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## Selective Recognition of Bis-Imidazoles by Complementary Bis-Metal Ion Complexes[1]

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Metal ion complexes that bind protein surfaces at exposed coordinating ligands can be exploited in selective protein recognition. For example, immobilized metal-affinity chromatography (IMAC), a technique used extensively for protein purification,[2] discriminates proteins based on the nature and multiplicity of surface-exposed ligands, usually the imidazole moiety of histidine. To design complexes capable of selectively recognizing an individual protein or other target molecule, the spatial distribution of metal ions can be matched to the distribution of coordinating ligands on the target molecule. A similar proposal, when used as the basis for template polymerization in the presence of the target molecule, yielded solid, $Cu^{2+}$-containing polymers that could discriminate bis-imidazole "protein analogs" so similar that they could not be separated by reverse-phase HPLC.[3] The "rationally designed" model system reported here demonstrates that receptor complexes containing as few as two properly-positioned metal ions can selectively recognize target molecules with a complementary spatial distribution of metal-coordinating ligands.[4] Complexes such as these may have applications as receptors for biological molecules that are characterized by unique patterns of surface coordinating ligands.

Bis-imidazoles **1** and **2**, the target molecules used in previous template polymerization studies,[5] were also used for this investigation. The distances between the two N-3 atoms of the imidazole rings that are optimal for simultaneously coordinating the two metal ions of a bis-metal ion receptor were found to be 7.2-8.3 Å for **1** and 11.5-12.5 Å for **2** by computer modeling. 1-Benzylimidazole (**3**) was used as a control in the binding experiments. Two bis-mercury complexes **4** and **5** were designed to recognize bis-imidazole **2** in preference to **1**; the optimum distance between the two metal centers is 13 Å for **4** and 11 Å for **5**. The synthesis of the receptor **4** is outlined in Scheme I. Receptor **5** was prepared following the literature procedure.[6,7]

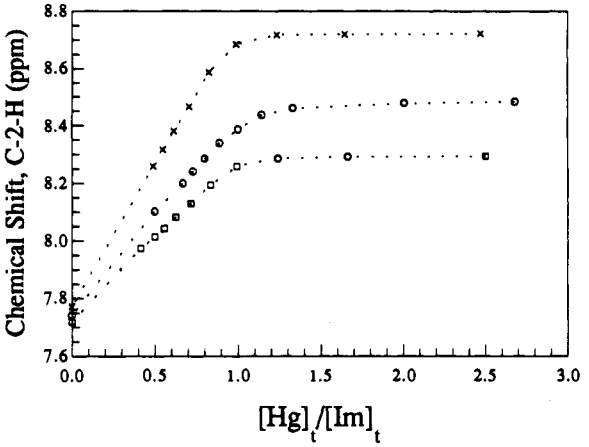
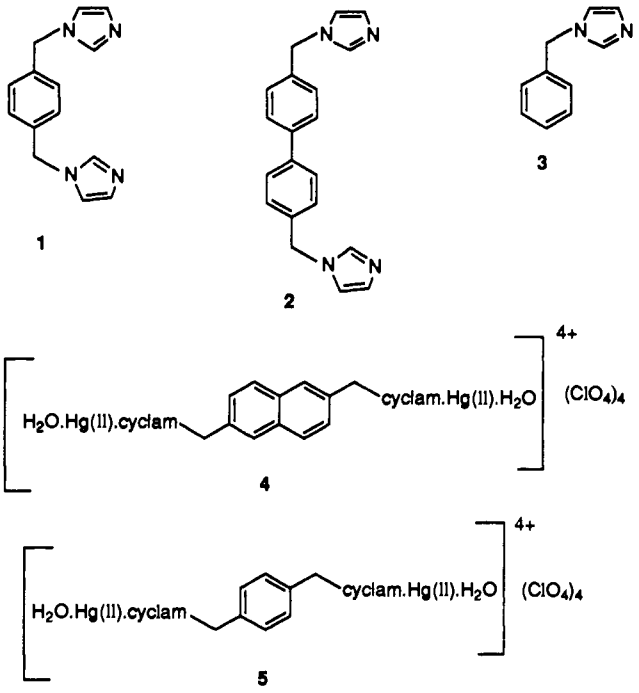



**Figure 1.** Imidazole C-2-H chemical shifts for the titration of bis-metal ion complex **4** with imidazole derivatives **1** (□), **2** (×), and **3** (○). Solutions of **4** in DMSO-$d_6$ were titrated with increasing amounts of **1** (initial concentration of **4** = 16.9 mM), **2** (initial concentration of **4** = 16.7 mM), and **3** (initial concentration of **4** = 16.4 mM).




Titrations of receptor complexes **4** and **5** (~15 mM in DMSO-$d_6$) with target imidazoles **1**, **2**, and **3** were monitored by $^1$H-NMR spectroscopy. In the absence of the bis-mercury receptor, the C-2-H and C-4-H resonances of **2** appear only 0.02 ppm downfield of the C-2-H and C-4-H resonances of **3**. These resonances are strongly affected by interaction with the metal complexes (see Figures 1 and 2). In the presence of stoichiometric amounts of bis-mercury complex **4**, the C-2-H of **2** is shifted downfield by 0.24 ppm with respect to the C-2-H of **3** (Figure 1); in contrast, the C-4-H of **2** is shifted upfield by 0.1 ppm with respect to the C-4-H of **3** (Figure 2). These chemical shifts are consistent with the positioning of the aromatic rings of **2** and **4** one on top of the other in a cyclic complex which places the C-2-H of **2** in the deshielding zone and the C-4-H in the shielding zone for the naphthalene ring current of **4**. That the phenyl ring protons of **2** are also shifted upfield by about 0.8 ppm at metal:imidazole

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(1) Dedicated to Sri B. R. Mitra on his 75th birthday.

(2) For recent examples see: Zhang, Z.; Tong, K.-T.; Belew, M.; Pettersson, T.; Janson, J.-C. *J. Chromatogr.* **1992**, *604*, 143-155. Skerra, A.; Pfitzinger, I.; Pluckthun, A. *Bio/Technology* **1991**, *9*, 273-278. Arnold, F. H. *Bio/Technology* **1991**, *9*, 151-156.

(3) Dhal, P. K.; Arnold, F. H. *J. Am. Chem. Soc.* **1991**, *113*, 7417-7418.

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(7) All new compounds were characterized by $^1$H- and $^{13}$C-NMR spectra and satisfactory mass spectral or elemental analyses.

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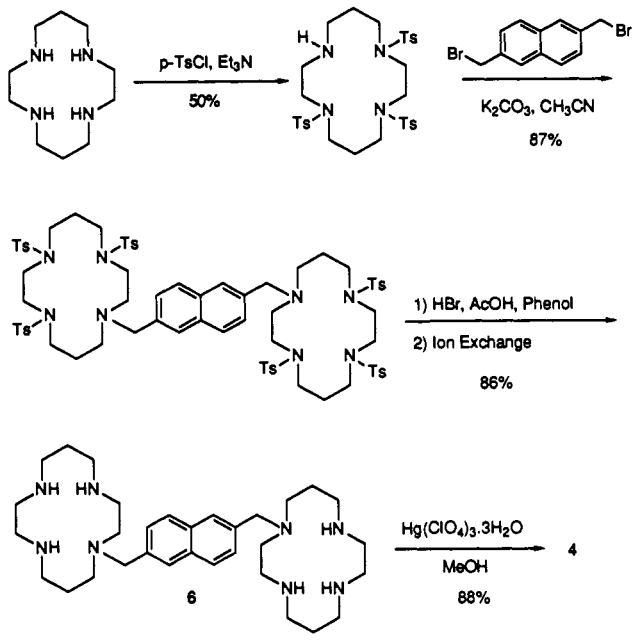
**Scheme I**




ratios below 1:1 provides corroborating evidence for the formation of the cyclic complex.[8] Molecular models indicate that these changes in chemical shift would not be expected for cyclic or linear oligomeric species (e.g., $\mathbf{4}_n\mathbf{.2}_n$). No such effects were observed in the titration of receptor **4** with either **1** or **3**. NMR titration of the metal-free receptor **6** with bis-imidazole **2** indicates that the 1:1 cyclic complex does not form in the absence of the metal ions. Titration of metal complex **5** with bis-imidazole **2** did not exhibit such definitive evidence for the formation of a cyclic structure. The $^1$H-NMR spectra of 1:1 mixtures of **5** and **2** were identical over a 10-fold concentration range (1–20 mM), arguing against the formation of oligomeric or polymeric species.

Most of the titration curves exhibit a rather sharp transition at 1:1 metal:imidazole ratios, indicating that the equilibrium binding constants are large compared to the inverse of the concentrations used ($\gg$100 M$^{-1}$) and therefore cannot be determined accurately from the titration results. Binding selectivities for the target imidazoles, on the other hand, can be determined from the competition between two imidazole derivatives for binding to a bis-mercury receptor.[9] Competitive titration experiments indicate that **4** binds the larger bis-imidazole **2** in preference to **1**, but is unable to distinguish between bis-imidazole **1** and 1-benzylimidazole (**3**) (Figure 3). The simple model used to analyze the titration data is shown below.

$$\mathbf{1} + \mathbf{4} \overset{K_{a1}}{\rightleftharpoons} [\mathbf{1.4}]$$

$$\mathbf{2} + \mathbf{4} \overset{K_{a2}}{\rightleftharpoons} [\mathbf{2.4}]$$

$$\frac{[\mathbf{1.4}]}{[\mathbf{2.4}] + [\mathbf{1.4}]} = \frac{(K_{a1}/K_{a2})([\mathbf{1}]/[\mathbf{2}])}{1 + (K_{a1}/K_{a2})([\mathbf{1}]/[\mathbf{2}])} = \frac{\alpha_{1,2}([\mathbf{1}]/[\mathbf{2}])}{1 + \alpha_{1,2}([\mathbf{1}]/[\mathbf{2}])}$$

The binding selectivities obtained from Figure 3 are listed in Table I. Complex **4** exhibits a 10-fold preference for binding bis-imidazole **2** over **1**; in metal complex **5** this preference increases to 14-fold (concentration of **2** is ~10 mM). Receptor **5** binds its target bis-imidazole 25 times more tightly than 1-benzylimidazole.

These binding selectivities are quite high, particularly for chromatographic applications where separation factors of ~2 yield high-resolution separations. Theoretically, however, the selectivities could be much larger.[10] There are four carbon–carbon single bonds capable of rotating freely in each of **1**, **2**, **4**, and **5**. In addition to imperfect matching of the metal ion spacing to the

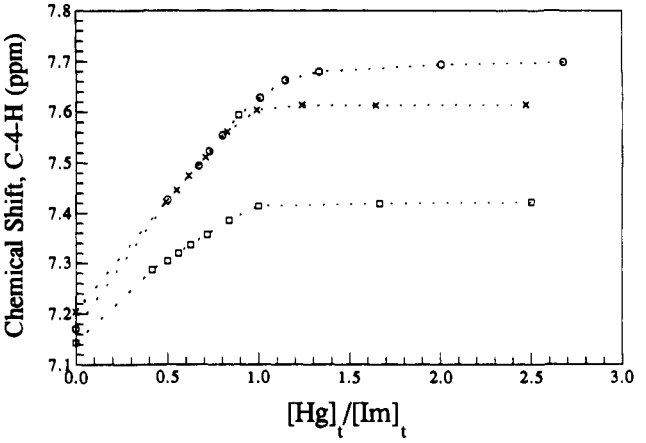



**Figure 2.** C-4-H chemical shifts for the titration of bis-metal ion complex **4** with imidazole derivatives **1** (□), **2** (×), and **3** (○). Concentrations are the same as in Figure 1.

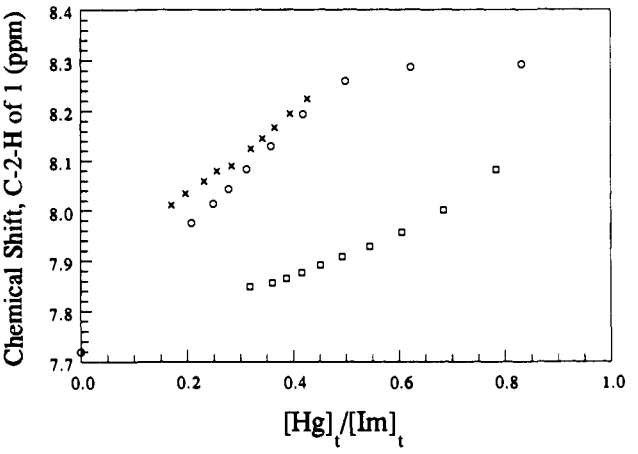



**Figure 3.** Chemical shifts (C-2-H) of **1** in competition experiments: a solution of 1:1 **4** and **1** (concentration = 15.0 mM in DMSO-$d_6$) was titrated with **3** (×), and a mixture of 1:1 **4** and **2** (concentration = 14.6 mM in DMSO-$d_6$) was titrated with **1** (□). C-2-H chemical shifts for the titration of **4** with **1** (○).

**Table I.** Selectivity of Bis-Metal Receptors **4** and **5** toward 1-Benzylimidazole (**3**) and Bis-Imidazoles **1** and **2** in Competitive Titration Experiments

| selectivity | complex **4** | complex **5** |
|---|---|---|
| $\alpha_{2,1}$ | 10 | 14 |
| $\alpha_{1,3}$ | 1 | 1.7 |
| $\alpha_{2,3}$ | 10 | 25 |

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(9) These NMR experiments cannot distinguish fast-exchanging mixed-ligand complexes of the type **4.2.3** or **4.2.1**. The upfield shifts of the phenyl ring protons of **2** in the competition experiments (e.g., **4** + **2** + **3** or **4** + **2** + **1**) are very similar to those of the titration experiment (i.e., **4** + **2**), indicating that the concentrations of any mixed-ligand complexes are small compared to the concentration of the cyclic complex.

(10) If the two imidazole moieties of **2** bind independently to the bis-metal complex **4**, the apparent binding constant would be twice the binding constant for 1-benzylimidazole (**3**) (reflecting the increased probability of interaction due to the availability of the additional binding site in **2**). If the two imidazoles of **2** bind *simultaneously* to the two metal centers of **4**, the binding constant can be much larger. If no additional entropy is lost upon simultaneous binding, compared to the binding of two molecules of **3** to **4**, the apparent binding constant for the interaction between **2** and **4** can be as high as $K_1K_2$, where $K_1$ and $K_2$ are the first and second binding constants for 1-benzylimidazole (**3**) with the bis-mercury complex **4**. The first binding constant ($K_1$) for **3** and **4** will be similar to the coordination of the first imidazole moiety of **2** to one metal center of **4**. $K_2$ for the interaction of **3** and **4** is ~1000 M$^{-1}$. Therefore the theoretical maximum selectivity for **2** versus **3** can be as much as 1000.

spacing between imidazole nitrogens, freezing of the rotations of these bonds may be responsible for reducing the selectivities.

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## Preparation of Lanthanide Tellurolates and Evidence for the Formation of Cluster Intermediates in Their Thermal Decomposition to Bulk Metal Tellurides

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The transformation of molecular compounds into solid-state materials is an increasingly important process.[1] Surprisingly little is known of the mechanisms involved, as these are generally gas- or solid-phase reactions that take place at elevated temperatures. We recently described a homogeneous solution model for the decomposition of metal chalcogenolates to chalcogenides represented by eq 1. Thus, treatment of the zirconium or hafnium

$$[M(ER)_2]_n \rightarrow [ME]_n + nER_2 \qquad (E = S, Se, Te) \quad (1)$$

tellurolates $M(TeR)_4$ [R = $Si(SiMe_3)_3$] with excess of the donor ligand dmpe [dmpe = 1,2-bis(dimethylphosphino)ethane] produced the unusual terminal telluride species $M(=Te)(TeR)_2(dmpe)_2$ and $TeR_2$.[2]

Working under the assumption that the combination of a hard, electropositive metal and a soft, polarizable tellurolate ligand will make for reactive M-Te bonds, we have been studying the synthesis and reactivity of lanthanide tellurolates. Although compounds of this type are extremely rare,[3,4] interest in them heightened recently with the realization that they may be of use as precursors to solid-state lanthanide(II) chalcogenides.[4,5]

Here we describe the synthesis of reactive homoleptic lanthanide(III) tellurolates which, in the absence of stabilizing donor ligands, decompose to form novel molecular telluride-tellurolate clusters.[6] In addition, we show that these isolable intermediates are converted to bulk lanthanide tellurides on pyrolysis.

Tellurolysis[2,7] of the trivalent metal amide derivatives $M[N(SiMe_3)_2]_3$ (M = La, Ce)[8] with 3 equiv of $HTeSi(SiMe_3)_3$ in hexane resulted in a slow color change from orange to brown (Scheme I).[9] Monitoring the lanthanum reaction by $^1H$ NMR spectroscopy in benzene-$d_6$ at 20 °C revealed that after ca. 2 h both starting materials had disappeared and that a single new product **1** ($^1H$ NMR, $\delta$ 0.55 ppm; $^{125}Te$ NMR, $\delta$ 1018 ppm) had formed together with 3 equiv of $NH(SiMe_3)_2$.[10] The homoleptic complex is thermally unstable (see below); however, $^1H$ NMR spectroscopy showed that addition of excess dmpe resulted in immediate quantitative conversion to the stable adduct **3**; this material was subsequently isolated as yellow crystals from preparative scale reactions in hexane,[11] and the paramagnetic cerium derivative (**4**) ($\mu_{eff}$ = 2.28 $\mu_B$) was obtained similarly.[10] Isolated yields of analytically pure **3** and **4** were >75%, and no byproducts were detected.

At 23 °C, the $^1H$ NMR spectrum of the diamagnetic lanthanum derivative **3** shows a broad singlet for the three equivalent tellurolate ligands and broad peaks due to the dmpe methyl and methylene groups.[10] On lowering of the temperature to -84 °C, the tellurolate ligands gave rise to two peaks integrating to 54 and 27 protons and the dmpe ligands showed two broad peaks that integrated to 12 protons each. (The methylene resonances were, presumably, too broad to be detected.) Over the same temperature range, $^{13}C$ NMR data showed three peaks at 23 °C (due to dmpe methylenes, methyls, and the tellurolate ligands) whereas at -84 °C a total of six resonances, resulting from the inequivalent ends of the dmpe ligands and two types of tellurolate ligand, were evident. The $^{31}P$ NMR spectra were also temperature dependent, showing a broad singlet at 23 °C that split into two narrower peaks of equal intensity at -84 °C.[10] Finally, $^{125}Te$ NMR spectra at -70 °C showed two broad singlets of relative intensity 2:1; no $^{125}Te$ NMR signal was observed at room temperature. These NMR data are indicative of stereochemical nonrigidity on the NMR time scale, even down to rather low temperatures. NMR data ($^1H$, $^{13}C$, and $^{31}P$) for the cerium derivative **4** show similar temperature dependent behavior but with resonances that are paramagnetically shifted.

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(5) These materials are of wide interest as a result of their unusual magnetic and electronic properties. See: *Handbook of the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L. R., Eds.; North-Holland: Amsterdam, 1979 and references therein.

(6) We could find only one other example of a crystallographically characterized telluride-tellurolate cluster: $[Fe_4Te_4(TePh)_4]^{3-}$. See: Simon, W.; Wilk, A.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1009.

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(9) All reactions were conducted under an atmosphere of purified argon using dry, oxygen-free solvents.

(10) Selected charactization data. **1**: $^1H$ NMR ($C_7D_8$, 300 MHz, 21 °C) $\delta$ 0.55 (s); $^{13}C\{^1H\}$ NMR ($C_7D_8$, 75.5 MHz, 21 °C) $\delta$ 2.77; $^{125}Te\{^1H\}$ NMR ($C_7D_8$, 94.6 MHz, 21 °C) $\delta$ 1018 (s, $\Delta\nu_{1/2}$ = 57 Hz). **3**: $^1H$ NMR ($C_7D_8$, 400 MHz, 23 °C) $\delta$ 1.46 (s, 8 H), 1.44 (s, 24 H), 0.45 (s, 81 H); $^{13}C\{^1H\}$ NMR ($C_7D_8$, 75.5 MHz, 23 °C) $\delta$ 32.0, 16.1, 1.80; $^{31}P\{^1H\}$ NMR ($C_7D_8$, 162 MHz, 23 °C) $\delta$ -29.4 (s, $\Delta\nu_{1/2}$ = 312 Hz); $^1H$ NMR ($C_7D_8$, 400 MHz, -84 °C) $\delta$ 1.64 (s, 12 H, $\Delta\nu_{1/2}$ = 10 Hz), 1.13 (s, 12 H, $\Delta\nu_{1/2}$ = 10 Hz), 0.68 (s, 27 H, $\Delta\nu_{1/2}$ = 5.7 Hz), 0.52 (s, 54 H, $\Delta\nu_{1/2}$ = 5.2 Hz); $^{13}C\{^1H\}$ NMR ($C_7D_8$, 75.5 MHz, -84 °C) $\delta$ 32.4, 23.4, 16.3 ($\Delta\nu_{1/2}$ = 14 Hz), 14.8, 1.81, 1.44; $^{31}P\{^1H\}$ NMR ($C_7D_8$, 162 MHz, -84 °C) $\delta$ -21.9 (s, 1 P, $\Delta\nu_{1/2}$ = 57 Hz), -34.0 (s, 1 P, $\Delta\nu_{1/2}$ = 49 Hz); $^{125}Te\{^1H\}$ NMR ($C_7D_8$, 94.6 MHz, -70°C) $\delta$ -894 (s, 1 Te, $\Delta\nu_{1/2}$ = 290 Hz), -1074 (s, 1 Te, $\Delta\nu_{1/2}$ = 155 Hz). Anal. Calcd for $C_{39}H_{113}P_4Si_{12}Te_3La$: C, 29.9; H, 7.28. Found: C, 29.9; H, 7.35. **4**: $^1H$ NMR ($C_7D_8$, 400 MHz, 23 °C) $\delta$ 5.87 (s, 8 H, $\Delta\nu_{1/2}$ = 30 Hz), 4.07 (s, 24 H, $\Delta\nu_{1/2}$ = 14 Hz), -0.28 (s, 81 H, $\Delta\nu_{1/2}$ = 32 Hz); $^{13}C\{^1H\}$ NMR ($C_7D_8$, 75.5 MHz, 23 °C) $\delta$ 33.4 ($\Delta\nu_{1/2}$ = 8.5 Hz), 21.4 ($\Delta\nu_{1/2}$ = 12 Hz), 1.44 ($\Delta\nu_{1/2}$ = 3.9 Hz); $^1H$ NMR ($C_7D_8$, 400 MHz, -78 °C) $\delta$ 11.45 (s, 4 H, $\Delta\nu_{1/2}$ = 55 Hz), 8.51 (s, 4 H, $\Delta\nu_{1/2}$ = 59 Hz), 7.65 (s, 12 H, $\Delta\nu_{1/2}$ = 44 Hz), 5.38 (s, 12 H, $\Delta\nu_{1/2}$ = 35 Hz), 1.16 (s, 27 H, $\Delta\nu_{1/2}$ = 9.8 Hz), -2.12 (s, 54 H, $\Delta\nu_{1/2}$ = 8.1 Hz); $^{13}C\{^1H\}$ NMR ($C_7D_8$, 75.5 MHz, -78 °C) $\delta$ 28.2 ($\Delta\nu_{1/2}$ = 31 Hz), 22.0, 3.08 ($\Delta\nu_{1/2}$ = 8.5), -1.17 ($\Delta\nu_{1/2}$ = 4.8 Hz); $^{31}P\{^1H\}$ NMR ($C_7D_8$, 122 MHz, -78 °C) $\delta$ 765.5 ($\Delta\nu_{1/2}$ = 262 Hz), 652.2 ($\Delta\nu_{1/2}$ = 186 Hz). Anal. Calcd for $C_{39}H_{113}P_4Si_{12}Te_3Ce$: C, 29.9; H, 7.27. Found: C, 29.9; H, 7.15. IR data for **5**: 1244 (s), 858 (s), 832 (s), 742 (w), 688 (m), 623 (m) $cm^{-1}$. IR data for **6**: 1306 (w), 1256 (w), 858 (m), 836 (s), 746 (w), 735 (w), 722 (w), 689 (m), 623 (m) $cm^{-1}$.

(11) See supplementary material for further details.

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