Synthesis and Structures of Cadmium Carboxylate and Thiocarboxylate Compounds with a Sulfur-Rich Coordination Environment: Carboxylate Exchange Kinetics Involving Tris(2-mercapto-1-t-butyldimidazolyl)hydroborato Cadmium Complexes, [TmBu\textsuperscript{1}]Cd(O\textsubscript{2}CR)

Ava Kreider-Mueller, Patrick J. Quinlivan, Jonathan S. Owen,* and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027, United States

Supporting Information

ABSTRACT: A series of cadmium carboxylate compounds in a sulfur-rich environment provided by the tris(2-tert-butyldimercaptoimidazolyl)hydroborato ligand, namely, [TmBu\textsuperscript{1}]CdO\textsubscript{2}CR, has been synthesized via the reactions of the cadmium methyl derivative [TmBu\textsuperscript{1}]CdMe with RCO\textsubscript{2}H. Such compounds mimic aspects of cadmium-substituted zinc enzymes and also the surface atoms of cadmium chalcogenide crystals, and have therefore been employed to model relevant ligand exchange processes. Significantly, both \textsuperscript{1}H and \textsuperscript{19}F NMR spectroscopy demonstrate that the exchange of carboxylate groups between [TmBu\textsuperscript{1}]Cd(κ\textsuperscript{2}-O\textsubscript{2}CR) and the carboxylic acid RCO\textsubscript{2}H is facile on the NMR time scale, even at low temperature. Analysis of the rate of exchange as a function of concentration of RCO\textsubscript{2}H indicates that reaction occurs via an associative rather than dissociative pathway. In addition to carboxylate compounds, the thiocarboxylate derivative [TmBu\textsuperscript{1}]Cd(κ\textsuperscript{2}-SC(O)Ph) has also been synthesized via the reaction of [TmBu\textsuperscript{1}]CdMe with thiobenzoic acid. The molecular structure of [TmBu\textsuperscript{1}]Cd(κ\textsuperscript{2}-SC(O)Ph) has been determined by X-ray diffraction, and an interesting feature is that, in contrast to the carboxylate derivatives [TmBu\textsuperscript{1}]Cd(κ\textsuperscript{2}-O\textsubscript{2}CR), the thiocarboxylate ligand binds in a κ\textsuperscript{1} manner via only the sulfur atom.

INTRODUCTION

The investigation of cadmium in sulfur-rich coordination environments is of relevance to areas as diverse as cadmium-substituted zinc enzymes\textsuperscript{1} and cadmium chalcogenide nanocrystals. With regards to the latter, the surface functionalization of metal chalcogenide nanocrystals via ligand exchange\textsuperscript{2} is of considerable importance to their use in applications such as optoelectronic devices and biological imaging.\textsuperscript{3} Specifically, the coordination of ligands to nanocrystal surfaces has profound effects on their electronic properties including photoluminescence quantum yield,\textsuperscript{4} thermal relaxation of excited carriers,\textsuperscript{5} and trapping of electrical carriers.\textsuperscript{6} Since carboxylic acids are commonly used as surfactants in the synthesis of cadmium-chalcogenide nanocrystals,\textsuperscript{7} the nature of the interaction of the carboxyl group with the nanocrystal surface and the ability to undergo exchange reactions is of considerable importance. In this regard, recent studies concerned with CdSe quantum dots employing oleic acid as the surfactant have shown that (i) the capping ligands are oleate rather than oleic acid, and (ii) the oleate ligands undergo self-exchange with excess oleic acid.\textsuperscript{7c} The complexity of nanocrystal surfaces, however, has limited quantitative studies of ligand exchange kinetics.\textsuperscript{8,9} Therefore, to provide data of relevance to carboxylate exchange on nanocrystal surfaces, and also the lability of cadmium in sulfur-rich active sites of enzymes, we sought to investigate systems that are more amenable to mechanistic investigations, namely, those of small molecules that feature cadmium in a sulfur-rich environment. In addition, since thiocarboxylates are precursors to cadmium sulfide materials,\textsuperscript{10,11} we have also investigated a corresponding thiobenzoate derivative.

RESULTS AND DISCUSSION

Tris(2-mercaptoimidazolyl)hydroborato ligands, [Tm\textsuperscript{8}] (Figure 1),\textsuperscript{12–16} have recently emerged as a popular class of L\textsubscript{X}\textsuperscript{17} [S\textsubscript{3}] donors that provide a sulfur-rich coordination environment. In this regard, we have previously used the t-butyl derivative [TmBu\textsuperscript{3}] to synthesize a variety of zinc,\textsuperscript{18,19} cadmium,\textsuperscript{20,21} and mercury\textsuperscript{22} complexes to investigate aspects of the chemistry of these metals in biological systems, which ranges from the beneficial use of zinc in enzymes to mechanisms of mercury detoxification. An understanding of the kinetics and thermodynamics associated with ligand coordination and exchange involving these metal sites is paramount for fully understanding the chemistry of these systems. Likewise, recognizing that the [S\textsubscript{3}] coordination environment of cadmium in [([Tm\textsuperscript{8}]Cd) compounds also resembles the surface metal atoms of the [111] and [001] facets of cadmium chalcogenides...
with, respectively, zinc blende and wurtzite structures,
we rationalized that this class of compounds can also be employed
to model ligand exchange processes on cadmium chalcogenide
nanocrystal surfaces. Therefore, we have (i) synthesized a series
of cadmium carboxylate compounds \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\) and (ii)
investigated the dynamics of carboxylate exchange.

1. Synthesis and Structural Characterization of Cadmium
Carboxylate Compounds \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\).

Although a variety of \([\text{TmBu}^\text{Bu}]\text{CdX}\) complexes are known,
there are no reports of structurally characterized carboxylate derivatives.\(^{25}\)
A series of such compounds, namely, \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\) \([R = \text{C}_6\text{H}_4\text{-4-Me}, \text{C}_6\text{H}_4\text{-4-F}, \text{C}_6\text{H}_4\text{-3,5-F}_2, \text{C}_6\text{H}_4\text{-2,6-F}_2, 9\text{-anthryl (9-An), n-C}_1\text{H}_{17}, \text{and C}_3\text{H}_6\text{Ph}]\), may, nevertheless, be
synthesized via the reactions of \([\text{TmBu}^\text{Bu}]\text{CdMe}_2\) with \text{RCO}_2\text{H}
(Scheme 1). Furthermore, \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\) may also be
obtained via reactions of \([\text{TmBu}^\text{Bu}]\text{Na}\)\(^{15,26}\) with cadmium
carboxylate compounds as generated by treatment of \text{RCO}_2\text{H}
with \text{Me}_2\text{Cd} (Scheme 2).\(^{7,7}\)

The molecular structures \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\) \([R = \text{C}_6\text{H}_4\text{-4-Me}, \text{C}_6\text{H}_4\text{-4-F}, \text{C}_6\text{H}_4\text{-3,5-F}_2, \text{C}_6\text{H}_4\text{-2,6-F}_2, 9\text{-anthryl}, \text{C}_3\text{H}_6\text{Ph}]\) have been determined by X-ray diffraction, as illustrated in
Figures 2–7. Selected bond lengths and angles are summarized
in Tables 1 and 2. Carboxylate ligands can bind to a single metal
center via bidentate, anisobidentate, or unidentate coordination
modes that, by analogy to nitrate ligands,\(^{28–30}\) can be identi-
fiied by the magnitude of the difference in \text{M–O} bond lengths \((\Delta d)\)
and \text{M–O–C} bond angles \((\Delta \theta)\), as summarized in Table 3.
Adopting this classification, the carboxylate coordination modes
in \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\) are identified as bidentate since both
(i) the differences in \text{Cd–O} bond lengths \((0.02–0.25 \text{ Å})\) are less
than 0.3 Å and (ii) the differences in \text{O–Cd–C} bond angles
\((0.7°–11.5°)\) are less than 14° (Table 4). As such, the cadmium
centers of each of the \([\text{TmBu}^\text{Bu}]\text{Cd(O}_2\text{CR})\) complexes are
classified as five-coordinate. Analysis of the compounds listed
in the Cambridge Structural Database indicates that the majority

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**Scheme 1**

**Scheme 2**
of nonbridging cadmium benzoate compounds are also bidentate (Figures 8 and 9). For example, 66.8% of the compounds have $\Delta d$ values $\leq 0.3 \, \text{Å}$.\textsuperscript{31} Despite the overall similarity in the structures of $\left[\text{TmBu}^+\right]\text{CdO}_2\text{C(C}_6\text{H}_4\text{-4-Me)}$, there are subtle differences in the cadmium coordination geometries. For example, the $\tau_5$ five-coordinate geometry indices\textsuperscript{32} of $\left[\text{TmBu}^+\right]\text{CdO}_2\text{C(O}_2\text{CR)}$ range from 0.10 ($R = \text{C}_6\text{H}_3\text{-2,6-F}_2$) to 0.45 ($R = \text{C}_3\text{H}_6\text{Ph}$), as summarized in Table 4. In view of the fact that an idealized trigonal bipyramid has a $\tau_5$ index of 1.00, while an idealized square pyramid has a $\tau_5$ index of 0.00, it is evident that there is a transition from a square pyramidal geometry to a structure that is midway between these idealized geometries. Interestingly, the structural variation of the cadmium center is linked to the bidenticity of the carboxylate ligand, as
illustrated by the correlation between the \( \tau_5 \) index and \( \Delta d \) (Figure 11), although it should be noted that there is some scatter in the data. Thus, the transition from a square pyramidal geometry towards a trigonal bipyramidal geometry is accompanied by a general increase in the asymmetry of the carboxylate ligand.

Another noteworthy feature of the arylcarboxylate compounds pertains to the torsion angle between the aryl and carboxylate groups. Specifically, the torsion angle between these groups (Table 2) falls into two classes, i.e., those in which the two groups are close to coplanar (\( \leq 15^\circ \)) and those in which they are closer to orthogonal (\( \geq 66^\circ \)). As would be expected, these torsion angles are dictated by the presence of ortho substituents, such that the two compounds with largest torsion angles are \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(\text{C}_6\text{H}_4-2,6-\text{F}_2)\) and \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(9-\text{An})\), as illustrated in Figures 5 and 6. These torsion angles, however, have little influence on the bidenticity of the carboxylate ligand.

Metal carboxylate \( \nu(\text{CO}_2)_{\text{asym}} \) and \( \nu(\text{CO}_2)_{\text{sym}} \) IR absorptions can be used, in principle, to differentiate between unidentate

![Table 1. Selected Bond Lengths for \([\text{TmBut}^{\text{Bu}}]\text{Cd}(\kappa^2-\text{O}_2\text{CR})\)]

| compound                  | d(Cd−S_{S1}), Å | d(Cd−S_{S2}), Å | d(Cd−S_{S3}), Å | d(Cd−O_{X1}), Å | d(Cd−O_{X2}), Å |
|---------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(\text{C}_6\text{H}_4-4-\text{Me})\) | 2.5225(6)       | 2.5503(7)       | 2.5414(7)       | 2.5544(7)       | 2.5870(6)       |
| \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(\text{C}_6\text{H}_4-4-F)\) | 2.5436(6)       | 2.5442(7)       | 2.5609(6)       | 2.2782(17)      | 2.4601(17)      |
| \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(\text{C}_6\text{H}_4-3,5-\text{F}_2)\) | 2.5333(4)       | 2.5351(4)       | 2.5728(5)       | 2.2595(13)      | 2.5069(14)      |
| \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(\text{C}_6\text{H}_4-2,6-\text{F}_2)\) | 2.5321(10)      | 2.5450(9)       | 2.5521(10)      | 2.351(3)        | 2.371(3)        |
| \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(9-\text{An})\) | 2.5226(9)       | 2.5504(9)       | 2.5661(9)       | 2.266(2)        | 2.465(2)        |
| \([\text{TmBut}^{\text{Bu}}]\text{CdO}_2\text{C}(\text{C}_3\text{H}_6\text{Ph})\) | 2.5179(12)      | 2.5394(13)      | 2.6095(13)      | 2.244(4)        | 2.447(4)        |

![Table 2. Selected Bond Angle Data for \([\text{TmBut}^{\text{Bu}}]\text{Cd(O}_2\text{CR})\)]

| coordination mode     | \( \Delta d \), Å | \( \Delta \theta \),° |
|-----------------------|-------------------|------------------------|
| unidentate            | >0.6              | >28                    |
| anisobidentate        | 0.3−0.6           | 14−28                  |
| bidentate             | <0.3              | <14                    |

\( \Delta d = d(\text{Cd−O}_{2X2}) − d(\text{Cd−O}_{2X1}) \)

\( \Delta \theta = \theta(\text{Cd−O}_{2X1}−\text{C}) − \theta(\text{Cd−O}_{2X2}−\text{C}) \)

\( \tau_5 = (\beta − \alpha)/60 \), where \( \beta − \alpha \) is the difference between the two largest angles.

![Table 3. Criteria for Assigning Carboxylate Coordination Modes]

| coordination mode     | \( \Delta d \), Å | \( \Delta \theta \),° |
|-----------------------|-------------------|------------------------|
| unidentate            | >0.6              | >28                    |
| anisobidentate        | 0.3−0.6           | 14−28                  |
| bidentate             | <0.3              | <14                    |

\( \Delta d = d(\text{Cd−O}_{2X2}) − d(\text{Cd−O}_{2X1}) \)

\( \Delta \theta = \theta(\text{Cd−O}_{2X1}−\text{C}) − \theta(\text{Cd−O}_{2X2}−\text{C}) \)

\( \tau_5 = (\beta − \alpha)/60 \), where \( \beta − \alpha \) is the difference between the two largest angles.

![Figure 8. Distribution of \( \Delta d \), i.e., \( d(\text{Cd−O}_{2X2}) − d(\text{Cd−O}_{2X1}) \), values for nonbridging benzoate compounds listed in the Cambridge Structural Database. The values on the x-axis indicate the maximum value of \( \Delta d \) in the bin.](image-url)
and bidentate coordination modes, although discrimination at the borderlines is not straightforward. In this regard, although $\nu(CO)$ absorptions for $[\text{TmBu}^+]\text{Cd}(\kappa^2\text{O}_2\text{CR})$ cannot be readily identified due to interference by other absorptions, $\nu(CO)_{sym}$ can be identified in the region of 1535–1567 cm$^{-1}$. These values are, nevertheless, consistent with the bidentate coordination modes observed by X-ray diffraction. For example, bidentate coordination modes are usually characterized by $\nu(CO)_{sym}$ values that are typically less than 1575 cm$^{-1}$.30

2. Synthesis and Structural Characterization of a Cadmium Thiobenzoate Complex, $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$. Similar to the carboxylate compounds, the thiobenzoate complex $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$ can be synthesized by treatment of $[\text{TmBu}^+]\text{CdMe}$ with thiobenzoic acid (Scheme 1). $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$ is characterized by an absorption at 1550 cm$^{-1}$ in the IR spectrum that may be assigned to $\nu(CO)$, which is in the range observed for other thiocarboxylate compounds.33–36 For example, $\text{Cd}[\text{SC(O)}\text{Ph}]_2$ is characterized by absorptions at 1580 and 1597 cm$^{-1}$.33

The molecular structure of $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$ has been determined by X-ray diffraction as illustrated in Figure 10.

As with carboxylate compounds, thiocarboxylate ligands can adopt a variety of coordination modes, including (i) unidentate and bidentate coordination to a single metal and (ii) several bridging modes.36,37 In this regard, with respect to coordination of the thiobenzoate ligand, the $\text{Cd}–\text{O}$ interaction (2.982 Å) is substantially longer than the $\text{Cd}–\text{S}$ bond (2.478 Å).38 Thus, whereas the carboxylate ligands in $[\text{TmBu}^+]\text{Cd}[\kappa^2\text{O}_2\text{CR}]$ coordinate in a bidentate manner, it is evident that the thiobenzoate ligand in $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$ coordinates in a S-bound unidentate fashion. As such, the cadmium center adopts a distorted tetrahedral geometry with a $\tau$ value of 0.39.

In accord with the X-type41 nature of the $\text{Cd}–\text{SC(O)}\text{Ph}$ interaction in $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$, the $\text{Cd}–\text{S}$ bond involving the thiobenzoate ligand (2.478 Å) is shorter than the average value for those involving the $\text{L}_2^1\ X^1[\text{TmBu}^+]$ ligand (2.53–2.59 Å, average = 2.56 Å). A similar trend is also observed for $[\text{TmBu}^+]\text{CdSPh}$, in which the $\text{Cd}–\text{SPh}$ bond (2.4595(7)) is shorter than the average $\text{Cd}–\text{S}$ bond for the $[\text{TmBu}^+]$ ligand (2.565 Å).39

Further comparison of the denticity of the thiobenzoate ligand with other compounds requires consideration of the different covalent radii of oxygen and sulfur. Specifically, whereas the denticity of a carboxylate ligand can be simply ascertained by evaluating the difference in the two $\text{M}–\text{O}$ bond lengths ($\Delta d$), the evaluation of the coordination mode of a thiocarboxylate ligand requires the different covalent radii of oxygen and sulfur to be taken into account when employing the corresponding $\Delta d_{\text{S}–\text{O}}$ values, as defined by $d(\text{Cd}–\text{S}) – d(\text{Cd}–\text{O})$. Thus, on the basis of the covalent radius of sulfur (1.05 Å) being 0.39 Å larger than that of oxygen (0.66 Å), $\Delta d_{\text{S}–\text{O}}$ values less than 0.39 Å can be considered to be indicative of primary coordination via sulfur. Correspondingly, $\Delta d_{\text{S}–\text{O}}$ values greater than 0.39 Å are indicative of primary coordination via oxygen, while a value of 0.39 Å may be classified as a “symmetric” thiocarboxylate complex. Adopting the $\Delta d$ value of 0.3 Å (Table 3) employed in the classification of nitrate and carboxylate ligands as an upper limit for bidentate coordination of these O$_2$ donor ligands, a $\Delta d_{\text{S}–\text{O}}$ value of 0.69 Å (i.e., 0.39 Å + 0.30 Å) may be established as an upper limit for bidentate thiocarboxylate coordination, in which the primary

Figure 9. Distribution of $\Delta \theta$ values, i.e., (Cd–O$_1$–C) – (Cd–O$_2$–C), for nonbridging benzoate compounds listed in the Cambridge Structural Database. The values on the x-axis indicate the maximum value of $\Delta \theta$ in the bin.

Figure 10. Molecular structure of $[\text{TmBu}^+]\text{Cd}[\kappa^1\text{SC(O)}\text{Ph}]$. DOI: 10.1021/acs.inorgchem.5b00017
coordination is via oxygen. Correspondingly, a lower limit for bidentate thiocarboxylate coordination corresponds to a \( \Delta d_{\text{S-O}} \) value of 0.09 Å (i.e., 0.39 Å – 0.30 Å), in which the primary coordination is via sulfur. Thus, bidentate thiocarboxylate coordination can be identified by values of \( \Delta d_{\text{S-O}} \) in the range 0.09–0.69 Å. Similarly, adopting the value of 0.6 Å to differentiate between symmetric bidentate and unidentate coordination modes of carboxylate ligands (Table 3), S-bound unidentate ligands can be classified by values of \( \Delta d_{\text{S-O}} < -0.21 \) Å (i.e., 0.39 Å – 0.60 Å), while O-bound unidentate ligands can be classified by values of \( \Delta d_{\text{S-O}} > 0.99 \) Å (i.e., 0.39 Å + 0.60 Å), with anisobidentate variants being characterized by intermediate values (Table 5). On this basis, the \( \Delta d_{\text{S-O}} \) value of –0.50 Å for \([\text{TmBu}]^+{\text{Cd}}[\kappa^1\text{SC(O)Ph}]^{-}\) is clearly in accord with the aforementioned unidentate S-bound thiobenzoate classification.

To provide additional context for the \( \Delta d_{\text{S-O}} \) value of –0.50 Å for \([\text{TmBu}]^+{\text{Cd}}[\kappa^1\text{SC(O)Ph}]^{-}\), the distribution of values for non-bridging metal thiocarboxylate compounds listed in the Cambridge Structural Database has been analyzed, as summarized in Figures 12–14. Examination of the distribution for all metal thiocarboxylate compounds (Table 6 and Figure 12) indicates that most popular category is S-unidentate (78.8%), followed by S-anisobidentate (10.8%) and bidentate (10.3%). Significantly, there is only one metal thiocarboxylate compound that exhibits an O-unidentate coordination mode, namely, (15-crown-5)-Ca\([\kappa^1\text{SC(O)Me}][\kappa^1\text{OC(S)Me}])^{-}\), as illustrated by a value of \( \Delta d_{\text{S-O}} = 2.44 \) Å.45 Cadmium exhibits a distribution that is narrower than observed for all metals (Figure 13), and there is a shift from a preference for S-unidentate coordination for all metals towards S-anisobidentate coordination for cadmium: S-unidentate (11.5%), S-anisobidentate (54.1%), and bidentate (34.4%). A similar distribution is observed for cadmium thiobenzoate compounds, with S-anisobidentate (64.7%) being the most common (Figure 14). Of particular note, none of the previously reported cadmium thiobenzoate compounds possess as much unidentate character as that of \([\text{TmBu}]^+{\text{Cd}}[\kappa^1\text{SC(O)Ph}]^{-}\), for which \( \Delta d_{\text{S-O}} \) is –0.50 Å. For example, the closest value to that for \([\text{TmBu}]^+{\text{Cd}}[\kappa^1\text{SC(O)Ph}]^{-}\) is for polymeric \({\text{Cd}}[\kappa^1\text{SC(O)Ph}]-\mu-4,4′\text{-bipyridine})_n\), for which \( \Delta d_{\text{S-O}} \) is –0.25 Å.46 Furthermore, only one metal thiocarboxylate, namely, the mercury

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**Table 5. Classification of Thiocarboxylate Coordination Modes**

| coordination mode | \( \Delta d_{\text{S-O}}, \text{Å} \) |
|-------------------|---------------------------------|
| S–unidentate       | < –0.21                         |
| S–anisobidentate  | –0.21 – 0.09                    |
| bidentate         | 0.09 – 0.69                     |
| O–anisobidentate  | 0.69 – 0.99                     |
| O–unidentate      | > 0.99                          |

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**Figure 12.** Distribution of metal thiocarboxylate compounds according to the value of \( \Delta d_{\text{S-O}} \) as defined by \( d(\text{M–S}) – d(\text{M–O}) \). The values on the x-axis indicate the maximum value of \( \Delta d_{\text{S-O}} \) in the bin. Note that there is only one example of O–unidentate coordination, which is marked with an asterisk.
compound [Me₄N][Hg(SC(O)Ph)₃] has a more negative $\Delta d_{S-O}$ value ($\sim$0.62 Å), i.e., a greater degree of S-unidenticity, than that for [TmBu₃]Cd[k¹-SC(O)Ph].

While the adoption of S-unidentate, rather than O-unidentate, coordination of thiobenzoate to cadmium in [TmBu₃]Cd[k¹-SC(O)Ph] may be attributed to hard–soft principles and the thiophilicity of cadmium, the observation that there are no examples of well-defined O-unidentate compounds listed in the Cambridge Structural Database for any metal suggests that this view is overly simplistic. An alternative simple explanation to rationalize both (i) S-unidentate coordination in [TmBu³]-Cd[k¹-SC(O)Ph] and (ii) the general absence of O-unidentate coordination in the literature, is to recognize that S-unidentate coordination retains a C\(\equiv\)O double bond, whereas O-unidentate coordination retains a C\(\equiv\)S double bond. Thus, in view of the fact that the combination of a C\(\equiv\)O double bond and a C–S single bond is ca. 30 kcal mol\(^{-1}\) thermodynamically more favorable than a combination comprising a C\(\equiv\)S double bond and a C–O single bond, it is evident that coordination of a metal to S would be preferred unless the X–O bond were to be more than 30 kcal mol\(^{-1}\) stronger than the corresponding X–S bond.

In support of this suggestion, it is pertinent to note that thiocarboxylic acids exist as a tautomeric mix of thiol and thioxo forms RC(O)SH and RC(S)OH, of which the former are the

### Table 6. Distribution of Metal Thiocarboxylate According to the Value of $\Delta d_{S-O}$, as Defined by $d(M-S) - d(M-O)$

| Coordination Mode | M[SC(O)R] (%) | Cd[SC(O)R] (%) | Cd[SC(O)Ph] (%) |
|------------------|---------------|----------------|-----------------|
| S-unidentate     | 78.76         | 34.42          | 17.65           |
| S-anisobidentate | 10.77         | 54.10          | 64.71           |
| Bidentate        | 10.32         | 11.48          | 17.65           |
| O-anisobidentate | 0.00          | 0.00           | 0.00            |
| O-unidentate     | 0.15          | 0.00           | 0.00            |
predominant forms in the solid state and in nonpolar solvents.\textsuperscript{50,51} While this observation is difficult to reconcile in terms of hard—soft principles (since hard H\textsuperscript{+} preferentially coordinates to the soft sulfur atom of $[RC(OS)]^-$, rather than to the hard oxygen atom), it can be readily reconciled in terms of the differences in C=E and C=E (E = O, S) bond energies.\textsuperscript{49,50} Given that an O–H bond is not stronger than a corresponding S–H bond by more than 30 kcal mol\textsuperscript{−1}.\textsuperscript{52}

3. Carboxylate Ligand Exchange Between $[\text{TmBu}]\text{Cd(O}_2\text{C}−\text{Ar})$ and $\text{ArCO}_2\text{H}$. Dynamic NMR spectroscopy provides, in principle, a method to investigate exchange of carboxylate groups between the carboxylate $[\text{TmBu}]\text{Cd(O}_2\text{C}−\text{R})$ and the carboxylic acid $\text{RCO}_2\text{H}$. For example, the $^1\text{H}$ NMR spectrum of a mixture of $[\text{TmBu}]\text{Cd(O}_2\text{C}-\text{p-Tol})$ and $\text{p-TolCO}_2\text{H}$ at room temperature exhibits exchange-averaged signals for the para-tolyl (p-Tol) groups, as illustrated for the hydrogen atoms ortho\textsuperscript{53} to the carboxyl groups in Figure 15.

![Figure 15](image)

**Figure 15.** $^1\text{H}$ NMR spectrum of (a) $[\text{TmBu}]\text{Cd(k^2-O}_2\text{C-p-Tol})$, (b) $\text{p-TolCO}_2\text{H}$, and (c) a mixture of $[\text{TmBu}]\text{Cd(k^2-O}_2\text{C-p-Tol})$ and $\text{p-TolCO}_2\text{H}$ at room temperature in $d_6$-toluene. For clarity, only the hydrogen atoms ortho to the carboxyl groups are shown.

While this observation is of considerable significance because it demonstrates that carboxylate exchange is facile, it does not permit a detailed quantification of the exchange. Rather, it merely provides a lower estimate for the exchange rate because the exchange-averaged signal exhibits no line broadening and is in the fast-exchange region.\textsuperscript{54} Specifically, since the chemical shift difference between pairs of ortho hydrogens in $[\text{TmBu}]\text{Cd(O}_2\text{C}-\text{p-Tol})$ and $\text{p-TolCO}_2\text{H}$ is 0.41 ppm (i.e., $\Delta\nu = 205$ Hz at 500 MHz), it is evident that the rate constant for site exchange is $>1 \times 10^3$ s\textsuperscript{−1}.\textsuperscript{55} Nevertheless, upon cooling, the rate of exchange slows down sufficiently that the exchange-averaged signal broadens (Figure 16). However, at the lowest temperature investigated, the rate is still sufficiently fast that decoalescence is not observed and that the exchange remains in the fast regime, with a single signal. Although rate data may be extracted from these spectra, the situation is complicated by the fact that the chemical shift of the exchange-averaged signal varies significantly as a function of temperature, ranging from 8.22 ppm at room temperature to 8.46 ppm at 188 K. The origin of the temperature dependence of the exchange-averaged signal is that the chemical shifts of both $[\text{TmBu}]\text{Cd(k^2-O}_2\text{C-p-Tol})$ and $\text{p-TolCO}_2\text{H}$ are also temperature-dependent.

![Figure 16](image)

**Figure 16.** $^1\text{H}$ NMR spectrum of a mixture of $[\text{TmBu}]\text{Cd(k^2-O}_2\text{C-p-Tol})$ and $\text{p-TolCO}_2\text{H}$ as a function of temperature. For clarity, only the hydrogen atoms ortho to the carboxyl groups are shown.

For example, the chemical shift of the ortho hydrogen atoms of $[\text{TmBu}]\text{Cd(O}_2\text{C-p-Tol})$ varies from 8.41 ppm at room temperature to 8.70 ppm at 188 K, while that for $\text{p-TolCO}_2\text{H}$ varies from 8.00 ppm at room temperature to 8.15 at 188 K. Adopting the chemical shift values of 8.70 and 8.15 at 188 K for $[\text{TmBu}]\text{Cd(O}_2\text{C-p-Tol})$ and $\text{p-TolCO}_2\text{H}$, respectively, the first order rate constant for site exchange is calculated to be $3.0 \times 10^2$ s\textsuperscript{−1} (Figure 17).\textsuperscript{56}

![Figure 17](image)

**Figure 17.** $^1\text{H}$ NMR spectrum (500 MHz) of (a) $[\text{TmBu}]\text{Cd(k^2-O}_2\text{C-p-Tol})$, (b) $\text{p-TolCO}_2\text{H}$, and (c) a mixture of $[\text{TmBu}]\text{Cd(k^2-O}_2\text{C-p-Tol})$ and $\text{p-TolCO}_2\text{H}$ at 188 K. For clarity, only the hydrogen atoms ortho to the carboxyl groups are shown. The first-order rate constant for site exchange is $3.0 \times 10^2$ s\textsuperscript{−1}.

In view of the fact that it was not possible to observe decoalescence of $[\text{TmBu}]\text{Cd(O}_2\text{C-p-Tol})$ and $\text{p-TolCO}_2\text{H}$ by $^1\text{H}$ NMR spectroscopy, our attention turned to the use of $^{19}\text{F}$ NMR spectroscopy to probe exchange between $[\text{TmBu}]\text{Cd(O}_2\text{C}−\text{Ar})$ and $\text{ArCO}_2\text{H}$. Specifically, since the chemical shift range for $^{19}\text{F}$ is much greater than that for the $^1\text{H}$ nucleus in typical compounds,\textsuperscript{57} $^{19}\text{F}$ NMR spectroscopy provides a means to quantify the kinetics of reactions that are too rapid to be measured by line-shape analysis of the corresponding $^1\text{H}$ NMR spectra. For example, while the $^1\text{H}$ chemical shifts of the ortho
hydrogens\textsuperscript{58} of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{O}_2\text{CArF})$ (8.34 ppm) and Ar$^3\text{CO}_2\text{H}$ (7.79 ppm) differ by 0.94 ppm (i.e., 278 Hz at 500 MHz, 11.7 T), the $^{19}\text{F}$ NMR chemical shifts differ by 6.45 ppm (i.e., 3,035 Hz at 470.59 MHz, 11.7 T). As such, $^{19}\text{F}$ NMR spectroscopy is capable of measuring kinetics in this system that are an order of magnitude faster than can be measured by $^1\text{H}$ NMR spectroscopy. Thus, while an exchange-averaged $^{19}\text{F}$ NMR signal is observed for a mixture of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{O}_2\text{CArF})$ and Ar$^3\text{CO}_2\text{H}$ at room temperature (Figure 18), decoalescence into two distinct signals can be achieved at low temperature (Figure 19).\textsuperscript{59}

Although the ability to observe spectra in both the fast- and slow-exchange regimes permits kinetics measurements via line-shape analysis over a large range of temperature (Figure 19 and Table 7),\textsuperscript{60} the interpretation of the kinetics data is dependent on the exchange mechanism. In this regard, two simple mechanistic possibilities for the exchange process include (i) an associative pathway in which the carboxylic acid is intimately involved in the rate-determining step and (ii) a dissociative pathway in which the rate-determining step only involves $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{O}_2\text{CArF})$. To distinguish between these possibilities, the dynamics were studied as a function of the concentration of Ar$^3\text{CO}_2\text{H}$ at 195 K. For example, if Ar$^3\text{CO}_2\text{H}$ were not to be involved prior to, or during, the rate-determining step, the line width of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{O}_2\text{CArF})$ would not be influenced by the concentration of Ar$^3\text{CO}_2\text{H}$; in contrast, the line width of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{O}_2\text{CArF})$ would increase if Ar$^3\text{CO}_2\text{H}$ were to be involved in the rate-determining step. Significantly, the data illustrated in Figure 20 and Table 8 indicate that the exchange rate is dependent on the concentration of Ar$^3\text{CO}_2\text{H}$, thereby signaling an associative rather than dissociative pathway.\textsuperscript{61}

Table 7. Rate of Carboxylate Exchange between $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})$ and Ar$^3\text{CO}_2\text{H}$ as a Function of Temperature\textsuperscript{a}

| T, K | rate, Ms\textsuperscript{-1} |
|------|--------------------------|
| 263  | 245                      |
| 253  | 150                      |
| 241  | 65                       |
| 231  | 33                       |
| 221  | 24                       |
| 213  | 13                       |
| 202  | 5                        |
| 195  | 2.5                      |

\textsuperscript{a}Rates correspond to a solution at room temperature that is composed of $[[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})]$ (9.1 $\times$ 10$^{-4}$ M) and [Ar$^3\text{CO}_2\text{H}$]$_T$ (9.1 $\times$ 10$^{-4}$ M).

Figure 18. $^{19}\text{F}$ NMR spectra of (a) Ar$^3\text{CO}_2\text{H}$, (b) $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})$, and (c) a mixture of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})$ and Ar$^3\text{CO}_2\text{H}$ at room temperature (ArF = C$_6$H$_4$-4-F).

Figure 19. Variable-temperature $^{19}\text{F}$ NMR spectra obtained for a 1:1 mixture of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})$ (●) and Ar$^3\text{CO}_2\text{H}$ (Ar$^3$ = 4-C$_6$H$_4$F) (◆) in C$_7$D$_8$.

Figure 20. $^{19}\text{F}$ NMR spectra obtained for a mixture of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})$ (●) and Ar$^3\text{CO}_2\text{H}$ (Ar$^3$ = 4-C$_6$H$_4$F) (◆) with different concentrations of the latter in C$_7$D$_8$: (a) 1:1, (b) 1:2, (c) 1:3, and (d) 1:4 molar ratios of $[\text{TmBu}^{\text{III}}]\text{Cd}(\text{kappa}-\text{O}_2\text{CArF})$ and Ar$^3\text{CO}_2\text{H}$ and Table 8 indicate that the exchange rate is dependent on the concentration of Ar$^3\text{CO}_2\text{H}$, thereby signaling an associative rather than dissociative pathway.\textsuperscript{61}
[1.95 × 10⁻⁴] Cd(κ²-O₂CArF) and Ar²CO₂H as a Function of Concentration at 195 K

| [Cd]/M⁺ | Ar²CO₂H/M⁺ | Ar²CO₂H/M⁺ rate, Ms⁻¹ |
|---------|-------------|------------------------|
| 9.10 × 10⁻⁴ | 9.10 × 10⁻⁴ | 1.47 × 10⁻⁸ | 25 |
| 9.10 × 10⁻⁴ | 1.80 × 10⁻⁵ | 2.07 × 10⁻⁸ | 6 |
| 9.10 × 10⁻⁴ | 2.70 × 10⁻⁵ | 2.53 × 10⁻⁸ | 10 |
| 9.10 × 10⁻⁴ | 3.60 × 10⁻⁵ | 2.92 × 10⁻⁸ | 14 |

*Cd* is a straight line with a slope of 1.86 versus ln[ArFCO₂H].

 Several possibilities exist for an associative mechanism. For example, one possibility is that [Cd]Cd(κ²-O₂CArF) and Ar²CO₂H undergo direct metathesis in which protonation of the carboxylate oxygen is accompanied by formation of a new Cd–O bond, as illustrated in Figure 21.62 A second possibility is that ArFCO₂H undergo direct metathesis in which protonation of the carboxylate oxygen is accompanied by formation of a new Cd–O bond, as illustrated in Figure 21.62

![Figure 21](Image)

**Figure 21.** Possible transition states for carboxylate exchange that are consistent with first- and second-order dependence on R²CO₂H.

[TmBu⁺]Cd(κ²-O₂CArF) forms a hydrogen-bonded adduct with Ar²CO₂H, namely, [TmBu⁺]Cd(κ²-O₂CArF)–HO₂CArF, thereby creating a leaving group, i.e., [Ar²CO₂HO₂CArF]⁺, which is better than a carboxylate (Figure 21).62,63 While each of these mechanisms are characterized by rate laws that have different dependence on total carboxylic acid concentrations, identifying the rate law is complicated by the fact that Ar²CO₂H exists in equilibrium with the hydrogen-bonded dimer (Ar²CO₂H)₂.64,65 As such the concentration of Ar²CO₂H requires consideration of the equilibrium constant for association of the acid (Kassoc), which can be estimated as 2.11 × 10⁶ on the basis that (i) the value of Kassoc is 1.95 × 10⁶ at 296 K,64 and (ii) ΔS is −16 e.u.66 A plot of ln(rate) versus ln[Ar²CO₂H] may be fit to a straight line with a slope of 2.51 (Figure 22), which is clearly indicative of a nonfirst-order dependence on [Ar²CO₂H]. However, on the basis that [Ar²CO₂H] is an estimate, we do not consider it prudent to interpret the slope as providing a precise value for the order of this reaction.

Phenomenologically, the rate can also be expressed in terms of total carboxylic acid concentration [Ar²CO₂H], in which case no distinction is made with respect to the form of the carboxylic acid (monomer or dimer) in solution. For this scenario, a plot of ln(rate) versus ln[Ar²CO₂H] may be fit to a straight line with a slope of 1.26. Correspondingly, a plot of rate versus ([TmBu⁺]Cd(O₂CArF))²[Ar²CO₂H]₁⁻²⁶ through the origin is characterized by a slope of 1.86 × 10⁷ M⁻¹⁻⁸ s⁻¹ for kassoc (Figure 23). While the empirical expression rate = kassoc[([TmBu⁺]Cd(O₂CArF))²[Ar²CO₂H]₁⁻²⁶] has no mechanistic significance,67 it is of value in allowing one to estimate an exchange rate as a function of total carboxylic acid concentration, which is of use in predicting reactivity (vide infra).

Although ligand exchange at group 12 metal centers has been investigated in a variety of systems,68–73 the most relevant comparison is with the tris(pyrazolyl)hydroborato compound [Tp³⁺]Cd(O₂CMe).25 In this regard, the observation of an associative mechanism for [TmBu⁺]Cd(O₂CArF) is of interest in view of the fact that the exchange of acetate between the tris(pyrazolyl)hydroborato compound, [Tp³⁺]Cd(O₂CMe) and [Na(krypto-221)][Me₃CO₂], as observed by ¹³C NMR spectroscopy, was proposed to be dissociative.25,74 Exchange was also observed between the cyclohexene oxide (CHO) adduct [Tp³⁺]Cd(O₂CMe)(CHO) and acetic acid, but the mechanism was not addressed;25 thus, further comparison with [TmBu⁺]Cd(O₂CArF) is not possible.

The observation that ligand exchange involving [TmBu⁺]Cd(O₂CArF) is very facile is of relevance to the fact that cadmium carbonic anhydrase also exhibits a sulfur-rich coordination environment involving cysteine thiolate groups25 and thus indicates that such an environment is consistent with catalytic turnover.
|     | [Tm\(^{6+}\)]CdO\(_2\)C(C\(_6\)H\(_4\)-4-Me)·0.5MeCN | [Tm\(^{6+}\)]CdO\(_2\)C(C\(_6\)H\(_4\)-4-F)·2(C\(_6\)H\(_6\)) | [Tm\(^{6+}\)]CdO\(_2\)C(C\(_6\)H\(_3\)-2,6-F\(_2\)) | [Tm\(^{6+}\)]CdO\(_2\)C(C\(_6\)H\(_3\)-3,5-F\(_2\))·(Et\(_2\)O) | [Tm\(^{6+}\)]CdO\(_2\)C(C\(_6\)H\(_4\)Ph)·(C\(_6\)H\(_6\)) | [Tm\(^{6+}\)]CdO\(_2\)C(9-An)·(C\(_6\)H\(_6\)) | [Tm\(^{6+}\)]CdSC(O)Ph·(C\(_6\)H\(_6\)) |
|-----|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| lattice | triclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | triclinic |
| formula | C\(_{60}\)H\(_{85}\)B\(_2\)Cd\(_2\)N\(_{13}\)O\(_4\)S\(_6\) | C\(_{40}\)H\(_{50}\)BCd\(_3\)N\(_6\)O\(_2\)S\(_3\) | C\(_{28}\)H\(_{37}\)BCd\(_3\)F\(_2\)N\(_6\)O\(_2\)S\(_3\) | C\(_{32}\)H\(_{47}\)BCd\(_3\)F\(_2\)N\(_6\)O\(_3\)S\(_3\) | C\(_{31}\)H\(_{45}\)BCdN\(_6\)O\(_2\)S\(_3\) | C\(_{42}\)H\(_{49}\)BCdN\(_6\)O\(_2\)S\(_3\) | C\(_{34}\)H\(_{45}\)BCdN\(_6\)O\(_4\)S\(_4\) |
| formula weight | 1491.19 | 885.25 | 747.03 | 821.15 | 753.12 | 889.26 | 805.21 |
| space group | P\(\overline{1}\) | P\(2_1/n\) | P\(2_1/n\) | P\(2_1/c\) | P\(2_1/c\) | P\(2_1/c\) | P\(\overline{1}\) |
| a/Å | 14.618(2) | 12.9391(17) | 11.0195(8) | 18.2044(11) | 11.4701(15) | 10.7547(9) | 11.0621(16) |
| b/Å | 14.677(2) | 13.6148(18) | 11.0195(8) | 18.2044(11) | 11.4701(15) | 10.7547(9) | 11.0621(16) |
| c/Å | 19.035(3) | 24.852(4) | 30.106(2) | 18.9143(11) | 15.472(2) | 22.323(2) | 15.950(2) |
| \(\alpha\)/deg | 67.915(2) | 90 | 90 | 90 | 90 | 90 | 90 |
| \(\beta\)/deg | 89.636(2) | 104.782(2) | 90.4850(10) | 90.5360(10) | 97.844(2) | 113.1060(10) | 87.140(2) |
| \(\gamma\)/deg | 67.224(2) | 90 | 90 | 90 | 90 | 90 | 90 |
| V/Å\(^3\) | 3442.8(8) | 4233.2(10) | 3328.2(4) | 3805.8(4) | 3464.5(8) | 4207.1(6) | 1862.6(4) |
| Z | 2 | 4 | 4 | 4 | 4 | 4 | 2 |
| temperature (K) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| radiation (\(\lambda\), Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| \(\rho\) (calcld), g cm\(^{-3}\) | 1.348 | 1.389 | 1.491 | 1.433 | 1.451 | 1.404 | 1.436 |
| \(\mu\) (Mo K\(\alpha\)), mm\(^{-1}\) | 0.854 | 0.709 | 0.891 | 0.788 | 0.853 | 0.711 | 0.847 |
| \(\theta\) max, deg | 28.28 | 30.66 | 30.61 | 30.51 | 30.83 | 30.68 | 30.51 |
| no. of data collected | 48 367 | 65 990 | 53 280 | 60 420 | 54 741 | 67 089 | 29 077 |
| no. of data used | 17 098 | 13 067 | 10 252 | 11 617 | 10 769 | 13 021 | 11 263 |
| no. of parameters | 813 | 500 | 401 | 448 | 410 | 563 | 437 |
| \(R_1\) \([I > 2\sigma(I)]\) | 0.0310 | 0.0384 | 0.0526 | 0.0290 | 0.0660 | 0.0526 | 0.0447 |
| \(wR_2\) \([I > 2\sigma(I)]\) | 0.0655 | 0.0768 | 0.0846 | 0.0669 | 0.1035 | 0.0885 | 0.0807 |
| \(R_1\) \([all\ data]\) | 0.0470 | 0.0622 | 0.1238 | 0.0394 | 0.1699 | 0.1205 | 0.0749 |
| \(wR_2\) \([all\ data]\) | 0.0723 | 0.0868 | 0.1045 | 0.0728 | 0.1312 | 0.1099 | 0.0909 |
| GOF | 1.020 | 1.033 | 1.002 | 1.035 | 1.012 | 1.003 | 1.013 |
| \(R_{int}\) | 0.0359 | 0.0555 | 0.1345 | 0.0323 | 0.1691 | 0.1292 | 0.0406 |
As an illustration of the facility of ligand exchange, the pseudo-first-order rate constant for the reaction of [TmBu]CdO2C(C6H4) in a 1 M solution of Ar2CO2H76 is calculated to be 1.86 × 10−6 s−1, which corresponds to a lifetime of 54 ns. For comparison, this lifetime is comparable to the exciton lifetimes in cadmium chalcogenide nanocrystals.77

Also of relevance to the present study, the kinetics of carboxylate exchange involving cadmium selenide nanocrystals has likewise been investigated.78 In this regard, while the exchange between oleic acid and physisorbed oleic acid is rapid on the NMR time scale, exchange with the bound oleate is slow. Exchange between oleic acid and physisorbed oleic acid is rapid on the NMR time scale, exchange with the bound oleate is slow. For comparison, this lifetime is comparable to the exciton lifetimes in cadmium chalcogenide crystals. The facility of ligand exchange processes in this coordination environment has been probed via exchange reactions with the corresponding carboxylic acid, RCO2H, which indicates that it is rapid on the NMR time scale, even at low temperature. Furthermore, the exchange reaction occurs via an associative rather than dissociative pathway. In addition to carboxylate compounds, the thio carboxylate derivative [TmBu]Cd(O2CSS[C(CH3)3])2 has also been synthesized via the reaction of [TmBu]CdMe with thiobenzoic acid, and, in contrast to the carboxylate derivatives [TmBu]CdO2C(κ2-O,C-R), the thio-carboxylate ligand binds in a κ2 manner via only the sulfur atom.

### EXPERIMENTAL SECTION

#### General Considerations

All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under a nitrogen atmosphere,79 except where otherwise stated. Solvents were purified and degassed by standard procedures. NMR solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 Avance III, Bruker 400 Cyber-enabled Avance III, and Bruker 500 DMX spectrometers.1H NMR chemical shifts are reported in ppm relative to SiMe4 (δ = 0) and were referenced internally with respect to the proto solvent impurity (δ = 7.16 for CDCl3 and 7.26 for CHCl3).79 13C NMR spectra are reported in ppm relative to SiMe4 (δ = 0) and were referenced internally with respect to the solvent (δ = 128.06 for CDCl3 and 77.16 for CDC13).79 19F NMR spectra are reported in ppm relative to CFCl3 (δ = 0) and were referenced internally with respect to a C6F6 standard (δ = 128.06 for C6D6 and 77.16 for CDCl3).79 Coupling constants are reported in hertz. IR spectra were recorded on a Nicolet 6700 FT-IR Spectrometer, and the data are reported in cm−1. Mass spectra were obtained on a JEOL-JMS-HX110H Tandem Double-Focusing Mass Spectrometer with a 10 kV accelerated voltage equipped with a fast-atom bombardment (FAB) ion source. Carboxylic acids were obtained from Aldrich, and 4-fluorobenzoic acid was recrystallized from a solution in EtOH/H2O (50:50) prior to use. Me2Cd was obtained from Strem and distilled prior to use.

### X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection, and refinement parameters are summarized in Table 9. The structures were solved using direct methods and standard difference map techniques, and they were refined by full-matrix least-squares procedures on F2 with SHELXTL (Version 2008/4).81

#### Synthesis of [TmBu]CdO2C(C6H4-4-Me).

As a solution of [TmBu]CdMe2 (201 mg, 0.33 mmol) in C6H6 (ca. 9 mL) was treated with 4-methylbenzoic acid (56 mg, 0.41 mmol), resulting in immediate effervescence. The solution was stirred at room temperature for 1 h, after which period the volatile components were removed in vacuo, and the resulting powder was washed with Et2O (ca. 2 mL), yielding [TmBu]CdO2C(C6H4-4-Me) as a white solid (157 mg, 65%). Crystals of [TmBu]CdO2C(C6H4-4-Me) suitable for X-ray diffraction were obtained from a solution in MeCN. Anal. Calc. for [TmBu]CdO2C(C6H4-4-Me): C, 48.0%; H, 5.7%; N, 11.6%. Found: C, 47.5%; H, 5.7%; N, 11.3%. 1H NMR (CD2D): 1.52 [s, 27H of HB(C6H4ON(C(CH3)3)])-CS3], 1.98 [s, 3H of CdO2C(C4H6(CH3))], 6.42 [d, JHH = 5, 3H of HB(C6H4N(C(CH3)3))CS3], 6.68 [d, JHH = 2, 3H of HB(C6H4N(C(CH3)3))CS3], 6.95 [d, JHH = 8, 2H of CdO2C(C4H6(CH3))], 8.60 [d, JHH = 8, 2H of CdO2C(C4H6(CH3))], 13C {1H} NMR (C6D6): 21.4 [1C, CdO2C(C6H4(CH3))], 28.9 [9C, HB(C6H4N(C(CH3)3))CS3], 59.5 [3C, HB(C6H4N(C(CH3)3))CS3], 117.0 [3C, HB(C6H4N(C(CH3)3))CS3], 122.9 [3C, HB(C6H4N(C(CH3)3))CS3], 128.6 [2C, CdO2C(C4H6(CH3))], 131.5 [2C, CdO2C(C4H6(CH3))], 132.9 [1C, CdO2C(C4H6(CH3))], 140.4 [1C, CdO2C(C4H6(CH3))], 157.6 [t, JCH = 9, 3C, HB(C6H4N(C(CH3)3))CS3], 175.1 [1C, CdO2C(C4H6(CH3))], IR data for [TmBu]CdO2C(C6H4-4-Me) (ATR, cm−1): 3183 (w), 2977 (w), 2923 (w), 2914 (w), 2324 (w), 2161 (w), 2051 (w), 1980 (w), 1800 (w), 1735 (s), 1682 (w), 1548 (w), 1397 (w), 1358 (w), 1293 (m), 1253 (m), 1229 (m), 1195 (m), 1195 (s), 1172 (s), 1132 (m), 1119 (m), 1099 (m), 1061 (m), 1047 (m), 1021 (m), 984 (w), 929 (w), 860 (m), 821 (m), 787 (m), 767 (s), 727 (s), 687 (s), 639 (w), 621 (m), 589 (m), 552 (m), 493 (w), 476 (m) FAB-MS: m/z = 591.1 [M − O(C4H6(CH3))]+, M = [TmBu]CdO2C(C4H6(CH3)).

(b) A solution of Me2Cd (36 μL, 0.50 mmol) in C6H6 (ca. 4 mL) was treated with [TmBu]Na15 (251 mg, 0.50 mmol) while stirring. 4-Methylbenzoic acid (137 mg, 1.01 mmol) was added to the reaction mixture, resulting in vigorous effervescence and the immediate formation of a cloudy yellow precipitate. The mixture was stirred for 45 min and filtered. The volatile components were removed in vacuo to give [TmBu]CdO2C(C6H4-4-Me) as a white solid (150 mg, 41%).

(c) A solution of 4-methylbenzoic acid (1.402 g, 10.30 mmol) in toluene (ca. 5 mL) was stirred and treated slowly with Me2Cd (370 μL, 5.14 mmol), resulting in the immediate formation of a thick gummy precipitate. Pentane (ca. 20 mL) was added, and the mixture was stirred at room temperature for 30 min to convert the gummy precipitate into a more tractable powder. After this period, the precipitate was isolated by filtration using a frit, washed with pentane (2 × 10 mL), and dried in vacuo to yield [TmBu]CdO2C(C6H4-4-Me) as a white solid (1.886 g, 96%).

### Conclusions

In summary, the tris-(2-tert-butylmercaptoimidazoyl)hydroborato ligand has been used to obtain a series of cadmium carboxylate compounds in a sulfur-rich environment, namely, [TmBu]CdO2C(κ2-O,C-R), which serve as mimics for both cadmium-substituted zinc enyzmes and also the surface atoms of cadmium chalcogenide crystals. The facility of ligand exchange processes in this coordination environment has been probed via exchange reactions with the corresponding carboxylic acid, RCO2H, which indicates that it is rapid on the NMR time scale, even at low temperature. Furthermore, the exchange reaction occurs via an associative rather than dissociative pathway. In addition to carboxylate compounds, the thio-carboxylate derivative [TmBu]CdMe with thiobenzoic acid, and, in contrast to the carboxylate derivatives [TmBu]CdO2C(κ2-O,C-R), the thio-carboxylate ligand binds in a κ2 manner via only the sulfur atom.
CdO,C(C6-H-F)], 8.47 [m, 2H of CdO,C(C6-H-F)], 1.33 \{^{1}H\} NMR (C_{3}D_{2}): 28.9 \{9C, HB\{C_{2}N_{2}H_{2}\[C(CH_{3})_{3}\]CS}\}, 59.5 \{3C, HB\{C_{2}N_{2}H_{2}\[C(CH_{3})_{3}\]CS}\}, 111.4 \{ \delta_{J_{C-C}} = 20, 2C, CdO,C(C_{3}-H-F)\}, 117.0 \{3C, HB\{C_{2}N_{2}H_{2}\[C(CH_{3})_{3}\]CS}\}, 123.0 \{3C, HB\{C_{2}N_{2}H_{2}\[C(CH_{3})_{3}\]CS}\\}, 131.8 \{ \delta_{J_{C-C}} = 3, 1C, CdO,C(C_{4}-H-F)\}, 133.6 \{ \delta_{J_{C-F}} = 9, 2C, CdO,C(C_{4}-H-F)\}, 157.3 \{ \delta_{J_{C-C}} = 9, 3C, HB\{C_{2}N_{2}H_{2}\[C(CH_{3})_{3}\]CS}\\}, 165.0 \{ \delta_{J_{C-F}} = 247, 1C, CdO,C(C_{4}-H-F)\}, 173.8 \{1C, CdO,C(C_{4}-H-F)\], 1.34 \{^{13}F\} NMR (C_{3}D_{2}): -113.2. IR data for [TmBut\{CdO,C(C_{3}-H-F)\} (ATR, cm^{-1}): 3177 (w), 3145 (w), 2979 (m), 2920 (w), 2862 (w), 2147 (w), 2324 (w), 2289 (w), 2399 (w), 2162 (w), 2116 (w), 2051 (w), 1981 (w), 1608 (w), 1602 (m), 1546 (m), 1507 (w), 1483 (m), 1438 (w), 1426 (m), 1397 (s), 1370 (s), 1365 (vs), 1305 (m), 1255 (w), 1232 (s), 1192 (vs), 1175 (s), 1115 (m), 1133 (w), 1087 (m), 1070 (w), 1030 (w), 1016 (w), 989 (w), 929 (w), 864 (m), 785 (s), 757 (s), 735 (s), 724 (s), 685 (s), 621 (s), 587 (m), 550 (m), 493 (m), 457 (m). FAB-MS: m/z = 591.2 [M - CdO,C(C_{3}-H-F)]\}, M = [TmBut\{CdO,C(C_{3}-H-F)\}\].

(b) A solution of Me_{2}Cd (36.6 mg, 0.50 mmol) in C_{6}H_{6} (ca. 4 mL) was treated with [TmBut\{Na\}]^{+} (247 mg, 0.49 mmol) while stirring. 4-Fluorobenzoic acid (134 mg, 0.95 mmol) was added to the reaction mixture, resulting in vigorous effervescence and the immediate formation of a white jellylike precipitate. The mixture was stirred for 30 min and allowed to settle for 30 min. After this period, the mixture was filtered, and the volatile components were removed from the solution to give [TmBut\{CdO,C(C_{4}-H-F)\} as a white solid (124 mg, 36%).

**Synthesis of [TmBut\{CdO,C(C_{3}-H-F, 3,5-F-\}]**. A solution of [TmBut\{CdMe_{2}O\}] (470 mg, 0.67 mmol) in C_{6}H_{6} (ca. 10 mL) was treated with 3.5-fluorobenzoic acid (107 mg, 0.67 mmol), resulting in immediate effervescence. The mixture was stirred at room temperature for 30 min, after which the volatile components were removed in vacuo, and the resulting powder was washed with Et_{2}O (ca. 2 mL) to yield [TmBut\{CdO,C(C_{3}-H-F, 3,5-F-)\} as a white solid (0.25 g, 50%). Crystals of [TmBut\{CdO,C(C_{3}-H-F, 3,5-F-)\} suitable for X-ray diffraction were obtained by cooling a solution in Et_{2}O. Anal. Calcld for [TmBut\{CdO,C(C_{3}-H-F, 3,5-F-)\}: C, 46.8%; H, 5.8%; N, 10.2%. Found: C, 46.2%; H, 6.0%; N, 11.2%. Crystals of [TmBut\{CdO,C(C_{3}-H-F, 3,5-F-)\} suitable for X-ray diffraction were obtained from Et_{2}O. Anal. Calcld for [TmBut\{CdO,C(C_{3}-H-F, 3,5-F-)\}: C, 49.7%; H, 5.5%; N, 10.6%. \{^{13}C\} NMR (C_{6}D_{6}): 1.52 \{ 

## Article

**Inorganic Chemistry**

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Synthesis of \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\). A solution of \([\text{TmBu}]_2\text{CdMe}_2\) (105 mg, 0.17 mmol) in \(C_6H_6\) (ca. 9 mL) was treated with tetradecanoyl (myristic) acid (40 mg, 0.18 mmol), resulting in immediate effervescence. The mixture was stirred vigorously at room temperature for 45 min. After this period, the reaction mixture was heated to 80°C for an additional 30 min. The mixture was cooled to room temperature, filtered, and the resulting solid was washed with a mixture (48:1:2) of Et_2O (ca. 0.5 mL) and pentane (ca. 2 mL), yielding \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\) (201 mg, 0.33 mmol) in \(C_6H_6\) (ca. 9 mL) was treated with thiobenzoic acid (48:1:2) to yield \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\) as a pale yellow solid (159 mg, 66%). Crystals of \([\text{TmBu}]_2\text{CdSO}_4\) suitable for X-ray diffraction were obtained via vapor diffusion of pentane into a solution in benzene. Anal. Calc for \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\): C, 46.3%; H, 5.4%; N, 11.6%. Found: C, 47.0%; H, 5.2%; N, 11.4%.}

**H NMR (CD_{2}D_{6})**: 1.52 [s, 27H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.39 [s, 27H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.53 [s, 27H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 2.68 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.68 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.89 [s, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 2.60 [d, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.64 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.68 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.89 [s, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 2.60 [d, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}].

**Synthesis of \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\)**: A solution of \([\text{TmBu}]_2\text{CdMe}_2\) (201 mg, 0.33 mmol) in \(C_6H_6\) (ca. 9 mL) was treated with tetradecanoyl (myristic) acid (48 mg, 0.18 mmol), resulting in immediate effervescence. The mixture was stirred at room temperature for 45 min. After this period, the volatile components were removed in vacuo, and the resulting powder was washed with a mixture of Et_2O (ca. 0.5 mL) and pentane (ca. 2 mL), yielding \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\) (201 mg, 0.33 mmol) in \(C_6H_6\) (ca. 9 mL) was treated with thiobenzoic acid (48 mg, 0.18 mmol), resulting in immediate effervescence. The mixture was stirred vigorously at room temperature for 45 min. After this period, the volatile components were removed in vacuo, and the resulting powder was washed with a mixture of Et_2O (ca. 0.5 mL) and pentane (ca. 2 mL), yielding \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\) as a pale yellow solid (159 mg, 66%). Crystals of \([\text{TmBu}]_2\text{CdSO}_4\) suitable for X-ray diffraction were obtained via vapor diffusion of pentane into a solution in benzene. Anal. Calc for \([\text{TmBu}]_2\text{CdO}_2(C(C_6H_4-F))\): C, 46.3%; H, 5.4%; N, 11.6%. Found: C, 47.0%; H, 5.2%; N, 11.4%.}

**H NMR (CD_{2}D_{6})**: 1.52 [s, 27H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.39 [s, 27H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.53 [s, 27H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 2.68 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.68 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.89 [s, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 2.60 [d, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.64 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.68 [d, \_J_{H,H} = 2, 3H of HB\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 1.89 [s, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}], 2.60 [d, \_J_{H,H} = 2, 2H of CD\{C_{2}N_{2}H_{2}[C(CH_{3})_{3}]\}].
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