Main-Group Chemistry

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A Short Bi=Bi Bond Supported by a Metalloid Group 13 Ligand**

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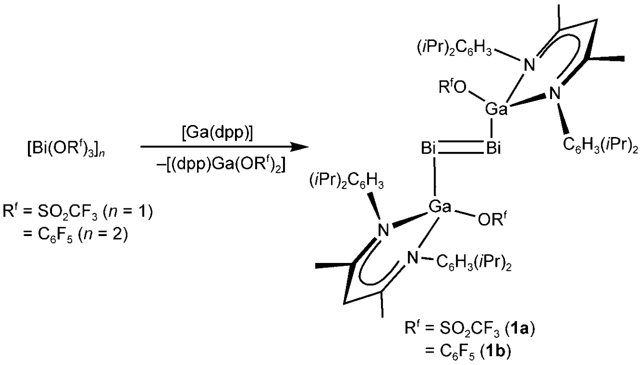
Multiple bonds between main-group metals have brought much attention for more than the last two decades owing to both inherent fundamental chemistry and applications in synthesis.[1] Particularly the isolation and structural characterization of multiply bonded Group 15 elements has posed a challenge to synthetic chemists. The first structurally characterized compound with a bismuth–bismuth double bond was discovered by Tokitoh et al. in 1997; it was prepared by treating sterically crowded tbtBiCl$_2$ (tbt = 2,4,6-[(Me$_3$Si)$_2$CH]$_3$C$_6$H$_2$) with Li$_2$Se and subsequent reduction of resulting (tbtBiSe)$_3$ with three equivalents of (Me$_2$N)$_3$P.[2] Subsequently, it was shown that RBi=BiR (R = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ or bbt, 4-(SiMe$_3$)$_3$C-2,6-[(Me$_3$Si)$_2$CH]$_2$C$_6$H$_2$) can also be obtained by the controlled reduction of the corresponding monoorganyl bismuth dihalides with magnesium.[3]

The "next generation"[4] of molecules with metal–metal multiple bonds between main-group elements was introduced by the recent and most notable reports on (NHC)E=E(NHC) species (E = Si[5a] or BH[5b,c], NHC = [CH(2,6-*i*Pr$_2$C$_6$H$_3$)-N]$_2$C:). These unusual molecules were obtained by reduction of the adducts (NHC)SiCl$_4$ and (NHC)BBr$_3$ with KC$_8$. Similar reduction of (NHC)PCl$_3$ or (NHC′)PCl$_3$ (NHC′ = [CH(2,4,6-Me$_3$C$_6$H$_2$)N]$_2$C:) resulted in a singly bonded diphosphorus moiety supported by NHC or NHC′ ligands.[6] However, NHC-stabilized multiple bonds of heavier main-group elements have not yet been realized. Nevertheless, fine tuning of NHC-type ligands could well be a successful synthetic strategy to access molecules with such units.[1]

It has been shown that the Group 13 metal-substituted NHC analogue [Ga(ddp)] (ddp = CH[MeC(2,6-*i*Pr$_2$C$_6$H$_3$)N]$_2$)[7,8] reacts as a selective, yet very potent, reducing agent. At the same time, it acts as a strong σ-donor ligand, quite compatible with the electrophilic nature of heavy main-group metals. For example, the synthesis of the Zintl type clusters [{(ddp)Ga(Cl)}$_2$Sn$_7$] and [{(ddp)Ga(Cl)}$_4$Sn$_{17}$] involves the reduction and coordination of SnCl$_2$ by [Ga(ddp)].[9] According to this strategy, we have now achieved the reduction of Bi(OSO$_2$CF$_3$)$_3$ and [{Bi(OC$_6$F$_5$)$_3$(toluene)}$_2$][10] by [Ga(ddp)] to yield [(R^{f}O)(ddp)GaBi=BiGa(ddp)(OR^f)] (R^f = SO$_2$CF$_3$ (**1a**), C$_6$F$_5$ (**1b**)), which represents a new type of dibismuthene stabilized by NHC-related ligands.

The reactions between two equivalents of [Ga(ddp)] and Bi(OSO$_2$CF$_3$)$_3$ and between six equivalents of [Ga(ddp)] and [{Bi(OC$_6$F$_5$)$_3$(toluene)}$_2$] gave purple crystals of **1a** (yield 29–32%) and **1b** (yield 63%; Scheme 1), respectively. The byproduct, which is generated in stoichiometric amounts, was characterized in each case as [(ddp)Ga(OR^f)$_2$]. Molecules **1a** and **1b** are soluble in polar organic solvents. The purple color rapidly disappears when the solids or solutions are exposed to air, owing to oxidation.[2] Reaction of [Ga(ddp)] with other commercially available bismuth salts such as BiX$_3$ (X = Cl, Br, I) under various conditions resulted in the reduction of Bi^{III} to metallic bismuth. Interestingly, the reduction of [(NHC)Bi(OSO$_2$CF$_3$)$_3$] using [Co(C$_5$H$_5$)$_2$] gives metallic bismuth, while [Ga(ddp)] as the reducing agent leads to **1a** in high yields.



Scheme 1. Synthesis of **1a** and **1b**.

The ^{1}H and ^{13}C NMR spectra of **1a** and **1b** show the expected signals for the β-diketiminate ligand.[7] Additional signals for the triflate group in **1a** (δ = 171.4 ppm) and the OC$_6$F$_5$ group in **1b** (δ = 173.61, 145.16, 144.0, 138.07 ppm) were observed in the ^{13}C NMR spectra. In the IR spectrum of **1a**, the triflate vibrations were detected at 1386(s) and 1200(s) cm^{-1}, suggesting the presence of covalently linked monodentate triflate groups.[11] Solution and solid-state UV/

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[**] Organo Group 13 complexes of d-block elements 59. For 58, see: T. Cadenbach, C. Gemel, T. Bollermann, R. A. Fischer, *Inorg. Chem.* **2009**, *48*, 5021–5026. G.P. is grateful for a stipend from the Alexander von Humboldt Foundation.

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Vis spectra of **1a** (see the Supporting Information for details) exhibit two absorption bands, each showing a distinct shoulder, while in **1b** only the weaker band shows this splitting. The UV/Vis absorptions of **1a** and **1b** are in the range of those of known aryl dibismuthenes.[1a] Compound **1a** was selected for electrochemical characterization. A THF solution containing $(Bu_4N)PF_6$ was studied by cyclic voltammetry (CV) and showed only one completely reversible redox wave with a half-wave potential $E_{1/2} = -1.2$ V versus Ag^+/Ag (see the Supporting Information). These data indicate that **1a** is more easily reduced than the series of dipnictenes (bbt)E=E(bbt) (E = P −1.84 V, Sb −1.65 V, Bi −1.79 V).[12] In contrast, **1b** is not easily reduced at this potential (reversible $E_{1/2} = -2.60$ V vs. Ag^+/Ag; irreversible $E_{pc} = -2.31$ V vs. Ag^+/Ag).

The structural features of **1a** and **1b** are very similar (Figure 1).[13,14] Therefore, only the solid-state structure of **1a** is discussed. It reveals a monomeric molecule with a bismuth–bismuth double bond in which each bismuth center is tethered by a $Ga(ddp)(OSO_2CF_3)$ ligand. The GaBi=BiGa moiety is planar and contains a center of inversion. The two Ga(ddp)-(OSO_2CF_3) ligands are located *trans* to each other. The aromatic groups in the β-diketiminate ligands are positioned above and below the GaBi=BiGa backbone. The gallium atom is connected to the two nitrogen atoms of the β-diketiminate ligand, one triflate oxygen atom, and one bismuth center in a distorted tetrahedral fashion. The triflate groups are found *trans* to each other with respect to the approximate plane generated by the {(ddp)GaBi=BiGa(ddp)} moiety. Note that the triflate and OC_6F_5 groups have no interaction with the bismuth center, as confirmed by the chemical shift values of these groups in the ^{13}C NMR spectra (see above). However, some π interaction of the $C_6H_3(i\text{Pr})_2$ rings of the ddp ligand with the bismuth centers may be present in the solid state, with average Bi−C distances of 3.673 Å for **1a** and 3.869 Å for **1b**. The Bi=Bi bond lengths in **1a** (2.8111(2) Å) and **1b** (2.8182(4) Å) are slightly shorter than those in the series of aryl dibismuthenes ArBi=BiAr (2.8206(8)–2.8699(6) Å; Ar = 2,4,6-$[(SiMe_3)_2CH]_3C_6H_2$,[2] 4-$(SiMe_3)_3C$-2,6-$[(SiMe_3)_2CH]_2C_6H_2$,[3c] 2,6-$(2,4,6\text{-}Me_3C_6H_2)_2$-$C_6H_3$[3a]). The Bi=Bi bond in **1a** is 0.1789 Å (**1b** 0.1718 Å) shorter than the Bi−Bi single bond of $Ph_2Bi{-}BiPh_2$ (2.990(2) Å).[15] The Ga−Bi bonds (2.655(1) Å (**1a**), 2.693(6) Å (**1b**)) are considerably shorter than the sum of the covalent radii for Ga and Bi (2.76 Å) and than the corresponding bond in the covalently linked Ga/Bi molecule $[\{Me_2GaBi(SiMe_3)_2\}_3]$ (2.744(1)–2.783(1) Å).[16] The Ga-Bi-Bi bond angle (90.56(1)°) in **1a** is smaller than in **1b** (95.521(16)°). These angles in **1a** and **1b** are only slightly lower than the C-Bi-Bi bond angle reported for ArBi=BiAr[2,3] and are comparable to the C-Si-Si bond angle (93.37(5)°) of (NHC)Si=Si(NHC).[5a] The torsion angles Ga-Bi-Bi-Ga in **1a** (180.0(1)°) and **1b** (180.0(18)°) are similar to those reported for C-Bi-Bi-C (180°).[2,3] The metrics of the Ga(ddp) backbone are typical of those found in other Ga(ddp) complexes.[8] The Ga−O1 bond in **1a** (2.027(1) Å) is somewhat longer than that of **1b** (1.897(39) Å) and is more comparable to the distance observed in $[(ddp)Ga(OSO_2CF_3)(PPh_2)]$ (1.979(6) Å).[17] The fluoride atoms of the triflate and C_6F_5 groups show weak F⋯H interactions with the aryl and *i*Pr C−H groups (see the Supporting Information).

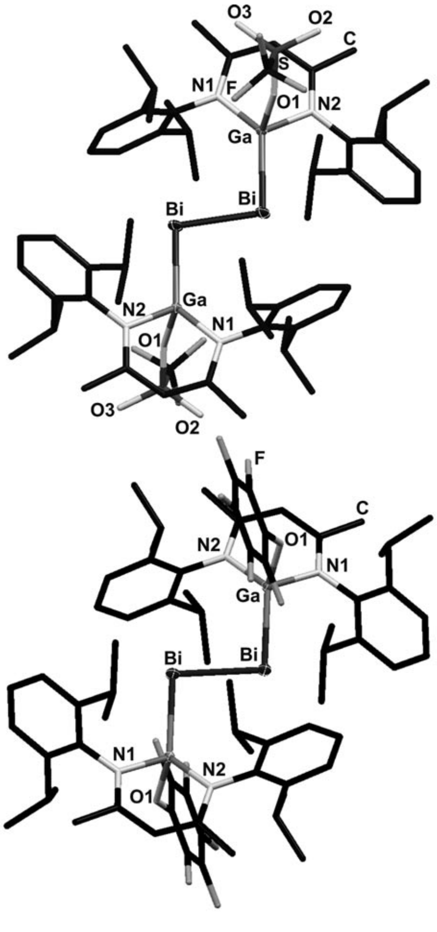

Figure 1. Molecular structure of **1a** (top) and **1b** (bottom). Selected bond lengths [Å] and angles [°] for **1a**: Bi=Bi 2.8111(2), Ga–Bi 2.655(1), Ga–N2 1.933(1), Ga–N1 1.922(1), Ga–O1 2.027(1); Ga-Bi-Bi 90.56(1), N1-Ga-N2 97.59(2), N1-Ga-Bi 133.437(1), N2-Ga-Bi 118.141(1), Bi-Ga-O1 103.63(2). Selected bond lengths [Å] and angles [°] for **1b**: Bi=Bi 2.8182(4), Ga–Bi 2.6930(6), Ga–N1 1.944(4), Ga–N2 1.961(4), Ga–O 1.897(39); Ga-Bi-Bi 95.521(16), N1-Ga-N2 95.43(17), N1-Ga-Bi 127.81(12), N2-Ga-Bi 114.86(13), Bi-Ga-O1 117.33(11).

Geometry optimizations (BP86/TZ2P level) for the *cis* and *trans* isomers of the model dibismuthenes [LBi=BiL] (L = $Ga(F)(C_3H_5N_2)$; **1**-L), $[LBi{=}BiL]^{2+}$ (L = $Ga(C_3H_5N_2)$; **1**-L^{2+}), $[C_6H_5Bi{=}BiC_6H_5]$ (**1**-Ph), and $[CH_3Bi{=}BiCH_3]$ (**1**-Me) were performed to elucidate the bonding situation in **1a** and **1b**.[18] The optimized geometries and the full set of calculated data are given in the Supporting Information. The most stable forms of **1**-L, **1**-L^{2+}, **1**-Ph, and **1**-Me lie in the *trans* orientations. Notably, the molecule **1**-L exhibits two types of *trans* isomers (C_1 and C_s) owing to a slight twist in the Bi−Ga bond; the C_s isomer is slightly higher in energy (ca. 0.7 $kcal\,mol^{-1}$) than the C_1 isomer. The optimized structural parameters for the C_1 isomer of **1**-L are in good agreement with the experimentally determined data of **1a** and **1b**. The calculated Wiberg bond orders P(Bi−Bi) of the compounds in the *trans* conformation **1**-L (1.91), **1**-L^{2+} (1.90), **1**-Ph (1.91), and **1**-Me (1.96) suggest Bi−Bi double bonds, while the P(Ga−Bi) values, which are between 0.99 for **1**-L and 0.86 for **1**-Ph, indicate Bi–Ga single bonds. The contour line diagram of the Laplacian distribution $\nabla^2\rho(r)$[24] of **1**-L at the GaBiBiGa plane depicts bond-critical points for Ga–Bi and Bi=Bi bonds (Figure 2). The calculated energy density at the Ga–Bi bond-critical point ($H(r_b) = -0.022$ Hartree Å^{-3}) is higher than the Bi=Bi bond-critical point ($H(r_b) = -0.016$ Hartree Å^{-3}). Figure 2 shows that there is an area of charge concentration ($\nabla^2\rho(r) < 0$; solid lines) in the middle of the Ga–Bi bonds in **1**-L, which suggests rather nonpolar bonds. Energy decomposition analyses (EDA)[25] for the bismuth–bismuth bond in the *trans* isomers of **1**-L, **1**-L^{2+}, **1**-Ph, and **1**-Me show a consistent picture for the orbital term, with approximately 78% σ and 22% π bonding. The calculated data clearly support a typical covalent bonding situation between Ga and Bi and preclude a description as a contact ion pair [Bi=Bi]$^{2-}$[Ga(OR^f)ddp]$^{2+}$ corresponding to a Bi^{-I}, Ga^{III} formulation. We favor a description as Bi^I, in agreement with the general bonding situation of known aryl dibismuthenes ArBi=BiAr. From this point of view, the Bi$_2^{2+}$ units of **1a** and **1b** are stabilized by two neutral [Ga(ddp)] ligands in which the Ga centers are made electrophilic by the formation of the Bi–Ga donor–acceptor bond. The two counteranions OR^f coordinate to the Ga centers and contribute to the overall steric shielding of the central dibismuthene unit. This coordination, however, does not change the formal oxidation state Ga^I. The species [(NHC)Bi=Bi(NHC)]$^{2+}$ proved to be elusive, at least in our hands to date, which may be due to the much less electrophilic character of coordinated carbene carbon atoms of NHC ligands in comparison to the Group 13 metal congeners.[26]

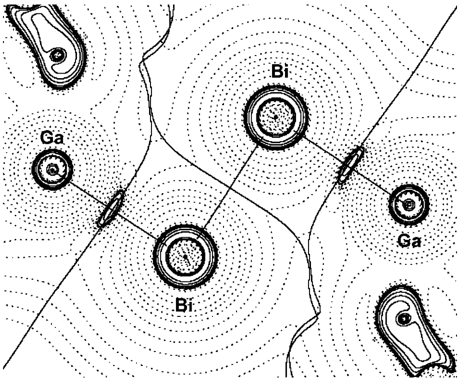

Figure 2. Contour line diagrams $\nabla^2\rho(r)$ of the *trans* (C_1) isomer of **1**-L at the GaBiBiGa plane. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$).

In summary, the new dibismuthenes **1a** and **1b** were derived from the commercially available bismuth triflate and bismuth aryloxide in acceptable yields by employing [Ga(ddp)] as both an efficient reducing agent and a stabilizing or trapping ligand for reactive species. Apart from the shortest known dibismuthene bond, the title compounds demonstrate the unique synthetic potential of low-coordinate Group 13 NHC analogues in main-group chemistry.

Experimental Section

1a: A Schlenk tube was charged with [Ga(ddp)] (0.1 g, 0.2052 mmol) and $Bi(OSO_2CF_3)_3$ (0.067 g, 0.1028 mmol). Fluorobenzene (2 mL) was added to this solid mixture at room temperature under vigorous stirring. The color of the reaction mixture immediately changed from yellow to purple. The mixture was stirred for 15 min, heated to 50 °C, cooled to room temperature, filtered, and the filtrate layered with hexane (2 mL) to yield purple crystals of **1a**. Yield: 29–32% (based on $Bi(OSO_2CF_3)_3$). IR (KBr): $\tilde{\nu}_{OSO_2CF_3} = 1386$(s) and 1200(s) cm^{-1}. ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 7.08$–7.04, 6.87–6.81 (m, 12H, Ar CH), 5.20 (s, 2H, γ-CH), 3.84 (sept, 4H, C*H*(Me)$_2$), 2.66 (sept, 4H, C*H*(Me)$_2$), 1.68 (s, 12H, CH_3), 1.37 (d), 1.21 (d), 0.89 ppm (dd) (48H, CH(*Me*)$_2$); ^{13}C NMR (C_6D_6, 62.8952 MHz): $\delta = 171.38$ (OSO_2CF_3), 146.75 (*C*(2,6-*i*Pr$_2$C$_6$H$_3$)-N), 143.13 (*C*Me), 140.46 [*o*-*C*(2,6-*i*Pr$_2$C$_6$H$_3$)], 126.25 [*p*-*C*(2,6-*i*Pr$_2$C$_6$H$_3$)], 124.86 [*m*-*C*(2,6-*i*Pr$_2$C$_6$H$_3$)], 101.87 (γ-*C*), 29.25, 28.61, 28.07, 27.44 (*C*HMe$_2$), 25.79 (CH*Me*$_2$), 24.96, 24.89 (C*Me*), 24.44, 24.40 ppm (CH*Me*$_2$). UV/Vis (toluene): λ (ε) = 515 (1889), 482 (1793), 685 (321), 631 nm (300 M^{-1}cm^{-1}). UV/Vis (solid): λ = 408, 498, 628, 676. Elemental analysis calcd (%) for $C_{60}H_{82}Bi_2F_6Ga_2N_4O_6S_2$ (1690.87): C 42.62, H 4.89, N 3.31, S 3.79; found: C 44.14, H 4.94, N 4.20, S 3.63; the comparatively high deviation of the carbon value is explained by the disturbing influence of fluorine.

1b: Hexane (2 mL) was added to a mixture of [Ga(ddp)] (0.1 g, 0.2052 mmol) and [{Bi(OC$_6$F$_5$)$_3$(toluene)}$_2$] (0.058 g, 0.0342 mmol) cooled at −30 °C for 30 min. The resulting yellow turbid solution was stirred at this temperature for 30 min and then allowed to warm slowly to room temperature. The color of the reaction mixture changed to purple. The mixture was stirred at room temperature for 1 h, toluene (0.5 mL) was added, the mixture was filtered, and the clear purple filtrate was stored at 8 °C to give purple crystals of **1b.** Yield: 63% (based on [{Bi(OC$_6$F$_5$)$_3$(toluene)}$_2$]). ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 7.12$ (s), 7.09 (s), 7.00 (d), 6.97 (m, 12H, Ar CH), 5.03 (s, 2H, γ-CH), 3.48 (sept, 4H, C*H*(Me)$_2$), 2.70 (sept, 4H, C*H*(Me)$_2$), 1.62 (s, 12H, CH_3), 1.10 (dd), 0.97 (d), 0.89 ppm (dd, 48H, CH(*Me*)$_2$); ^{13}C NMR (C_6D_6, 62.8952 MHz): $\delta = 173.61$ (O-*C*(C$_6$F$_5$)), 169.14 (*C*(2,6-*i*Pr$_2$C$_6$H$_3$)-N), 145.16 (*o*-*C*(C$_6$F$_5$)), 144.0 (*m*-*C*(C$_6$F$_5$)), 143.08 (*C*Me), 141.78 [*o*-*C*(2,6-*i*Pr$_2$C$_6$H$_3$)], 138.07 (*p*-*C*(C$_6$F$_5$)), 125.60 [*p*-*C*(2,6-*i*Pr$_2$C$_6$H$_3$)], 124.88, 124.72 [*m*-*C*(2,6-*i*Pr$_2$C$_6$H$_3$)], 99.38, 98.30 (γ-*C*), 29.64, 28.57, 27.92 (*C*HMe$_2$), 26.03, 25.92 (CH*Me*$_2$), 24.79, 24.41, 24.38, 24.27 (C*Me*), 23.98, 23.63 ppm (CH*Me*$_2$). UV/Vis (toluene): λ(ε) = 512 (4422), 658 (152), 701 nm (155 M^{-1}cm^{-1}). UV/Vis (solid): λ = 506, 643, 694 nm. Elemental analysis calcd (%) for $C_{70}H_{82}Bi_2F_{10}Ga_2N_4O_2$ (1758.84): C 47.80, H 4.70, N 3.19; found: C 52.09, H 5.15, N 3.12; the comparatively high deviation of the carbon value is explained by the disturbing influence of fluorine.

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[13] Crystal structure analyses (Oxford Excalibur 2 diffractometer): The structural solution and refinement was performed using the programs SHELXS-97 and SHELXL-97.[14] a) X-ray crystal structure analysis of **1a**: $C_{44}H_{98}Bi_2F_6Ga_2N_4O_6S_2$, $M = 1514.78$, triclinic, space group $P\bar{1}$, $a = 12.0267(3)$, $b = 12.1652(5)$, $c = 14.3667(4)$ Å, $\alpha = 109.301(3)$, $\beta = 92.378(2)$, $\gamma = 119.069(3)°$, $V = 1681.08(9)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.496\ g\,cm^{-3}$, $T = 108(2)$ K, $F(000) = 752$, $\mu(Mo_{K\alpha}) = 6.128\ mm^{-1}$, plate crystal, 12478 reflections measured, 7267 unique ($R_{int} = 0.0204$), 370 parameters, $R_1 = 0.0285$ ($I > 2\sigma(I)$), $wR_2 = 0.0604$ ($I > 2\sigma(I)$), GOF = 0.975; b) X-ray crystal structure analysis of **1b**: $C_{70}H_{82}Bi_2F_{10}Ga_2N_4O_2$, $M = 1758.80$, monoclinic, space group $C2/c$, $a = 20.4373(12)$, $b = 13.0412(8)$, $c = 27.6080(16)$ Å, $\beta = 106.319(6)°$, $V = 7061.8(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.654\ g\,cm^{-3}$, $T = 111(2)$ K, $F(000) = 3456$, $\mu(Mo_{K\alpha}) = 5.795\ mm^{-1}$, plate crystal, 23541 reflections measured, 6230 unique ($R_{int} = 0.0677$), 406 parameters, $R_1 = 0.0377$ ($I > 2\sigma(I)$), $wR_2 = 0.0698$ ($I > 2\sigma(I)$), GOF = 1.010. CCDC 728867 (**1a**), and 728868 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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