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Synthesis of a Tetrahomodioxacalix[4]arene Tetraamide and the Crystal Structure of Its Lead Ion Complex

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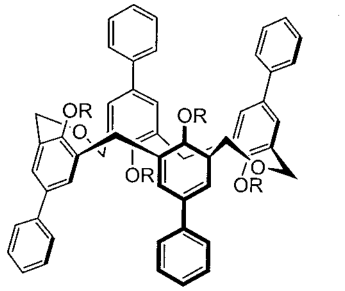
The 1,4-alternate tetrahomodioxacalix[4]arene tetraamide **4** with four *p*-phenyl groups on its upper rim was synthesized. In two-phase metal picrate extraction, **4** exhibited Pb^{2+} selectivity with formation of a 1:1 complex in chloroform. In the solid-state structure of the **4**·$Pb(Pic)_2$ complex, Pb^{2+} is bound by the carbonyl oxygens of two adjacent amide groups and an aryl−alkyl ether oxygen atom of one of these amide-containing substituents. The crystal structure and ^1H NMR spectrum of the **4**·Pb^{2+} complex reveals π-metal ion complexation of one aromatic ring in the ligand with Pb^{2+}.

Introduction

Calixarenes are synthetic macrocycles with a varying ring sizes that have received a great deal of attention in recent years.[1−3] They are of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures. In contrast to calix[4]arenes, homooxacalix[4]arenes that contain extra oxygen atoms in the macrocyclic ring have received little attention, mainly because they can be synthesized only in relatively low overall yields.[4−6] Gutsche and co-workers prepared tetrahomodioxa-*p-tert*-butylcalix[4]arene in 44% yield by dehydration of a bishydroxymethylated dimer of *p-tert*-butylphenol, which was synthesized by a multistep reaction sequence starting with the bromination of *p-tert*-butylphenol.[6] There have only been limited studies of the solution conformations, solid-state structures, and complexation properties of homooxacalix[4]arenes.[7−10] Masci and Saccheo[11] reported that the main conformation of tetrahomodioxa-*p-tert*-butylcalix[4]arene tetramethyl ether is 1,4-alternate based on temperature-dependent NMR spectral analysis. Recently, we described a facile two-step synthesis of tetrahomodioxa-*p*-phenylcalix[4]arene by refluxing bishydroxymethylated *p*-phenylphenol in xylene[12] and the solid-state structure of its tetraester **5**.[13] In this paper, we report the synthesis of tetrahomodioxa-*p*-phenylcalix[4]arene tetraamide **4**, its two-phase metal picrate extraction behavior compared to **5**, and the solid-state structure of its complex with lead picrate.



R
4 $CH_2CON(Et)_2$
5 CH_2CO_2Et

Results and Discussion

The synthetic route to **4** is depicted in Scheme 1. When a mixture of *p*-phenylphenol, 35% formaldehyde, and

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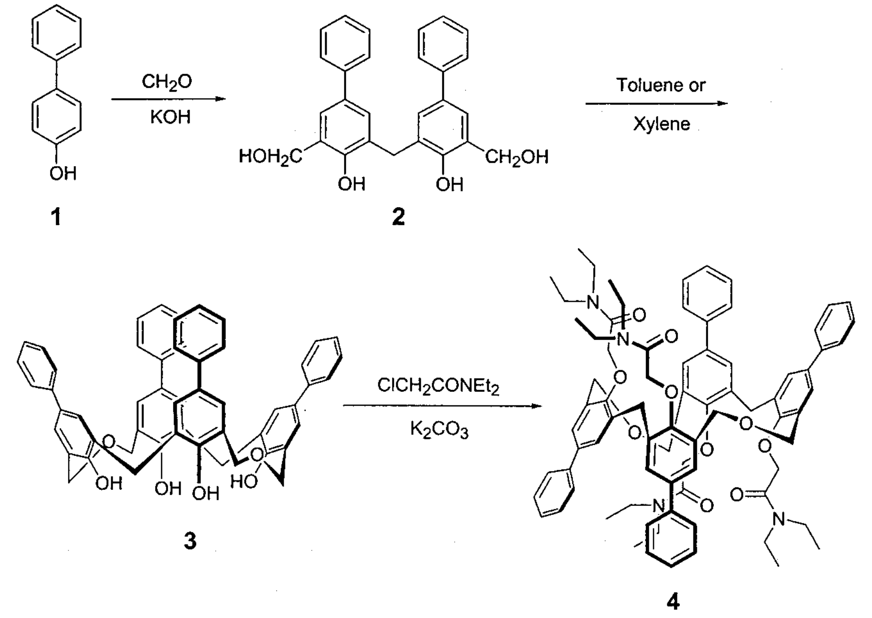
Scheme 1. Synthetic Route to Tetrahomodioxacalix[4]arene Tetraamide 4



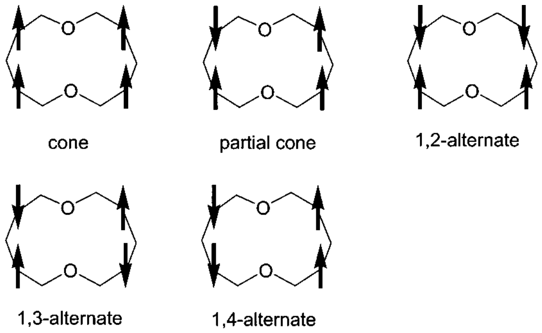


Figure 1. Conformations of tetrahomodioxacalix[4]arene.

KOH was stirred for 4 days at 40 °C, dimer diol **2** was obtained in 55% yield by the published procedures.[14,15] Refluxing of **2** in xylene with removal of water by a Dean–Stark trap afforded the tetrahomodioxacalix[4]arene **3** in 79% yield.[12] Reaction of **3** with excess *N*,*N*-diethyl chloroacetamide and K_2CO_3 in MeCN gave a 45% yield of tetraamide **4** as a crystalline solid.

As shown in Figure 1, **4** can exist in five limiting conformations (symmetrical cone, partial cone, 1,2-alternate, 1,3-alternate, and 1,4-alternate) instead of the four limiting conformations for calix[4]arenes. The conformation of **4** was probed by NMR spectroscopy. In the 600 MHz ^{1}H NMR spectrum (Figure 2A), the methylene protons of the ArCH_2Ar bridge showed two AB doublets at δ 5.40 and δ 3.57 with a geminal coupling constant of 13.2 Hz. The chemical shift difference of $\Delta\nu = 1098$ Hz was unusually wide. An AB pattern for the dimethylenic protons of ArCH_2OCH_2Ar appeared at δ 4.69 and 4.15, with a geminal coupling constant of 14.46 Hz and a chemical shift difference of $\Delta\nu = 324$ Hz. Another AB pattern for the methylene protons of ArOCH_2CON(Et)$_2$ appeared at δ 4.92 and 4.59 with a geminal coupling constant of 11.4 Hz and a chemical shift difference of $\Delta\nu = 202.3$ Hz. The ^{13}C NMR spectrum showed a single peak from a carbonyl carbon, one peak at 72.12 ppm for the ArCH_2O bridge methylene carbons and one peak at 32.65 ppm for the ArCH_2Ar bridge carbons. For the partial cone, 1,2-alternate and 1,3-alternate conformers, in which two adjacent benzene rings are in an anti orientation, an additional methylene bridge carbon peak at around 37 ppm would be anticipated. Thus, the spectral pattern for **4** is consistent with either a cone or 1,4-alternate conformation in which the two adjacent phenyl rings connected by a dimethyleneoxy group are inverted. The position of the methylenic bridge carbons of ArCH_2Ar at 32.65 ppm indicates that these two adjacent benzene rings are in a syn orientation.[16] In temperature-depend-

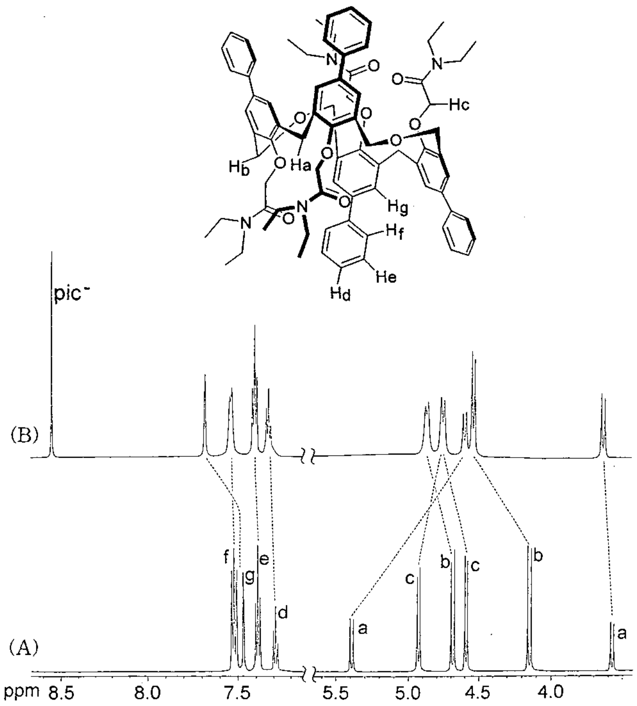


Figure 2. ^{1}H NMR spectra for Ligand **4** and the **4·Pb**(Pic)$_2$ complex.

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Table 1. Metal Picrate Extraction by Homooxacalixarene Tetraamide 4 and Tetraester 5

	extractability (%) for cations								
ligand	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ag^+	Pb^{2+}	Sr^{2+}	Ba^{2+}
4	0.06	0.13	1.80	0.84	3.28	11.89	37.59	3.04	6.22
5	1.26	1.24	2.24	1.17	2.01	0.99	0.83	1.31	0.94

ent ^{1}H NMR spectra of **4** in $CDCl_3$ from −20 to +50 °C, no spectral changes were observed. This revealed a fixed cone or 1,4-alternate conformation for **4**. A solid-state structure of its Pb^{2+} complex (vide supra) showed that **4** exists in a fixed 1,4-alternate conformation.

It has been noted that for calix[*n*]arene ester and amide derivatives, the latter are stronger metal ion complexing agents.[17,18] To obtain insight into the metal ion affinity of homooxacalixarene-based ligands, extractabilities of alkali, alkaline earth, and transition metal ions by tetraamide **4** and tetraester **5** were determined by the metal picrate extraction method. The data presented in Table 1 show higher extractability of Pb^{2+}, Ag^+, and Ba^{2+} by tetraamide **4** than tetraester **5** with pronounced selectivity of **4** for Pb^{2+}. It is noteworthy that both cone-shaped calix[4]arene tetraamide and tetraester compounds exhibit high extractability for Na^+ because of the hole-size selectivity and the rigidity of the ionophoric cavity, but poor extractability for Pb^{2+}.[17] In sharp contrast, the 1,4-alternate monooxacalixarene tetraamide **4** gave poor extractability for Na^+, but high Pb^{2+} extractability.

To determine the stoichiometry of the **4**·Pb^{2+} complex, extraction equilibrium parameters were determined as reported previously.[19−25] The stoichiometric coefficient (q) and extraction constant (K_{ex}) were determined from a plot of log D_M/[Pic^-]$_a$ vs log [**4**]$_o$. This plot gave a straight line with a slope of unity (q), which demonstrates formation of a 1:1 complex of **4** with Pb^{2+} and log $K_{ex}^{Pb} = 4.42$.

In view of the extraction selectiviy of **4** for Pb^{2+}, a solid-state structure of the complex was determined to probe the mode of complexation. A suitable single crystal of the **4**·lead picrate complex was grown by slow evaporation of a CH_2Cl_2−MeOH solution of lead picrate and **4**. The solid-state structure and data are given in Figure 3 and Table S1 (Supporting Information), respectively. Immediately evident is the 1,4-alternate conformation of the ligand in the complex. Since the amide group is sufficiently bulky to inhibit the *oxygen-through-the annulus rotation*,[19] the free ligand must also be in the 1,4-alternate conformation (vide infra). In agreement with the picrate extraction results, one Pb^{2+} is complexed by one molecule of **4**. In the complex, the carbonyl oxygens of two adjacent amide groups and the aryl−alkyl ether oxygen of one of the amide-containing substituents are directed toward Pb^{2+} to form the complex. The phenolic oxygen of one picrate anion also coordinates with the Pb^{2+}. The distances between Pb^{2+}−O7, −O9, and −O6 as well as Pb^{2+}−C7−C11 (mean = 4.486 Å) are listed in Table 2. There seems to be marked cation−π interaction between Pb^{2+} and the rotated aromatic calixarene ring *C* (C7−C11) with Pb^{2+} positioned over the center of the aromatic ring. To the best of our knowledge, this is the first example of a solid-state structure in which a homooxacalixarene encapsulates Pb^{2+}.

The ^{1}H NMR spectrum of **4**·$Pb(Pic)_2$ is shown in Figure 2B. Two sets of triplets at δ 7.28 (H_p of *p*-phenyl, H_d), δ 7.39 (H_m of *p*-phenyl, H_e) and the singlet at δ 7.53 (H_o of *p*-phenyl, H_f) in **4** are slightly shifted to δ 7.32, 7.40, and 7.53, respectively, in the complex. Interestingly, the two doublet AB patterns at δ 7.50 and 7.46 for the *m*-hydrogens (H_g) of the calixarene aromatic groups in **4** are shifted downfield to δ 7.68 and collapse into a broad singlet in the complex, suggesting that the *m*-carbons of the two pairs of benzene rings are involved in the complexation. This broad singlet indicates that complexation and decomplexation of Pb^{2+} is fast on the NMR time scale. The large distance between the two AB doublets at δ 5.40 and δ 3.57 for the methylenic protons (H_a) of the ArCH_2Ar bridge of the free ligand **4** decreases upon complexation to δ 4.60 and 3.63 with $\Delta\nu = 582$ Hz. In addition, the AB pattern of the oxamethylenic protons (H_b) of ArCH_2OCH_2Ar at δ 4.69 and 4.15 with a chemical shift difference of $\Delta\nu = 324$ Hz is shifted downfield to δ 4.87 and 4.54 and narrowed ($\Delta\nu = 198$ Hz). Another AB pattern for the methylenic protons (H_c) of ArOCH_2CON-$(Et)_2$ with $\Delta\nu = 202.3$ Hz in **4** changed to a doublet at δ 4.76 in the complex. These observations indicate that the ligand conformation in the complex is somewhat flexible in solution with Pb^{2+} undergoing rapid and complexation and decomplexation on the NMR time scale.

Conclusions

Tetrahomodioxacalix[4]arene tetraamide **4** was synthesized in reasonable yield and found to be in the cone or 1,4-alternate conformation based on its ^{1}H and ^{13}C NMR spectra. Compared with the analogous homooxacalixarene tetraester **5**, the tetraamide **4** selectively binds Pb^{2+} over alkali, alkaline earth, ammonium, and transition metal ions with formation of a 1:1 complex. In the solid-state structure of **4**·$Pb(Pic)_2$, the ligand is in the 1,4-alternate conformation. The Pb^{2+} is bound to the carbonyl oxygens of two adjacent amide substituents and an aryl−alkyl ether oxygen of one of them. It also appears that Pb^{2+} is positioned over the center of one aromatic ring of the ligand with π-metal ion interaction. In solution, the complex shows exchange between complexed and uncomplexed forms on a 600 MHz NMR time scale.

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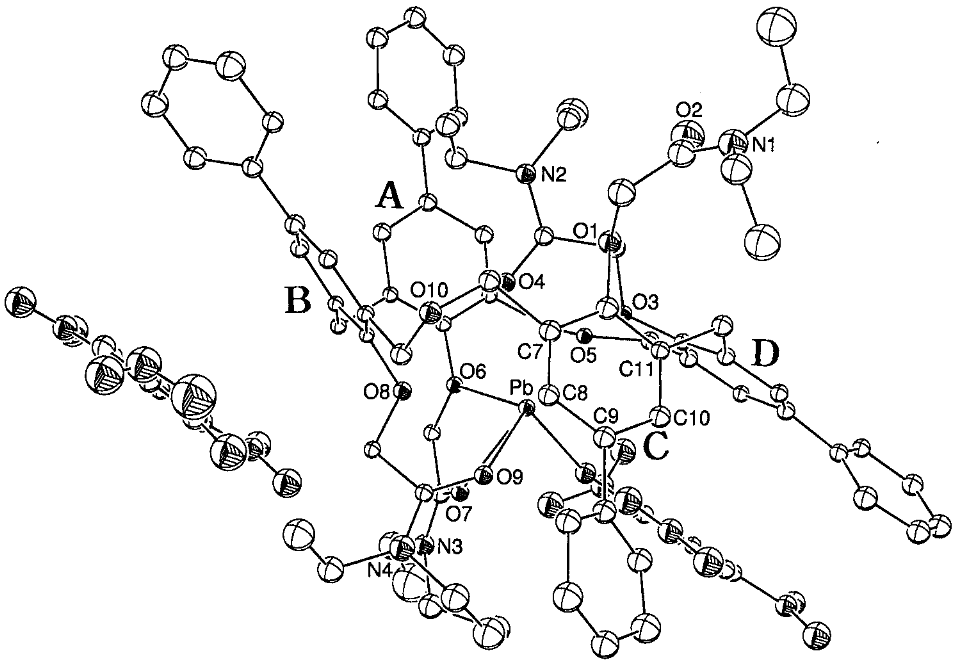

Figure 3.

Table 2. Distances (Å) between Pb^{2+} and Selected Oxygen and Aromatic Carbon Atoms in $4 \cdot Pb^{2+}(Pic^-)_2$

Pb−O(9)	2.451(12)	Pb−C(7)	4.406 (18)
Pb−O(7)	2.471(11)	Pb−C(8)	4.586 (16)
Pb−O(11)	2.499(11)	Pb−C(9)	4.659 (17)
Pb−O(6)	2.577(9)	Pb−C(10)	4.487(16)
Pb−O(4)	2.708(10)	Pb−C(11)	4.292 (15)
Pb−O(8)	2.746(9)		

Experimental Section

Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Melting points were taken in evacuated amd sealed capillary tubes with a Mel-Temp apparatus. IR spectra were determined with a Nicolet Impact 400 FT-IR spectrometer as KBr pellets. ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX 600 spectrometer. Chemical shifts are recorded in parts per million relative to TMS as an internal standard.

The 3-(3-hydroxymethyl-5-phenylsalicyl)-5-phenyl-2-hydroxybenzyl alcohol (**2**) was prepared in 55% yield following the published procedure.[26,27] The 7,13,21,27-tetraphenyl-29,30,31,-32-tetrahydroxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene (**3**) was prepared in 79% yield from bishydroxymethylated dimer of *p*-phenylphenol as described elsewhere:[7] mp 236−237 °C (lit.[7] mp 236−237 °C).

7,13,21,27-Tetraphenyl-29,30,31,32-tetrakis(diethylcarbamoyl)methoxy-2,3-16,17-tetrahomo-3,17-dioxacalix[4]arene (4). To a solution of **3** (932 mg, 1.18 mmol) in dry MeCN (160 mL) was added 2.52 g of anhydrous K_2CO_3 followed by 2.0 mL of *N,N*-diethylchloroacetamide. The mixture was refluxed for 48 h and evaporated in vacuo. The residue was acidified with dilute HCl and the mixture was extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with water, dried over $MgSO_4$ and evaporated in vacuo. The residue was triturated with MeOH to give 513 mg (35%) of the **4** as a white, crystalline solid with mp 276 °C. An additional 147 mg (12%) of pure product was isolated by flash chromatography of the residue obtained by evaporation of filtrate on silica gel with MeOH−$CHCl_3$ (10:1) as eluent: IR (KBr) 1658 cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 7.50 (AB d, 8 H, H_m of calix-Ar), 7.28 (t, 4 H, H_p of *p*-phenyl), 7.39 (t, 8 H, H_m of *p*-phenyl), 7.53 (d, 8 H, H_o of *p*-phenyl), 5.41 (d, 2 H, Ar*CH*$_2$Ar, J = 13.2 Hz), 4.92 (d, 4 H, ArO*CH*$_2$CON, J = 11.2 Hz), 4.69 (d, 4 H, Ar*CH*$_2$O*CH*$_2$Ar, J = 14.6 Hz), 4.61 (d, 4 H, ArO*CH*$_2$CON, J = 11.2 Hz), 4.15 (d, 4 H, Ar*CH*$_2$O*CH*$_2$Ar, J = 14.6 Hz), 3.59 (d, 2 H, Ar*CH*$_2$Ar, J = 13.2 Hz), 3.30 (sextet, 4 H, N*CH*$_2$CH$_3$, J = 7.3, 6.8 Hz), 3.07 (sextet, 4 H, N*CH*$_2$CH$_3$, J = 7.3, 6.8 Hz), 2.74 (sextet, 4 H, N*CH*$_2$CH$_3$, J = 7.3, 6.8 Hz), 2.63 (sextet, 4 H, N*CH*$_2$CH$_3$, J = 7.3, 6.8 Hz), 0.97 (t, 12 H, NCH$_2$*CH*$_3$, J = 6.8 Hz), 0.63 (t, 12 H, NCH$_2$*CH*$_3$, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) 167.72 (*C*=O), 157.23, 140.18, 135.96, 135.53, 130.06, 129.19, 129.04, 128.69, 126.92, 126.58 (Ar), 72.12, 67.90 (*C*H$_2$), 40.55, 39.85 (N*C*H$_2$), 32.65 (Ar*C*H$_2$Ar), 13.56, 12.96 (*C*H$_3$) ppm. Anal. Calcd for $C_{78}H_{88}O_{10}N_4$: C, 75.46; H, 7.14. Found: C, 75.42; H, 7.05.

Metal Picrate Extraction. Metal picrates were prepared by reaction of picric acid with the appropriate metal carbonate.[28,29] To determine the extractability of the ligand for a metal picrate, an aqueous solution (2.0 mL) containing 0.20 mM metal picrate and a chloroform solution (2.0 mL) of the extractant (0.10 mM) was shaken for 30 min at 25 °C. The concentration of picrate anion extracted from the aqueous phase into the organic layer was determined by UV spectrophotometry (λ_{max} = 373 nm). Three independent experiments were carried out for each combination of ligand and metal picrate. The extractability values listed in Table 1 are averages.

To measure the complex ratio from the mass balance of Pb^{2+} and the stoichiometric coefficient between extractant and lead picrate, extraction equilibrium parameters (the distribution ratio of lead picrate (D_M), the extraction equilibrium constant (K_{ex}) and the stoichiometric coefficient between extractant and lead picrate) were determined. An aqueous solution (20.0 mL) containing 0.20 mM lead picrate and a chloroform solution (20.0 mL) of the extractant (0.050−0.80 mM) was shaken at 25 °C.[29] The concentration of picrate anion extracted from the aqueous phase into the organic layer was determined by UV spectrophotometry (λ_{max} = 373 nm).

Solid-State Structure. Yellow crystals of **4**·Pb(Pic)$_2$ were obtained by slow evaporation of solvent of a solution of **4** and lead picrate in CH_2Cl_2−MeOH. A crystal of 0.462 × 0.363 ×

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0.066 mm was mounted and aligned on an Enraf-Nonius Cad-4 diffractometer.[30] The triclinic cell parameters were refined by setting angles of 23 reflections with $11.46 < \theta < 13.59°$. A total of 15 423 independent reflections were collected in the range $2 < \theta < 25°$ with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique at room temperature. The data were corrected for L−p, decay, and empirical absorption effects, and 6775 reflections satisfied the condition $F_o \geq 4\sigma(F_o)$. The structure was solved by direct methods with the space group P-1 with $Z = 2$ and was refined with SHELX97.[31,32] All hydrogen atoms were placed in their calculated positions and allowed to ride on their parent carbon atoms. The residual electron-density maximum is 1.09 Å from the Pb atom.

NMR Studies. The ^{1}H NMR sample of the lead picrate complex of **4** was prepared as follows. A mixture of **4** (20.0 mg) and excess lead picrate (at least 5 equiv) in $CDCl_3$ (1.0 mL) was stirred for 1 h. After filtration of the excess lead picrate, the resultant $CDCl_3$ solution was analyzed by 600-MHz ^{1}H NMR spectroscopy along with HOMO and HETERO COSY techniques.

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Supporting Information Available: Additional table (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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