Cadmium Compounds with an [N$_2$C] Atrane Motif: Evidence for the Generation of a Cadmium Hydride Species

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Supporting Information

ABSTRACT: Tris(2-pyridylthio)methane ([Tptm]H) has been employed to synthesize a series of cadmium carbatrane compounds that feature an [N$_2$C] coordination environment. Specifically, [Tptm]H reacts with Cd[N(SiMe$_3$)$_2$]$_2$ to afford [Tptm]CdN(SiMe$_3$)$_2$, which thereby provides access to other derivatives. For example, [Tptm]CdN(SiMe$_3$)$_2$ reacts with CO$_2$ to form [{[Tptm]Cd(μ-NCO)}$_2$] and (ii) Me$_3$SiOH and Ph$_3$SiOH to form [{κ$_3$-Tptm}Cd(μ-O$Si$Me$_3$)]$_2$ and [Tptm]-CdOSiPh$_3$, respectively. The siloxide compound [{κ$_3$-Tptm}Cd(μ-O$Si$Me$_3$)]$_2$ reacts with Me$_3$SiX (X = Cl, Br, O$_2$CMe) to give [Tptm]CdX, while the reaction with PhSiH$_3$ in the presence of CO$_2$ generates the formate complex, [Tptm]CdO$_2$CH, thereby providing evidence for the generation of a proposed cadmium hydride intermediate, [{[Tptm]CdH}].

Whereas zinc is of pivotal importance to human health, its congeners, cadmium and mercury, are toxic. As such, an appreciation of the different reactivities of these metals in a common environment is essential for achieving a complete understanding of the origin of the toxicity of cadmium and mercury. The beneficial nature of zinc in biological systems is a consequence of (i) its catalytic and structural roles in enzymes and proteins and (ii) its ability to serve as a signaling ion in regulation. With respect to the former, the active sites of many zinc enzymes exhibit a nitrogen-rich coordination environment, as exemplified by carbonic anhydrase, the first zinc enzyme to be discovered. Since synthetic analogues are of much value in providing insight into the structures and mechanism of metalloenzymes, we have employed tris(3-tert-butyl-5-methylpyrazolyl)hydroborato, [Tp$^t$-Bu,Me $^-$], and tris(2-pyridylthio)methyl, [Tptm], ligands to provide three nitrogen donors to mimic the active site of carbonic anhydrase, including the first structural characterization of mononuclear zinc bicarbonate compounds, namely, [Tp$^t$-Bu,Me]$^-$ZnOCO$_2$H and [Tptm]ZnOCO$_2$H$_5$. Here we describe the application of the [Tptm] ligand to cadmium chemistry, thereby demonstrating how zinc and cadmium exhibit significant differences in this nitrogen-rich system.

Access to tris(2-pyridylthio)methylcadmium compounds is provided by the reaction of tris(2-pyridylthio)methane ([Tptm]-H)$^-$ with Cd[N(SiMe$_3$)$_2$]$_2$ to afford [Tptm]CdN(SiMe$_3$)$_2$ (1), as illustrated in Scheme 1. The molecular structure of [Tptm]CdN(SiMe$_3$)$_2$ has been determined by single-crystal X-ray diffraction (Figure 1), which clearly demonstrates that the [Tptm] ligand coordinates in a κ$^4$ manner, thereby resulting in an atrane motif. In this regard, the structure of the cadmium carbatrane compound [Tptm]CdN(SiMe$_3$)$_2$ is very distinct from that of the zinc counterpart for which $^1$H NMR spectroscopy
demonstrates that the ligand coordinates in a \( \kappa^3 \) manner.\(^{6a,8}\) Despite the presence of the atrane motif in \([\text{Tptm}]\text{CdN(SiMe}_3\text{)}\text{2}\), however, the coordination geometry is markedly distorted from a trigonal bipyramidal geometry towards a square-pyramidal geometry, as illustrated by the average value of 0.19 for the \( \tau \) five-coordinate geometry index\(^ {11}\) for the two crystallographically independent molecules. \([\text{Tptm}]\text{CdN(SiMe}_3\text{)}\text{2}\) is a useful precursor for other cadmium derivatives, as illustrated by the reaction with \( \text{CO}_2 \) to form the isocyanate complex \({[\text{Tptm}]\text{Cd}(\mu-\text{NCO})}\)\(_2\) (2; Scheme 1), which has been structurally characterized by X-ray diffraction (Figure 2). While the reactivity of \([\text{Tptm}]\text{CdN(SiMe}_3\text{)}\text{2}\) towards \( \text{CO}_2 \) is similar to that of the zinc counterpart \([\text{Tptm}]\text{Zn-}\text{NCO}\), the \( \mu \)-isocyanate complex \({[\text{Tptm}]\text{Cd}(\mu-\text{NCO})}\)\(_2\) exhibits \( \kappa^4 \) coordination. Not only do \({[\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\) and \([\text{Tptm}]\text{CdOSiPh}_3\) illustrate the dramatic impact of varying the substituents on silicon, but the structure of \({[\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\) is also of note because it provides another example of the difference between the zinc and cadmium systems: specifically, the zinc complex \([\text{Tptm}]\text{ZnOSiMe}_3\) is monomeric, whereas \([\text{Tptm}]\text{CdOSiPh}_3\) is dinuclear with bridging siloxide ligands. As such, \([\text{Tptm}]\text{ZnOSiMe}_3\) resembles \([\text{Tptm}]\text{CdOSiPh}_3\) more than the trimethylsiloxide derivative, \({[\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\).

In addition to the different coordination modes of the \( \text{OSiPh}_3 \) and \( \text{OSiMe}_3 \) ligands, the \([\text{Tptm}]\text{CdOSiPh}_3\) ligands to \([\text{Tptm}]\text{CdOSiPh}_3\) and \({[\text{k}^3-\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\) also adopt different coordination modes. Thus, whereas \([\text{Tptm}]\text{CdSiOH}\) exhibits an atrane motif with \( \kappa^3 \) coordination, \({[\text{k}^3-\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\) exhibits \( \kappa^4 \) coordination. Not only do \({[\text{k}^3-\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\) and \([\text{Tptm}]\text{CdSiOH}\) illustrate the dramatic impact of varying the substituents on silicon, but the structure of \({[\text{k}^3-\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\) is also of note because it provides another example of the difference between the zinc and cadmium systems: specifically, the zinc complex \([\text{Tptm}]\text{ZnOSiMe}_3\) is monomeric, whereas \([\text{Tptm}]\text{CdOSiPh}_3\) is dinuclear with bridging siloxide ligands. As such, \([\text{Tptm}]\text{ZnOSiMe}_3\) resembles \([\text{Tptm}]\text{CdOSiPh}_3\) more than the trimethylsiloxide derivative, \({[\text{k}^3-\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\).

The molecular structures of \([\text{Tptm}]\text{CdOSiPh}_3\)\(_2\) (Scheme 1), the iodide compound, \([\text{Tptm}]\text{CdI}\), has been obtained by metathesis of \([\text{Tptm}]\text{Li}\) with \( \text{CdI}_2 \). X-ray diffraction studies demonstrate that the halide compounds, \([\text{Tptm}]\text{CdX} (X = \text{Cl}, \text{Br}, \text{I})\),\(^ {15}\) have approximate trigonal-bipyramidal geometries,\(^ {19}\) while \([\text{Tptm}]\text{CdO}_2\text{CMe}\) exhibits a distorted octahedral geometry with bidentate coordination of the acetate ligand (Figure 4), as indicated by the magnitude of the deviation in the \( \text{Cd}--\text{O} \) bond lengths (\( \Delta d = 0.22 \text{ Å} \)).\(^ {20}\) In this regard, it is evident that the cadmium complex \([\text{Tptm}]\text{CdO}_2\text{CMe}\) exhibits a greater degree of bidenticity than does the zinc counterpart \([\text{Tptm}]\text{ZnO}_2\text{CMe}\), for which \( \Delta d = 0.44 \text{ Å} \).\(^ {6a}\) \({[\text{k}^3-\text{Tptm}]\text{Cd}(\mu-\text{OSiMe}_3)}\)\(_2\) also reacts with \( \text{PhSiH}_3\), which, in the presence of \( \text{CO}_2 \), produces the formate compound \([\text{Tptm}]\text{CdO}_2\text{CH}\) (8). By analogy to the zinc system,\(^ {6a}\) the formation of \([\text{Tptm}]\text{CdO}_2\text{CH}\) is proposed to occur via the intermediacy of a cadmium hydride species, \([\text{Tptm}]\text{CdH}\), that is trapped by \( \text{CO}_2 \) to generate a formate derivative. While cadmium formate compounds are known,\(^ {21}\) the synthesis of \([\text{Tptm}]\text{CdO}_2\text{CH}\) is novel because it is the first example of the formation of a cadmium formate by the proposed insertion of.
CO\textsubscript{2} into a cadmium hydride bond. Such reactivity is of relevance to the discovery of potential methods for functionalizing CO\textsubscript{2}.

Also of note, the formate ligand of [Tptm]CdO\textsubscript{2}CH coordinates in a bidentate manner (Δd = 0.22 Å), which is not only in contrast to the zinc counterpart, [Tptm]ZnO\textsubscript{2}CH, which exhibits a well-defined unidentate coordination mode (Δd = 0.63 Å), but also in contrast to other cadmium formate compounds. For example, the smallest Δd for a mononuclear cadmium formate compound listed in the CSD has a value of 0.75 Å.

The proposed intermediacy of a cadmium hydride species is noteworthy because such species are not well preceded and their reactivity has been little investigated. For example, there are only two structurally characterized cadmium hydride compounds listed in the CSD, namely, the terphenyl compounds Ar\textsubscript{3}CdH and Ar\textsubscript{3}Cd(μ-H)\textsubscript{2}, as reported by Power et al. In addition, spectroscopic evidence has been presented by Reger et al. for the tris(pyrazolyl)hydroborate compound [Tp\textsubscript{2}Bu\textsubscript{5}]CdH. With respect to the reactivity of these complexes, [Ar\textsubscript{3}Cd(μ-H)]\textsubscript{2} is unstable at room temperature and decomposes to [Ar\textsubscript{3}Cd\textsubscript{2}]\textsubscript{2}, an observation that is in accord with the paucity of cadmium hydride compounds.

With the exception of \{[ɛ\textsuperscript{3}-Tptm]Cd(μ-OSiMe\textsubscript{3})\}\textsubscript{2}, each of the cadmium compounds described above features an atrane motif in which the [Tptm] ligand coordinates in a κ\textsuperscript{3} manner. While tetradentate tripodal ligands that give rise to atrane structures are common, the majority feature an L-type donor as the bridgehead, as exemplified by tris(2-pyridyl)amine. Tetradentate tripodal ligands that feature X-type or Z-type bridgeheads have received comparatively little attention, but also in contrast to other cadmium formate compounds. For example, the smallest Δd for a mononuclear cadmium formate compound listed in the CSD has a value of 0.75 Å.

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The Cd–C and Cd–N bond length data pertaining to coordination of the [Tptm] ligand for the above [Tptm]CdX compounds are summarized in Table 1. Examination of these data illustrate that, despite (i) the different coordination modes of the [Tptm] ligand and (ii) the different steric demands of X, the Cd–C (2.33–2.38 Å) and Cd–N\textsubscript{av} (2.29–2.37 Å) bond lengths exhibit relatively little variation. For example, the Cd–C bond lengths vary from 2.332(6) Å for [Tptm]CdN(SiMe\textsubscript{3})\textsubscript{2} to 2.383(7) Å for [Tptm]Cd(O\textsubscript{2}CMe), while the average Cd–N bond lengths range from 2.285 Å for [Tptm]CdOSiPh\textsubscript{3} to 2.368 Å for [Tptm]CdN(SiMe\textsubscript{3})\textsubscript{2}. In most cases, the Cd–C bond length is slightly longer than the average Cd–N bond length.
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(13) The NMR spectra of [(Tptm)Cd(µ-NCO)]2 and (kα-Tptm)-Cd(µ-O[Me2S]4)2 indicate that the pyridyl groups are chemically equivalent at room temperature.

(14) With respect to this structural distinction, examination of the literature indicates that the NCO ligand can coordinate to a metal via a variety of modes, which include a kα terminal (bound through either nitrogen or oxygen), a µ–kα bridge (bound through either nitrogen or oxygen), and a µ–(O,N)–kα bridge in an end-to-end manner bound through both nitrogen and oxygen; of these coordination modes, only approximately 7% exhibit the bridging mode observed for [(Tptm)- Cd(µ-NCO)]2 and there are only two cadmium examples with this coordination mode.14c Listed in the Cambridge Structural Database (CSD, Version S.374).

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