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Synthesis, Structure and Reactivity of Organometallic Complexes of Sm(II)*

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Abstract

The synthesis of $(C_5Me_5)_2Sm(THF)_2$ by metal vapor methods provided the first soluble organometallic Sm(II) complex. This compound allowed the development of the chemistry of the highly reducing Sm(II) ion in an organometallic environment. The unique combination of physical properties associated with $(C_5Me_5)_2Sm(THF)_2$, *i.e.* high reduction potential, oxophilicity, solubility, and 4f valence orbitals, allows this compound to do reductive chemistry not possible with other one electron reducing agents. The reactivity of $(C_5Me_5)_2Sm(THF)_2$ with a variety of unsaturated substrates including CO, alkynes, diynes, alkenes, isocyanides and azo compounds is discussed. Recent results on the chemistry of the unusual bent metallocene $(C_5Me_5)_2Sm$ is presented. The synthetic, structural and reactivity features of organometallic Sm(II) complexes are compared and contrasted with the known chemistry of trivalent organometallic complexes.

Introduction

Some years ago, as part of a general program to explore low valent lanthanide chemistry, we began to study the organometallic chemistry of the lanthanide metals in the formally zero oxidation state, *i.e.*, the chemistry of the elemental metals [1]. Metal vapor reaction techniques [2] were employed and unsaturated hydrocarbon substrates were chosen as reagents. Unsaturated hydrocarbons were of interest because of their importance in organometallic chemistry in general and because, prior to 1975, they were not considered as viable substrates/ligands in the lanthanide field.

The metal vapor studies showed that the lanthanides had quite an extensive reaction chemistry with unsaturated hydrocarbons. Evidence for oxidative addition of C–H, C–C bond-breaking and bond-making processes, polymerization, reduction, and dehydrogenation was obtained [1, 3]. Soluble, thermally stable complexes were also obtainable in many cases, but their physical and spectroscopic properties precluded definitive structural analysis.

The metal vapor studies indicated that unsaturated hydrocarbon substrates were viable reagents and suggested new experiments to explore this chemistry. One experiment of this type was designed to obtain more definitive evidence on oxidative addition of C–H [4]. Samarium vapor was reacted with C_5Me_5H to try to make species such as 'C_5Me_5SmH'. Evidence for such reactivity was obtained, but more importantly this metal vapor system provided $(C_5Me_5)_2Sm(THF)_2$ [5] and $(C_5Me_5)_2Sm$ [6]. $(C_5Me_5)_2Sm(THF)_2$ was the first soluble organometallic complex of Sm(II) and allowed exploitation of the strong reducing power of this oxidation state [Sm(III)/Sm(II) = −1.5 V *versus* NHE [7]] in an organometallic complex. $(C_5Me_5)_2Sm$ was the first structurally characterized f element analog of ferrocene and proved to have an unusual bent structure [8]. Both of these complexes have had a significant impact on organometallic lanthanide chemistry.

One of the best examples of the high reactivity achievable via organosamarium(II) chemistry is the reaction of $(C_5Me_5)_2Sm(THF)_2$ with CO [9]. One product of this reaction is the dimer $[(C_5Me_5)_4Sm_2(THF)(O_2C{-}C{=}C{=}O)]_2$ in which six CO molecules have been reduced by four electrons as they are homologated into two ketenecarboxylate units. Complete cleavage of one CO triple bond apparently occurs in this reaction to give the central, oxygen-free carbon of the C–C=C skeleton. Although CO cleavage is thought to occur in heterogeneous Fischer–Tropsch systems [10], this rarely occurs in homogeneous systems, particularly those in which two or more C–C bonds are also formed [11]. Comparison of this CO reduction with those by other reducing agents suggests that $(C_5Me_5)_2Sm(THF)_2$ is a unique reducing agent in the Periodic Table. The combination of strong reducing power, oxophilicity, solubility, and lack of d valence orbitals is not duplicated by any other reducing agent presently available.

$(C_5Me_5)_2Sm(THF)_2$ also shows high reactivity in its reactions with $C_6H_5C{\equiv}CC_6H_5$ and $C_6H_5N{=}NC_6H_5$

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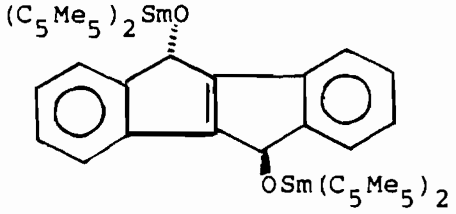
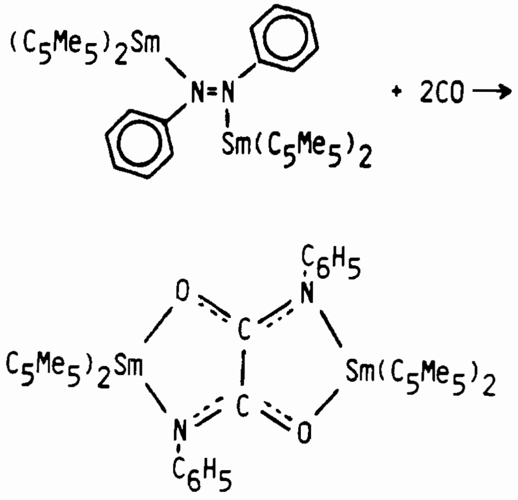
and the subsequent reactions of these products with CO. $(C_5Me_5)_2Sm(THF)_2$ reacts with $C_6H_5C{\equiv}CC_6H_5$ to form the unusual black Sm(III) complex $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ [12]. This complex then reacts with CO in a remarkably facile stereospecific synthesis of the tetracyclic hydrocarbon shown below [13].



$(C_5Me_5)_2Sm(THF)_2$ reacts with $C_6H_5N{=}NC_6H_5$ to form another trivalent complex with an unusual color, $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$, and this complex also has an unusual structure [14]. The molecule contains N–C(phenyl) distances stretched by over 0.1 Å and has both samarium atoms asymmetrically placed close to the *ortho* hydrogens of a single phenyl ring. Like $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$, $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ reacts with two molecules of CO. In this case, however, a different result is obtained [eqn. (1) [15]].



(1)

The overall transformation accomplished by treating azobenzene with $(C_5Me_5)_2Sm(THF)_2$ and then CO is an unusual four-center bond-breaking and bond-making sequence in which NN and CO multiple bonds are broken and two C–N and one C–C bond are formed.

Similarly unusual reactivity is observed when $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ are treated with dienes, alkenes, diynes, isocyanides and azines. In several cases, direct parallels exist between these results and possible reaction pathways considered for the metal vapor reactions discussed earlier. Parallels with alkali metal chemistry are also sometimes observed, but the greater solubility of the organosamarium(II) reagent usually allows interesting extensions of the basic chemistry to occur. Clearly, unsaturated hydrocarbons can have extensive chemistry with the lanthanide elements, and $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ are key reagents in this regard.

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