Reactivity of the Substituted Butadienes, Isoprene and Myrcene, with Decamethylsamarocene

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The interaction of the substituted diene monomers isoprene, C_5H_8, and myrcene, $C_{10}H_{16}$, with a lanthanide was probed by examining their chemistry with $(C_5Me_5)_2Sm$. $CH_2{=}CHC(Me){=}CH_2$ reacts with $(C_5Me_5)_2Sm$ to form the bimetallic $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, **1**. Both $(C_5Me_5)_2Sm$ components in **1** exhibit trivalent metrical parameters. One Sm is oriented toward all four of the dienyl carbon atoms at distances of 2.604(9)−2.799(8) Å, and the other Sm interacts with only two carbons at distances of 2.544(9) and 2.674(9) Å. $CH_2{=}CHC({=}CH_2)CH_2CH_2CH{=}CMe_2$ reacts with $(C_5Me_5)_2Sm$ to form $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(CH_2)CH_2CH_2CHCMe_2]$, **2**, which is similar in structure to **1**. The double bond of the pendant olefinic substituent attached to the diene in myrcene does not coordinate. The structures of **1** and **2** are compared to the $(C_5Me_5)_2Sm/PhC{\equiv}CPh$ bimetallic reaction product $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^1{:}\eta^1\text{-}PhCCPh]$, **3**, which also contains two $(C_5Me_5)_2Sm$ units attached to an unsaturated hydrocarbon, but has equivalent trivalent $(C_5Me_5)_2Sm$ units. Each Sm in **3** interacts with the reduced $(PhC{\equiv}CPh)^{2-}$ primarily through a 2.52−2.54 Å Sm−C bond, although an ortho phenyl carbon is oriented toward each metal at a distance of >2.96 Å.

Introduction

One of the special aspects of lanthanide-based polymerization chemistry is that neodymium catalysts have been found to polymerize butadiene and isoprene to >98% *cis*-1,4-polybutadienes.[1−6] Since natural rubber is comprised primarily of *cis*-1,4-polyisoprene, this polymerization is of considerable importance.[7,8] Unfortunately, little is known about the details of these polymerizations including how the substrate dienes interact with the lanthanides.[1,8]

One approach to identifying basic lanthanide/unsaturated hydrocarbon interactions involves the divalent samarium metallocenes[9] $(C_5Me_5)_2Sm(THF)_2$[10] and $(C_5Me_5)_2Sm$.[11] These metallocenes have been found to interact with a variety of unsaturated hydrocarbons to form fully characterizable products. Styrene,[12] stilbene,[12] anthracene,[13] pyrene,[13] diphenylacetylene,[14] and diphenylbutadiyne[15] are converted to 2:1 metal/substrate complexes of general formula $[(C_5Me_5)_2Sm]_2[\text{substrate}]$, propene is converted to the allyl complex $(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH_2)$,[16] and butadiene is selectively dimerized to the bis-allyl species $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2CHCHCH_2CH_2CHCHCH_2]$.[16] Except for ethylene, which is polymerized by these compounds,[11,17] and diphenylacetylene, which did not form a crystalline product,[14] detailed structural information has been obtainable via X-ray crystallography for all of these decamethylsamarocene hydrocarbon complexes. The trivalent $(C_5Me_5)_2Sm$ unit appears to be particularly useful in generating crystalline materials, and it has even been used to stabilize a nonclassical carbonium ion.[18]

To examine further the interactions of dienes with lanthanides and to probe the generality of the dimerization of butadiene by $(C_5Me_5)_2Sm$, the reactions of $(C_5Me_5)_2Sm$ with the substituted butadienes, isoprene, $CH_2{=}CHC(Me){=}CH_2$, and myrcene, $CH_2{=}CHC({=}CH_2)CH_2CH_2CH{=}CMe_2$, have been examined. It was of interest to determine if the methyl substituent in isoprene changed the chemistry from that of butadiene, since isoprene and butadiene polymerizations are usually conducted under similar conditions. The natural

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product myrcene, found in bayberry plants, was examined since it has a pendant olefinic functionality attached to the butadiene framework. It was conceivable that this pendant olefin could coordinate to the metal and possibly mimic intermediates in the diene polymerization reactions, since these are generally envisioned to contain not only anionic allylic but also neutral diene coordination.[1−5] The isoprene and myrcene results are also compared to the recently determined structure of the $(C_5Me_5)_2Sm/PhC{\equiv}CPh$ reaction product, which had eluded crystallization for many years, but which now has been found to form a related bimetallic unsaturated hydrocarbon complex.

Experimental Section

The chemistry described below was performed under argon with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Solvents were purified as previously described.[19] $(C_5Me_5)_2Sm$[17] and $[(C_5Me_5)_2Sm]_2[PhCCPh]$[14] were prepared as described in the literature. Isoprene (Aldrich) and myrcene (Aldrich) were dried with 3 Å molecular sieves and vacuum distilled. ^1H and ^{13}C NMR spectra were obtained using an Omega 500 MHz and a GN 500 MHz NMR spectrometer at 25 °C. Infrared spectra were recorded as thin films[20] on a ASI ReactIR 1000 spectrometer. Complexometric analyses were performed as previously described.[21]

Synthesis of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, 1. In an argon-filled glovebox, isoprene (0.016 g, 0.240 mmol) in 2 mL of toluene at −36 °C was added to a green solution of $(C_5Me_5)_2Sm$ (0.100 g, 0.238 mmol) in 3 mL of toluene at −36 °C. The color changed from green to dark red in minutes as the reaction was stirred at room temperature. The solution was subsequently kept at −36 °C overnight. Removal of toluene by rotary evaporation gave a brown-red solid. This solid was dissolved in hexane and the solution centrifuged to remove any insoluble materials. Red crystals of **1** (0.096 g, 89%) suitable for X-ray crystallography were grown at −36 °C after 20 h. ^1H NMR (C_6D_6, 25 °C): δ 1.25 (C_5Me_5). ^{13}C NMR (C_6D_6, 25 °C): δ 120.4 (C_5Me_5), 20.2 ($C_5\mathit{Me}_5$). Calcd for $C_{45}H_{68}Sm_2$: Sm, 33.1. Found: Sm, 33.9. IR: 2961m, 2910s, 2856s, 2725w, 1494w, 1440s, 1382s, 1258s, 1146w, 1089w, 1061w, 1023m, 980w, 803s, 699m cm^{-1}.

Synthesis of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(CH_2)CH_2CH_2CHC(Me)_2]$, 2. **2** was synthesized as described for **1** from $(C_5Me_5)_2Sm$ (0.061 g, 0.145 mmol) and myrcene (0.01 g, 0.073 mmol). Red, X-ray quality crystals of **2** (0.065 g, 92%) were grown at −36 °C. ^1H NMR (C_6D_6, 25 °C): δ 1.38 (C_5Me_5). ^{13}C NMR (C_6D_6, 25 °C): δ 120.7 (C_5Me_5), 24.9 ($C_5\mathit{Me}_5$). Calcd for $C_{50}H_{76}Sm_2$: Sm, 30.8. Found: Sm, 31.7. IR: 2961m, 2910s, 2860s, 2725w, 1640w, 1567w, 1494w, 1440s, 1378m, 1258m, 1162w, 1089w, 1058w, 1023m, 980m, 888w, 834w, 807w, 699s cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for 1, 2, and 3. $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, 1. A red crystal of approximate dimensions 0.07 × 0.09 × 0.19 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[22] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT[23] and SADABS[24] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[25] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the centrosymmetric orthorhombic space group *Pbca*, which was later determined to be correct.

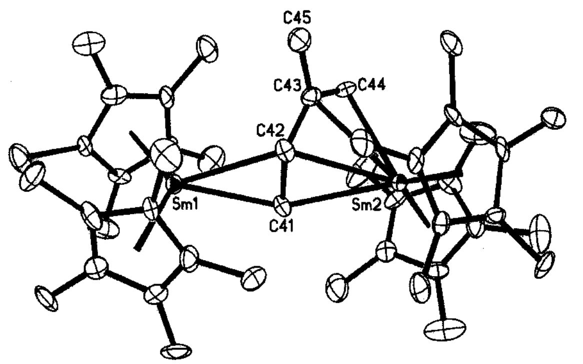

Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, **1**, shown at the 50% probability level.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[26] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.1189 and GOF = 1.025 for 436 variables refined against 5921 data (0.90 Å resolution). As a comparison for refinement on F, R1 = 0.0467 for those 4033 data with $I > 2.0\sigma(I)$.

$[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(CH_2)CH_2CH_2CHC(CH_3)_2]$, 2. A red crystal of approximate dimensions 0.15 × 0.18 × 0.22 mm was handled as described for **1** except that 20 s/frame scan time was used. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that the centrosymmetric space group *C*2/*c* was correct. Hydrogen atoms were located from a difference Fourier map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0806 and GOF = 1.028 for 773 variables refined against 11 227 data. As a comparison for refinement on F, R1 = 0.0336 for those 7967 data with $I > 2.0\sigma(I)$.

$[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^1{:}\eta^1\text{-}PhCCPh]$, 3. A dark purple crystal of approximate dimensions 0.07 × 0.17 × 0.25 mm, crystallized from pentane at −31 °C, was handled as described for **1** except that 25 s/frame scan time was used. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbca*, which was later determined to be correct. There were two independent molecules of the formula present. There was also one-half molecule of pentane solvent present per formula unit. At convergence, wR2 = 0.0883 and GOF = 1.060 for 1054 variables refined against 16 922 data (0.85 Å resolution). As a comparison for refinement on F, R1 = 0.0384 for those 12 707 data with $I > 2.0\sigma(I)$.

Results

Isoprene and Myrcene Reactivity with $(C_5Me_5)_2Sm$. Isoprene reacts in minutes with $(C_5Me_5)_2Sm$ in toluene at −36 °C to generate a brown-red solution which displays a single C_5Me_5 resonance at δ 1.25 ppm

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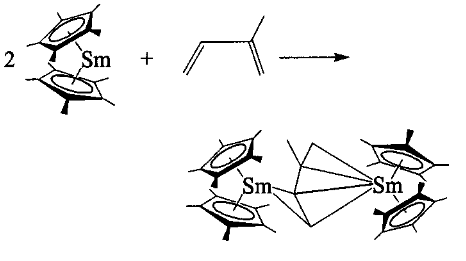
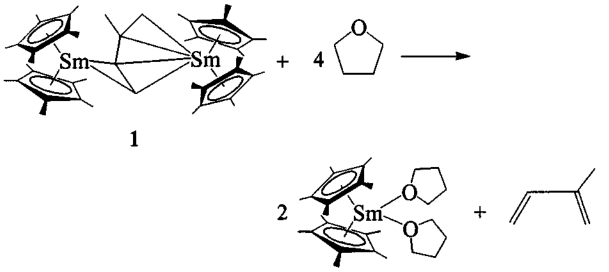
in its ^{1}H NMR spectrum. The ^{13}C NMR spectrum contained a ring carbon resonance at δ 120.4 and a methyl carbon resonance at δ 20.2 ppm, identified by DEPT studies, that are consistent with the presence of Sm(III) and not Sm(II).[16] An X-ray crystal structure determination was carried out to identify the product and revealed that the reaction forms $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, **1**, Figure 1, eq 1.



(1)

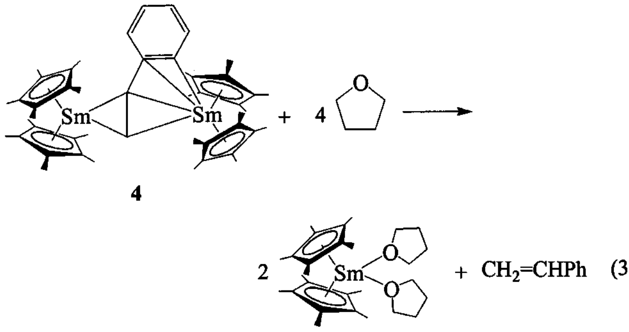
1

Attempts to run this reaction at room temperature gave complicated mixtures which were not separable into pure components. Addition of THF to **1** quantitatively regenerated a purple solution whose color and NMR spectra were consistent with that of $(C_5Me_5)_2Sm(THF)_2$, eq 2.[10]

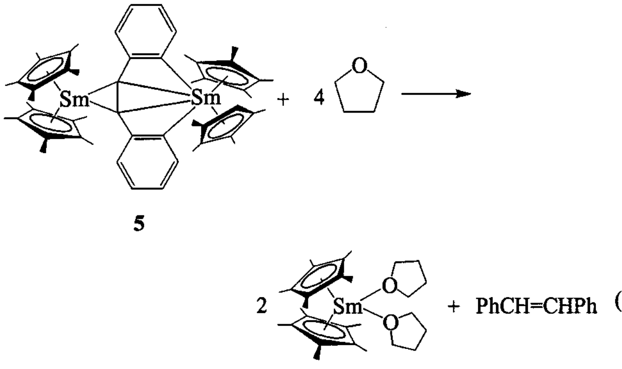


(2)

Similar reactions occur with $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh]$, **4**, and $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh]$, **5**, the products of treating styrene and stilbene with $(C_5Me_5)_2Sm$; that is, **4** and **5** react with THF to form $(C_5Me_5)_2Sm(THF)_2$ and the free olefin, eq 3 and eq 4.[12]



(3)



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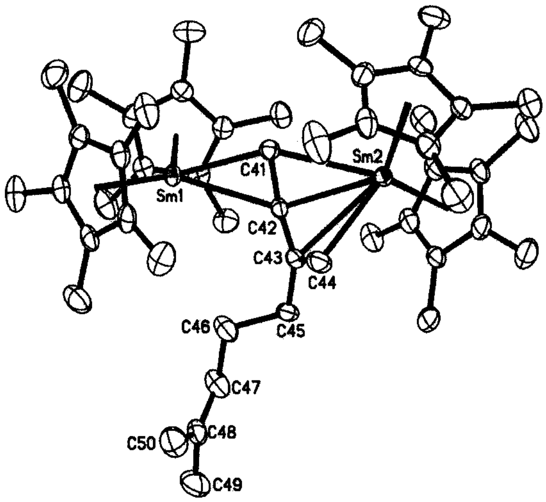
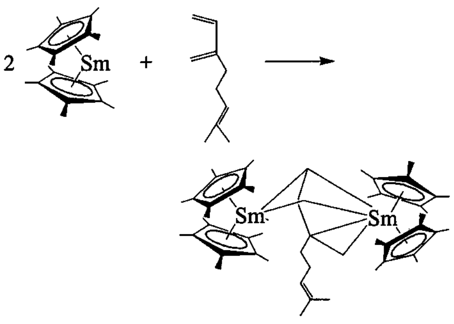


Figure 2. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(CH_2)CH_2CH_2CHC(Me)_2]$, **2**, shown at the 50% probability level.

The reaction of myrcene with $(C_5Me_5)_2Sm$ is analogous to that of isoprene. The product is also red-brown, a C_5Me_5 resonance is observed in the ^{1}H NMR spectrum at δ 1.38 ppm, and the ^{13}C NMR spectrum is consistent with a Sm(III) product. The complex was identified by X-ray crystallography as $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHC(CH_2)CH_2CH_2CHC(Me)_2]$, **2**, Figure 2, eq 5. In a fashion similar to **1**, addition of THF to **2** regenerates the Sm(II) complex $(C_5Me_5)_2Sm(THF)_2$ and myrcene, eq 6.



(5)

2

$$\mathbf{2} + 4\ THF \rightarrow 2\ (C_5Me_5)_2Sm(THF)_2 + CH_2{=}CHC({=}CH_2)CH_2CH_2CH{=}CMe_2 \quad (6)$$

The reaction of diphenylacetylene with Sm(II) is similar to eqs 1 and 3 except that $(C_5Me_5)_2Sm(THF)_2$ can be used as the starting material; that is, the product is not decomposed by THF. Although the $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^1{:}\ \eta^1\text{-}PhCCPh]$, **3**, product was made many years ago, structural characterization has been difficult due to its high solubility in alkanes. Crystals were ultimately obtained from pentane at −31 °C, and the structure is shown in Figure 3.

Structural Studies. Complexes **1**−**3** are similar in that they contain two trivalent $(C_5Me_5)_2Sm$ units complexed to an organic substrate. In this respect they are like many 2:1 Sm/substrate complexes formed by Sm(II) metallocenes and unsaturated hydrocarbons,[9,12,15] including the products of reaction with styrene, $(C_5$-

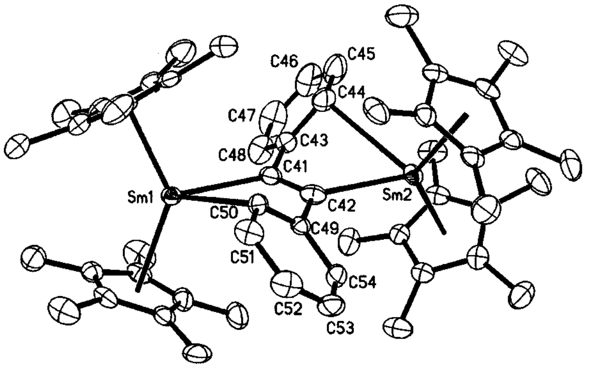


Figure 3. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^1\text{:}\eta^1\text{-PhCCPh}]$, **3**, shown at the 50% probability level.

Table 1. X-ray Data Collection Parameters[a] for $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2\text{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, 1, $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2\text{:}\eta^4\text{-}CH_2CHC(CH_2)\text{-}CH_2CH_2CHC(CH_3)_2]$, 2, and $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^1\text{:}\eta^1\text{-PhCCPh}]$, 3

empirical formula	$C_{45}H_{68}Sm_2$ **1**	$C_{50}H_{76}Sm_2$ **2**	$C_{54}H_{70}Sm_2\cdot 1/2C_5H_{12}$ **3**$\cdot 1/2C_5H_{12}$
fw	909.69	977.81	1055.87
temp (K)	158(2)	163(2)	163(2)
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pbca*	C2/*c*	*Pbca*
a (Å)	18.8904(17)	37.985(3)	23.3208(7)
b (Å)	18.4966(17)	10.0673(7)	19.8008(6)
c (Å)	23.594(2)	24.5941(17)	42.9886(13)
α (deg)	90	90	90
β (deg)	90	99.6340(10)	90
γ (deg)	90	90	90
volume (Å^3)	8243.8(13)	9272.2(11)	19850.9(10)
Z	8	8	16
ρ_{calcd} (Mg/m^3)	1.466	1.401	1.413
μ (mm^{-1})	2.849	2.539	2.378
R1[b] [$I > 2.0\sigma(I)$)]	0.0467	0.0366	0.0384
wR2[c] (all data)	0.1189	0.0806	0.0883

[a] Radiation: Mo Kα (μ = 0.71073 Å). Monochromator: highly oriented graphite. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Bond Distances (Å) in $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2\text{:}\eta^4\text{-}CH_2CHC(Me)CH_2]$, 1, $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^2\text{:}\eta^4\text{-}CH_2CH\text{-}C(CH_2)\text{-}CH_2CH_2CHC(CH_3)_2]$, 2, and $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^1\text{:}\eta^1\text{-PhCCPh}]$, 3[a]

	1	2	3
Sm(1)−C(41)	2.544(9)	2.5294(4)	2.521(6)
Sm(1)−C(42)	2.674(9)	2.672(4)	
Sm(1)−C(50)			2.966(6)
Sm(2)−C(41)	2.714(8)	2.749(4)	
Sm(2)−C(42)	2.723(9)	2.717(4)	2.532(6)
Sm(2)−C(43)	2.799(8)	2.803(4)	
Sm(2)−C(44)	2.604(9)	2.632(4)	3.052(7)
Sm(1)−Cnt(1)	2.419	2.441	2.461
Sm(1)−Cnt(2)	2.438	2.449	2.448
Sm(2)−Cnt(3)	2.506	2.512	2.462
Sm(2)−Cnt(4)	2.508	2.504	2.466
C(41)−C(42)	1.483(12)	1.475(5)	1.351
C(42)−C(43)	1.402(12)	1.401(5)	
C(43)−C(44)	1.395(13)	1.397(6)	
C(43)−C(45)	1.497(12)	1.513(5)	
C(42)−C(49)			1.483(8)
C(41)−C(43)			1.481(8)

[a] Cnt(1) is the ring centroid for C(1)−C(5), Cnt(2) is the ring centroid for C(11)−C(15), Cnt(3) is the ring centroid for C(21)−C(25), and Cnt(4) is the ring centroid for C(31)−C(35).

$Me_5)_2Sm(\mu\text{-}\eta^2\text{:}\eta^4\text{-}CH_2CHPh)$, **4**, and stilbene, $(C_5Me_5)_2\text{-}Sm(\mu\text{-}\eta^2\text{:}\eta^4\text{-PhCHCHPh})$, **5**.[12] Of these five complexes **1**−**5**, only **3** has a structure in which the two metals within the complex have similar coordination environments. In each of the other complexes, one $(C_5Me_5)_2Sm$ unit is coordinated to only two carbon atoms which formed a double bond in the starting material. The other $(C_5Me_5)_2Sm$ unit interacts more extensively with several carbon atoms of the hydrocarbon ligand.

The four C−C distances of the hydrocarbon unit originating from isoprene in **1** are identical within experimental error to the analogous distances in **2**. In each compound, the longest C−C bond is the C(43)−C(45) linkage to the methyl (1.513(5) Å) or $Me_2C{=}CH\text{-}CH_2CH_2\text{-}$ (1.497(12) Å) substituent. These distances are in the sp^3−sp^2 single bond range.[27] The next longest C−C bond in each structure is C(41)−C(42) (1.475(5) Å in **1** and 1.483(12) Å in **2**), the two-carbon portion of the ligand that interacts with both $(C_5Me_5)_2Sm$ units. This C−C linkage has been significantly lengthened; for example, the analogous C=C distance in butadiene is 1.36 Å.[27] The other former C=C double bond in the diene precursors, C(43)−C(44) (1.397(6) Å in **1** and 1.395(13) Å in **2**), which is close only to Sm(2), is lengthened compared to the free diene, but not as much. The C(42)−C(43) bonds (1.401(5) Å in **1** and 1.402(12) Å in **2**) are also shorter than the analogue in butadiene, 1.45 Å.[27] These data along with the NMR and metrical parameters of the $(C_5Me_5)_2Sm$ units (see below), which show them to be trivalent, are consistent with the formation of a delocalized diene dianion in both complexes.

The two $(C_5Me_5)_2Sm$ moieties in **1** exhibit different structural features consistent with their different coordination numbers, and a similar situation is found in **2**. Hence, the Sm(1) metallocene, which is coordinated to only two carbons of the substrate, has (ring centroid)−Sm−(ring centroid) angles of 134.2° for **1** and 135.7° for **2**. These are larger than those of the Sm(2) metallocene (126.8° for **1** and 127.8° for **2**), which must be more bent to accommodate coordination to four carbon atoms. For similar reasons, the Sm(1)−C(C_5Me_5) average distances, 2.609(9) Å in **1** and 2.600(4) Å in **2**, are shorter than those of Sm(2)−C(C_5Me_5), 2.710(9) Å in **1** and 2.725(4) Å in **2**.

The analogous Sm−C bonds in **1** and **2** are also quite similar. The shortest Sm−C bond involves lower coordinate Sm(1): Sm(1)−C(41) is 2.529(4) Å in **1** and 2.544(9) Å in **2**. These distances can be compared with the 2.484(14) and 2.528(8) Å Sm−C single bond distances in $(C_5Me_5)_2SmMe(THF)$[28] and $(C_5Me_5)_2Sm(CH_2Ph)\text{-}(THF)$,[29] respectively. The Sm(1)−C(42) distances are longer: 2.672(4) Å in **1** and 2.674(9) Å in **2**. Sm(2) on the other hand has three Sm−C distances in the 2.71−2.81 Å range and one shorter connection to the reduced diene, the Sm(2)−C(44) bond: 2.632(4) Å in **1** and 2.604(9) Å in **2**.

Comparison of the Sm−C distances in **1** and **2** with those in the analogous structure of the styrene complex,

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4, shows some striking similarities. The Sm(1) distances are very similar [2.537(15) and 2.647(15) Å in **4**], as are some but not all of the Sm(2) distances (2.674(15), 2.732(15), 2.850(16), and 2.772(17) Å in **4**). A major difference between the structures is that the closest Sm(2)−C distance in **4**, the 2.674(15) Å length, is to the analogue of C(41) not to the analogue of C(44).

The structure of **3** also suggests that diphenylacetylene has been reduced to a $(PhC{=}CPh)^{2-}$ dianion since the 1.351(9) Å C(41)−C(42) distance is in the C═C double bond region.[27] Consistent with this, the 2.738(6) Å average Sm−C(C_5Me_5) bond length and the 134.4° (ring centroid)−Sm−(ring centroid) angle are normal for trivalent $(C_5Me_5)_2Sm$ complexes.[30] Each samarium has one close contact to the $(PhC{=}CPh)^{2-}$ dianion: Sm(1)−C(41), 2.521(6) Å, and Sm(2)−C(42), 2.532(6) Å. Since these distances are similar to the 2.484(14) and 2.528(8) Å Sm−C single bonds in $(C_5Me_5)_2SmMe(THF)$[28] and $(C_5Me_5)_2Sm(CH_2Ph)(THF)$,[29] **3** displays a rather conventional interaction with this organic ligand. In addition to these primary contacts, two of the phenyl ring carbons are oriented toward the samarium centers at distances of 2.966(6) Å [Sm(1)−C(50)] and 3.052(7) Å [Sm(2)−C(44)]. Since these distances are over 0.2 Å longer than the Sm−C(C_5Me_5) distances, the interaction must be weak. In comparison, in the styrene product, **4**, Sm−C(phenyl ring) distances of 2.772(17) and 2.850(16) Å were observed.[12]

Discussion

In contrast to butadiene, which is dimerized by $(C_5Me_5)_2Sm$, isoprene and myrcene form 2:1 $[(C_5Me_5)_2Sm]_2$(diene) complexes, **1** and **2**, which are more analogous to the styrene and stilbene products, **4** and **5**. **1**, **2**, **4**, and **5** are all similar in that they are trivalent samarium complexes that can be converted back to Sm(II) by addition of THF. They also contain two distinct types of Sm centers: one $(C_5Me_5)_2Sm$ metallocene is bound to only two carbons of a former double bond and the other $(C_5Me_5)_2Sm$ unit interacts more extensively with the hydrocarbon unit. The THF reactivity and the structural asymmetry are both unusual. The structures of the isoprene and myrcene products show that this type of reactivity and structure is clearly not limited to aryl-substituted olefins. In addition, these results show that the position of the carbon of closest approach to the $(C_5Me_5)_2Sm$ unit interacting with several carbons can differ depending on the presence of an alkyl or aryl substituent.

In contrast, the $(C_5Me_5)_2Sm/PhC{\equiv}CPh$ product, **3**, does not convert back to Sm(II) upon addition of THF and the structure does not have a $(C_5Me_5)_2Sm$ unit interacting with either an extended series of carbon atoms or with just two carbons of an unsaturated bond. **3** has a structure more like a simple alkyl complex $(C_5Me_5)_2SmR$ with a single Sm−C interaction for each $(C_5Me_5)_2Sm$. This is more similar to the $[(C_5Me_5)_2Sm]_2(RC_4R)$ complexes derived from diynes: in each of these structurally chararacterized systems (R = Ph and CH_2CH_2Ph),[12,15] there is one close Sm−C distance in the single bond range and the other distances are 2.68−2.97 Å.

The structures of **1**−**5** plus the butadiene dimerization product, $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2CHCHCH_2CH_2CHCHCH_2]$, indicate that the specific substituent on the unsaturated carbon−carbon bond can have a significant influence on the structure of the lanthanide metallocene complex. This suggests that even in a well-controlled environment of a metallocene, considerable variation in olefin lanthanide interaction can occur.

Conclusion

$(C_5Me_5)_2Sm$ does not reductively dimerize isoprene and myrcene as occurs with butadiene. Instead, 2:1 $[(C_5Me_5)_2Sm]_2$(substrate) complexes are formed that have structural and chemical similarities to styrene and stilbene products. Although, $(C_5Me_5)_2Sm$ reduces $PhC{\equiv}CPh$ to a similar 2:1 product, the metal interacts with the hydrocarbon via two simple single Sm−C bonds rather than in the polyhapto manner of isoprene and myrcene.

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Supporting Information Available: Atomic coordinates, thermal parameters, and complete bond distances and angles; listing of observed and calculated structure factor amplitudes for compounds 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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