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Inorganic Chemistry
Note

Synthesis and Characterization of Novel Mononuclear Cadmium Thiolate Complexes in a Sulfur-Rich Environment

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Introduction

The tendency to bridge metal centers and form extended structures is one of the distinctive traits of metal thiolate coordination chemistry.[1] Cadmium thiolate complexes are no exception, and many intricate cluster and polymeric species, some of which have interesting optoelectronic properties, have been prepared in recent years.[2] In contrast, mononuclear cadmium thiolate complexes, structurally authenticated examples of which include trigonal planar $[Cd(SR)_3]^-$ and tetrahedral $[Cd(SR)_4]^{2-}$ and $Cd(SR)_2L_2$ derivatives,[3] are less common. Such molecular species have been synthesized primarily as model compounds in the study of zinc enzymes[4] because of the favorable spectroscopic (e.g., NMR) properties of cadmium relative to zinc.[5] To prepare well-defined monothiolate complexes of cadmium in a sulfur-rich environment, we decided to use the anionic tris(mercaptoimidazolyl)borate (Tm^R) ligand system, recently introduced[6] as a soft counterpart of the versatile tris(pyrazolyl)borate family of ligands (Figure 1).[7] Several Tm^R ligands have been successfully applied to zinc bioinorganic chemistry,[8] and our own contributions to this area include the syntheses of the new bulky benzyl- and *p*-tolyl-substituted ligands Tm^{Bz} and $Tm^{p\text{-}Tol}$ and their corresponding group 12 metal complexes $(Tm^R)MBr$ (M = Zn, Cd).[9] In particular, we considered that the complex $(Tm^{p\text{-}Tol})CdBr$, because of

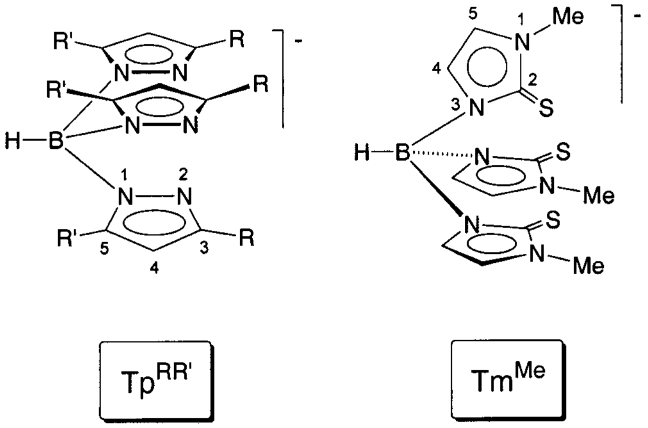

Figure 1. Trofimenko's tris(pyrazolyl)borate ($Tp^{RR'}$) and Reglinski's original tris(2-mercapto-1-methylimidazolyl)borate (Tm^{Me}) ligands.

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its steric bulk, good solubility in common organic solvents, and ease of preparation in excellent yield, would be an ideal starting material for the preparation of the desired mononuclear cadmium thiolate compounds. That turned out to be the case, and we report in this paper the synthesis and characterization of the first series of neutral monothiolate complexes of cadmium of general formula (Tm$^{p\text{-Tol}}$)CdSR, compounds which provide a rare opportunity to compare directly the simultaneous binding of both thione and thiolate donor groups at a single metal center.[10]

Results and Discussion

The cadmium thiolate complexes (Tm$^{p\text{-Tol}}$)CdSR (R = Bz, Ph, *p*-Tol, C_6F_5) were readily prepared by reacting benzene or acetonitrile solutions of (Tm$^{p\text{-Tol}}$)CdBr with equimolar amounts of the corresponding thallium thiolates Tl(SR), as shown in eq 1. The desired products were isolated in very

$$(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdBr} + \mathrm{Tl(SR)} \xrightarrow[-\mathrm{TlBr}]{\mathrm{C_6H_6\ or\ MeCN}} (\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSR} \tag{1}$$

good yield (80−90%) after separating by filtration in each case the insoluble thallous bromide byproduct. While this protocol seems to work well for primary alkyl and aryl thiolates, the corresponding reaction with Tl(SBu^t) failed to give any isolable products. The new cadmium thiolate complexes are all fairly air-stable white solids, only moderately soluble in benzene or toluene but very soluble in more polar solvents such as dichloromethane, chloroform, tetrahydrofuran, acetone, acetonitrile, *N,N′*-dimethylformamide, and dimethyl sulfoxide. They were characterized by a combination of analytical and spectroscopic methods, including elemental analyses (CHN) and IR and NMR spectroscopies. The IR spectra of all three arylthiolate complexes show single $\nu_{\mathrm{B-H}}$ absorptions of medium intensity close to 2404 cm^{-1}, values which are shifted some 30 cm^{-1} to lower frequencies relative to (Tm$^{p\text{-Tol}}$)CdBr and ~54 cm^{-1} lower than the corresponding value seen for the less electron-withdrawing benzylthiolate derivative (Tm$^{p\text{-Tol}}$)CdSBz. ^{1}H and ^{13}C NMR data for the series (Tm$^{p\text{-Tol}}$)CdSR, excluding the thiolate signals, are not only virtually identical to those of (Tm$^{p\text{-Tol}}$)CdBr but also indicative of the magnetic equivalency on the NMR time scale of the three mercaptoimidazolyl groups in the Tm$^{p\text{-Tol}}$ ligands and thus provide evidence for the existence of mononuclear tetrahedral complexes in solution.

Single crystals suitable for an X-ray diffraction study of the phenylthiolate derivative (Tm$^{p\text{-Tol}}$)CdSPh were obtained by slow evaporation at room temperature of a benzene solution of the complex. As shown in Figure 2, the four-coordinate complex exhibits in the solid state a distorted tetrahedral geometry akin to those of (Tm$^{\mathrm{Bz}}$)MBr (M = Zn, Cd)[9] and other complexes of general formula (Tm$^{\mathrm{R}}$)ZnX,[8] with the three mercaptoimidazolyl groups distributed in a propeller-like arrangement around the pseudo-C_3 axis that contains the boron and cadmium atoms. Even though the steric bulk provided by the *p*-tolyl substituents evidently contributes to the stabilization (i.e., monomeric nature) of (Tm$^{p\text{-Tol}}$)CdSPh, the phenylthiolate ligand is still considerably bent at sulfur (Cd−S−C ≈ 96.6°).[11] In addition, whereas the average S_{Tm}−Cd−S_{Tm} bond angle in (Tm$^{p\text{-Tol}}$)CdSPh (97.9°) deviates ~6° further from the ideal tetrahedral angles than do the corresponding values found in either (Tm$^{\mathrm{Bz}}$)CdBr (103.1°) or (Tm$^{\mathrm{Ph}}$)ZnSPh (105.3°), the average S_{Tm}−Cd−SPh angle in (Tm$^{p\text{-Tol}}$)CdSPh (119.3°) is about 5° larger than the S_{Tm}−M−X angles in either (Tm$^{\mathrm{Bz}}$)CdBr or (Tm$^{\mathrm{Ph}}$)ZnSPh. The observation of more distorted structures in the (Tm$^{\mathrm{R}}$)CdX complexes, despite the larger size of cadmium relative to zinc, can be therefore attributed to the geometric constraints of the tridentate ligands, a phenomenon that is also precedented in group 12 metal tris(pyrazolyl)borate chemistry.[12]

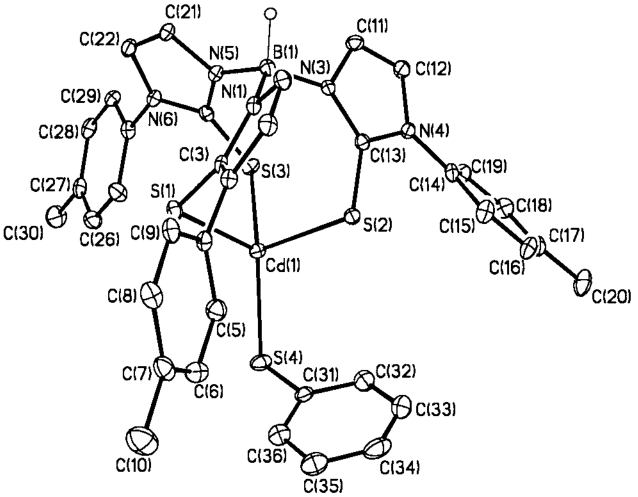

Figure 2. Molecular structure of (Tm$^{p\text{-Tol}}$)CdSPh. Selected bond lengths (Å) and angles (deg): Cd(1)−S(1) 2.529(5), Cd(1)−S(2) 2.477(5), Cd(1)−S(3) 2.516(5), Cd(1)−S(4) 2.573(4); S(1)−Cd(1)−S(2) 96.01(9), S(1)−Cd(1)−S(3) 97.91(15), S(1)−Cd(1)−S(4) 122.21(11), S(2)−Cd(1)−S(3) 99.89(11), S(2)−Cd(1)−S(4) 114.04(15), S(3)−Cd(1)−S(4) 121.78(6), Cd(1)−S(1)−C(3) 101.63(13), Cd(1)−S(2)−C(13) 100.55(18), Cd(1)−S(3)−C(23) 101.01(16), Cd(1)−S(4)−C(31) 96.62(16).

The Cd−S_{Tm} bond distances, in the range 2.477(5)−2.529(5) Å, are slightly shorter than those seen in (Tm$^{\mathrm{Bz}}$)CdBr [2.515(1)−2.569(1) Å], the only other structurally characterized cadmium tris(mercaptoimidazolyl)borate complex that we are aware of.[13] Furthermore, the Cd−SPh bond distance

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(10) The related phenyltris[(*tert*-butylthio)methyl]borate zinc phenylthiolate complex (PhTt$^{\mathrm{tBu}}$)ZnSPh, which contains both thioether and thiolate ligands, has recently been prepared as a model compound for the active center in methionine synthases: Chiou, S.-J.; Innocent, J.; Riordan, C. G.; Lam, K.-C.; Liable-Sands, L.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 4347−4353.

(11) For comparison, the Cd−S−C angles in homoleptic $[\mathrm{Cd(SR)_4}]^{2-}$ complexes are in the range 106−110°, and the Zn−S−C angle in (Tm$^{\mathrm{Ph}}$)ZnSPh is 102.8°. See refs 3d−g and 8b, respectively.

(12) For example, the average N−M−I angles in the iodo complexes (Tp$^{i\mathrm{Pr}_2}$)MI (M = Zn,[12a] Cd[12b]) are 123.2° and 128.0°, respectively. (a) Han, R.; Looney, A.; McNeill, K.; Parkin, G.; Rheingold, A. L.; Haggerty, B. S. *J. Inorg. Biochem.* **1993**, *49*, 105−121. (b) Looney, A.; Saleh, A.; Zhang, Y.; Parkin, G. *Inorg. Chem.* **1994**, *33*, 1158−1164.

(13) The octahedral bis(mercaptoimidazolyl)(pyrazolyl)borate complex Cd(pzBm$^{\mathrm{Me}}$)$_2$ has, in addition to two relatively weak Cd···H−B contacts at ~2.6 Å, four Cd−S bond lengths in the range 2.526(1)−2.572(1) Å. See: Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Hascall, T.; Parkin. G. *Inorg. Chem.* **2000**, *39*, 4240−4243.

[2.573(4) Å] appears to be the longest reported so far for such interactions in cadmium complexes containing terminal thiolate ligands, values which are typically between 2.42 and 2.55 Å.[2,3] All the remaining interatomic distances (i.e., B—N, S—C, C—N, and C—C) are within normal ranges.

Conclusions

In summary, four rare examples of mononuclear cadmium monothiolate complexes $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSR}$ (R = Bz, Ph, *p*-Tol, C_6F_5) have been readily prepared and fully characterized. The X-ray structure of the phenylthiolate derivative revealed that all the Cd—S bond distances and Cd—S—C bond angles are fairly similar, an observation that lends support to the notion that the thione groups in Tm^{R} ligands can be regarded as "masked" thiolate groups. We are currently exploring the synthesis and reactivity (e.g., protonation and alkylation reactions) of these and additional sulfur-rich complexes $(\mathrm{Tm}^{\mathrm{R}})\mathrm{MSR}'$ (M = Cd, Hg), studies which are primarily aimed at modeling the biologically relevant scission of cysteine thiolate residues and concomitant formation of thioethers or thiols in a variety of zinc metalloenzymes.[8b,14]

Experimental Section

General Considerations. All reactions were performed under dry, oxygen-free nitrogen in an Innovative Technology System One-M-DC glovebox or under argon using a combination of high-vacuum and Schlenk techniques.[15] Solvents were purified and degassed by standard procedures, and all commercially available reagents were used as received. Whereas the complex $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdBr}$ was prepared as published,[9] the thallium thiolates Tl(SR) were obtained using a modification of the procedure reported for the synthesis of various thallium phenoxides[16] by reacting Tl(OEt) with a slight excess of the corresponding thiols in pentane; the bright yellow (R = Bz, Ph, *p*-Tol) or off-white (R = C_6F_5) solids were isolated in 90−95% yield, dried in vacuo for at least 3 h, and stored in the glovebox. ^{1}H and ^{13}C NMR spectra were obtained on General Electric QE 300 or Varian Gemini (300 MHz) FT spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$ ppm) and were referenced internally with respect to the solvent resonances (^{1}H, δ 5.32 for $CDHCl_2$; ^{13}C, δ 53.8 for CD_2Cl_2); coupling constants are given in hertz. IR spectra were recorded as KBr pellets on a Bio-Rad 175C FT spectrophotometer and are reported in reciprocal centimeters. Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

Synthesis of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSBz}$. A yellow suspension of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdBr}$ (0.23 g, 0.30 mmol) and $Tl(SCH_2C_6H_5)$ (0.10 g, 0.31 mmol) in benzene (25 mL) was stirred for 2 h, and the resulting brownish yellow suspension was filtered. The solvent was removed under reduced pressure from the colorless filtrate to give a white solid, which was washed with pentane (2 × 5 mL) and dried in vacuo for 1 h (0.20 g, 82%). Mp = 160 °C (dec). NMR data (in CD_2Cl_2): ^{1}H d 2.39 (s, 9 H, $NC_6H_4CH_3$), 3.59 (br s, 2 H, CH_2), 6.80−7.35 (m, 23 H, $NC_6H_4CH_3$ + imidazole *H* + $SCH_2C_6H_5$), B*H* not located; ^{13}C d 21.3 (q, $^1J_{\mathrm{C-H}} = 127$, 3 C, $C_6H_4CH_3$), 31.7 (t, $^1J_{\mathrm{C-H}} = 155$, 1 C, CH_2), 121.2 (d, $^1J_{\mathrm{C-H}} = 199$, 3 C, imidazole *C*), 124.6 (d, $^1J_{\mathrm{C-H}} = 201$, 3 C, imidazole *C*), 126.9 (d, $^1J_{\mathrm{C-H}} = 160$, 1 C, C_p in $SCH_2C_6H_5$), 127.1 (d, $^1J_{\mathrm{C-H}} = 157$, 6 C, C_o or C_m in *p*-Tol), 128.3 (d, $^1J_{\mathrm{C-H}} = 160$, 2 C, C_o or C_m in $SCH_2C_6H_5$), 128.7 (d, $^1J_{\mathrm{C-H}} = 160$, 2 C, C_o or C_m in $SCH_2C_6H_5$), 129.9 (d, $^1J_{\mathrm{C-H}} = 160$, 6 C, C_o or C_m in *p*-Tol), 135.5 (s, 3 C, C_p in *p*-Tol), 138.9 (s, 3 C, C_{ipso} in *p*-Tol), 158.7 (s, 3 C, *C*=S). IR data: 2458 ($\nu_{\mathrm{B-H}}$). Anal. Calcd for $C_{37}H_{35}BCdN_6S_4$: C, 54.5; H, 4.3; N, 10.3. Found: C, 54.4; H, 4.5; N, 10.3%.

Synthesis of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSPh}$. A yellow suspension of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdBr}$ (0.25 g, 0.32 mmol) and $Tl(SC_6H_5)$ (0.10 g, 0.32 mmol) in benzene (20 mL) was stirred for 2 h, and the resulting grayish yellow suspension was filtered. The solvent was removed under reduced pressure from the colorless filtrate to give a white solid, which was washed with pentane (2 × 8 mL) and dried in vacuo for 2 h (0.23 g, 90%). Mp = 232 °C (dec). NMR data (in CD_2Cl_2): ^{1}H d 2.40 (s, 9 H, $NC_6H_4CH_3$), 6.84−7.32 (m, 23 H, $NC_6H_4CH_3$ + imidazole *H* + SC_6H_5), B*H* not located; ^{13}C d 21.3 (q, $^1J_{\mathrm{C-H}} = 127$, 3 C, $C_6H_4CH_3$), 121.4 (d, $^1J_{\mathrm{C-H}} = 198$, 3 C, imidazole *C*), 122.4 (d, $^1J_{\mathrm{C-H}} = 162$, 1 C, C_p in SC_6H_5), 124.8 (d, $^1J_{\mathrm{C-H}} = 195$, 3 C, imidazole *C*), 127.1 (d, $^1J_{\mathrm{C-H}} = 163$, 6 C, C_o or C_m in *p*-Tol), 128.1 (d, $^1J_{\mathrm{C-H}} = 153$, 2 C, C_o or C_m in SC_6H_5), 130.0 (d, $^1J_{\mathrm{C-H}} = 160$, 6 C, C_o or C_m in *p*-Tol), 133.1 (d, $^1J_{\mathrm{C-H}} = 157$, 2 C, C_o or C_m in SC_6H_5), 135.4 (s, 3 C, C_p in *p*-Tol), 139.6 (s, 3 C, C_{ipso} in *p*-Tol), 143.3 (s, 1 C, C_{ipso} in SC_6H_5), 158.3 (s, 3 C, *C*=S). IR data: 2405 ($\nu_{\mathrm{B-H}}$). Anal. Calcd for $C_{36}H_{33}BCdN_6S_4$: C, 54.0; H, 4.2; N, 10.5. Found: C, 54.1; H, 4.1; N, 10.4%.

Synthesis of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdS}\text{-}p\text{-}C_6H_4Me$. A yellow suspension of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdBr}$ (0.28 g, 0.36 mmol) and Tl(S-*p*-C_6H_4Me) (0.12 g, 0.36 mmol) in acetonitrile (25 mL) was stirred for 2 h, and the resulting beige suspension was filtered. Concentration of the colorless filtrate under reduced pressure to ∼3 mL and addition of diethyl ether (20 mL) resulted in the separation of a white solid, which was isolated by decantation, washed with diethyl ether (2 × 10 mL), and dried in vacuo for 1 h (0.25 g, 85%). Mp = 242 °C (dec). NMR data (in CD_2Cl_2): ^{1}H d 2.21 (s, 3 H, $SC_6H_4CH_3$), 2.41 (s, 9 H, $NC_6H_4CH_3$), 6.66−7.30 (m, 22 H, $NC_6H_4CH_3$ + imidazole H + $SC_6H_4CH_3$), B*H* not located; ^{13}C d 20.9 (q, $^1J_{\mathrm{C-H}} = 126$, 1 C, $SC_6H_4CH_3$), 21.3 (q, $^1J_{\mathrm{C-H}} = 127$, 3 C, $NC_6H_4CH_3$), 121.4 (d, $^1J_{\mathrm{C-H}} = 198$, 3 C, imidazole *C*), 124.8 (d, $^1J_{\mathrm{C-H}} = 199$, 3 C, imidazole *C*), 127.1 (d, $^1J_{\mathrm{C-H}} = 163$, 6 C, C_o or C_m in $NC_6H_4CH_3$), 128.9 (d, $^1J_{\mathrm{C-H}} = 156$, 2 C, C_o or C_m in $SC_6H_4CH_3$), 130.0 (d, $^1J_{\mathrm{C-H}} = 160$, 6 C, C_o or C_m in $NC_6H_4CH_3$), 133.1 (d, $^1J_{\mathrm{C-H}} = 161$, 2 C, C_o or C_m in $SC_6H_4CH_3$), 135.5 (s, 3 C, C_p in $NC_6H_4CH_3$), 139.6 (s, 3 C, C_{ipso} in $NC_6H_4CH_3$), 158.4 (s, 3 C, *C*=S), C_{ipso} and C_p in $SC_6H_4CH_3$ not located. IR data: 2405 ($\nu_{\mathrm{B-H}}$). Anal. Calcd for $C_{37}H_{35}BCdN_6S_4$: C, 54.5; H, 4.3; N, 10.3. Found: C, 54.3; H, 4.4; N, 10.1%.

Synthesis of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSC_6F_5}$. A white suspension of $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdBr}$ (0.20 g, 0.26 mmol) and $Tl(SC_6F_5)$ (0.11 g, 0.27 mmol) in benzene (10 mL) was stirred for 1.5 h, and the resulting yellowish suspension was filtered. The solvent was removed from the colorless filtrate under reduced pressure to give a white solid, which was washed with pentane (6 × 10 mL) and dried in vacuo for 4 h (0.20 g, 86%). Mp = 222 °C (dec). NMR data (in CD_2Cl_2): ^{1}H d 2.42 (s, 9 H, $NC_6H_4CH_3$), 7.00−7.33 (m, 18 H, $NC_6H_4CH_3$ + imidazole *H*), B*H* not located; ^{13}C d 21.3 (q, $^1J_{\mathrm{C-H}} = 127$, 3 C, $C_6H_4CH_3$), 121.5 (d, $^1J_{\mathrm{C-H}} = 198$, 3 C, imidazole *C*), 124.9 (d,

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Table 1. Crystallographic Data for (Tm$^{p\text{-Tol}}$)CdSPh

formula	$C_{36}H_{33}BCdN_6S_4$
fw	801.13
cryst color, habit	colorless block
cryst syst	monoclinic
space group	$P2_1/n$ (no. 14)
T, K	173(2)
a, Å	15.01(4)
b, Å	15.32(4)
c, Å	15.18(4)
β, deg	90.00(5)
V, Å^3	3489(14)
Z	4
D_c, g cm^{-3}	1.525
μ (Mo Kα), cm^{-1}	9.02
θ_{max}, deg	29.90
no. of data	8055
no. of parameters	441
R1/wR2 [$I > 2\sigma(I)$] [a]	0.0595/0.1003
R1/wR2 (all data) [a]	0.0719/0.1025

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

$^1J_{C-H}$ = 190, 3 C, imidazole *C*), 127.1 (d, $^1J_{C-H}$ = 163, 6 C, C_o or C_m in *p*-Tol), 130.0 (d, $^1J_{C-H}$ = 160, 6 C, C_o or C_m in *p*-Tol), 135.3 (s, 3 C, C_p in *p*-Tol), 139.8 (s, 3 C, C_{ipso} in *p*-Tol), 147.5 (d, $^1J_{C-F}$ = 232, 1 C, C_{ipso} in SC_6F_5), 157.9 (s, 3 C, *C*=S); C_o, C_m, and C_p in SC_6F_5 not located. IR data: 2403 (ν_{B-H}). Anal. Calcd for $C_{36}H_{28}BCdF_5N_6S_4$: C, 48.5; H, 3.2; N, 9.4. Found: C, 48.6; H, 3.3; N, 9.3%.

X-ray Structure Determination. A summary of crystal data collection and refinement parameters for (Tm$^{p\text{-Tol}}$)CdSPh is given in Table 1. A crystal suitable for data collection was selected and mounted with epoxy cement on the tip of a fine glass fiber and immediately placed in the cold nitrogen stream. A data set was collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector using Mo Kα radiation (λ = 0.710 73 Å). Despite the appearance of higher symmetry, the monoclinic space group $P2_1/n$ was chosen on the basis of photographic and intensity data. Solution in the reported space group yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library.[17]

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of (Tm$^{p\text{-Tol}}$)CdSPh. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Sheldrick, G. M. Siemens XRD: Madison, WI.