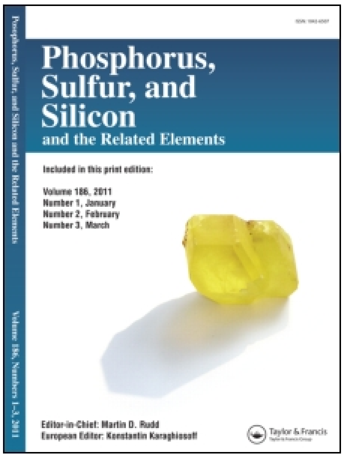

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Main Group and Transition Metal-Selenolate Complexes: Rings to Clusters

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The utility of silylated selenium reagents Se(R)SiMe$_3$ in synthesizing polynuclear metal-selenolate complexes, [M-ER]$_n$, is illustrated. This paper describes the synthesis and characterization of transition metal and bismuth-selenolate complexes.

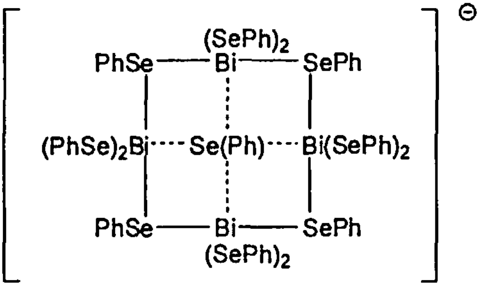
Keywords: cluster; selenolate; silylated reagents; metal

INTRODUCTION

Interest in metal-selenolate complexes can be attributed to advances on many fronts including their use as reagents in organic synthesis,[1] precursors to metal-selenide extended solids and thin films [2] and the photophysics of nanometer-sized metal-selenide-selenolate complexes.[3] Synthetic routes into transition metal selenolate complexes include the insertion of elemental selenium into metal-carbon bonds, oxidative addition of R_2E_2 onto late transition metal centers, the reaction of alkali metal-chalcogenolates or chalcogenols with transition metal-halide complexes and the reaction of silylated chalcogen reagents with metal-salts.[4] The latter method proceeds with the generation of X-$SiMe_3$, which remains in solution, thus facilitating isolation and crystallization of the formed "M-ER" complexes.

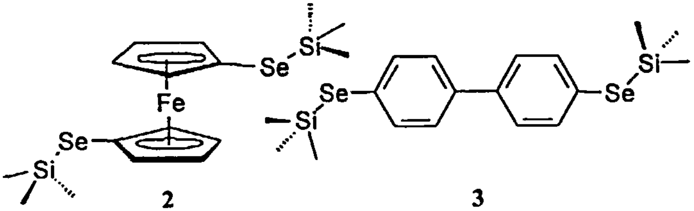
RESULTS AND DISCUSSION

The reactions of Se(R)$SiMe_3$ complexes and metal salts to yield M-Se bonds is a widely applicable, to both transition and main group metals. Thus the reaction of $BiBr_3$ with three equivalents Se(Ph)$SiMe_3$ with solubilizing PPr_3 ligands results in the displacement of the Bi-Br bonds and the formation $[Bi_4(\mu\text{-}SePh)_5(SePh)_8][HPPr_3]$ **1** in moderate yields, after work-up in protic solvents.[5] The formation of **1** illustrates the effectiveness of silyl reagents in displacing (in this case three) halide ligands from the starting metal, and the effectiveness of Se(Ph) ligands in bridging (in this case non-bonded main group) metal centers. The formation of **1** was accompanied by the isolation of bismuth metal and Ph_2Se_2 in the reaction mixtures, accounting for the low yields of the polynuclear complex.



1

The synthesis of $Se(R)SiMe_3$ reagents is readily carried out by insertion of elemental Se into C-Li or C-MgX bonds, followed by reaction with $ClSiMe_3$ to yield alkyl- and aryltrimethylsilylselenoethers in workable yields.[6] We have also demonstrated that it is possible to use similar synthetic strategies to synthesize bis(trimethylsilyl)chalcogenolates. Thus 1,1-bis(trimethylsilylseleno)ferrocene **2** and 4,4'-bis(trimethylsilylseleno)biphenyl **3** were prepared in 65% and 56% yields, respectively, from the corresponding dilithiodiselenolate salts.[7]



2

3

The organometallic complex **2** was isolated from the reaction of $ClSiMe_3$ and $[Fe(\eta^5-C_5H_5SeLi)_2\cdot(TMEDA)]$ in pentane at 0 °C.

After removal of LiCl, the filtrate was concentrated slowly to afford X-ray quality golden orange crystals of **2**. The cyclic voltammogram of **2** displayed (Figure 1) one irreversible oxidation wave at +0.375 V (*vs.* SCE), complicated by the deposition of the material onto the electrode surface. This deposit of **2** onto the electrode is presumably a consequence of the Se-Si bonds as other $[Fe(\eta^5\text{-}C_5H_4ER)_2]$ complexes do not display this behavior.[8]

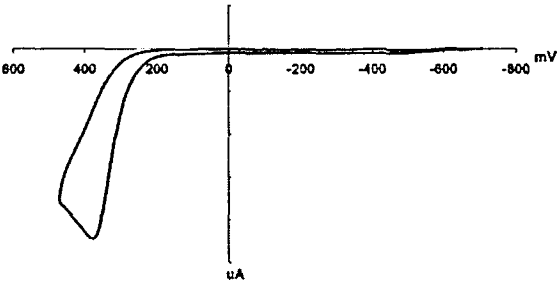
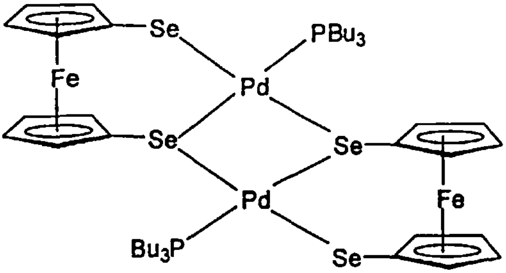


FIGURE 1. Cyclic voltammogram of **2** in THF solution (scan rate 100 mV s^{-1}).

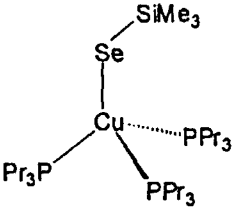
The reaction of **2** and *trans*-$PdCl_2(PBu_3)_2$ proceeds with the expected displacement of the two chloride ligands and the formation of Pd-Se bonds. Concomitant with the formation of these bonding interactions, two Se centers adopt a (preferred) bridging coordination mode *via* the displacement of a PBu_3 ligand from the platinum centers and the formation of $[Pd_2(PBu_3)_2\{\mu_2\text{-}Fe(\eta^5\text{-}C_5H_4Se)_2\}_2]$ **4** in good yield. The structure of **4** is comprised of two ferrocenyl units at the periphery of a planar Pd_2Se_4 array that contains a central Pd_2Se_2 ring, the connectivity confirmed with a single crystal X-ray diffraction analysis.[9]



4

The cyclic voltammogram of 4 in DMF/0.1 M Bu_4NBF_4 displayed two reversible, one-electron oxidation waves at +0.354 V and +0.560 V (*vs.* SCE), demonstrating electronic communication between the two iron centres, mediated by the $C_5SePdSeC_5$ linkages.

In addition to the synthesis of silylselenoethers, the related tri-n-propylphosphine stabilized copper-trimethylsilylselenolate complex **5** was prepared in good yield from $(Pr_3P)_3CuOAc$ and $Se(SiMe_3)_2$ at low temperatures.[10] The tetrahedral molecules contain a terminally bonded $E\text{-}SiMe_3$ moiety that can be displaced. Complex **5** thus acts as a source of “metallaselenolate” in ternary nanocluster materials.[10] This is made possible due to the lability of the phosphine ligands, and the preformed Cu-Se bond in **5**. Additional M-E (metal-chalcogen) sources of this type are actively being targeted for ternary nanocluster synthesis.



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