Protonation of Electron-rich Diphosphazane-bridged Derivatives of Dicobalt Octacarbonyl: Crystal Structure of $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4{\cdot}CH_2Cl_2$†

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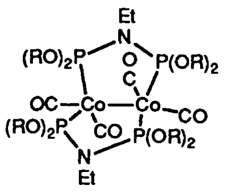
Protonation of $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) proceeds without CO loss to give $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$. Proton n.m.r. spectroscopic data, as well as an *X*-ray structure determination of $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4$, confirm the presence of a bridging hydride ligand. Both cobalt atoms are trigonal bipyramidal but the overall conformation is staggered as evidenced by P–Co–Co–P torsion angles of 34.7(1) and 35.7(1)°. Attempts to form a dihydrido species by addition of H^- merely served to deprotonate the cation with formation of the starting complex and H_2.

We have recently reported the syntheses of diphosphazane ligand-bridged derivatives of $[Co_2(CO)_8]$ of formula $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**1**; R = CH_2, Me, or Pr^i)[1] and the crystal and molecular structure of $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$[2] in particular. Being electron-rich, these compounds are expected to be susceptible to electrophilic attack and to display similar reactivity patterns to those exhibited by the closely related $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe or Ru; R = Me or Pr^i) complexes.[3] Of interest here is the reaction of $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with protons; we wished to ascertain whether a cobalt analogue of $[M_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$(M = Rh[4]orIr[5])wouldform, *i.e.* whether decarbonylation would occur with formation of a bridging hydride, bridging carbonyl species. Indeed, reaction of $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with halogens has been shown to lead to CO loss and formation of cations of the type $[Co_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = Cl, Br, or I)[6] but, of course, a bridging halogen atom is considered to be a three-electron donor, whereas the proton will not contribute any electrons to the metal-atom valency shell.

Results and Discussion

Reaction of the $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) complex in methanol with acids such as HPF_6, HBF_4, and HCl rapidly afforded a new compound which exhibited strong peaks in the ν(CO) region of the i.r. spectrum at 2 020, 1 986 (R = Me) or 2 010, 1 977 cm^{-1} (R = Pr^i) measured in dichloromethane. Isolation of a red crystalline solid from the reaction of $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ in methanol with HPF_6, and its subsequent characterisation as $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (**2**, PF_6) confirmed that in all these reactions the electron-rich neutral compound is readily protonated without loss of CO ligand. The ^1H n.m.r. spectrum of the $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Me or Pr^i) cation shows a regular quintet centred at δ −10.55 (R = Me) or −10.61 (R = Pr^i), measured in $CDCl_3$, indicative of a bridging hydride ligand which couples with four equivalent phosphorus atoms. A single broad resonance at δ 153.52 p.p.m. in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the cation (relative to H_3PO_4 and measured in $CDCl_3$) confirms that the phosphorus atoms are equivalent, at least at room temperature.



(1)

In order to establish the structure of cation (**2**) unambiguously an *X*-ray diffraction study was carried out. The crystals used were of the BPh_4^-, rather than the PF_6^-, salt since it proved impossible to grow crystals of the latter suitable for *X*-ray analysis. Single crystals of (**2**, BPh_4) were grown from a solution of (**2**, PF_6) in dichloromethane–light petroleum to which $NaBPh_4$ had been added. The Figure gives a perspective view of (**2**) while Table 1 lists selected interatomic distances and angles and, in particular, the angles at each cobalt atom. The cobalt atoms are bridged by the two diphosphazane ligands as well as by the hydrogen atom, the latter being reliably located in an electron-density map and its position refined. The co-ordination at each cobalt atom is completed by two carbonyl groups resulting in a trigonal-bipyramidal geometry at each metal atom which is nearly regular, see Table 1. In this description one cobalt atom is *not* considered to take-up a co-ordination site in the co-ordination sphere of the other, the implication being that there is little orbital overlap along the line joining the two cobalt atoms (see below).

The Co(1)···Co(2) distance of 2.736(1) Å is significantly longer than the values reported for cobalt metal[7] (2.522 Å), $[Co_2(CO)_8]$[8] (2.522 and 2.525 Å), $[Co_2(\eta^5\text{-}C_5H_5)(\mu\text{-}$

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† Bis(μ-2-ethyl-1,1,3,3-tetramethoxodiphosphazane-*PP′*)-μ-hydrido-bis(dicarbonylcobalt) tetraphenylborate–dichloromethane (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

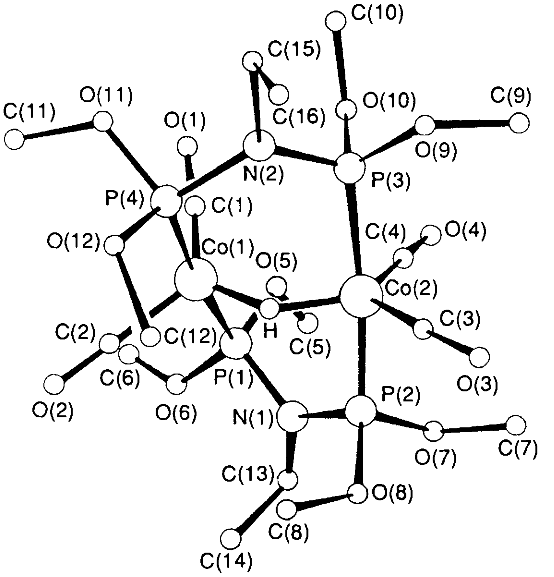
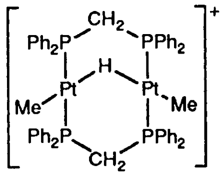


Figure. Stereochemistry of $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$, (**2**)

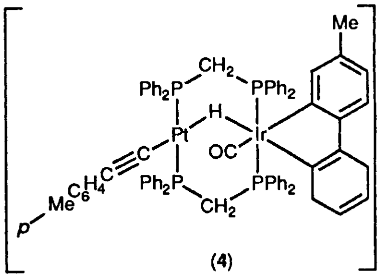
Table 1. Selected interatomic distances (Å) and angles (°) for $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4\cdot CH_2Cl_2$

Co(1) ··· Co(2)	2.736(1)	P(1) ··· P(2)	2.820(3)
P(3) ··· P(4)	2.817(3)		
Co(1)–P(1)	2.152(2)	Co(2)–P(2)	2.136(2)
Co(1)–P(4)	2.147(2)	Co(2)–P(3)	2.145(2)
Co(1)–C(1)	1.757(10)	Co(2)–C(3)	1.759(11)
Co(1)–C(2)	1.775(9)	Co(2)–C(4)	1.772(11)
Co(1)–H	1.56(8)	Co(2)–H	1.50(7)
P(1)–Co(1)–P(4)	173.0(1)	P(1)–Co(2)–P(3)	174.6(1)
P(1)–Co(1)–C(1)	91.1(3)	P(2)–Co(2)–C(3)	92.1(3)
P(1)–Co(1)–C(2)	91.8(3)	P(2)–Co(2)–C(4)	90.7(3)
P(1)–Co(1)–H	93(3)	P(2)–Co(2)–H	88(3)
P(4)–Co(1)–C(1)	90.3(3)	P(3)–Co(2)–C(3)	92.1(3)
P(4)–Co(1)–C(2)	93.2(3)	P(3)–Co(2)–C(4)	90.7(3)
P(4)–Co(1)–H	81(3)	P(3)–Co(2)–H	87(3)
C(1)–Co(1)–C(2)	122.2(4)	C(3)–Co(2)–C(4)	124.2(4)
C(1)–Co(1)–H	129(3)	C(3)–Co(2)–H	104(4)
C(2)–Co(1)–H	108(3)	C(4)–Co(2)–H	132(4)
Co(1)–H–Co(2)	127(6)		

$PMe_2)(CO)_4]$[9] [2.593(1) Å], $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ [2.635(1) Å],[2] and $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)]$[10] [2.637(1) Å]. On this basis any interaction between the cobalt atoms would appear to be weak, although it should be noted that a single hydride bridge is considered to lengthen a metal–metal bond.[11] Also noteworthy is that, assuming precise *dsp*³ hybridisation at both cobalt atoms, the hybrid orbital at each cobalt atom involved in overlap with the hydrogen 1*s* orbital does not point directly at the bridging hydrogen atom, but at the centre of the CoHCo triangle. This is evident from the larger C(1)–Co(1)–H [129(3)°] and C(4)–Co(2)–H [132(4)°] angles compared to C(2)–Co(1)–H [108(3)°] and C(3)–Co(2)–H [104(4)°]. As Bau *et al.*[12] have noted, this result provides evidence for at least a degree of metal–metal overlap in a closed M–H–M system (M = metal). Nevertheless, in the structure represented in the Figure the vector between the cobalt atoms is omitted because this better reflects the trigonal-bipyramidal co-ordination at each cobalt atom.[13]



(**3**)



(**4**)

The Co–H distances in (**2**) of 1.56(8) and 1.50(7) Å are somewhat shorter than the values determined by neutron diffraction for the triply bridging hydride in $[FeCo_2(\mu_3\text{-}H)(CO)_9\{P(OMe)_3\}_3]$[14] of 1.728(3), 1.731(3), and 1.742(3) Å. As Bau *et al.*[12] have noted, M–H distances measured by *X*-ray methods are often 0.1—0.2 Å shorter than their true values and this is probably the case here. Nevertheless, the *X*-ray evidence indicates a symmetrically bridging hydride, as does the observation that there is no change in either the ^1H or the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum when the temperature is varied between room temperature and −90 °C. This is in contrast to the situation in $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)]$[10] where the Co–H distances of 1.37(8) and 1.84(7) Å differ significantly.

Two *X*-ray structure determinations have been reported of dinuclear complexes in which the two metal atoms are bridged by two bidentate donor ligands ($Ph_2PCH_2PPh_2$ in both cases) and by a single hydride ligand, *viz.* $[Pt_2(\mu\text{-}H)Me_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$[15] (**3**) and $[(p\text{-}MeC_6H_4C{\equiv}C)Pt(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}H)Ir(CO)\{C{=}C(C_6H_3Me)CH_2CH{=}CHCH_2\}]^+$[16] (**4**), but in neither case was it possible to locate the bridging hydrogen atom.

The P–M–M–P torsion angles (M = metal) in these two complexes are 0(1) and 4.5(1)° in complex (**3**) and 10.1 and 6.1° in (**4**) which may be compared with values for the P–Co–Co–P torsion angles in (**2**) of 34.7(1) and 35.7(1)°. Viewed down the M–M bond it is apparent that the structures of (**3**) and (**4**) are nearly eclipsed whereas (**2**) adopts a staggered conformation. It would appear that increased intramolecular non-bonded repulsions in (**2**), compared to (**3**) and (**4**), associated with the Co ··· Co distance of 2.736(1) Å being significantly shorter than the Pt ··· Pt distances of 2.932(1) Å in (**3**) and the Pt ··· Ir distance of 2.948(1) Å in (**4**), are responsible for the severe twisting of the diphosphazane ligands about the Co ··· Co vector.

The formal relationship of the cation (**2**) to the neutral complexes $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Me)P(OMe)_2\}_2]$ and $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ is simply the addition of H^+ across the Co ··· Co vector; no change in electron count has taken place. Yet both neutral complexes have unsymmetrical structures in that the geometries at each cobalt atom are different;[2,17] thus the presence of a bridging hydride appears to impose identical co-ordination environments on each cobalt atom. Also interesting is that CO loss does not occur in the reaction of H^+ with $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Prⁱ), *i.e.* the cobalt analogues of $[M_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ (M = Rh[4] or Ir[5]) do not form.

Several attempts were made to convert $[Co_2(\mu\text{-}H)(CO)_4(\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Me or Prⁱ) into a dihydrido species using a variety of hydride sources, *e.g.* $NaBH_4$ and KH, both at room temperature and at low temperature (−70 °C). In every case the cation was rapidly deprotonated with formation of $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Prⁱ) and H_2. Clearly, the bridging hydride is very acidic.

Table 2. Fractional atomic co-ordinates (× 10^4) for $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4\cdot CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	3 045(1)	1 040(1)	3 255(1)	C(14)	712(7)	−498(4)	1 540(8)
Co(2)	2 037(1)	1 814(1)	1 853(1)	C(15)	4 851(5)	2 549(4)	2 917(7)
P(1)	1 793(1)	723(1)	3 131(1)	C(16)	4 978(7)	2 516(5)	1 974(8)
P(2)	1 074(1)	1 119(1)	1 245(1)	B	7 387(5)	450(4)	2 472(6)
P(3)	3 075(1)	2 446(1)	2 553(1)	C(17)	7 266(4)	878(3)	1 549(5)
P(4)	4 211(1)	1 440(1)	3 255(2)	C(18)	6 530(5)	1 251(4)	1 143(6)
N(1)	1 048(4)	616(3)	2 042(4)	C(19)	6 381(6)	1 634(4)	358(7)
N(2)	4 074(4)	2 162(3)	2 857(5)	C(20)	6 987(7)	1 631(5)	−35(7)
O(1)	3 361(5)	1 652(4)	5 031(5)	C(21)	7 738(7)	1 294(5)	334(8)
O(2)	3 629(5)	−217(3)	3 232(6)	C(22)	7 865(6)	901(4)	1 136(6)
O(3)	2 057(5)	2 118(4)	52(5)	C(23)	7 615(4)	960(3)	3 328(5)
O(4)	933(4)	2 459(3)	2 603(6)	C(24)	8 449(5)	1 204(4)	3 782(5)
O(5)	1 409(3)	1 163(3)	3 681(4)	C(25)	8 667(5)	1 646(4)	4 474(6)
O(6)	1 723(3)	49(3)	3 501(4)	C(26)	8 049(5)	1 881(4)	4 760(6)
O(7)	97(3)	1 331(3)	787(4)	C(27)	7 194(5)	1 663(4)	4 320(6)
O(8)	1 094(4)	721(3)	391(4)	C(28)	6 987(5)	1 217(3)	3 608(5)
O(9)	3 176(3)	3 014(2)	1 969(4)	C(29)	8 159(4)	−65(3)	2 691(5)
O(10)	2 993(4)	2 742(3)	3 452(4)	C(30)	8 810(4)	−186(3)	3 578(5)
O(11)	4 993(3)	1 538(3)	4 252(4)	C(31)	9 434(5)	−652(4)	3 743(6)
O(12)	4 711(3)	1 092(3)	2 715(5)	C(32)	9 415(6)	−1 015(4)	3 001(6)
C(1)	3 214(5)	1 418(5)	4 315(6)	C(33)	8 765(5)	−931(4)	2 107(6)
C(2)	3 404(5)	273(4)	3 221(7)	C(34)	8 152(5)	−461(4)	1 973(5)
C(3)	2 067(6)	1 991(4)	762(6)	C(35)	6 488(4)	59(3)	2 281(5)
C(4)	1 365(5)	2 194(4)	2 320(7)	C(36)	6 284(5)	−147(4)	3 023(5)
C(5)	527(6)	1 099(5)	3 638(8)	C(37)	5 554(6)	−528(4)	2 859(6)
C(6)	2 176(7)	−119(5)	4 491(7)	C(38)	5 016(6)	−686(4)	1 963(6)
C(7)	−181(7)	1 829(5)	110(8)	C(39)	5 215(5)	−499(4)	1 228(6)
C(8)	1 892(7)	406(5)	468(7)	C(40)	5 935(5)	−125(4)	1 386(5)
C(9)	2 457(6)	3 460(4)	1 559(7)	Cl(1)	8 957(2)	2 351(2)	7 532(2)
C(10)	3 617(7)	3 179(5)	4 066(7)	Cl(2)	7 365(3)	1 762(2)	7 296(4)
C(11)	5 392(6)	998(6)	4 863(8)	C(41)	7 868(7)	2 472(6)	7 317(8)
C(12)	4 281(7)	880(5)	1 759(7)	H	2 688(47)	1 307(36)	2 236(52)
C(13)	372(5)	112(4)	1 779(7)				

Experimental

Materials.—The complex $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) was synthesised as reported previously.[1] All other reagents used were of analytical grade.

Synthesis of $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$. Hexafluorophosphoric acid (65% aqueous solution, 1—2 cm^3) was added dropwise to a stirred methanol solution (25 cm^3) of $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (0.200 g, 2.40 × 10^{-4} mol). After *ca.* 30 min the solution was filtered through Celite; reduction of the volume of the filtrate and cooling (−10 °C) gave a red crystalline precipitate (0.19 g, 95%) (Found: C, 23.5; H, 4.4; N, 3.6. $C_{16}H_{35}Co_2F_6N_2O_{12}P_5$ requires C, 23.1; H, 4.2; N, 3.4%), $\nu_{max.}$(CO) at 2 040 (sh), 2 020s, and 1 986s cm^{-1} (dichloromethane). N.m.r. (80 MHz, 22 °C, in CD_2Cl_2): ^1H, δ −10.55 (q, μ-H), 1.19 (t, NCH_2CH_3), 3.37 (qnt, NCH_2CH_3), and 3.73 (t, $POCH_3$); $^{31}P\text{-}\{^1H\}$, δ 153.49 p.p.m. (s, relative to H_3PO_4).

Crystallisation of $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4\cdot CH_2Cl_2$. Sodium tetraphenylborate (*ca.* 0.1 g), dissolved in the minimum of methanol, was added to a solution of $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]PF_6$ (0.05 g, 6.0 × 10^{-5} mol) in dichloromethane (*ca.* 25 cm^3). Light petroleum (b.p. 40—60 °C) was added dropwise until the solution appeared slightly turbid and the solution was then cooled (−10 °C). Red crystals suitable for *X*-ray analysis grew over 2—3 d; $\nu_{max.}$(CO) 2 037w, 2 018s, and 1 986s cm^{-1} (dichloromethane).

Crystallographic Studies.—Crystal data. $C_{41}H_{57}BCl_2Co_2N_2O_{12}P_4$, *M* = 1 093.3, monoclinic, space group $P2_1/c$, a = 16.849(5), b = 21.654(8), c = 15.533(5) Å, β = 113.48(5)°, U = 5 198(4) Å^3, Z = 4, D_c = 1.397 g cm^{-3}, $F(000)$ = 2 264, λ = 0.710 69 Å, μ(Mo-K_α) = 9.2 cm^{-1}, crystal size 0.58 × 0.69 × 0.39 mm.

Data collection. Unit-cell parameters and intensity data were obtained by previously detailed procedures,[18] using a CAD4 diffractometer operating in the ω—2θ scan mode, with graphite-monochromated Mo-K_α radiation. A total of 7 432 unique reflections were collected in the range 2 ⩽ θ ⩽ 23°, of which 4 671 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption using the azimuthal-scan method.[19]

Structure solution and refinement. The cobalt atoms were located from a three-dimensional Patterson function. Subsequent Fourier syntheses revealed the positions of all the remaining non-hydrogen atoms in the complex. All the atom positions located thus far were refined, with anisotropic thermal parameters assigned to atoms in the cation and isotropic thermal parameters to the atoms in the anion; *R* at this stage was below 0.10. A Fourier difference synthesis calculated at this stage using low-angle data only showed clearly the presence of the dichloromethane solvent molecule as well as a hydrogen atom bridging the two cobalt atoms. These atoms were included in the final refinement. The chlorine atoms were assigned anisotropic thermal parameters, the carbon atom of the solvent molecule and the hydrogen atom isotropic ones. A final full-matrix, least-squares refinement (451 variables) using the weighting scheme $w = K/[\sigma^2(F) + 0.002F^2]$ [$\sigma(F)$ from counting statistics, K = 1.28] converged at R = 0.062, and R' = 0.071 (maximum shift/e.s.d. in the last cycle = 0.60; 0.41 for the hydrogen-atom position). A final Fourier difference map calculated at this stage was featureless with a maximum peak height of 0.3 e Å^{-3}. All computations were made using the program SHELX.[20] The Figure was plotted using the program PLUTO.[21]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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