■ **Chlorophosphinidene**

Two Structurally Characterized Conformational Isomers with Different C—P Bonds

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Dedicated to Professor Didier Astruc on the occasion of his 70th birthday

Abstract: The cyclic alkyl(amino) carbene (cAAC) bonded chlorophosphinidene (cAAC)P—Cl (**2/2′**) was isolated from the direct reaction between cAAC and phosphorus trichloride (PCl_3). Compound **2/2′** has been characterized by NMR spectroscopy and mass spectrometry. ^{31}P NMR investigations [$\delta \approx 160$ ppm (major) and $\delta \approx 130$ ppm (minor)] reveal that there are two different P environments of the P—Cl unit. X-ray single-crystal determination suggests a co-crystallization of two conformational isomers of (cAAC)P—Cl (**2/2′**); the major compound possessing a cAAC—PCl unit with C_{cAAC}—P 1.75 Å. This C—P bond length is very close to that of $(NHC)_2P_2$ [NHC = N-heterocyclic carbene]. The residual density can be interpreted as a conformational isomer with a shorter C_{cAAC}—P bond similar to a non-conjugated phosphaalkene [R—P=CR_2]. Our study shows an unprecedented example of two conformational isomers with different $C_{carbene}$—element bonds. Additionally, Br (**3c/3c′**), I (**4c/4c′**), and H (**5c/5c′**) analogues [(Me_2-cAAC)P—X; X = Br (**3**), I (**4**), H (**5**)] of **2c/2c′**[(Me_2-cAAC)P—Cl] were also synthesized and characterized by NMR spectroscopy suggesting similar equilibrium in solution. The unique property of cAAC and the required electronegativity of the X (X = Cl, Br, I, and H) atom play a crucial role for the existence of the two isomers which were further studied by theoretical calculations.

Since the synthetic reports of stable and isolable singlet *N*-heterocyclic carbenes (NHCs) in 1988 by Bertrand et al.[1] and in 1991 by Arduengo et al.,[2] syntheses and characterization of several stable carbenes have been reported.[3] The use of carbenes has brought numerous breakthroughs in the field of homogenous catalysis[4] and NHCs have been utilized as strong σ-donors in different fields of chemistry.[5] The carbene carbon atom of an NHC is bound to two σ-withdrawing and π-donating nitrogen atoms.[5] Consequently, the accumulation of electron density in the p_z-orbital of the carbene carbon atom is reasonably high leading to the weak π-accepting property of NHC.[6] Theoretical studies as well as experimental evidence have shown that non-negligible π-back-donation occurs in the bonding between NHCs and transition metals.[7] The syntheses of cyclic alkyl(amino) carbenes (cAACs)[8] were reported in 2005 by Bertrand et al. One σ-withdrawing and π-donating nitrogen atom of an NHC is replaced by a σ-donating quaternary carbon atom in cAAC leading to a lower lying LUMO. cAACs are superior ligands for the stabilization of various unstable chemical species,[9] radicals,[10] and elements in their different oxidation states[11] due to their stronger π-accepting properties. This is energetically advantageous for acceptance of π-back donation from the element bound to the carbene carbon atom (C_{cAAC}) of cAAC (see the Supporting Information).[3b, 12, 13] The electronic properties of C_{cAAC} and the accumulation of electron densities on the elements (E) are very important since they control the chemical behavior of the cAAC-containing compounds.[3b, 13] Phosphaalkenes are a class of compounds (Scheme 1) with a C=P double bond.[14] They can be represented by two conformational isomers (**X** and **Y**, Scheme 1).[15–17] The form **X** corresponds to a typical phosphaalkene showing a formal P=C double bond, whereas form **Y** corresponds to a carbene–phosphinidene adduct having a P—C coordinate bond with two lone pairs of electrons at the phosphorus atom (Scheme 1).

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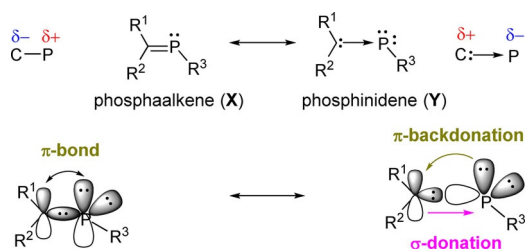E-mail: dstalke@chemie.uni-goettingen.de
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Scheme 1. Two extreme canonical structures and bonding situation of the carbene–phosphinidene adducts.

Scheme 2. The bonding situations of previously known carbene–phosphorus containing compounds with experimental chemical shift values.

The electronic polarization is opposite to each other. The phosphorus atom of the carbene–phosphinidene is electron rich due to the stronger C:→P σ-donation and C←:P π-back-donation which are polar in nature. The C=P double bond of the phosphaalkene is less polar and the phosphorus atom is comparatively electron deficient (Scheme 1) since the electronegativity of carbon (2.5) is higher than that of phosphorus (2.1).[15] This reverse polarity of the electron density is also reflected in the ^{31}P NMR data.[15–17a] The C2-amino substituents at R^1 or R^2 favor the resonance form **Y** and the reverse is true for C2-amino substituents at R^3 (favoring **X**).[15, 17a]

The effect of halide substituents at phosphorus has rarely been reported.[17b] The (cAAC)PX is certainly an interesting starting material for the preparation of a variety of cAAC–phosphinidene compounds.[17c] A number of unusual chemical reactions of cAACs have been reported.[3b, 9–13] The direct reaction of cAAC with PCl$_3$ in a 2:1 molar ratio led to the isolation of cAAC–chlorophosphinidene (cAAC)P–Cl (**2/2′**). The Br (**3 c/3 c′**), I (**4 c/4 c′**), and H (**5 c/5 c′**) analogues of **2/2′** were also synthesized (Scheme S2) and characterized by NMR spectroscopy. The NHC analogues have not been described yet. Herein, we report the synthesis and characterization of **2/2′**, and the existence of two conformational isomers of type **X** and type **Y** which have been characterized by X-ray single-crystal diffraction and confirmed by NMR studies.

NHC formed a stable adduct with trichlorophosphane [(NHC)PCl$_3$, **A**] when this was reacted in a 1:1 molar ratio.[18, 19] Carbene–phenylphosphinidene (**B**) was obtained when pentaphenylcyclopentaphosphane was reacted with NHC.[19, 20] The cationic phosphinidene (**C**) was isolated when trichlorophosphane was treated with three equivalents of NHC.[21] The C–P bonds of compounds **A**–**C** are coordinate σ-bonds (C$_{NHC}$→P) (Scheme 2). NHC- or cAAC-stabilized bisphosphinidenes (**D**, **E**) were obtained when the (NHC)PCl$_3$ adduct was reduced with three equivalents of KC$_8$[19] in THF, or cAAC was directly reacted with P$_4$ in a 4:1 molar ratio.[10b, 22] Theoretical calculations and ^{31}P NMR studies led to the conclusion that the electronic properties of **D** and **E** are very different[10b, 19] although they are analogous (carbene)$_2$P$_2$ adducts. Compound **D** prefers the **Y**-type[19] resonance structure (**D** in Scheme 2), while its cAAC-analogue likes to have the **X**-type resonance form (**E′**, Scheme 2).[10b, 22] Thus, the ^{31}P chemical shift values are very different ($δ = -52$ to -73 ppm for **D** and $δ = +59.4$ ppm for **E′**).[10b, 22] The phosphorus atoms of **D** are upfield shifted when compared with those of **E′**. The ^{31}P chemical shift value of **D** is
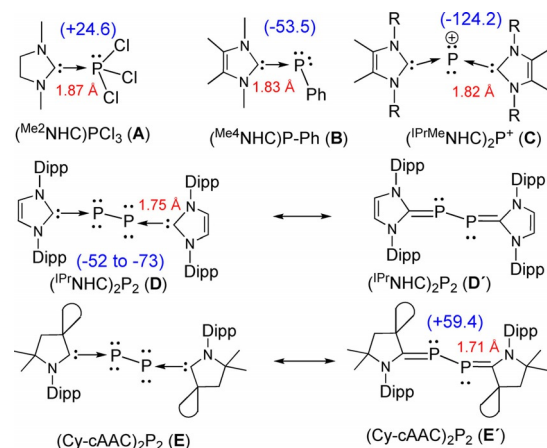
close to that of **B** (C$_{NHC}$–P 1.83 Å, $δ = -53.5$ ppm).[19, 20] The ^{31}P chemical shift value of (Cy-cAAC)P–Ph (C$_{cAAC}$–P 1.73 Å, $δ = +68.9$ ppm) is low field shifted when compared with that of the NHC analogue **B**.[17a]

Trichlorophosphine (PCl$_3$) was added drop by drop to the THF solution of cAAC (**1**) (Scheme 3) at room temperature in a 1:1 molar ratio. The solution was stirred for three hours to
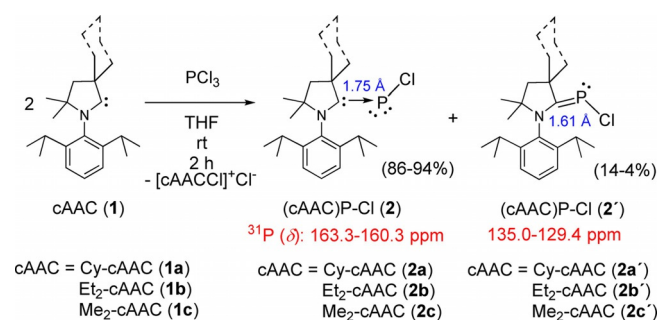

Scheme 3. Syntheses of compounds **2 a–c/2 a′–c′**.

obtain a yellow solution, which was dried under evacuation and extracted with *n*-hexane. The concentrated *n*-hexane solution was stored at $-32\,°C$ in a deep-freezer leading to yellow rods of compound (cAAC)P–Cl (**2/2′**) (Scheme 3) in 28 % yield instead of the (cAAC)PCl$_3$ adduct. This suggests the elimination of [cAACCl]$^+$Cl$^-$ as a side product.[18, 21] A NHC analogue of this salt was obtained when NHC was allowed to react with PCl$_3$ in a 3:1 molar ratio leading to the isolation of salt **C** (Scheme 2). The yield of **2/2′** increased to 60 % when the equivalent of cAAC was doubled. [(cAAC)$_2$P]$^+$Cl$^-$ is not obtained when cAAC is reacted with PCl$_3$ in a 1:3 molar ratio at room temperature. Moreover, the direct reaction of (cAAC)P–Cl (**2/2′**) with another equivalent of cAAC or NHC does not produce [(cAAC)$_2$P]$^+$Cl$^-$ or [(cAAC)(NHC)P]$^+$Cl$^-$.[18, 21]

The yellow rods of compounds **2 a-c/2 a′–c′** are stable in air for several hours. They are stable for several months under an inert atmosphere at room temperature. Compounds **2 a–c** melt

at 145 °C under an inert atmosphere. Compounds **2a/2a′** (*m/z* 391.2205 (100%) [*M*$^+$]), **2b/2b′** (*m/z* 379.2 [*M*$^+$]), and **2c/2c′** (*m/z* 351.1887 (100%) [*M*$^+$]), respectively, were characterized by electron spray ionization (ESI) or electron ionization (EI) mass spectrometry (see Supporting Information).

The structure of **2/2′** was confirmed by X-ray single-crystal diffraction. X-ray structure determination of compound (cAAC)P—Cl (**2/2′**) (cAAC = Cy-cAAC, **2a/2a′**; Et₂-cAAC, **2b/2b′**; Me₂-cAAC,**2c/2c′**) showed similar molecular data. The X-ray structure of **2a/2a′** is herein described (for **2b/2b′** and **2c/2c′** see the Supporting Information). Compound **2a** crystallizes in the triclinic space group $P\bar{1}$ (Figure 1). The P—Cl unit is
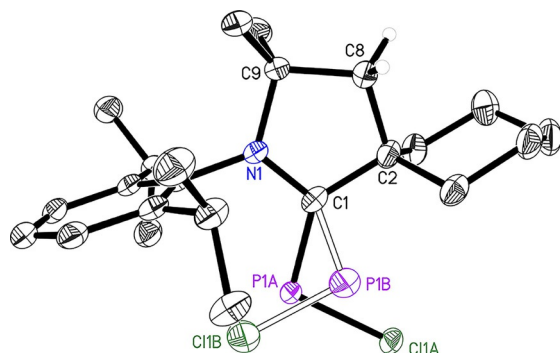
Figure 1. The molecular structure of compound **2a/2a′** with major isomer **2a** in solid and minor **2a′** in hollow bonds. Hydrogen atoms except at C8 are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental [calculated at M06-2X/def2-SVP] bond lengths [Å] and angles [°]:C1—P1A 1.7513(15) [1.752], C1—P1B 1.615(4) [1.615], C1—N1 1.3632(18) [1.359/1.376], P1A—Cl1A 2.0982(7) [2.098], P1B—Cl1B 2.048(5) [2.046]; C1-P1A-Cl1A 104.51(5) [104.5], C1-P1B-Cl1B 98.0(2) [98.1].

disordered. The major component (site occupation factor of ca. 85% in **2a** and ca. 95% in **2b** and **2c**) shows a C$_{cAAC}$—P1A distance of 1.7513(15) Å and a C$_{cAAC}$-P1A-Cl1A angle of 104.51(5)° (Table S1). In accordance with the NMR data, the residual density (see below) is interpreted as a conformational isomer with a much smaller C$_{cAAC}$—P1B distance and also a much smaller C$_{cAAC}$-P1B-Cl1B angle. Both phosphorus atoms of **2a** and **2a′** reside in the same plane formed by N1, C1, and C2 (see Figure 1). All three structures show the same tendency but because of the low occupancy of the minor component, the uncertainty of the bond lengths and angles is much higher than the estimated standard deviation. Therefore, any detailed discussion of geometrical features is excluded.

The previously reported adducts (Scheme 2, **A**–**C**) display C$_{cAAC}$—P bonds (1.82–1.87 Å) which are significantly longer than those in non-conjugated phosphaalkenes (1.65–1.67 Å).[16] The C—P bond length of the major conformation (**2a**) is similar to those in (Cy-cAAC)₂P₂ (1.71 Å), (Cy-cAAC)P—Ph (1.73 Å),[17] and (ᶦPrNHC)₂P₂ (1.75 Å).[19] Selected bond parameters of both forms (**2a/2a′**) are given in the caption of Figure 1 and in Table S1.

The existence of two conformational isomers of compounds **2a–c/2a′–c′** was further supported by ¹H, ¹³C, ³¹P, and ¹⁵N NMR spectroscopy in solution. The ¹³C NMR spectra of **2a–c/2a′–c′** show a doublet in each case at $\delta = 210.05$ ($J_{C–P} = 104.4$ Hz)

(**2a**), 208.22 ppm ($J_{C–P} = 102.6$ Hz) (**2b**), and 210.91 ppm ($J_{C–P} = 101.4$ Hz) (**2c**), respectively (for major resonance forms of **2**). They are far down field shifted when compared to those of the free cAAC ligands (304–310 ppm).[8] The corresponding ¹³C NMR chemical shift values of the minor conformational isomers (**2a′–c′**) were not observed possibly due to the low concentration. The ³¹P NMR spectra of **2a–c/2a′–c′** display two distinct resonances at $\delta = 163.39$ (**2a**) and 135.04 ppm (**2a′**), $\delta = 160.32$ (**2b**) and 131.09 ppm (**2b′**), $\delta = 161.92$ (**2c**) and 129.42 ppm (**2c′**), respectively.[17b] The ³¹P NMR chemical shift values are downfield shifted when compared with those of (Cy-cAAC)P—Ph (+68.9 ppm)[17] and (Cy-cAAC)₂P₂ (+59.4 ppm, **E′**)[10b, 22] but upfield shifted when compared with a number of values $\delta = 230–420$ ppm of non-polarized phosphaalkenes.[16a] The presence of the chlorine atom at the phosphorus atom has an important influence. The electronegativity (3.0) of the chlorine atom is higher than that of the P atom (2.1), which causes a downfield shift of the ³¹P nucleus of **2**. The 1,3-bond correlated ¹H–¹⁵N HMBC spectrum of the major isomer (**2a–c**) shows a doublet due to further coupling with the ³¹P nuclei, $I = 1/2$ at $\delta = -249.99$ ($J_{N–P} = 378$ Hz) (**2a**), -247.37 ($J_{N–P} = 390$ Hz) (**2b**), and -248.61 ppm ($J_{N–P} = 375$ Hz), respectively. The corresponding ¹⁵N ($I = 1/2$) NMR chemical shift values of the minor conformational isomers **2a′–c′** are $\delta = -237.24$ (**2a′**), -234.44 (**2b′**) and -234.11 ppm (**2c′**), respectively, which are upfield shifted compared to those of the major conformational isomers (see the Supporting Information). These ¹⁵N NMR chemical shift values are upfield shifted when compared with that of the free cAAC ligand (-159.0 ppm). The above-mentioned spectroscopic data of the two conformational isomers of (cAAC)P—Cl (**2/2′**) further support their existence in solution (see Supporting Information for all NMR spectra of compounds **2a–c**). Similarly, Br (**3c/3c′**), I (**4c/4c′**), and H (**5c/5c′**) analogues of **2** were also characterized by NMR spectroscopy (see Supporting Information). To get further insight in the equilibrium between the two isomers, temperature-dependent ³¹P NMR were recorded for **2a/2a′** (see Supporting Information), which revealed that there is nearly no change in the molar ratio of **2a/2a′**. This suggests that the temperature does not have any effect within the reported temperature range (238, 283, 313 K) on the equilibrium of the two conformational isomers of compound **2**. Moreover, we have studied the ³¹P NMR spectra of different samples obtained by fractional crystallization, which revealed minor changes in the molar ratio of **2a/2a′**.

Some of the cAAC-containing radicals [(cAAC˙)₂SiCl₂ and (cAAC˙)SiCl₃] possess more than one polymorph.[10c, d] Recently, it has been observed that the (cAAC)₂Pd⁰ complex displays a crystalochromism effect. The color of the (cAAC)₂Pd⁰ complex dramatically changes from dark maroon to bright green when the C$_{cAAC}$-Pd-C$_{cAAC}$ angle is sharpened by 6°.[23] The ²⁹Si NMR spectrum of (Cy-cAAC)₂Si₂ shows two resonances at $\delta = 190.1$ and 318.3 ppm due to the presence of two different silicon atoms in the solid state which is averaged out in solution (249.1 ppm).[24] Notably, the C$_{cAAC}$—Si bond lengths of (Cy-cAAC)₂Si₂ are significantly different. The dark blue colored cAAC-dichlorosilylene stabilized phosphinidene (P-Tip) [(cAAC)→SiCl₂→P-Tip, Tip = triisopropylphenyl] displays

a strong intramolecular charge transfer (ICT) transition due to the electronic transition from the $\pi_{P=Si}$ type orbital to the low lying LUMO (π^*_{C-N}) of cAAC.[25] The above-mentioned examples have in common that they exhibit unusual electronic properties due to the presence of cAACs as ligands.

Singlet and triplet-state optimizations[26] at the R/U-M06-2X/def2-SVP level of theory showed that all the conformers possess a singlet electronic ground state. The relative stabilization energies of the major halo conformers (2c–4c) with the respective minor conformers (2c′–4c′) are significantly higher than that of the hydro conformers [10.3 (2c/2c′), 8.5 (3c/3c′), 10.5 kcal mol⁻¹ (4c/4c′), 4.2 (5c/5c′)], as substantiated by the conformer ratios. The C_{cAAC}–N bond lengths in the 2c–5c and 2c′–5c′ conformers are 1.359–1.361 and 1.372–1.376 Å, which are slightly longer than that of free cAAC (1.309 Å). This confirms that stronger π back-donation from phosphorus to the C_{cAAC} disrupts the delocalization of the lone pair on the adjacent nitrogen atom to the vacant $2p_z$ orbital of the carbene carbon ($C_{cAAC}\leftarrow$N back-donation). The C_{cAAC}–N bonds show single-bond occupancies of 1.978–1.982 e. The C_{cAAC}–P bonds exhibit σ and π occupancies of 1.950–1.969/1.971–1.974 e and 1.947–1.969/1.966 e in 2c--5c/2c′--5c′, respectively (see Table S13). The C_{cAAC}–P σ-bonded electron density is polarized towards the more electronegative C_{cAAC} center (C_{cAAC}: 62–67%), while the π-bonded electron density is almost equally shared (C_{cAAC}: 45–47%) between the bonding partners except in 2c and 3c (C_{cAAC}: 40/42%). In 2c′–5c′, C_{cAAC} utilizes an sp²-hybrid orbital having greater s-character for C_{cAAC}–P σ-bond formation, giving rise to significantly shorter C_{cAAC}–P bonds. The Wiberg bond indices calculated for C_{cAAC}–P bonds are 1.535/1.626 (2c/2c′), 1.525/1.630 (3c/3c′), 1.516/1.638 (4c/4c′), 1.601/1.681 (5c/5c′), suggesting significant double-bond type character. The greater π back-donation from phosphorus to cAAC in 2c′–5c′compared to 2c–5c is reflected from the group charges on the carbenes [−0.095/−0.238 (2c/2c′), −0.085/−0.241 (3c/3c′), −0.076/−0.249 (4c/4c′), −0.083/−0.193 (5c/5c′)]. The calculated electron density [$\rho(r)$] at the (3,−1) bond critical points (BCPs) of C_{cAAC}–P bonds [0.168–0.171 in 2c–5c; 0.199–0.204 in 2c′–5c′] along with the respective Laplacian [$\nabla^2\rho(r)$: +0.233 to +0.310 in 2c–5c; +0.544 to +0.588 in 2c′–5c′] indicate a closed-shell interaction (Table S19). The energy density values for C_{cAAC}–P bonds at the BCPs suggest a larger covalent contribution to the donor–acceptor bonds in 2c′–5c′ ($H_b = -0.691$–0.710) than in 2c–5c ($H_b = -0.547$–0.556).[27]

The calculated ³¹P chemical shifts in all the conformers are in good agreement with the experimental values (Table S22). In all the conformers, phosphorus has the major contribution in the HOMOs, which are π orbitals of C_{cAAC}–P bonds. The C_{cAAC}–P π^* orbitals are the LUMOs in 2c/2c′, 3c′, and 5c; LUMO+1 in 3c and 4c/4c′; LUMO+2 in 5c′ (Figure S8). As pointed out by Weber, the smaller HOMO–LUMO gap (0.2–0.3 eV) in 2c–5c than 2c′–5c′may give rise to significant downfield shifts of the phosphorus atoms in the former conformers.[15]

In summary, we have shown that π-accepting cyclic alkyl(amino) carbenes (cAACs) react with trichlorophosphane at room temperature to produce cAAC–chlorophosphinidenes

(2a–c). They are well-characterized by NMR spectroscopy and mass spectrometry. Their structures are confirmed by X-ray single-crystal diffraction. The crystals of 2a–c are stable in air for several hours and stable for months under an inert atmosphere at room temperature. Interestingly, this series of compounds (cAAC)P–Cl (2a–c) exist as two conformational isomers: phosphaalkenes and phosphinidenes (X and Y; Scheme 1) both in the solid state and in solution. The former is the minor isomer, while the latter is the major conformational isomer. Additionally, Br (3c/3c′), I (4c/4c′), and H (5c/5c′) analogues [(Me₂-cAAC)P–X; X = Br (3), I (4), H (5)] of 2c/2c′ also show similar equilibrium in solution. To the best our knowledge the existence of two extreme resonance forms of any carbene–phosphinidene was not yet reported.

Experimental Section

See Supporting Information for the syntheses of compounds 2a–c. Crystal data for 2a at 100(2) K: $C_{23}H_{35}ClNP$, $M = 391.94$ g mol⁻¹, $0.17\times0.13\times0.11$ mm, triclinic, $P\bar{1}$, $a = 8.868(2)$ Å, $b = 10.197(2)$ Å, $c = 12.260(2)$ Å, $\alpha = 86.77(2)°$, $\beta = 82.10(2)°$, $\gamma = 88.59(2)°$, $V = 1096.2(4)$ Å³, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.254$ mm⁻¹, $\theta_{max} = 28.272°$, 26 769 reflections measured, 5430 independent ($R_{int} = 0.0310$), $R1 = 0.0408$ [$I > 2\sigma(I)$], $wR2 = 0.1097$(all data), residual density peaks: 0.447 to -0.256 eA⁻³, CCDC: 1498552.[35] See Supporting Information for the crystal data of 2b and 2c. CCDC: 1498554 and 1498553.[35] All crystals were selected under cooling, using a X-Temp2 device.[28] The data were integrated with SAINT.[29] A multi-scan absorption correction and a 3λ correction[30] were applied using SADABS.[31] The structures were solved by SHELXT[32] and refined on F^2 using SHELXL[33] in the graphical user interface SHELXLE.[34]

Computational Details: See Supporting Information.

Conflict of interest

The authors declare no conflict of interest.

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