

Cadmium Compounds with an $[N_3C]$ Atrane Motif: Evidence for the Generation of a Cadmium Hydride Species

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S Supporting Information

ABSTRACT: Tris(2-pyridylthio)methane ([Tptm]H) has been employed to synthesize a series of cadmium carbatrane compounds that feature an $[N_3C]$ coordination environment. Specifically, [Tptm]H reacts with $Cd[N(SiMe_3)_2]_2$ to afford [Tptm]CdN(SiMe₃)₂, which thereby provides access to other derivatives. For example, [Tptm]CdN(SiMe₃)₂ reacts with (i) CO₂ to form {[Tptm]Cd(μ -NCO)}₂ and (ii) Me₃SiOH and Ph₃SiOH to form {[κ^3 -Tptm]Cd(μ -OSiMe₃)}₂ and [Tptm]-CdOSiPh₃, respectively. The siloxide compound {[κ^3 -Tptm]Cd(μ -OSiMe₃)}₂ reacts with Me₃SiX (X = Cl, Br, O₂CMe) to give [Tptm]CdX, while the reaction with PhSiH₃ in the presence of CO₂ generates the formate complex, [Tptm]CdO₂CH, thereby providing evidence for the generation of a proposed cadmium hydride intermediate, {[Tptm]CdH}.

Whereas zinc is of pivotal importance to human health,¹ its congeners, cadmium and mercury, are toxic.² 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.¹ 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 analogues³ are of much value in providing insight into the structures and mechanism of metalloenzymes,⁴ 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}]ZnOCO₂H and [Tptm]ZnOCO₂H.^{5,6} 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)⁷ with $Cd[N(SiMe_3)_2]_2$ to afford [Tptm]CdN(SiMe₃)₂ (1), as illustrated in Scheme 1. The molecular structure of [Tptm]CdN(SiMe₃)₂ has been determined by single-crystal X-ray diffraction (Figure 1), which clearly demonstrates that the

Scheme 1

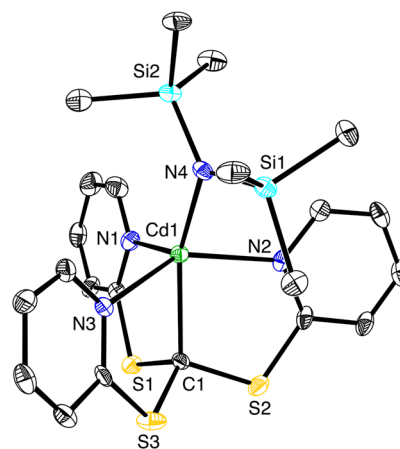
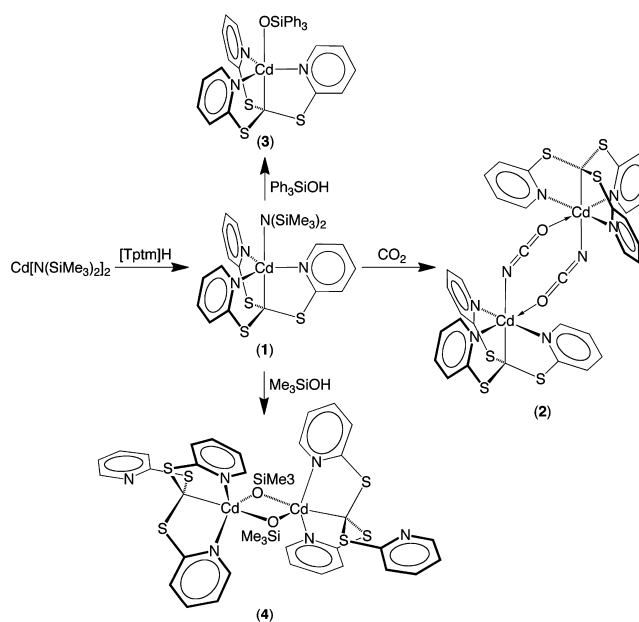


Figure 1. Molecular structure of [Tptm]CdN(SiMe₃)₂.

[Tptm] ligand coordinates in a κ^4 manner,⁸ thereby resulting in an atrane motif.^{9,10} In this regard, the structure of the cadmium carbatrane compound [Tptm]CdN(SiMe₃)₂ is very distinct from that of the zinc counterpart for which ¹H NMR spectroscopy

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demonstrates that the ligand coordinates in a κ^3 manner.^{6a,8} Despite the presence of the atrane motif in $[\text{Tptm}]\text{CdN}(\text{SiMe}_3)_2$, 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 τ_5 five-coordinate geometry index¹¹ for the two crystallographically independent molecules.

$[\text{Tptm}]\text{CdN}(\text{SiMe}_3)_2$ is a useful precursor for other cadmium derivatives, as illustrated by the reaction with 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 $[\text{Tptm}]\text{CdN}(\text{SiMe}_3)_2$ towards

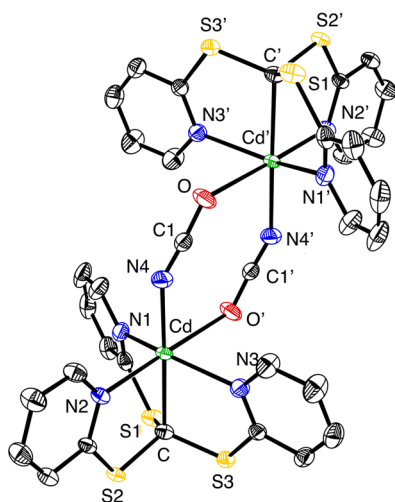


Figure 2. Molecular structure of $\{[\text{Tptm}]\text{Cd}(\mu\text{-NCO})\}_2$.

CO_2 is similar to that of the zinc counterpart $[\text{Tptm}]\text{ZnN}(\text{SiMe}_3)_2$,^{6a,12} a most interesting difference is that the cadmium complex $\{[\text{Tptm}]\text{Cd}(\mu\text{-NCO})\}_2$ is dinuclear with bridging NCO ligands, whereas the zinc complex $[\text{Tptm}]\text{Zn}(\text{NCO})$ possesses a terminal NCO ligand.^{13,14}

The Cd–N bond of $[\text{Tptm}]\text{CdN}(\text{SiMe}_3)_2$ is subject to facile protolytic cleavage, as illustrated by the reactions with Ph_3SiOH and Me_3SiOH to afford the siloxides $[\text{Tptm}]\text{CdOSiPh}_3$ (**3**) and $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ (**4**), respectively (Scheme 1). The molecular structures of $[\text{Tptm}]\text{CdOSiPh}_3$ ¹⁵ and $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ (Figure 3) have been determined by X-ray diffraction and reveal several notable features. For example, while the Ph_3SiO ligand coordinates in a terminal manner, the Me_3SiO ligand coordinates in a μ_2 manner, thereby resulting in a dimeric

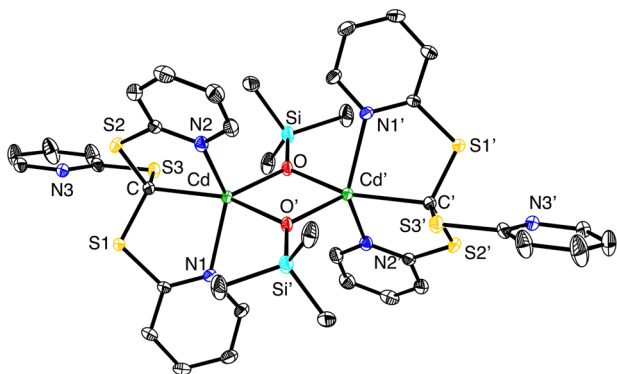


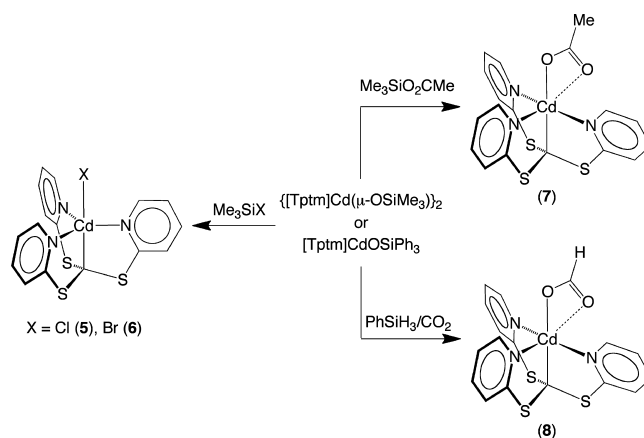
Figure 3. Molecular structure of $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$.

structure. The observation of both of these coordination modes is noteworthy because there is only one other cadmium siloxide compound listed in the Cambridge Structural Database (CSD),^{14d} namely $\text{Cd}_4\text{I}_4(\text{OSiMe}_3)(\text{NPET}_3)_3$,¹⁶ and it is tetranuclear with a triply bridging μ_3 -siloxide ligand.^{17,18}

In addition to the different coordination modes of the OSiPh_3 and OSiMe_3 ligands, the $[\text{Tptm}]$ ligands of $[\text{Tptm}]\text{CdOSiPh}_3$ and $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ also adopt different coordination modes. Thus, whereas $[\text{Tptm}]\text{CdOSiPh}_3$ exhibits an atrane motif with κ^4 coordination, $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ exhibits κ^3 coordination. Not only do $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ and $[\text{Tptm}]\text{CdOSiPh}_3$ illustrate the dramatic impact of varying the substituents on silicon, but the structure of $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ 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, with a terminal siloxide ligand. As such, $[\text{Tptm}]\text{ZnOSiMe}_3$ more resembles $[\text{Tptm}]\text{CdOSiPh}_3$ than the trimethylsiloxide derivative, $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$.

The trimethylsiloxide derivative $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ also provides access to a variety of cadmium compounds. For example, $\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ reacts with Me_3SiX ($\text{X} = \text{Cl}, \text{Br}, \text{O}_2\text{CMe}$) to form the halide and acetate derivatives $[\text{Tptm}]\text{CdCl}$, $[\text{Tptm}]\text{CdBr}$, and $[\text{Tptm}]\text{CdO}_2\text{CMe}$ (**5–7**), as illustrated in Scheme 2. The iodide compound, $[\text{Tptm}]\text{CdI}$, has

Scheme 2



also been obtained by metathesis of $[\text{Tptm}]\text{Li}$ with CdI_2 . X-ray diffraction studies demonstrate that the halide compounds, $[\text{Tptm}]\text{CdX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$),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 difference in the Cd–O bond lengths ($\Delta d = 0.22 \text{ \AA}$).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 $\Delta d = 0.44 \text{ \AA}$.^{6a}

$\{[\kappa^3\text{-Tptm}]\text{Cd}(\mu\text{-OSiMe}_3)\}_2$ also reacts with PhSiH_3 , which, in the presence of 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 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

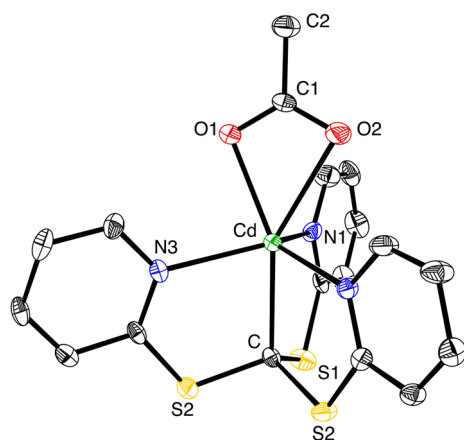


Figure 4. Molecular structure of 5.

CO₂ into a cadmium hydride bond. Such reactivity is of relevance to the discovery of potential methods for functionalizing CO₂.²² Also of note, the formate ligand of [Tptm]CdO₂CH coordinates in a bidentate manner ($\Delta d = 0.22$ Å), which is not only in contrast to the zinc counterpart, [Tptm]ZnO₂CH, which exhibits a well-defined unidentate coordination mode ($\Delta d = 0.63$ Å),^{6a} but also in contrast to other cadmium formate compounds. For example, the smallest Δd for a mononuclear formate compound listed in the CSD has a value of 0.75 Å.^{21f}

The proposed intermediacy of a cadmium hydride species is noteworthy because such species are not well precedented 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^{*}CdH and [Ar'Cd(μ -H)]₂, as reported by Power et al.²³ In addition, spectroscopic evidence has been presented by Reger et al. for the tris(pyrazolyl)hydroborate compound [Tpt^{t-Bu}]CdH.²⁴ With respect to the reactivity of these complexes, [Ar'Cd(μ -H)]₂ is unstable at room temperature and decomposes to [Ar'Cd]₂,^{23b} an observation that is in accord with the paucity of cadmium hydride compounds.

With the exception of {[κ^3 -Tptm]Cd(μ -OSiMe₃)}₂, each of the cadmium compounds described above features an atrane motif in which the [Tptm] ligand coordinates in a κ^4 manner. While tetradentate tripodal ligands that give rise to atrane structures are common, the majority feature an L-type²⁵ donor as the bridgehead,^{9,10,26} as exemplified by tris(2-pridyl)amine.^{26b,27} Tetradentate tripodal ligands that feature X-type or Z-type bridgeheads have received comparatively little attention,^{28–30} such that the carbatrane compounds described herein, with transannular Cd–C interactions, represent a notable development in cadmium chemistry.

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_{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(SiMe₃)₂ to 2.383(7) Å for [Tptm]Cd(O₂CMe), while the average Cd–N bond lengths range from 2.285 Å for [Tptm]CdOSiPh₃ to 2.368 Å for [Tptm]CdN(SiMe₃)₂. In most cases, the Cd–C bond length is slightly longer than the average Cd–N bond length. For

Table 1. Cd–C and Cd–N Bond Lengths in [Tptm]CdX Derivatives

	$d(\text{Cd}-\text{C})/\text{\AA}$	$d(\text{Cd}-\text{N}_{\text{av}})/\text{\AA}$
[Tptm]CdN(SiMe ₃) ₂	2.332(6)	2.368
	2.343(6)	2.372
{[κ^3 -Tptm]Cd(μ -OSiMe ₃)} ₂	2.334(4)	2.334
[Tptm]CdOSiPh ₃	2.337(10)	2.285
{[Tptm]Cd(μ -NCO)} ₂	2.347(4)	2.314
[Tptm]CdO ₂ CMe	2.383(7)	2.320
[Tptm]CdO ₂ CH	2.370(9)	2.316
[Tptm]CdCl	2.372(6)	2.312
[Tptm]CdBr	2.368(6)	2.303
[Tptm]CdI	2.363(11)	2.322

comparison, zinc compounds that feature the {[Tptm]Zn} atrane motif exhibit a similar trend in terms of their Zn–C (2.11–2.22 Å) and Zn–N_{av} (2.04–2.14 Å) bond lengths,³¹ with the Zn–C bond length being slightly longer. As would be expected, the Cd–C and Cd–N_{av} bonds are longer than the corresponding bond lengths for zinc, with values that are comparable to the difference in the covalent radii (ca. 0.2 Å) of zinc and cadmium.³² The larger size of cadmium is, therefore, one factor that is responsible for the different types of structures that are described above, such as (i) the adoption of a dinuclear octahedral structure for {[Tptm]Cd(μ -NCO)}₂ and a mononuclear five-coordinate structure for the zinc counterpart [Tptm]ZnNCO and (ii) greater degrees of bidenticity in the cadmium carboxylate compounds [Tptm]CdO₂CR (R = H, Me) than in the zinc derivatives.

In summary, the reaction of [Tptm]H with Cd[N(SiMe₃)₂]₂ affords [Tptm]CdN(SiMe₃)₂, which thereby provides access to a series of other carbatrane compounds that possess an [N₃C] coordination environment. Structural characterization by X-ray diffraction reveals significant differences with zinc counterparts, such as the observation that the NCO ligands in {[Tptm]Cd(μ -NCO)}₂ bridge two cadmium centers whereas the NCO ligand in [Tptm]ZnNCO is terminal, and further illustrates the versatility of [Tptm] as a supporting ligand.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02196.

Experimental details (PDF)

X-ray crystallographic data in CIF format (ZIP)

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Notes

The authors declare no competing financial interest.

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- (13) The NMR spectra of {[Tptm]Cd(μ-NCO)}₂ and {κ³-Tptm}-Cd(μ-OSiMe₃)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 κ¹ terminal (bound through either nitrogen or oxygen), a μ–κ¹ bridge (bound through either nitrogen or oxygen), and a μ–(O,N)–κ² bridge in an end-to-end manner bound through both nitrogen and oxygen;^{14a} 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^{14b,c} listed in the Cambridge Structural Database (CSD, Version 5.37).^{14d} (a) Mahendrasinh, Z.; Ankita, S.; Kumar, S. B.; Escuer, A.; Suresh, E. Cyanato bridged binuclear nickel(II) and copper(II) complexes with pyridylpyrazole ligand: Synthesis, structure and magnetic properties. *Inorg. Chim. Acta* **2011**, *375*, 333–337. (b) Hegemann, C.; Tyrre, W.; Neudorfl, J. M.; Mathur, S. Synthetic and structural investigations on the reactivity of the Cd–I bond in [ICd{Zr₂(OPrⁱ)₉}] to construct new mixed-metal alkoxides. *Organometallics* **2013**, *32*, 1654–1664. (c) Solanki, A.; Sadhu, M. H.; Kumar, S. B.; Mitra, P. Zinc(II) and cadmium(II) complexes with N₄-coordinate pyrazole based ligand: Syntheses, characterization and structure. *J. Mol. Struct.* **2014**, *1076*, 475–482. (d) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2016**, *B72*, 171–179.
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