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Template Synthesis of Platinum Complexes with Benzoxazolin-2-ylidene Ligands

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Dedicated to Prof. Jan Reedijk on the occasion of his 65th birthday

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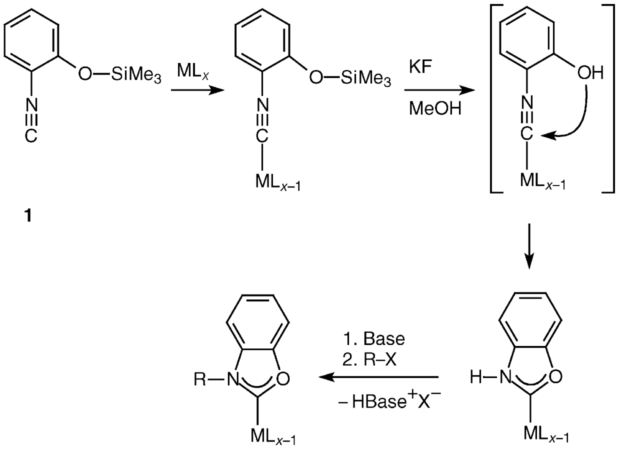
2-(Trimethylsiloxy)phenyl isocyanide (**1**) reacted with *cis*-[$PtCl_2(PPh_3)_2$] (**2**), and subsequent hydrolysis of the O–$SiMe_3$ bond yielded *trans*-[Pt(benzoxazolin-2-ylidene)Cl$(PPh_3)_2$]Cl (**3**). Reaction of dinuclear complex [Pt(μ-Cl)(dppe)]$_2$(CF_3SO_3)$_2$ (**4**) [dppe = 1,2-bis(diphenylphosphanyl)ethane] with two equivalents of **1** did not yield the expected monocarbene complex but the dicarbene complex [Pt(benzoxazolinato-2-ylidene)(benzoxazolin-2-ylidene)(dppe)](CF_3SO_3) (**5**). A single-crystal X-ray diffraction study showed that complex **5** contains one deprotonated and one protonated heterocarbene ligand. The two carbene ligands are linked by a N–H···N hydrogen bond which forces them in a sterically unfavored coplanar arrangement.

Introduction

The reaction of coordinated isocyanides[1] with N- or O-nucleophiles constitutes the oldest method for the preparation of complexes with heteroatom-stabilized carbene ligands.[2] Many examples for this carbene synthesis have been reported in the literature.[3] This type of template synthesis only works if the isocyanide is coordinated to a late transition metal or a transition metal in a high oxidation state, which reduces metal-to-ligand (d→p)π backbonding and thus activates the isocyanide for the attack by a nucleophile.

We have shown that 2-(trimethylsiloxy)phenyl isocyanide (**1**)[4] is a suitable starting material for the synthesis of complexes with N,O-stabilized carbene ligands.[5] Coordination of **1** to suitable transition metals, followed by cleavage of the O–$SiMe_3$ bond, leads to an intramolecular nucleophilic attack of the hydroxy group at the isocyanide carbon atom and to the formation of a complex with the benzoxazolin-2-ylidene ligand. The subsequent *N*-alkylation of this ligand is unproblematic (Scheme 1). A large number of complexes with NH,O- and NR,O-stabilized carbene ligands containing W,[6,7] Cr,[7] Pt, Pd,[8] B,[9] Fe,[10] and Re[11] have been prepared in addition to some platinum complexes with the six-membered benzo[1,3]oxazin-2-ylidene.[12] The intramolecular attack of the hydroxy group at the isocyanide carbon atom is influenced by metal-to-ligand d→π* backbonding. No cyclization is observed in the case of strong backbonding, which, upon O–$SiMe_3$ bond cleavage, leads to the complexes with the 2-hydroxyphenyl isocyanide ligand, which is known to be unstable in the free state.[11,13a–13c]



Scheme 1. Cyclization reaction of 2-(trimethylsiloxy)phenyl isocyanide.

The cyclization of β-functionalized isocyanides can also be applied for the synthesis of cyclic diaminocarbenes. Complexes with benzannulated[14] N-heterocyclic carbene (NHC) ligands have been prepared by this method, which turns out to be an alternative to the generation of such complexes from cyclic carbene precursors.[15] The cyclization reaction of 2-functionalized isocyanides has been used

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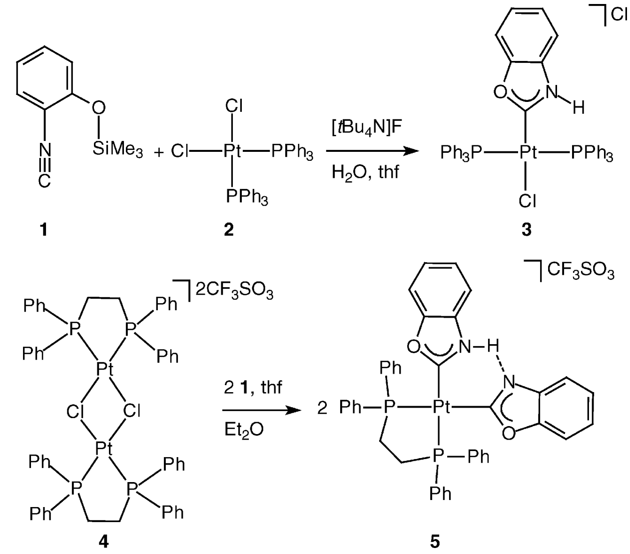
for the generation of complexes with cyclic tetra(diaminocarbene),[16] saturated imidazolidin-2-ylidene,[17] and diaminocarbene ligands derived from a six-membered heterocycle.[18]

In this contribution, we report on the synthesis of monocarbene complex **3** and dicarbene complex **5** that were obtained upon Si–O bond cleavage in the corresponding [2-(trimethylsiloxy)phenyl isocyanide]platinum(II) complexes (Scheme 2).



Scheme 2. Synthesis of complexes **3** and **5**.

Results and Discussion

The reaction of one equivalent of 2-(trimethylsiloxy)phenyl isocyanide (**1**) with *cis*-dichloridobis(triphenylphosphane)platinum(II) (**2**) in the presence of fluoride anions yielded *trans*-(benzoxazolin-2-ylidene)chloridobis(triphenylphosphane)platinum(II) chloride (**3**) as a colorless powder, which was isolated without further purification (Scheme 2).

The ^{31}P NMR spectrum of **3** exhibits one resonance for the phosphorus atoms at $\delta = 16.5$ ppm with a $^{1}J(^{31}\mathrm{P},^{195}\mathrm{Pt})$ coupling constant of 2511 Hz. This is a clear indication for a *trans* orientation of the phosphane ligands, since the *cis*-orientation would give rise to two different ^{31}P resonances with two different $^{1}J(^{31}\mathrm{P},^{195}\mathrm{Pt})$ coupling constants. The resonance of the hydrogen atom that is bound to the nitrogen atom of the carbene ring is shifted strongly downfield to $\delta = 16.40$ ppm in the ^{1}H NMR spectrum.

The molecular structure of $\mathbf{3}\cdot 3\mathrm{CH_2Cl_2}$ (Figure 1) was determined by single-crystal X-ray diffraction. Complex **3** resides on a crystallographic mirror plane. The benzoxazolin-2-ylidene ligand, as well as atoms Pt, Cl1, Cl2, and HN, are located on that mirror plane. Atom Cl2 forms a hydrogen bond to atom HN [bond lengths N–HN 0.85(7) Å; HN···Cl2 2.155 Å]. Similar hydrogen bonds have been observed previously.[19] The formation of the N–HN···Cl2 hydrogen bond together with the downfield shift observed for proton HN in the ^{1}H NMR spectrum are indicative of a strong polarization of the N–HN bond.

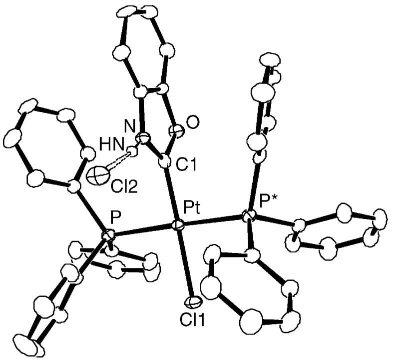


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and bond angles [°]: Pt–Cl1 2.3526(12), Pt–P 2.3168(9), Pt–C1 1.945(5), N–HN 0.85(7), HN···Cl2 2.155; Cl1–Pt–P 89.58(2), Cl1–Pt–C1 177.71(15), P–Pt–P* 175.72(5), P–Pt–C1 90.34(2), N–C1–O 108.3(4), N–HN···Cl2 170.9.

The platinum atom in **3** exhibits an almost square-planar coordination geometry, and the phosphane ligands are arranged *trans* to each other [angle P–Pt–P* 175.72(5)°] in contrast to the *cis* configuration observed in the starting material **2**. As expected, the carbene ring plane is oriented almost perfectly perpendicular to the Pt/C/P$_2$/Cl plane. This is caused by the steric demand of the carbene ring and the phenyl rings of the phosphane ligands.

The Pt–C$_{\mathrm{carbene}}$ bond length [1.945(5) Å] falls in the range observed previously for Pt-NHC complexes[16] and the N–C1–O angle [108.3(4)°] also assumes a value that is typical for complexes with the benzoxazolin-2-ylidene ligand.[10,11]

The molecular structure of **3** shows that a chlorido ligand in the *cis*-diphosphane complex **2** must have been initially replaced by isocyanide **1**. After cleavage of the O–SiMe$_3$ bond and cyclization to the benzoxazolin-2-ylidene ligand, complex **3** has a *trans*-configuration of the phosphane ligands. Such a rearrangement of the phosphane ligands from the *cis* to the *trans* configuration has been reported previously for the synthesis of *trans*-[Pd(benzoxazolin-2-ylidene)Cl(PPh$_3$)$_2$]Cl and *cis*-[Pd(benzoxazolin-2-ylidene)I$_2$(PPh$_3$)] by using *trans*-[PdX$_2$(PPh$_3$)$_2$] (X = Cl, I) as a starting material.[19a] In these cases, the carbene ligand avoids the *trans* position to the phosphane ligands. This behavior has steric as well as electronic reasons, as other examples of platinum carbene complexes with phosphane and halide ligands have shown.[20]

The *cis*–*trans* rearrangement of the phosphane ligands observed during the synthesis of **3** can be prevented by using a starting material with a bidentate chelating phosphane ligand like dppe. With that in mind, [PtCl$_2$(dppe)] was synthesized and converted into the dinuclear complex **4** by chloride abstraction with AgCF$_3$SO$_3$. It was hoped that the reaction of **4** with two equivalents of **1** would lead to cleavage of the µ-chlorido bridges with formation of the monoisocyanide and subsequently the monocarbene complex in *cis* configuration. Surprisingly, the reaction of **4** with two equivalents of **1** followed by O–SiMe$_3$ bond cleavage gave the *cis*-dicarbene complex **5** in 44% yield (Scheme 2).

The ^{31}P NMR signal of the *cis*-arranged phosphorus atoms was observed at δ = 45.9 ppm with a $^{1}J(^{31}\mathrm{P},^{195}\mathrm{Pt})$ coupling constant of 2259 Hz. The two carbene carbon atoms are apparently chemically equivalent. The ^{13}C NMR spectrum shows a doublet at δ = 184.1 ppm. This doublet is caused by an AXX′-spin system, which actually leads to a doublet of doublets due to coupling of the carbene carbon atoms to the phosphorus atoms. The ^{1}H NMR spectrum, however, shows only one resonance for N–H protons at δ = 13.60 ppm, which is significantly shifted upfield relative to the N–H resonance found in the ^{1}H NMR spectrum of **3**. In addition, the IR spectrum exhibits no absorption for an N–H stretching vibration in the expected range between 3000 and 3500 cm^{-1}. On the basis of these observations it is reasonable to assume that only one carbene ligand is protonated at the nitrogen atom, while the other one is deprotonated and the single proton is located in between the two nitrogen atoms of the two carbene ligands. We have described previously an iron complex containing a protonated and an unprotonated benzoxazolin-2-ylidene ligand.[13b]

Crystals of solvate **5**·thf can be obtained from a concentrated thf solution. The molecular structure of **5**·thf has been determined by single-crystal X-ray diffraction, and the results are depicted in Figure 2 together with selected bond lengths and angles.

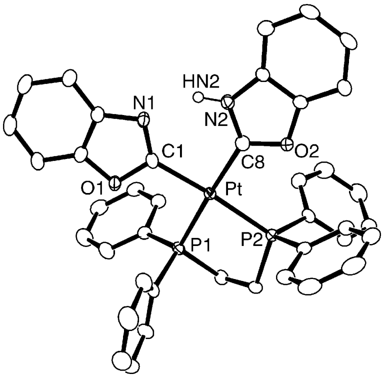


Figure 2. Molecular structure of **5** (all hydrogen atoms except for HN2 and the $CF_3SO_3^-$ anion are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: Pt–P1 2.2953(8), Pt–P2 2.3039(8), Pt–C1 2.041(3), Pt–C8 2.009(3), N2–HN2 0.90(5), HN2···N1 1.89(5), O1–C1 1.385(3), O2–C8 1.349(4), N1–C1 1.307(4), N2–C8 1.337(4); P1–Pt–P2 84.53(3), P1–Pt–C1 92.12(9), P1–Pt–C8 175.43(9), P2–Pt–C1 175.81(9), P2–Pt–C8 92.59(9), C1–Pt–C8 90.91(12), O1–C1–N1 111.8(2), O2–C8–N2 107.6(3).

Complex **5** contains a platinum atom surrounded in a slightly distorted square-planar fashion by the P_2C_2 donor set. While the P1–Pt–P2 angle is, as expected, slightly smaller than 90°, a C1–Pt–C8 angle of 90.91(12)° was found. In spite of the steric demand of the carbene ligands, they are arranged in an unexpected coplanar geometry of the carbene ring planes with a dihedral angle of only 8.3(2)°. Bis(NHC) complexes of square-planar metal centers normally exhibit carbene ligands that are arranged almost perpendicular to the metal coordination plane. The coplanar arrangement in **5** is due to the protonation status of the carbene ligands. Since only one carbene ligand is protonated at the nitrogen atom [distance N2–HN2 0.90(5) Å], this hydrogen atom can form a hydrogen bridge to the nitrogen atoms N1 of the unprotonated, anionic NHC ligand [distance HN2···N1 1.89(5) Å], thus enforcing the unusual coplanar arrangement of the NHC ligands.

We assume that the formation of the N2–HN2···N1 hydrogen bridge is the driving force for the arrangement of the carbene ligands in the sterically unfavorable coplanar arrangement. The molecular structure of **5** can be regarded as the first example for the influence of intramolecular hydrogen bonds on the conformation of bis(NHC) complexes. It also confirms that the rotation of the NHC ligands around the Pt–C bonds is facile.

The difference in the protonation states of the NHC ligands in **5** manifests itself in different geometric parameters for the heterocycles. The deprotonated benzoxazolin-2-ylidene ligand exhibits a shorter N–C$_{\mathrm{carbene}}$ [N1–C1 1.307(4) Å vs. N2–C8 1.337(4) Å] and a longer O–C$_{\mathrm{carbene}}$ [O1–C1 1.385(3) Å vs. O2–C8 1.349(4) Å] bond length than the protonated one. *N*-Deprotonation of a coordinated benzoxazolin-2-ylidene apparently hampers electron delocalization within the five-membered heterocycle. This is also detectable for the O–C–N angles where the typical angle for a benzoxazolin-2-ylidene [107.6(3)°][1] was found for the protonated ligand while the deprotonated ligand shows an enlarged O–C–N angle of 111.8(2)°. The C ligands in **5** can therefore also be classified as an oxazolyl and an NHC ligand. Complexes with a related set of ligands have been described previously.[13b,13d]

The Pt–C$_{\mathrm{carbene}}$ bond lengths in dicarbene complex **5** are slightly longer than those observed for monocarbene complex **3** and are slightly different: a longer Pt–C$_{\mathrm{carbene}}$ separation is found for the deprotonated benzoxazolin-2-ylidene ligand [Pt–C1 2.041(3) Å, Pt–C8 2.009(3) Å].

Conclusions

Isocyanide ligand **1** is capable of replacing chlorido ligands from platinum complexes **2** and **4**. After coordination of **1**, the metal center activates the isocyanide ligand for a subsequent intramolecular nucleophilic attack. For the synthesis of **3**, cleavage of the O–SiMe$_3$ bond by a catalytic amount of fluoride ions resulted in the liberation of the hydroxy group, which subsequently attacked the isocyanide function to form complex **3**. Water added to the reaction mixture led to the formation of the protonated benzoxazolin-2-ylidene ligand. During the synthesis of **3**, a rearrangement of the phosphane ligands from the *cis* configuration in **2** to the *trans* configuration in **3** was observed. The formation of the carbene ligand in **3** was promoted by the addition of tetrabutylammonium fluoride (TBAF), while spontaneous cyclization of the isocyanide ligands has been observed during the formation of **5**. At this time, we do not know which (catalytic) agent in the reaction mixture caused

O–$SiMe_3$ bond cleavage. However, the cleavage reaction must have proceeded with high efficiency as the isolated yield of **5** is 44% (full conversion under the selected reaction conditions would lead to a yield of 50%). The strong activation of isocyanide ligands for a nucleophilic attack by coordination to Pt^{II} has been described previously.[16]

If possible, the benzoxazolin-2-ylidene ligand avoids the *trans*-position to a phosphane ligand. The molecular structure of **5** shows an unusual coplanar arrangement of the NHC ligands which is enforced by an intramolecular N–H···N hydrogen bond.

Experimental Section

General Considerations: All operations were performed in an atmosphere of dry argon by using standard Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker AC 200 (200 MHz) or a Varian U 400 (400 MHz) spectrometer and are reported relative to TMS as internal standard. 2-(Trimethylsiloxy)phenyl isocyanide (**1**) was synthesized as described previously.[4] The syntheses of the starting compounds, *cis*-dichloridobis(triphenylphosphane)platinum(II) (**2**)[21] and dichlorido[1,2-bis(diphenylphosphanyl)ethane]platinum(II)[22] have been described. Microanalytical data for complexes **4** and **5** could not be obtained because of the presence of fluorine-containing counterions.

***trans*-(Benzoxazolin-2-ylidene)chloridobis(triphenylphosphane)platinum(II) Chloride (3):** To a stirred suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.30 g, 0.38 mmol) in thf (60 mL) was added 2-(trimethylsiloxy)phenyl isocyanide (**1**) (0.08 g, 0.42 mmol) at –40 °C. The mixture was stirred at this temperature for 2 h. Subsequently, a small amount of Bu_4NF (10 mg) and water (0.1 mL), were added. The solution was stirred at ambient temperature for an additional 0.5 h. By then, a colorless precipitate had formed, which was separated by filtration. It was washed with a small amount of thf (5 mL) and dried in vacuo. Yield: 0.20 g (0.24 mmol, 64%). Crystals of **3**·$4CH_2Cl_2$ were obtained by cooling a saturated solution of **3** in dichloromethane. Spectral data for the solvent-free compound: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 16.40 (s, 1 H, NH), 7.79–7.00 (m, 34 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 134.8, 134.3, 131.3, 131.1, 130.8, 129.7, 129.0, 128.7, 128.3, 127.9, (Ar-C) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 16.5 [$^{1}J(^{31}P,^{195}Pt)$ = 2511 Hz] ppm.

Di-μ-chloridobis[1,2-bis(diphenylphosphanyl)ethane]diplatinum(II) Bis(trifluoromethanesulfonate) (4): Dichlorido[1,2-bis(diphenylphosphanyl)-ethane] platinum(II) (0.90 g, 1.35 mmol) was suspended in acetone (60 mL). To this suspension was slowly added a solution of silver trifluoromethanesulfonate (0.42 g, 1.63 mmol) in acetone (10 mL). The mixture was stirred for 12 h at ambient temperature with exclusion of light, and the silver chloride formed was subsequently removed by filtration. The filtrate was reduced to 1/3 of the original volume. This solution was poured into diethyl ether (50 mL). Complex **4** precipitated as a colorless powder, which was isolated by filtration. The compound can be recrystallized from acetone/diethyl ether. Yield: 0.62 g (0.40 mmol, 59%). ^{1}H NMR (200 MHz, $[D_6]$acetone): δ = 7.85–7.65 (m, 40 H, Ar-H), 3.08 (s, 8 H, CH_2) ppm. ^{31}P NMR (81 MHz, $[D_8]$acetone): δ = 52.3 [$^{1}J(^{31}P,^{195}Pt)$ = 3780 Hz] ppm.

(Benzoxazolinato-2-ylidene)(benzoxazolin-2-ylidene)[1,2-bis(diphenylphosphanyl)ethane]platinum(II) Trifluoromethanesulfonate (5): To a stirred suspension of **4** (0.10 g, 64 μmol) in thf (3 mL) was added at ambient temperature a solution of **1** (0.03 g, 141 μmol) in thf (1 mL). The suspension turned rapidly into a clear solution. After stirring for 15 min the solution was reduced to 1/2 of the original volume and layered with the same amount of diethyl ether. After two days at ambient temperature colorless crystals of the solvate **5**·C_4H_8O had formed. These were collected by filtration and washed with a small amount of diethyl ether. Yield: 0.03 g (31 μmol, 44%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 13.60 (s, 1 H, NH), 7.84–7.03 (m, 28 H, Ar-H), 2.59 (m, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 184.1 (dd, J = 120 Hz, carbene-C), 134.8, 134.3, 133.5, 130.3, 126.2, 117.0, 113.3 (Ar-C), 30.6 (CH_2) ppm. ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 45.9 ($^{1}J(^{31}P,^{195}Pt)$ = 2259 Hz) ppm.

X-ray Diffraction Studies: Diffraction data for **3**·$3CH_2Cl_2$ and **5**·thf were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 123(2) K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[23] program package. Structure solutions were found with the SHELXS-97[24] package by using the heavy-atom method and were refined with SHELXL-97[25] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. CCDC-691289 (**3**·$3CH_2Cl_2$) and -691290 (**5**·C_4H_8O) 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.

Crystal Data for 3·$3CH_2Cl_2$: $C_{46}H_{41}Cl_8NOP_2Pt$, M = 1164.43, μ = 3.553 mm^{-1}, ρ = 1.650 g cm^{-3}, orthorhombic, *Pnma*, Z = 4, a = 21.948(3) Å, b = 21.903(3) Å, c = 9.7535(11) Å, V = 4688.9(9) Å^3, 52616 measured reflections, 7021 unique reflections (R_{int} = 0.0965), R = 0.0434, wR = 0.0803 for 5565 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions (except for HN where the positional parameters were refined in the least-squares procedure). The asymmetric unit contains 1/2 molecule of **3** and 1.5 molecules of CH_2Cl_2.

Crystal Data for 5·C_4H_8O: $C_{45}H_{41}F_3N_2O_6P_2PtS$, M = 1051.89, μ = 3.536 mm^{-1}, ρ = 1.665 g cm^{-3}, triclinic, $P\bar{1}$, Z = 2, a = 10.5857(15) Å, b = 13.457(2) Å, c = 15.859(2) Å, α = 86.814(3)°, β = 74.630(3)°, γ = 74.377(3)°, V = 2097.6(5) Å^3, 24428 measured reflections, 12077 unique reflections (R_{int} = 0.0333), R = 0.0339, wR = 0.0785 for 11148 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions (except for HN2 where the positional parameters were refined in the least-squares procedure). The asymmetric unit contains one molecule of **5** and one molecule of thf.

Acknowledgments

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