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Simple synthesis and structure characterization of a phosphoniomethylidyne tantalum(V) complex

Nazhen Liu [1], Gengyu Zhu [1], Hongjian Sun, Xiaoyan Li *

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China

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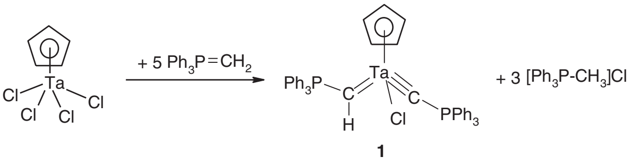
ABSTRACT

A high-valent phosphoniomethylidyne tantalum complex $[(C_5Me_4H)Ta(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**3**) was obtained via transylidation reactions of $(C_5Me_4H)TaCl_4$ with 5 equivalents of the phosphorus ylide $Ph_3P=CH_2$. The addition of strong base $Li(N(SiMe_3)_2$ is beneficial to the transylidation reaction and improves the yield of complex **3**. The ylide adduct complex $[(C_5Me_4H)TaCl_4(CH_2PPh_3)]$ (**4**) as the reaction intermediate was isolated through the reaction of $(C_5Me_4H)TaCl_4$ with one equivalent of the phosphorus ylide $Ph_3P=CH_2$. Both complexes **3** and **4** were structurally characterized by X-ray single crystal diffraction. A comparison on the preparation and properties of the phosphoniomethylidyne tantalum complexes with different supporting ligands, $[CpTa(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**1**) (Cp = cyclopentadieneyl ligand), $[(C_5Me_4H)Ta(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**3**) (C_5Me_4H = tetramethylcyclopentadienyl ligand) (**3**) and $[Cp^*Ta(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**2**) (Cp^* = pentamethylcyclopentadienyl ligand) was discussed.

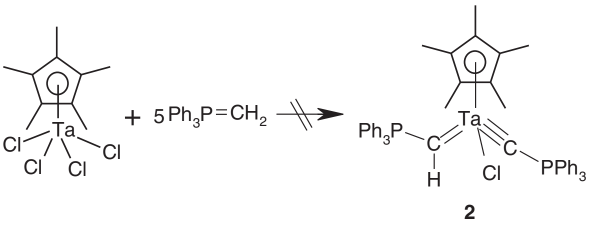
The study on metal carbyne complex is always an interesting topic in current research of organometallic chemistry. Metal carbyne complexes can be used in alkyne metathesis reaction. Compared to the chemistry of metal carbene complexes, the chemistry of metal carbyne complexes is less developed because they are more difficult to synthesize than carbene complexes. The first bridged dinuclear titanium(IV) phosphonio carbyne complex was obtained from titanium tetrachloride via transylidation reaction [1]. Employing the transylidation method, we successfully prepared the phosphoniomethylidyne complex of tungsten [2], rhenium [3] and niobium [4] with a d^0 electron configuration.

We prepared the phosphoniomethylidyne complex of tantalum with a d^0 electron configuration, $[(C_pTa(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**1**) [5], supported by cyclopentadienyl ligand. This is the first report of a stable tantalum complex with a terminal $[Ta\equiv C\text{-}PR_3]$ function (Eq. (1)).

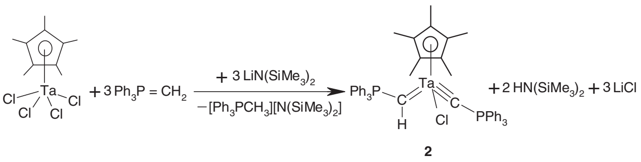


(1)

Under similar reaction conditions, the transylidation reaction of Cp^*TaCl_4 with the ylide $Ph_3P=CH_2$ did not occur. The expected phosphoniomethylidyne complex $[(Cp^*Ta(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**2**) was not obtained (Eq. (2)) [6]. Complex **2** was only formed with the participation of a strong base, $LiN(SiMe_3)_2$ (Eq. (3)) [6].



(2)



(3)

In order to clarify the influence of the substituents on the cyclopentadienyl ring upon the synthesis and stability of the corresponding phosphoniomethylidyne tantalum complexes, herein we report our progress in the synthesis and characterization of a new tantalum

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* Corresponding author. Tel.: +86 531 88361350; fax: +86 531 88564464.
E-mail address: xli63@sdu.edu.cn (X. Li).

[1] The first two authors contributed equally to this work.

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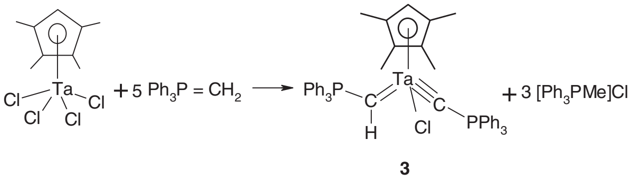
phosphoniomethylidyne complex $[(C_5Me_4H)Ta(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**3**) with tetramethylcyclopentadienyl group as supporting ligand.

The reaction of $(C_5Me_4H)TaCl_4$ with 5 equivalents of the phosphorus ylide $Ph_3P=CH_2$ lead to phosphoniomethylidyne tantalum complex **3** (Eq. (4)) [7]. Crystallization in pentane at 0 °C afforded **3** as orange crystals with a 30% yield.



(4)

Complex **3** was characterized by NMR spectroscopy. In the ^1H NMR spectra the proton signal of C_5Me_4H appears at 5.46 ppm as a singlet. The metal-bound α-CH function (Ta=C*H*) is located at 4.50 ppm as a triplet with $|^2J_{PH} + {}^4J_{PH}| = 2.7$ Hz. Two types of protons of the methyl groups on the cyclopentadienyl ring appear at 2.13 and 2.06 ppm, respectively. The ^{31}P NMR spectra of complex **3** show two doublets for $[Ta=CH\text{-}PPh_3]$ and $[Ta\equiv C\text{-}PPh_3]$ at 22.3 and −25.9 ppm with a coupling constant $^4J_{PP} = 5.5$ Hz. In comparison with the chemical shifts of the phosphorus resonances of complexes $[CpTa(\equiv CPPh_3)(=CH\text{-}PPh_3)Cl]$ (**1**) (23.7, −21.7 ppm) [5] and $[Cp^*Ta(\equiv C\text{-}PPh_3)(=CH\text{-}PPh_3)Cl]$ (**2**) (22.0, −30.0 ppm) [6], the corresponding values of complex **3** are between them. This trend is also reflected in the data of the ^{13}C NMR spectra of complexes **3**, **2** and **1**. The ^{13}C NMR resonance for carbyne carbon ($[Ta\equiv C\text{-}PPh_3]$) shows at 208.0 (**1**) [5], 202.1 (**3**) and 198.6 (**2**) ppm [6], respectively.

The molecular structure of complex **3** is shown in Fig. 1 with selected bond distances and angles [8]. The Ta atom is tetra-coordinated with the center of tetramethylcyclopentadienyl group acting as one vertex of the tetrahedron. The Ta1–C47 distance of 2.060(4) Å in the moiety of $[Ta=CH\text{-}PPh_3]$ is comparable with the tantalum–carbon double bond (2.040(6) Å in complex **1** [5]. The Ta1–C46 distance of 1.880(5) Å in the moiety of $[Ta\equiv C\text{-}PPh_3]$ lies within the range of the expected values for a metal–carbon triple bond (1.849(8) Å in $[Cp^*Ta(\equiv C\text{-}Ph)(PMe_3)_2Cl]$ [9], 1.850(5) Å in $[Ta(\equiv C\text{-}CMe_3)(H)(dmpe)_2(ClAlMe_3)]$ [10] and 1.853 Å in **1** [5]. Due to the stronger electron-donating ability of the four methyl groups on the tetramethylcyclopentadienyl ring in comparison to the cyclopentadienyl group, the bond distances of Ta≡C, Ta=C in complex **3** are longer than those in complex **1** [5].

Upon the basis of our previous investigation [2–6], the transylidation reaction is likely to proceed via the hexa-coordinate classical ylide adduct $[(C_5Me_4H)TaCl_4(CH_2\text{-}PPh_3)]$ (**4**) (Scheme 1). Complex **4** is deprotonated by 2 equivalents of $Ph_3P=CH_2$ molecules to provide phosphoniomethylidyne complex **5** and methyltriphenyl phosphonium chloride. In the presence of another 2 equivalents of $Ph_3P=CH_2$ complex **5** was transformed to the end product **3**.

In order to catch intermediate **4** the reaction of $(C_5Me_4H)TaCl_4$ with one equivalent of $Ph_3P=CH_2$ was carried out in toluene [11]. After the workup complex **4** was isolated as yellow crystals. The molecular geometry is shown in Fig. 2 with selected bond distances and angles [12]. X-ray single crystal diffraction studies show that complex **4** has a hexa-coordinate octahedron geometry. The four chloride ligands are in the equatorial plane while the ylide carbon atom and the tetramethylcyclopentadienyl ligand are in the axial positions. The bond length Ta1–C1 (2.337(3) Å) in complex **4** is longer than those (Ta1–C47 2.060(4) Å and Ta1–C46 1.880(5) Å) in complex **3**. This distinction indicates that the Ta1–C1 bond is a single bond in complex **4**.

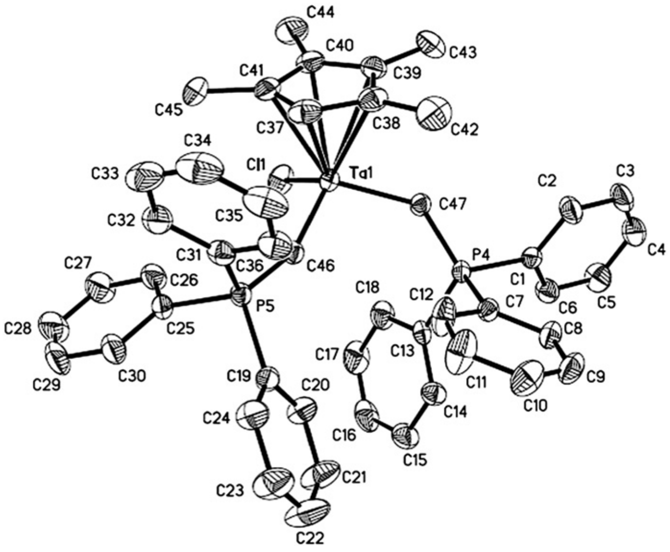
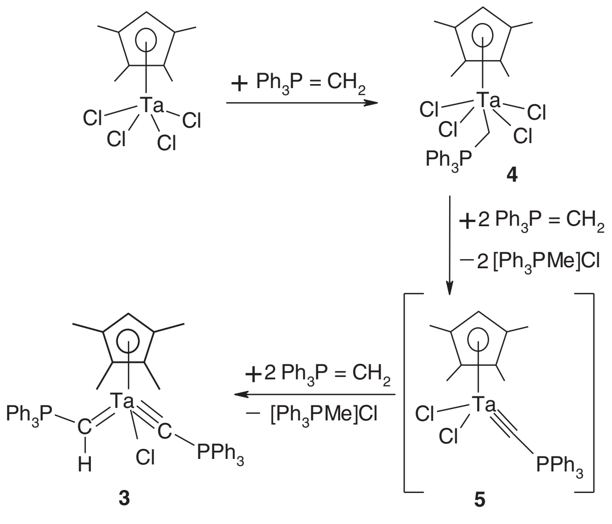


Fig. 1. Molecular structure of **3** and selected bond distances (Å) and angles (°): Ta1–C47 2.060(4), Ta1–C46 1.880(5), Ta1–Cl1 2.4060(13), C47–P4 1.697(4), C46–P5 1.684(5), Ta1–C37 2.375(5), Ta1–C38 2.445(5), Ta1–C39 2.563(5), Ta1–C40 2.551(5), Ta1–C41 2.430(5), Ta1–C47–P4 134.3(3), Ta1–C46–P5 155.7(3), C46–Ta1–Cl1 103.29(15), and C47–Ta1–Cl1 105.04(13).

The efforts to isolate intermediate **5** failed when complex **2** was treated with 3 equivalents of $Ph_3P=CH_2$ or when complex **4** reacted with 2 equivalents of $Ph_3P=CH_2$ in toluene. From the experimental results it was found that the transylidation reaction and the formation yield of the phosphoniomethylidyne tantalum complexes strongly depend upon the substituents on the cyclopentadienyl ring. Complex **1** without substituent on the Cp ring was obtained in 4 d in the yield of 34% [5], complex **3** with four methyl groups on the Cp ring was obtained in 15 d in the yield of 30%, but complex **2** with five methyl groups on the Cp ring could not be formed through the transylidation reaction of Cp^*TaCl_4 with 5 equivalents of $Ph_3P=CH_2$ [6]. This result is consistent with the decreasing of the acidity of ylide methylene protons of the ylide adducts from $[CpTa(CH_2\text{-}PPh_3)Cl_4]$, $[(C_5Me_4H)Ta(CH_2\text{-}PPh_3)Cl_4]$ to $[Cp^*Ta(CH_2\text{-}PPh_3)Cl_4]$, with the increase in the number of methyl groups on the cyclopentadienyl ring. This trend is



Scheme 1. Proposed formation mechanism of complex **3**.

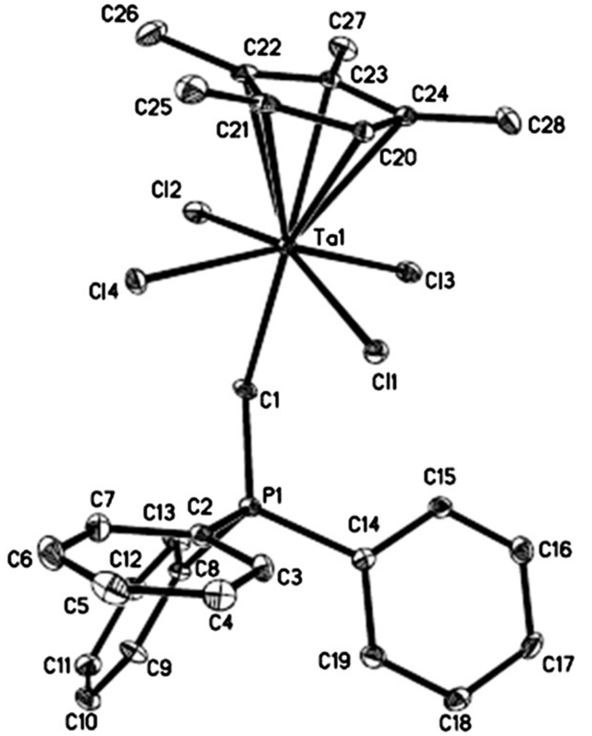
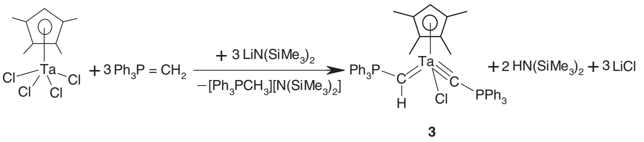


Fig. 2. Molecular structure of **4** and selected bond distances (Å) and angles (°): Ta1–C1 2.337(3), C1–P1 1.773(3), P1–C14 1.802(4), P1–C8 1.827(3), P1–C2 1.804(4), Ta1–Cl1 2.4073(9), Ta1–Cl2 2.4289(9), Ta1–Cl3 2.4516(12), Ta1–Cl4 2.4045(12), Ta1–C1–P1 132.22(18), C1–Ta1–Cl1 80.74(9), C1–Ta1–Cl2 74.96(9), C1–Ta1–Cl3 78.68(10), C1–Ta1–Cl4 77.55(10), C1–P1–C2 115.90(16), C1–P1–C8 107.86(15), and C1–P1–C14 114.53(17).

also in accordance with the strength of basicity of the cyclopentadienyl ligands.

A strong base, $LiN(SiMe_3)_2$, was added to the reaction of $(C_5Me_4H)TaCl_4$ with $Ph_3P{=}CH_2$ to improve the yield of complex **3** because the basicity of the phosphorus ylide $Ph_3P{=}CH_2$ is weaker than that of $LiN(SiMe_3)_2$ (Eq. (5)) [7]. With the addition of 3 equivalents of $LiN(SiMe_3)_2$ and 3 equivalents of $Ph_3P{=}CH_2$ complex **3** could be quantitatively obtained within 12 h.



(5)

In conclusion, a high-valent phosphoniomethylidyne tantalum complex **3** with tetramethylcyclopentadienyl as a supporting ligand was obtained via transylidation reactions of $(C_5Me_4H)TaCl_4$ with 5 equivalents of $Ph_3P{=}CH_2$. With the addition of 3 equiv of $LiN(SiMe_3)_2$ and 3 equiv of $Ph_3P{=}CH_2$ complex **3** could be quantitatively obtained. The ylide adduct complex **4** was obtained as an intermediate through the reactions of $(C_5Me_4H)TaCl_4$ with one equivalent of $Ph_3P{=}CH_2$. Complexes **3** and **4** were structurally characterized by single crystal X-ray diffraction. A comparison of the phosphoniomethylidyne tantalum complexes with different ancillary ligands (**1** with Cp; **3** with tetramethylcyclopentadienyl and **2** with Cp*) was discussed.

Acknowledgment

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Appendix A. Supplementary material

CCDC-793860 (**3**) and CCDC-793859 (**4**) contain the supplementary crystallographic data for complexes **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html. Supplementary data associated with this article can be found, in the online version at http://dx.doi.org/10.1016/j.inoche.2012.10.017.

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[7] Synthesis of **3**. Method a: To the solution of $(C_5Me_4H)TaCl_4$ [13–15] (1.2 g, 2.70 mmol) in 30 mL of toluene was added $Ph_3P{=}CH_2$ [16] (3.7 g, 13.40 mmol) in 30 mL of toluene at 0 °C. After 15 d of stirring at room temperature, the resulting suspension was filtered. Toluene was evaporated under vacuo and the residue was extracted with pentane and diethyl ether. The product was crystallized as orange crystals from pentane. Yield: 0.72 g (30%). Anal. calcd for $C_{47}H_{44}TaClP_2$ (**3**; 887.21 g/mol): C, 63.63; H, 5.00. Found: C, 63.82; H, 4.99. ^1H NMR (300 MHz, C_6D_6, 300 K, ppm): 2.06 (d, $^4J_{HH}=8.1$ Hz, 6H, $C_5\mathit{Me}_4H$), 2.13 (d, $^5J_{HH}=3.6$ Hz, 6H, $C_5\mathit{Me}_4H$), 4.50 (t′, $|^2J_{PH}+{}^4J_{PH}|=2.7$ Hz, 1H, $Ta{=}C\mathit{H}$), 5.46 (s, 1H, $C_5Me_4\mathit{H}$), 6.96–8.04 (m, 30H, $P\mathit{Ph}_3$). ^{31}P NMR (121 MHz, C_6D_6, 300 K, ppm): −25.9 (d, $^4J_{PP}=5.5$ Hz, 1P, $TaC\mathit{P}Ph_3$), 22.3 (d, $^4J_{PP}=5.5$ Hz, 1P, $TaCH\mathit{P}Ph_3$). ^{13}C NMR (75 MHz, C_6D_6, 300 K, ppm): 11.4 (s, $C_5\mathit{Me}_4H$), 14.1 (s, $C_5\mathit{Me}_4H$), 65.8 (s, $\mathit{C}Me$, C_5Me_4H), 99.4 (s, $\mathit{C}H$, C_5Me_4H), 112.2 s, 113.8 s, 117.6 s, 118.4 s, 119.0 s, 119.7 s, 130.0 (d, $^4J_{P,C}=2.3$ Hz), 130.3 (d, $^4J_{P,C}=3.0$ Hz), 133.2 (d, $^3J_{P,C}=9.0$ Hz), 134.2 (d, $^3J_{P,C}=9.0$ Hz), 135.1 (d, $^4J_{P,C}=2.0$ Hz), 135.4 s, 136.2 (d, $^4J_{P,C}=2.0$ Hz),136.5 s, 202.2 (t′, $|^1J_{P,C}+{}^3J_{P,C}|=12.8$ Hz,$Ta{\equiv}\mathit{C}$). Method b: To a suspension of $(C_5Me_4H)TaCl_4$ (0.90 g, 2.03 mmol) in 30 mL of toluene was added 1.68 g (6.08 mmol) of $Ph_3P{=}CH_2$ in 20 mL of toluene at 0 °C. The reaction mixture was stirred at room temperature for 3 h, and the resulting suspension was treated with a solution of 1.02 g (6.09 mmol) $LiN(SiMe_3)_2$ in 20 mL of toluene at −78 °C. The reaction solution was allowed to warm slowly to room temperature and stirred for an additional 12 h. Removal of the precipitate by filtration furnished a bright red solution containing **3** analyzed by ^{31}P NMR spectroscopy. Yield: 100% confirmed by ^{31}P NMR.

[8] Crystallographic data for **3**. $C_{47}H_{44}TaClP_2$, Mr = 887.21, monoclinic, space group P2(1)/n, $a=10.7345(10)$ Å, $b=27.758(3)$ Å, $c=14.4496(14)$ Å, $V=4095.9(7)$ Å^3, T = 298 K, Z = 4, Dc = 1.439 g/cm^3, $\mu=2.858$ mm^{-1}. A total of 22,717 reflections were collected, 8458 unique ($R_{int}=0.0287$), R1 = 0.0293 (for 8458 reflections with I > 2 sigma(I)), wR2 = 0.0712 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

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[11] Synthesis of **4**. To the solution of $(C_5Me_4H)TaCl_4$ (0.60 g, 1.35 mmol) in 20 mL of toluene was added $PPh_3P{=}CH_2$ (0.37 g, 1.35 mmol) in 20 mL of toluene at 0 °C. The reaction mixture gradually changed from yellow to brown. After 12 h of stirring at room temperature, the suspension was filtered. Toluene was evaporated in vacuo and the residue was extracted with pentane and diethyl ether. Crystallization at 0 °C afforded complex **4** as yellow crystals suitable for X-ray diffraction analysis. Yield: 0.68 g (70.6%). Anal. calcd for $C_{28}H_{30}TaCl_4P$ (**4**; 720.24 g/mol): C, 46.69; H, 4.20. Found: C, 47.01; H, 4.02. ^1H NMR (300 MHz, C_6D_6, 300 K, ppm): 2.22 (s, 6H, $C\mathit{H}_3$), 2.56 (s, 6H, $C\mathit{H}_3$), 4.01 (d, $^2J_{P,H}=15.9$ Hz, 2H, $PC\mathit{H}_2$), 5.84 (s, 1 H, $C_5Me_4\mathit{H}$), 6.90–7.80 (m, 15H, $P\mathit{Ph}_3$). ^{31}P NMR (121 MHz, C_6D_6, 300 K, ppm): 34.1 (s, $\mathit{P}Ph_3$).

[12] Crystallographic data for **4**. $C_{28}H_{30}TaCl_4P$, Mr = 720.24, monoclinic, space group P2(1)/c, $a=15.525(3)$ Å, $b=12.036(2)$ Å, $c=15.618(3)$ Å, $V=2725.6(9)$ Å^3, T = 298 K, Z = 4, Dc = 1.755 g/cm^3, $\mu=4.500$ mm^{-1}. A total of 15,051 reflections were collected, 5474 unique ($R_{int}=0.0887$), R1 = 0.0228 (for 5474 reflections with I > 2 sigma(I)), wR2 = 0.0645 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

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