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Communications

Formation of Metal–Chalcogen Bonds by the Reaction of Metal Alkyls with Silyl Chalcogenides

Mild chemical reactions that result in the formation of metal–non-metal bonds are important to the synthesis of both molecular and solid-state compounds. The longer the list of reactions that form covalent bonds between inorganic elements, the more versatile and general the synthesis methodology will be. This will lead in turn to its application to a wider variety of practical problems. Recently, we have been studying metal chalcogenides as model systems, hoping to find new reactions that will be useful in materials synthesis.[1] The simplest of the solid-state metal chalcogenides are the so-called II–VI materials, the one-to-one binary compounds containing a group IIB metal and a group VIB non-metal. These materials not only are technologically important but also are chemically and structurally simple and are therefore attractive as synthesis targets in model studies.

A number of reactions that give bonds between group IIB metals and chalcogens have been known for quite some time. Three of these (in which the solid-state compound CdSe is used as the example product) are shown in eq 1–3.[2-4] All of these reactions

$$CdSO_4 + Na_2Se \xrightarrow[-Na_2SO_4]{} CdSe \tag{1}$$

$$CdMe_2 + H_2Se \xrightarrow[-2CH_4]{} CdSe \tag{2}$$

$$CdCl_2 + Se(SiMe_3)_2 \xrightarrow[-2Me_3SiCl]{} CdSe \tag{3}$$

are very useful and are of widespread importance, but there are some limitations to their utility. Reactions 1 and 3 use ionic reagents. This limits the media in which the reactions can be conducted; they can generally not be run in organic solvents or in the gas phase. Reaction 2 does not suffer from this restriction, but the hydrogen chalcogenides are quite dangerous, being gaseous (at standard temperature and pressure) and highly toxic. In this communication, we report the use of an alternative reaction. In the dealkylsilylation reaction (an example of which is shown in eq 4), a simple metal alkyl and a silyl chalcogenide react to form

$$CdMe_2 + Se(SiMe_3)_2 \xrightarrow[-2SiMe_4]{} CdSe \tag{4}$$

a metal–chalcogen covalent bond and a carbon–silicon bond. All of the reagents are organic derivatives that are reasonably volatile; therefore, these reactions can be run in organic solvents or adapted to the vapor phase. The silyl chalcogenides, while still probably as toxic as the hydrogen chalcogenides, are liquids and are therefore safer. Using this method, we have been able to prepare II–VI solid-state compounds as well as metal–chalcogenide molecular compounds.

The solid-state compound CdSe can be prepared easily from the reaction of dimethylcadmium with bis(trimethylsilyl)selenium (hereafter, $Se(TMS)_2$) in toluene, heptane, THF, or dichloromethane.[5] Combination of the two reagents leads to the precipitation of a red-brown solid. When this solid is heated to 400 °C under vacuum, it quickly turns black. This black solid is identified by powder X-ray diffraction as polycrystalline CdSe. On the basis of the facts that no intense X-ray diffraction is seen and that no volatile materials evolve on heating, and on its color,[6] we believe that the red-brown solid is either amorphous CdSe or nanocrystalline CdSe in which the crystallite size is on the order of 50–75 Å.

In toluene, the rate of the reaction of $CdMe_2$ with $Se(TMS)_2$ is slow enough that the process can be followed by proton NMR spectroscopy. As the resonances due to the starting materials recede, one and only one new peak appears, and that peak is coincident with that due to $SiMe_4$. (Subsequent GC/MS analysis confirms the identification of this product as tetramethylsilane.) It is encouraging that no other proton-containing species are seen at any time during this reaction.

We have extended this synthesis to include the other II–VI materials ZnSe and CdTe (eq 5 and 6, Table I). This shows that

$$ZnEt_2 + Se(SiMe_3)_2 \xrightarrow[-2SiEtMe_3]{} ZnSe \tag{5}$$

$$CdMe_2 + Te(Si^iPrMe_2)_2 \xrightarrow[-2Si^iPrMe_3]{} CdTe \tag{6}$$

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(1) (a) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200. (b) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245. (c) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228. (d) Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52.

(2) See, for example, Fojtik, A.; Weller, H.; Kock, U.; Henglein, A. *Ber. Bunsen-Ges, Phys. Chem.* **1984**, *88*, 969.

(3) See, for example: Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 255.

(4) (a) Abel, E. W.; Jenkins, C. R. *J. Organomet. Chem.* **1968**, *14*, 285. (b) Schleich, D. M.; Martin, M. J. *J. Solid State Chem.* **1986**, *64*, 359–64. (c) Martin, M. J.; Qiang, G. H.; Schleich, D. M. *Inorg. Chem.* **1988**, *27*, 2804–8. For additional examples of dehalosilylations see: (d) Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277. (e) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706. (f) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Chem. Mater.* **1989**, *1*, 4.

(5) $CdMe_2$ (88 mg, 0.62 mmol; used as purchased from Alfa) and $Se(SiMe_3)_2$ (140 mg, 0.62 mmol; prepared as in ref 7) were combined in dry dichloromethane (1.0 mL). There was an immediate reaction to give a red-brown solid. The mixture was stirred at room temperature for 4 h and then filtered to give 109 mg of dry powder. This powder was annealed in vacuo (400 °C, 4 h) to give polycrystalline CdSe (108 mg, 0.56 mmol, 91%). The X-ray powder diffraction pattern shown by this material was recorded on a Rigaku Miniflex diffractometer. This pattern is identical with that shown by commercially available CdSe.

(6) 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.

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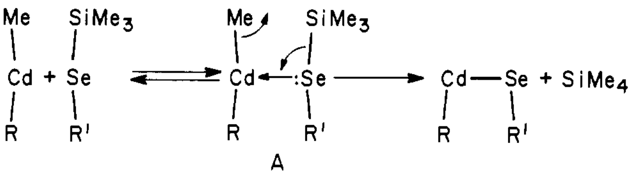
Table I

			reaction		annealing		
product	reagents	solvent	time	temp	time	temp	yield[a]
CdSe	$CdMe_2 + Se(TMS)_2$	CH_2Cl_2	4 h	*b*	4 h	400 °C	91 %
CdTe	$CdMe_2 + Te(IPDMS)_2$	CH_2Cl_2	15 min	*b*	2 h	400 °C	88 %
ZnSe	$ZnEt_2 + Se(TMS)_2$	Cl_3CCH_3	45 min	75 °C	18 h	400 °C	97 %

[a] Based on molecular starting materials. [b] Room temperature.

Scheme I



zinc alkyls are as useful in this process as those of cadmium, and that the tellurium compound, $Te(Si(iPr)Me_2)_2$ (hereafter, $Te(IPDMS)_2$)[7] is as useful in this sense as is $Se(TMS)_2$.

Dealkylsilylation is also useful in molecule synthesis. Our initial results are summarized in eq 7. The reaction of $CdMe_2$ with 2

$$CdMe_2 + 2PhESiMe_3 \xrightarrow[-2SiMe_4]{} \underset{1}{Cd(EPh)_2} \qquad (7)$$

$$(E = S, Se, Te)$$

equiv of $PhESiMe_3$ gives $Cd(EPh)_2$ (**1**).[8] The S and Se compounds are identical with those prepared by independent routes.[9-11]

We are not aware of previous reports of dealkylsilylations of the sort described above (although they bear some resemblance to the reaction of methyllithium with trimethylsilyl chloride to give tetramethylsilane and lithium chloride). The dealkylsilylation is a hybrid of the metathetical reactions 2 and 3, and arguing strictly by analogy, the process may be viewed either as protolytic (eq 2) with the trimethylsilyl group acting as the acid, or as a nucleophilic displacement at Si (eq 3) with the methyl group replacing chloride as the nucleophile.

The solvent has a dramatic effect on the rate of dealkylsilylation. The formation of CdSe in dichloromethane is instantaneous at room temperature. At comparable concentrations in toluene, the reaction is fairly slow, taking days to go to completion. In saturated hydrocarbons, the reaction is very slow, having a half-life of weeks at room temperature. Finally, there is no observable reaction between $CdMe_2$ and $Se(TMS)_2$ when the two are combined as neat liquids. Rates for the analogous reactions with $PhSeSiMe_3$ follow a similar trend. On the basis of these observations, we support a pathway in which the fundamental chemical step is that shown in Scheme I. We suggest that the reaction partners (MeCdR and Me_3SiSeR' in Scheme I, where R and R' are Me and $SiMe_3$, respectively, for the initial step and are fragments of the growing CdSe array in subsequent steps) form a coordination complex (A in Scheme I) which then eliminates the silane in a unimolecular way through a dipolar transition state. Although we have no direct proof for this proposal, the simplicity of the reaction (as indicated by the NMR study) argues against a less selective process such as one involving radicals.

The thermochemistry of these reactions is worth comment. We estimate that the Se–Si bond in $Se(TMS)_2$ is roughly 35 kcal/mol weaker than the C–Si bond in $SiMe_4$.[12] Since the average Cd–C bond in $CdMe_2$ is 33 kcal/mol,[13c] the dealkylsilylation must be quite exothermic. An additional consideration is that while the central atoms in both $CdMe_2$ and $Se(TMS)_2$ are two-coordinate, they are up to four-coordinate in the products. The strong donor–acceptor interactions (which are responsible for the insolubility of the products) further promote metal–chalcogen bond formation.

In bulk form, the II–VI compounds are all available in arbitrarily high purity via a number of simple routes, and for that reason, we made no attempt to optimize the dealkylsilylation for the preparation of the simple solid-state compounds. The utility of the general reaction will be in molecular synthesis and in vapor-phase processing. As mentioned above, all of the reagents in these reactions are volatile, and since the byproduct alkylsilanes are fairly inert, the dealkylsilylation is potentially applicable to the preparation of thin films of II–VI compounds by vapor-phase epitaxy. The attraction of the liquid source compounds is in their safety. Although the toxicity of the silyl chalcogenide compounds has not been established, they are safer if only because of their lower vapor pressure—an accident with these liquid sources is more easily contained than a similar accident with a pressurized toxic gas.

The use of the silyl tellurides highlights a particularly useful side of dealkylsilylation. Hydrogen telluride and tellurols (RTeH) are much less stable than the analogous sulfur and selenium compounds[14] and are therefore inconvenient for either materials or molecular synthesis. Silyl tellurides are easily prepared, purified, and handled, making them attractive synthesis reagents.

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Registry No. CdSe, 1306-24-7; $CdMe_2$, 506-82-1; $Se(TMS)_2$, 4099-46-1; $SiMe_4$, 75-76-3; $ZnEt_2$, 557-20-0; ZnSe, 1315-09-9; $Te(Si^iPrMe_2)_2$, 123676-74-4; CdTe, 1306-25-8; $PhSeSiMe_3$, 33861-17-5; $PhTeSiMe_3$, 73296-31-8; $Cd(SePh)_2$, 120138-29-6; $Cd(TePh)_2$, 123676-75-5; $PhSSiMe_3$, 4551-15-9; $Cd(SPh)_2$, 21094-83-7.

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(7) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1354–6.

(8) To $CdMe_2$ (0.20 g, 1.41 mmol) dissolved in CH_2Cl_2 (20 mL) was added $PhTeSiMe_3$ (0.80 g, 2.80 mmol). A yellowish precipitate began to form immediately. After 48 h, heptane (20 mL) was added to the mixture; the precipitate was collected by filtration and dried under vacuum to give a light yellow solid (0.50 g, 67%). Mp: yellows at 182 °C, goes red at 230 °C, and goes black at 280 °C. Anal. Calcd for $C_{12}H_{10}CdTe_2$: C, 27.6; H, 1.93; Cd, 21.5; Te, 48.9. Found (Schwarzkopf): C, 26.8; H, 1.89; Cd, 21.9; Te, 49.1. ^1H NMR (NC_5D_5, 30 °C): δ 7.97 (d, 2 H), 6.94 (t, 1 H), 6.75 (t, 2 H). Under identical conditions, $Cd(SePh)_2$[10] and $Cd(SPh)_2$[9] can be isolated as white solids in 81% and 58% yields respectively.

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(11) For a related tellurium complex see ref 1a.

(12) This estimate is based on data in ref 13. Comparison of data in ref 13a,b shows that the S–H and S–C bonds are 10–15 kcal/mol stronger than the corresponding Se–H and Se–C bonds, respectively. In ref 13a, the strength of the S–Si bond is given as 54 kcal/mol. Assuming that the sulfur to selenium comparison is valid, this gives a Se–Si bond strength of 39–44 kcal/mol. Reference 13c gives the Si–C bond strength as 77 kcal/mol, resulting in the difference cited in the text.

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(14) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1980; p 511. (b) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1974; p 58.

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