# **ORGANOMETALLICS**

# Synthesis, Structure, and Reactivity of a Thorium Metallocene Containing a 2,2'-Bipyridyl Ligand

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**Supporting Information** 

**ABSTRACT:** The reduction of  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}ThCl_{2}$  (1) with potassium graphite in the presence of 2,2'-bipyridine gives the purple thorium bipy metallocene  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}Th(bipy)$  (2) in good yield. Complex 2 has been characterized by various spectroscopic techniques, elemental analysis, and single-crystal X-ray diffraction. Complex 2 is a good synthon for low-valent thorium, as shown by the reactivity with silver halides, trityl chloride, pyridine-N-oxide, RN<sub>3</sub>, 9-diazofluorene, and diphenyl diselenide, yielding the halide metallocenes  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}ThX_{2}$ 



(X = CI (1), F (3), Br (4)), oxo metallocene  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ ThO(py) (5), imido metallocenes  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th=NR (R = p-tolyl (6), Ph<sub>3</sub>C (7), Me<sub>3</sub>Si (8), (9-C<sub>13</sub>H<sub>8</sub>)=N (9)), and selenido complex  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th(SePh)<sub>3</sub>(bipy) (10a), in quantitative conversions.

# INTRODUCTION

2,2'-Bipyridine (bipy) and its derivatives have been ubiquitously employed in coordination chemistry, and a wealth of very detailed information regarding the electrochemical and spectroscopic properties of the corresponding coordination complexes is available in the chemical literature.<sup>1</sup> In these complexes, the 2,2'-bipyridyl ligand can exist in three different oxidation states; that is, the neutral 2,2'-bipyridyl can accept either one or two electrons into its  $\pi^*$  orbitals to form the  $\pi$ -radical monoanion [bipy]<sup>•-</sup> and the diamagnetic dianion [bipy]<sup>2-</sup>, respectively (Figure 1).<sup>1</sup> While bipy complexes of main group, lanthanide,



**Figure 1.** Neutral 2,2'-bipyridyl (bipy),  $\pi$ -radical monoanion [bipy]<sup>•-</sup>, and dianion [bipy]<sup>2-</sup>.

and transition metals have been extensively studied,<sup>1</sup> only a small number of actinide complexes have been reported that contain a reduced bipyridyl ligand.<sup>2,3</sup> In most actinide complexes 2,2'-bipyridyl remains redox innocent and therefore does not participate in redox chemistry with the metal center. Recently, the uranium bipy metallocene  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}U(bipy)$  has been shown to be a useful precursor for the preparation of the oxo and *p*-tolylimido metallocenes  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}U=O$  (monomeric in gas phase) and  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}U=N(p-tolyl)$  (monomeric in gas and solid phase), respectively.<sup>4</sup> Encouraged by the interesting chemistry of this uranium bipy metallocene, and by the fact that, to the best of our knowledge, no examples

of thorium metallocenes with an anionic bipy ligand have been reported,<sup>3</sup> we have recently initiated a research program in this area. Herein, we report on some observations concerning the chemistry of a thorium bipy metallocene.

# RESULTS AND DISCUSSION

Synthesis of [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2). Treatment of an excess of KC<sub>8</sub> with a 1:1 mixture of 2,2'-bipyridine and  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ ThCl<sub>2</sub> (1) in cyclohexane solution gives the purple bipy metallocene  $[\eta^5-1,2,4-(Me_3C)_3 C_5H_2$  Th(bipy) (2) in 82% yield (Scheme 1). Complex 2 is soluble in and readily recrystallized from an *n*-hexane solution. Crystals of 2 are air and moisture sensitive, but can be stored without degradation in a dry nitrogen atmosphere. Complex 2 has been fully characterized by various spectroscopic techniques, elemental analysis, and single-crystal X-ray diffraction. The narrow <sup>1</sup>H NMR resonances with chemical shifts in the range of 0-10 ppm and well-resolved coupling patterns are consistent with a diamagnetic molecule. This implies that 2 is a Th(IV) metallocene, in which the bipy ligand serves as a dianion. The four resonances assigned to the bipy ligand are significantly shifted upfield in comparison with those in free bipy, and the ratio of bipy to Cp ligand is 1:2.

The molecular structure of 2 is shown in Figure 2, and selected bond distances and angles are listed in Table 1. The cyclopentadienyl rings adopt a nearly eclipsed conformation. To the best of our knowledge, 2 is the first structurally characterized thorium complex with a bipy anion. As observed by other authors,<sup>2,5,6q</sup> the acceptance of electrons into the

Received:October 21, 2011Published:January 5, 2012





Figure 2. Molecular structure of 2 (thermal ellipsoids drawn at the 35% probability level).

lowest unoccupied molecular orbital of neutral bipy results in shortening of the C(5)-C(6) bond and in flattening of the

bipyridyl ligand. The bending angle<sup>6q</sup> of the bipy ligand in **2** is 141°, which is close to that found in  $(\eta^{5}-C_{5}H_{5})_{2}Zr(bipy)$  (143°).<sup>6q</sup> The C(5)–C(6) distance is 1.382(8) Å, and the shortening of ca. 0.10 Å relative to the value found in neutral bipy (1.490(3) Å)<sup>7</sup> is consistent with a C==C double bond.<sup>5k</sup> A similar value was observed in the known complexes [Yb( $\mu^{2}$ -bipy)(thf)<sub>2</sub>]<sub>3</sub> (1.41 Å),<sup>5a</sup> [Na<sub>2</sub>(bipy)(dme)<sub>2</sub>]<sub>∞</sub> (1.38 Å),<sup>5b</sup> [Li-(THF)<sub>4</sub>][Al(bipy)<sub>2</sub>] (1.36 Å),<sup>5g</sup> [Li(THF)<sub>4</sub>]<sub>2</sub>[Zr(bipy)<sub>3</sub>] (1.36(1) Å),<sup>5c</sup> and Tp\*Y(bipy)(THF)<sub>2</sub> (1.35 Å) (Tp\* = hydrotris(3,5-dimethylpyrazolyl)borate),<sup>5f</sup> in which the bipy ligands are unambiguously described as dianionic.

**Reactivity Studies.** Complexes containing redoxnoninnocent ligands exhibit fascinating electronic structures and/or unusual reactivity patterns.<sup>5d,i,k,l,8</sup> In contrast to group 4 metals,<sup>6</sup> low-valent thorium chemistry is virtually unexplored with a few exceptions describing Th(III) organometallic complexes.<sup>9</sup> This is due to very negative reduction potentials of the Th(IV)/Th(III) and Th(III)/Th(II) couples.<sup>10</sup> Therefore, the synthesis of low-valent Th complexes is rather challenging. However, the high reactivity of low-valent thorium complexes has been demonstrated by *in situ* reduction of appropriate Th(IV) precursors.<sup>11</sup> In this context Gambrotta and co-workers have chosen an interesting approach by preparing thorium naphthalene complexes, which act as well-defined Th(II) synthons. The reaction chemistry in these

Table 1. Selected Distances	(Å)	and Angles (	(deg)	for Com	pounds 2–4.	7.8	and	$10a^{a}$
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compound	C(Cp)-Th (av)	C(Cp)-Th (range)	Cp(cent)– Th (av)	Th-X (av)	Cp(cent)–Th– Cp(cent)	X-Th-X
2	2.881(5)	2.811(5) to 2.988(5)	2.614(5)	2.344(5)	134.5(5)	73.4(2)
3	2.835(9)	2.795(9) to 2.898(9)	2.563(9)	2.126(5)	143.6(3)	103.1(2)
4	2.835(4)	2.760(3) to 2.943(4)	2.565(4)	2.785(1)	139.8(1)	96.8(1)
7	2.903(3)	2.785(3) to 3.059(3)	2.641(3)	2.034(2)	133.5(3)	
8	2.873(4)	2.764(3) to 3.034(4)	2.612(4)	2.035(3)	144.9(4)	
10a	2.855(6)	2.786(6) to 2.939(6)	2.589(6)	Th–N 2.609(5), Th–Se 2.938(8)		N-Th-N 62.3(2), Se-Th-Se 85.3(1), 99.9(1), and 150.5(1)

<sup>a</sup>Cp = cyclopentadienyl ring.

## Organometallics

Scheme 2



systems is induced by the electrons in the reduced dianionic naphthalene moitety.<sup>12</sup> Therefore, the "stored" electrons in the dianionic bipyridyl ligand of 2 might also be used for synthetic chemistry. This approach is analogous to the idea advocated for  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2U(bipy)$ , which is a synthetically useful U(II) synthon.<sup>4</sup> We have recently shown how thorium imido metallocenes can be prepared via amine elimination from thorium diamido metallocenes.<sup>13</sup> However, this synthetic approach using amine elimination is very dependent on the steric demands of the employed amino ligands.<sup>13</sup> In addition, the thorium imido metallocenes are good starting materials for the preparation of thorium oxo and sulfido metallocenes.<sup>14</sup> However, 2 might be an easily accessible and more flexible synthetic alternative for the preparation of these species. Therefore, we investigated the reactivity of 2 with a series of oxidizing reagents. For example, 2 reacts cleanly with silver halides to give the halide metallocenes  $[\eta^{5}-1,2,4-(Me_{3}C)_{3} C_{5}H_{2}]_{2}ThX_{2}$  (X = Cl (1), F (3),<sup>15</sup> Br (4)) in quantitative conversion (Scheme 1). The conversions are measured by integrating the <sup>1</sup>H NMR resonances against an internal standard. The pure halide complexes may be readily separated from free bipy, which is the only organic byproduct, by recrystallization from an *n*-hexane solution, and the isolated preparative scale yield is 91% for 3 and 96% for 4, respectively. Likewise, the treatment of 2 with trityl chloride quantitatively results in the choride complex 1, along with the byproducts neutral bipy and Gomberg's dimer  $Ph_3CCH(C_2H_2)_2C=CPh_2^{16}$  (Scheme 1). The formation of Gomberg's dimer and neutral bipy implies that the free radical  $Ph_3C^{\bullet}$  is formed on oxidation of the [bipy]<sup>2–</sup> anion by Ph<sub>3</sub>C<sup>+</sup>.

Encouraged by this initial screening, we investigated the reactivity of 2 with pyridine-N-oxide and organic azides RN<sub>3</sub>. Similar to the uranium bipy metallocene  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2U(bipy),^4$ 2 reacts cleanly to give quantitatively the oxo metallocene  $[\eta^{5}-1,2,4 (Me_3C)_3C_5H_2$  ThO(py) (5) and imido metallocenes [ $\eta^5$ -1,2,4- $(Me_3C)_3C_5H_2]_2$ Th=NR (R = p-tolyl (6), Ph<sub>3</sub>C (7), Me<sub>3</sub>Si (8)), respectively (Scheme 1). Complex 8 is a nice example of a molecule that is not readily available via the previously reported amine elimination route.<sup>13,17</sup> Unfortunately, although the reaction of 2 with azido compounds yields quantitatively imido metallocenes and N2, the reaction of 2 with diazoalkane compounds does not form the carbene complex  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th=  $(9-C_{13}H_8)$  under similar reaction conditions. For example, treatment of 2 with 1 equiv of 9-diazofluorene gives the hydrazido/ imido complex  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}Th=N-N=$  $(9-C_{13}H_8)$  (9) in quantitative conversion (Scheme 1). Under similar reaction conditions, 2 also breaks Se-Se bonds to give selenido complexes. For example, reaction of 2 with 1 equiv of Article

PhSeSePh results in Se–Se bond cleavage and ligand redistribution to yield  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]Th(SePh)_{3}(bipy)$ (10a) and  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{3}Th(SePh)$  (10b) in quantitative conversion (Scheme 2).

The complexes **3**, **4**, 7–9, and **10a** are stable in dry nitrogen atmosphere, while they are moisture sensitive. They have been characterized by various spectroscopic techniques and elemental analyses (see Experimental Section for details). In addition, the solid-state structures of complexes **3**, **4**, 7, **8**, and **10a** have been further confirmed by single-crystal X-ray diffraction. The ORTEP diagrams of  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ -ThF<sub>2</sub> (**3**) and  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ -ThBr<sub>2</sub> (**4**) are shown in Figures 3 and 4, and selected bond distances and angles are



Figure 3. Molecular structure of 3 (thermal ellipsoids drawn at the 35% probability level).



Figure 4. Molecular structure of 4 (thermal ellipsoids drawn at the 35% probability level).

listed in Table 1. The orientation of the cyclopentadienyl rings in 3 and 4 is nearly eclipsed, similar to that in  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}-C_{5}H_{2}]_{2}ThCl_{2}$ ,<sup>13</sup> and the two X-groups (X = F, Br) are oriented on either side of the eclipsed Me<sub>3</sub>C groups such that the molecule has idealized  $C_{2}$  symmetry. The average Th–F distance is 2.126(5) Å. The average Th–Br distance of 2.785(1) Å is very close to that (2.800(2) Å) found in  $(\eta^{5}-C_{5}Me_{5})_{2}ThBr_{2}$ .<sup>18</sup>

The solid-state crystal structures of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ -Th=NCPh<sub>3</sub> (7) and  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th=NSiMe<sub>3</sub> (8) are shown in Figures 5 and 6. In each molecule, the Cp rings are nearly staggered, the average Th-C(Cp) distance is



Figure 5. Molecular structure of 7 (thermal ellipsoids drawn at the 35% probability level).



Figure 6. Molecular structure of 8 (thermal ellipsoids drawn at the 35% probability level).

2.903(3) Å for 7 and 2.873(4) Å for 8, respectively, and the angle Cp(cent)–Th–Cp(cent) is 133.5(3)° for 7 and 144.9(4)° for 8, respectively. The short Th–N distances (2.034(2) Å for 7 and 2.035(3) Å for 8) and the approximately linear angles (Th–N–C (168.3(2)°) for 7 and Th–N–Si (175.8(2)°) for 8) are consistent with a Th=N double bond,<sup>19</sup> which are comparable to those found in the thorium imido metallocenes ( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th=N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(thf), with the Th–N distance of 2.045(8) Å and the Th–N–C angle of 171.5(7)°,<sup>20</sup> and [ $\eta^{5}$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th=N(*p*-tolyl) (6), with the Th–N distance of 2.038(3) Å and the Th–N–C angle of 172.8(3)°.<sup>13</sup>

The single-crystal X-ray diffraction analysis shows that in a molecule of  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]Th(SePh)_{3}(bipy)$  (10a) the Th<sup>4+</sup> ion is  $\eta^{5}$ -bound to one Cp-ring and  $\sigma$ -coordinate to two nitrogen atoms of the neutral bipy ligand and three

selenium atoms from three PhSe groups in a distorted-octahedral geometry (Figure 7) with an average Th-C(ring)



Figure 7. Molecular structure of 10a (thermal ellipsoids drawn at the 35% probability level).

distance of 2.855(6) Å and an average Th–Se distance of 2.938(8) Å. The average Th–N distance is 2.609(5) Å, which is longer than that found in 2 (2.344(5) Å). The pyridyl rings are twisted with respect to each other, with a torsion angle of  $6.3(1)^{\circ}$ . The distance C(23)–C(24) is  $1.484(9)^{\circ}$ , which is close to those found in free bipy (1.490(3) Å)<sup>7</sup> and Tp\*LaCl<sub>2</sub>(bipy) (1.484(8) Å) (Tp\* = hydrotris(3,5-dimethylpyrazolyl)-borate),<sup>5f</sup> while it is longer than that found in 2 (1.382(8) Å).

# CONCLUSIONS

In conclusion, the first bipy thorium metallocene,  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}Th(bipy)$  (2), has been prepared and structurally characterized, in which the bipy ligand serves as a dianion. It serves as a useful Th(II) synthon and reacts cleanly with silver halides, trityl chloride, pyridine-*N*-oxide, diphenyl diselenide, organic azides, and diazoalkanes such as 9-diazofluorene, leading to halido, oxo, selenido, and imido complexes. These initial results demonstrate how redox-noninnocent ligands can be employed to synthesize organoactinide metallocenes with terminal multiple bonds that are not readily available by other synthetic means. The reaction chemistry of actinide complexes with redox-noninnocent ligands is currently being explored.

# EXPERIMENTAL SECTION

General Procedures. All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Pyridine-N-oxide and 2,2'-bipyridine were purified by sublimation prior to use.  $KC_{8}^{21} p-CH_{3}C_{6}H_{4}N_{3}^{22} [\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}ThCl_{2}(1)^{13} and 9$ diazofluorene<sup>23</sup> were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer.  $^1H,\ ^{13}C\{^1\dot{H}\},$  and  $^{19}F$  NMR spectra were recorded on a Bruker AV 400 spectrometer at 400, 100, and 376 MHz, respectively. All chemical shifts are reported in  $\delta$  units with reference to the residual protons of the deuterated solvents, which are internal standards, for proton and carbon chemical shifts, and to external  $FCCl_3$  (0.00 ppm) for fluorine chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Preparation of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th(bipy) (2). KC<sub>8</sub> (1.05 g, 7.8 mmol) was added to a cyclohexane (20 mL) solution of  $[\eta^5-1,2,4-$ (Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>ThCl<sub>2</sub> (1; 2.00 g, 2.6 mmol) and 2,2'-bipyridine (bipy; 0.41 g, 2.6 mmol) with stirring at room temperature. After this solution was stirred overnight at 60 °C the solvent was removed. The residue was extracted with *n*-hexane (10 mL  $\times$  3) and filtered. The volume of the filtrate was reduced to 10 mL; purple crystals of 2 were isolated when this solution was kept at room temperature for two days. Yield: 1.82 g (82%). Mp: 118–120 °C (dec). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.59 (d, J = 6.8 Hz, 2H, bipy), 7.08 (d, J = 9.6 Hz, 2H, bipy), 6.28 (s, 4H, ring CH), 6.08 (m, 2H, bipy), 5.29 (t, J = 6.0 Hz, 2H, bipy), 1.45  $(s, 36H, (CH_3)_3C), 1.32$   $(s, 18H, (CH_3)_3C).$  <sup>13</sup>C{<sup>1</sup>H} NMR  $(C_6D_6):$ δ 144.5, 143.7, 142.9, 122.6, 121.6, 116.0, 114.4, 102.5, 34.5, 34.3, 33.5, 32.6. IR (KBr, cm<sup>-1</sup>): v 2958 (s), 2857 (m), 1594 (s), 1486 (m), 1389 (s), 1359 (s), 1256 (s), 1119 (s), 811 (s). Anal. Calcd for C44H66N2Th: C, 61.81; H, 7.78; N, 3.28. Found: C, 61.76; H, 7.74; N, 3.32.

Reaction of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th(bipy) (2) with AgCl. NMR Scale. AgCl (5.8 mg, 0.04 mmol) was added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th(bipy) (2; 17 mg, 0.02 mmol) and  $C_6D_6$  (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ ThCl<sub>2</sub> (1) (<sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  6.56 (*s*, 4H, ring CH), 1.59 (*s*, 36H, (CH<sub>3</sub>)\_3C), 1.31 (*s*, 18H, (CH<sub>3</sub>)\_3C))<sup>13</sup> along with those of 2,2'-bipyridine (<sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  8.72 (d, J = 8.0 Hz, 2H), 8.53 (d, J = 4.0 Hz, 2H), 7.22 (t, J = 1.8 Hz, 2H), 6.68 (m, 2H)) were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

**Preparation of** [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>ThF<sub>2</sub> (3). Method A. AgF (0.38 g, 3.0 mmol) was added to a toluene (20 mL) solution of [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2; 1.28 g, 1.5 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from purple to colorless. After the solution was stirred at room temperature overnight, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to -20 °C, yielding colorless crystals of 3, which were isolated by filtration. Yield: 1.01 g (91%). Mp: 123–125 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.37 (s, 4H, ring CH), 1.56 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>C), 1.37 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 143.2, 142.7, 117.4, 34.6, 33.4, 32.8, 32.5. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): δ 136.7 (s). IR (KBr, cm<sup>-1</sup>): ν 2961 (s), 1582 (m), 1458 (s), 1391 (s), 1362 (s), 1260 (s), 1086 (s), 1022 (s), 798 (s). Anal. Calcd for C<sub>34</sub>H<sub>58</sub>F<sub>2</sub>Th: C, 55.42; H, 7.93. Found: C, 55.37; H, 7.88.

**Method B. NMR Scale.** AgF (5.1 mg, 0.04 mmol) was added to a J. Young NMR tube charged with  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th(bipy) (2; 17 mg, 0.02 mmol) and  $C_{6}D_{6}$  (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to 3 along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

**Preparation of** [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>ThBr<sub>2</sub> (4). Method A. This compound was prepared as colorless crystals from the reaction of [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2; 1.28 g, 1.5 mmol) and AgBr (0.57 g, 3.0 mmol) in toluene (20 mL) and recrystallization from an *n*-hexane solution by a similar procedure to the synthesis of 3. Yield: 1.24 g (96%). Mp: 139–141 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.65 (s, 4H, ring CH), 1.61 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>C), 1.29 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 148.6, 147.6, 119.5, 35.5, 34.1, 34.0, 32.4. IR (KBr, cm<sup>-1</sup>): ν 2961 (s), 2895 (m), 1597 (m), 1458 (s), 1393 (s), 1358 (s), 1260 (s), 1237 (s), 1020 (s), 798 (s). Anal. Calcd for C<sub>34</sub>H<sub>58</sub>Br<sub>2</sub>Th: C, 47.56; H, 6.81. Found: C, 47.62; H, 6.78.

**Method B. NMR Scale.** AgBr (7.6 mg, 0.04 mmol) was added to a J. Young NMR tube charged with  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th(bipy) (2; 17 mg, 0.02 mmol) and  $C_{6}D_{6}$  (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to 4 along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

Reaction of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th(bipy) (2) with Ph<sub>3</sub>CCI. NMR Scale. Ph<sub>3</sub>CCI (11 mg; 0.04 mmol) was added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th(bipy) (2; 17 mg, 0.02 mmol) and C<sub>6</sub>D<sub>6</sub> (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ ThCl<sub>2</sub> (1)<sup>13</sup> along with those of Ph<sub>3</sub>CCH(C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>C= CPh<sub>2</sub> (<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.29 (m, 3H, phenyl), 7.00 (m, 22H, phenyl), 6.43 (d, *J* = 9.8 Hz, 2H, CH), 5.92 (d, *J* = 9.8 Hz, 2H, CH), 4.92 (s, 1H, CH))<sup>16</sup> and 2,2' bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

Reaction of  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}I_{2}Th(bipy)$  (2) with Pyridine-*N*-Oxide. NMR Scale. Pyridine-*N*-oxide (2 mg, 0.02 mmol) was added to a J. Young NMR tube charged with  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}Th(bipy)$  (2; 17 mg, 0.02 mmol) and  $C_{6}D_{6}$  (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}Th(O)(py)$ (5) (<sup>1</sup>H NMR ( $C_{6}D_{6}$ ):  $\delta$  8.78 (m, py), 6.94 (m, py), 6.64 (m, py), 6.48 (d, *J* = 3.4 Hz, 2H, ring CH), 5.92 (d, *J* = 3.4 Hz, 2H, ring CH), 1.60 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.59 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.18 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C))<sup>12</sup> along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

**Reaction of**  $[\eta^{5}$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2) with *p*-TolylN<sub>3</sub>. NMR Scale. A C<sub>6</sub>D<sub>6</sub> (0.3 mL) solution of *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub> (2.6 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^{5}$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2; 17 mg, 0.02 mmol) and C<sub>6</sub>D<sub>6</sub> (0.2 mL). The color of the solution immediately changed from purple to colorless, and resonances due to  $[\eta^{5}$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th= N(*p*-tolyl) (6) (<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.12 (d, *J* = 8.0 Hz, 2H, aryl), 6.52 (s, 4H, ring CH), 6.48 (d, *J* = 8.0 Hz, 2H, aryl), 2.33 (s, 3H, tolylCH<sub>3</sub>), 1.52 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>C), 1.44 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C))<sup>11</sup> along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

Preparation of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th=NCPh<sub>3</sub>·C<sub>6</sub>H<sub>6</sub>  $(7 \cdot C_6 H_6)$ . Method A. A benzene (10 mL) solution of Ph<sub>3</sub>CN<sub>3</sub> (0.43 g, 1.5 mmol) was added to a benzene (20 mL) solution of  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th(bipy) (2; 1.28 g, 1.5 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from purple to colorless. After the solution was stirred at room temperature for 0.5 h, the solution was filtered. The volume of the filtrate was reduced to 5 mL, and colorless crystals of  $7 \cdot C_6 H_6$  were isolated when this solution was kept at room temperature for two days. Yield: 1.47 g (95%). Mp: 194–196 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.78 (d, J = 7.2 Hz, 6H, Ph), 7.22 (t, J = 7.2 Hz, 6H, Ph), 7.15 (s, 6H, benzene) 7.02 (t, J = 7.2 Hz, 3H, Ph), 6.98 (s, 2H, ring CH), 6.03 (s, 2H, ring CH), 1.50 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.49 (s, 18H,  $(CH_3)_3C$ ), 1.38 (s, 18H,  $(CH_3)_3C$ ). <sup>13</sup>C{<sup>1</sup>H} NMR  $(C_6D_6)$ :  $\delta$  153.2, 140.1, 140.0 133.9, 129.4, 128.0, 127.8, 127.5, 127.2, 124.6, 117.7, 115.5, 81.6, 34.9, 34.3, 33.9, 32.6. IR (KBr, cm<sup>-1</sup>):  $\nu$  2961 (s), 1595 (m), 1474 (s), 1457 (s), 1387 (s), 1360 (s), 1260 (s), 1095 (s), 1021 (s), 804 (s). Anal. Calcd for C<sub>59</sub>H<sub>79</sub>NTh: C, 68.51; H, 7.70; N, 1.35. Found: C, 68.49; H, 7.78; N, 1.32.

**Method B. NMR Scale.** Ph<sub>3</sub>CN<sub>3</sub> (6 mg; 0.02 mmol) was added to a J. Young NMR tube charged with  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th(bipy) (2; 17 mg, 0.02 mmol) and C<sub>6</sub>D<sub>6</sub> (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to 7 along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

Preparation of [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th=NSiMe<sub>3</sub> (8). Method A. This compound was prepared as colorless crystals from the reaction of [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2; 1.28 g, 1.5 mmol) and Me<sub>3</sub>SiN<sub>3</sub> (0.18 g, 1.5 mmol) in benzene (20 mL) and recrystallization from an *n*-hexane solution by a similar procedure to the synthesis of 7. Yield: 1.00 g (85%). Mp: 196–198 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.15 (s, 4H, ring CH), 1.53 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>C), 1.51 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 0.26 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 134.8, 128.3, 127.7, 34.4, 33.9, 32.7, 32.6, 4.7. IR (KBr, cm<sup>-1</sup>): ν 2962 (s), 2862 (m), 1574 (m), 1459 (m), 1363 (m), 1260 (s), 1097 (s), 1019 (s), 798 (s). Anal. Calcd for C<sub>37</sub>H<sub>67</sub>NSiTh: C, 56.53; H, 8.59; N, 1.78. Found: C, 56.46; H, 8.63; N, 1.72.

Tabl	le 2.	Crystal	Data a	nd Ex	perimental	Parameters	for (	Compound	s 2–4	, 7,	8,	and	10a
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	2	3	4	$7 \cdot C_6 H_6$	8	10a·THF
formula	C444H66N2Th	$C_{34}H_{58}F_2Th$	C34H58Br2Th	C <sub>59</sub> H <sub>79</sub> NTh	C37H67NSiTh	C49H60N2OSe3Th
fw	855.03	736.84	858.66	1034.27	786.05	1161.91
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_{1}/c$	$P2_{1}2_{1}2_{1}$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$
a (Å)	18.609(4)	10.171(2)	10.632(1)	10.729(1)	10.248(2)	10.456(1)
b (Å)	12.831(3)	17.003(2)	20.767(2)	23.149(1)	19.685(4)	30.093(4)
c (Å)	17.548(4)	19.449(3)	32.426(3)	21.743(1)	21.358(4)	17.748(2)
$\beta$ (deg)	102.84(1)	90	98.70(1)	112.64(1)	114.91(1)	123.45(1)
V (Å <sup>3</sup> )	4085.1(4)	3363.3(9)	7077.1(12)	4984.0(5)	3724.8(13)	4659.3(9)
Ζ	4	4	8	4	4	4
$D_{\rm calc}~({\rm g/cm^3})$	1.390	1.455	1.612	1.378	1.402	1.656
$\mu$ (Mo/K $\alpha$ ) <sub>calc</sub> (cm <sup>-1</sup> )	3.680	4.464	6.492	3.030	4.059	5.580
size (mm)	$0.30 \times 0.20 \times 0.20$	$0.24\times0.22\times0.20$	$0.42 \times 0.36 \times 0.28$	$0.17 \times 0.15 \times 0.08$	$0.21\times0.20\times0.10$	$0.25 \times 0.20 \times 0.15$
F(000)	1736	1480	3376	2120	1600	2272
$2\theta$ range (deg)	3.88 to 55.02	4.52 to 55.76	2.54 to 63.82	3.52 to 55.28	4.14 to 55.38	3.86 to 50.50
no. of reflns, collected	23 416	32 324	69 346	29 665	22 106	23 357
no. of unique reflns	9241 ( $R_{\rm int} = 0.0608$ )	7998 ( $R_{\rm int} = 0.0686$ )	22 526 ( $R_{\rm int} = 0.0428$ )	11 450 $(R_{int} = 0.0433)$	$8575 (R_{int} = 0.0494)$	8431 $(R_{\rm int} = 0.0800)$
no. of obsd reflns	6937	7402	19 799	9391	6675	6230
no. of variables	442	353	703	568	382	514
$abs_{corr} (T_{max'} T_{min})$	0.53, 0.40	0.47, 0.41	0.26, 0.17	0.79, 0.63	0.69, 0.48	0.49, 0.34
R	0.046	0.069	0.039	0.030	0.033	0.043
R <sub>w</sub>	0.102	0.163	0.083	0.060	0.062	0.075
$R_{\rm all}$	0.069	0.071	0.047	0.042	0.050	0.067
Gof	1.01	1.04	1.06	1.00	0.98	0.97

**Method B. NMR Scale.** Me<sub>3</sub>SiN<sub>3</sub> (2.3 mg; 0.02 mmol) was added to a J. Young NMR tube charged with  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th-(bipy) (2; 17 mg, 0.02 mmol) and C<sub>6</sub>D<sub>6</sub> (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to 8 along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

Preparation of  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}Th=N-N=(9-C_{13}H_{8})$ (9). Method A. A benzene (10 mL) solution of 9-diazofluorene (0.31 g, 1.5 mmol) was added to a benzene (20 mL) solution of  $[\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(bipy) (2; 1.28 g, 1.5 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from purple to brown. After the solution was stirred at room temperature for 0.5 h, solvent was removed and the brown solid was exposed to vacuum overnight at 50 °C in a water bath. The residue was extracted with *n*-hexane (10 mL  $\times$  3) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to -20 °C, yielding brown microcrystals of 9, which were isolated by filtration. Yield: 0.96 g (72%). Mp: 86–88 °C. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  9.12 (d, J = 7.6 Hz, 1H, aryl), 8.02 (d, J = 7.6 Hz, 1H, aryl), 7.98 (d, J = 7.6 Hz, 1H, aryl), 7.93 (d, J = 7.6 Hz, 1H, aryl), 7.51 (q, J = 7.6 Hz, 2H, aryl), 7.33 (t, J = 7.6 Hz, 1H, aryl), 7.26 (t, J = 7.6 Hz, 1H, aryl), 6.37 (s, 2H, ring CH), 6.32 (s, 2H, ring CH), 1.46 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.37 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.32 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 142.7, 136.4, 135.9, 135.4, 135.3, 127.2, 127.1, 124.8, 124.6, 124.5, 124.4, 124.3, 123.1, 123.0, 120.3, 119.3, 117.2, 34.5, 34.3, 33.7, 33.0, 32.9, 31.7. IR (KBr, cm<sup>-1</sup>): v 2962 (s), 1580 (m), 1457 (m), 1384 (s), 1260 (s), 1090 (s), 1019 (s), 798 (s). Anal. Calcd for C<sub>47</sub>H<sub>66</sub>N<sub>2</sub>Th: C, 63.35; H, 7.47; N, 3.14. Found: C, 63.30; H, 7.38; N, 3.22.

**Method B. NMR Scale.** 9-Diazofluorene (4 mg; 0.02 mmol) was added to a J. Young NMR tube charged with  $[\eta^{5}-1,2,4-(Me_{3}C)_{3}C_{5}H_{2}]_{2}$ Th(bipy) (2; 17 mg, 0.02 mmol) and  $C_{6}D_{6}$  (0.5 mL). The color of the solution immediately changed from purple to brown, and resonances due to 9 along with those of 2,2'-bipyridine were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

Preparation of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]Th(SePh)_3(bipy)·THF (10a·THF). Method A. A benzene (10 mL) solution of PhSeSePh (0.47 g, 1.5 mmol) was added to a benzene (20 mL) solution of <math>[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th(bipy) (2; 1.28 g, 1.5 mmol) with stirring at room temperature. During the course of the reaction, the color of the

solution changed from purple to yellow. After the solution was stirred at room temperature for 0.5 h, solvent was removed and the yellow residue was extracted with THF (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to -20 °C, yielding yellow crystals **10a** THF, which were isolated by filtration. Yield: 0.59 g (34% based on Th). Mp: 158–160 °C (dec). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.35 (m, 2H, bipy), 7.20 (m, 2H, bipy), 7.18 (m, 2H, bipy), 6.94 (s, 2H, ring CH), 6.60 (m, 12H, phenyl), 6.32 (m, 5H, phenyl and bipy), 3.60 (m, 4H, thf), 1.93 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.75 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.39 (m, 4H, thf). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  152.7, 150.3, 147.9, 146.5, 139.1, 137.5, 135.7, 128.3, 123.9, 123.5, 121.5, 120.6, 67.5, 35.8, 35.0, 34.8, 32.7, 25.5. IR (KBr, cm<sup>-1</sup>):  $\nu$  2962 (s), 1581 (m), 1472 (m), 1454 (m), 1358 (m), 1260 (s), 1097 (s), 1019 (s), 798 (s). Anal. Calcd for C<sub>49</sub>H<sub>60</sub>N<sub>2</sub>OSe<sub>3</sub>Th: C, 50.65; H, 5.20; N, 2.41. Found: C, 50.72; H, 5.18; N, 2.42.

Method B. NMR Scale. PhSeSePh (6 mg; 0.02 mmol) was added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2$ Th-(bipy) (2; 17 mg, 0.02 mmol) and  $C_6D_6$  (0.5 mL). The color of the solution immediately changed from purple to yellow, and resonances due to 10a along with those of  $[\eta^5-1,2,4-(Me_3C)_3C_5H_2]_3Th(SePh)$ (10b) (<sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  8.73 (d, J = 8.2 Hz, 1H, phenyl), 8.53 (d, J = 4.1 Hz, 1H, phenyl), 7.57 (d, J = 6.6 Hz, 2H, phenyl), 7.53 (d, J =6.9 Hz, 1H, phenyl), 6.48 (s, 1H, ring CH), 6.45 (s, 1H, ring CH), 6.26 (s, 1H, ring CH), 6.21 (d, J = 2.0 Hz, 1H, ring CH), 5.97 (d, J =1.6 Hz, 1H, ring CH), 5.71 (d, J = 2.0 Hz, 1H, ring CH), 1.51 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.49 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.39 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.28 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.26 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>C), 1.18 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.11 (s, 9H,  $(CH_3)_3C$ , 1.08 (s, 9H,  $(CH_3)_3C$ )) were observed by <sup>1</sup>H NMR spectroscopy (100% conversion). 10b was not isolated as a pure compound on a synthetic scale, since it was an oily residue and very soluble in solvents such as benzene and *n*-hexane and 10a could not be removed completely.

**X-ray Crystallography.** Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffractometer at 150(2) K or on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71070 Å). An empirical absorption correction was applied using the SADABS program.<sup>24</sup> All structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXL-97

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program package.<sup>25</sup> All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for 2-4, 7, 8, and 10a are summarized in Table 2. Selected bond lengths and angles are listed in Table 1.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

<sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the new molecules. X-ray crystallographic data, in CIF format, for compounds 2-4, 7, 8, 10a, and 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 20972018, 21074013, 21172022), the Program for New Century Excellent Talents in University (NCET-10-0253), the Fundamental Research Funds for the Central Universities (China), and the Deutsche Forschungsgemeinschaft (DFG) through the Emmy-Noether program (WA 2513/2-1). We thank Dr. Haibin Song and Dr. Xuebin Deng for their help with the crystallography, and Prof. Richard A. Andersen for helpful discussions.

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