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Communications

A Heterocumulene Metathesis Route to Cd[ESiMe₃]₂ and Passivated CdE (E = S and Se) Nanocrystals

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The preparation and investigation of well-defined clusters and nanocrystals of ME semiconductors, where M = Zn, Cd, Hg, and Pb and E = S, Se, and Te, have been the focus of considerable attention given that the ability to fine-tune the fundamental electronic and optical properties of these structures by simply varying size, rather than composition, makes them highly attractive for a variety of possible applications.¹ In this pursuit, trialkylsilylchalcogenides and -chalcogenolates have played key roles in the development of low-temperature routes to these materials. For instance, the bis(trialkylsilyl)chalcogenides, [R₃Si]₂E (E = S, Se, and Te), have been used as convenient chalcogenide atom-transfer reagents in the formation of ME nano-

crystals from metal halides.^{1a} More recently, Arnold and co-workers² have shown that the cadmium tris-(trimethylsilyl)silylchalcogenolates, {Cd[ESi(SiMe₃)₃]₂}₂ (E = S, Se, and Te), which undergo facile eliminations of E[Si(SiMe₃)₃]₂, can serve as low-temperature, single-source molecular precursors to CdE bulk materials and thin films. To explore the full extents and limitations of this latter condensation process further and, more specifically, for the possible production of CdE nanocrystals, it is desirable to have a range of readily available Cd[ESiR₃]₂ starting materials for study. Unfortunately, the acquisition of such compounds by conventional salt elimination and protolytic ligand metathesis reactions is hampered by (a) the general lack of the pure reagents, M'ESiR₃ (M' = Li, Na, K) and HESiR₃, respectively, except where E = S and/or R is a bulky ligand,^{3,4} and (b) the known problems associated with obtaining salt-free compounds using the former synthetic method. Accordingly, in light of our recent successes in using heterocumulene metathesis to prepare group 14 s² trimethylsilylanolates from metal trimethylsilylamides that are then subsequently employed to obtain polynuclear metal oxo clusters via (Me₃Si)₂O eliminations,^{5,6} we initiated a program to determine if heterocumulene metathesis could be extended as a synthetic tool to prepare Cd[ESiR₃]₂ compounds under

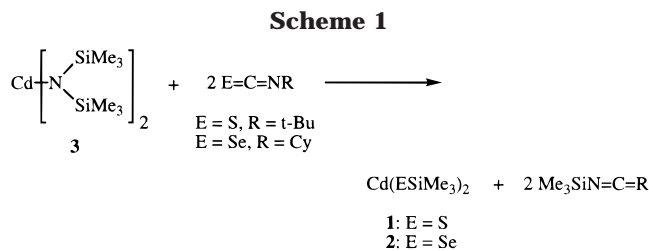
(1) (a) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046–3050. (i) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183–188. (b) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403–409. (c) Herron, N.; Calabrese, J. C.; Farneth, W. E. *Science* **1993**, *259*, 1426. (d) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715. (e) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335. (f) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226–13239. (g) Yang, J. P.; Qadri, S. B.; Ratna, B. R. *J. Phys. Chem.* **1996**, *100*, 17255–17259. (h) Trindade, T.; O'Brien, P. *Chem. Mater.* **1997**, *9*, 523–530.

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(3) NaSSiMe₃ can be prepared in low yield and has been used to prepare metal trimethylsilylthiolates; see, for example: (a) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809–3812. (b) Liang, H.-C.; Shapley, P. A. *Organometallics* **1996**, *15*, 1331–1333.

(4) For the use of HSSiPh₃, see: (a) Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Toomey, L. M. *Organometallics* **1996**, *15*, 3653–3658. For the use of HSSi(OBu)₃, see: Wojnowski, W.; Becker, B.; Walz, L.; Peters, K.; Peters, E. M.; von Schnering, H. G. *Polyhedron* **1992**, *11*, 607–612.

(5) (a) Sita, L. R.; Babcock, J. R.; Xi, R. *J. Am. Chem. Soc.* **1996**, *118*, 10912–10913. (b) Xi, R.; Sita, L. R. *Inorg. Acta Chim.* **1998**, *270*, 118–122. (c) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1998**, *120*, 5585–5586.



mild and salt-free conditions by employing thio- and selenoiscyanates, SCNR and SeCNR, respectively, as chalcogenide atom-transfer reagents. Herein, we now report the first success of this program that details the direct preparation of the previously unknown compounds, $[\text{Cd}(\text{ESiMe}_3)_2]_n$ (E = S and Se) (**1** and **2**, respectively), from readily available $\text{Cd}[\text{N}(\text{SiMe}_3)_2]_2$ (**3**)⁷ that proceeds according to Scheme 1. Importantly, we further document that if this metathesis process is conducted in the presence of trioctylphosphine oxide (TOPO), high yields of TOPO-passivated CdE nanocrystals that exhibit strong room-temperature emission can be obtained at 25 °C via TOPO-induced condensation of **1** and **2**. Given the efficiencies by which both of these processes occur, heterocumulene metathesis now holds promise as a new synthetically attractive route to other metal trialkylsilylthiolates and -selenolates, and thereby, other classes of ME clusters, nanocrystals, and bulk materials.

To begin, addition of 2 equiv of *tert*-butylisothiocyanate, Bu^tNCS , to a solution of **3** in toluene at 25 °C resulted in the rapid formation of a nearly white insoluble material and the carbodiimide, $\text{Bu}^t\text{N}=\text{C}=\text{NSiMe}_3$, thus indicating that metathesis had occurred. This was confirmed by isolation of the insoluble product which was revealed to be pure **1** on the basis of chemical analysis.⁸ Following this metathesis process by ¹H NMR spectroscopy showed that it proceeded quantitatively; however, it was also noted that, if the reaction was allowed to stand for much longer times, there was growth of a resonance corresponding to $(\text{Me}_3\text{Si})_2\text{S}$, with a concomitant yellowing of the material, thereby suggesting that condensation was slowly occurring, potentially as a result of small traces of impurities.⁹ A similar reaction between **3** and 2 equiv of cyclohexyliselenocyanate, CyNCS_e , prepared from cyclohexylisocyanide and selenium metal,¹⁰ led to an immediate precipitation of an orange material and the appearance in the ¹H NMR spectrum of both $\text{CyN}=\text{C}=\text{NSiMe}_3$ and a new resonance presumed to be $(\text{Me}_3\text{Si})_2\text{Se}$. Subsequent isolation and characterization of this orange material revealed that, while metathesis was complete (i.e., no nitrogen present), **2** had apparently undergone facile condensations to provide a material that is best de-

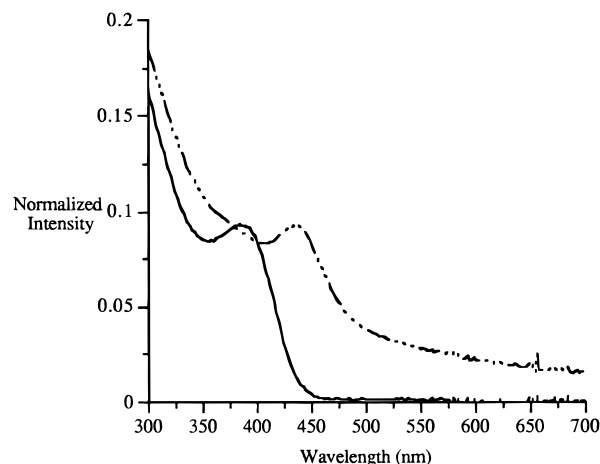


Figure 1. Electronic spectra for TOPO-passivated CdS (solid line) and CdSe (dash-dotted line) nanocrystals.

scribed as being $[\mathbf{2} \cdot (\text{CdSe})_n]$. Unfortunately, all attempts to limit the extent of this condensation of **2** were unsuccessful.

To obtain soluble coordination complexes of **1** and **2**, metathesis was carried out in the presence of several types of σ -donors, and these were found to dramatically affect the outcome of the reaction in different ways. First, addition of 1.2 equiv of tetramethylethylenediamine (TMEDA) to the initial solution of **3** attenuated the rate of metathesis to such an extent that it became possible to cleanly produce, and spectroscopically characterize in solution, the heteroleptic compound $\{\text{Cd}[\text{N}(\text{SiMe}_3)_2](\text{SSiMe}_3)\}_n$ (**4**) [¹H NMR (400 MHz, benzene-*d*₆, 25 °C) δ 0.19 (s, 18 H), 0.43 (s, 9H); ¹¹³Cd{¹H} NMR (88.8 MHz, benzene-*d*₆) δ 426 ppm], that arises from mono-metathesis.¹¹ Although attempts to isolate **4** in solid form resulted in disproportionation to **1** and **3**, this compound could nonetheless be used to prepare, through protolysis with HXR, other solution-stable heteroleptic cadmium compounds, such as $\{\text{Cd}[\text{XR}](\text{SSiMe}_3)\}_n$ [$\text{X} = \text{O}$, R = 2,6-di-*tert*-butyl-4-methylphenyl, ¹¹³Cd{¹H} NMR δ 375 ppm; X = O, R = SiPh₃, δ 398 ppm; and X = S, R = SiPh₃, δ 355 ppm]. Finally, treatment of **4** with 1 equiv of Bu^tNCS resulted in, once more, rapid formation of insoluble **1**.

Surprisingly, replacement of TMEDA with 1 equiv of trioctylphosphine oxide (TOPO) as the σ -donor additive resulted in the metathesis reaction taking a different course. In this case, both reactions of **3** with Bu^tNCS and CyNCS_e in toluene provided colored, but clear, solutions: yellow in the case of Bu^tNCS and orange in the case of CyNCS_e . Upon removal of the toluene in vacuo, it was found that the crude products could be freely dissolved in pentane, and the electronic spectra of these solutions indicated that these cadmium-containing materials were, in fact, comprised of TOPO-passivated CdE (E = S and Se) nanocrystals (λ_{max} 384 for CdS and 438 nm for CdSe) that are, on average, 1.5–2.0 nm in diameter (see Figure 1).^{1e–h} This conclusion was further verified for the CdS(TOPO) material by first replacing the coordinated TOPO with coordinated dodecanethiol by dissolving and stirring the material in the latter reagent for 18 h. After the volatiles were removed

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(8) Anal. Calcd for $\text{C}_6\text{H}_{18}\text{S}_2\text{Si}_2\text{Cd}$: C, 22.32; H, 5.62. Found: C, 22.64; H, 5.29.

(9) Amines are known to catalyze the condensation of metal alkoxides; see: McGeary, M. J.; Wedlich, R. C.; Coan, P. S.; Folting, K.; Caulton, K. G. *Polyhedron* **1992**, *11*, 2459–2473.

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(11) It is assumed that, at 25 °C, **4** is in rapid equilibrium in solution with its TMEDA complex.

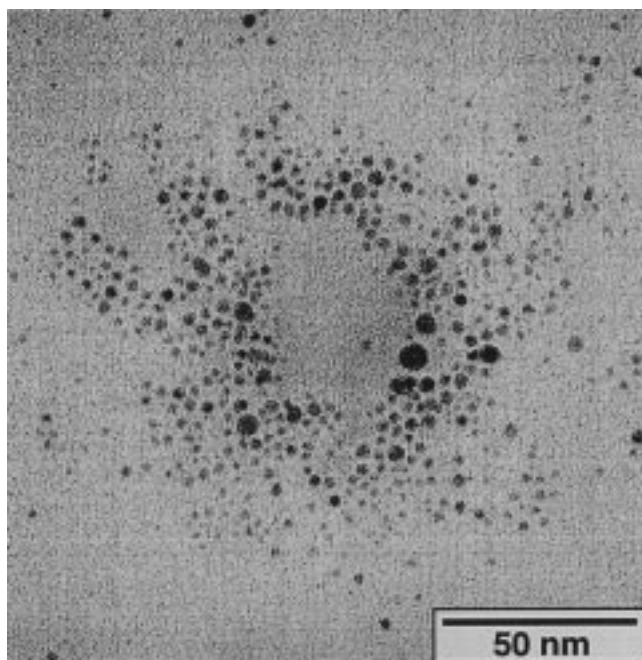


Figure 2. TEM of dodecanethiol-passivated CdS nanocrystals prepared at room temperature.

in vacuo, the crude product was purified by multiple (ca. 3×) toluene/ethanol precipitations until both ^1H NMR (benzene- d_6) and IR spectroscopy showed excess TOPO and dodecanethiol to be absent. This purified material was then subjected to transmission electron microscopy (TEM), which served to provide the average size and polydispersity of the nanocrystals. As shown in Figure 2, the dodecanethiol-passivated CdS nanocrystals were indeed found to be roughly 1.5–2.0 nm in diameter, but there also appeared to be a broad range of sizes present. However, it is important to point out that, at the present time, no attempts have yet been made to either modify reaction conditions that might lead to different size selectivities or to obtain more monodisperse samples through size-selective precipitations. Finally, of major significance was the finding that the dodecanethiol-passivated CdS nanocrystals exhibited strong room-temperature emission which suggests that, as formed by the present method, they possess few surface defect sites (see Figure 3).^{1b,f}

In conclusion, we have demonstrated the first use of heterocumulene metathesis as a synthetic tool that

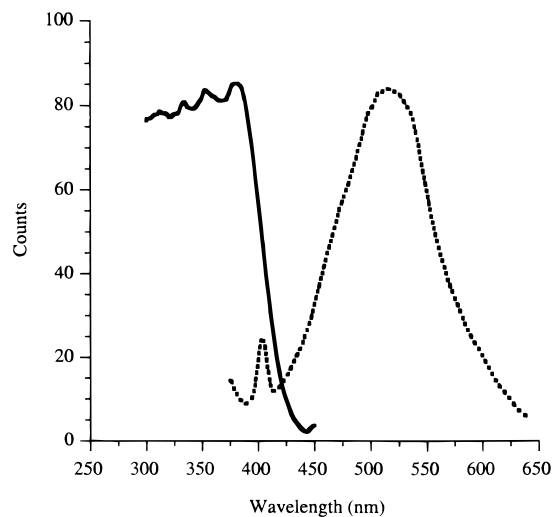


Figure 3. Excitation (solid) and emission (dotted) spectra for dodecanethiol-passivated CdS nanocrystals prepared according to the text. Note: the small maximum at 402 nm is an instrumental artifact.

can be used to prepare metal trimethylsilylthiolates and -selenolates under mild conditions. In the present study, it is noteworthy that passivated CdS and CdSe nanocrystals can be obtained at room temperature from the readily available starting material $\text{Cd}[\text{N}(\text{SiR}_3)_2]_2$ ($\text{R} = \text{Me}$). We are now in the process of modifying both the nature of the SiR_3 group and the reaction conditions in order to provide a higher degree of control over size distributions. In addition, we are exploring the use of heterocumulene metathesis for the preparation of passivated, low band gap, PbE clusters and nanocrystals for which few synthetic methods are currently available.^{1g} The results of these investigations will be reported in due course.

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