Transition-Metal–Silicon Bonds

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Metallasilatranes: Palladium(II) and Platinum(II) as Lone-Pair Donors to Silicon(IV)**

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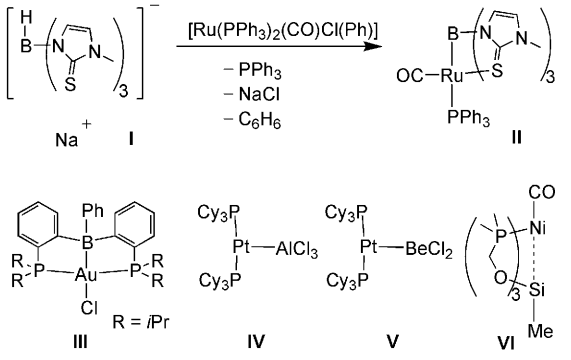
Transition-metal (TM) σ-basicity,[1] that is, an electron-rich transition-metal atom formally acting as a lone pair σ-donor towards an electrophilic site, is becoming a more and more popular principle in transition-metal coordination chemistry. In this context, Hill et al. moved into a novel field when they presented their "Sting of the Scorpion" in 1999 (Scheme 1, top).[2] In their first so-called metallaboratrane **II** the ruthenium atom has a lone pair directed towards the Lewis acidic boron atom (according to isolobal considerations). Within the past decade numerous examples of metallaboratranes followed and have been reviewed and commented on recently.[3] Although further buttressing clamps (e.g., 7-azaindole instead of methimazole)[4] are under investigation for metallaboratrane syntheses, these still rely on the oxidative addition of a B−H bond. The direct formation of metallametallatranes, that is, cage compounds comprising Au→B, Au→Ga, and Au→Al interactions (**III**), was reported by Bourissou et al.[5] Braunschweig et al. reported on the compounds **IV** and **V** exhibiting $\mathrm{Pt^0 \rightarrow Al^{III}}$ and $\mathrm{Pt^0 \rightarrow Be^{II}}$ interactions (Scheme 1, bottom) and related gallium-containing systems as examples for the straightforward formation of TM→E interactions (E = main-group element),[6] and Fischer et al. reported compounds containing $\mathrm{Rh^I \rightarrow Ga^{III}}$ bonds.[7]



Scheme 1. Selected examples of transition-metal base complexes with electrophilic main-group-element sites.

Whereas above examples exhibit transition metal σ-donation towards electron-deficient Lewis acidic sites (e.g., Be, B, Al, Ga), similar interactions towards Lewis acidic centers which formally contain an octet shell (e.g., $\mathrm{Si^{IV}}$ with at least four additional substituents) should in principle be feasible. First steps date back to the work of Grobe et al., who already proposed the potential capability of electron-rich Ni, Pd, and Pt complexes to establish donor interactions to transannular located silicon atoms (e.g., **VI**, Scheme 1).[8] Unfortunately, these initial approaches towards metallasilatranes yielded compounds which exhibit rather long M–Si separations (ca. 3.5–4 Å). We now report on the first hypercoordinate silicon complexes which contain electron-rich transition-metal atoms as formal lone-pair σ-donors in their ligand spheres. These compounds are accessible in good yield, and strong electronic interactions between the Si atom and the $\mathrm{Pd^{II}}$ or $\mathrm{Pt^{II}}$ atoms in their donor sphere are demonstrated by X-ray diffraction analyses and ^{29}Si NMR spectroscopy.

Methimazolylsilanes, bearing the 2-mercapto-1-methylimidazolide ligand as a buttress capable of bridging hard and soft metal sites, were already considered as an entry into metallasilatrane chemistry in our recent studies.[9] Whereas in an initial attempt, $\mathrm{Pt^0}$ underwent oxidative addition into the methimazole C=S bond under formation of a carbene complex, the present report shows that $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$ indeed react with methimazolylsilanes under formation of metallasilatranes.

Reaction of $\mathrm{SiCl_4}$ with 2-mercapto-1-methylimidazole (methimazole, Hmt) supported by triethylamine provides access to silanes $\mathrm{ClSi(mt)_3}$ and $\mathrm{Si(mt)_4}$ (Scheme 2, top). The molecular structures of these silanes, as determined by X-ray crystallography,[10] clearly show the tetracoordination of the Si atoms. The S-donor sites remain in distances between 3.30 and 3.35 Å from the Si atoms. Whereas $\mathrm{Si(mt)_4}$ appears stable in aprotic solution (e.g., anhydrous chloroform), silane $\mathrm{ClSi(mt)_3}$ undergoes ligand exchange in chloroform solution, thus giving the silanes $\mathrm{Cl_2Si(mt)_2}$, $\mathrm{ClSi(mt)_3}$, and $\mathrm{Si(mt)_4}$ (approximate molar ratio 1:5:1 as determined from the ^{29}Si NMR signals at $\delta = -41.2$, -50.5, and -59.1 ppm, respectively) as potential reactants for transition-metal complexes.

Although $\mathrm{ClSi(mt)_3}$ remains the predominant silane species in chloroform solutions of this compound, $\mathrm{[PdCl_2(PPh_3)_2]}$ and *cis*-$\mathrm{[PtCl_2(PPh_3)_2]}$ are susceptible to coordination of $\mathrm{Si(mt)_4}$ generated in the exchange equilibrium (Scheme 2,

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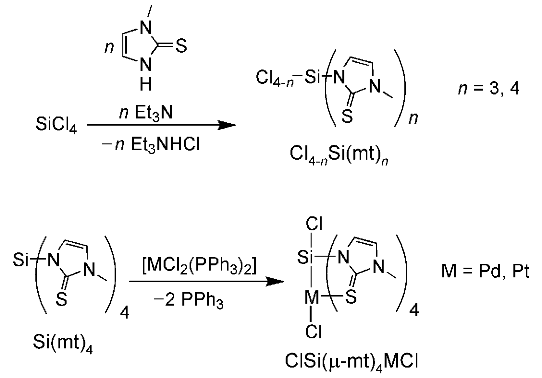


Scheme 2. Syntheses of methimazolylsilanes (top) and metallasilatranes (bottom).

bottom), thus furnishing the cage-like compounds [ClSi(μ-mt)$_4$PdCl] and [ClSi(μ-mt)$_4$PtCl], respectively, whereas Cl$_2$Si(mt)$_2$ remains in solution (as evidenced by ^{29}Si NMR spectroscopy). The molecular structures of [ClSi(μ-mt)$_4$PdCl] (Figure 1)[11,12] and [ClSi(μ-mt)$_4$PtCl] show great similarities to one another.

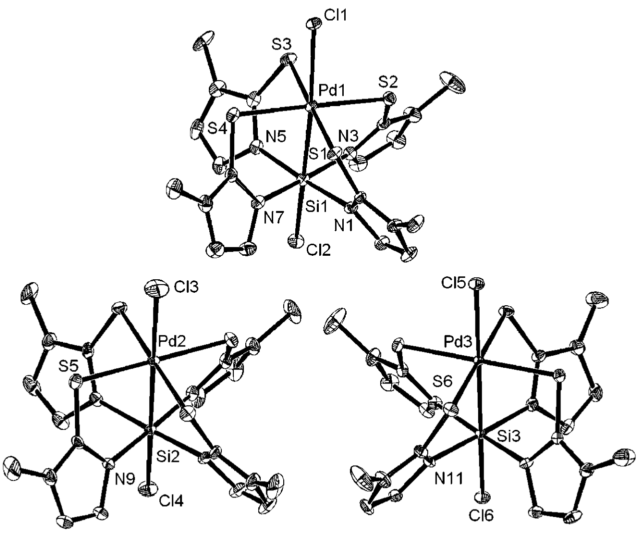
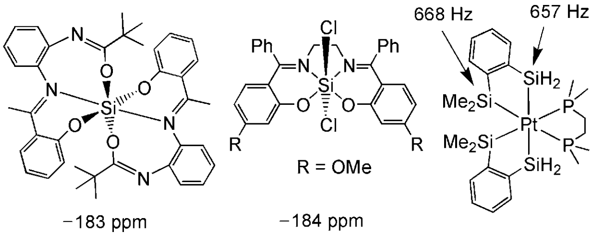


Figure 1. ORTEP representation of the three crystallographically independent molecules of [ClSi(μ-mt)$_4$PdCl] in the crystal structure of [ClSi(μ-mt)$_4$PdCl]$_3$·8CHCl$_3$.[11,12] (Thermal ellipsoids are set at 30% probability). For clarity the hydrogen atoms are omitted. The asymmetric unit comprises an entire molecule [ClSi(μ-mt)$_4$PdCl] (top) and two quarters of such molecules, the Si–Pd axes of which, are located on crystallographically imposed fourfold axes. The molecular structures of [ClSi(μ-mt)$_4$PtCl][11,12] are very similar.

The crystal structures of these novel paddlewheel-shaped compounds comprise three independent (but similar to one another) molecular arrangements. The Pd–Si and Pt–Si bond lengths range from 2.527(2)–2.569(1) and from 2.447(3)–2.469(2) Å, respectively. These short intermetallic bonds are accommodated by pronounced tilt angles of the opposing methimazolyl groups relative to each other (ranging from 50.4(3) to 53.0(2)°). This is a direct indication of the favorability of the Pd–Si (or Pt–Si) interaction because idealized C_{4v} symmetry would reduce interligand steric interactions but require a lengthening of the M–Si bond. The fact that the molecules twist into the more compact C_4-symmetric structure to allow a closer M–Si approach provides circumstantial evidence of the thermodynamic contribution of this bond off-setting the steric factors. The Si atoms are almost in plane with the four surrounding N atoms, and the same holds for the location of the Pd and Pt atoms within the square plane of four S atoms (maximum deviations from these least-squares planes: Si 0.064(2), Pd 0.016(1), Pt 0.032(2) Å). The Si–N bond lengths (1.888(3)–1.917(5) Å) are in a typical range for Si–N bonds in hexacoordinate Si compounds, and the same applies to the Si–Cl bonds (2.151(1)–2.211(4) Å) with the longer Si–Cl bonds being in the Pt complexes, which exhibit a notably shorter *trans*-disposed M–Si bond. This Si–Cl bond elongation already hints at pronounced donor strength of the Pt atom in [ClSi(μ-mt)$_4$PtCl]. Further evidence is provided below.

Whereas a structurally related tin compound[13] was discovered merely in traces and only characterized by X-ray diffraction and mass spectroscopy, [ClSi(μ-mt)$_4$PdCl] and [ClSi(μ-mt)$_4$PtCl] were deliberately prepared and in good yield, thus allowing insights into the TM→E bonding features. The ^{29}Si cross-polarization/magic-angle spinning (CP/MAS) NMR spectrum of [ClSi(μ-mt)$_4$PdCl] exhibits three signals ($\delta = -180.0$, -182.6, -183.4 ppm) in ratio 1:4:1, as determined by peak deconvolution. Thus, the solid-state ^{29}Si NMR spectrum is in accord with the crystal structure of this compound, which comprises three crystallographically independent Si sites in this ratio. The ^{29}Si NMR shifts of [ClSi(μ-mt)$_4$PdCl] are surprisingly similar to other hexacoordinate Si complexes, which bear only main-group (potentially σ- and π-) donor atoms in the Si coordination sphere (Scheme 3).[14] Thus, the Pd atom is clearly acting as a donor towards the Si atom rather than being merely in ligand-constrained close proximity.



Scheme 3. Selected hexacoordinate Si complexes and their ^{29}Si NMR shifts[14] and a hexacoordinate platinum silyl compound with its $^1J_{\mathrm{Pt,Si}}$ coupling constants.[15]

The Pt–Si separations in the structure of [ClSi(μ-mt)$_4$PtCl], which are systematically shorter than the respective Pd–Si distances in [ClSi(μ-mt)$_4$PdCl], already indicate a potentially enhanced shielding of the ^{29}Si nuclei in the Pt compound. Indeed, ^{29}Si CP/MAS NMR spectroscopy revealed a notable upfield shift of the resonance signals. The presence of three signals in ratio 1:1:4 is not as obvious as in case of the related Pd compound since some of them are obscured by ^{195}Pt satellites. Peak deconvolution, however, allowed for a proper interpretation of the spectrum ($\delta = -213.2$, -216.8, -218.5 ppm). The peak analysis delivered different half-widths (broader signals for the Si nuclei on crystallographically imposed fourfold axes), which might indeed be present as a result of symmetry-imposed disorders within the molecules which are located on these special crystallographic positions. Furthermore, the $^{1}J_{Si,Pt}$ coupling constants can be derived from the spectrum (860, 810, and 806 Hz). They are of the same order of magnitude as those reported for other hexacoordinate Pt compounds bearing Si atoms in their coordination sphere (Scheme 3).[15] In addition to the ^{29}Si NMR shifts of compounds [ClSi(μ-mt)$_4$PdCl] and [ClSi(μ-mt)$_4$PtCl], which are typical of Si atoms attached to six σ- and π-donor atoms, the ^{195}Pt satellites of the Pt compounds indicate a strong electronic Si–Pt interaction.

These results demonstrate the silicon atom's demand for an additional lone pair, when incorporated with such cage-like compounds. The fixation of the Pd and Pt atoms in [ClSi(μ-mt)$_4$PdCl] and [ClSi(μ-mt)$_4$PtCl] by the soft methimazole sulfur donor arms (the ClSi(μ-mt)$_4^-$ moiety is thus an eight-electron-donor ligand) together with the lone-pair attraction towards the Lewis acidic Si center suggest the picture of an octopus feeding on its prey.

We have shown that the silane Si(mt)$_4$ is capable of accommodating strong TM→Si interactions with σ-basic transition-metal sites. Furthermore, a great variety of neutral Group 14 or even Group 15 element (E) compounds E(clamp)$_n$, where "(clamp)" is a suitable heterobidentate chelator monodentately bound to E, may in future serve the role as starting materials for numerous heterobimetallic complexes including formally σ-dative TM→E bonds. These compounds contribute to the understanding of the special features of TM→E complexes. In addition, the class of TM–E heterobimetallic compounds,[16] some of which are under consideration for catalytic applications, may thus benefit from the increasing number of heterobimetallic bonding modes between transition-metal and main-group elements that are becoming available. The M−Cl functions of the above [ClM(μ-mt)$_4$M′Cl] compounds allow for substitution and thus functionalization of these complexes. This makes them attractive starting materials for further investigations, which are currently under way. Thus, the platinum- or palladium-bound chlorine atoms may, for example, be replaced by other donor atoms, as shown for iodide.[17] From the view point of silicon coordination chemistry, in which unusual coordination patterns are occasionally found[18] or highlights such as pentacoordinate Si compounds with five different main-group element donor atoms attached to silicon are discovered,[19] the metallasilatranes presented herein represent a striking novelty.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using anhydrous solvents. The chemicals used were commercially available. The syntheses of ClSi(mt)$_3$ and Si(mt)$_4$ from SiCl$_4$, methimazole, and triethylamine are given in the Supporting Information.

[ClSi(μ-mt)$_4$PdCl]: In a Schlenk tube ClSi(mt)$_3$ (0.23 g, 0.57 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (0.20 g, 0.285 mmol) were layered with chloroform (5 mL) and stored for 2 weeks, whereupon red crystals of [ClSi(μ-mt)$_4$PdCl] had formed (PPh$_3$ and Cl$_2$Si(mt)$_2$ remain in solution, the latter was identified by ^{29}Si NMR spectroscopy, $\delta = -41.2$ ppm). The supernatant solution was removed with a cannula, and the solid product was washed with chloroform (3 mL) and briefly dried in vacuo. Yield: 0.20 g (0.21 mmol of [ClSi(μ-mt)$_4$PdCl] as [ClSi(μ-mt)$_4$PdCl]$_3$·7 CHCl$_3$, 75 %), ^{29}Si CP/MAS NMR (79.5 MHz, ν_{spin} 4 kHz): $\delta = -180.0$, -182.6, -183.4 ppm (ratio 1:4:1); Elemental analysis (%) calcd for $C_{55}H_{67}Cl_{27}N_{24}S_{12}Si_3Pd_3$: C 23.51, H 2.40, N 11.96, S 13.69; found: C 23.56, H 2.42, N 12.11, S 13.32.

[ClSi(μ-mt)$_4$PtCl]: The same procedure as above with ClSi(mt)$_3$ (0.23 g, 0.57 mmol) and *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.23 g, 0.29 mmol). Yellow crystals of [ClSi(μ-mt)$_4$PdCl] formed. The supernatant solution was removed with a cannula, and the solid product was washed with chloroform (3 mL) and briefly dried in vacuo. Yield: 0.23 g (0.22 mmol of [ClSi(μ-mt)$_4$PtCl] as [ClSi(μ-mt)$_4$PtCl]$_3$·7 CHCl$_3$, 77 %), ^{29}Si CP/MAS NMR (79.5 MHz, ν_{spin} 4 kHz): $\delta = -213.2$, -216.8, -218.5 ppm (ratio 1:1:4) with $^{1}J_{Si,Pt} = 810$, 806, 860 Hz, respectively; Elemental analysis (%) calcd for $C_{55}H_{67}Cl_{27}N_{24}S_{12}Si_3Pt_3$: C 21.48, H 2.21, N 10.93, S 12.51; found: C 21.46, H 2.21, N 11.16, S 12.47.

Alternative routes to [ClSi(μ-mt)$_4$PdCl], the ^{29}Si CP/MAS NMR spectra of [ClSi(μ-mt)$_4$PdCl and [ClSi(μ-mt)$_4$PtCl] as well as for the Cl–I exchange in [ClSi(μ-mt)$_4$PtCl] are given in the Supporting Information.

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[10] Crystal structure analysis of ClSi(mt)$_3$:. $C_{12}H_{15}ClN_6S_3Si$, $M_r = 403.03$, $T = 100(2)$ K, monoclinic, space group $C2/c$, $a = 18.8561(3)$, $b = 7.8183(1)$, $c = 24.6127(4)$ Å, $\beta = 101.272°$, $V = 3558.48(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.505$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.640$ mm^{-1}, $F(000) = 1664$, $2\theta_{max} = 62.0°$, 36647 collected reflections, 5613 unique reflections ($R_{int} = 0.0275$), 208 parameters, $S = 1.037$, $R_1 = 0.0286$ ($I > 2\sigma(I)$), wR_2(all data) = 0.0731, max./min. residual electron density +0.465/−0.330 e Å^{-3}. Crystal structure analysis of Si(mt)$_4$·2.23 CHCl$_3$: $C_{18.23}H_{22.23}Cl_{6.69}N_8S_4Si$, $M_r = 746.92$, $T = 200(2)$ K, orthorhombic, space group $Pccn$, $a = 15.5889(3)$, $b = 28.1039(6)$, $c = 14.8782(4)$ Å, $V = 6518.3(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.522$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.903$ mm^{-1}, $F(000) = 3034.1$, $2\theta_{max} = 50.0°$, 24382 collected reflections, 5733 unique reflections ($R_{int} = 0.0429$), 412 parameters, $S = 1.122$, $R_1 = 0.0483$ ($I > 2\sigma(I)$), wR_2(all data) = 0.1312, max./min. residual electron density +0.558/−0.393 e Å^{-3}. The asymmetric unit includes three chloroform sites, one of which in close proximity to a center of inversion, so that the principle formula is Si(mt)$_4$·2.5 CHCl$_3$. Refinement of the site occupancy factors however, revealed less chloroform occupancy. CCDC 748274 (ClSi(mt)$_3$) and CCDC 748271 (Si(mt)$_4$·2.23 CHCl$_3$) 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.

[11] Crystal structure analysis of [ClSi(μ-mt)$_4$PdCl]$_3$·8 CHCl$_3$: $C_{56}H_{68}Cl_{30}N_{24}Pd_3S_{12}Si_3$, $M_r = 2929.03$, $T = 150(2)$ K, tetragonal, space group $P4nc$, $a = b = 19.2135(3)$, $c = 27.9235(9)$ Å, $V = 10308.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.887$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.626$ mm^{-1}, $F(000) = 5816$, $2\theta_{max} = 55.0°$, 82194 collected reflections, 11849 unique reflections ($R_{int} = 0.0500$), 506 parameters, $S = 1.072$, $R_1 = 0.0338$ ($I > 2\sigma(I)$), wR_2(all data) = 0.0768, Flack parameter 0.01(2), max./min. residual electron density +0.673/−0.490 e Å^{-3}. Crystal structure analysis of [ClSi(μ-mt)$_4$PtCl]$_3$·8 CHCl$_3$: $C_{56}H_{68}Cl_{30}N_{24}Pt_3S_{12}Si_3$, $M_r = 3195.10$, $T = 150(2)$ K, tetragonal, space group $P4nc$, $a = b = 19.2415(2)$, $c = 27.9371(6)$ Å, $V = 10343.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.052$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 5.152$ mm^{-1}, $F(000) = 6200$, $2\theta_{max} = 56.6°$, 104835 collected reflections, 12891 unique reflections ($R_{int} = 0.0528$), 519 parameters, $S = 1.066$, $R_1 = 0.0318$ ($I > 2\sigma(I)$), wR_2(all data) = 0.0820, Flack parameter 0.012(4), max./min. residual electron density +1.002/−0.765 e Å^{-3}. Note: The chloroform content expressed in the formulae [ClSi(μ-mt)$_4$MCl]$_3$·8 CHCl$_3$ (corresponding to 32 chloroform molecules per unit cell) is an approximation. Elemental analyses support chloroform content of at least [ClSi(μ-mt)$_4$MCl]$_3$·7 CHCl$_3$. The crystals were, however, found to decompose under loss of solvent. The above two crystal structures include heavily disordered solvent of crystallization (chloroform). Only a limited number of these chloroform molecules could be refined in reasonable quality (10 per unit cell). After initial refinement the non-refined chloroform sites were accounted for in a SQUEEZE treatment as implemented in WinGX Platon.[12] This procedure yielded 1187 superfluous electrons per unit cell for the [ClSi(μ-mt)$_4$PdCl] structure, 1303 electrons per unit cell for the [ClSi(μ-mt)$_4$PtCl] structure, corresponding to 20.5 and 22.5 CHCl$_3$ molecules, respectively. Thus, the maximum number of chloroform molecules found per unit cell (10 refined + 22 from SQUEEZE) was considered as the constituting solvent of crystallization in above crystal structures and included in the formulae as required for numerical absorption correction. CCDC 748272 ([ClSi(μ-mt)$_4$PdCl]$_3$·8 CHCl$_3$) and CCDC 748275 ([ClSi(μ-mt)$_4$PtCl]$_3$·8 CHCl$_3$) 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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[17] For example, the reaction of [ClSi(μ-mt)$_4$PtCl] with potassium iodide allows for the selective substitution of the platinum-bound Cl atom. This initial result is confirmed by a X-ray crystallographic analysis of such a cage-like compound, namely [ClSi(μ-mt)$_4$PtI]·2.5 Me$_2$SO (with partial OH-occupancy of the Cl-site, site occupancy factor 0.30, the origin of the OH groups is not clear yet): $C_{42}H_{70.6}Cl_{1.4}I_2N_{16}O_{5.6}Pt_2S_{13}Si_2$, $M_r = 2055.91$, $T = 100(2)$ K, monoclinic, space group $P2_1/c$, $a = 16.0699(2)$, $b = 11.1591(2)$, $c = 19.4309(3)$ Å, $\beta = 93.494(1)°$, $V = 3477.98(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.963$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 5.438$ mm^{-1}, $F(000) = 2002$, $2\theta_{max} = 70.0°$, 86657 collected reflections, 15261 unique reflections ($R_{int} = 0.0419$), 357 parameters, $S = 1.056$, $R_1 = 0.0251$ ($I > 2\sigma(I)$), wR_2(all data) = 0.0486, max./min. residual electron density +0.764/−1.418 e Å^{-3}. CCDC 748273 contains 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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