Monatshefte für Chemie 130, 717–723 (1999)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Coordination Chemistry of 2,6-*Bis*(oxazolinyl)-pyridine Ruthenium Complexes

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Summary. The cationic complex [*mer*,*trans*-Ru(*pybox*)$(PPh_3)_2Cl]^+$ (**1**; *pybox* = 2,6-*bis*(oxazolinyl)-pyridine has been prepared by the reaction of either $Ru(PPh_3)_4Cl_2$ or $Ru(PPh_3)_3Cl_2$ with stoichiometric amounts of *pybox*. In solution, **1** is substitutionally labile liberating to some extent PPh_3 to give the neutral complex [*mer*,*cis*-Ru(*pybox*)$(PPh_3)Cl_2$] (**2**). The isomeric complex [*mer*,*trans*-Ru(*pybox*)$(PPh_3)Cl_2$] (**3**) has been afforded by the reaction of $[Ru(cymene)Cl_2]_2$ (cymene = 4-isopropyl toluene) with 2 equiv. of *pybox* and PPh_3 in refluxing toluene. Complex **3** is thermodynamically less stable than **2** and is quantitatively converted to **2** at elevated temperature. The X-ray structure of $\mathbf{2} \cdot (C_2H_5)_2O$ is reported.

Keywords. Ruthenium; *Bis*(oxazolinyl)pyridine; Coordination chemistry; Isomerization.

Koordinationschemie von Ruthenium-2,6-*bis*(oxazolinyl)pyridinkomplexen

Zusammenfassung. Der kationische Komplex [*mer*,*trans*-Ru(*pybox*)$(PPh_3)_2Cl]^+$ (**1**; *pybox* = 2,6-*bis*(oxazolinyl)pyridin) wurde durch die Reaktion von $Ru(PPh_3)_4Cl_2$ oder $Ru(PPh_3)_3Cl_2$ mit einem Äquivalent *pybox* hergestellt. In Lösung ist **1** substitutionslabil und setzt in geringem Maße PPh_3 frei. Es entsteht dabei der neutrale Komplex [*mer*,*cis*-Ru(*pybox*)$(PPh_3)Cl_2$] (**2**). Die isomere Verbindung [*mer*,*trans*-Ru(*pybox*)$(PPh_3)Cl_2$] (**3**) wurde durch Reaktion von $[Ru(Cumol)Cl_2]_2$ (Cumol = 4-Isopropyltoluol) mit zwei Äquivalenten *pybox* und PPh_3 in siedendem Toluol erhalten. Die Verbindung **3** ist thermodynamisch weniger stabil als **2** und kann bei höherer Temperatur quantitativ in **2** überführt werden. Eine Röntgenstrukturanalyse von $\mathbf{2} \cdot (C_2H_5)_2O$ wird präsentiert.

Introduction

Ruthenium complexes containing the anionic NN′N″ terdentate ligand trispyrazolylborate (*Tp*) have received considerable interest in recent years [1]. For instance, it has been shown that the Ru*Tp* fragment facilitates the formation of reactive vinylidene complexes which are able to promote C–C coupling reactions between alkynes and olefins [2]. It is interesting to note that all Ru*Tp* complexes are typically octahedral with *Tp* adopting exclusively a facial coordination

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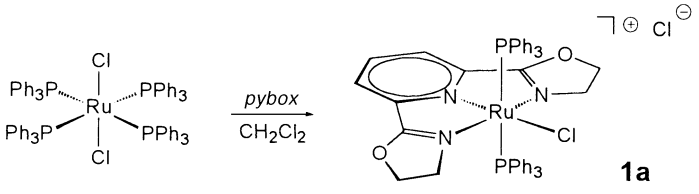
geometry, similar to the *Cp* and *Cp** ligands. The application of other terdentate ligands such as 2,2′,2″-terpyridine (*trpy*) [3] or 2,6-*bis*(dimethylaminomethyl)pyridine (*bdp*) [4] has received much less attention. In the present work we will report on the synthesis and characterization of ruthenium complexes containing the NN′N″ terdentate ligand 2,6-*bis*(oxazolinyl)pyridine (*pybox*) which, in contrast to *Tp*, prefers a meridional arrangement. The resulting complexes might thus exhibit a different reactivity. In fact, substituted 2,6-*bis*(oxazolinyl)pyridine ligands have become important chiral coligands in ruthenium chemistry such as in the asymmetric catalytic cyclopropanation of olefins and diazoacetates [5].

Results and Discussion

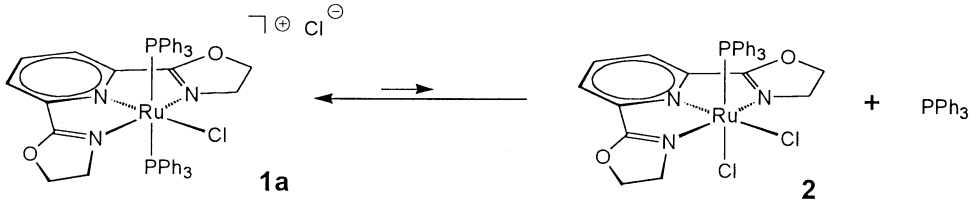
Treatment of either $Ru(PPh_3)_4Cl_2$ or $Ru(PPh_3)_3Cl_2$ with stoichiometric amounts of *pybox* in CH_2Cl_2 gives, upon workup, [*mer*, *trans*-Ru(*pybox*)$(PPh_3)_2$Cl]Cl (**1a**) in 56% isolated yield. **1a** has been characterized by elemental analysis, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The *mer*, *trans* arrangement of the PPh_3 ligands is readily apparent from the ^{31}P{^{1}H} NMR spectrum by the singlet at 22.0 ppm. Furthermore, in the ^{1}H NMR spectrum the CH_2 groups vicinal to the oxygen and nitrogen atoms of the *pybox* ligand exhibit only two sets of oxazoline protons centered at 4.36 (4H) and 3.65 ppm (4H), respectively (Scheme 1). When the above reaction is performed in the presence of 1 equiv. of either $NaBPh_4$ or $AgCF_3SO_3$, the compounds [*mer*,*trans*-Ru(*pybox*)$(PPh_3)_2$Cl]BPh_4 (**1b**) and [*mer*,*trans*-Ru(*pybox*)$(PPh_3)_2$Cl]CF_3SO_3 (**1c**) are obtained in yields of 60 and 40%, respectively.

The yield of **1** is moderate due to the formation of two by-products exhibiting resonances at 25.5 and 42.8 ppm in the ^{31}P{^{1}H} NMR spectrum. While we were unable to isolate or identify the first by-product, the second one has been isolated and characterized as [*mer*,*cis*-Ru(*pybox*)$(PPh_3)Cl_2$] (**2**) (*vide infra*). These results are in contrast to the reactions of $Ru(PPh_3)_3Cl_2$ with 2,6-*bis*(diphenylphosphinomethyl)pyridine (*pnp*) [6], *bdp* [3], and *trpy* [4] where only monophosphine complexes were obtained. In the first two cases the *mer*, *trans*-isomer was isolated in the latter case the *mer*,*cis*-complex was obtained.

In solution, **1a** is substitutionally labile liberating some PPh_3 and forming **2** (Scheme 2). This equilibrium depends strongly on the solvent. Thus, whereas in acetone no evidence for the formation of **2** was found, in $CDCl_3$ about 10% of **2** are present according to ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. When **1a** is refluxed in toluene, **2** is formed in about 30% yield. At room temperature no free PPh_3 could be detected by ^{31}P NMR spectroscopy, pointing to a rapid equilibrium on the NMR



Scheme 1



Scheme 2

time scale (101.26 MHz), whereas at lower temperature the signal of free PPh_3 was detected at −4.8 ppm.

Addition of excess chloride in the form of KCl or Bu_4NCl does not affect the position of the equilibrium. On the other hand, in the presence of extra added PPh_3, the formation of **2** was completely suppressed. It is interesting to note that in $CHCl_3$ even **1b** and **1c** give **2**, albeit with less than 5% conversion. In addition, also small amounts of a not yet identified compound were observed ($^{31}P\{^1H\}$ NMR: 30.0 ppm). Characterization of **2** was performed by NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of **2** gives rise to four characteristic multiplets centered at 4.80 (2H), 4.57 (2H), 4.24 (2H), and 3.92 ppm (2H).

In attempting to grow crystals of **1a** suitable for an X-ray study, crystals of **2** in the form of the solvate $\mathbf{2}\cdot(C_2H_5)_2O$ were obtained by slow diffusion of diethyl ether into a solution of **1a** in CH_2Cl_2 [7]. A structural view is shown in Fig. 1 with

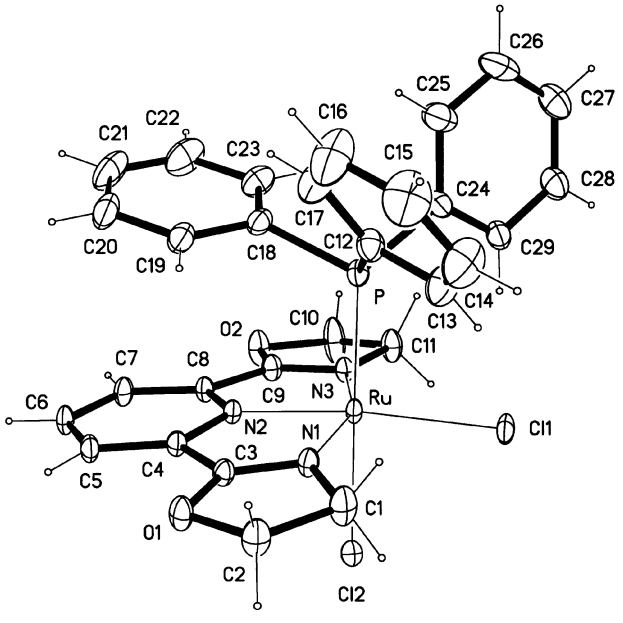
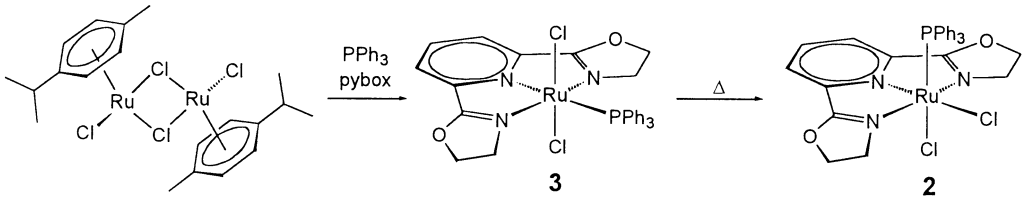


Fig. 1. Structural view of [*mer,cis*-Ru(*pybox*)(PPh_3)Cl_2]$\cdot(C_2H_5)_2O$ ($\mathbf{2}\cdot(C_2H_5)_2O$) showing 20% probability thermal ellipsoids ($(C_2H_5)_2O$) omitted for clarity); selected bond lengths (Å) and angles (°): Ru-N(1) 2.078(2), Ru-N(2) 1.963(2), Ru-N(3) 2.112(2), Ru-P 2.275(1), Ru-Cl(1) 2.423(1), Ru-Cl(2) 2.464(1), N(1)-Ru-N(2) 78.1(1), N(2)-Ru-N(3) 78.0(1), N(1)-Ru-N(3), 156.0(1), N(2)-Ru-Cl(1) 172.5(1), P-Ru-Cl(2) 177.5(1), Cl(1)-Ru-Cl(2) 88.3(1)



Scheme 3

important bond lengths and angles reported in the caption. The coordination polyhedron of Ru is a distorted octahedron with P-Ru-Cl(2) and N(2)-Ru-Cl(1) angles of 177.5(1) and 172.5(1)°, respectively, and a distinctly smaller N(1)-Ru-N(3) angle of 156.0(1)°. The two Ru-N bond lengths *trans* to one another are significantly longer (Ru-N(1) = 2.078(2) Å, Ru-N(3) = 2.112(2) Å) than that *trans* to the equatorial chloride ligand (Ru-N(2) = 1.963(2) Å). The Ru-Cl bond lengths are 2.423(1) and 2.464(1) Å for the equatorial Cl(1) and for the axial Cl(2), respectively. The *pybox* ligand is not perfectly planar but somewhat curved (oxazolinyl rings relative to the pyridine ring are bent away from the PPh_3 ligand). The rms. deviation from planarity is 0.084 Å for non-hydrogen atoms. Such deviations from planarity for the meridional ligand are not uncommon among Ru(*pybox*) and Ru(*trpy*) complexes. Apart from packing, they can be attributed to some strain release in the coordinated tridentate ligand.

The isomeric complex [*mer*,*trans*-Ru(*pybox*)(PPh_3)Cl_2] (**3**) derives from the reaction of $[Ru(cymene)_2Cl_2]_2$ (cymene = 4-isopropyl toluene) with 2 equiv. of *pybox* and PPh_3 in refluxing toluene in 50% isolated yield. Besides, also the known complex Ru(cymene)(PPh_3)Cl_2 [11] and **2** were formed in 35 and 12% yield, respectively (Scheme 3). It may be noted that the established procedure for preparing complexes of the type [*mer*,*cis*-Ru(*pybox*)(L)Cl_2] (*L* = CO, ethylene) [5b] proved to be unsuccessful. Thus, treatment of $[Ru(cymene)_2Cl_2]_2$ with *pybox* (2 equiv.) for a few minutes in CH_2Cl_2 subsequent addition of *L* (2 equiv.), and stirring for 2 h at room temperature gave only poor yields for $L = PPh_3$. This may be attributable to the stability of Ru(cymene)(PPh_3)Cl_2. Characterization of **3** was again accomplished by a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of **3** is significantly different from that of **2**, exhibiting two triplets centered at 4.74 (4H) and 3.49 ppm (4H) which are assigned to the CH_2 groups vicinal to the oxygen and nitrogen atoms. The ^{31}P NMR resonance is found at low field (46.7 ppm) which is characteristic for a phosphine residue bonded *trans* to the pyridine moiety [3a]. Complex **3** turned out to be thermodynamically less stable than **2**. In fact, **2** could be obtained even quantitatively upon refluxing a solution of **3** in toluene for 5 h.

We have previously shown that the related complex Ru*Tp*(PPh_3)$_2$Cl (*Tp* = *tris*pyrazolylborate) forms vinylidene complexes of the types Ru*Tp*(PPh_3)(=C=CHR)Cl and [Ru*Tp*(PPh_3)$_2$(=C=CHR)]$^+$ of which the first are able to promote C–C coupling reactions [2, 8]. Thus, we reasoned that Ru(*pybox*)(vinylidene) complexes might exhibit interesting reactivities in this regard. However, any attempt to synthesize Ru(*pybox*)(=C=CHPh)Cl_2 and [Ru(*pybox*)(=C=CHPh)(PPh_3)Cl]$^+$ from reactions of HC≡CPh with **2** or **3** was unsuccessful.

Experimental

General

All manipulations were performed under an inert atmosphere of argon using *Schlenk* techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [9]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. TLC was performed on Riedel-deHaen TLC-sheets silica gel 60 F 254 (layer thickness 0.2 mm). For column chromatography, silica gel purchased from Merck, grade 60, 70–230 mesh, 60 Å was used. $Ru(PPh_3)_4Cl_2$ [10], $[RuCl_2(p\text{-cymene})]_2$ [11], and *pybox* [12] were prepared according to the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to internal $SiMe_4$ and external H_3PO_4 (85%). Microanalyses were done by Microanalytical Laboratories, University of Vienna.

[mer,trans-Ru(pybox)(PPh$_3$)$_2$Cl]Cl (**1a**)

A solution of $Ru(PPh_3)_4Cl_2$ (300 mg, 0.246 mmol) in CH_2Cl_2 (5 cm^3) was treated with *pybox* (56 mg, 258 mmol) and stirred for 2 h at room temperature. The volume of the solution was reduced to about 1 cm^3 and **1a** was precipitated upon addition of Et_2O. The crude product was purified by column chromatography (20 g silica gel, eluent 1/40 (v/v) EtOH/CH_2Cl_2) collecting the yellow band. The product was then recrystallized from acetone.

Yield: 126 mg (56%); $C_{47}H_{41}Cl_2N_3O_2PRu$ (882.81 g/mol); calcd.: C 63.95, H 4.68, N 4.76; found: C 64.23, H 4.88, N 4.51; ^1H NMR (δ, $CDCl_3$, 20°C): 7.99 (t, $^3J_{HH} = 8.1$ Hz, 1H, py^4), 7.57–7.50 (m, 2H), 7.40–7.24 (m, 30H), 4.36 (t, $^3J_{HH} = 9.5$ Hz, 4H), 3.65 (t, $^3J_{HH} = 9.5$ Hz, 4H) ppm; $^{13}C\{^1H\}$ NMR (δ , $CDCl_3$, 20°C): 167.7 (2C, ox^2), 148.1 (2C, $py^{2,6}$), 134.3 (py^4), 133.8 (pt, $^2J_{PC} = 5.3$ Hz, 12C, $PPh_3^{2,6}$), 131.6 (pt, $^1J_{PC} = 20.0$ Hz, 6C, PPh_3^1), 131.0 (6C, PPh_3^4), 129.3 (pt, $^3J_{PC} = 4.5$ Hz, 12C, $PPh_3^{3,5}$), 127.0 (2C, $py^{3,5}$), 72.4 (*ox*), 53.2 (*ox*) ppm; $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 22.0 ppm.

[mer,trans-Ru(pybox)(PPh$_3$)$_2$Cl]BPh$_4$ (**1b**)

This complex has been prepared analogously to **1a** except that 1 equiv. of $NaBPh_4$ was added to the reaction mixture.

Yield: 61%, $C_{71}H_{61}BClN_3O_2P_2Ru$ (1197.57 g/mol); calcd.: C 71.21, H 5.13, N 3.51; found: C 71.04, H 5.32, N 3.71.

[mer,trans-Ru(pybox)(PPh$_3$)$_2$Cl]SO$_3$CF$_3$ (**1c**)

1c was prepared analogously to **1a** except that 1 equiv. of $AgCF_3SO_3$ was added to the reaction mixture and the eluent was slowly changed during eluation from 1/40 (v/v) EtOH/CH_2Cl_2 to 1/1 (v/v) EtOH/CH_2Cl_2.

Yield: 39%; $C_{48}H_{41}ClF_3N_3O_5PRuS$ (996.43 g/mol); calcd.: C 57.86, H 4.15, N 4.22; found: C 57.99, H 4.28, N 4.21; NMR spectra according to **1a**.

[mer,cis-Ru(pybox)(PPh$_3$)Cl$_2$] (**2**)

A solution of **3** (50 mg, 0.077 mmol) in toluene (4 cm^3) was heated for 4.5 h at reflux. After evaporation of the solvent, the crude reaction product was transferred to a glass frit and washed with Et_2O (3×2 cm^3) and dried *in vacuo*.

Yield: 43 mg (86%); $C_{29}H_{26}Cl_2N_3O_2PRu$ (651.50 g/mol); calcd.: C 53.46, H 4.02, N 6.45; found: C 53.74, H 3.99, N 6.21; ^1H NMR (δ, $CDCl_3$, 20°C): 7.71–7.64 (m, 6H), 7.40–7.18 (m, 12H), 4.89–

4.78 (m, 2H, *ox*), 4.63–4.52 (m, 2H, *ox*), 4.31–4.17 (m, 2H, *ox*), 3.98–3.85 (m, 2H, *ox*) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 168.1 (2C, ox^2), 151.8 (2C, $py^{2,6}$), 134.9 (py^4), 133.6 (d, $^2J_{PC} = 10.0$ Hz, 6C, $PPh_3^{2,6}$), 133.4 (d, $^1J_{PC} = 43.4$ Hz, 3C, PPh_3^1), 130.1 (d, 3C, $^4J_{PC} = 2.3$ Hz, PPh_3^4), 128.7 (d, $^3J_{PC} = 9.3$ Hz, 6C, $PPh_3^{3,5}$), 124.1 (2C, $py^{3,5}$), 72.4 (*ox*), 52.9 (*ox*) ppm; $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 46.7 ppm; $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20°C): 42.8 ppm.

[mer,trans-Ru(pybox)(PPh_3)Cl_2] (**3**)

Method a: A solution of $[RuCl_2(p\text{-cymene})]_2$ (192 mg, 0.316 mmol) and *pybox* (137 mg, 0.631 mmol) in CH_2Cl_2 (8 cm^3) was stirred at room temperature for 1 h. The dark red solution was treated with PPh_3 (166 mg, 0.631 mmol) and heated under reflux for 2 h. The volume of the violet reaction mixture was reduced to about 2 cm^3, and upon addition of Et_2O a dark red precipitate was formed which was collected on a glass frit and washed with Et_2O (5×2 cm^3). The crude product (360 mg) was redissolved in 1.5 cm^3 of CH_2Cl_2 and purified by column chromatography (30 g silica gel, eluent 1/20 (v/v) MeOH/CH_2Cl_2) collecting the band at $R_f = 0.19$ (dark violet). The solvent was evaporated to dryness resulting in a dark violet solid which was washed with Et_2O (2×2 cm^3) and dried under vacuum. Yield: 120 mg (29%).

Method b: A solution of $[RuCl_2(p\text{-cymene})]_2$ (192 mg, 0.316 mmol), PPh_3 (166 mg, 0.631 mmol), and *pybox* (137 mg, 0.631 mmol) in toluene (8 cm^3) was heated under reflux for 1 h. The volume of the violet reaction mixture was reduced to 2 cm^3, and upon addition of Et_2O a dark red precipitate was formed which was collected on a glass frit and washed with Et_2O (5×2 cm^3). The crude product was purified by column chromatography as described in Method a.

Yield: 210 mg (51%); $C_{29}H_{26}Cl_2N_3O_2PRu$ (651.50 g/mol); calcd.: C 53.46, H 4.02, N 6.45; found: C 53.54, H 4.29, N 6.31; ^1H NMR (δ, $CDCl_3$, 20°C): 7.99–7.74 (m, 9H), 7.40–7.36 (m, 9H), 4.74 (t, $^3J_{HH} = 9.6$ Hz, 4H, *ox*), 3.49 (t, $^3J_{HH} = 9.6$ Hz, 4H, *ox*) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 167.3 (d, $J_{PC} = 3.3$ Hz, 2C, ox^2), 149.3 (d, $^3J_{PC} = 1.4$ Hz, 2C, $py^{2,6}$), 137.2 (d, $^1J_{PC} = 38.2$ Hz, 3C, PPh_3^1), 135.5 (d, $^2J_{PC} = 10.0$ Hz, 6C, $PPh_3^{2,6}$), 135.0 (py^4), 129.8 (d, $^4J_{PC} = 2.4$ Hz, 3C, PPh_3^4), 128.3 (d, $^3J_{PC} = 9.1$ Hz, 6C, $PPh_3^{3,5}$), 123.2 (d, $^4J_{PC} = 2.4$ Hz, 2C, $py^{3,5}$), 71.7 (*ox*), 54.7 (*ox*) ppm; $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 46.7 ppm.

X-Ray structure determination of [mer,cis-Ru(pybox)(PPh_3)Cl_2]·$(C_2H_5)_2O$ (**2**·$(C_2H_5)_2O$)

A red platy crystal (0.46×0.30×0.06 mm) of **2**·$(C_2H_5)_2O$ ($C_{29}H_{26}Cl_2N_3O_2$)·$(C_2H_5)_2O$, $Fw = 725.59$, monoclinic, space group $P2_1/c$, $a = 15.699(2)$, $b = 11.294(2)$, $c = 19.436(4)$ Å, $\beta = 104.90(1)°$, $V = 3330(1)$ $Å^3$, $Z = 4$, d(calcd) = 1.447 g/cm^3, $T = 298$ K) was used for data collection with a Siemens/Bruker SMART CCD diffractometer (sealed X-ray tube, MoK_α radiation, graphite monochromator, 0.3° ω-scan frames; $\theta = 2$–27°, $-20 \le h \le 20$, $-14 \le k \le 13$, $-17 \le l \le 24$, 18926 reflections collected, 7243 reflections independent, $R_{int} = 0.022$, correction for absorption by multiscan method and program SADABS, transmission factors 0.76–0.93). The structure was solved with direct methods using the program SHELXS86 [13] and was refined on F^2 with the program SHELXL93 [14] using anisotropic displacement factors for non-hydrogen atoms. Hydrogen atoms were inserted in idealized positions and refined riding with the atoms to which they were bonded. The occupancy of the diethyl ether solvent molecule was allowed to vary (final value 1.06(1)) in order to account for a partial replacement of diethyl ether by some CH_2Cl_2. Final $R1 = 0.046$ and $wR2 = 0.082$ for all 7243 independent reflections and 390 varied parameters. $R1 = 0.031$ for the 5855 data with $F^2 > 2\sigma(F^2)$. Excursions in final difference *Fourier* map between −0.60 and 0.56 e$Å^{-3}$. Additional material to the structure determination may be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, referring to the deposition number CSD-408748, the names of the authors, and citation of the present paper.

Acknowledgements

Financial support by the *Jubiläumsfonds der Oesterreichischen Nationalbank* is gratefully acknowledged (Project No. 6474).

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Received November 17, 1998. Accepted (revised) December 22, 1998