

The Transition Metal Complexes of Stannylenes

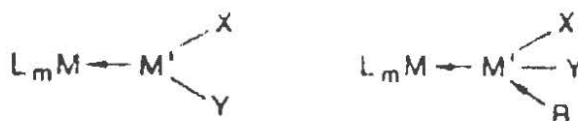
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Stannylenes are units of divalent tin bound to two organic or halide residues. Interest in these compounds has grown in recent years as researchers seek to expand their understanding of main group elements, particularly in their less common oxidation state. While numerous articles have been published on the chemistry of transition metal carbenes, much less information is available on their tin analogs.

When freshly prepared, most stannylenes exist in the monomeric form but unless the ligands on tin are sufficiently bulky, they rapidly polymerize [1]. The methylcyclopentadienyl, cyclopentadienyl [2] and amido [3] stannylenes exist as monomers due to the steric bulk and electronic characteristics of the ligands. The bis(trimethylsilyl)methyl [4] and β -ketoenolato complexes exist as loosely bound dimers in the solid state and in solution a monomer-dimer equilibrium is observed.



The transition metal complexes of stannylenes exist primarily in two forms--base stabilized and non-base stabilized. The organic ligands on tin are small (Me, *t*-Bu) in the base stabilized compounds of group VI metals [5] but can be larger ($\text{CH}(\text{SiMe}_3)_2$, β -ketoenolates) for group VIII metals [6]. These compounds are stabilized by the π donation of the base electrons to the tin. These stannylene complexes can be synthesized only if a coordinating solvent is present and they decompose if the base is removed. The bis-cyclopentadienyl stannylene forms a dimer with enneacarbonyl-diiron where the Cp rings have changed from penta- to mono-hapto [7].

Group VI metal carbonyls can form complexes with stannylenes of intermediate and large steric bulk that do not require a molecule of base to stabilize. These compounds exist for the stannylenes Cp_2Sn , $(\text{MeCp})_2\text{Sn}$ [8], $[\text{CH}(\text{SiMe}_3)_2]_2\text{Sn}$ [9], and $(\beta\text{-ketoenolato})_2\text{Sn}$ [10]. The stability of these compounds is due to the strong π -bonding between the tin and the metal.

^{119}Sn Mössbauer spectroscopy has proven to be a useful tool in probing the bonding in these compounds. The monomeric stannylenes exhibit rather large isomer shifts corresponding to divalent tin [11]. Upon complexation, the isomer shifts decrease and the quadrupolar splitting values increase markedly [12]. These changes suggest synergic metal-tin back-bonding from the d-orbitals on the metal to the p or d orbitals of tin. Infrared and nuclear magnetic resonance data for these compounds indicate that there is a strong π -interaction and support such a bonding scheme.

Despite these results, a conclusive and satisfactory explanation of the bonding in these compounds is not yet available. The lack of reactivity studies of transition metal stannylene complexes may, in part, account for this deficiency. Future research comparing the reactivity of stannylene complexes to carbene complexes can be useful in understanding the chemistry of group XIV compounds.

References

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