Organometallic Chemistry

Polydentate coordination of the thallium atom in complexes with chiral amidinylcyclopentadienyl ligands

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The chiral thallium amidinium cyclopentadiene-*N*-ylide complexes $[C_5(CO_2Me)_4\{ArNC(Ar')NAr\}]Tl$ were synthesized and structurally characterized by X-ray diffraction analysis and NMR spectroscopy. In these complexes, an unusual mode of coordination of the thallium atom was found, *viz.*, the thallium atom is coordinated by both the side-chain nitrogen atom (N—Tl, 2.833(6) Å) and the π system of the cyclopentadienyl ring (Tl—Cp, 2.887(4) Å; η^5-bonding).

Key words: thallium complexes, cyclopentadienyl ligands with a donor side chain, amidines, chirality, X-ray diffraction analysis.

Cyclopentadienylthallium complexes are important precursors of organic and organometallic compounds.

Recently,[1,2] we have prepared the first chiral *N*-amidine-functionalized cyclopentadienyl ligands $[C_5(CO_2Me)_4\{ArNC(Ar')NAr\}]H$ and their gold(I)- and mercury(II)-containing complexes characterized by bidentate coordination of the metal (hydrogen) atom by both the cyclopentadienyl fragment and the side-chain nitrogen atom. Such chiral *N*-functionalized cyclopentadienyl complexes with additional intramolecular coordination of the metal atom by the side-chain nitrogen atom are attractive as catalysts for asymmetric syntheses.[3—5]

The aim of the present study was to synthesize stable chiral cyclopentadienylthallium(I) complexes containing the amidinyl substituents in the five-membered ring, *viz.*, *N,N'*-diaryl-*N*-thallium-benz(α-naphth)amidinium-*N'*-[2,3,4,5-tetra(methoxycarbonyl)cyclopentadien-1-yl]ides, and to study their structures in the solid state and in solutions by X-ray diffraction analysis and NMR spectroscopy.

Results and Discussion

Treatment of *N,N'*-diaryl-*N*-methoxycarbonylbenz(α-naphth)amidinium-*N'*-[2,3,4,5-tetra(methoxycarbonyl)cyclopentadien-1-yl]ides (**1**) with a methanolic solution of TlOH afforded *N,N'*-diaryl-*N*-thalliumbenz(α-naphth)amidinium-*N'*-[2,3,4,5-tetra(methoxy-

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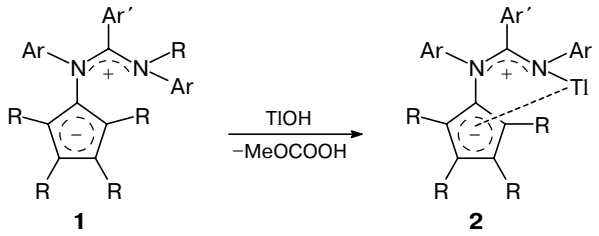
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 852—856, May, 2001.

1066-5285/01/5005-890 $25.00

carbonyl)cyclopentadien-1-yl]ides (**2**) in 85—87% yields. The reactions were accompanied by elimination of the *N*-methoxycarbonyl group (Scheme 1).

Scheme 1



R = CO_2Me; Ar = 4-MeC_6H_4; Ar′ = 1-$C_{10}H_7$ (**a**), 2-ClC_6H_4 (**b**), 2-Cl-6-MeC_6H_3 (**c**)

Complexes **2** exist as yellow crystals resistant to oxidation with atmospheric oxygen and moisture and are readily soluble in most organic solvents.

The crystal structure of thallium derivative **2c** was established by X-ray diffraction analysis (Fig. 1). This compound exists as a zwitterion as evidenced by the close values of the C—C bond lengths in the cyclopentadienyl ring and the N—C(14) bond lengths in the amidine fragment (Table 1).

The structure of ylide **2c** is characterized by the *Z* configuration of the amidine fragment, the coordination of the Tl atom by the nitrogen atom of the amidine fragment (N(21)—Tl 2.833(6) Å), and short distances between the Tl atom and the C atoms of the cyclopentadienyl ring. The plane of the amidine fragment is almost perpendicular to the plane of the cyclopentadienyl ring (the C(5)—C(1)—N(6)—C(14) torsion angle is 76.7°) due to which the distances between the Tl atom

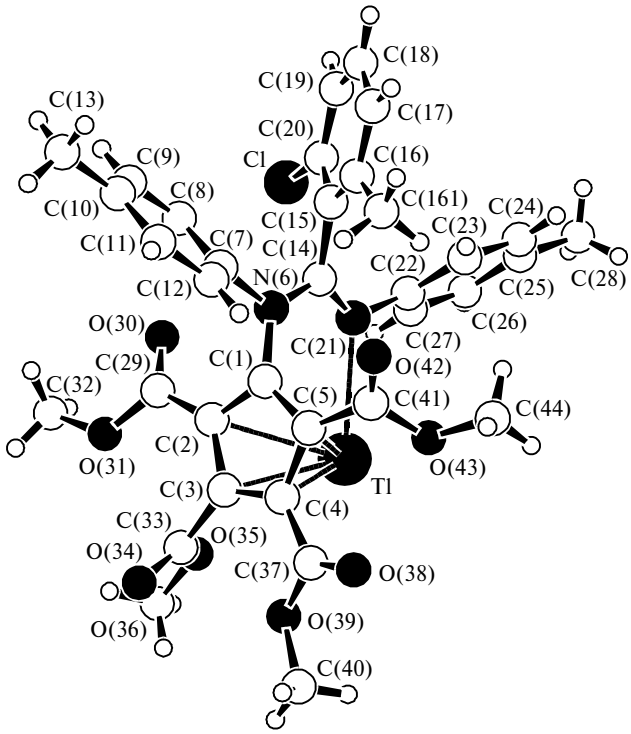


Fig. 1. Molecular structure of compound **2c**.

and the C atoms of the five-membered ring are rather short (Fig. 2):

Bond	Tl—C(1)	Tl—C(2)	Tl—C(3)	Tl—C(4)	Tl—C(5)
d/Å	3.18	3.15	3.10	3.08	3.13

These short distances are indicative of strong attractive interaction due to π-bonding of the η^5 type between the

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the structure of ylide **2c**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Tl—N(21)	2.833(6)	C(14)-N(6)—C(7)	123.9(6)	C(1)—C(5)—C(4)	106.6(6)
Cl—C(20)	1.714(11)	C(14)—N(6)—C(1)	119.1(6)	C(1)—C(5)—C(41)	121.4(7)
N(6)—C(14)	1.374(10)	C(7)—N(6)—C(1)	116.7(6)	C(4)—C(5)—C(41)	131.9(8)
N(6)—C(7)	1.431(10)	C(14)—N(21)—C(22)	122.3(6)	C(12)—C(7)—N(6)	119.3(8)
N(6)—C(1)	1.431(10)	C(14)—N(21)—Tl	132.3(5)	C(8)—C(7)—N(6)	121.3(8)
N(21)—C(14)	1.283(10)	C(22)—N(21)—Tl	105.4(5)	N(21)—C(14)—N(6)	119.8(7)
N(21)—C(22)	1.413(10)	C(5)—C(1)—C(2)	109.0(6)	N(21)—C(14)—C(15)	124.1(7)
C(1)—C(5)	1.402(11)	C(5)—C(1)—N(6)	126.6(7)	N(6)—C(14)—C(15)	116.0(7)
C(1)—C(2)	1.422(10)	C(2)—C(1)—N(6)	124.4(7)	C(20)—C(15)—C(14)	123.4(8)
C(2)—C(3)	1.400(10)	C(3)—C(2)—C(1)	106.1(6)	C(16)—C(15)—C(14)	119.5(8)
C(2)—C(29)	1.478(11)	C(3)—C(2)—C(29)	127.9(7)	C(15)—C(16)—C(161)	130.3(10)
C(3)—C(4)	1.373(11)	C(1)—C(2)—C(29)	126.0(7)	C(17)—C(16)—C(161)	107.5(11)
C(3)—C(33)	1.506(11)	C(4)—C(3)—C(2)	110.3(7)	C(15)—C(20)—Cl	122.2(7)
C(4)—C(5)	1.431(11)	C(4)—C(3)—C(33)	126.8(7)	C(19)—C(20)—Cl	115.4(9)
C(4)—C(37)	1.474(11)	C(2)—C(3)—C(33)	122.8(7)	C(27)—C(22)—N(21)	119.3(8)
C(5)—C(41)	1.492(12)	C(3)—C(4)—C(5)	107.9(7)	N(21)—C(22)—C(23)	122.6(8)
C(14)—C(15)	1.502(10)	C(3)—C(4)—C(37)	126.0(8)	O(34)[b]—Tl—N(21)	99.0(2)
Tl—O(34)[a]	2.788(6)	C(5)—C(4)—C(37)	126.1(8)	C(33)—O(34)—Tl[a]	144.7(6)

[a] The symmetry transformation $x + 1/2, -y + 1/2, -z + 1$.
[b] The symmetry transformation $x - 1/2, -y + 1/2, -z + 1$.

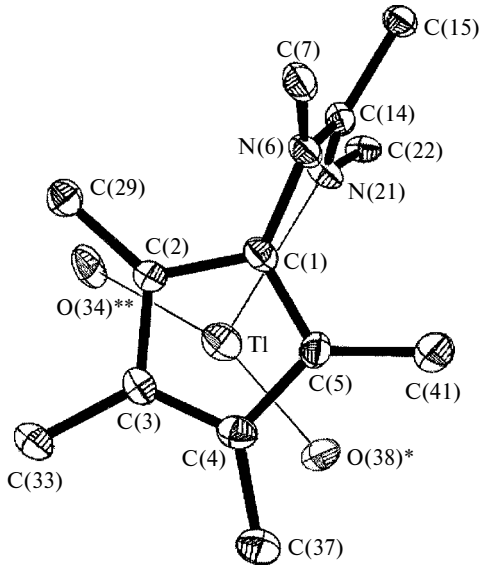


Fig. 2. Projection of molecule **2c** illustrating η^5-coordination of the Tl atom by the cyclopentadienyl ring. O* and O** are the carbonyl oxygen atoms of two adjacent molecules. The distances/Å: Tl—center of Cp is 2.887(4), Tl—O(38)* is 3.092(8), and Tl—O(34)** is 2.788(6).

thallium atom and the negatively charged cyclopentadienyl ring (the distance between the Tl atom and the center of the Cp ring is 2.887(4) Å).

In the crystal structure, the Tl atom is additionally coordinated by the carbonyl oxygen atoms of two adjacent molecules (the Tl—O(38)* and Tl—O(34)** bond lengths are 3.092(8) and 2.788(6) Å, respectively) (see Fig. 2).

It should be noted that the H and Au atoms in the $[C_5(CO_2Me)_4\{ArNC(Ar')NAr\}]H$ ligands and their complexes with $AuPPh_3$, respectively, are covalently bound to the amidine N atom and are additionally η^1- and η^2-coordinated by the π system of the Cp ring (the H—C(1), Au—C(1), and Au—C(5) bond lengths are 2.46(8), 2.938, and 3.116 Å, respectively).[1,2] In complex **2c**, the Tl atom is η^5-bound to the π system of the Cp ring resulting in weakening of the Tl—N bond compared to the H—N and Au—N bonds in the $[C_5(CO_2Me)_4\{ArNC(Ar')NAr\}]H$ ligand and in its Au^I complex, respectively. This weakening is manifested in a lesser degree of equalization of the bond lengths in the amidine fragment of ylide **2c** (the N(6)—C(14) and N(21)—C(14) bond lengths are 1.374 and 1.283 Å, respectively), whereas these distances in the initial ligand are virtually equal (1.320 and 1.315 Å [1]).

The cyclopentadienylthallium derivatives containing *N*-functionalized side chains, which have been described previously,[4,5] *viz.*, $C_5R_4(CH_2CH_2NMe_2)Tl$ (R = H or Me) and $C_5H_4[CH(Ph)CH(Me)NMe_2]Tl$, differ from compound **2** in that the Tl atom in the former derivatives is coordinated only by the π system of the cyclopentadienyl ring and does not form a bond with the N atom. In pentamethoxycarbonylcyclopentadienylthallium, the Tl atom has the coordination number of 5 and is coordinated to two vicinal carbonyl O atoms of one anion and three O atoms of other anions. In the crystal, the carbonyl O atoms of each anion are coordinated to four different metal atoms (see Fig. 3).[6]

Molecule **2c** is sterically overcrowded, and two methoxycarbonyl groups are rotated with respect to the plane of the cyclopentadienyl ring. The torsion angles in the structure are as follows.

Angle	α/deg
C(1)—C(2)—C(29)—O(30)	22.9
C(2)—C(3)—C(33)—O(35)	72.7
C(3)—C(4)—C(37)—O(39)	15.2
C(1)—C(5)—C(41)—O(42)	45.6

The Cl atom and the *o*-Me group in the aryl substituent at the C(14) atom are bent upward. The bond angles have the following values:

Angle	ω/deg	Angle	ω/deg
C(15)—C(20)—Cl	122.2	C(15)—C(16)—C(161)	130.3
C(19)—C(20)—Cl	115.4	C(17)—C(16)—C(161)	107.5

In the *Z*-amidine fragment, both tolyl groups are rotated with respect to the plane of the amidine moiety (the C(14)—N(6)—C(7)—C(8) and C(14)—N(21)—C(22)—C(23) torsion angles are 50.9° and 53.5°, respectively). In spite of this conformation of the *N*-tolyl fragments, the bulky 2,6-substituted aryl group at the C(14) atom cannot be located in the plane of the amidine fragment and deviates from this plane because of steric hindrances (the N(6)—C(14)—C(15)—C(16) torsion angle is 63.3°) resulting in the chirality of the structure of ylide **2c**.

According to the data of X-ray diffraction analysis, ^1H and ^{13}C NMR spectroscopy, and IR spectroscopy, complexes **2a—c** exist as zwitterions both in the solid state and in solutions.

The IR spectra of compounds **2a—c** have no absorption bands corresponding to the C=N bonds and the C=C bonds of the cyclopentadienyl ring. The carbonyl groups are manifested as four absorption bands because the the methoxycarbonyl substituents are located at different angles with respect to the plane of the cyclopentadienyl ring and, hence, are nonequivalent (Table 2).

In the ^{13}C NMR spectra of complexes **2a—c** (see the Experimental section), all signals for the C atoms of the cyclopentadienyl ring are observed at δ 105—123. The negative charge is localized on the Cp ring, which is confirmed by the fact that the above-mentioned signals are shifted upfield compared to the signals for the sp^2-hybridized carbon atoms of the Cp ring in 5-methyl-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene[7] (δ 140.62 and 145.46). The signals for the C atoms of the amidine NCN groups are observed at δ 159—161, which is characteristic of the positively charged C atoms. These data agree with the ylide structure of compound **2** in solution. The coordination of the Tl atom by

Table 2. Characteristics of complexes **2a—c**

Compound	Found / Calculated (%)					Molecular formula	IR, Nujol mulls, ν/cm^{-1}	^1H NMR at 298 K (CD_3CN), δ		
	C	H	Cl	N	Tl			Me (s)	OMe (s, 3 H)	Ar (m)
2a	53.61 53.69	3.99 3.91	—	3.23 3.30	23.99 24.04	$C_{38}H_{33}N_2O_8Tl$	1730, 1700, 1695, 1690, 1580, 1520, 1480, 1200, 1180	1.91 (3 H), 1.96 (3 H)*, 1.98 (3 H), 2.02 (3 H)	3.64, 3.75, 3.83, 3.84*, 3.71, 3.73, 3.76, 3.87	6.34—8.10 (15 H)*, 6.48—8.27 (15 H)
2b	48.88 48.94	3.70 3.62	4.19 4.25	3.29 3.36	24.55 24.49	$C_{34}H_{30}ClN_2O_8Tl$	1740, 1730, 1710, 1700, 1600, 1520, 1500, 1410, 1220, 1180	2.15 (6 H)	3.66, 3.67, 3.74, 3.80	6.55—7.60 (12 H)
2c	49.49 49.54	3.75 3.80	4.23 4.18	3.36 3.30	24.15 24.09	$C_{35}H_{32}ClN_2O_8Tl$	1750, 1740, 1705, 1700, 1590, 1520, 1510, 1410, 1220, 1200, 1190	2.14 (6 H), 2.20 (3 H)	3.65, 3.67, 3.73, 3.79	6.50—7.65 (11 H)

* $CDCl_3$ as the solvent.

the cyclopentadienyl moiety is manifested in the downfield shifts of the signals for the C atoms of the five-membered ring compared to the corresponding signals of the 1-(*N,N′*-di(*p*-tolyl)-α-naphthamidinyl)-2,3,4,5-tetra(methoxycarbonyl)cyclopentadienide anion.[2] Previously, an analogous criterion has been used as a proof that the π system of the Cp ring is involved in coordination (see Refs. 3—5 and references cited therein).

According to the ^1H and ^{13}C NMR spectral data, both the protons and the C atoms of the methoxycarbonyl groups in complexes **2a—c** containing the bulky α-naphthyl or *o*-substituted aryl fragments at the C atom of the amidine moiety are magnetically nonequivalent (see Table 2). Analogously, the C(2)—C(5) atoms of the cyclopentadienyl ring give four different signals in the ^{13}C NMR spectra. These facts are indicative of the absence of the symmetry plane in molecules **2a—c** and, hence, of their chiral structures. Unlike compounds **2a—c**, the ylides $[C_5(CO_2Me)_4\{ArNC(Ph)NAr\}]H$ and their analogs containing the phenyl substituent at the carbon atom of the amidine group[1,2] possess the C_s symmetry.

No changes were found in the NMR spectra of compounds **2a—c** upon heating of their solutions in acetonitrile-d_3 to 80 °C, which is evidence for their rather high stability.

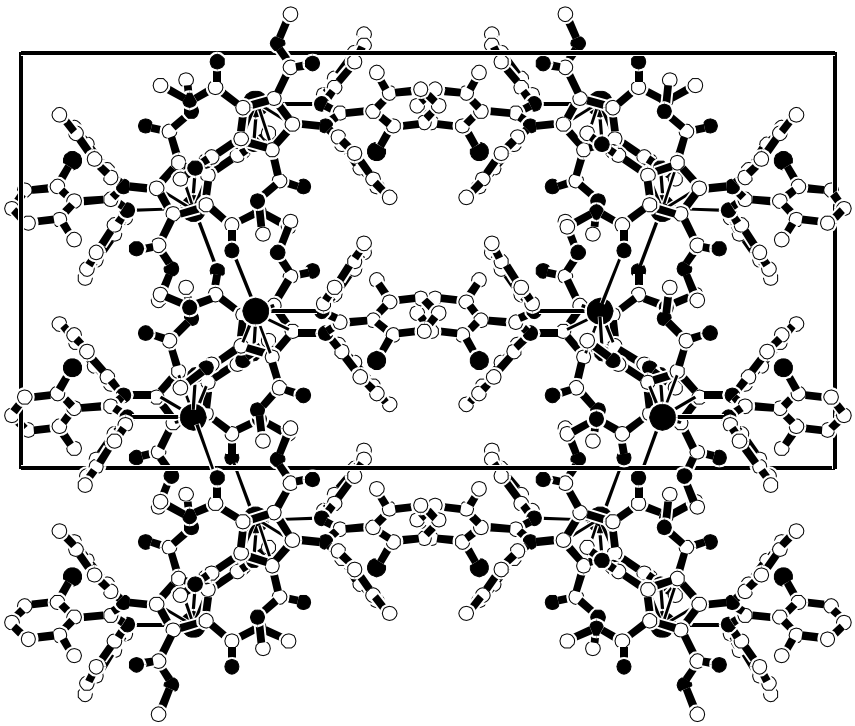


Fig. 3. Unit cell of the crystal structure of compound **2c**.

To summarize, the Tl atom in complexes **2** is coordinated in a polydentate fashion by the "hard" donor, *viz.*, by the side-chain N atom of the amidine moiety, and by the "soft" donor, *viz.*, by the π system of the Cp ring (η^5-bonding). This mode of coordination of the thallium atom has not been observed previously in related compounds. Such an unusual coordination is favored by the fact that the plane of the amidine fragment adopting the *Z* configuration is perpendicular to the plane of the Cp ring due to the presence of the bulky methoxycarbonyl and aryl substituents. The high energy barrier hinders rotation of the α-naphthyl or *o*-substituted aryl groups about the C—C bond of the amidine moiety. All these factors are responsible for the stability of the chiral structures of thallium derivatives **2**.

Experimental

The ^{1}H NMR spectra of solutions of the complexes (0.05 mol L^{-1}) were recorded on a Bruker AM spectrometer operating at 300 MHz. The ^{13}C NMR spectra of solutions of the complexes (0.5 mol L^{-1}) were measured on a Bruker AM spectrometer operating at 75.47 MHz with Me_4Si as the internal standard. The IR spectra were recorded on a Specord IR-75 instrument in Nujol mulls. The mass spectra were measured on an HP 5995 A spectrometer (direct inlet of the sample, EI, 70 eV, 60 °C). Methanol and benzene were purified according to standard procedures.[8]

***N,N′*-diaryl-*N*-thallium-benz(α-naphth)amidinium-*N′*-[2,3,4,5-tetra(methoxycarbonyl)cyclopentadien-1-yl]ides (2a—c) (general procedure).** Ylide **1** (5 mmol), which was obtained according to a procedure reported previously,[9] was added to a solution of freshly prepared TlOH [10] (5 mmol) in MeOH (80 mL). The reaction mixture was stirred at 40 °C for 1 h. Then the solvent was removed *in vacuo* and the residue was crystallized by hot filtration from benzene (**2a**) or MeOH (**2b** and **2c**). The yields were 85—87%. Yellow crystals, m.p. 208—209 °C (**2a**), 186—187 °C (**2b**), and 237—238 °C (**2c**).

^{13}C NMR ($CDCl_3$), δ. **2a**: 20.1, 20.4 (Me); 51.1, 51.4, 51.5, 51.9 (OMe); 106.1, 112.7, 114.8, 121.8 (C(1)—C(5), $Cp_{ring.}$); 122.3, 124.4, 125.6, 125.6, 125.8, 126.4, 128.0, 128.2, 128.8, 129.1, 129.3, 130.0, 131.4, 131.9, 132.4, 134.8, 140.9, 143.5 (Ar); 161.4 (NCN); 164.5, 165.6, 166.3, 167.9 (C=O). **2b:** 20.4, 20.6 (Me); 51.0, 51.4, 51.5, 51.9 (OMe); 105.5, 113.4, 114.2, 122.6 (C(1)—C(5), $Cp_{ring.}$); 122.6, 125.8, 125.9, 128.2, 128.4, 128.8, 129.1, 129.9, 131.7, 132.1, 132.3, 133.3, 135.0, 140.7, 142.8 (Ar); 159.4 (NCN); 164.3, 165.3, 166.1, 168.0 (C=O).

X-ray diffraction analysis of complex 2c. Crystals of **2c** ($C_{35}H_{32}ClN_2O_8Tl$) are orthorhombic, M = 848.45, space group *Pbca*, at 20 °C a = 10.9598(4), b = 17.8091(6), c = 34.8492(12) Å, α = 90.0°, β = 90.0°, γ = 90.0°, V = 6802.0(4) Å^3, Z = 8, d_{calc} = 1.657 g cm^{-3}. The X-ray diffraction data were collected on a Bruker SMART diffractometer equipped with a CCD detector (T = 293(2) K, graphite monochromator, Mo-Kα radiation, λ = 0.71073 Å). The absorption coefficient was 4.881 mm^{-1}; F(000) 3344; θ 2.20—29.03°; the limiting indices $-14 \le h \le 13$, $-15 \le k \le 23$, $-47 \le l \le 45$; 36579 measured reflections; 8320 independent reflections (R_{int} 0.0549); semiempirical absorption correction from ψ scans; maximum and minimum transmissions were 0.284 and 0.202, respectively. The refinement was performed by the least-squares method using 8221 reflections; 0 restraints, 425 parameters refined, GOOF based on F^2 was 1.268; the final R factors using reflections with $I > 2\sigma(I)$ were R_1 = 0.0853, wR_2 = 0.1655; the R factors based on all data were R_1 = 0.0937, wR_2 = 0.1705, Δf_{max} = 2.225, −1.369 e/Å^3. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The selected lengths and bond angles in the structure of **2c** are given in Table 1. The atomic coordinates, bond lengths, bond angles, and thermal parameters were deposited with the Cambridge Structural Database.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-33062, 99-03-33505, and 00-15-97320).

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Received February 15, 2001