Group 14 Compounds

Triple Bond to Lead: Synthesis and Characterization of the Plumbylidyne Complex *trans*-[Br(PMe$_3$)$_4$Mo≡Pb–C$_6$H$_3$-2,6-Trip$_2$]**

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Carbon forms multiple bonds to many other elements and these bonds are the origin of the rich and versatile chemistry of many organic and organometallic compounds. In contrast, the heavier Group 14 elements Si, Ge, Sn, and Pb reluctantly participate in multiple bonding.[1] Since the discovery of the first stable compounds with a Si=C bond (silene)[2] and a Si=Si bond (disilene) in 1981,[3] several methods have been developed for the synthesis of the heavier Group 14 element homologues of alkenes, and their unusual structures and properties have been studied in detail.[4] Recently, the first compounds featuring a triple bond to linear-coordinated germanium or tin were reported. These include the germylidyne complexes [(η^5-C$_5$H$_5$)(CO)$_2$M≡Ge–R] (M = Cr, Mo, W; R = C$_6$H$_3$-2,6-Trip$_2$ (Trip = C$_6$H$_2$-2,4,6-*i*Pr$_3$), C$_6$H$_3$-2,6-Mes$_2$ (Mes = C$_6$H$_2$-2,4,6-Me$_3$))[5] and *trans*-[X(dppe)$_2$M≡Ge–(η^1-C$_5$Me$_5$)] (M = Mo, W; X = Cl, Br, I; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$)[6] and the stannylidyne complexes *trans*-[Cl(L)$_4$W≡Sn–C$_6$H$_3$-2,6-Mes$_2$] (L = PMe$_3$, L$_2$ = dppe).[7] In addition, first stable germanium and tin analogues of the alkynes, E$_2$(C$_6$H$_3$-2,6-Dipp$_2$)$_2$ (Dipp = C$_6$H$_3$-2,6-*i*Pr$_2$), could be isolated.[8] Both compounds display a *trans*-bent geometry and short E–E distances, thus suggesting, in combination with theoretical calculations, an E–E bond order of approximately two.[8,9] In contrast, no π bonding was found in the homologous lead derivative Pb$_2$(C$_6$H$_3$-2,6-Trip$_2$)$_2$, which features a Pb–Pb single bond and a lone electron pair at each lead center.[10] This change in bonding from germanium to lead can be traced back to the decrease in the π-bond strengths upon descending Group 14,[11] and to the decreasing hybridization of the s and p orbitals,[12] which, in the case of lead, is further diminished by relativistic effects.[13] Therefore it is not surprising, that doubly-bonded lead compounds are rare,[14] and compounds that feature a triple bond to lead are not known to date.[15] We report herein the synthesis and characterization of the plumbylidyne complex *trans*-[Br(PMe$_3$)$_4$Mo≡Pb–C$_6$H$_3$-2,6-Trip$_2$], which is the first com-

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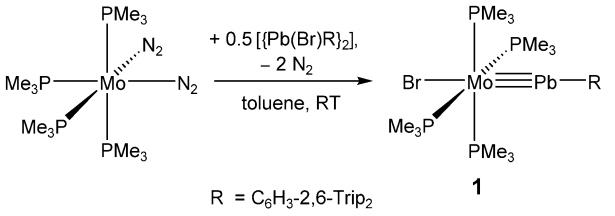
pound containing a triple bond to a main-group element of the sixth row.

Treatment of the dinitrogen complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$[16] with the aryl lead(II) bromide $\{Pb(Br)C_6H_3\text{-}2,6\text{-}Trip_2\}_2$[17] in toluene at ambient temperature was accompanied by gas evolution and a color change from orange to brown to give the plumbylidyne complex **1** (Scheme 1).[18] IR monitoring of the reaction and the ^1H and



Scheme 1. Synthesis of the plumbylidyne complex **1**.

$^{31}P\{^1H\}$ NMR spectra of the crude product obtained after completion of the reaction revealed the concomitant formation of three by-products, which, by comparison with authentic samples, were identified to be $[Mo(N_2)(PMe_3)_5]$ (**2**),[16] *trans*-$[MoBr_2(PMe_3)_4]$ (**3**)[19] and C_6H_4-1,3-$Trip_2$.[18] Compound **1** was separated from the by-products upon fractional crystallization from pentane and isolated as a red-brown, microcrystalline solid in 54% yield. The plumbylidyne complex **1** exhibits remarkable thermal stability, and decomposes upon heating above 194 °C. However, **1** is very air-sensitive, its red solutions in pentane turning rapidly orange upon exposure to air.

Complex **1** was characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and IR spectroscopy, and its molecular structure was determined by a single crystal X-ray diffraction study.[18,20] The $^{31}P\{^1H\}$ NMR spectrum displays a singlet resonance for the equivalent PMe_3 ligands at $\delta = -17.1$ ppm, which appears at higher field than that of the analogous germylidyne and stannylidyne complexes *trans*-$[Cl(PMe_3)_4Mo{\equiv}E{-}R]$ (E = Ge, R = C_5Me_5: $\delta_P = -1.5$ ppm; E = Sn, R = C_6H_3-2,6-Mes_2: $\delta_P = -0.85$ ppm). The ^1H NMR spectrum shows the expected proton resonances of the *m*-terphenyl substituent and the PMe_3 ligands in the intensity ratio 1:4. The most characteristic signal in the $^{13}C\{^1H\}$ NMR spectrum of **1** is that of the lead-bonded carbon atom at very low field ($\delta = +280.6$ ppm). The molecular structure of **1** reveals a distorted octahedral complex with a *trans* arrangement of the plymbylidyne and the bromo ligand (Br-Mo-Pb 179.02(4)°; Figure 1). Two *trans* bonded PMe_3 ligands (P1 and P3) are orthogonal to the Mo–Br bond axis, whereas the other two PMe_3 ligands (P2 and P4) are inclined by 11.6° (mean value) to the bromo ligand. This geometric distortion of the $M(PMe_3)_4$ fragment results from steric interactions between the PMe_3 ligands, and is also observed in the stannylidyne complex *trans*-$[Cl(PMe_3)_4W{\equiv}Sn{-}C_6H_3$-2,6-$Mes_2]$.[7] The most striking structural features of **1** are the very short Mo–Pb bond (2.5495(8) Å) and the almost linear coordination geometry at lead (Mo-Pb-C_{aryl} 177.8(2)°), which suggests the presence of a triply bonded lead atom (Figure 1). In fact, the Mo–Pb distance in **1** is the

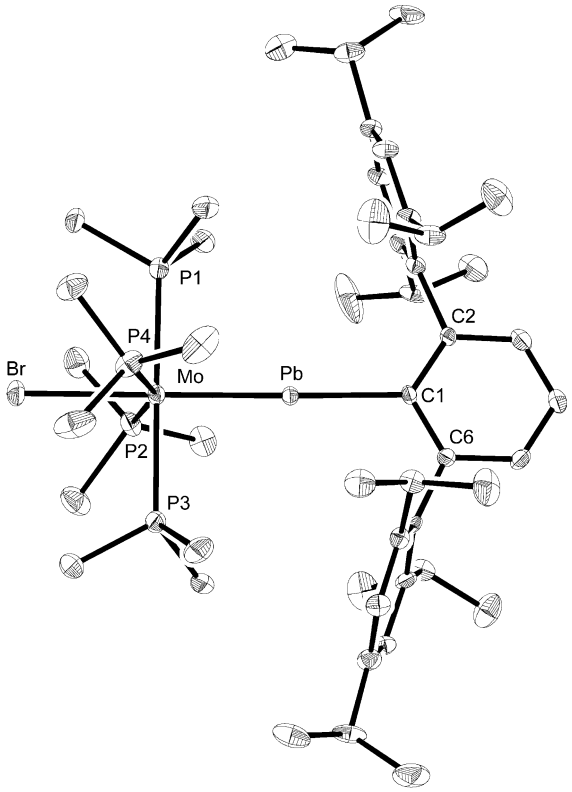


Figure 1. DIAMOND plot of the molecular structure of **1** in the solid state. The thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo-Pb 2.5495(8), Mo-Br 2.677(1), Mo-P1 2.478(2), Mo-P2 2.490(2), Mo-P3 2.489(2), Mo-P4 2.495(3), Pb-C1 2.277(7); Mo-Pb-C1 177.8(2), Br-Mo-Pb 179.02 (4), Br-Mo-P1 90.37(6), Br-Mo-P2 78.74(6), Br-Mo-P3 90.30(6), Br-Mo-P4 78.02(7), Pb-C1-C2 123.4(6), Pb-C1-C6 119.1(5), C2-C1-C6 117.5(6).

shortest reported so far for a Mo–Pb bond.[21] It is about 0.43 Å shorter than the Mo–Pb bond of the molybdenoplumbylene $[Pb\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}C_6H_3$-2,6-$Trip_2]$ (2.9845(7) Å) that features a two-coordinate lead(II) center with bent geometry,[22] or the Mo–Pb single bonds of the dimolybdenoplumbylenes $[Pb\{Mo(\eta^5\text{-}C_5Me_5)(CO)_3\}_2(THF)]$ (2.989(2) and 3.019(2) Å) and $[(Pb\{Mo(\eta^5\text{-}C_5Me_5)(CO)_3\}_2)_2]$ (2.935(1) and 2.989(1) Å), both of which contain trigonal-pyramidal-coordinated lead(II) centers.[23] Two-coordinate lead compounds with a linear coordination geometry are extremely rare,[24] by far the most examples exhibiting a V-shaped geometry.[17,22,23,25]

Gradient corrected density functional theory (DFT) calculations of the model compounds *trans*-$[Br(PH_3)_4Mo{\equiv}E{-}Ph]$ (**1-Pb**, E = Pb; **1-C**, E = C) were carried out without symmetry restraints by using the exchange correlation functional BP86 with various basis sets (LANL2DZ, TZ2P), and the calculated electronic structures were analyzed by various quantum-chemical methods to compare the Mo–E triple bonds (Table 1 and 2).[18] Both compounds adopt essentially a C_{2v} symmetric minimum structure and display a linear geometry at the E atom as found in **1** and in most carbyne complexes.[26] The calculated Mo–Br and Mo–E distances of **1-Pb** and **1-C** compare well with the experimental values of **1**

Table 1: Selected calculated bonding parameters[a] of *trans*-[Br(PH$_3$)$_4$-Mo≡E–Ph] (**1-Pb**, E = Pb, **1-C**: E = C).

	Mo-E [Å]	Mo-P [Å]	E-C [Å]	Mo-Br [Å]	Mo-E-C [°]
1-Pb	2.5218	2.4922	2.2210	2.6837	180.0
1-C	1.8126	2.5058	1.4544	2.7999	180.0

[a] BP86/LANL2DZ.

and *trans*-[Br(dppe)$_2$Mo≡C–SiMe$_3$] (Mo–Br 2.731(2) Å; Mo–C 1.82(1) Å),[27] respectively. The relaxed potential-energy profile for bending at the E atom reveals that the bending energy increases continuously in both compounds with increasing deviation of the Mo-E-C array from linearity (Figure 2). The bending energy reaches a value of

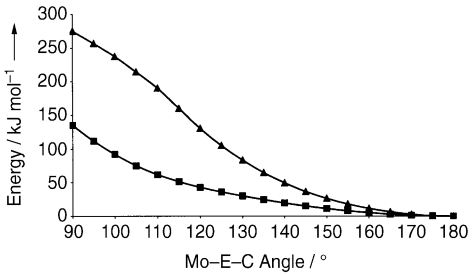


Figure 2. Energy (kJ mol^{-1}) as a function of bending at the E atom in *trans*-[Br(PH$_3$)$_4$Mo≡Pb–Ph] (■) and *trans*-[Br(PH$_3$)$_4$Mo≡C–Ph] (▲) (BP86/LANL2DZ).

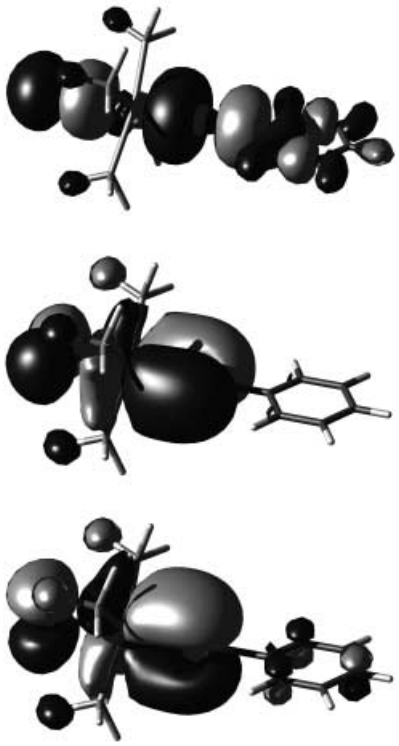


Figure 3. Kohn–Sham orbitals of the σ component (top), the in-plane π component (middle), and the out-of-plane π component (bottom) of the Mo–Pb triple bond in *trans*-[Br(PH$_3$)$_4$Mo≡Pb–Ph] (BP86/TZ2P).

134.1 kJ mol^{-1} in the plumbylidyne complex **1-Pb** at a bonding angle of 90° and in the carbyne complex **1-C** a value of 272.1 kJ mol^{-1}. The orbital analysis of **1-Pb** and of **1-C** shows a σ-type, an in-plane π-type (π_{in}), and an out-of-plane π-type (π_{out}) molecular orbital that contributes to the formation of a Mo–E triple bond (Figure 3).

Analysis of the electronic charge distribution by using the natural bond orbital (NBO) partitioning scheme,[28] reveals that **1-Pb** and **1-C** have an optimal Lewis structure with a Mo–E triple bond, that is composed of one σ component of a_1 symmetry and two nearly degenerate π components of b_2 and b_1 symmetry, respectively.[29] The Mo–E σ bonds result from the overlap of a molybdenum sd^n hybrid orbital (**1-Pb**, $n = 1.65$; **1-C**, $n = 2.48$) with a sp^x hydrid orbital of E (**1-Pb**, $x = 0.72$; **1-C**, $x = 0.81$), and are polarized towards the element E, the σ-bond polarization being similar in both compounds. In comparison, both π-bonding contributions to the Mo–E triple bonds are formed from the interactions of pure molybdenum d orbitals and p orbitals of the element E, and are polarized towards the molybdenum center (Table 2). The Mo–Pb

Table 2: Results of the bonding analyses of *trans*-[Br(PH$_3$)$_4$Mo≡E–Ph] (**1-Pb**, E = Pb, **1-C**: E = C).

	NPA partial charges[a]	occ.	NBO[b] %(Mo)	hyb.	%(E)	hyb.	WBI	BDE [kJ mol^{-1}][c]	EDA[d] [kJ mol^{-1}] ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{int}
1-Pb											−562.9 (49.0%);	
	Mo: −1.42	σ: 1.728	36.0	$sd^{1.65}$	64.0	$sp^{0.72}$					−115.1 ($\Delta E_\sigma(a_1)$)	
	Pb: +1.06	π_{in}: 1.886	78.0	d	22.0	p	1.51	195.2	+390.7	−586.0	−217.6 ($\Delta E_\pi(b_2)$)	−758.2
	[Pb-Ph]: +0.54	π_{out}: 1.847	79.1	d	20.9	p					−219.5 ($\Delta E_\pi(b_1)$)	
1-C											−1316.3 (60.3%)	
	Mo: −0.80	σ: 1.908	36.4	$sd^{2.48}$	63.6	$sp^{0.81}$					−217.8 ($\Delta E_\sigma(a_1)$)	
	E: +0.05	π_{in}: 1.846	59.6	d	40.4	p	2.08	549.4	+960.7	−867.1	−546.7 ($\Delta E_\pi(b_2)$)	−1222.7
	C-Ph: −0.04	π_{out}: 1.786	59.1	d	40.9	p					−544.8 ($\Delta E_\pi(b_1)$)	

[a] Natural population analysis. [b] Natural bond orbital analysis of the Mo–E bonds: NBO occupancy, bond polarization in %Mo and %E, orbital hydridization and Wiberg bond index. [c] Homolytic Gibbs free dissociation energy (298.15 K, 1 atm) of the Mo–E bond to the fragments in their electronic ground states (ZPE corrected). [d] Energy decomposition analysis (BP86/TZ2P): Pauli repulsion (ΔE_{Pauli}), electrostatic interaction (ΔE_{elstat}), orbital interaction (ΔE_{orb}), and total interaction energy (bond-snapping energy) between the fragments [Mo(PH$_3$)$_4$Br]$^-$ and [E-Ph]$^+$ in the complex; the values in parentheses are the percentage contribution of ΔE_{orb} to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb}$) reflecting the covalent character of the Mo–E bond; $\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb}$; $\Delta E_{orb} = \Delta E_\sigma(a_1) + \Delta E_\pi(b_1) + \Delta E_\pi(b_2)$, the contribution of $\Delta E(a_2)$ to ΔE_{orb} is very small.

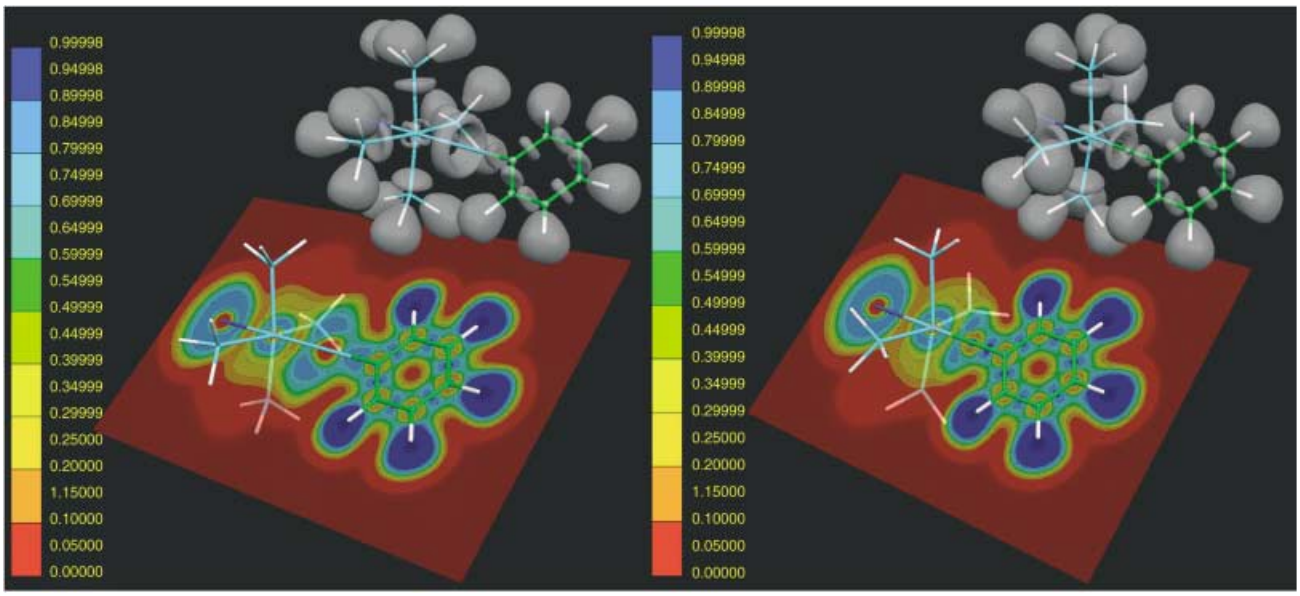


Figure 4. A 2D cross section in the phenyl plane (bottom) and 3D representation (top) of the electron localization function (ELF) in *trans*-[Br(PH$_3$)$_4$Mo≡Pb–Ph] (**1-Pb**) (left picture) and *trans*-[Br(PH$_3$)$_4$Mo≡C–Ph] (**1-C**; right picture) (BP86/LANL2DZ). The colors at each point of the 2D images correspond to the ELF values given in the color bar on the left side of both pictures and range from dark blue (ELF = 1.0) to dark red (ELF = 0). The 3D isosurface plots correspond to an ELF value of 0.85.

π bonds are more polarized than the Mo–C π bonds. Consequently, the plumbylidyne ligand carries a more positive partial charge (+0.54) than the carbyne ligand (−0.04), and the molybdenum center carries in the plumbylidyne complex a higher negative charge (−1.42) than in the carbyne complex (−0.80; Table 2). The higher polarity of the Mo–Pb triple bond is also reflected in the lower Wiberg bond index (WBI; Mo–Pb, 1.51; Mo–C 2.08).[30] Accordingly, the energy required to cleave the Mo–E bond (bond-dissociation energy, BDE) to give the relaxed fragments {Mo(PH$_3$)$_4$Br} and {E–Ph} in their ^{4}A″ and ^{2}A′ electronic ground states, respectively, decreases sharply from the carbyne complex **1-C** (549.4 kJ mol^{-1}) to the plumbylidyne complex **1-Pb** (195.2 kJ mol^{-1}). The Mo–Pb bond-dissociation energy of **1-Pb** is, however, considerably higher than the calculated Pb–Pb bond dissociation energy of *trans* bent Pb$_2$H$_2$ (80 kJ mol^{-1}),[9c] thus suggesting that lead forms a comparatively strong triple bond in **1**.

The bonding interactions between the closed-shell fragments {Mo(PH$_3$)$_4$Br}$^-$ and {E–Ph}$^+$ were analyzed with the energy-decomposition analysis (EDA) method (Table 2). The overall interaction energy ΔE_{int} is smaller in the plumbylidyne complex **1-Pb** than in the carbyne complex **1-C**. In addition, the contribution of the orbital-interaction term ΔE_{orb} to the total attractive interactions is smaller in **1-Pb**, which reflects, in full agreement with the results of the NBO analyses, the lower covalent character of the Mo–Pb triple bond (49.0 %) relative to that of the Mo–C triple bond (60.3 %). Furthermore, breakdown of the covalent bonding energy ΔE_{orb} into contributions of the {Mo(PH$_3$)$_4$Br}$^-$←PbR$^+$ σ donation (ΔE_σ) and the {Mo(PH$_3$)$_4$Br}$^-$→PbR$^+$ π back-donation ($\Delta E_\pi(b_2) + \Delta E_\pi(b_1)$) reveals that the two almost degenerate π bonds make the major contribution to the ΔE_{orb} term (**1-Pb**, 79 % of ΔE_{orb}; **1-C**, 83 % of ΔE_{orb}), thus providing additional evidence for the presence of a Mo–E triple bond in **1-Pb** and **1-C**.

No significant differences were found between the electron-localization functions (ELF) of **1-Pb** and **1-C**, which suggests a similar bonding situation (Figure 4). The Mo–E triple bond domains are characterized in both complexes by a cylindrical torso-shaped region of localized electrons (ELF = 0.85), as found for the triple bond in acetylene.[31] The torus is, however, shifted towards the E atom owing to the polarity of the Mo–E triple bonds and the different atomic numbers of the elements in **1-C**.

The present work shows that stereoelectronically well defined transition-metal fragments are capable of stabilizing triple bonds even to those main-group elements that have persistently resisted such bonding. The existence of **1** provides another challenge to the so called "double-bond rule",[1] and opens up new perspectives in the chemistry of unsaturated lead compounds.

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[18] The experimental section including the synthesis, full characterization and the crystallographic data of **1**, IR and NMR spectroscopic data of the starting materials and the by-products of the reaction leading to **1**, and details of the electronic structure calculations of **1-Pb** and **1-C** can be found in the Supporting Information.

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[20] Crystal structure determination of **1**: $C_{48}H_{85}BrMoP_4Pb$, $M_r = 1169.08$; dark red crystals ($0.56 \times 0.48 \times 0.44$ mm) from a concentrated pentane solution upon cooling from room temperature to +4 °C, $T = 180(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, monoclinic, space group $I2/a$, $a = 20.990(4)$, $b = 21.403(3)$, $c = 25.763(5)$ Å, $\alpha = \gamma = 90$, $\beta = 97.24(2)°$, $V = 11482(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.353$ g cm^{-3}, $2\theta_{max} = 51°$, $\mu = 3.982$ mm^{-1}, $F(000) = 4736$, 39387 reflections, 10424 unique reflections, 520 parameters, GOF = 0.929, $R_1 = 0.0565$ [$I > 2\sigma(I)$], $wR_2 = 0.1421$, min./max. residual electron density −1.264/2.766 e Å^{-3}. CCDC-229986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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