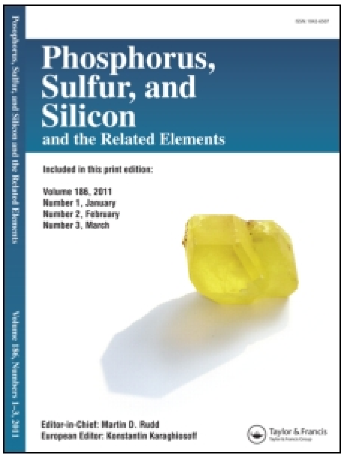

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CHALCOGENOAMIDES: CONVENIENT PREPARATIONS AND REACTIONS WITH METAL COMPOUNDS

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New Al-E (E: S, Se, Te) reagents, mixtures of $(^{i}Bu_2AlE)_2$ and $(^{i}BuAlE)_n$, were produced by the reaction of $^{i}Bu_2AlH$ with elemental chalcogens. They directly convert amides to chalcogenoamides. Seleno- and telluroamides serve as the ligands in their metal complexes or react with MAc_2 (M: Zn, Cd, Hg) to give MSe or MTe powders.

Keywords: aluminum-sulfur; aluminum-selenium; aluminum-tellurium; chalcogenoamides; metal selenides; metal tellurides

INTRODUCTION

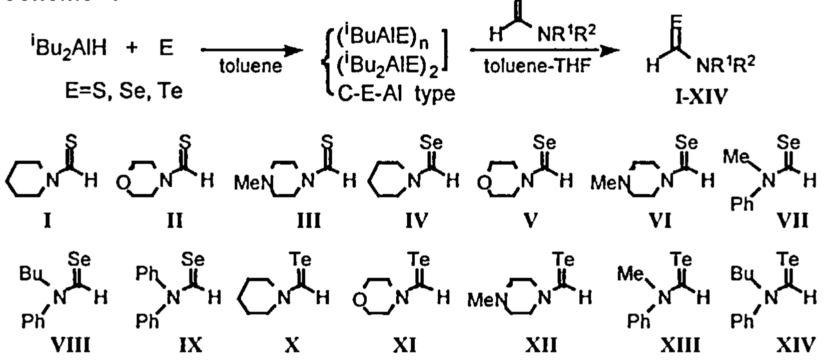
Cadmium telluride (CdTe) is considered to be one of the next-generation semiconducting materials.[1] Based upon the experience with metal sulfide and selenide semiconducting thin films (eqs.1, 2),[2] telluro-carbonyls could be useful in the preparation of metal telluride films.

$$Me(H_2N)C{=}S \quad + \quad MX_2 \xrightarrow{\hspace{2em}} \underset{\text{(M: Cu, Zn, Cd, Pb, etc.)}}{\text{MS thin films}} \qquad (1)$$

$$Me_2N(H_2N)C{=}Se \quad + \quad MX_2 \xrightarrow{\hspace{2em}} \text{MSe thin films} \qquad (2)$$

Free tellurocarbonyls [3] are still difficult to prepare, although the chemistry of organotellurium compounds has been studied for a long time.[4] We have recently described the syntheses and crystal stuctures of two telluroamides.[3f] The synthetic procedure involves the reaction of amides with bis(dimethylaluminum) telluride or selenide, $(Me_2Al)_2E$ (E: Te or Se),[5] in which aluminum plays a key role to replace the carbonyl oxygen with a Te or Se atom. In this paper, we report that new Al-E reagents, a mixture of $(^iBu_2AlE)_2$ and $(^iBuAlE)_n$ (E: S, Se, Te), undergo reaction with amides and convert them to thio-, seleno-, and telluroamides (Scheme 1). Also, the properties of selenoamides and telluroamides as ligands in metal complexes or as precursors of metal selenides and tellurides have been investigated.

Scheme 1



RESULTS AND DISCUSSION

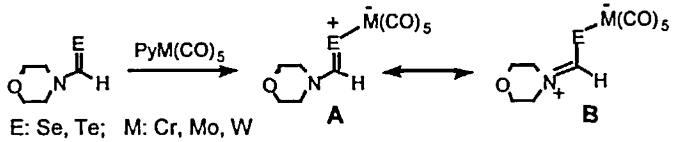
Under an argon atmosphere, a mixture of $^{i}Bu_2AlH$ (1.5 M solution in toluene) and one equivalent of Se or Te powder was heated at 120-130_C for 1-2h. Mass spectrometry confirmed that hydrogen and isobutane gases were evolved from the reaction. This indicated the formation of $(^{i}Bu_2AlE)_2$ and $(^{i}BuAlE)_n$. ^{1}H NMR measurement showed that only a small amount of C-Se-Al or C-Te-Al type compound was formed (a doublet at δ 2.65 ppm arising from CH_2 bonded to Se; a doublet at δ 3.4 from CH_2-Te). All other signals appeared at the same region as (but they are more complicated than) those observed for the starting material $^{i}Bu_2AlH$.

Because of its exothermic nature, the reaction between $^{i}Bu_2AlH$ and sulfur was carried out at lower temperatures. After stirring at 5-10_C for 1h and then 30-40_C for 2h, all sulfur dissolved to give a white suspension, a mixture of several Al-S compounds.

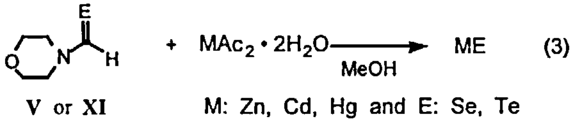
These reagents are too unstable to be purified or fully characterized. They may be utilized, as prepared, *in situ*. By reaction with these reagents, amides were efficiently converted to the corresponding thio-, seleno-, and telluroamides (**I-XIV**) in the yields of 49-70%. All sulfur and selenium compounds demonstrated the expected spectral and analytical data. Tellurium compounds showed the expected NMR (^{1}H, ^{13}C, ^{125}Te) and mass spectra, but did not give good elemental analyses due to decomposition.

The availability of seleno- and telluroamides has enabled us to investigate their metal complexes. 4-Selenoformylmorpholine (**V**) and 4-telluroformylmorpholine (**XI**) underwent reaction with $PyM(CO)_5$ in THF to afford $C_5H_9NOE\text{-}M(CO)_5$ where E is Se or Te and M is Cr, Mo, or W (Scheme 2).[6] Their structures are better described as resonance forms **A** and **B**, of which **B** is the more important.

Scheme 2



One of the applications of organochalcogen compounds is to be used for solid-state material synthesis. Steigerwald and co-workers have used R_3PTe [7a-c] and $(^iPrMe_2Si)_2Te$ [7d] to prepare metal tellurides (MTe, M is Pd, Hg, Co, Cd). In this work, we have found that 4-telluroformylmorpholine (**XI**) and 4-selenoformylmorpholine (**V**) react with MAc_2 (M is Zn, Cd, Hg) in methanol solution to give MTe and MSe powders in 95-98% yields (eq.3). When heated at 300_C for 2h, both red CdTe and CdSe powders turned black. They were indentified as cubic crystalline CdTe and hexagonal CdSe by powder XRD.



Acknowledgments

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