Indeed, taken with the fact that the $Y_3(OR)_7Cl_2(THF)_2$ to $Y_{14}(OR)_{28}Cl_{10}O_2(THF)_4$ conversion is quantitative in retaining chloride, one could begin to develop an argument that halophilicity is an important factor in yttrium *tert*-butoxide systems. The formation of $Y_3(OR)_8Cl(THF)_2$ instead of $Y_3(OR)_9(THF)_2$ (analogous to $La_3(OR)_9(THF)_2$[3]) from the reaction of YCl_3 with 3NaOR can be explained in terms of steric factors. The formation of $Y(OR)Cl(THF)_5^+$ instead of $Y(OR)_2(THF)_5^+$ cannot be explained in this way. Neither can steric arguments explain the reluctance of **4** to react with NaOR to form $Y(OR)_2(THF)_5^+$.

The importance of halophilicity is likely to be part of a more general set of principles for yttrium and lanthanide alkoxide chemistry that will be revealed as more chemistry is developed. These undoubtedly will help explain the complicated reaction chemistry observed in this system.

Conclusion

The synthesis of the cationic *tert*-butoxide complexes **2–4** has considerably broadened the scope of known yttrium alkoxide chemistry in terms of structural types and reactivity patterns. The identification of bimetallic and highly solvated monometallic complexes in an area previously dominated by trimetallic species demonstrates the importance of the net charge on yttrium alkoxide complexes in governing the chemistry. More generally, this suggests that the amount of ligand electron density that is delivered to the metal will significantly influence which complexes are formed and how they will react.

In terms of reactivity, these studies have reinforced the idea that a terminal chloride ligand can be a reactive entry point to chemical derivatization. In addition, these reactions have demonstrated that monometallic and bimetallic intermediates are available and can be isolated for use as starting materials in subsequent synthesis. The utility of these cationic complexes in the synthesis of heteropolymetallic complexes is under study.

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Supplementary Material Available: Tables of crystal data, ORTEP diagrams, atomic positional parameters, bond distances and angles, thermal parameters, and hydrogen atom coordinates for the yttrium complexes (37 pages); listing of structure factor amplitudes (72 pages). Ordering information is given on any current masthead page.

Reactivity of $(C_5Me_5)_2Sm$ and Related Species with Alkenes: Synthesis and Structural Characterization of a Series of Organosamarium Allyl Complexes[1]

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Abstract: The reactivity of $(C_5Me_5)_2Sm$ (**1**) with alkenes has been examined and compared with that of $(C_5Me_5)_2Sm(THF)_2$ (**2**) and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (**3**). **1** reacted rapidly with a variety of alkenes in hexane or toluene to form allyl complexes and alkane byproducts. Reactions with propene, butene, and allylbenzene formed $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**4**), $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (**5**), and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (**6**), respectively, in 85–95% yield. Complexes **4–6** were also prepared in similar yield from **3** and the appropriate alkene in hexane. The corresponding alkane was again the byproduct. Reactions of **3** with these alkenes in toluene formed $(C_5Me_5)_2Sm(CH_2C_6H_5)$ exclusively. **1** reacted with 1,3-butadiene and 1,5-hexadiene to form the bis-allyl complexes $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (**7**) and $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{-})]_2$ (**8**). In contrast, **3** reacted with butadiene to form **5**. **2** reacts like **1** with allylbenzene and 1,3-butadiene to form **6** and **7**. **2** is not very reactive with propene and forms complex mixtures of products with butene and 1,5-hexadiene. Complex **4** crystallizes from hexane in the tetragonal space group $I\bar{4}$ (no. 82; S_4^2) with unit cell parameters $a = 23.1043$ (36) Å, $c = 8.4586$ (12) Å, $V = 4515$ (1) Å^3, and $Z = 8$ for $D_{calcd} = 1.36$ g cm^{-3}. Least-squares refinement of the model based on 1894 observed reflections converged to $R_F = 4.7\%$. Complex **5** crystallizes from hexane in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 15.9367$ (41) Å, $b = 17.7780$ (32) Å, $c = 16.7024$ (48) Å, $\beta = 101.381$ (20)°, $V = 4639$ (2) Å^3, and $Z = 8$ for $D_{calcd} = 1.36$ g cm^{-3}. Least-squares refinement of the two crystallographically independent molecules based on 4688 observed reflections converged to $R_F = 7.5\%$. Complex **6** was crystallized from hexane at −34 °C as the 1,3-dihydroisobenzofuran adduct $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$, **6′**, in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 10.3851$ (16) Å, $b = 17.357$ (3) Å, $c = 17.703$ (2) Å, $\beta = 95.785$ (12)°, and $V = 3174.9$ (8) Å^3 with $Z = 4$ for $D_{calcd} = 1.38$ g cm^{-3}. Least-squares refinement of the model based on 6964 observed reflections converged to $R_F = 3.1\%$. Complex **7** crystallizes from toluene/hexane in the orthorhombic space group *Pbca* (no. 61; D_{2h}^{15}) with unit cell parameters $a = 16.5911$ (26) Å, $b = 29.8565$ (49) Å, $c = 18.0130$ (25) Å, $V = 8923$ (2) Å^3, and $Z = 8$ for $D_{calcd} = 1.41$ g cm^{-3}. Least-squares refinement of the model based on 4134 observed reflections converged to $R_F = 6.9\%$. Complex **8** crystallizes from hexane in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 13.953$ (12) Å, $b = 8.445$ (4) Å, $c = 18.635$ (10) Å, $\beta = 102.85$ (5)° and $V = 2143$ (2) Å^3 with $Z = 2$ for $D_{calcd} = 1.43$ g cm^{-3}.

The reduction, oligomerization, and polymerization of alkenes is an important area of chemistry and efforts are continually being made to develop better methods to manipulate these unsaturated hydrocarbon substrates.[2] Recently, we initiated a study[1,3] of the reactivity of $(C_5Me_5)_2Sm$ (**1**)[4] with alkenes both to determine if

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the unusual bent structure of **1**[4,5] would provide new ways to transform alkenes and to further probe the chemistry of **1**. Complex **1** differs from other one-electron reducing agents in several ways. In contrast to alkali metals, it is soluble in alkanes. In contrast to transition-metal complexes, it has a $4f^6$ electron configuration instead of a d^n configuration. In contrast to other organo f-element complexes,[6] it has a much more open coordination environment.

The first well-defined results obtained on the chemistry of **1** with alkenes involved the reduction of cyclopentadiene by **1** to form hydrogen and the cyclopentadienide ion in $(C_5Me_5)_2Sm(C_5H_5)$.[3] This reaction paralleled alkali metal chemistry. However, the second product isolated from this system, the mixed-valent complex $(C_5Me_5)_2Sm^{III}(\mu\text{-}C_5H_5)Sm^{II}(C_5Me_5)_2$, does not have an alkali metal analogue. The crystal structure of the latter complex revealed how the $(C_5Me_5)_2Sm$ unit could initially approach the unsaturated hydrocarbon electron density in the $C_5H_5^-$ ion. Further information in this regard was obtained from the crystal structures of the Lewis acid base adducts of $MeC{\equiv}CMe$ and $C_2H_4Pt(PPh_3)_2$ with the ytterbium analogue of **1**, $(C_5Me_5)_2Yb$.[7,8] Since Yb(II) is a weaker reducing agent than Sm(II),[9,10] only weak interactions were observed, but η^2-approach of neutral unsaturated hydrocarbons to the f-element bent metallocene was established. Recently, the initial stages of the reaction of **1** with alkenes have been revealed in the structures of the styrene and stilbene complexes $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$.[11] In these complexes, each samarium atom has a significant η^2-interaction with the alkene double bond, and in each complex one of the samarium atoms also interacts with the arene rings.

In this report, we describe reactions of $(C_5Me_5)_2Sm$ with unsaturated hydrocarbons which proceed beyond the simple coordination stage. Reactions of **1** with simple alkenes and dienes are described which lead to a variety of mono- and bimetallic allyl complexes. The reactions of these substrates with the solvated analogue of **1**, $(C_5Me_5)_2Sm(THF)_2$ (**2**), have also been examined to study the effect of the extra solvating ligands. Since the observed reaction pathways could occur via samarium hydride intermediates, the reactions of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, **3**,[12] with these substrates have also been studied. The comparisons with **2** and **3** suggest that the $(C_5Me_5)_2Sm$ unit can provide an unusual coordination environment for the manipulation and derivatization of alkenes.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques.

Solvents were purified as previously described.[13] Propene, *trans*-2-butene, *cis*-2-butene and 1,3-butadiene were purified by using columns of $CaSO_4$ (Drierite) and MnO on vermiculite. Phthalan (1,3-dihydroisobenzofuran), allylbenzene, and 1,5-hexadiene were dried with 4 Å molecular sieves, degassed on a high vacuum line by freeze–pump–thaw cycles, and vacuum distilled by using a liquid nitrogen bath. $(C_5Me_5)_2Sm$,[4] $(C_5Me_5)_2Sm(THF)$,[14] $(C_5Me_5)_2Sm(THF)_2$,[15,16] and $[(C_5Me_5)_2SmH]_2$[12] were made according to the literature. $(C_5Me_5)_2Sm$ must be handled in an ether-free glovebox. Physical measurements were obtained as previously described.[13,17] ^{13}C NMR spectra were obtained on a GN-500 MHz spectrometer and variable-temperature NMR data were obtained on a GE-300 MHz spectrometer. Most reactions were carried out in a 100-mL glass tube fitted with a high vacuum greaseless stopcock. This will be called a 100-mL reaction vessel in the Experimental Section.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (4) from $(C_5Me_5)_2Sm$ (1). In the glovebox, $(C_5Me_5)_2Sm$ (0.203 g, 0.436 mmol) was dissolved in 6 mL of toluene to give a dark green solution which was placed in a 100-mL reaction vessel equipped with a Teflon stir bar. The apparatus was attached to a Schlenk line, and the pressure was reduced by opening it to vacuum until the solution bubbled. Addition of 1 atm of propene to the stirred reaction mixture caused an immediate color change to red. After 5 min, the excess propene was removed, the flask was returned to the glovebox, and the solvent was removed by rotary evaporation. The resulting red powder was extracted with hexane to yield a red supernatant and a small amount of a yellow solid which was identified as $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[18] by ^1H NMR spectroscopy. Hexane was removed from the red supernatant by rotary evaporation to leave **4** as a red microcrystalline powder (0.209 g, 94%) which was identified by X-ray crystallography: ^1H NMR (cyclohexane-d_{12}) δ 15.55 (br s, $CH_2C\mathit{H}CH_2$, 1 H), 7.04 (d, J_{HH} = 12.1 Hz, $C\mathit{H}_2CHC\mathit{H}_2$, 2 H), 3.58 (d, J_{HH} = 7.8 Hz, $C\mathit{H}_2CHC\mathit{H}_2$, 2 H), 1.29 (s, C_5Me_5, 15 H), 1.08 (s, C_5Me_5, 15 H); ^{13}C NMR (benzene-d_6) δ 175.7 (d, J_{CH} = 144 Hz, $CH_2\mathit{C}HCH_2$), 115.6 (s, C_5Me_5), 113.7 (s, C_5Me_5), 25.6 (t, J_{CH} = 142 Hz, $\mathit{C}H_2CH\mathit{C}H_2$), 15.1 (q, J_{CH} = 124 Hz, $C_5\mathit{Me}_5$), 14.8 (q, J_{CH} = 126 Hz, $C_5\mathit{Me}_5$); ^1H NMR (cyclohexane-d_{12}) with excess proteo-tetrahydrofuran added δ 14.98 (br s, $CH_2C\mathit{H}CH_2$, 1 H), 5.32 (v br s, $C\mathit{H}_2CHC\mathit{H}_2$, 4 H), 1.19 (s, C_5Me_5, 30 H); magnetic susceptibility $\chi_M^{295K} = 1186 \times 10^{-6}$ (cgs); μ_{eff}^{295K} = 1.68 μ_B; IR (KBr) 3075 w, 2900 s, 2870 s, 2735 w, 1540 w, 1445 s, 1380 s, 1240 m, 1015 m, 770 s, 710 w, 670 m cm^{-1}. Anal. Calcd for $SmC_{23}H_{35}$: Sm, 32.55; C, 59.81; H, 7.64. Found: Sm, 32.80; C, 59.58; H, 7.51.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (4) from $[(C_5Me_5)_2SmH]_2$ (3). In the glovebox, $[(C_5Me_5)_2SmH]_2$ (0.061 g, 0.072 mmol) was added to 5 mL of hexane to give an orange suspension which was placed in a 100-mL reaction vessel and handled as described above. Addition of 1 atm of propene over the stirred reaction quickly generated a dark red solution. After 15 min, the excess propene was removed, the flask was returned to the glovebox, and the solution was filtered to yield a red supernatant and a small amount of an orange solid. The solvent was removed from the red supernatant by rotary evaporation to leave a red microcrystalline powder (0.057 g, 86%), which was found to be pure $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ by ^1H NMR spectroscopy.

Analysis of the Gases Formed in the Conversion of 1 to 4. In the glovebox, $(C_5Me_5)_2Sm$ (0.050 g, 0.119 mmol), 10 mL of toluene, and a Teflon stir bar were placed in a 100-mL reaction vessel equipped with a side arm sealed with a Kontes high vacuum greaseless valve and a septum for reagent addition. The flask was attached to a high vacuum line (2×10^{-5} Torr) and degassed by five freeze–pump–thaw cycles. Propene (8.8 mL, 0.357 mmol) was added by syringe through the side arm, and the frozen solution was allowed to warm to room temperature. The gases were collected by Toepler pump (0.129 mmol, 54%) and determined to be a 1.0:0.8 molar mixture of propene:propane by mass spectrometry.

Analysis of the Gases Formed in the Conversion of 3 to 4. In the glovebox, $[(C_5Me_5)_2SmH]_2$ (0.052 g, 0.061 mmol), 10 mL of hexane, and a Teflon stir bar were placed in a 100-mL reaction vessel equipped as described above. Propene (6.0 mL, 0.244 mmol) was added following the above procedure. The gases (0.066 mmol, 54%) were collected by Toepler pump and determined to be a 1.0:0.3 molar mixture of propane:propene by mass spectrometry.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (5) from 1. $(C_5Me_5)_2Sm$ (0.068 g, 0.16 mmol) was dissolved in 5 mL of toluene and handled as described above in the **1** to **4** conversion. Addition of 1 atm of *trans*-2-butene to the stirred solution caused an immediate color change to orange-red. After 30 min, the excess *trans*-2-butene was removed, and the solvent was

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removed by rotary evaporation, leaving a red, slightly tacky powder. The red powder was extracted with hexane to yield a red supernatant and a small amount of a yellow solid which was discarded. Rotary evaporation of the hexane left **5** as a red slightly sticky microcrystalline powder (0.075 g, 97%). X-ray quality crystals were obtained from hexane at −34 °C. In a similar fashion, $(C_5Me_5)_2Sm$ in toluene was reacted with 1 atm of *cis*-2-butene to generate pure **5**: ^1H NMR (benzene-d_6) δ 14.73 (br s, $CHHC\mathit{H}CH(CH_3)$, 1 H), 10.90 (br s, $C\mathit{H}HCHCH(CH_3)$, 1 H), 7.57 (br s, $CH\mathit{H}CHCH(CH_3)$, 1 H), 6.03 (br s, $CHHCHC\mathit{H}(CH_3)$, 1 H), −4.61 (br s, $CHHCHCH(C\mathit{H}_3)$, 3 H), 1.10 (s, C_5Me_5, 30 H); tentative assignments assuming accidental degeneracy of the C_5Me_5 resonances; ^1H NMR (benzene-d_6) with excess proteo-tetrahydrofuran added δ 14.69 (br s, $CHHC\mathit{H}CH(CH_3)$, 1 H), 9.28 (br s, $C\mathit{H}_2CHCH(CH_3)$, 2 H), 6.02 (br s, $CHHCHC\mathit{H}(CH_3)$, 1 H), −4.60 (br s, $CHHCHCH(C\mathit{H}_3)$, 3 H), 1.10 (s, C_5Me_5, 30 H); ^{13}C NMR (benzene-d_6) δ 114.12 (s, C_5Me_5), 14.97 (q, J_{CH} = 125 Hz, $C_5\mathit{Me}_5$); magnetic susceptibility $\chi_M^{295K} = 1267 \times 10^{-6}$ (cgs); $\mu_{eff}^{295K} = 1.74\ \mu_B$; IR (KBr) 2910 s, 2860 s, 1550 w, 1440 m, 1380 m, 1255 w, 1150 w, 1080 m, 1025 m, 790 m cm^{-1}. Anal. Calcd for $SmC_{24}H_{37}$: Sm, 31.59. Found: Sm, 32.6.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (5) from 3. In the glovebox, $[(C_5Me_5)_2SmH]_2$ (0.039 g, 0.046 mmol) was added to 5 mL of hexane and handled as described in the **3** to **4** conversion. The solution immediately began to darken upon addition of 1 atm of *trans*-2-butene. After 30 min, the excess *trans*-2-butene was removed, and the solution was filtered to yield a red supernatant and a small amount of a yellow solid. The solvent was removed from the red supernatant by rotary evaporation, leaving a red, slightly sticky, microcrystalline powder (0.043 g, 98%), which was found to be pure **5** by ^1H NMR spectroscopy. In a similar fashion, $[(C_5Me_5)_2SmH]_2$ in hexane was reacted with 1 atm of *cis*-2-butene to generate pure **5**.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (6) from $(C_5Me_5)_2Sm(THF)$. In the glovebox, $(C_5Me_5)_2Sm(THF)$ (0.242 g, 0.49 mmol) was suspended in 15 mL of hexane. Addition of $CH_2CHCH_2C_6H_5$, (0.15 mL, 1.13 mmol) to the stirred solution caused an immediate color change to red. After 3 h, the solution was centrifuged to yield a red solution and a small amount of a dark brownish-black solid. The solvent of the red solution was removed by rotary evaporation to yield an oily red solid (0.23 g, 88%). The red oil was dissolved in hexane with a few drops of phthalan (1,3-dihydroisobenzofuran, OC_8H_8) and cooled to −34 °C to generate crystals suitable for a single-crystal X-ray crystallographic study. The volatiles from the above reaction were analyzed by mass spectrometry and found to contain propylbenzene: ^1H NMR of desolvated complex (benzene-d_6) δ 15.55 (br s, $CHHC\mathit{H}CH(C_6H_5)$, 1 H), 10.17 (br s, $C\mathit{H}HCHCH(C_6H_5)$, 1 H), 6.55 (br s, $CHHCHC\mathit{H}(C_6H_5)$, 1 H), 6.43 (t, J_{HH} = 7.3 Hz, H_p-$CHHCHCH(C_6\mathit{H}_5)$, 1 H), 5.71 (t, J_{HH} = 7.4 Hz, H_m-$CHHCHCH(C_6\mathit{H}_5)$, 2 H), 5.32 (br s, $CH\mathit{H}CHCH(C_6H_5)$, 1 H), 3.92 (d, J_{HH} = 7.6 Hz, H_o-$CHHCHCH(C_6\mathit{H}_5)$, 2 H), 1.17 (br s, C_5Me_5, 15 H), 0.72 (br s, C_5Me_5, 15 H); ^1H NMR of phthalan adduct (benzene-d_6) δ 15.44 (br s, $CHHC\mathit{H}CH(C_6H_5)$, 1 H), 6.53 (t, J_{HH} = 7.3 Hz, H_p-$CHHCHCH(C_6\mathit{H}_5)$, 1 H), 6.53 (br s, $CHHCHC\mathit{H}(C_6H_5)$, 1 H), 5.71 (t, J_{HH} = 7.6 Hz, H_m-$CHHCHCH(C_6\mathit{H}_5)$, 2 H), 3.94 (d, J_{HH} = 7.8 Hz, H_o-$CHHCHCH(C_6\mathit{H}_5)$, 2 H), 0.95 (s, C_5Me_5, 30 H). Note that two of the hydrogen resonances of the allyl moiety were not found and are assumed to be lost in the base line due to fluxionality (see below). In addition, the phthalan molecule does not appear as a coordinated solvent, but as a free ether: ^{13}C NMR (benzene-d_6) δ 165.4 (d, J_{CH} = 143 Hz, allyl C), 146.0 (s, allyl C), 128.1 (d, J_{CH} = 153 Hz, aryl C), 117.3 (d, J_{CH} = 160 Hz, aryl C), 115.2 (s, C_5Me_5), 114.4 (d, J_{CH} = 156 Hz, aryl C), 48.7 (d, J_{CH} = 137 Hz, allyl C), 15.7 (q, J_{CH} = 125 Hz, $C_5\mathit{Me}_5$); magnetic susceptibility $\chi_M^{295K} = 1423 \times 10^{-6}$ (cgs); $\mu_{eff}^{295K} = 1.84\ \mu_B$; IR (KBr) of the phthalan solvate 2920–2860 s, 1595 m, 1550 s, 1500 m, 1440 s, 1380 m, 1285 w, 1245 s, 1180 m, 1020 w, 990 s, 890 w, 875 m, 790 s, 770 s, 750 s, 695 s, 645 m cm^{-1}. Anal. Calcd for $SmC_{37}H_{47}O$: Sm, 22.84; C, 67.53; H, 7.20; O, 2.43. Found: Sm, 23.10; C, 67.47; H, 7.21; O, 2.22.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (6) from 1. In the glovebox, allylbenzene (159 μL, 1.200 mmol) was added to a stirred solution of $(C_5Me_5)_2Sm$ (0.253 g, 0.600 mmol) in 10 mL of toluene. The solution immediately turned red. After 15 min, the solvent and volatiles were removed by vacuum distillation and were analyzed by gas chromatography–mass spectrometry. The volatiles contained allylbenzene and propylbenzene in a 1:1.2 ratio. **6** (358 mg) was isolated in 91% yield.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (6) from 3. In the glovebox, $[(C_5Me_5)_2SmH]_2$ (0.043 g, 0.050 mmol) was suspended in 5 mL of hexane. Upon addition of allylbenzene (40 μL, 0.30 mmol) to the stirred solution, the solution began to turn red. After 1 h, the solvent was removed by vacuum distillation leaving an oily red solid. The solid was extracted with hexane yielding a yellow solid and a red solution. Rotary evaporation left an oily red solid (0.040 g, 74%) which was determined to be desolvated **6** by ^1H NMR spectroscopy. The volatile products of the reaction were analyzed by mass spectrometry and were determined to contain allylbenzene and propylbenzene in a 1.0:0.8 molar ratio.

$[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (7) from 2. $(C_5Me_5)_2Sm(THF)_2$ (0.214 g, 0.38 mmol) was suspended in 10 mL of hexane to give a dark purple suspension which was placed in a 100-mL, round-bottomed flask equipped with a gas inlet and a Teflon stir bar. The pressure in the reaction vessel was reduced until the solution bubbled. Butadiene (1 atm) was placed over the stirred solution causing an immediate color change to deep red and causing all components to go into solution. During the next 3 h, a red-orange precipitate was deposited. Excess butadiene was removed, and the solution was filtered to yield a red supernatant which was discarded and **7** as a red-orange microcrystalline powder (0.131 g, 73%): ^1H NMR (benzene-d_6) δ 14.07 (br s, $(CHHC\mathit{H}CHCHH\text{-})_2$, 2 H), 10.10 (br s, $(C\mathit{H}HCHCHCHH\text{-})_2$, 2 H), 6.73 (br s, $(CH\mathit{H}CHCHCHH\text{-})_2$, 2 H), 5.27 (br s, $(CHHCHC\mathit{H}CHH\text{-})_2$, 2 H), 0.90 (s, C_5Me_5, 60 H), −6.77 (br s, $(CHHCHCHC\mathit{H}H\text{-})_2$, 2 H), −8.07 (br s, $(CHHCHCHCH\mathit{H}\text{-})_2$, 2 H); ^1H NMR (benzene-d_6) with excess proteo-tetrahydrofuran added δ 14.09 (br s, $(CH_2C\mathit{H}CHCH_2\text{-})_2$, 2 H), 8.38 (br s, $C\mathit{H}_2CHCHCH_2\text{-})_2$, 4 H), 5.24 (br s, $(CH_2CHC\mathit{H}CH_2\text{-})_2$, 2 H), 0.92 (s, C_5Me_5, 60 H), −7.04 (br s, $(CH_2CHCHC\mathit{H}_2\text{-})_2$, 4 H); ^{13}C NMR (THF-d_8) δ 159.2 (d, J_{CH} = 140 Hz, CH of C_8H_{12}), 155.2 (d, J_{CH} = 141 Hz, CH of C_8H_{12}), 117.1 (s, C_5Me_5), 111.1 (s, C_5Me_5), 38.1 (t, J_{CH} = 124 Hz, CH_2 of C_8H_{12}), 28.9 (t, J_{CH} = 122 Hz, CH_2 of C_8H_{12}), 17.8 (q, J_{CH} = 125 Hz, $C_5\mathit{Me}_5$), 16.6 (q, J_{CH} = 125 Hz, $C_5\mathit{Me}_5$); magnetic susceptibility $\chi_M^{298K} = 1160 \times 10^{-6}$ (cgs); $\mu_{eff}^{298K} = 1.67\ \mu_B$; IR (KBr) 2870 s, 1550 w, 1535 w, 1438 m, 1378 m, 1255 w, 1188 m, 1080 w, 1015 w, 988 w, 786 m, 670 m cm^{-1}. Anal. Calcd for $Sm_2C_{48}H_{72}$: Sm, 31.66. Found: Sm, 31.8.

$[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (7) from 1. In the glovebox, $(C_5Me_5)_2Sm$ (0.255 g, 0.61 mmol) was suspended in 15 mL of hexane to give a dark green suspension which was treated with butadiene as described above. A red-orange microcrystalline powder (0.230 g, 80%) was isolated and determined to be pure **7** by ^1H NMR spectroscopy.

$[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{-})]_2$ (8) from 1. In the glovebox, 1,5-hexadiene (40 μL, 0.337 mmol) was added to a stirred solution of $(C_5Me_5)_2Sm$ (0.141 g, 0.336 mmol) in 10 mL of toluene. The solution immediately turned red-purple. After 10 min, the solvent was removed leaving a dark purple solid, which was suspended in 10 mL of hexane. Filtration gave a dark red supernatant and **8** as a dark purple solid (0.048 g, 78%). A separate reaction involving 75 mg (0.179 mmol) of **1** was carried out on a high vacuum line attached to a Toepler pump. No evolved hydrogen was collected: ^1H NMR (benzene-d_6) δ 1.22 (s, C_5Me_5, 30 H), 0.88 (s, C_5Me_5, 30 H); ^1H NMR (benzene-d_6) upon addition of excess proteo-THF δ 1.04 (s, C_5Me_5, 60 H); ^{13}C NMR (benzene-d_6) δ 114.4, 112.5 (C_5Me_5), 15.6, 15.2 ($C_5\mathit{Me}_5$). Assignments were made by using a DEPT NMR experiment.[19] Complex **8** was too insoluble to obtain a coupled ^{13}C NMR spectrum or to obtain a ^{13}C NMR spectrum containing resonances for the C_6H_8 unit: IR (KBr) 2980 s, 2920 s, 2870 s, 1530 m, 1440 m, 1380 m, 1260 w, 1240 m, 1130 w, 1020 m, 995 w, 815 w, 800 w, 685 s cm^{-1}. Anal. Calcd for $Sm_2C_{46}H_{68}$: Sm, 32.62. Found: Sm, 32.4.

Ethene Polymerization Reactions. All polymerization reactions were carried out by using a 3 oz. Fisher-Porter aerosol pressure apparatus.[17] The reactions were pressurized with 40 psi of ethene. The reaction of ethene with $(C_5Me_5)_2Sm$ (**1**), $(C_5Me_5)_2Sm(THF)_2$ (**2**), $[(C_5Me_5)_2SmH]_2$ (**3**), $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**4**), and $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (**7**) gave polyethylene. Only **1** and **2** catalyzed the polymerization for a significant period of time. Polymer samples obtained from **1** and **3** were characterized by GPC in trichlorobenzene (at the Unocal Science and Technology Division, Brea, CA) and were found to have a high polydispersity.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (4). A bright red crystal with approximate dimensions 0.10 × 0.20 × 0.40 mm was mounted in a thin-walled glass capillary under nitrogen and accurately aligned on a Syntex $P2_1$ automated four-circle diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was accomplished by techniques similar to those of Churchill.[20] Room temperature (23 °C) intensity data were collected by using the θ-2θ scan technique with Mo Kα radiation. Final cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space, all having $21° < 2\theta < 30°$. Details are given in the Supplementary Material.

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The complex crystallizes in the noncentrosymmetric tetragonal space group $I\bar{4}$ [S_4^2; no. 82]. This space group was determined to be correct by successful solution and refinement of the structure. All 2158 data were corrected for the effects of absorption and for Lorentz and polarization factors and reduced to unscaled $|F_o|$ values. The data were placed on an approximate absolute scale by means of a Wilson plot. Those 1894 data having $|F_o| > 3.0\sigma(|F_o|)$ were considered observed and used in subsequent calculations.

The structure was solved by direct methods by using the program MITHRIL;[21] the position of the samarium atom was located from an "E-map". The positions of all remaining independent non-hydrogen atoms were determined from a series of difference-Fourier syntheses. All crystallographic calculations were performed by using our locally modified version of the UCLA Crystallographic Computing Package.[22] The structure was refined by using full-matrix least-squares methods (anisotropic thermal parameters were included for all non-hydrogen atoms). The weighting scheme using $p = 0.05$ has been previously described.[23] Hydrogen atoms were placed in calculated idealized positions with d(C–H) = 0.95 Å.[24] The model converged with $R_F = 4.7\%$, $R_{wF} = 5.0\%$, and GOF = 1.36 for 217 variables refined against 1894 data. A final difference-Fourier map was featureless. Final fractional coordinates for all structures in this paper are given in the Supplementary Material.

The analytical scattering factors of Cromer and Waber[25a] for the neutral atoms (C, H, Sm) were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[25b] were included.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (5). A dark red crystal of approximate dimensions 0.14 × 0.25 × 0.33 mm was studied as described above for **4** except a Nicolet P3 automated four-circle diffractometer was used. All 6594 data were corrected as described above for **4**. A careful survey of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ [C_{2h}^5; no. 14], is thus uniquely defined.

The structure was solved by direct methods (SHELXTL PLUS)[26] and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with $R_F = 7.5\%$, $R_{wF} = 7.5\%$, and GOF = 1.12 for 451 variables refined against those 4688 data with $|F_o| > 2.0\sigma(|F_o|)$, ($R_F = 4.5\%$, $R_{wF} = 5.7\%$ for those 3409 data with $|F_o| > 6.0\sigma(|F_o|)$). The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0017(|F_o|)^2$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 1.16$ e Å^{-3}.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_4H_8)$ (6'). A dark red crystal of approximate dimensions 0.30 × 0.31 × 0.45 mm was immersed in Paratone-N (Exxon), mounted on a glass fiber, transferred to the Syntex P2$_1$ diffractometer equipped with a modified LT-1 apparatus, and handled as described above for **4**. Data (7742) were collected at 213 K and corrected as described above for **4**. A careful survey of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group, $P2_1/c$ [C_{2h}^5; no. 14], is thus uniquely defined.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Refinement of positional and thermal parameters (isotropic for hydrogen atoms) led to convergence with $R_F = 3.1\%$, $R_{wF} = 3.0\%$, and GOF = 1.34 for 541 variables refined against those 6964 data with $|F_o| > 0$ ($R_F = 2.2\%$, $R_{wF} = 2.8\%$ for those 5969 data with $|F_o| > 6.0\sigma(|F_o|)$). $\sum w(|F_o| - |F_c|)^2$ was minimized with $w^{-1} = \sigma^2(|F_o|) + 0.0002(|F_o|)^2$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.54$ e Å^{-3}.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{–})]_2$ (7). A dark red crystal with approximate dimensions 0.10 × 0.40 × 0.62 mm was handled as described above for **5**. All 7896 unique data were corrected as described above, and those 4134 data having $|F_o| > 4.0\sigma(|F_o|)$ were considered observed and used in subsequent calculations.

A careful survey of a preliminary data set revealed the systematic extinctions $hk0$ for $h = 2n + 1$, $h0l$ for $l = 2n + 1$, and $0kl$ for $k = 2n + 1$. The space group is therefore uniquely defined as the centrosymmetric orthorhombic space group $Pbca$ [D_{2h}^{15}; no. 61].

The structure was solved and refined as described above for **4**. At convergence, the discrepancy indices were $R_F = 6.9\%$, $R_{wF} = 6.7\%$, and GOF = 1.50 for 451 variables. A final difference-Fourier map showed no significant features.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{–})]_2$ (8). A dark purple plate was mounted in a 0.1 mm capillary and handled as described above for **5**. A full structural determination was carried out, but, due to the small size of the crystal and the subsequent low intensity of the data collected, the structural determination was not of sufficient quality to obtain reliable distance and angle data. However, the connectivity of the structure was definitely determined. The following unit cell data were obtained: space group $P2_1/c$, a = 13.953 (12) Å, b = 8.445 (4) Å, c = 18.653 (10) Å, β = 102.85 (5)°, and V = 2143 (2) Å^3 with $Z = 2$ for D_{calcd} = 1.43 g cm^{-3}. R values obtained were $R_F = 6.4\%$, $R_{wF} = 8.5\%$ for 1525 reflections with $|F_o| > 6.0\sigma(|F_o|)$.

Results

Propene Reactions. Synthesis and Characterization of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (4). Propene is the simplest alkene to give isolable monomeric products with $(C_5Me_5)_2Sm$ (**1**). Ethene could not be used for this purpose since it is rapidly polymerized by **1**, $(C_5Me_5)_2Sm(THF)_2$ (**2**),[27,28] and $[(C_5Me_5)_2SmH]_2$ (**3**). When a dark green solution of **1** in toluene was exposed to 1 atm of propene, it reacted instantly to form ruby red, hexane soluble **4** in nearly quantitative yield (eq 1). The reaction to produce

$$\underset{\mathbf{1}}{(C_5Me_5)_2Sm} + \text{excess } H_2C{=}CHCH_3 \rightarrow \underset{\mathbf{4}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)} + CH_3CH_2CH_3 \tag{1}$$

4 also proceeds cleanly to completion if only a few equivalents of propene are used instead of an excess. Analysis of the gaseous byproducts of this reaction by Toepler pump revealed that only propane is produced during the reaction. If only 1 equiv of propene was used, the reaction solution did not achieve the characteristic red color of **4**. Instead a dark brown solution was obtained which could be converted to **4** if an additional equivalent of propene was added. The reaction of **1** with 20 psi of propene produced hydrocarbon oligomers of propene with molecular weights up to 350 (identified by GC-MS). Consistent with this, **4** polymerized ethene. The reaction of $(C_5Me_5)_2Sm(THF)_2$ (**2**) with 1 atm of propene did not produce **4**.

Complex **4** was also prepared from the reaction of a hexane suspension of $[(C_5Me_5)_2SmH]_2$ (**3**) with 1 atm of propene (eq 2).

$$0.5\underset{\mathbf{3}}{[(C_5Me_5)_2SmH]_2} + \text{excess } H_2C{=}CHCH_3 \rightarrow \underset{\mathbf{4}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)} + CH_3CH_2CH_3 \tag{2}$$

This reaction is like the $(C_5Me_5)_2Sm$ reaction in that more than 1 equiv of propene per samarium atom was needed for the reaction to proceed to completion. If only 1 equiv of propene was used, unreacted **3** remained in the reaction mixture as an orange precipitate. The addition of a second equivalent of propene caused the precipitate from the unreacted **3** to disappear. A Toepler pump experiment was carried out on a reaction with 2 equiv of propene, and it was found that only propane was produced during the reaction.

Even though **4** is extremely soluble in alkane solvents, it is a tractable solid which can be readily crystallized. An X-ray crystallographic study identified **4** as an η^3-allyl complex (Figure 1). Structural details will be described in a later section. The presence of two C_5Me_5 signals and separate signals for the syn and anti protons of the allyl group in the ^{1}H NMR spectrum indicates that, in the absence of coordinating solvents, **4** exists in solution as a static η^3-allyl structure. The infrared spectrum contains a stretch at 1540 cm^{-1} which can be assigned to the

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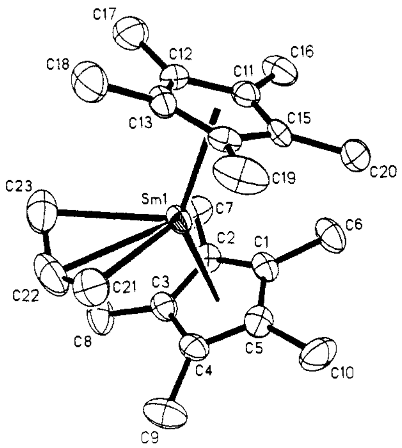

Figure 1. ORTEP diagram of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**4**) with thermal ellipsoids drawn at the 30% probability level.

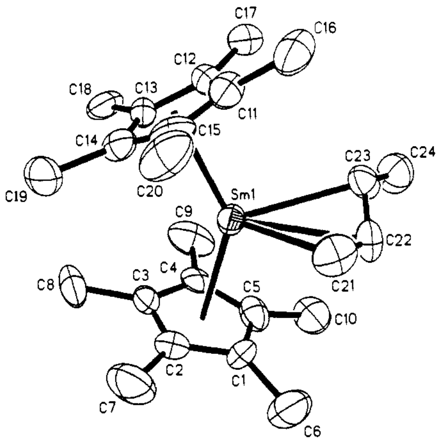

Figure 2. ORTEP diagram of one of the crystallographically independent molecules of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (**5**) with thermal ellipsoids drawn at the 40% probability level.

delocalized C–C stretch of an η^3-allyl unit.[29,30] High-temperature ^{1}H NMR spectroscopy up to 70 °C in cyclohexane-d_{12} was carried out, but no change in the spectrum was observed with the increasing temperature. The addition of a coordinating solvent, such as tetrahydrofuran, causes both the C_5Me_5 signals and the syn and anti signals to coalesce. This coalescence is assumed to occur through a THF adduct of **4** in which the allyl moiety can shift to an η^1 mode of binding. The lack of any signals in the ^{1}H NMR spectrum for a coordinated THF molecule suggests than an equilibrium is present between **4** and its THF adduct.

The chemistry of **4** is consistent with the availability of an η^1-allyl binding mode. For example, **4** dissolved in hexane reacted with 1 atm of H_2 to produce $[(C_5Me_5)_2SmH]_2$ (**3**). As described above, **4** dissolved in hexane catalyzed the polymerization of ethene. However, when **4** was dissolved in THF, no polymerization of ethene was observed. Presumably, when **4** is dissolved in THF, the open coordination site required for the catalytic behavior is blocked. **4** has also been found to react with 75 psi of CO, but the crystalline product of this reaction has not as yet been identified.

Butene Reactions. Synthesis and Characterization of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (5). A solution of $(C_5Me_5)_2Sm$ in toluene instantly reacted with 1 atm of *trans*-2-butene or *cis*-2-butene to form ruby red, hexane soluble **5** in nearly quantitative yield (eq 3). Complex **5** could also be generated in

$$\underset{\mathbf{1}}{(C_5Me_5)_2Sm} + \text{excess } CH_3CH{=}CHCH_3 \rightarrow \underset{\mathbf{5}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)} + CH_3CH_2CH_2CH_3 \quad (3)$$

quantitative yield from the reaction of a suspension of $[(C_5Me_5)_2SmH]_2$ in hexane with 1 atm of *trans*-2-butene or *cis*-2-butene (eq 4). The reaction of **3** with 1,3-butadiene also

$$0.5\underset{\mathbf{3}}{[(C_5Me_5)_2SmH]_2} + \text{excess } CH_3CH{=}CHCH_3 \rightarrow \underset{\mathbf{5}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)} + CH_3CH_2CH_2CH_3 \quad (4)$$

$$0.5\underset{\mathbf{3}}{[(C_5Me_5)_2SmH]_2} + H_2C{=}CHCH{=}CH_2 \rightarrow \underset{\mathbf{5}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)} \quad (5)$$

produced **5** (eq 5), but $(C_5Me_5)_2Sm(THF)_2$ did not react with 1 atm of butene to form **5**. As with the propene reactions, the butene reactions could be done with just a few equivalents of butene per samarium atom, and in these reactions, the byproduct was the alkane, in this case, butane. The reaction of **1** with 10 psi of butene gave hydrocarbon oligomers with molecular weights up to 450.

Like **4**, complex **5** is extremely soluble in alkanes. However, **5** differs from **4** in that it tends to be oily, and it does not easily form crystals. Nevertheless, X-ray crystallographic data were obtained, and the η^3-allyl structure (described later) is shown in Figure 2. The ^{1}H NMR spectrum of **5** contains separate signals assignable to the syn and anti protons on the allyl moiety, but the two expected C_5Me_5 resonances are observed as a single signal. A low-temperature ^{1}H NMR study of **5** in toluene-d_8 down to −80 °C did not freeze out more than one C_5Me_5 environment. The infrared spectrum contains a stretch at 1550 cm^{-1} indicative of an η^3-allyl unit. It appears that the addition of the methyl substituent on the allyl group increases the steric bulk of the ligand such that the structure is less rigid in solution. This decreased rigidity may result in less favorable crystal packing which manifests itself as lower crystallinity. As with **4**, the addition of the coordinating solvent THF to **5** causes the NMR signals for the syn and anti protons to coalesce.

Allylbenzene Reactions. Synthesis and Characterization of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (6). Solutions of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ reacted instantly with an excess of $H_2C{=}CHCH_2Ph$ to produce dark red, hexane soluble **6** in excellent yield. The monosolvate $(C_5Me_5)_2Sm(THF)$, which is readily generated from **2** on a rotary evaporator,[14] was also examined in this case and gives similar results. Propylbenzene was the only byproduct formed in these reactions. The stoichiometry of the reaction of $(C_5Me_5)_2Sm$ with allylbenzene was investigated by using a 2:1 ratio of $H_2C{=}CHCH_2Ph$ to **1**. GC–MS analysis of the organic products revealed allylbenzene and propylbenzene in a 1:1.2 ratio. This is consistent with the net 3:2 CH_2CHCH_2Ph:**1** stoichiometry given in eq 6. Complex **6** is also

$$2(C_5Me_5)_2Sm(THF)_{0-2} + 3H_2C{=}CHCH_2Ph \rightarrow 2\underset{\mathbf{6}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)} + CH_3CH_2CH_2Ph \quad (6)$$

formed when a suspension of $[(C_5Me_5)_2SmH]_2$ in hexane reacts with 2 equiv of allylbenzene (eq 7). As in the samarium(II)-based reactions, propylbenzene is the byproduct of this reaction.

$$0.5\underset{\mathbf{3}}{[(C_5Me_5)_2SmH]_2} + 2H_2C{=}CHCH_2Ph \rightarrow \underset{\mathbf{6}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)} + CH_3CH_2CH_2Ph \quad (7)$$

Complex **6** is extremely soluble in alkane solvents and is isolated as a red oil. It can only be obtained as a tractable solid when it is recrystallized in the presence of a coordinating ether such as tetrahydrofuran or phthalan (1,3-dihydroisobenzofuran, OC_8H_8). X-ray crystallographic data were obtained on the phthalan adduct $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$, **6′**, and again an η^3-allyl structure was observed (Figure 3). The ^{1}H NMR

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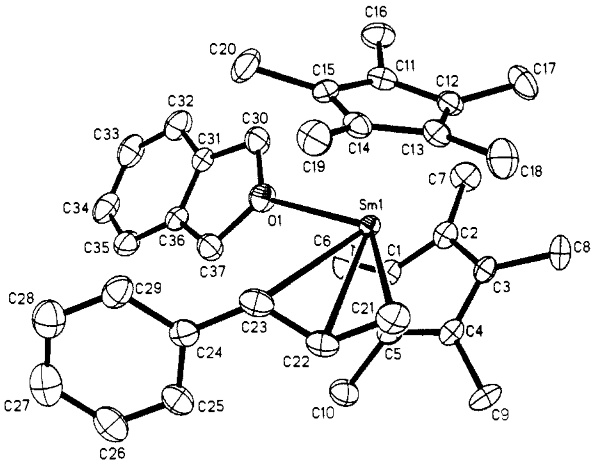


Figure 3. ORTEP diagram of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$ (**6′**) with thermal ellipsoids drawn at the 40% probability level.

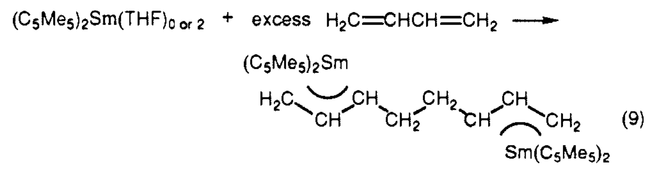
spectrum of **6** contains distinct peaks for the syn and anti protons and two peaks for the C_5Me_5 rings. The C_5Me_5 peaks have a half height line width of 26 Hz which is larger than that of **4** (10 Hz). In view of the change in crystallinity observed with the addition of a methyl substituent on the allyl moiety when going from **4** to **5**, it is not surprising that the addition of the phenyl substituent causes complex **6** to be an oil. It is only by adding a coordinating ether that a crystallizable, rigid structure is obtained. Addition of a coordinating ether to an NMR sample of **6** causes both the C_5Me_5 peaks and the syn and anti peaks to coalesce. The infrared spectrum of the solvated complex is less definitive, since there are stretches at 1550 and 1500 cm^{-1} indicative of an η^3-allyl structure, but there is also a stretch at 1595 cm^{-1} which is in the η^1-allyl region.[29,30]

Reaction of $[(C_5Me_5)_2SmH]_2$ with Alkenes in Toluene. When **3** was dissolved in toluene instead of suspended in hexane, it reacted differently with alkenes. Instead of forming the allyl complexes described above, toluene solutions of **3** reacted instantly with alkenes to produce the orange-red η^1-metalated benzyl complex, $(C_5Me_5)_2Sm(CH_2Ph)$ (eq 8). The benzyl complex was

$$0.5[(C_5Me_5)_2SmH]_2 + \text{alkene} \xrightarrow{\text{toluene}} (C_5Me_5)_2Sm(CH_2Ph) \qquad (8)$$

isolated in pure form after a reaction time of only a few minutes. It has been previously determined that **3** requires a much longer reaction time (i.e., days) to generate the benzyl complex from toluene in the absence of an alkene coreagent.[31]

1,3-Butadiene Reactions. Synthesis and Characterization of $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (7). When $(C_5Me_5)_2Sm(THF)_2$ or $(C_5Me_5)_2Sm$ were suspended in hexane, they instantly reacted with 1 atm of 1,3-butadiene to produce a deep red, hexane soluble complex. Upon stirring, a red-orange precipitate of **7** formed (eq 9).



$$(C_5Me_5)_2Sm(THF)_{0\,\text{or}\,2} + \text{excess } H_2C{=}CHCH{=}CH_2 \longrightarrow (C_5Me_5)_2Sm\text{–}H_2C\text{–}CH\text{–}CH\text{–}CH_2\text{–}CH_2\text{–}CH\text{–}CH\text{–}CH_2\text{–}Sm(C_5Me_5)_2 \qquad (9)$$

7

Complex **7** is moderately soluble in toluene and can be recrystallized from a toluene/hexane mixture as deep red crystals. X-ray crystallography revealed that **7** is a bis-allyl samarium complex formed by dimerizing butadiene (Figure 4). The ^1H NMR spectrum of **7** is highly dependent on the solvent and the temperature. In arenes at room temperature, separate peaks are observed for the six independent protons on the C_8 fragment, but there is only one C_5Me_5 resonance. This peak is somewhat broad, however, which suggests that there probably are several similar conformations that **7** can adopt in solution. The addition of THF to an NMR sample of **7** causes the C_5Me_5 peak to sharpen, and an equilibration of the methylene protons of the C_8 moiety is seen. This presumably occurs through an η^3–η^1 fluxional process. If the ^1H NMR spectrum is taken in THF-d_8 four C_5Me_5 environments are observed, and ten signals are observed for the C_8-protons. The two major C_5Me_5 peaks are in a 1:1 ratio and are assigned to one molecule in which the two C_5Me_5 ligands on each samarium atom experience a different magnetic environment, as in **4**. When the THF-d_8 sample is cooled to −40 °C, only this latter conformation is observed. This latter low-temperature THF-d_8 ^1H NMR spectrum can be duplicated in toluene-d_8 at low temperature (−20 °C). The infrared spectrum of **7** has stretches at 1550 and 1535 cm^{-1} in the η^3-allyl region.

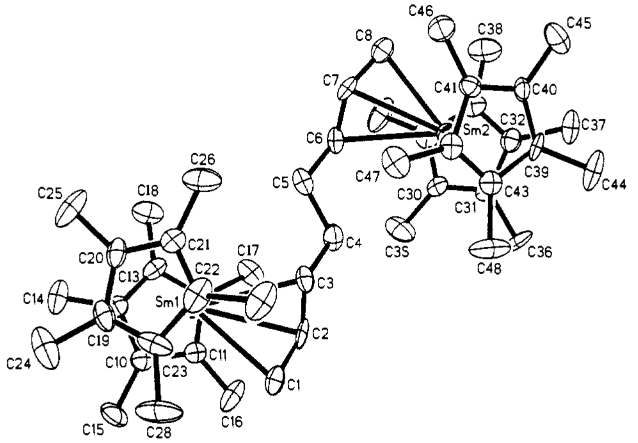


Figure 4. ORTEP diagram of $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (**7**) with thermal ellipsoids drawn at the 30% probability level.

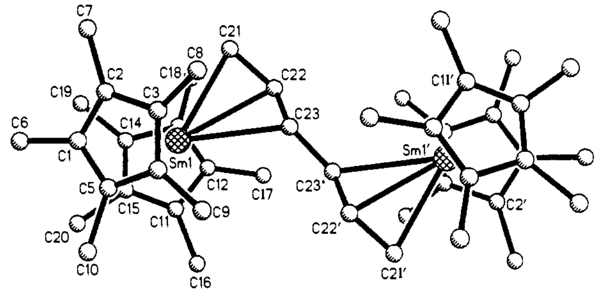


Figure 5. Molecular structure of $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{-})]_2$ (**8**).

The chemistry of **7** is analogous to that of the simple allyl complex **4** in that it polymerizes ethene and reacts with 1 atm of H_2 to produce $[(C_5Me_5)_2SmH]_2$. As with **4**, the ability of **7** to participate in these reactions suggests that **7** can adopt an η^1-conformation.

1,5-Hexadiene Reactions. Synthesis and Characterization of $[(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH\text{-})]_2$ (8). When $(C_5Me_5)_2Sm$ was treated with 1,5-hexadiene in toluene, a dark purple compound, **8**, was produced in 75% yield. Complex **8** is only marginally soluble in arenes and when dissolved in THF forms a red-orange THF solvated derivative. An X-ray crystallographic investigation revealed that **8** is a bis-allyl complex like **7**, except that it is derived from one (not two) molecule of the diene substrate (Figure 5). The major byproduct of the reaction of **1** with 1,5-hexadiene was the red hexane soluble propylallyl complex $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPr)$ (**9**) (eq 10). **9** could not be separated from the other hexane soluble byproducts in reaction 10 but was independently synthesized from **1** and 1-hexene (eq 11). The reaction of **3** with 1,5-hexadiene gave a mixture of products with a distribution opposite that of the **1**/1,5-hexadiene reaction. The major portion of the reaction mixture was a red hexane soluble mixture containing **9**. Complex **8** was observed only as a minor byproduct.

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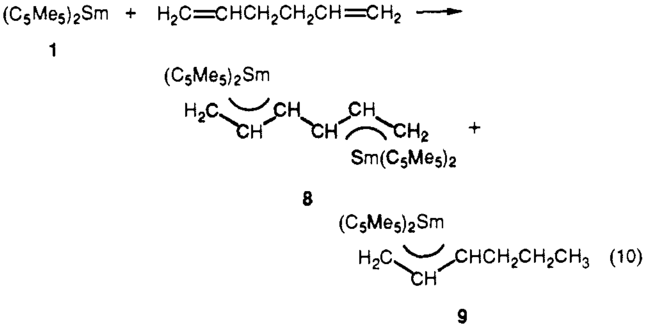
(31) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Manuscript in preparation.



$$\underset{\mathbf{1}}{(C_5Me_5)_2Sm} + H_2C{=}CH_2CH_2CH_2CH_2CH_3 \rightarrow \underset{\mathbf{9}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPr)} \quad (11)$$

The ^1H NMR spectrum of **8** is similar to that of **4** in that it contains two C_5Me_5 resonances, but it differs from that of **7** which contains a single C_5Me_5 resonance. Presumably, since the $(C_5Me_5)_2Sm$ units are closer together due to the shorter C_6 ligand, the fluxional processes necessary to produce a single C_5Me_5 environment as in **7** are blocked by unfavorable steric interactions. As with all of the allyl systems, the addition of THF causes the two C_5Me_5 resonances to coalesce.

Generalizations on the Structures of the $(C_5Me_5)_2Sm(\eta^3\text{-allyl})$ Complexes. A summary of the bond distances and angles observed in **4**, **5**, **6′**, and **7** is given in Table II. Complete bond distance and angle data are given in the Supplementary Material. The crystallographic data set obtained on **8** was not of high enough quality to include in this discussion due to the small size of the crystal, but the connectivity of the atoms in **8** was unambiguously determined. In complexes **4**, **5**, **6′**, **7**, and **8**, each samarium atom is surrounded by two η^5-C_5Me_5 rings and an η^3-allyl ligand. Complex **6′** differs in that it has an additional ligand, phthalan, in the coordination sphere. The fact that complex **6**, which has the most sterically bulky allyl ligand, can accommodate an extra ligand may seem surprising. However, it has been shown that the trivalent $(C_5Me_5)_2Sm$ unit is flexible in regard to coordination environment.[32,33] For example, several sets of $(C_5Me_5)_2Sm^{III}$ complexes are known in which both *n*-coordinate and $(n + 1)$-coordinate species containing the same *n*-coordinate ligand set can be crystallographically characterized.[33] The existence of a solvated derivative of **6** suggests that ether adducts of complexes **4**, **5**, **7**, and **8** could also form. More importantly, the solvation of **6** demonstrates that there is room to coordinate another ligand or reactive substrate adjacent to the allyl ligand in these complexes.

Table II shows that the average samarium–$C(C_5Me_5)$ distances, 2.724 (30)–2.772 (24) Å, fall in the 2.68–2.77 Å range typical for trivalent $(C_5Me_5)_2Sm$ complexes.[3] As expected, the most sterically crowded molecule, **6′**, has the longest Sm–$C(C_5Me_5)$ distance. The 134.6–140.3° range of (C_5Me_5 centroid)–Sm–(C_5Me_5 centroid) angles in **4**–**7** extend the top end of the previously observed span of 130–139°.[34] Consistent with the steric demands of the allyl ligands, **6′**, has the smallest angle in this group. The C(allyl CH_2)–Sm–C(allyl CHR) angles also follow this pattern and range from 52.1 (1)° for complex **6′** to 57.1 (8)° for complex **4**. The $C(CH_2)$–C(CH)–C(CHR) angles are identical within experimental error (range: 124.2(18)–127.6(15)°) and are typical for η^3-allyl ligands.[35-38] The angular orientation of the allyl ligand to the metal in each of these complexes is also in the normal range. This can be measured by the dihedral angle between the plane defined by the three carbon atoms of the allyl ligand and the plane defined by the metal and the two outer carbon atoms in the allyl ligand. These angles are 116.4° for **4**, 119.1° and 118.3° for the two independent molecules of **5**, 109.3° for **6′**, and 113.3° and 117.4° for Sm(1) and Sm(2), respectively, in **7**.

The C–C and Sm–C distances involving the allyl ligands are not all equal and suggest that there is a slight trend toward the localization of charge on $C(CH_2)$. The distances do not differ by more than 3σ, however. In all cases, the Sm–$C(CH_2)$ distance has the shortest numerical Sm–C(allyl) value. In addition, in all cases the $C(CH_2)$–C(CH) distance is slightly longer than the C(CH)–C(CHR) distance. This asymmetry is consistent with the facile η^3–η^1 conversions which appear to occur in these molecules and has been observed previously in the structure of $(C_5H_5)Zr(\eta^3\text{-}CH_2CHCH_2)_3$.[39]

In the unsubstituted allyl complex **4**, the Sm–C(CH) distance is the longest Sm–C(allyl) distance. A similar situation is observed in $(C_5Me_5)U(\eta^3\text{-}CH_2CHCH_2)_3$.[40] In contrast, it is more common in transition-metal complexes to find that the metal–(central carbon) distance is the shortest of the three metal–carbon lengths.[35-38] Disorder clouds this issue[40] in $(^iPrO)_2U(\eta^3\text{-allyl})_3$,[41] and no consistent pattern is observed in $[Li(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$.[42] However, in the substituted allyl samarium complexes **5**, **6′**, and **7**, there is an increase in the Sm–C(allyl) distances across the allyl unit with Sm–$C(CH_2)$ < Sm–C(CH) < Sm–C(CHR). It is possible that the substituted carbon atom occupies the position farthest from the samarium due to the steric demands of the substituent.

Discussion

Propene, Butene, and Allylbenzene Reactions. $(C_5Me_5)_2Sm$ reacts with simple alkenes larger than ethene to form allyl complexes in high yield. Allyl complexes are well-known in organolanthanide chemistry,[42-47] although prior to this study, only one allyl lanthanide complex, the quite complicated $[Li(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$,[42] had been characterized by X-ray diffraction. Previously, structural assignments were made by NMR and IR spectroscopy, and in some cases even with diamagnetic complexes, the data were ambiguous. With these paramagnetic samarium systems, it was essential to have crystallographic data. The structures presented here establish that η^3-coordination occurs and suggest that even in the solid state, there may be a tendency toward charge localization which would lead to $\eta^3 \rightleftarrows \eta^1$ interconversions. The NMR studies of these allyl complexes show that spectral assignment must take into account the presence of coordinating solvents and the temperature.

The first syntheses of allyl lanthanide complexes involved the reaction of trivalent lanthanide halides with Grignard reagents.[43] More recently, allyl complexes have been prepared from trivalent alkyl and hydride species.[44-47] The formation of allyl complexes

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Table I. Crystallographic Data for **4**, **5**, **6′**, and **7**[a]

complex	**4**	**5**	**6′**	**7**
formula	$C_{23}H_{35}Sm$	$C_{24}H_{37}Sm$	$C_{37}H_{47}OSm$	$C_{48}H_{72}Sm_2$
mol wt	461.9	475.9	658.1	949.9
space group	$I\bar{4}$ (no. 82; $S_4{}^2$)	$P2_1/n$	$P2_1/c$	*Pbca* (no. 61; $D_{2h}{}^{15}$)
cell constants				
a, Å	23.1043 (36)	15.9367 (41)	10.3851 (16)	16.5911 (26)
b, Å		17.7780 (32)	17.357 (3)	29.8565 (49)
c, Å	8.4586 (12)	16.7024 (48)	17.703 (2)	18.0130 (25)
β, deg		101.381 (20)	95.785 (12)	
cell volume, Å^3	4514.7 (15)	4639 (2)	3174.9 (8)	8922.7 (24)
mols/unit cell	8	8	4	8
D_{calcd}, g cm^{-3}	1.36	1.36	1.377	1.41
temp, K	295	296	213	295
μ_{calcd}, cm^{-1}	26.1	25.4	18.8	26.5
transmission, coeff min–max	0.16–0.22	0.47–0.53	0.33–0.39	0.22–0.31
R_F, %	4.7	7.5	3.1	6.9
R_{wF}, %	5.0	7.5	3.0	6.7

[a] Radiation for all structures was Mo Kα; $\bar{\lambda}$ = 0.71073 Å.

Table II. Interatomic Bond Distances (Å) and Angles (deg) for the $(C_5Me_5)_2Sm(\eta^3\text{-allyl})$ Complexes **4**, **5**, 6′, and **7**[a]

complex	**4**	**5**	**7**[b]	6′
formula	$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$	$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$	$[(C_5Me_5)_2Sm(\mu,\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$	$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$
Sm–C(ring)	2.724 (30)	2.727 (20), 2.729 (30)	2.725 (27), 2.728 (27)	2.772 (24)
Cn–Sm–Cn[c]	140.3	138.9, 139.1	138.7, 137.8	134.6
C(A)–Sm–C(C)	57.1 (8)	55.6 (5), 56.5 (5)	54.2 (6), 55.8 (6)	52.1 (1)
Sm–C(A)[a]	2.630 (15)	2.551 (17), 2.579 (17)	2.575 (17), 2.560 (17)	2.643 (3)
Sm–C(B)	2.668 (18)	2.689 (16), 2.659 (15)	2.680 (16), 2.686 (15)	2.769 (2)
Sm–C(C)	2.643 (18)	2.715 (14), 2.674 (16)	2.730 (17), 2.721 (16)	2.922 (3)
C(A)–C(B)	1.465 (32)	1.401 (22), 1.392 (22)	1.377 (24), 1.431 (24)	1.396 (4)
C(B)–C(C)	1.369 (32)	1.358 (24), 1.380 (25)	1.363 (24), 1.348 (22)	1.359 (4)
C–C–C	125.6 (20)	126.3 (15), 127.6 (15)	124.2 (18), 125.9 (16)	126.3 (3)

[a] The allyl carbon atoms are labeled as follows: $\eta^3\text{-}C^AH_2C^BHC^CHR$. [b] The complexes are listed in order of increasing steric requirements. [c] Cn = centroid of cyclopentadienyl ring.

from divalent organolanthanide precursors had not been observed before this study was initiated.[1,48] One can envisage several ways by which $(C_5Me_5)_2Sm$ can react with an alkene to form an allyl complex. Since some of these pathways involve trivalent samarium hydride intermediates, we also examined the reactions of the most relevant hydride, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (**3**),[12] with the same substrates, and these will be discussed first.

The reactions of hexane suspensions of **3** with propene, *cis*- and *trans*-2-butene, and allylbenzene, which form **4**–**6** and the appropriate alkane, can be explained by the sequence shown for propene in eqs 12–14. The same scheme was proposed earlier

$$0.5[(C_5Me_5)_2SmH]_2 + H_2C{=}CHCH_3 \rightarrow (C_5Me_5)_2Sm(CH_2CH_2CH_3) \quad (12)$$

$$(C_5Me_5)_2Sm(CH_2CH_2CH_3) + H_2C{=}CHCH_3 \rightarrow \underset{\text{A}}{(C_5Me_5)_2Sm(CH_2CH_2CH_3)(H_2C{=}CHCH_3)} \quad (13)$$

$$(C_5Me_5)_2Sm(CH_2CH_2CH_3)(H_2C{=}CHCH_3) \rightarrow (C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2) + CH_3CH_2CH_3 \quad (14)$$

for the synthesis of allyl lanthanum and neodymium complexes from hydride precursors.[46] The first step in this scheme, the 1,2-addition of a lanthanide hydride to an alkene (eq 12), is well-established in lanthanide chemistry.[46,49-51] Less precedent existed for the second step, the coordination of an alkene to a trivalent lanthanide complex (eq 13), although the existence of transient intermediates such as A were reasonable in many systems. The crystal structure of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2Ph)(OC_8H_8)$, **6′**, which demonstrates that a Sm^{3+} ion can accommodate two $\eta^5\text{-}C_5Me_5$ groups, an η^3-allyl ligand, *and* an additional ligand, shows that an alkyl alkene samarium complex such as A is quite reasonable sterically. The third step in the sequence, the metalation of the alkene (eq 14), again has ample precedent in the extensive metalation chemistry observed for organolanthanide alkyl complexes.[6,52-57]

The reaction of **3** with these alkenes in toluene to form the benzyl complex $(C_5Me_5)_2Sm(CH_2Ph)$ (eq 8) is also consistent with the above sequence. On the basis of the high metalation reactivity of the solvated complex, $(C_5Me_5)_2SmMe(THF)$,[56] and the reactivity of sterically unsaturated lanthanide alkyls in general,[6,58] one would expect unsolvated $(C_5Me_5)_2Sm(CH_2CH_2CH_3)$ to readily metalate toluene (eq 15).

$$(C_5Me_5)_2SmCH_2CH_2CH_3 + C_6H_5CH_3 \rightarrow (C_5Me_5)_2Sm(CH_2C_6H_5) + CH_3CH_2CH_3 \quad (15)$$

The reactivity of **3** with 1,3-butadiene to form **5** (eq 5) is also consistent with the above discussion. 1,2-Addition of the H–Sm bond to one double bond forms the methyl allyl complex directly. $[(C_5Me_5)_2LaH]_2$ reacts similarly.[46]

With this background, the formation of allyl complexes from $(C_5Me_5)_2Sm$ and alkenes can be discussed. Figure 6 shows three possible pathways for this type of transformation exemplified with propene. Scheme I (in Figure 6) shows the direct metalation of the alkene to form the allyl complex and hydrogen. This is the

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(48) Professor T. J. Marks informs us that his group has also studied the reaction of $(C_5Me_5)_2Sm$ with propene: Marks, T. J. 44th Northwest Regional ACS Meeting, Reno Sparks, NV, June 1989, 20. Nolan, S. P.; Stern, D.; Marks, T. J. 196th ACS National Meeting, Los Angeles, CA, Sept. 1988, INOR 378.

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reaction pathway observed in the reaction of $(C_5Me_5)_2Sm$ with cyclopentadiene.[3] This scheme is unlikely since the observed byproduct of the alkene reactions is an alkane and not hydrogen.

In Scheme II (in Figure 6), the first part of the overall sequence involves the formal abstraction of hydrogen from the alkene by $(C_5Me_5)_2Sm$ to form a samarium(III) hydride and an allyl radical. Each of these intermediates can undergo further reaction. The allyl radical can (a) react with a second samarium(II) molecule to produce the observed samarium allyl product, (b) undergo a dimerization reaction, or (c) abstract hydrogen from the solvent to regenerate the alkene and produce a solvent radical, which will carry out more radical-based chemistry. The samarium(III) hydride can react with a second equivalent of alkene to generate a samarium alkyl complex like A above which would metalate a third equivalent of alkene to produce the observed samarium allyl complex. If the allyl radical reacts according to pathway (a) and the samarium hydride reacts as described above, the reaction stoichiometry matches that observed in the formation of **6**; i.e., 2 mol of $(C_5Me_5)_2Sm$ react with 3 mol of alkene to form 2 mol of $(C_5Me_5)_2Sm(\eta^3\text{-allyl})$ and 1 mol of alkane.

The major problem with Scheme II is that reactions in toluene should form $(C_5Me_5)_2Sm(CH_2Ph)$. The Sm(III) hydride complex in Scheme II should have chemistry similar to that observed for **3**, and, if anything, it should be more reactive. Hence, Sm(III) alkyls should form which should metalate toluene as observed in the reactions of **3** with alkenes and as observed for $(C_5Me_5)_2SmMe(THF)$.[17]

In Scheme III (in Figure 6) $(C_5Me_5)_2Sm$ adds to propene to produce a samarium(III)-substituted radical. This step is consistent with the polymerization chemistry observed in the reaction of $(C_5Me_5)_2Sm$ with ethene and with the butadiene dimerization observed in the reaction of $(C_5Me_5)_2Sm$ with 1,3-butadiene (see below). These Sm(III)-substituted radicals could disproportionate to produce 1 mol of the observed samarium allyl complex and a samarium alkyl complex. The samarium alkyl complex could react with another mol of alkene to yield a second mol of the samarium allyl complex and 1 mol of the alkane as in Scheme II. Scheme III, like Scheme II, matches the observed reaction stoichiometry. Scheme III also has the same problem identified in Scheme II, i.e., if Sm(III) alkyl complexes are present, $(C_5Me_5)_2SmCH_2Ph$ should be formed in toluene. Since this is not observed, Scheme III is also inadequate.

Indeed, any scheme which contains free $(C_5Me_5)_2Sm(\text{alkyl})$ moieties will fail to match the experimental results because these complexes will certainly metalate toluene. Any scheme which involves a free $(C_5Me_5)_2SmH$ unit in the presence of alkene is similarly unacceptable, since it will generate a reactive alkyl complex. On the other hand, it is difficult to imagine a metal-based reaction involving the formal transfer of a hydrogen atom from each of two alkenes to a third alkene which does not involve either a metal alkyl or metal hydride intermediate! The results strongly suggest that the $(C_5Me_5)_2Sm$-based transformation of 3 mol of alkene to 1 mol of alkane and 2 mol of allyl ligand occurs within a site in which toluene cannot access reactive samarium hydride and alkyl intermediates. It is unlikely that such a site could be provided by the $(C_5Me_5)_2Sm$ unit alone. However, recent results involving the reactivity of $(C_5Me_5)_2Sm$ with aryl-substituted alkenes suggest a possible explanation involving two $(C_5Me_5)_2Sm$ units.

$(C_5Me_5)_2Sm$ reacts with styrene and stilbene to form $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^4\text{:}\eta^2\text{-}CH_2CHPh)$ (**9**) and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^4\text{:}\eta^2\text{-}PhCHCHPh)$ (**10**), respectively.[11] The structures of these complexes are shown in Figure 7. In both cases, two $(C_5Me_5)_2Sm$ units coordinate to the carbon–carbon alkene bond. This is consistent with the 2:1 $(C_5Me_5)_2Sm$:(unsaturated substrate) stoichiometries observed in the products of reactions of $(C_5Me_5)_2Sm(THF)_{0.2}$ with the unsaturated substrates $PhC{\equiv}CPh$,[12] $PhN{=}NPh$,[59,60] $pyCH{=}CHpy$,[61] and $N{\equiv}N$.[62] In view of all of these 2:1 structures, it seems likely that the reactions between **1** and alkenes also could involve the formation of 2:1 intermediates, i.e., $[(C_5Me_5)_2Sm]_2(\text{alkene})$ complexes. If such intermediates are formed, then the four pentamethylcyclopentadienyl groups could provide the protected site which prevents the toluene solvent from being metalated by the alkyl and hydride intermediates involved in the observed alkene hydrogen transfer chemistry.

Figure 8 shows a scheme which may explain the experimental observations. In intermediate **B**, the propene is oriented in a way to mimic the observed structure of **9**. In this orientation, the C–H activation needed to form the allyl product seems readily available. Moreover, a second $(C_5Me_5)_2Sm$ unit is present which can accept the allyl ligand generated by C–H cleavage. To meet the requirement that no free Sm(III) hydrides or alkyls are formed, several other steps must occur before the bimetallic unit comes apart. First, the coordination of a second molecule of propene to the bimetallic hydride complex C must occur. Complexes **6′** and **10** suggest that there is room for coordination of a second alkene. If hydrogen transfer to this second propene to form the propyl complex D occurs while the bimetallic complex remains intact, the existence of a free Sm–H unit is avoided. If the propyl ligand in D abstracts another hydrogen atom while within the protected tetracyclopentadienyl environment of the bimetallic complex, the observed propane can be formed without having a free samarium alkyl unit. This second hydrogen abstraction could occur in two ways. The propyl ligand could metalate the coordinated allyl ligand to form a $SmCH_2CHCHSm$ unit containing a $C_3H_4^{2-}$ ion which could react with the third molecule of propene to generate the observed 2 mol of the allyl complex and the propane. Alternatively, the third molecule of propene could coordinate to one of the samarium atoms in D and be directly metalated to form a second allyl ligand. The bimetallic complex would dissociate at this point to the observed 2 mol of **4**. Again, the structures of **6′** and **10** suggest that there is room to coordinate this third molecule of propene. Obviously, the intimate details of this scheme are speculative. However, a scheme of this type would allow the transfer of two hydrogen atoms from two propene molecules to a third propene molecule without the formation of a free Sm(III) alkyl or hydride unit which would metalate toluene. It is possible that two $(C_5Me_5)_2Sm$ units provide a dynamic tetrakis(pentamethylcyclopentadienyl) cavity which allows this chemistry to occur.

Diene Reactions. The reaction of $(C_5Me_5)_2Sm$ with 1,3-butadiene to form primarily **7** is consistent with the observed chemistry of butadiene with alkali metals[63] and previously observed similarities between $(C_5Me_5)_2Sm$ and the alkali metals.[3,10] However, in contrast to the $(C_5Me_5)_2Sm$-based ethene polymerization reaction and the many alkali metal butadiene polymerization reactions, the $(C_5Me_5)_2Sm$/1,3-butadiene reaction stops at the dimer stage. Dimerization of 1,3-butadiene can be achieved with sodium under special conditions[64] as evidenced by subsequent CO_2 reactions which give C_8 diacids. The reaction of $K[(C_5H_5)_2V]$,[65] $NiBrMe(PPr^i_3)_2$,[66] and $[Pd(C_3H_5)OAc]_2/HOAc$[67] with

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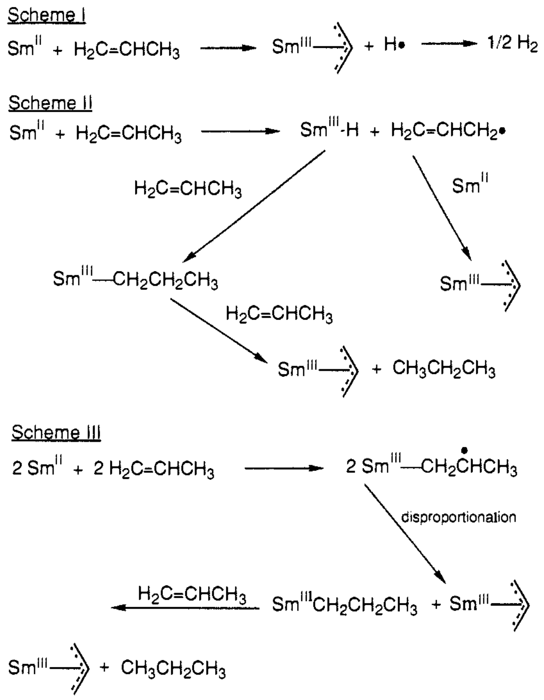
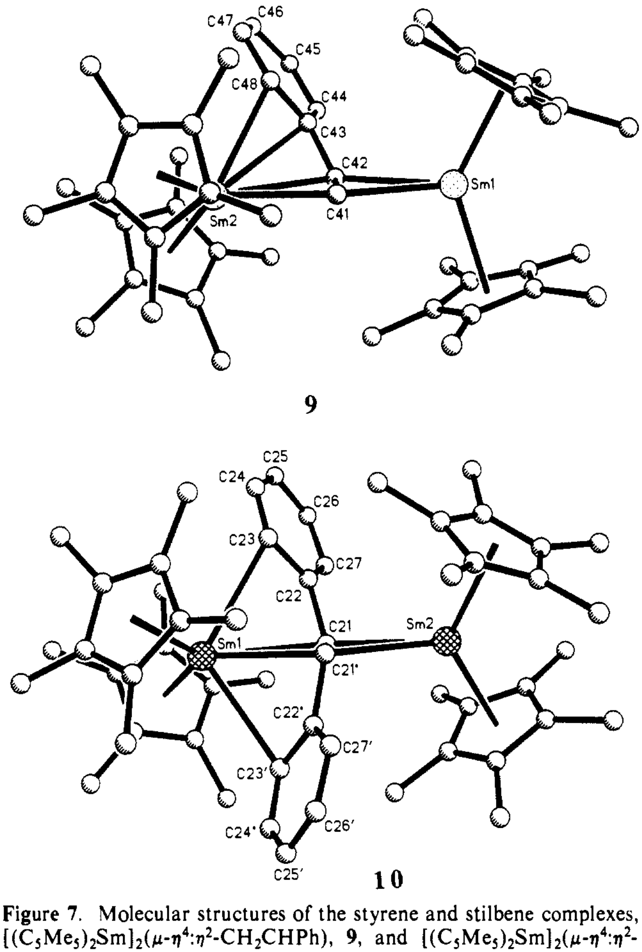


Figure 6. Possible reaction pathways for the formation of $(C_5Me_5)_2Sm$(allyl) complexes from $(C_5Me_5)_2Sm$ and alkenes.



9

10

Figure 7. Molecular structures of the styrene and stilbene complexes, $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^4:\eta^2\text{-}CH_2CHPh)$, 9, and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^4:\eta^2\text{-}PhCHCHPh)$, 10, respectively.

1,3-butadiene have also generated linear bis-allyl C_8H_{12} ligands which have been crystallographically identified.

It is possible that a bimetallic intermediate of the type discussed for the alkene reaction sequence in Figure 8 is the reason that this butadiene reduction stops at the C_8H_{12} stage. A complex such as $[(C_5Me_5)_2Sm]_2C_4H_6$ may form, a second butadiene molecule

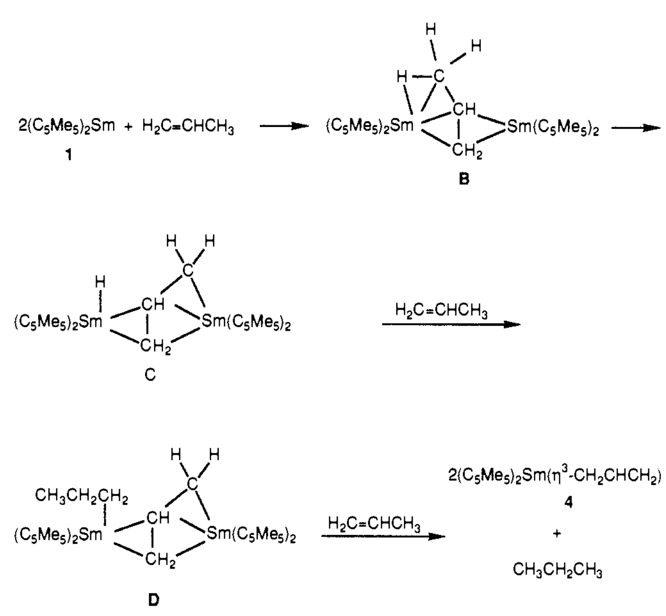


Figure 8. Possible reaction pathway for conversion of 3 mol of propene to propane and two allyl complexes within a tetracyclopentadienyl cavity generated from two $(C_5Me_5)_2Sm$ units.

may coordinate, and clean C–C bond formation may occur within the $[(C_5Me_5)_2Sm]_2$ cage. However, since butadiene is sufficiently different from the alkene substrates discussed above, there is no need to discuss a common reaction pathway.

The reaction of $(C_5Me_5)_2Sm$ with 1,5-hexadiene to form **8** was chosen to see if a $(C_5Me_5)_2Sm$-substituted 5-hexenyl radical would form and cyclize to a cyclopentylmethyl complex.[68-70] This is not observed and although not definitive, this is more evidence against Scheme III in Figure 6. With our present data, it is not possible to determine if the hydrogen transfer which occurs in the formation of **8** occurs in the same way as it does in the formation of **4–6**.

$(C_5Me_5)_2Sm$ vs $(C_5Me_5)_2Sm(THF)_2$. In general, **1** is more reactive than **2** with any given substrate as expected from the greater degree of steric unsaturation in **1**.[10] It is interesting to note that although **2** readily reacts with ethene and butadiene, it fails to form **4** and **5** from propene and butene in the facile manner achievable by **1**. Yet, **2** reacts with the more highly substituted substrate, allylbenzene. Since dissociation of one molecule of THF from **2** to form $(C_5Me_5)_2Sm(THF)$ occurs readily, it is clear that **2** can easily provide one open coordination position for an incoming substrate. The differences in substrate reactivity may arise because some substrates can coordinate further and displace the other THF, whereas other substrates cannot.

Conclusion

$(C_5Me_5)_2Sm$ reacts rapidly and quantitatively with alkenes to form allyl complexes via pathways which do not involve free $(C_5Me_5)_2SmH$ or $(C_5Me_5)_2Sm$(alkyl) intermediates. The observed facile hydrogen transfer between unsaturated hydrocarbons may occur within a dynamic tetracyclopentadienyl cavity provided by two $(C_5Me_5)_2Sm$ groups. The structures of the $(C_5Me_5)_2Sm$ complexes of styrene and stilbene and the isolation of $(C_5Me_5)_2Sm(CH_2CHCHPh)$ as a phthalan adduct indicates that there is room for coordination of additional substrate molecules to a $(C_5Me_5)_2Sm$(allyl) moiety as needed in a cage reaction scheme. The fact that $(C_5Me_5)_2Sm(THF)_2$ does not have the same reactivity as $(C_5Me_5)_2Sm$ demonstrates the importance of reagents and reaction conditions free of coordinating solvents in these Sm(II) reactions. Hence, one of the experimental consequences of the unusual, bent structure of the unsolvated $(C_5Me_5)_2Sm$ may

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be that the ligand deficient samarium centers readily form 2:1 $(C_5Me_5)_2$Sm:(unsaturated substrate) complexes. The tetracyclopentadienyl cavity generated in this way may provide an environment in which reactions not possible in bulk solution can occur. The formation of dynamic tetracyclopentadienyl cavities of this type may be available in other systems and should be pursued as a means of accomplishing rapid, quantitative cage chemistry without constructing a rigid enclosure.

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Supplementary Material Available: Tables of crystal data, final fractional coordinates, hydrogen atom coordinates, bond distances and angles, and thermal parameters (45 pages); tables of observed and calculated structure factors (74 pages). Ordering information is given on any current masthead page.

Molecular Hydrogen Complexes. 6. The Barrier to Rotation of η^2-H_2 in $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ (M = W, Mo; R = Cy, *i*-Pr): Inelastic Neutron Scattering, Theoretical, and Molecular Mechanics Studies

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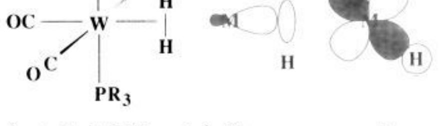
Abstract: Inelastic neutron scattering (INS) studies, electronic structure calculations, and molecular mechanics have been carried out on a series of molecular hydrogen complexes, $M(CO)_3(\eta^2\text{-}H_2)(PR_3)_2$ (M = Mo, W, R = c-C_6D_{11}; M = W, R = *i*-C_3D_7), in order to determine relative electronic versus steric (ligand bulk) effects on the barrier to rotation of the H_2 ligand. Low-lying vibrational excitations were identified with INS, and high-resolution spectrometers were used to measure the rotational tunneling splitting of the librational ground state on the solid complexes at 4 K. Replacement of the W by Mo changed the latter splitting by about a factor of 3, from 0.89 to 2.82 cm^{-1}. Variation of the phosphine on the other hand changed the frequency by less than 20%. The torsional transitions observed in the range 300–400 cm^{-1} are consistent with the tunneling transitions for a simple double-minimum potential with one angular degree of freedom for the rotation. The barrier heights hindering the H_2 rotation were determined from these measurements to be 2.4 kcal/mol (M = W, R = *i*-Pr), 2.2 kcal/mol (M = W, R = Cy), and 1.5–1.7 kcal/mol (M = Mo, R = Cy). Ab initio electronic structure calculations showed that the electronic component yields barriers of 1.4–1.8 kcal/mol for M = W and R = H, of 0.8 kcal/mol for M = W and R = Me, and of 0.6 kcal/mol for M = Mo and R = H. The present calculations show the simple double-minimum potential with the minima parallel to the P–M–P axis, which is indeed observed to be the equilibrium position for the H_2 in the crystallographic studies. Molecular mechanics (MM2) calculations showed no direct steric effects arising from the bulky phosphine ligands on the H_2 rotational barrier but did show an additional orientational preference (0.6–1.4 kcal/mol) for the H_2 along the P–M–P axis. The sum of the calculated ab initio and MM2 barriers agreed remarkably well with the observed INS values.

The nature of bonding of the dihydrogen ligand to transition metals is of major significance because $M(\eta^2\text{-}H_2)$ represents the prototype for ligand coordination solely via interaction of a metal center with a σ-bonding electron pair ("σ-bond complex").[1,2] This three-center, two-electron bonding is electron-deficient similar to boron hydrides and serves as a model for as yet unisolated alkane complexes (C–H coordination). Theoretical studies[3] indicate that the primary interaction is donation of electron density from the H–H σ bond to an empty metal orbital and that a lesser degree of metal to H_2 σ^* back-bonding analogous to metal to olefin π^* back-donation also occurs. The latter stabilizes the side-on (η^2) coordination mode and ultimately facilitates cleavage of the H–H bond to give dihydride complexes in oxidative addition reactions (Chart I). An experimental probe of the electronic details of dihydrogen coordination is clearly desirable. η^2-H_2 undergoes a remarkably wide variety of ligand dynamics, including rapid rotation about the M–H_2 axis.[1] The presence and magnitude of an energy barrier to rotation that is electronic in origin would offer

Chart I



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