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Palladium Complexes with the Tridentate Dianionic Ligand Pyridine-2,6-bis(thiocarboxylate), pdtc. Crystal Structure of (n-Bu$_4$N)[Pd(pdtc)Br]

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Introduction

Interest in the chemistry of complexes containing pyridine-2,6-dicarboxylic acid (dipicolinic acid, H$_2$dipic) and its dinegative anion (dipic) has led to the preparation of a large number of bivalent or trivalent transition metal complexes in which the dipic ligand[1] may be coordinated in various ways. The meridional tridentate form[2] is the most common, but there are a few examples of other coordination modes such as facial coordination,[3] bridging of two metal atoms,[4] polymerization of chelate complexes by coordination of the carbonyl oxygen atom,[5] and bidentate N–O coordination.[6]

Less attention has been paid to the sulfur analog pyridine-2,6-bis(thiocarboxylic) acid (H$_2$pdtc), a natural product of some strains of *Pseudomonas putida* when grown under condition of iron deficiency,[7] and only recently a few octahedral complexes with Fe, Co, and Ni, containing the ligand coordinated in the meriditional tridentate form, have been reported.[8,9] Some of these complexes were made as models to explain some intricate reactions in biological systems or to elucidate the influence of the ligand structure on the unusually low values for Ni(III)/Ni(II) redox potentials found in [NiFe] hydrogenases.

The combination of a flat tridentate ligand such as pdtc with a metal with square-planar coordination should give rise to structures (Figure 1) which have a net dipolar moment in the direction of the N–Pd–L bonds (usually attempts to produce complexes with a net dipolar moment of the type *trans*-[PdX$_2$L^{1}L^2] lead to rearrangement to a mixture of *trans*-[PdX$_2$L$^1{}_2$] and *trans*-[PdX$_2$L$^2{}_2$]). This, along with the rather anisotropic shape of the structure, can induce interesting physical properties in the materials. In fact the related compound K[Pt(dipic)Cl] has been shown to give rise to the formation of gels in water, whereas the use of appropriate ligands L or/and the introduction of long chains in the *para* carbon of the pyridinic ring should give rise to rodlike molecules of potential interest in the field of metal-containing liquid crystals.[10,11] Thus, pursuing our interest in palladium chemistry and in metal-containing liquid crystals,[12] we have started the study of these systems and report here the synthesis of the first complexes of palladium(II) with the tridentate ligand pdtc.

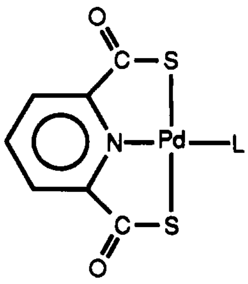

Figure 1.

Experimental Section

Literature methods were used to prepare [Pd(acac)$_2$][13] and pyridine-2,6-bis(thiocarboxylic) acid.[14] C, H, and N analyses were carried out on a Perkin-Elmer 240 microanalyzer. All new compounds gave satisfactory elemental analyses. IR spectra were recorded on a Perkin-Elmer 833 spectrophotometer using Nujol mulls between polyethylene sheets. ^{1}H NMR spectra were recorded on a Bruker AC-80 instrument. Melting points were determined using a polarizing Leitz microscope provided with a heating device.

Preparation of [Pd(pdtc)]$_2$ (1). [Pd(acac)$_2$] (1.00 g, 3.28 mmol) and pyridine-2,6-bis(thiocarboxylic) acid (0.654 g, 3.28 mmol) were stirred in CHCl$_3$ (40 mL) for 24 h. The orange precipitate was collected on a frit, washed with chloroform (3 × 10 mL), and dried in vacuo. Yield: 0.907 g (91%). IR (Nujol, cm^{-1}): $\nu_{C=O}$ 1695, 1642.

Preparation of [Pd(pdtc)py] (2). Method a. To a suspension of **1** (0.1 g, 0.165 mmol) in acetone (10 mL) was added pyridine (0.5 mL), and the mixture was stirred overnight. The resulting yellow orange precipitate was filtered out, washed with acetone (2 × 3 mL) and then diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 0.107 g (85%). IR (Nujol, cm^{-1}): $\nu_{C=O}$ 1631, 1606.

Method b. Pyridinium pyridinium-2,6-bis(thiocarboxylate) (0.654 g, 2.35 mmol) and [Pd(acac)$_2$] (0.715 g, 2.35 mmol) were stirred overnight in CHCl$_3$ (30 mL). The resulting yellow-orange precipitate was collected on a frit, washed with chloroform (3 × 10 mL) and then acetone (2 × 5 mL), and dried in vacuo. Yield: 0.809 g (90%).

Preparation of [Pd(pdtc)PPh$_3$] (3). To a stirred suspension of **1** (0.100 g, 0.165 mmol) in dichloromethane (20 mL) was added PPh$_3$ (0.087 g, 0.33 mmol). When a clear solution was formed, it was filtered and concentrated in vacuo to a small volume. Slow addition of diethyl ether produced yellow crystals of **3**. Yield: 0.155 g (86%). IR (Nujol, cm^{-1}): $\nu_{C=O}$ 1633, 1622.

Complexes **4**–**6** were prepared in similar yields from **1** and the appropriate ligand. **4**: Yield 81%; IR (Nujol, cm^{-1}) $\nu_{C=O}$ 1640, 1607,

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ν_{CN} 2234. **5**: Yield 89%; IR (Nujol, cm^{-1}) $\nu_{\mathrm{C=O}}$ 1633, 1620, ν_{CN} 2252. **6**: yield 80%; IR (Nujol, cm^{-1}) $\nu_{\mathrm{C=O}}$ 1633, 1629, ν_{CN} 2218.

Preparation of [Pd(Mepdtc)I] (7). To a suspension of **1** (0.5 g, 0.823 mmol) in acetone (50 mL) was added MeI (5 mL), and the mixture was stirred for 10 days in the dark. The resulting orange-red precipitate was decanted, washed with acetone (3 × 10 mL) and then diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 0.40 g (54%). IR (Nujol, cm^{-1}): $\nu_{\mathrm{C=O}}$ 1721, 1636.

Preparation of (*n*-Bu$_4$N)[Pd(pdtc)Br] (8). Complex **1** (0.50 g, 0.823 mmol) and (*n*-Bu$_4$N)Br (0.531 g, 1.647 mmol) in acetone (40 mL) were stirred at room temperature for 1 day, whereupon an orange-red solution was formed, which was filtered through Celite and concentrated to ca. 5 mL under reduced pressure. Addition of diethyl ether (50 mL) afforded compound **8** as orange crystals, which were recrystallized from acetone–diethyl ether. Yield: 0.978 g (95%). IR (Nujol, cm^{-1}): $\nu_{\mathrm{C=O}}$ 1630, 1621, $\nu_{\mathrm{Pd-Br}}$ 259.

Preparation of (*n*-Bu$_4$N)[Pd(pdtc)CN] (9). Freshly prepared silver cyanide [obtained from AgNO$_3$ (65 mg) and KCN (25 mg)] and **8** (0.2 g, 0.32 mmol) in acetone (30 mL) were stirred overnight in the dark. The AgBr precipitate was filtered off, and the yellow solution was concentrated. Addition of diethyl ether gave a lemon-yellow solid, which was recrystallized from acetone–diethyl ether. Yield: 0.172 g (94%). IR (Nujol, cm^{-1}): $\nu_{\mathrm{C=O}}$ 1636, 1629, ν_{CN} 2131.

Preparation of (*n*-Bu$_4$N)[{Pd(Pdtc)}$_2$(μ-CN)] (10). A mixture of **9** (0.15 g, 0.262 mmol) and **1** (0.079 g, 0.13 mmol) in acetone was stirred for 2 days to give an orange solution. Evaporation of the solvent in vacuo and washing of the resulting solid with 1:1 dichloromethane–diethyl ether (3 × 5 mL) afforded **10** as a yellow-orange solid, which was recrystallized from acetone–diethyl ether. Yield: 0.17 g (74%). IR (Nujol, cm^{-1}): $\nu_{\mathrm{C=O}}$ 1626, ν_{CN} 2186.

Preparation of (*n*-Bu$_4$N)[Pd(pdtc)(SCN)] (11). Compound **8** (0.075 g, 0.12 mmol) and KSCN (0.014 g, 0.14 mmol) were stirred in acetone (10 mL) for 1 h. A white precipitate of KBr was formed. The solvent was then evaporated to dryness and the residue extracted with dichloromethane (2 × 10 mL). The yellow solution was filtered through Celite to remove the insoluble KBr and concentrated in vacuo. Addition of diethyl ether produced yellow crystals of **11**. Yield: 0.0544 g (75%). IR (Nujol, cm^{-1}): $\nu_{\mathrm{C=O}}$ 1619, ν_{CN} 2108.

X-ray Structural Determination. Crystals were grown by slow diffusion of Et$_2$O into a concentrated acetone solution of **8**. The diffraction intensities of an approximately 0.65 × 0.40 × 0.30 mm crystal were collected on a Philips PW1100 diffractometer with monochromatized Mo Kα radiation (λ = 0.710 73 Å) by using the ω–2θ scan technique with ω-scan width of (0.9 + 0.34 tan θ)°. Lattice parameters were obtained by least squares from the setting angles of 25 reflections in the range $16 \le \theta \le 17°$. During the data collections two standard reflections were measured every 2 hours. A total of 2358 reflections were collected in the $1 \le \theta \le 25°$ range ($-15 \le h \le 15, 0 \le k \le 27, 0 \le l \le 10$). The agreement factor between equivalent reflections was 0.023. A total of 1426 reflections with $I \ge 3\sigma(I)$ were used for the structure refinement. The minimum and maximum peaks in the final difference Fourier map correspond to −0.52 and 0.69 e Å^{-3}, respectively. The structure was solved by direct methods and subsequent Fourier maps. Refinements were carried out by least-squares methods, in two blocks. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were found on a difference map, their coordinates were refined, and they were given an overall isotropic thermal parameter. An absorption correction was applied with the program DIFABS[15] (correction coefficients were in the range 1.01–1.08) from CRYSTALS.[16] Atomic scattering factors were taken from ref 17. An extinction correction was not necessary. Further crystallographic details are given in Table 1, and positional parameters are collected in Table 2.

Table 1. Crystallographic Data for (*n*-Bu$_4$N)[Pd(pdtc)Br]

chem formula	$C_{23}H_{39}BrN_2O_2PdS_2$	V, Å^3	2764(1)
fw	626.0	Z	4
cryst system	Monoclinic	ρ_{calc}, g cm^{-3}	1.50
space group	$C2/c$	μ, cm^{-1}	22.6
a, Å	13.642(3)	temp, °C	18
b, Å	23.258(1)	R^a	0.039
c, Å	9.293(1)	$R_w{}^b$	0.041
β, deg	110.38(2)		

[a] $R = \sum|\Delta F|/\sum F_o$. [b] $R = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2}$; $w = 1$.

Table 2. Atomic and Thermal Parameters (Å^2) in (*n*-Bu$_4$N)[Pd(pdtc)Br]

atom	x/a	y/b	z/c	U(eq)^a
Pd(1)	0.0000	0.16343(3)	0.2500	0.0484
S(1)	−0.1247(1)	0.1573(1)	0.3617(2)	0.0685
Br(1)	0.0000	0.26628(5)	0.2500	0.0825
N(1)	0.0000	0.0760(3)	0.2500	0.0504
O(1)	−0.1955(5)	0.0589(3)	0.4165(8)	0.1026
C(1)	−0.1361(6)	0.0842(4)	0.3671(9)	0.0737
C(2)	0.0666(6)	0.0488(3)	0.1942(9)	0.0666
C(3)	0.067(1)	−0.0102(4)	0.197(1)	0.0885
C(4)	0.0000	−0.0390(6)	0.2500	0.0947
N(2)	0.0000	0.3110(3)	0.7500	0.0423
C(5)	0.0989(5)	0.2744(3)	0.8022(8)	0.0462
C(6)	0.1113(6)	0.2327(3)	0.6858(9)	0.0632
C(7)	0.2064(7)	0.1953(4)	0.759(1)	0.0736
C(8)	0.2269(9)	0.1536(5)	0.653(1)	0.0938
C(9)	0.0068(5)	0.3483(3)	0.8900(8)	0.0472
C(10)	−0.0815(6)	0.3898(3)	0.8698(9)	0.0586
C(11)	−0.0635(7)	0.4225(4)	1.017(1)	0.0709
C(12)	−0.1515(9)	0.4645(4)	1.005(1)	0.0862

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

The synthesis and structures of the new complexes are summarized in Scheme 1.

Neutral pdtc Complexes. The reaction of [Pd(acac)$_2$] with an equimolar amount of H$_2$pdtc in chloroform produces a yellow-orange precipitate. The analytical results for the compound reveal a Pd(pdtc) stoichiometry consistent with the dimeric structure **1** proposed in Scheme 1, where each pdtc ligand is coordinated to one palladium in an η^3-S,N,S′ chelate fashion and one sulfur atom is involved in the formation of bridges to the other palladium atom. A similar binuclear structure has been proposed for (pyridine-2,6-dimethanethiolato)nickel(II).[18]

Unfortunately the product is only very sparingly soluble in noncoordinating solvents, which precludes obtaining molecular weight determinations or single crystals for X-ray confirmation of the structure. For the same reason its ^{1}H NMR spectrum could only be obtained in deuterated DMSO and shows an AB$_2$ pattern revealing that splitting of the dimer by DMSO has occurred. However, the observation in the IR spectrum in the solid state of two well-separated $\nu_{\mathrm{C=O}}$ bands, one of them at the rather high wavenumber of 1695 cm^{-1}, strongly supports the structure proposed with two different thiocarboxylate groups; an increase in $\nu_{\mathrm{C=O}}$ is to be expected for the thiocarboxylate group in which the sulfur atom is involved in bridge formation.

Reaction of **1** with neutral ligands L (L = py, PPh$_3$, CNBu^t, CNC$_8$H$_{17}$, CNC$_6$H$_4$OC$_8$H$_{17}$-*p*) in acetone yields the mononuclear compounds **2–6**. These complexes are noticeably more soluble than the parent dimer, and their ^{1}H NMR spectra show the expected AB$_2$ pattern for the pdtc ring protons. Their IR spectra show the two expected $\nu_{\mathrm{C=O}}$ absorptions C_{2v}, A$_1$ + B$_1$) well below 1650 cm^{-1}. Alternatively, the pyrdine complex **2** can be obtained from [Pd(acac)$_2$] and the pyridinium salt of pyridinium-2,6-bis(thiocarboxylate), in a reaction where the two protonated pyridine rings behave as acids toward acac. The facile displacement of the pyridine ligand in compound **2** by phosphines or isonitriles can also be used as an alternative way to obtain the corresponding complexes. Although both **5** and **6** show relatively low melting points (152 and 167 °C, respectively), they melt to an isotropic liquid and do not display liquid-crystalline behavior. This suggests

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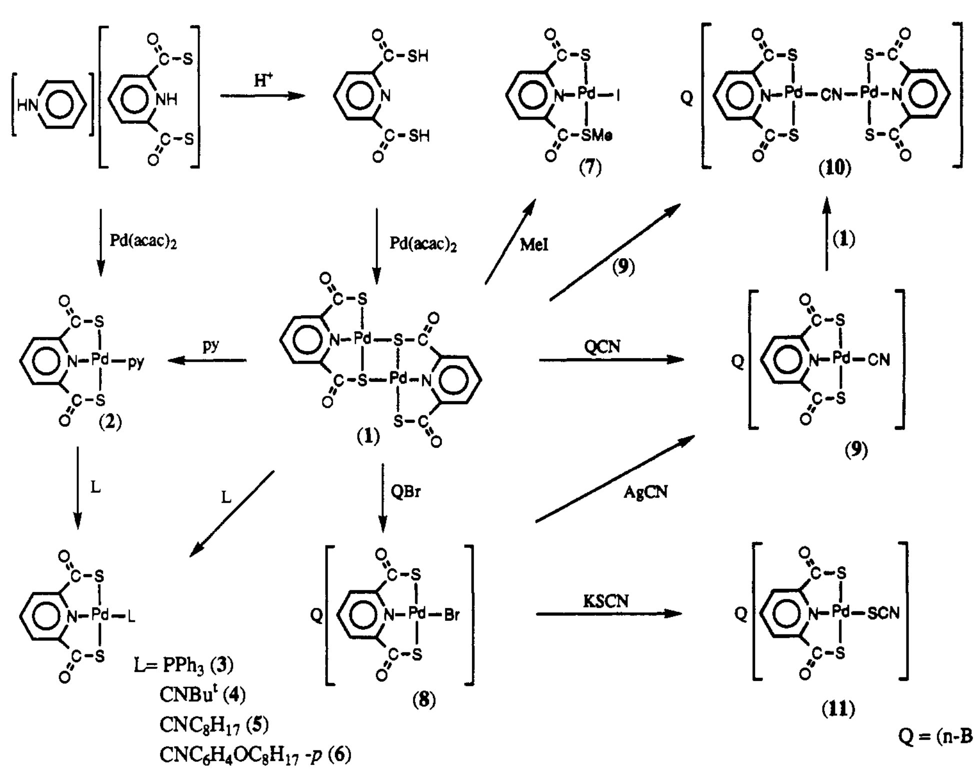
Scheme 1



that substitution in the pyridine ring of the pdtc ligand is probably necessary in order to obtain liquid crystals based on this chemical system.

Complex **1** reacts with MeI to give **7**, which shows two $\nu_{C=O}$ bands. The one at 1721 cm^{-1} corresponds to the thioester moiety formed by methylation of one sulfur atom, and the other at 1636 cm^{-1} supports a chelating thiocarboxylate moiety where the sulfur atom is not involved in bridge formation. The four-coordination of palladium can be satisfied either by formation of a $(\mu\text{-I})_2$-bridged dimer with a pendant thiocarboxylic ester group or, as shown in Scheme 1, in a monomer where the thioester group is coordinated to palladium. The mass spectrum of **7** exhibits the molecular ion at m/z 445 with the appropriate isotopic distribution for Pd, supporting the monomeric structure.

Ionic pdtc Complexes. The dimeric complex **1** can be cleaved by different coordinating anions to give anionic complexes. Thus, the reaction of a suspension of **1** in acetone with (n-Bu$_4$N)Br gives (n-Bu$_4$N)[Pd(pdtc)Br] (**8**), whose structure has been determined by X-ray diffraction and is discussed below. Treatment of **8** with AgCN, or cleavage of **1** with (n-Bu$_4$N)CN, affords (n-Bu$_4$N)[Pd(pdtc)CN] (**9**).

The lone pair of coordinated cyano group in **9** is also able to cleave the dimer **1**. Thus the reaction between **1** and **9** affords the single-bridged anionic dimer (n-Bu$_4$N)[{Pd(pdtc)}$_2$(μ-CN)] (**10**); this produces a shift of ν_{CN} from 2131 cm^{-1} in **9** to 2186 cm^{-1} in **10**. The ^{1}H NMR spectrum of **10** shows two sets of signals of the aromatic protons arising from the two inequivalent AB$_2$ systems in the complex.

Reaction of **8** with a 1 molar equiv of KSCN leads to exchange of the bromide. The values of 2108 cm^{-1} for ν_{CN}, and 431 cm^{-1} for δ_{NCS}, support S-coordination of the thiocyanato group,[19] as expected for the soft environment of palladium in **11**.

Structure of [Pd(pdtc)Br]⁻. The X-ray structure and numbering scheme for the anion in complex **8** are shown in Figure 2. Selected bond lengths and angles are given in Table 3.

The structure shows a palladium complex with C_2 symmetry, Pd(1), Br(1), N(1), and C(4) lying on a crystallographic 2-fold rotational axis. The palladium environment is strictly planar, and the square-planar coordination makes an angle of 1.6° with the best mean-square plane of the pyridine ring. The structure

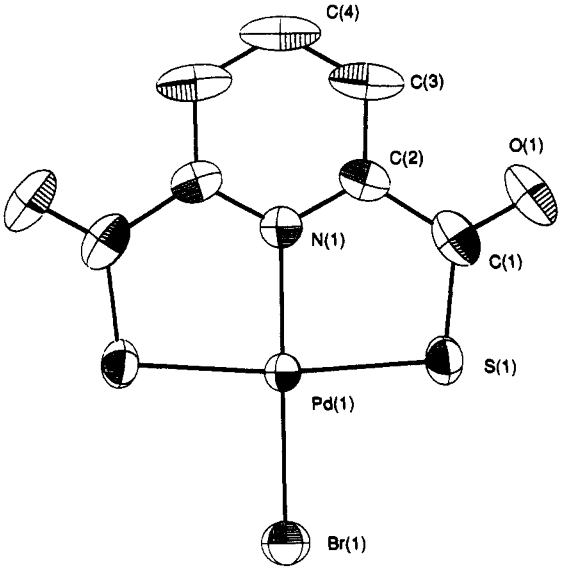


Figure 2.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [Pd(dptc)Br]⁻

Pd–S(1)	2.285(2)	Pd–Br	2.392(1)
Pd–N(1)	2.034(8)	S(1)–C(1)	1.711(9)
N(1)–C(2)	1.350(9)	O(1)–C(1)	1.214(9)
C(1)–C(2)	1.51(1)	C(2)–C(3)	1.37(1)
C(3)–C(4)	1.35(1)		
S(1)–Pd–S(1)′	172.9(1)	Br(1)–Pd–S(1)	93.56(6)
N(1)–Pd–S(1)	86.44(6)	N(1)–Pd–Br	180.00
C(1)–S(1)–Pd	99.5(3)	C(2)–N(1)–Pd	117.9(5)
C(2)–N(1)–C(2)′	124.2(10)	O(1)–C(1)–S(1)	125.0(8)
C(2)–C(1)–S(1)	117.1(6)	C(2)–C(1)–O(1)	117.9(9)
C(1)–C(2)–N(1)	119.0(7)	C(3)–C(2)–N(1)	117.1(10)
C(3)–C(2)–C(1)	123.8(10)	C(4)–C(3)–C(2)	120.5(13)
C(3)–C(4)–C(3)′	120.5(14)		

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can be compared with that of the related dipic complex $[Pd(dipic)Cl]^{1-}$,[6b] in which short Pt–N distances (in the range 1.88–1.91 Å for the three independent molecules in the crystal) and distortions from the idealized square-planar geometry around the metal ion (O–Pt–O angle is 162.3°) are imposed by the geometrical constraints of the tridentate dipic ligand. In the pdtc complex described here, the longer C–S distance, compared to C–O, reduces the strain in the metallacycles. This is reflected in the larger S–Pd–S angles (172.9°) and the Pd–N distance (2.034(8) Å), which is now within the range for Pd(II)–N bond distances (1.99–2.04 Å).[20] The length of the Pd–S bonds (2.285(2) Å) is noticeably shorter than those found in $[Pd(PMe_3)_2(S_2C_2O_2)]$[21] and $[Pd(S_2CPh)_2]$[22] (Pd–S(mean) = 2.33 Å), suggesting a very strong Pd–S interaction in the pdtc derivatives. The intramolecular distances and angles for the rest of the pdtc moiety are normal and compare well with those reported by Holm[9] for $[Ni(pdtc)_2]^-$, $[Ni(pdtc)_2]^{2-}$, and $[Co(pdtc)_2]^-$.

Conclusions

The pdtc dianionic ligand acts as a nicely behaved tridentate ligand toward palladium producing a rather stable strain-free chelation of the metal. The fourth coordination site can be filled by a lone pair from the sulfur atoms in a dimer or by a variety of neutral and anionic ligands to give monomers. The introduction of a long tail ligand (with or without an aryl ring) is not sufficient to induce mesogenic properties in the material, and further elaboration of the pdtc moiety (introduction of substituents in the *para* position of the ring) will be required.

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Supplementary Material Available: Tables of crystallographic data (Table S1), complete atomic coordinates (Table S2), anisotropic thermal parameters for non-hydrogens atoms (Table S3), bond distances and angles (Table S4), and microanalyses and ^1H NMR data (Table S5) (6 pages). Ordering information is given on any current masthead page.

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