group 13 complexes

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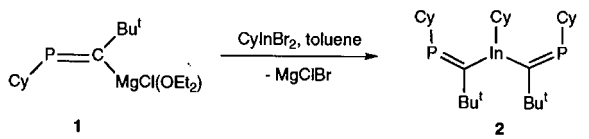
Abstract

The bisphosphavinyl indium complex, [CyIn{C(^{t}Bu)=PCy}$_2$], has been prepared from the reaction of two equivalents of [CyP=C(^{t}Bu)MgCl(OEt$_2$)] with CyInBr$_2$. Its crystal structure shows it to be monomeric with a trigonal planar indium centre. The reactions of [CyP=C(^{t}Bu)MgCl(OEt$_2$)] with MX$_3$, M = Al, Ga or In, X = Cl or Br, leads to facile phosphavinyl coupling reactions and the formation of the diphosphametallobicyclo[1.1.1]pentane complexes, [M{C$_2$(^{t}Bu)$_2$P$_2$Cy$_2$}{C(^{t}Bu)=PCy}], which contain terminal phosphavinyl ligands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphavinyl; Low coordination; Group 13; Group 15; Cage; Phosphorus; Heterocycle; Crystal structure

1. Introduction

Vinyl–Group 13 complexes, especially those of aluminium, have found a variety of applications in organometallic synthesis and have been utilised in a wide range of organic transformations [1]. We have recently embarked upon an investigation into the synthesis and reactivity of main group phosphavinyl complexes, [M{C(R)=PR}$_n$], M = main group element [2–4], which we hoped would include Group 13–phosphavinyl complexes as we believed these might find a similar range of applications as their vinyl counterparts. In this context, it is noteworthy that we have previously reported a general, high yielding synthetic route to a range of phosphavinyl Grignard reagents, e.g. [CyP=C(^{t}Bu)MgCl(OEt$_2$)] (**1**), Cy = cyclohexyl [2], which we have used as a transfer reagent in the preparation of the first bis-phosphavinyl tin complex, [SnMe$_2$\{C(^{t}Bu)=PCy\}$_2$] [3]. As a result of this work it seemed likely that metathesis reactions of **1** with Group 13 halide compounds would lead to hetero- and homoleptic phosphavinyl–group 13 complexes. The results of our efforts in this area are reported herein.



1 2

Scheme 1.

2. Results and discussion

In an attempt to prepare a heteroleptic phosphavinyl indium complex, two equivalents of **1** were reacted with in situ generated CyInBr$_2$ in toluene to yield the first example of a Group 13–phosphavinyl complex, **2**, in moderate yield (40%) after recrystallisation from toluene (Scheme 1). The compound is thermally stable and displays a low field singlet (δ 329 ppm) in its ^{31}P\{^{1}H\}-NMR spectrum which is in the region normally associated with metallophosphaalkenes [5]. This suggested that compound **2** had been formed as its *Z*,*Z*-isomer though the possibility of it existing in its *E*,*E*-form could not be ruled out.

In order to confirm its stereochemistry an X-ray crystal structure analysis was carried out. Its molecular structure (Fig. 1, Table 1) showed it to exist as its *Z*,*Z*-isomer. In addition the compound was found to be

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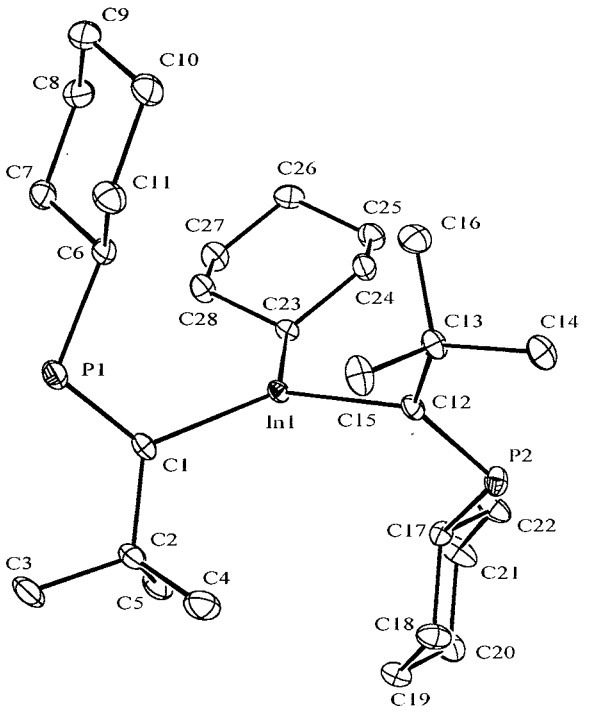


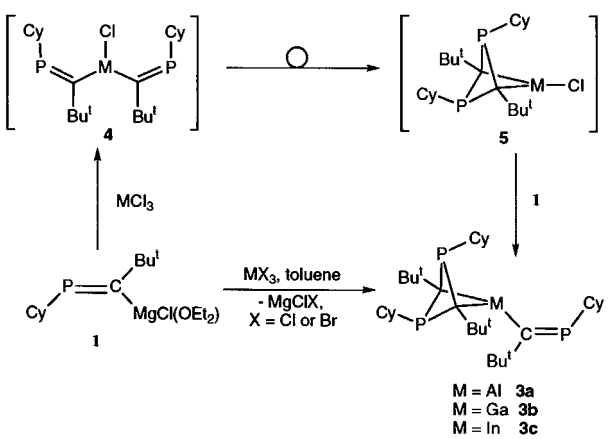
Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): In(1)–C(12), 2.175(4); In(1)–C(23), 2.183(4); In(1)–C(1), 2.191(4); P(1)–C(1), 1.664(4); P(1)–C(6), 1.867(5); P(2)–C(12), 1.677(4); P(2)–C(17), 1.865(4); C(1)–C(2), 1.534(6); C(12)–C(13), 1.515(5); C(12)–In(1)–C(23), 115.84(15); C(12)–In(1)–C(1), 121.57(15); C(23)–In(1)–C(1), 122.50(15); C(1)–P(1)–C(6), 105.4(2); C(12)–P(2)–C(17), 105.66(19); P(1)–C(1)–In(1), 122.7(2); P(2)–C(12)–In(1), 121.5(2).

monomeric with a trigonal planar indium centre (Σ angles about In(1) 359.9°). The geometry of both phosphavinyl fragments is similar and both the P(1)–C(1) and P(2)–C(12) bond lengths are in the normal region for localised P–C double bonds [5]. All other bond lengths and angles within the compound are in the normal ranges.

We also attempted the preparation of a series of homoleptic trisphosphavinyl–Group 13 complexes by the reaction of three equivalents of **1** with the appropriate Group 13 halide (Scheme 2). Unexpectedly, however, the reactions led to the formation of the novel diphosphametallobicyclo[1.1.1]pentane complexes, **3a**–**3c**, in low to moderate yields. We cannot be sure of the mechanism of formation of these compounds as the reactions proceeded too rapidly to observe any intermediates by ^{31}P-NMR spectroscopy. However, it is believed that the metal halide initially reacts with two equivalents of **1** to give the intermediate, **4**, which is structurally similar to **2**. This then undergoes a facile intramolecular phosphavinyl coupling reaction to give **5** which reacts with a third equivalent of **1** to give **3**. If this is the case, it is not known why **2** does not undergo a similar coupling to **4** but perhaps the bulk of the cyclohexyl group of **2** relative to the chloride ligand of **4** prevents this in some way. Of course the reaction could proceed via an intermediate trisphosphavinyl complex, [M{C(ᵗBu)=PCy}$_3$] prior to coupling, but our isolation of the phosphorus counterpart of **5**, i.e. M = P [6], from the analogous reaction of PCl_3 with three equivalents of **1** would suggest this is not the case. It is

Table 1
Summary of crystallographic data for complexes **2**, **3a** and **3b**

	2	**3a**	**3b**
Empirical formula	$C_{28}H_{51}InP_2$	$C_{33}H_{60}AlP_3$	$C_{33}H_{60}GaP_3$
M_r	564.45	576.70	619.44
Temperature (K)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$
Unit cell dimensions			
a (Å)	9.948(4)	10.514(2)	10.597(8)
b (Å)	11.435(4)	30.924(6)	31.032(6)
c (Å)	13.566(5)	11.490(2)	11.480(7)
α (°)	94.96(3)	90	90
β (°)	101.27(3)	115.40(3)	115.58(6)
γ (°)	96.16(4)	90	90
V (Å^3)	1495.5(10)	3374.7(11)	3405(3)
Z	2	4	4
Crystal size (mm)	$0.3\times0.2\times0.2$	$0.3\times0.4\times0.2$	$0.2\times0.2\times0.15$
Colour	Colourless	Yellow	Yellow
μ (mm^{-1})	0.910	0.222	0.969
F(000)	596	1264	1336
Reflections collected	5604	6396	6407
R_{int}	0.0138	0.0301	0.1468
Unique reflections	5359	6054	6094
Parameters varied	286	343	343
R [$I>2\sigma(I)$]	0.0454	0.0500	0.0653
R_w (all data)	0.0502	0.1375	0.2657



Scheme 2.

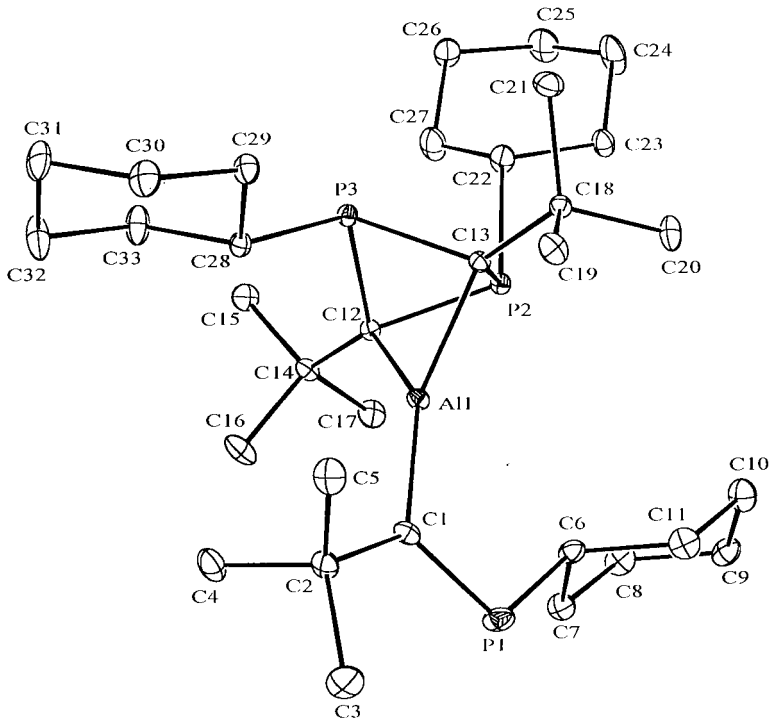


Fig. 2. Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): P(1)–C(1), 1.676(3); P(1)–C(6), 1.864(3); Al(1)–C(1), 1.960(3); Al(1)–C(12), 1.983(3); Al(1)–C(13), 1.958(3); P(2)–C(12), 1.896(3); P(2)–C(13), 1.912(3); P(3)–C(12), 1.895(3); P(3)–C(13), 1.915(3); C(6)–P(1)–C(1), 106.10(14); P(1)–C(1)–Al(1), 112.78(15); C(13)–Al(1)–C(12), 74.24(11); C(12)–P(3)–C(13), 77.27(12); C(12)–P(2)–C(13), 77.31(12); P(3)–C(12)–P(2), 86.58(12); P(3)–C(12)–Al(1), 85.25(11); P(2)–C(12)–Al(1), 86.05(11); P(2)–C(13)–P(3), 85.56(11); P(2)–C(13)–Al(1), 86.32; P(3)–C(13)–Al(1), 85.40(11).

worth noting that the formations of **3a**–**3c** are notionally related to the reactions of aluminium and gallium trialkyls with phosphaalkynes, P≡CR, which also do not lead to Group 13–trisphosphavinyl complexes via 1,2-additions, but instead to triphosphametallatobicyclo[3.2.0.0^{2,6}]heptenes, again via coupling reactions [7].

The spectroscopic data for **3a**–**3c** are similar and the $^{31}P\{^{1}H\}$-NMR spectrum of each displays a three signal pattern with a low field singlet in the expected region for metallophosphaalkenes [5]. Singlets for the chemically inequivalent saturated phosphorus centres were observed at higher field, though no two bond P–P couplings between the signals were evident. The reason for this apparently lies with the acute CPC angles, and thus a high degree of p-character to the bonds within the cage framework. All other spectroscopic data for **3a**–**3c** are consistent with the proposed structures.

The X-ray crystal structures of **3a** and **3b** were obtained and found to be isomorphous (Figs. 2 and 3, see Table 1). The compounds are monomeric with trigonal planar metal coordination environments (Σ angles about M − 359.9°) and metallodiphosphabicyclo[1.1.1]pentane cage frameworks. The CPC and CMC angles within the cages are acute (ca. 70–80°) and can be compared to the CPC angles [74.1(3)°] in the structurally similar triphosphabicyclo[1.1.1]pentane compound, ^{t}BuC{P(Cl)}$_3$C^{t}Bu [8]. The P(1)–C(1) bond lengths of the terminal phosphavinyl fragments in both the aluminium and gallium compounds are close to each other and consistent with localised P–C double bonds [5].

One of our current research goals is the linear polymerisation of phosphaalkynes. We are interested in this area as polyphosphaalkynes could be considered as analogues of polyacetylenes which have found a number of applications derived from their interesting electronic properties [9]. As compounds **3a**–**3c** have unsaturated three coordinate metal centres it seemed possible that their reaction with an excess of the phosphaalkyne, P≡C^{t}Bu, might lead to initial coordination at the metal centre followed by sequential insertion of the P≡C bond into the terminal M–C bond of the cage to give an unsaturated organophosphorus polymer chain. To investigate this possibility **3a** was reacted with P≡C^{t}Bu in a number of stoichiometries, however in all cases complex mixtures of soluble phosphorus containing products were obtained and therefore our efforts in this area have been abandoned.

3. Conclusions

We have prepared a number of novel compounds from the reactions of phosphavinyl Grignard reagents

with Group 13–halide complexes. These include the first examples of terminal phosphavinyl–Group 13 complexes, **2** and **3**, several examples of which, **3a**–**3c**, are formed via a facile phosphavinyl coupling reaction. We are currently extending this study to explore the interaction of **1** with other main group halides, initial results of which are showing remarkable differences between the chemistries of phosphavinyl and vinyl Grignard reagents. The outcome of these explorations will be the subject of a forthcoming publication.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity Ar or dinitrogen. Toluene was distilled over potassium then freeze–thaw degassed prior to use. ^{1}H- and ^{31}P-NMR spectra were recorded on either a Bruker AMX360 or Bruker DPX400 spectrometer in C_6D_6 and were referenced to the residual ^{1}H resonances of the solvent used (^{1}H-NMR) or to external 85% H_3PO_4, 0.0 ppm (^{31}P-NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under Ar, and are uncorrected. The elemental analysis of **2** was carried out at the Warwick Analytical Service. Reproducible elemental analyses of **3a**–**c** could not be obtained due to the air sensitivity of these compounds. ^{13}C data for **2** were difficult to obtain due to its low solubility in non-coordinating solvents. ^{13}C data for **3a**–**c** were difficult to interpret due to numerous overlapping peaks and phosphorus couplings. Compound **1** was prepared by a literature procedure [2]. All other reagents were used as received.

4.1. $CyIn\{C(^{t}Bu)=PCy\}_2$ (2)

To a suspension of $InBr_3$ (0.20 g) in toluene (20 ml) at −78°C was added CyMgCl (0.28 ml of 2 M Et_2O solution, 0.56 mmol). The resulting suspension was warmed to room temperature (r.t.) and stirred overnight. The solution was cooled to −78°C and to this was added a solution of **1** (0.35 g, 1.12 mmol) in toluene (10 ml). The resulting solution was warmed to r.t. and stirred for 6 h whereupon it was filtered and cooled to −30°C to yield colourless crystals of **2** (0.13 g, 40%), m.p. 74–76°C. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ 1.29 (s, 18H, ^{t}Bu), 1.0–1.9 (m, 33H, Cy). ^{31}P{^{1}H}-NMR (145.8 MHz, C_6D_6): δ 329 (P=C). IR (Nujol, ν cm^{-1}): 1023 (m), 802 (m) 727 (m), MS APCI; m/z: 482 ([M^+ − Cy], 15), 367 ([CyPC^{t}BuInC^{t}Bu$^+$], 100), 298 ([CyPC^{t}BuIn$^+$], 15%); Anal. Found: C, 58.99; H, 9.00. Calc. for $C_{28}H_{51}InP_2$: C, 59.90; H, 8.62%.

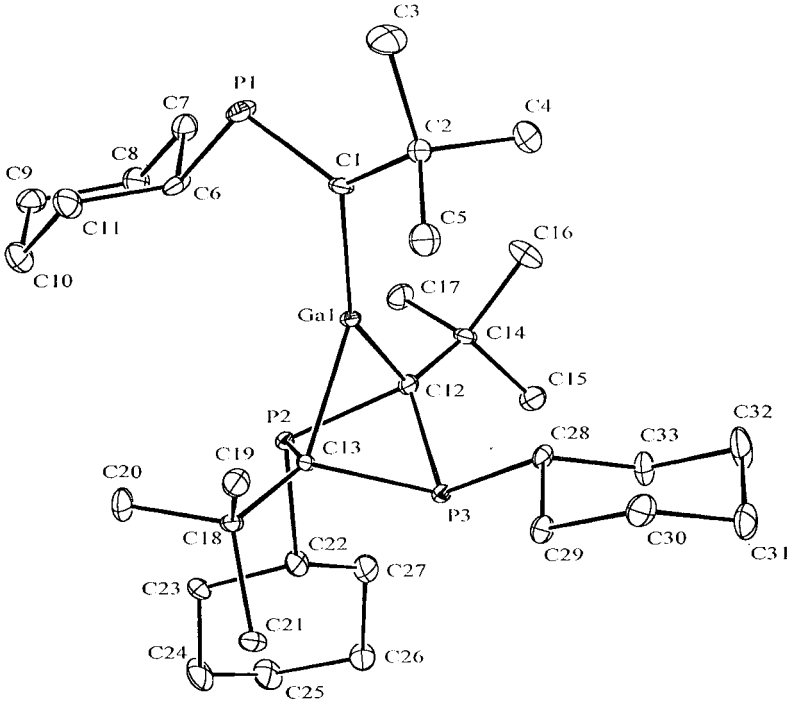


Fig. 3. Molecular structure of **3b**. Selected bond lengths (Å) and angles (°): P(1)–C(1), 1.683(7); P(1)–C(6), 1.879(8); Ga(1)–C(1), 1.968(7); Ga(1)–C(12), 2.023(8); Ga(1)–C(13), 2.005(7); P(2)–C(12), 1.892(7); P(2)–C(13), 1.957(8); P(3)–C(12), 1.882(8); P(3)–C(13), 1.947(8); C(1)–P(1)–C(6), 106.2(3); Ga(1)–C(1)–P(1), 115.7(4); C(13)–Ga(1)–C(12), 73.5(3); C(12)–P(2)–C(13), 77.5(3); C(12)–P(3)–C(13), 78.0(3); P(3)–C(12)–P(2), 87.4(3); P(3)–C(12)–Ga(1), 87.2(3); P(2)–C(12)–Ga(1), 85.7(3); P(3)–C(13)–P(2), 83.9(3); P(3)–C(13)–Ga(1), 86.0(3); P(2)–C(13)–Ga(1), 84.5(3).

4.2. $Al(C_2{}^tBu_2P_2Cy_2)\{C(^tBu)=PCy\}$ (3a)

To a suspension of $AlCl_3$ (0.05g, 0.37 mmol) in toluene (25 ml) at −78°C was added a solution of **1** (0.35 g, 1.11 mmol) in toluene (10 ml). The resulting suspension was warmed to r.t., stirred overnight and filtered. The filtrate was reduced and placed at −30°C to yield yellow crystals of **3a** (0.10 g, 49%), m.p. (dec.) 175 − 180°C. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ 0.95 (br. s, 18H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 0.92–2.21 (m, 33H, Cy). $^{31}P\{^1H\}$-NMR (145.8 MHz, C_6D_6): δ 23.6 (s, PCy), 37.9 (s, PCy), 353 (P=C). IR (Nujol, ν cm^{-1}): 1376 (m), 1260 (m) 1020 (m). MS APCI; m/z: 367 ([$P_2Cy_2C'_2Bu_2$], 100), 284 ([$P_2CyC'_2Bu_2$], 15%).

4.3. $Ga(C_2{}^tBu_2P_2Cy_2)\{C(^tBu)=PCy\}$ (3b)

To a suspension of $GaCl_3$ (0.06 g, 0.34 mmol) in toluene (25 ml) at −78°C was added a solution of **1** (0.35 g, 1.11 mmol) in toluene (10 ml). The resulting suspension was warmed to r.t., stirred overnight and filtered. The filtrate was reduced and placed at −30°C to yield yellow crystals of **3b** (0.03 g, 15%), m.p. (dec.) 115–118°C. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ 1.24 (br. s, 18H, ^{t}Bu), 1.75 (s, 9H, ^{t}Bu), 1.08–2.32 (m, 33H, Cy). $^{31}P\{^1H\}$-NMR (145.8 MHz, C_6D_6): δ 4.1 (s, PCy), 29.0 (s, PCy), 333 (P=C). IR (Nujol, ν cm^{-1}): 1376 (m), 1260 (m) 1092 (m), 800 (m). MS APCI; m/z: 454 [$M^+ - 2Cy$].

4.4. $In(C_2{}^tBu_2P_2Cy_2)\{C(^tBu)=PCy\}$ (3c)

To a suspension of $InBr_3$ (0.24 g, 0.68 mmol) in toluene (25 ml) at −78°C was added a solution of **1** (0.70 g, 2.2 mmol) in toluene (10 ml). The resulting suspension was warmed to r.t., stirred overnight and filtered. The filtrate was reduced and placed at −30°C to yield yellow crystals of **3c** (0.19 g, 42%), m.p. 74–76°C. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ 1.40 (br. s, 18H, ^{t}Bu), 1.72 (s, 9H, ^{t}Bu), 1.09–2.41 (m, 33H, Cy). $^{31}P\{^1H\}$-NMR (145.8 MHz, C_6D_6): δ 8.8 (s, PCy), 24.2 (s, PCy), 329 (P=C). IR (Nujol, ν cm^{-1}): 1377 (m), 1262 (m) 1018 (m). MS APCI; m/z: 367 ([$P_2Cy_2C'_2Bu_2$], 100), 298 ([CyPC$'$BuIn], 20%).

5. Crystallographic studies

All crystallographic measurements were made using an Enraf–Nonius CAD4 diffractometer. The structures of **2**, **3a** and **3b** were solved by direct methods and refined on F^2 by full-matrix least-squares (SHELX-97) [10] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Empirical absorption corrections were carried out by the DIFABS method [11]. The data for the structure of compound **3b** were weak but the fact that this structure is isomorphous to that of **3a** leaves no doubt about the gross molecular framework of the compound.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158733, 158734 and 158735 for compounds **2**, **3a** and **3b**, respectively. Copies of this information may be obtained free of charge 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).

Acknowledgements

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