

Synthesis and Reactivity of Trimethylsilylthiolate Compounds: Precursors for Heterometallic Complexes

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Final Seminar

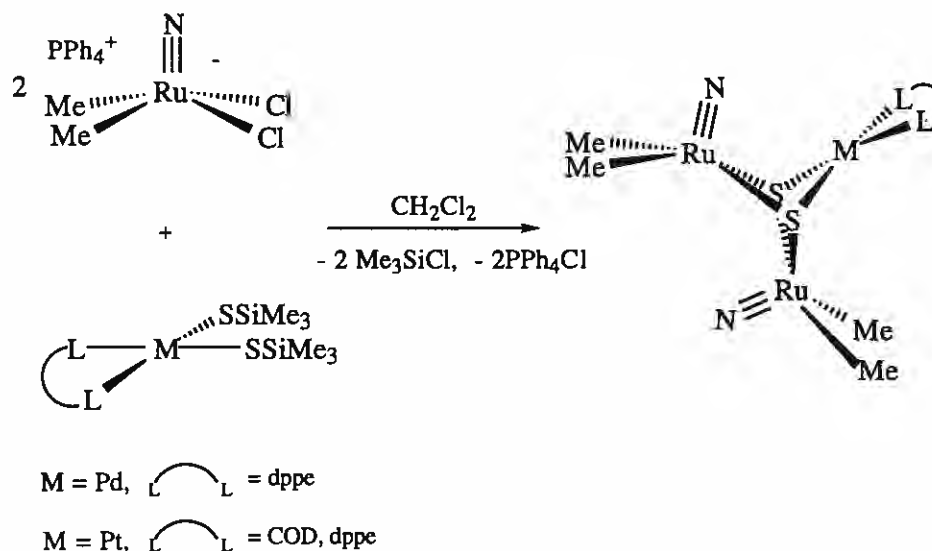
June 6, 1997

Heterometallic complexes may exhibit interesting reactivities because the different metal centers could act cooperatively in chemical transformations.¹ There are many strategies for synthesizing heterometallic complexes. Besides forming metal-metal bonds, bridge-assisted reactions can be used which employ ligands to bring two or more metal centers together. One of the rational syntheses of heteronuclear compounds with bridging sulfido ligands involves displacing a ligand on a metal center with a terminal sulfido ligand from another metal.² However, this strategy cannot be used when no terminal sulfido compounds exist for the metals involved in a target heterometallic complex.

Transition metal trialkylsilylthiolate complexes could be valuable precursors for synthesizing heterometallic compounds with bridging sulfido ligands. There are a number of stable transition metal organosilylthiolate complexes, but there have been no studies published on the reactivity of their sulfur-silicon bonds.³ The Si-Cl bond is much stronger than the Si-S bond in organosilicon compounds.⁴ Because of this, $(\text{Me}_3\text{Si})_2\text{S}$ reacts with a variety of transition metal chlorides to cleave the silicon-sulfur bond and form metal-sulfur complexes.⁵ Transition metal trialkylsilylthiolate complexes could react similarly with metal chlorides to form heterometallic complexes.

A series of palladium and platinum trimethylsilylthiolate complexes $(\text{dppe})\text{M}(\text{SSiMe}_3)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane; M = Pd, Pt) and $(\text{COD})\text{Pt}(\text{SSiMe}_3)_2$ (COD = 1,5-cyclooctadiene) have been synthesized, and all of them contain reactive Si-S bonds. The trimethylsilylthiolate compounds $(\text{dppe})\text{M}(\text{SSiMe}_3)_2$ (M = Pd, Pt) and $(\text{COD})\text{Pt}(\text{SSiMe}_3)_2$ react with $[\text{PPh}_4][\text{Ru}(\text{N})\text{Me}_2\text{Cl}_2]$ to form the corresponding heterometallic complexes (Scheme 1). The structure of $(\text{dppe})\text{Pt}(\mu_3\text{-S})_2\{\text{Ru}(\text{N})\text{Me}_2\}_2$ was confirmed by single crystal X-ray diffraction.

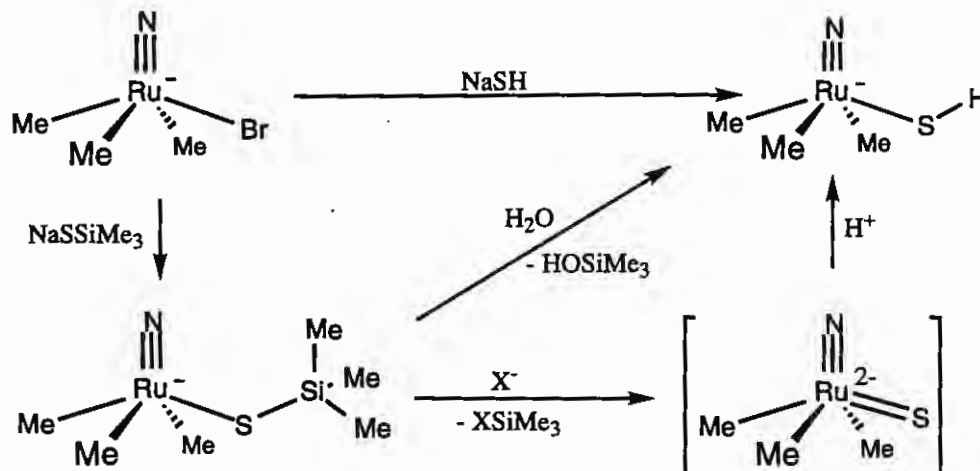
Scheme 1



The heterometallic complexes $(dppe)M(\mu_3-S)_2\{Ru(N)Me_2\}_2$ ($M = Pd, Pt$) and $(COD)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$ catalyze the O_2 oxidation of ethanol to acetaldehyde diethyl acetal at 100 °C and 40 psi O_2 . The most active catalyst is $(dppe)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$, which catalyzes the oxidation of 52 equivalents of ethanol under those conditions.

Other than serving as precursors for synthesizing heterometallic complexes, trimethylsilylthiolate compounds could also be used to synthesize metal sulfhydryl complexes. The nickel compound $(dppe)Ni(SSiMe_3)_2$ was synthesized, and it reacts with H_2O to form the previously-characterized $(dppe)Ni(SH)_2$ in good yield. Two Ru(VI) trimethylsilylthiolate compounds $[PPh_4][Ru(N)R_3(SSiMe_3)]$ ($R = CH_2SiMe_3, Me$) were also synthesized, and both of these complexes react with halide sources such as CsF or PPh_4Cl or with H_2O to form the corresponding sulfhydryl compounds $[PPh_4][Ru(N)R_3(SH)]$ (Scheme 2). Before these studies, no transition metal sulfhydryl complexes containing alkyl ligands have been reported. The structure of $[PPh_4][Ru(N)Me_3(SH)]$ was confirmed by single crystal X-ray diffraction.⁶

Scheme 2



References

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