Titanium Complexes Containing Bulky η^2-1,2,4-Triazolato Ligands

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The unusual η^2-coordination of a 1,2,4-triazolato ligand to a transition metal is described. The synthesized compounds $[Ti(\eta^2\text{-tz})_4]$ (**1**), $[(C_5Me_4CH_2Ph)Ti(\eta^2\text{-tz})Cl_2]$ (**2**), $[Cp^*Ti(\eta^2\text{-tz})Cl_2]$ (**3**) and $[Cp^*Ti(\eta^2\text{-tz})_3]$ (**4**) (tzH = 3,5-diisopropyl-1,2,4-triazole) were characterized by ^1H and ^{13}C NMR spectroscopy and, in the case of **1** and **2**, by X-ray crystallography. Both structures confirm the η^2-coordination of the ligand. In compound **1** all four ligands coordinate in an η^2 fashion leading to a metal center surrounded by eight nitrogen atoms. The core of the fragment formed by the central atom and the triazolato planes exhibits a distorted D_{2d} symmetry. A variable temperature NMR spectroscopy experiment performed on **1** confirms the occurrence of two different isopropyl groups at low temperature. The structure of compound **2** shows the geometry of the molecule in a distorted C_s symmetry, with the mirror plane perpendicular to the cyclopentadienyl and triazolato rings. The tz ligand is oriented in a *transoid* position relative to the benzyl substituent of the $C_5Me_4CH_2Ph$ group.

Introduction

Pyrazoles and triazoles represent a class of molecules with ideal ligand properties that allow a wide variety of structures and bonding options.[1−4] The preparation of the parent heterocycle is in most cases achieved by straightforward organic reactions, enabling easy tuning of the substituents attached to the five-membered ring.[5,6] In addition, they may act as neutral or monoanionic ligands. All these factors explain their extensive use in coordination chemistry. The most common bonding modes in these complexes are η^1, bridging between two metal atoms in a μ_2-η^1:η^1 fashion, or a μ_3-η^1:η^1:η^1 fashion for triazolato ligands. However, many different bonding modes have been found in recent years.[4,7−9] With pyrazolato ligands, an η^2-coordination has been found in complexes of f-block[10−15] and, quite unexpectedly, d-block metals[16−22] as well as with main group elements.[23−27] However, with triazolato ligands only one crystallographically established η^2-coordination has been reported, namely in a benzo-1,2,3-triazolato potassium salt, where an η^2-interaction was found in the solid-state structure.[28] No example of an η^2-1,2,4-triazolato ligand has been described as yet.[29]

Herein, we present a series of compounds that contain the unusual η^2-coordination of a 1,2,4-triazolato ligand. The complexes $[Ti(\eta^2\text{-tz})_4]$ (**1**), $[(C_5Me_4CH_2Ph)Ti(\eta^2\text{-tz})Cl_2]$ (**2**), $[Cp^*Ti(\eta^2\text{-tz})Cl_2]$ (**3**) and $[Cp^*Ti(\eta^2\text{-tz})_3]$ (**4**) (tz = 3,5-diisopropyl-1,2,4-triazolato) have been synthesized by the appropriate metathesis reaction and characterized by NMR spectroscopy, mass spectrometry and elemental analysis. In addition, the solid state structures of **1** and **2** were determined by X-ray crystallography.

Results and Discussion

Preparation of Titanium Compounds

The requirements for an ideal ligand system for high oxidation state early transition metals are steric bulk, to avoid oligomerization, and/or electron donating properties to stabilize the electrophilic metal center. Sterically demanding alkyl groups seem to meet those premises. We recently described the synthesis of a triazole ligand bearing bulky isopropyl groups in the 3,5-positions.[30]

The reaction of tetrakis(dimethylamido)titanium(IV) with four equivalents of tzH in toluene at room temperature gave $[Ti(\eta^2\text{-tz})_4]$ (**1**), isolated as yellow crystals from hexane in good yield [Equation (1)].

$$[Ti(NMe_2)_4] + 4\ tzH \xrightarrow[-4\ NHMe_2]{toluene} \underset{\mathbf{1}\ (68\ \%)}{[Ti(\eta^2\text{-tz})_4]} \qquad (1)$$

The reaction is fast, as the formation of $HNMe_2$ was immediately apparent. The compound is highly soluble in hydrocarbon solvents, and thus had to be crystallized from concentrated solutions at low temperatures. The highest peak in the mass spectrum was assignable to the monomeric molecular ion. This is consistent with the solid-state structure determined by X-ray crystallography (vide infra).

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The ^1H and ^{13}C NMR spectra at room temperature each exhibit one set of signals, indicating a highly symmetric coordination of the ligands. However, a variable temperature ^1H NMR spectroscopy experiment shows the signals to split into two sets with a coalescence temperature of approx. 200 K, pointing to an asymmetric coordination of the ligands at low temperature (Figure 1).

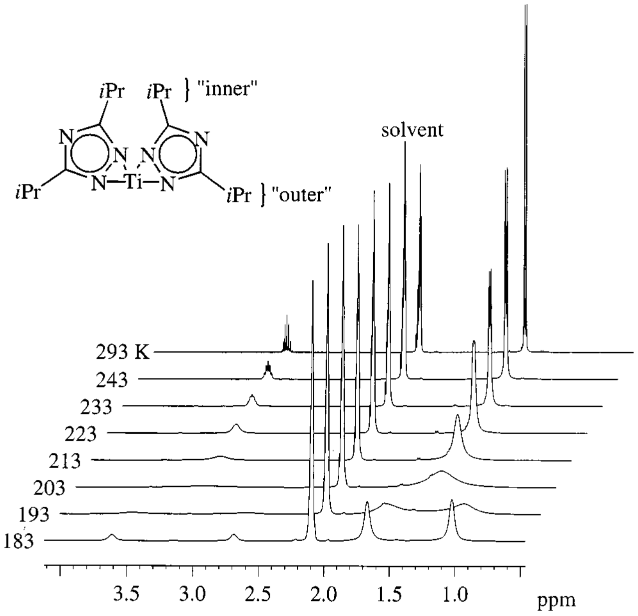
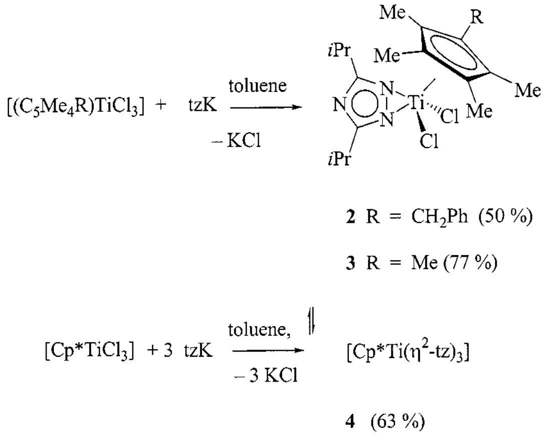


Figure 1. VT NMR spectra of **1** in [D$_8$]toluene; a fragment of **1** consisting of two coplanar triazolato ligands shows the two types of isopropyl groups

The spectrum at 183 K shows two relatively broad signals for six protons each ($\delta = 1.02$ and 1.67) and two signals for one proton each ($\delta = 2.69$ and 3.61) for two different isopropyl groups. A COSY NMR spectrum at 183 K reveals cross-peaks between the methyl signal at $\delta = 1.02$ and the CH signal at $\delta = 2.69$, while the resonance at $\delta = 1.67$ has a cross-peak with that at $\delta = 3.61$. The temperature could not be decreased further due to freezing of the solvent (toluene) thereby presumably preventing sharper signals that show the expected doublets and septuplets. With increasing temperature the structure apparently becomes more dynamic so that the room temperature spectrum shows only one averaged set of signals. The low-temperature spectrum is consistent with the solid-state structure determined by X-ray crystallography at 133 K, which shows two triazolato rings almost coplanar to each other, with the other two perpendicular to them. Two of the four nitrogen atoms coordinated to Ti in one plane form a large N−Ti−N angle [e.g. 169.25(6)° for N1−Ti1−N7], whereas the other two form a small one [e.g. 92.77(6)° N2−Ti1−N8]. This coordination leads to magnetically nonequivalent "inner" and "outer" isopropyl groups, which give rise to the two sets of signals.

The reaction of [(C$_5$Me$_4$CH$_2$Ph)TiCl$_3$] and [Cp*TiCl$_3$], respectively, with one equivalent of tzK in toluene at room temperature afforded the complexes [(C$_5$Me$_4$CH$_2$Ph)Ti(η^2-tz)Cl$_2$] (**2**) and [Cp*Ti(η^2-tz)Cl$_2$] (**3**) as red crystalline materials in medium to good yields (Scheme 1). The ^1H and ^{13}C NMR spectra show the coordination of one triazolato ligand in a symmetric fashion. The occurrence of an η^2-coordinated ligand was confirmed by the X-ray crystal structure analysis of **2** (vide infra). In the mass spectrum, the molecular ion could be detected indicating a thermal stability of the species.



Scheme 1

The analogous Cp derivative [CpTi(η^2-tz)Cl$_2$] can be formed by the same reaction procedure as above, producing orange crystals. The X-ray crystal structure determination confirms the connectivity as well as the η^2-coordination of the triazolato ligand, although the insufficient quality of the structural analysis due to disorder and twinning problems prevents the discussion of bond lengths and angles. These are general problems in these mixed Cp/tz as well as Cp*/tz systems, as several attempts with different crystals did not improve the structures. The combination of the steric properties of the two ligands seems to lead to disordered and twinned structures that can only be avoided by the substitution of a methyl by a benzyl group at the Cp* ring. The behavior of [CpTi(η^2-tz)Cl$_2$] in solution is unclear. NMR spectra of crystalline material in C$_6$D$_6$ show several signals in the Cp and isopropyl group region pointing to an instability in solution. Presumably the steric protection provided by the Cp group and the isopropyl groups is not large enough, giving rise to oligomeric structures in solution.

The treatment of [Cp*TiCl$_3$] with three equivalents of tzK in refluxing toluene for 2 h afforded the orange compound [Cp*Ti(η^2-tz)$_3$] (**4**) in high yield as shown in Scheme 1. NMR spectroscopic data as well as an attempted X-ray crystal structure analysis are consistent with the formation of a compound that contains three η^2-coordinated triazolato ligands. The addition of only two equivalents of tzK to [Cp*TiCl$_3$] gave mixtures of **3** and **4**, but no evidence was found for the formation of the monochloride species [Cp*Ti(η^2-tz)$_2$Cl] either by NMR spectroscopy or mass spectrometry.

Structural Studies

X-ray crystallography on a single crystal of **1** confirms a monomeric species with a titanium atom in a distorted tetrahedral environment, assuming the triazolato ligands occupy only one coordination site. All four ligands coordinate in an η^2 fashion, leading to a metal center surrounded by eight nitrogen atoms. Figure 2 shows an ORTEP view of **1**; crystallographic data are given in Table 1 and selected bond lengths and angles in Table 2.

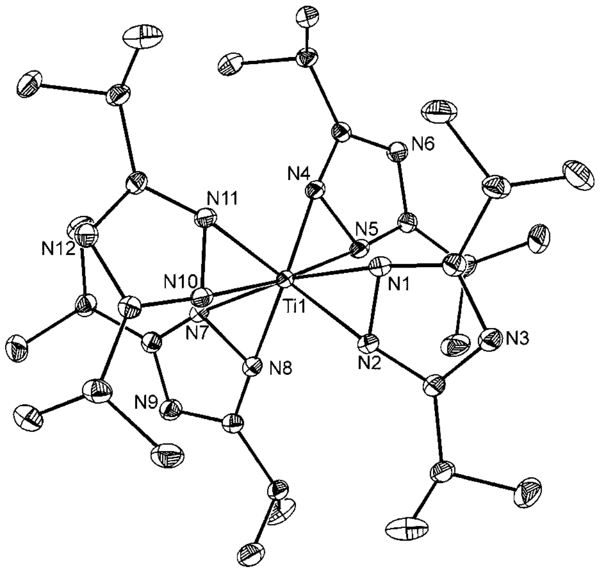


Figure 2. ORTEP view of **1** (thermal ellipsoids at the 50% probability level)

Table 1. Experimental crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{32}H_{56}N_{12}Ti$	$C_{24}H_{33}C_{12}N_3Ti$
Fw	656.79	482.33
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.826(2)	6.8029(14)
b (Å)	15.741(3)	12.361(3)
c (Å)	22.287(5)	14.845(3)
α (deg)		96.86(3)
β (deg)	90.89(3)	97.93(3)
γ (deg)		96.93(3)
V (Å^3)	3797.5(13)	1215.5(4)
Z	4	2
T (K)	133(2) K	133(2)
λ (Å)	0.71073	0.71073
$\rho_{\text{calcd.}}$ (mg/cm^3)	1.149	1.318
μ (mm^{-1})	0.263	0.588
Reflections measured	40821	10917
Reflections unique	6707 (R_{int} = 0.0527)	2830 (R_{int} = 0.0908)
$R1$ (%)	5.54	6.50
$wR2$ (%)	9.90	12.73

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Ti1−N1	2.1289(16)	Ti1−N2	2.0338(15)
Ti1−N4	2.0284(15)	Ti1−N5	2.0816(16)
Ti1−N7	2.1285(16)	Ti1−N8	2.0151(16)
Ti1−N10	2.1019(16)	Ti1−N11	2.0591(16)
N1−Ti1−N2	38.73(6)	N1−Ti1−N7	169.25(6)
N2−Ti1−N8	92.77(6)	N1−Ti−N5	86.41(6)
N1−Ti−N10	91.87(6)	N4−Ti1−N5	39.43(6)

The triazolato rings can be grouped approximately into two, almost orthogonal planes. The average planarity in each group is satisfied within a few degrees, as evidenced by, for example, the torsion angles of 174.07(1)° (N1−N2−Ti1−N8) and 175.79(1)° (N5−N4−Ti1−N10). Whereas the core of the fragment formed by the central atom and the triazolato planes exhibits a symmetry close to D_{2d}, the steric hindrance between adjacent isopropyl groups leads to a deviation from the perfect arrangement. The eight coordinated nitrogen atoms may be considered as forming two tetrahedra, a very flattened, almost planar one, [N5−Ti1−N10 = 172.56(6)° and N1−Ti1−N7 = 169.25(6)] and another elongated one [N2−Ti1−N8 = 92.77(6) and N4−Ti1−N11 = 94.83(6)]. The bond lengths in the former tetrahedron are longer than in the latter by approx. 0.1 Å. The most interesting features of the structure are the three-membered TiN_2 metallacycles, with Ti−N bond lengths between 2.0151(16) and 2.1289(16) Å and N−Ti−N angles between 38.73(6)° and 39.43(6)°. Comparison of the structure of **1** with that of the η^2-pyrazolato species $[Ti(\eta^2\text{-}3,5\text{-}Me_2pz)_4]$ employing a less bulky ligand, recently described by Winter and co-workers, reveals a similar geometry.[17] Apparently, steric hindrance seems not to be a prerequisite for the formation of the homoleptic species, whereas bulky substituents are important for the stability of the compounds **2−4**. Other titanium complexes with three-membered TiN_2 rings contain η^2-diazenido,[31] -diazo[32] or -hydrazido[33,34] ligands. Whereas the η^2-diazenido and -diazo ligands show similar structural features to those of **1**, the latter ones are slightly different in that the Ti−N bond lengths in η^2-hydrazido complexes differ by approx. 0.3 Å leading to a distinct tilting of the ligand.

The X-ray diffraction study of **2** confirms the η^2-coordination of the triazolato ligand. An ORTEP diagram is shown in Figure 3 and selected bond lengths and angles in

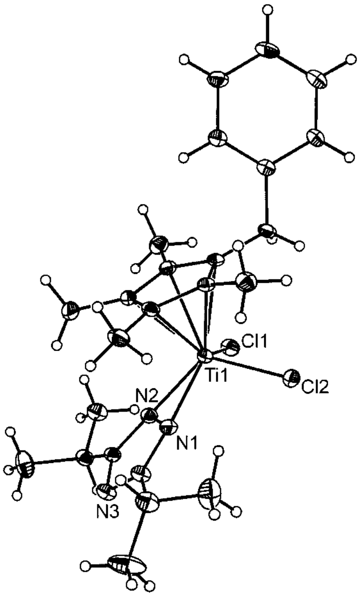


Figure 3. ORTEP view of **2** (thermal ellipsoids at the 50% probability level)

Table 3. Selected bond lengths (Å) and angles (°) for **2**

Ti1−N1	2.055(3)	Ti1−N2	2.061(3)
Ti1−Cl1	2.295(1)	Ti1−Cl2	2.284(1)
Ti1−C9	2.352(3)	Ti1−C10	2.357(4)
Ti1−C11	2.370(4)	Ti1−C12	2.384(4)
Ti1−C13	2.381(4)	N1−N2	1.372(4)
N1−Ti1−N2	38.95(12)	N1−Ti1−Cl1	123.97(10)
N2−Ti1−Cl1	91.91(10)	N1−Ti−Cl2	93.42(10)
N2−Ti1−Cl2	121.52(10)	Cl1−Ti1−Cl2	96.09(5)

Table 3. The structure shows the geometry of the molecule in a distorted C_s symmetry, with the mirror plane perpendicular to the Cp and tz rings.

The titanium atom is coordinated in a distorted tetrahedral geometry assuming that the Cp and tz ligand occupy only one coordination site. The tz ligand is oriented in a *transoid* position relative to the benzyl substituent of the Cp group for steric reasons. The bond lengths and angles of the three-membered TiN_2 ring are virtually identical to those in **1**, although the formal coordination number at Ti is smaller.

Conclusion

In summary, the unusual η^2-coordination of a triazolato ligand in a transition metal complex has been established. The formation of the symmetric homoleptic complex **1** as well as the less-symmetric heteroleptic systems **2**−**4** proves the relative stability of the η^2-pattern. The use of the potassium salt of the triazole enables a convenient route towards Ti^{IV} complexes for HSAB reasons.

Further investigations will concern the role of d electrons[22] in the stability of the η^2 pattern and an analysis of the related spectroscopic consequences, and we are also continuing to explore the coordination behavior and structural features of triazolato complexes of d-block metal ions.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen. All common reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise indicated. Melting points were determined on a Büchi B-540 melting point apparatus in sealed glass tubes and are uncorrected. NMR spectra were recorded on Bruker Avance 200 and Bruker Avance 500 spectrometers (for the VT NMR experiment). The chemical shifts are referenced to external $SiMe_4$. Mass spectra were recorded on a Finnigan MAT 8230 or Varian MAT CH5 spectrometer.

Preparation of $[Ti(\eta^2\text{-tz})_4]$ (1): A solution of $[Ti(NMe_2)_4]$ (0.58 g, 2.6 mmol) in toluene (75 mL) was added at room temperature to a suspension of tzH (1.59 g, 10.4 mmol) in toluene (20 mL). Evolution of dimethylamine was immediately apparent. The resulting yellow-brown solution was stirred overnight and then evaporated to dryness. The brown residue was extracted with hexane (50 mL) and filtered through Celite. The solvent was reduced to 10 mL and the product crystallized at −25 °C as yellow cubes (1.15 g, 68%). Crystals suitable for X-ray crystallography were grown from hexane at −25 °C. M.p. 98 °C. ^1H NMR (C_6D_6): δ = 1.30 [d, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$, 12 H], 3.14 [sept, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$, 1 H]. ^{13}C NMR (C_6D_6): δ = 21.9 [$CH(CH_3)_2$], 28.5 [$CH(CH_3)_2$], 163.1 (C ring). MS(EI): *m/z* (%) = 656 (5) [M^+], 504 (100) [M^+ − tz]. $C_{32}H_{56}N_{12}Ti$ (656.8): calcd. C 58.52, H 8.59, N 25.59; found C 58.07, H 8.64, N 25.15.

Preparation of $[(C_5Me_4CH_2Ph)Ti(\eta^2\text{-tz})Cl_2]$ (2): A suspension of tzK (0.18 g, 0.94 mmol) in toluene (15 mL) was added at room temperature to a solution of $[(C_5Me_4CH_2Ph)TiCl_3]$ (0.32 g, 0.88 mmol) in 20 mL of toluene and the resulting red suspension was stirred overnight. The solvent was then removed, the residual solid extracted with hexane and filtered through Celite. The volume was reduced to 20 mL and 0.21 g (50%) of the red compound crystallized at −25 °C. M.p. 82 °C. ^1H NMR (C_6D_6): δ = 1.38 [d, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$, 12 H], 1.83 (s, $CpCH_3$, 6 H), 2.01 (s, $CpCH_3$, 6 H), 3.10 [sept, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$, 2 H], 4.06 (s, CH_2, 2 H), 6.84 (m, Ph, 2 H), 7.0 (m, Ph, 2 H), 7.12 (m, Ph, 1 H). ^{13}C NMR (C_6D_6): δ = 13.5 (CpMe), 14.1 (CpMe), 21.8 [$CH(CH_3)_2$], 28.7 [$CH(CH_3)_2$], 34.6 (CH_2), 126.8 (C_{para} Ph), 128.4 (C_{meta} Ph), 128.9 (C_{ortho} Ph), 134.67 (Cp ring), 134.88 (Cp ring), 136.4 (Cp ring), 139.5 (C_{ipso} Ph), 165.6 (tz ring). MS(EI): *m/z* (%) = 481 (20) [M^+], 329 (100) [M^+ − tz]. $C_{24}H_{33}Cl_2N_3Ti$ (482.4): calcd. C 59.77, H 6.90, N 8.71; found C 59.42, H 6.92, N 8.44.

Preparation of $[Cp^*Ti(\eta^2\text{-tz})Cl_2]$ (3): The synthetic procedure used was analogous to **2** employing $[Cp^*TiCl_3]$ (0.51 g, 1.76 mmol) and tzK (0.36 g, 1.88 mmol). Yield: 0.55 g (77%). M.p. 132 °C. ^1H NMR (C_6D_6): δ = 1.37 [d, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$, 12 H], 1.87 (s, Cp*, 15 H), 3.07 [sept, $^3J_{H,H}$ = 7 Hz, $CH(CH_3)_2$, 2 H]. ^{13}C NMR (C_6D_6): δ = 13.6 (Cp* CH_3), 21.8 [$CH(CH_3)_2$], 28.6 [$CH(CH_3)_2$], 134.6 (Cp* ring), 165.5 (tz ring). MS(EI): *m/z* (%) = 405 (20) [M^+], 253 (100) [M^+ − tz]. $C_{18}H_{29}Cl_2N_3Ti$ (406.3): calcd. C 53.22, H 7.20, N 10.34; found C 53.68, H 7.24, N 10.10.

Preparation of $[Cp^*Ti(\eta^2\text{-tz})_3]$ (4): Toluene (30 mL) was added to a mixture of $[Cp^*TiCl_3]$ (0.47 g, 1.62 mmol) and tzK (0.96 g, 5.03 mmol). The mixture was stirred under reflux for 2 h, the solvent removed, the residual solid extracted with hexane and filtered through Celite. The volume was reduced to 20 mL and the compound crystallized as yellow needles at −25 °C. Yield: 0.65 g (63%). M.p. 151 °C. ^1H NMR (C_6D_6): δ = 1.22 [d, $^3J_{H,H}$ = 6 Hz, $CH(CH_3)_2$, 12 H], 1.77 (s, Cp*, 15 H), 3.05 [sept, $^3J_{H,H}$ = 6 Hz, $CH(CH_3)_2$, 6 H]. ^{13}C NMR (C_6D_6): δ = 12.5 (Cp* CH_3), 22.3 [$CH(CH_3)_2$], 28.6 [$CH(CH_3)_2$], 129.9 (Cp* ring), 162.8 (tz ring). MS(EI): *m/z* (%) = 639 (5) [M^+], 504 [M^+ − Cp*] 487 (40) [M^+ − tz]. $C_{34}H_{57}N_9Ti$ (639.8): calcd. C 63.83, H 8.98, N 19.70; found C 63.25, H 8.98, N 19.70.

X-ray Crystallographic Studies: The selected crystals were covered with oil and mounted on a glass fiber. The data for **1** were collected on a Stoe−Siemens−Huber four-circle-diffractometer coupled to a Siemens CCD area-detector and for **2** on a Stoe IPDS II-array detector system instrument, in both cases with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[35] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[36] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

CCDC-173074 (**1**) and CCDC-173075 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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