Reaction of electron-deficient triosmium cluster Os$_3$(CO)$_8${μ$_3$-Ph$_2$PCH(CH$_3$)P(Ph)C$_6$H$_4$}(μ-H) with HCl: X-ray structure of two isomers of Os$_3$(CO)$_8${μ-Ph$_2$PCH(CH$_3$)PPh$_2$}(μ-Cl)(μ-H)

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Treatment of electron-deficient Os$_3$(CO)$_8${μ$_3$-Ph$_2$PCH(CH$_3$)-P(Ph)C$_6$H$_4$}(μ-H) (**1**) with HCl at room temperature furnishes the adduct Os$_3$(CO)$_8${μ-Ph$_2$PCH(CH$_3$)PPh$_2$}(μ-Cl)(μ-H) (**2**) in almost quantitative yield via oxidative addition of H–Cl bond. Cluster (**2**) is electron-precise and contains bridging chloride and hydride ligands which rearranges upon heating at 110 °C to form isomeric (**3**). Both clusters have been characterized by a combination of elemental analyses, IR and NMR spectroscopic data together with single crystal X-ray diffraction studies.

Low-valent triosmium clusters readily react with a range of protic acids depending on the basicity of the cluster core.[1-15] For instance, Os$_3$(CO)$_{12}$ reacts with concentrated H$_2$SO$_4$ to give the cationic species[1-3] [Os$_3$(CO)$_{12}$(μ-H)]$^+$, whereas protonation of its relatively electron rich mono- and di-phosphine derivatives occurs more readily on treatment with weaker acids such as CF$_3$CO$_2$H.[9] In most cases, the incoming proton is disposed across an osmium-osmium vector to give simple cationic hydrido species, but coordination of the conjugate base to the osmium centers is not uncommon especially when the acids contain anions of coordinating nature. For example, reactions of the cyclometallated Os$_3$(CO)$_9$(μ$_3$-PPhC$_6$H$_4$)(μ-H)$_2$ with HX (X = F, Cl, Br, CF$_3$CO$_2$) proceed via initial protonation followed by coordination of the conjugate base to give Os$_3$(CO)$_9$(X)(μ$_3$-PPh$_2$)(μ-H)$_2$, whereas this cluster affords only the simple protonation product [Os$_3$(CO)$_9$(μ$_3$-PPhC$_6$H$_4$)(μ-H)$_3$]$^+$ when treated with HBF$_4$.[12]

The electron-deficient triosmium cluster Os$_3$(CO)$_8${μ$_3$-Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$}(μ-H), first prepared by Smith and co-workers upon decarbonylation of Os$_3$(CO)$_{10}$(μ-dppm), has attracted considerable interest for its catalytic potential as well as applications in organic synthesis.[16–22] This cluster has a formal electron count of 46 and reacts with various electron donor ligands under mild conditions relative to electron precise clusters.[23] It also reacts with a range of protic acids leading to a variety of products depending on the coordinating nature of the conjugate bases.[13] Recently, we have prepared the isostructural electron-deficient cluster Os$_3$(CO)$_8${μ$_3$-Ph$_2$PCH(CH$_3$)P(Ph)C$_6$H$_4$}(μ-H) (**1**) from the decarbonylation of Os$_3$(CO)$_{10}$(μ-dppmMe) [dppmMe = Ph$_2$PCH(CH$_3$)PPh$_2$]. The two faces of this cluster with respect to the metallic triangle are differentiated by the presence of methyl group on the backbone carbon of diphosphine.[24] We have initiated a study to investigate the reactivity of (**1**) with various electron donors and herein we report its reaction with HCl.

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. The synthesis of Os$_3$(CO)$_8${μ$_3$-Ph$_2$PCH(CH$_3$)P(Ph)C$_6$H$_4$)}(μ-H) (**1**)[24] and Ph$_2$PCH(Me)PPh$_2$[25] were carried out following literature procedure. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer while the NMR spectra were recorded on a DPX 400 instrument. The chemical shifts were referenced to residual solvent resonances or external 85% H$_3$PO$_4$ in ^{1}H and ^{31}P spectra respectively. Elemental analyses were carried out in the Microanalytical Laboratories of Wazed Miah Science Research Centre at Jahangirnagar University. Preparative thin layer chromatography was carried out on 1 mm plates prepared from silica gel GF254 (type 60, E. Merck) at Jahangirnagar University.

To study the reaction of $Os_3(CO)_8$ $\{\mu_3$-Ph_2 $PCH(CH_3)P(Ph)C_6H_4\}(\mu$-H$)$ (**1**) with HCl, the acid was passed through a CH_2Cl_2 (35 mL) solution of $Os_3(CO)_8\{\mu_3$-$Ph_2PCH(CH_3)P(Ph)C_6H_4)\}(\mu$-H$)$ (**1**) (125 mg, 0.105 mmol) for 2 min. The initial green solution turned red and the reaction mixture was then stirred for another 30 min at room temperature. The solvent was removed under reduced pressure and the residue yielded $Os_3(CO)_8$ $\{\mu$-$Ph_2PCH(CH_3)PPh_2\}(\mu$-Cl$)(\mu$-H$)$ (**2**) (121mg, 94%) as red crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C.

$Os_3(CO)_8\{\mu$-$Ph_2PCH(CH_3)PPh_2\}(\mu$-Cl$)(\mu$-H$)$ (**2**): Anal. (%): Calcd. for $C_{34}H_{25}ClOs_3O_8P_2$: C, 33.21; H, 2.05. Found: C, 33.94; H, 2.13. IR (v_{CO}, CH_2Cl_2): 2076 s, 2027 m, 2002 vs, 1982 sh, 1956 s, 1926 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.62 (m, 3H), 7.54-7.37 (m, 13H), 7.21 (m, 4H), 4.33 (m,1H), 1.06 (m, 3H), -12.93 (dd, J 31.6, 1.6 1H). ^{31}P$\{^1$H$\}$ NMR($CDCl_3$): δ: -1.8(d, J 48, 1P), -10.6 (d, J 48, 1P).

Thermolysis of $Os_3(CO)_8\{\mu$-$Ph_2PCH(CH_3)PPh_2\}$ $(\mu$-Cl$)(\mu$-H$)$ (**2**) was carried out as follows: $Os_3(CO)_8$ $\{\mu$-$Ph_2PCH(CH_3)PPh_2\}(\mu$-Cl$)(\mu$-H$)$ (**2**) (30 mg, 0.024 mmol) was heated in boiling toluene for 3 hours. The colour of the reaction mixture changed from orange to pale yellow during this time. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed three bands. The second band gave $Os_3(CO)_8$ $\{\mu$-$Ph_2PCH(CH_3)PPh_2\}(\mu$-Cl$)(\mu$-H$)$ (**3**) (21 mg, 70%) as pale yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4°C.

$Os_3(CO)_8\{\mu$-$Ph_2PCH(CH_3)PPh_2\}(\mu$-Cl$)(\mu$-H$)$ (**3**): Anal. (%): Calcd. for $C_{34}H_{25}ClOs_3O_8P_2$: C, 33.21; H, 2.05. Found: C, 34.04; H, 2.11. IR (v_{CO}, CH_2Cl_2): 2076 s, 2004 vs, 1995 sh, 1955 w, 1942 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 3H), 7.17 (m, 13H), 7.05 (m, 4H), 4.05 (m, 1H), 1.24 (m, 1H), -16.44 (t, J 11.0, 1H). ^{31}P$\{^1$H$\}$ NMR($CDCl_3$): δ -11.5 (s).
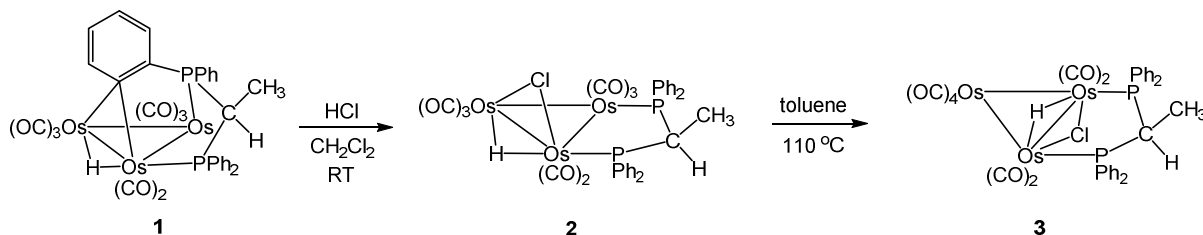
Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of (**2**) and (**3**) at 4 °C and mounted on a MiteGen loop with Apiezen grease at 277 K and 293 K for (**2**) and (**3**), respectively. Diffraction studies were carried out on a Rigaku XtaLab mini bench-top instrument. Data collection and data reduction was done with the "Crystal Clear" software of the instrument. The radiation source was graphite monochromated Mo-Kα (λ = 0.71073Å) radiation. The final cell parameters were determined from least squares refinement on 8324 and 2401 reflections for (**1**) and (**2**), respectively. Compounds (**1**) and (**2**) crystallized in orthorhombic (space group: *Pbca*) and monoclinic (space group: *P2$_1$/c*) crystal systems, respectively. Structures were solved by direct methods and expanded using Fourier techniques.[26] Crystals of both compounds were disordered as was apparent from the images. Compound (**2**) had many closely spaced faint reflections aside from intense circular ones. No twin law could be derived for this crystal. Compound (**3**) on the other hand had in general faint elliptically elongated reflections. This crystal was a poor diffractor as well. The C21 atom of compound (**2**) was refined by ISOR command, and all the carbon atoms of compound (**3**) were refined isotropically, since anisotropic refinement would result in non-positive definite. There was positive residual density near the metal atom locations which may be due to the inherent disorder in the lattice. All other non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in their expected positions using the HFIX command and were included in the final cycles of least squares with isotropic Uij related to the atoms ridden on. Structure solution and refinement was performed from within WINGX program suit.[27]

Results and discussion

Room temperature reaction between the electron-deficient $Os_3(CO)_8\{\mu_3$-$Ph_2PCH(CH_3)P(Ph)C_6H_4\}(\mu$-H$)$

Reactivity of $Os_3(CO)_8\{\mu_3$-$Ph_2PCH(CH_3)P(Ph)C_6H_4\}(\mu$-H$)$ (1) towards HCl

Scheme 1

(**1**) and HCl, followed by the usual work up, afforded only $Os_3(CO)_8\{\mu\text{-}Ph_2PCH(CH_3)PPh_2\}(\mu\text{-}Cl)(\mu\text{-}H)$ (**2**) in almost quantitative yield (Scheme 1). Multiple addition of chloride leading to osmium-osmium bond scission, as seen in a similar reaction between the electron-deficient $Os_3(CO)_8\{\mu_3\text{-}Ph_2PCH_2P(Ph)C_6H_4\}(\mu\text{-}H)$ and HCl, was not observed in this reaction.[13] Cluster (**2**) was formed by oxidative-addition of H–Cl bond to (**1**) with concomitant reductive-elimination of the metallated phenyl ring. It has been characterized by a combination of elemental analyses, infrared and NMR spectroscopic data and single crystal X-ray diffraction analysis.

The crystal data and structure refinement details for (**1**) and (**2**) are given in Table 1. The solid state molecular structure of (**2**) is depicted in Fig. 1 with the caption containing selected bond distances and angles. The molecule consists of a triosmium core ligated by eight terminally bonded carbonyls and each of the following three ligands bonded in bridging capacity: $Ph_2PCH(CH_3)PPh_2$, chloride and hydride. The osmium metals make an equilateral triangle with three equal Os–Os bond lengths [2.850(2), 2.840(3)
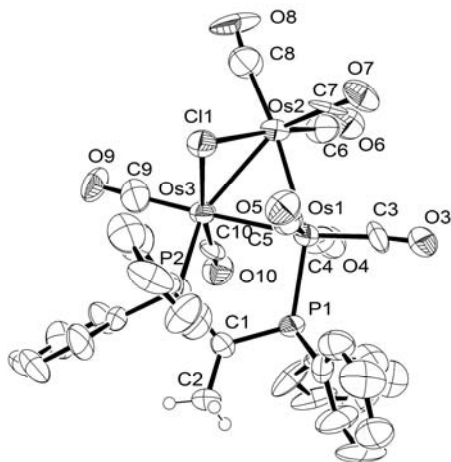
and 2.842(3) Å] and three Os–Os–Os angles of 60° [59.87(7), 60.20(4) and 59.93(5)°] within the experimental error. The chloride symmetrically bridges the same Os—Os edge [Os(2)—Cl(1) 2.465(7) and Os(3)—Cl(1) 2.479(7) Å] bridged by the hydride. The hydride ligand was not located from the structural study but is believed to span across this edge and

Fig. 1—The solid state molecular structure of $Os_3(CO)_8$ $\{\mu\text{-}Ph_2PCH(CH_3)PPh_2\}(\mu\text{-}Cl)(\mu\text{-}H)$ (**2**) showing 50% probability thermal ellipsoids. Ring hydrogen atoms are omitted for clarity. [Selected bond distances (Å) and angles (°): Os(1)—Os(2) 2.850(2), Os(1)—Os(3) 2.840(3), Os(2)—Os(3) 2.842(3), Os(2)—Cl(1) 2.465(7), Os(3)—Cl(1) 2.479(7), Os(1)—P(1) 2.339(7), Os(2)—P(2) 2.329(7); Os(1)—Os(2)—Os(3) 59.87(7), Os(1)—Os(3)—Os(2) 60.20(4), Os(2)—Os(1)—Os(3) 59.93(5), P(1)—Os(1)—Os(2) 153.07(17), P(1)—Os(1)—Os(3) 93.25(16), P(2)—Os(3)—Os(1) 86.35(16), P(2)—Os(3)—Os(2) 137.70(17), Os(2)—Cl(1)—Os(3) 70.17(18), Cl(1)—Os(2)—Os(3) 55.15(17), Cl(1)—Os(3)—Os(2) 54.68(17), Cl(1)—Os(2)—Os(1) 86.15(18), Cl(1)—Os(3)—Os(1) 86.09(15), Cl(1)—Os(2)—C(6) 171.1(11), Cl(1)—Os(2)—C(7) 97.8(10), C(8)—Os(2)—Os(3) 113.8(11), C(7)—Os(2)—Os(1) 86.0(8), C(9)—Os(3)—Os(2) 118.2(11), C(3)—Os(1)—Os(2) 109.6(10)].

Table 1—Crystal data and structure refinement details for compounds (**2**) and (**3**)

Comp.	(**2**)	(**3**)
Emp. formula	$C_{34}H_{24}ClO_8Os_3P_2$	$C_{34}H_{25}ClO_8Os_3P_2$
Formula w	1228.62	1229.57
Temp. (K)	277(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*P2₁/c*
Unit cell dimensions		
a (Å)	11.309(10)	9.469(10)
b (Å)	19.872(18)	16.730(18)
c (Å)	31.69(3)	24.90(3)
α (°)	90	90
β (°)	90	97.437(13)
γ (°)	90	90
Vol. (Å³)	7122(11)	3911(8)
Z	8	4
Density (calc.) (mg/m³)	2.292	2.095
Abs. coeff. (mm⁻¹)	10.892	9.918
F(000)	4536	2280
Crystal size (mm³)	0.27×0.21×0.09	0.20×0.15×0.07
Range for data collection (°)	2.05 to 25.00	3.14 to 22.50
Index ranges	$-6 \le h \le 13$, $-23 \le k \le 23$, $-37 \le l \le 32$	$-10 \le h \le 10$, $-18 \le k \le 17$, $-26 \le l \le 26$
Reflections collected	13171	19139
Ind. reflections [R_{int}]	5712 [$R_{int} = 0.0881$]	5068 [$R_{int} = 0.1440$]
Max. and min. transmission	0.4406 and 0.1570	0.5436 and 0.2417
Data/ restraints/ parameters	5712/ 0/ 428	5068/ 0/ 267
Goodness of fit on F^2	1.024	1.019
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0810$, $wR_2 = 0.1929$	$R_1 = 0.0685$, $wR_2 = 0.1387$
R indices (all data)	$R_1 = 0.1287$, $wR_2 = 0.2329$	$R_1 = 0.1266$, $wR_2 = 0.1663$
Largest diff. peak and hole (e. Å⁻³)	2.727 and −2.365	1.556 and −1.573

approximately lying within the metallic plane as evident from the widening of OC–Os–Os angles across this edge [C(8)─Os(2)─Os(3) 113.8(11), C(7)─Os(2)─Os(1) 86.0(8), C(9)─Os(3)─Os(2) 118.2(11) and C(3)─Os(1)─Os(2) 109.6(10)°]. The chloride occupies one of the axial coordination sites of both Os(2) and Os(3) and spatially oriented on the same face of the metallic plane with respect to the backbone methyl group. Overall the molecule is isostructural with its dppm analog $Os_3(CO)_8$-{μ-Ph$_2$PCH$_2$PPh$_2$}(μ-Cl)(μ-H)[13] with some subtle difference in molecular geometry. The solution spectroscopic data show that the molecule retains its solid state geometry in solution. The IR spectrum of (**2**) displays six carbonyl absorptions between 2076-1926 cm^{-1} indicating that all the carbonyls are terminally bonded to osmium centers. The $^{31}P\{^1H\}$ NMR spectrum exhibits two equally intense doublets at −1.77 and −10.62 ppm for the two inequivalent phosphorus atoms, whilst the ^1H NMR shows an upfield doublet at −12.93 ppm for the bridging hydride together with resonances for the phenyl, methyl and methine protons of the diphosphine.

Thermolysis of (**2**) in boiling toluene led to the formation of isomeric $Os_3(CO)_8${μ-Ph$_2$PCH(CH$_3$)-PPh$_2$}(μ-Cl)(μ-H) (**3**) in 70% yield. Clusters (**2**) and (**3**) differ in the position of bridging chloride and hydride ligands across Os–Os edges. Whilst these ligands bridge a separate edge in (**2**), they span the same edge bridged by the diphosphine in (**3**). Cluster (**3**) has also been characterized by IR and NMR spectroscopic data together with single crystal X-ray diffraction analysis.

An ORTEP diagram of the molecular structure of (**3**) is shown in Fig. 2 with the caption containing selected bond lengths and angles. The osmium metals make an approximate isosceles triangle with two short [Os(1)─Os(2) 2.814(3) and Os(1)─Os(3) 2.839(3) Å] and one relatively long metal-metal bonds [Os(2)─Os(3) 2.872(3) Å]. The diphosphine, chloride and hydride bridge the same Os–Os vector in (**3**) and among the eight carbonyls the remote osmium, Os(3), is coordinated to four while the rest are evenly distributed between Os(1) and Os(2). The Os–Cl bond lengths [Os(1)─Cl(1) 2.510(6) and Os(2)─Cl(1) 2.499(6) Å] are the same within experimental error, indicating that the chloride bridges the Os(1)─Os(2) edge symmetrically. The chloride occupies one of the axial coordination sites of both Os(1) and Os(2) and located on the opposite face of the metallic plane with

respect to the backbone methyl group of the diphosphine. The Os–P bond lengths in (**3**) [Os(1)─P(1) 2.378(6) and Os(2)─P(2) 2.385(6) Å] is *ca.* 0.05 Å longer compared to those observed in (**2**), probably due to the accommodation of chloride and hydride along the Os(1)─Os(2) edge. The molecule possesses a non-crystallographic mirror plane of symmetry passing through the remote osmium, Os(3), and bisecting Os(1)─Os(2) vector, and the gross structural features are very similar to its dppm analog $Os_3(CO)_8${μ-Ph$_2$PCH$_2$PPh$_2$}(μ-Cl)(μ-H)[13]. The spectroscopic data of (**3**) are consistent with the solid state structure indicating that the solid state structure persists in solution The IR spectrum shows carbonyl absorptions above 1850 cm^{-1} indicating the presence of only terminally bonded CO ligands in the molecule. The $^{31}P\{^1H\}$ NMR spectrum displays only a singlet at −11.5 ppm attributed to the equivalent phosphorus atoms of the diphosphine, whilst the ^1H NMR shows an triplet at −16.44 ppm for the bridging hydride together with resonances for the phenyl, methyl and methine protons of the diphosphine.
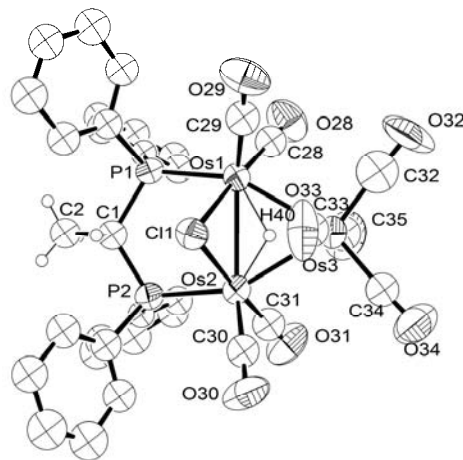

Fig. 2—The solid state molecular structure of $Os_3(CO)_8$ {μ-Ph$_2$PCH(CH$_3$)PPh$_2$}(μ-Cl)(μ-H) (**3**) showing 50% probability thermal ellipsoids. Ring hydrogen atoms are omitted for clarity. [Selected bond distances (Å) and angles (°): Os(1)─Os(2) 2.814(3), Os(1)─Os(3) 2.839(3), Os(2)─Os(3) 2.872(3), Os(1)─Cl(1) 2.510(6), Os(2)─Cl(1) 2.499(6), Os(1)─P(1) 2.378(6), Os(2)─P(2) 2.385(6), Os(1)─H(40) 1.90(10), Os(2)─H(40) 1.34(11), Os(3)─H(40) 1.74(10); Os(1)─Os(2)─Os(3) 59.89(6), Os(1)─Os(3)─Os(2) 59.04(4), Os(2)─Os(1)─Os(3) 61.07(8), P(1)─Os(1)─Os(2) 94.61(15), P(1)─Os(1)─Os(3) 155.55(13), P(2)─Os(2)─Os(1) 94.68(16), P(2)─Os(2)─Os(3) 154.45(14), Os(1)─Cl(1)─Os(2) 68.36(14), Cl(1)─Os(1)─Os(2) 55.64(13), Cl(1)─Os(2)─Os(1) 56.01(13), Cl(1)─Os(2)─Os(3) 84.70(13), Cl(1)─Os(1)─Os(3) 85.20(14), Cl(1)─Os(1)─C(28) 176.6(7), Cl(1)─Os(1)─C(29) 91.7(7)].

The present study shows that oxidative addition of HCl to the electron-deficient triosmium cluster (**1**) gives the electron-precise $Os_3(CO)_8\{\mu\text{-}Ph_2PCH(CH_3)PPh_2\}$-$(\mu\text{-}Cl)(\mu\text{-}H)$ (**2**) in which both cholride and hydride adopt bridging coordination mode thus acting as 3e and 1e donors, respectively, and span a different Os–Os edge with respect to the diphosphine. Cluster (**2**) undergoes rearrangement at high temperature to afford isomeric (**3**) in which all the bridging ligands span the same Os–Os edge. This rearrangement requires migration of both the bridging cholride and hydride ligands together with a carbonyl. The reactivity of (**1**) towards HCl is similar to that reported for its dppm analog $Os_3(CO)_8\{\mu_3\text{-}Ph_2PCH_2P(Ph)C_6H_4\}(\mu\text{-}H)$ except that multiple addition of chloride to (**1**) was not observed.

Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data centre. CCDC 1061837 and CCDC 1061838 contain supplementary crystallographic data for compounds (**2**) and (**3**) respectively. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

Acknowledgment

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