CO_2 Insertion Chemistry as a Probe of Organosamarium Allyl Reactivity

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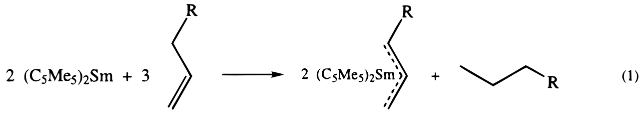
CO_2 reacts with $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, **1**, in toluene at room temperature and with $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = Me (**2**), Et (**3**)) in toluene at −78 °C to form $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CHR)]_2$ (R = H (**4**), Me (**5**) Et (**6**)) in >90% yield. In THF, **4**−**6** exist as solvated monometallic species, $(C_5Me_5)_2Sm(\mu^2\text{-}O_2CCH_2CH{=}CHR)(THF)$. Crystallization of **4** from hexanes gives a bimetallic complex which contains an eight membered SmOCOSmOCO ring. CS_2 reacts with **1** to form $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH_2CH{=}CH_2)$, **7**, which isomerizes to $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, **8**, in less than 48 h. COS reacts with **1** to form $(C_5Me_5)_2Sm(\eta^2\text{-}OSCCH_2CH{=}CH_2)$, **9**. Both **8** and **9** exist as monometallic species in THF, benzene, and toluene. Crystallization of **8** from toluene/phthalan gives a monometallic structure which contains a four-membered SmSCS ring. CO_2 also reacts with $(C_5Me_5)_2Sm(C_6H_5)$ in toluene to form $[(C_5Me_5)_2Sm(\mu\text{-}O_2CC_6H_5)]_2$, **10**, which is dimeric in toluene and exists as a solvated monomer in THF. **10** can also be made by the reduction of benzoic acid by $(C_5Me_5)_2Sm(THF)_2$ in THF. Similarly, reduction of terephthalic acid with 2 equiv of $(C_5Me_5)_2Sm(THF)_2$ produces $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}(O_2C)_2C_6H_4]$, **11**, which contains a single bridging $[(O_2C)_2C_6H_4]^{2-}$ unit and two four-membered SmOCO rings. X-ray crystal structures were obtained for **4**, **8**, **10**, and **11**.

Introduction

Allyl complexes are important in organometallic chemistry since they are often key intermediates in homogeneous catalysis and organic synthesis.[1,2] Organosamarium allyl complexes of the type $(C_5Me_5)_2Sm(CH_2CHCHR)$ are central species in samarium metallocene chemistry since they can arise from a variety of α-olefin and diene substrates and can initiate the polymerization of ethylene.[3,4,5] As shown in eqs 1−3, both divalent $(C_5Me_5)_2Sm(THF)_x$[6] (x = 0, 2) and trivalent $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$[7] complexes react with olefins to make allyl products of this type.[3]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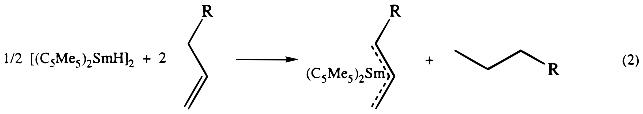
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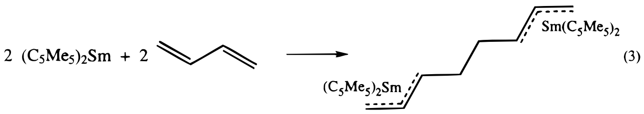
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All of the crystallographic studies of organosamarium metallocene allyl complexes obtained so far have shown that these ligands adopt η^3-structures in the solid state, even in the presence of coordinating solvents such as THF and phthalan.[3] However, NMR studies of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = H, Me, Ph) suggest that

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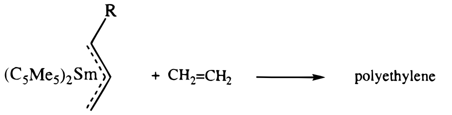
the η^3 structure interconverts to an η^1 form in solution in the presence of a coordinating ether.[3] Reactivity studies with ethylene,[3,8] eq 4, and hydrogen,[8] eq 5, and



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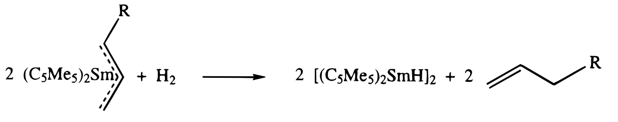

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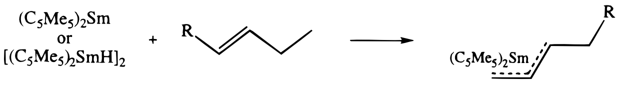

(6)

the isolation of terminal allyl complexes from reactions with internal olefins,[8] eq 6, also suggest that access to an η^1 form is facile. Further evidence for the accessibility of an η^1 form should be obtainable by definitively characterizing an insertion product in which the allyl unit has been converted to a $CH_2CH{=}CHR$ substituent attached to the inserted substrate. However, no definitive evidence of this type has been reported to date for the lanthanides.

We have recently found that under the proper and rather particular reaction conditions CO_2 can be used successfully as an insertion substrate in organosamarium chemistry.[9] This study showed that CO_2 had some advantages in organolanthanide chemistry over the common insertion reagent CO.[10] However, to date only a few other examples of CO_2 reactivity with organolanthanide complexes have been reported.[11,12] In contrast, CO_2 insertion is well-known in transition metal chemistry with examples involving metal allyl[13,14] as well as a variety of other metal ligand bonds.[15]

Accordingly, to probe the availability of an η^1-allyl form and to determine the utility of CO_2 as an insertion substrate with organolanthanide allyl complexes, we examined the reactions of CO_2 with the samarium allyl complexes $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = H (**1**), Me (**2**), Et (**3**)). In addition, analogous COS and CS_2 insertion chemistry was studied for comparison. CO_2 insertion into non-allylic samarium carbon bonds was also examined, and the synthesis of related carboxylates from the parent carboxylic acids was explored. These studies not only provided information about the reactivity of allylsamarium complexes but they also revealed some interesting monometallic/bimetallic equilibria and a synthetic route to olefin-substituted lanthanide metallocenes.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, the syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The preparation of $(C_5Me_5)_2Sm(THF)_2$,[16] $(C_5Me_5)_2Sm$,[17] $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$,[3] **1**, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_3)$,[3] **2**, and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_2CH_3)$,[8] **3**, and methods for drying solvents and taking physical measurements[18,19] have been described previously. $(C_5Me_5)_2Sm(C_6H_5)$ was prepared from $(C_5Me_5)_2Sm$ in a synthesis analogous to that of $(C_5Me_5)_2Sm(C_6H_5)(THF)$.[20] CS_2 was purchased from Fisher and dried over 4A molecular sieves prior to use. CO_2 (99.995% purity) and COS (96%+ purity) were purchased from Matheson and further purified by three freeze−pump−thaw cycles. Benzoic and terephthalic acid were purchased from Aldrich and vacuum-dried prior to use. ^{13}C and ^1H NMR analyses were carried out on a GN 500 spectrometer. Infrared analyses were carried out on a Perkin-Elmer 1600 series FTIR spectrometer. All C and H elemental analyses were conducted using a Carlo Erba instrument. All metal analyses were determined by complexometric titration.[19] Azobenzene (Aldrich, sublimed) was used as a standard in isopiestic molecular weight determinations using the Signer method.[21]

$[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2$, 4. In an argon-filled glovebox, a red solution of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, **1** (50 mg, 0.11 mmol), in ca. 10 mL of toluene and a stir bar were placed in a flask fitted with a high-vacuum greaseless stopcock. The flask was attached to a vacuum line and evacuated to the solvent vapor pressure. Excess CO_2 at 1 atm was admitted to the flask, and the solution turned yellow in less than 1 min. After the solution was stirred for 5 min, the flask was degassed and returned to the glovebox where solvent was removed to leave **4** as a yellow solid (53 mg, 96%). Mass spectrum: calcd for the monomer $(C_5Me_5)_2Sm(O_2CCH_2CH{=}CH_2)$, *m/e* 510.1894; found, *m/e* 510.1892. Anal. Calcd for $C_{24}H_{35}O_2Sm$: Sm, 29.73;

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C, 56.98; H, 6.97. Found: Sm, 30.1; C, 57.1; H, 6.92. Isopiestic molecular weight: calcd for $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CH_2)](THF)$, 578 g/mol; found in THF, 590 g/mol; calcd as $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CH_2)]_2$, 1011 g/mol; found in toluene, 1020 g/mol. ^{1}H NMR (C_6D_6): δ 2.71 (d, J_{HH} = 9.9 Hz, $O_2CCH_2CH{=}C\mathit{H}_{cis}H$, 1H), 2.35 (d, J_{HH} = 17 Hz, $O_2CCH_2CH{=}CH\mathit{H}_{trans}$, 1H), 1.58 (s, $C_5\mathit{Me}_5$, 30H), 0.48 (m, $O_2CCH_2C\mathit{H}{=}CH_2$, 1H), −1.58 (d, J_{HH} = 6.2 Hz, $O_2CC\mathit{H}_2CH{=}CH_2$, 2H). ^{1}H NMR (THF-$d_8$, major set of resonances): δ 6.09 (m, $O_2CCH_2C\mathit{H}{=}CH_2$, 1H), 5.24 (d, J_{HH} = 17 Hz, $O_2CCH_2CH{=}CH\mathit{H}_{trans}$, 1H), 5.15 (d, J_{HH} = 10.2 Hz, $O_2CCH_2CH{=}C\mathit{H}_{cis}H$, 1H), 3.27 (d, J_{HH} = 6.2 Hz, $O_2CC\mathit{H}_2CH{=}CH_2$, 2H), 1.31 (s, $C_5\mathit{Me}_5$, 30H). ^{1}H NMR (THF-d_8, minor set of resonances): δ 2.91 (d, J_{HH} = 9.9 Hz, $O_2CCH_2CH{=}C\mathit{H}_{cis}H$, 1H), 2.64 (d, J_{HH} = 17 Hz, $O_2CCH_2CH{=}CH\mathit{H}_{trans}$, 1H), 1.52 (s, $C_5\mathit{Me}_5$, 30H), 0.60 (m, $O_2CCH_2C\mathit{H}{=}CH_2$, 1H), −1.31 (d, J_{HH} = 6.2 Hz, $O_2CC\mathit{H}_2CH{=}CH_2$, 2H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 175 ($O_2\mathit{C}CH_2CH{=}CH_2$), 129 ($O_2CCH_2\mathit{C}H{=}CH_2$) 115 ($\mathit{C}_5Me_5$), 114 ($O_2CCH_2CH{=}\mathit{C}H_2$), 37.8 ($O_2C\mathit{C}H_2CH{=}CH_2$), 17.6 ($C_5\mathit{Me}_5$). ^{13}C{^{1}H} NMR (THF-d_8): δ 195 ($O_2\mathit{C}CH_2CH{=}CH_2$), 134 ($O_2CCH_2\mathit{C}H{=}CH_2$), 116 ($O_2CCH_2CH{=}\mathit{C}H_2$), 113 ($\mathit{C}_5Me_5$), 41.3 ($O_2C\mathit{C}H_2CH{=}CH_2$), 15.4 ($C_5\mathit{Me}_5$). IR (neat): 2907 m, 1571 s, 1415 s, 1255 w, 914 w, 602 w cm^{-1}. IR (benzene) ν_{CO} region: 1576 s, 1412 s cm^{-1}. IR (THF) ν_{CO} region: 1575 m, 1542 s, 1436 s cm^{-1}. Crystals of **4** suitable for X-ray diffraction were grown from a solution of hexanes at −36 °C.

Variable-Temperature ^{1}H NMR of 4. A sample of **4** (0.040 M) and THF-d_8 (0.022) was prepared in 50 μL of C_6D_6. ^{1}H NMR spectra were recorded over a temperature range of 295−340 K, and the temperature-dependent equilibrium between resonances at δ 1.31 and 1.51 was recorded A plot of ln K vs 1/T gave $\Delta H°$ = 17.6 kJ/mol and $\Delta S°$ = 8.7 J/(mol K).

$[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CHCH_3)]_2$, 5. Following the procedure described above, a red solution of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_3)$ (104 mg, 0.218 mmol) in ca. 10 mL of toluene was treated with CO_2 at 1 atm and −78 °C for ca. 20 min to form **5** as a yellow solid (107 mg, 94%). Anal. Calcd for $C_{25}H_{37}O_2Sm$: Sm, 28.92; C, 57.75; H, 7.17. Found: Sm, 28.0; C, 57.4; H, 7.2. Isopiestic molecular weight: calcd for $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CHCH_3)](THF)$, 592 g/mol; found in THF, 621 g/mol; calcd for $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CHCH_3)]_2$ 1040 g/mol; found in toluene, 998 g/mol. ^{1}H NMR (C_6D_6): δ 2.71 (m, $O_2CCH_2CH{=}C\mathit{H}CH_3$, 1H; selective decoupling of $O_2CCH_2CH{=}CHC\mathit{H}_3$, d, J_{HH} = 16 Hz, $O_2CCH_2CH{=}C\mathit{H}CH_3$, 1H), 1.60 (s, $C_5\mathit{Me}_5$, 30H), 0.20 (m, $O_2CCH_2C\mathit{H}{=}CHCH_3$, 1H; selective decoupling of $O_2CC\mathit{H}_2CH{=}CHCH_3$, d, J_{HH} = 16 Hz, $O_2CCH_2C\mathit{H}{=}CHCH_3$, 1H), −0.12 (d, J_{HH} = 6.0 Hz, $O_2CCH_2CH{=}CHC\mathit{H}_3$, 3H), −1.53 (d J_{HH} = 6.0 Hz, $O_2CC\mathit{H}_2CH{=}CHCH_3$, 2H). ^{1}H NMR (THF-$d_8$): δ 5.60 (m, $O_2CCH_2C\mathit{H}{=}C\mathit{H}CH_3$, 2H), 3.10 (m, $O_2CC\mathit{H}_2CH{=}CHCH_3$, 2H), 1.73 (m, $O_2CCH_2CH{=}CHC\mathit{H}_3$, signal overlap with THF prevented integration), 1.19 (s, C_5Me_5, 30H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 125 ($O_2CCH_2CH{=}\mathit{C}HCH_3$), 121 ($O_2CCH_2\mathit{C}H{=}CHCH_3$), 115 ($\mathit{C}_5Me_5$), 36.5 ($O_2C\mathit{C}H_2CH{=}CHCH_3$), 17.6 ($C_5\mathit{Me}_5$), 16.0 ($O_2CCH_2CH{=}CH\mathit{C}H_3$). ^{13}C{^{1}H} NMR (THF-d_8): δ 127, 126 ($O_2CCH_2\mathit{C}H{=}\mathit{C}HCH_3$), 113 ($\mathit{C}_5Me_5$), 40.0 ($O_2C\mathit{C}H_2CH{=}CHCH_3$), 18.1 ($O_2CCH_2CH{=}CH\mathit{C}H_3$), 15.7 ($C_5\mathit{Me}_5$). IR (neat): 2715 m, 1578 s, 1417 s, 1268 w, 815 w, 728 w cm^{-1}. IR (benzene) ν_{CO} region: 1574 s, 1419 m cm^{-1}. IR (THF) ν_{CO} region: 1573 s, 1540 m, 1424 m cm^{-1}.

$[(C_5Me_5)_2Sm(\eta\text{-}O_2CCH_2CH{=}CHCH_2CH_3)]_2$, 6. Following the procedure described for **4**, a red solution of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_2CH_3)$ (59.4 mg, 0.121 mmol) in ca. 10 mL of toluene was treated with CO_2 at 1 atm and −78 °C for ca. 20 min to form **6** as a yellow solid (62 mg, 98% yield). Anal. Calcd for $C_{26}H_{39}O_2Sm$: Sm, 28.16; C, 58.48; H, 7.36. Found: Sm, 28.5; C, 59.1; H, 7.3. Isopiestic molecular weight: calcd for $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CHCH_2CH_3)](THF)$, 606 g/mol; found in THF, 590 g/mol; calcd for $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CHCH_2CH_3)]_2$, 1068 g/mol; found in toluene, 1015 g/mol. ^{1}H NMR (benzene-d_6): δ 2.86 (m, $O_2CCH_2CH{=}C\mathit{H}CH_2CH_3$, 1H), 1.61 (s, $C_5\mathit{Me}_5$, 30H), 0.28 (m, $O_2CCH_2C\mathit{H}{=}CHCH_2CH_3$, 1H), 0.26 (m, $O_2CCH_2CH{=}CHC\mathit{H}_2CH_3$, 2H), −0.28 (d, J_{HH} = 7.0, $O_2CCH_2CH{=}CHCH_2C\mathit{H}_3$, 3H), −1.53 (d, J_{HH} = 7.0, $O_2CC\mathit{H}_2CH{=}CHCH_2CH_3$, 2H). ^{1}H NMR (THF-$d_8$): δ 5.66 (m, $O_2CCH_2C\mathit{H}{=}C\mathit{H}CH_2CH_3$, 2H), 3.11 (m, $O_2CC\mathit{H}_2CH{=}CHCH_2CH_3$, 2H), 2.09 (m, $O_2CCH_2CH{=}CHC\mathit{H}_2CH_3$, 2H), 1.20 (s, $C_5\mathit{Me}_5$, 30H), 1.06 (d, J_{HH} = 7.5 Hz, $O_2CCH_2CH{=}CHCH_2C\mathit{H}_3$, 3H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 132 ($O_2CCH_2CH\mathit{C}HCH_2CH_3$), 119 ($O_2CCH_2\mathit{C}HCHCH_2CH_3$), 115 ($\mathit{C}_5Me_5$), 36.7 ($O_2C\mathit{C}H_2CHCHCH_2CH_3$), 24.1 ($O_2CCH_2CHCH\mathit{C}H_2CH_3$), 17.7 ($C_5\mathit{Me}_5$), 12.2 ($O_2CCH_2CHCHCH_2\mathit{C}H_3$). ^{13}C{^{1}H} NMR (THF-d_8): δ 134, 124 ($O_2CCH_2\mathit{C}H{=}\mathit{C}HCH_2CH_3$), 113 ($\mathit{C}_5Me_5$), 40.2 ($O_2C\mathit{C}H_2CH{=}CHCH_2CH_3$), 26.5 ($O_2CCH_2CH{=}CH\mathit{C}H_2CH_3$), 15.7 ($C_5\mathit{Me}_5$), 14.3 ($O_2CCH_2CH{=}CHCH_2\mathit{C}H_3$). IR (neat): 2624.1 s, 1566.0 s, 1458.3 s, 1377.3 m, 1260.1 m, 1087.7 mb, 966.7 w, 803.5 w, 735.8 w cm^{-1}. IR (benzene) ν_{CO} region: 1572 s, 1419 s cm^{-1}. IR (THF) ν_{CO} region: 1570 s, 1544 m, 1435 s cm^{-1}.

$(C_2Me_5)_2Sm(\eta^2\text{-}S_2CCH_2CH{=}CH_2)$, 7. In an argon-filled glovebox, a red solution of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (250 mg, 0.542 mmol) in ca. 10 mL of hexanes and a stir bar were placed in a flask fitted with a high-vacuum greaseless stopcock. The flask was attached to a Schlenk line, evacuated to the solvent vapor pressure, and then refilled with nitrogen. Excess CS_2 was transferred to the flask via cannula resulting in an immediate color change to orange. The solution was stirred for 5 min, after which time excess CS_2 and solvent were evacuated leaving dark orange solids. The solids were returned to the glovebox and extracted with hexanes. The resulting red solution was evaporated leaving **7** as red solids (220 mg, 88%). Anal. Calcd for $C_{24}H_{35}S_2Sm$: Sm, 27.95; C, 53.57; H, 6.56. Found: Sm, 28.1; C, 53.4; H, 6.7. ^{1}H NMR (benzene-d_6): δ 7.15 (m, $S_2CCH_2C\mathit{H}{=}CH_2$, signal overlap with benzene prevented integration), 5.64 (d, J_{HH} = 17 Hz, $S_2CCH_2CH{=}CH\mathit{H}_{trans}$, 1H), 5.55 (d, J_{HH} = 9.5 Hz, $S_2CCH_2CH{=}C\mathit{H}_{cis}H$, 1H), 4.78 (d, J_{HH} = 7.0 Hz, $S_2CC\mathit{H}_2CH{=}CH_2$, 2H), 2.41 (m, $S_2CCH_2C\mathit{H}{=}CH_2$, 1H), 0.833 (s, $C_5\mathit{Me}_5$, 30H). ^{1}H NMR (THF-d_8): δ 5.40 (m, $S_2CCH_2C\mathit{H}{=}CH_2$, 1H), 5.20 (m, $S_2CCH_2CH{=}C\mathit{H}_2$, 2H), 1.79 ($S_2CC\mathit{H}_2CH{=}CH_2$, signal overlap with THF prevented integration), 1.15 (s, $C_5\mathit{Me}_5$, 30H). ^{13}C{^{1}H} (benzene-d_6): δ 280 ($S_2\mathit{C}CH_2CH{=}CH_2$), 135 ($S_2C\mathit{C}H_2CH{=}CH_2$), 119 ($\mathit{C}_5Me_5$), 118 ($S_2CCH_2CH{=}\mathit{C}H_2$), 64.3 ($S_2CCH_2\mathit{C}H{=}CH_2$), 18.4 ($C_5Me_5$). ^{13}C{^{1}H} (THF-$d_8$): δ 142 ($S_2CCH_2\mathit{C}H{=}CH_2$), 134 ($S_2CCH_2CH{=}\mathit{C}H_2$), 115 ($\mathit{C}_5Me_5$), 17.7 ($S_2C\mathit{C}H_2CH{=}CH_2$), 17.5 ($C_5\mathit{Me}_5$).

$(C_2Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, 8. In solution, compound **7** completely isomerizes to **8** in less than 48 h as observed by NMR spectroscopy. Crystals of **8** suitable for X-ray diffraction were grown from a mixture of toluene and phthalan. Anal. Calcd for $C_{24}H_{35}S_2Sm$: Sm, 27.95; C, 53.57; H, 6.56. Found: Sm, 27.6; C, 53.6; H, 6.4. Isopiestic molecular weight: calcd for $(C_5Me_5)_2Sm(S_2CCH{=}CHCH_3)$ 538 g/mol, found in THF, 510 g/mol; found in toluene, 673 g/mol. ^{1}H NMR (benzene-d_6): δ 7.78 (m, $S_2CC\mathit{H}{=}C\mathit{H}CH_3$, 2H), 1.87 (m, $S_2CCH{=}CHC\mathit{H}_3$, 3H), 0.898 (s, C_5Me_5, 30 H). ^{1}H NMR (THF-d_8): δ 6.82 (m, $S_2CCH{=}C\mathit{H}CH_3$, 1H), 6.39 (d, $S_2CC\mathit{H}{=}CHCH_3$, 1H), 1.93 (d, $S_2CCH{=}CHC\mathit{H}_3$, 3), 1.14 (s, C_5Me_5, 30H). ^{13}C{^{1}H} (benzene-d_6): δ 145,136 ($S_2C\mathit{C}H{=}\mathit{C}HCH_3$), 118 ($\mathit{C}_5Me_5$), 18.3 ($C_5\mathit{Me}_5$), 18.0 ($S_2CCH{=}CH\mathit{C}H_3$). ^{13}C{^{1}H} (THF-$d_8$): δ 143 ($S_2C\mathit{C}H{=}CHCH_3$), 135 ($S_2CCH{=}\mathit{C}HCH_3$), 116 (C_5Me_5), 17.7 ($S_2CCH{=}CH\mathit{C}H_3$), 17.5 ($C_5\mathit{Me}_5$). IR (neat): 2906 s, 1620 m, 1436 s, 1377 m, 1276 w, 1164 m, 1084 m, 974 m, 918 m cm^{-1}.

$(C_5Me_5)_2Sm[\eta^2\text{-}(OCS)CH_2CH{=}CH_2]$, 9. Following the procedure for **4**, a red solution of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, **1** (97.6 mg,0.211 mmol), in ca. 10 mL of toluene was treated with 1 atm of COS, which resulted in an orange solution. Solvent was removed leaving **9** as a viscous orange oil (97.9 mg, 89%). Anal. Calcd for $C_{24}H_{35}OSSm$: Sm, 29.04; Found: Sm, 29.4. Isopiestic molecular weight: calcd for $(C_5Me_5)_2Sm[(OCS)CH_2CH{=}CH_2]$, 522.0 g/mol; found in THF, 580 g/mol; found in toluene, 550 g/mol. ^{1}H NMR (benzene-d_6): δ 7.15 (m, $(OCS)CH_2C\mathit{H}{=}CH_2$, signal overlap with benzene prevented integration), 5.83 (d, J_{HH} = 8.7 Hz, (OCS)$CH_2CH{=}CHH_{trans}$, 1H), 5.59 (d, J_{HH} = 5 Hz, (OCS)$CH_2CH{=}CH_{cis}H$, 1H), 5.32 (d, J_{HH} = 7.15, (OCS)$CH_2CH{=}CH_2$), 0.79 (s, C_5Me_5, 30H). ^1H NMR (THF-d_8): δ 5.79 (m, (OCS)$CH_2CH{=}CH_2$, 1H), 4.98(m, (OCS)$CH_2CH{=}CH_2$, 2H), 3.0 (d, J_{HH} = 6.9 Hz, (OCS)CH_2-$CH{=}CH_2$, 2H), 1.18 (s, C_5Me_5, 30H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 251 ({OCS}$CH_2CH{=}CH_2$), 133 ({OCS}$CH_2CH{=}CH_2$), 119 (C_5Me_5), 118 ({OCS}$CH_2CH{=}CH_2$), 58 ({OCS}-$CH_2CH{=}CH_2$), 17.9 (C_5Me_5). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 232 ({OCS}$CH_2CH{=}CH_2$), 133 ({OCS}$CH_2CH{=}CH_2$), 117 ({OCS}$CH_2CH{=}CH_2$), 113 (C_5Me_5), 53 ({OCS}$CH_2CH{=}CH_2$). IR (neat): 2905 s, 1638 m, 1448 s, 1380 m, 1125 w, 1047 m, 919 m, 804 w cm^{-1}.

$[(C_5Me_5)_2Sm(\mu^2\text{-}O_2CC_6H_5)]_2$, 10. Following the procedure for **4**, a yellow solution of $(C_5Me_5)_2Sm(C_6H_5)$ (120 mg, 0.241 mmol) in ca. 10 mL of toluene was treated with 1 atm of CO_2. No notable color change resulted from the reaction. Solvent was removed leaving **10** as a yellow solid (121 mg, 93%). Crystals of **10** suitable for X-ray crystallographic studies were grown from hexanes. Anal. Calcd for $C_{27}H_{35}O_2Sm$: Sm, 27.75; C, 59.94; H, 6.51. Found: Sm, 28.4; C 60.2, H 6.4. Isopiestic molecular weight: calcd for $[(C_5Me_5)_2Sm(O_2CC_6H_5)](THF)$, 598 g/mol; found in THF, 623 g/mol; calcd for $[(C_5Me_5)_2Sm(O_2CC_6H_5)]_2$, 1083 g/mol; found in toluene, 1020 g/mol. ^1H NMR (benzene-d_6): δ 5.56 (t, J_{HH} = 7.5 Hz, *p*-C_6H_5, 1H), 4.84 (t, J_{HH} = 8 Hz, *m*-C_6H_5, 2H), 1.65 (s, C_5Me_5, 30H), −0.25 (d, J_{HH} = 8 Hz, *o*-C_6H_5, 2H). ^1H NMR (THF-d_8): δ 7.83 (d, J_{HH} = 8 Hz, *o*-C_6H_5, 2H), 7.48 (t, J_{HH} = 8 Hz, *p*-C_6H_5, 1H), 7.37 (t, J_{HH} = 8 Hz, *m*-C_6H_5, 2H), 1.20 (s, C_5Me_5, 30H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 131 (*p*-C_6H_5), 237 (*ipso*-C_6H_5), 126 (*o*-C_6H_5), 125 (*m*-C_6H_5), 115 (C_5Me_5), 17.9 (C_5Me_5). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 132 (*p*-C_6H_5), 130 (*o*-C_6H_5), 128 (*m*-C_6H_5), 113 (C_5Me_5), 14.5 (15.8 C_5Me_5) (*ipso* carbon not located). IR (neat): 3000 m, 2906 m, 1597 s, 1553 s, 1395 s, 1067 w, 1026 w, 717 m cm^{-1}. IR (benzene) ν_{CO} region: 1552 s, 1400 s cm^{-1}. IR (THF) ν_{CO} region: 1546 s, 1500 m, 1420 s cm^{-1}.

Synthesis of 10 from $(C_5Me_5)_2Sm(THF)_2$ and Benzoic Acid. In a nitrogen-filled glovebox, benzoic acid (26 mg, 0.22 mmol) was added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (104 mg, 0.22 mmol) in ca. 7−10 mL of THF. Within 10 min the solution color turned yellow. Removal of solvent by rotary evaporation left yellow solids. The benzene-d_8 ^1H NMR spectrum of the solids contained signals for **10** and C_5Me_5H. Recrystallization from hexanes left pure **10** (99 mg, 83%).

$[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}(O_2C)_2C_6H_4]$, 11. In a nitrogen-filled glovebox, terephthalic acid (15 mg, 0.089 mmol) was added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (100 mg, 0.18 mmol) in ca. 7−10 mL THF. The color of the solution changed to yellow in less than 1 min. Removal of the solvent left yellow-orange solids. Recrystallization of the solids from THF gave **11** as yellow plates (80 mg, 80%). ^1H NMR (THF-d_8): δ 7.81 (s, C_6H_4, 4H), 1.25 (s, C_5Me_5, 30H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 132 (*m*-C_6H_4), 115 (C_5Me_5), 14.5 (C_5Me_5) (*ipso* carbons not located). IR (solid state): 2912 m, 1573 s, 1384 s, 1050 m, 870 w cm^{-1}. IR (THF) ν_{CO} region: 1550 s br, 1420 m br, 1402 s br cm^{-1}. Since **11** appeared to lose solvent and crystals of **11** degraded due to cracking, analytical data were sought on solvent-free material. **11** was dissolved in toluene, and the solution was stirred for ca. 1 h. During that time, yellow solids precipitated from solution. The solids were removed via centrifugation and stirred again with fresh toluene for ca. 30 min. The solids were removed from the solvent via centrifugation, washed twice with hexanes, and dried under vacuum. Anal. Calcd for THF-free **11**, i.e., $C_{48}H_{64}O_4Sm_2$: Sm, 29.91; C, 57.32; H, 6.41. Found: Sm, 30.2; C 57.4, H 6.2.

X-ray Data Collection, Structure Determination, and Refinement. All crystallographic data were collected on a Siemens P4 diffractometer from crystals mounted on a glass fiber. The determination of diffraction symmetry, unit cell parameters, and crystal orientation were carried out by standard procedures.[22] Intensity data were collected by use of the $2\theta/\omega$ scan technique and processed with a local version of CARESS,[23] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out by use of SHELXTL, version 5.03.[24] All data were corrected for absorption on the basis of φ-scan profiles. The structures were solved by direct or Patterson methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included and were refined by use of the riding model. The analytical scattering factors for neutral atoms[25] were used throughout the analysis. Crystal data and selected experimental information are listed in Table 1.

Table 1. Experimental Data for the X-ray Diffraction Studies of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CHCH_2)]_2$, 4, $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH_2CHCH_2)$, 8, and $[(C_5Me_5)_2Sm(\mu\text{-}O_2CC_6H_5)]_2$, 10[a]

	4	**8**	**10**
formula	$C_{24}H_{35}O_2Sm$	$C_{24}H_{35}S_2Sm$	$C_{34}H_{43}O_2Sm$
fw	505.87	537.99	634.03
temp (K)	153(2)	153	293(2)
cryst system	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.7650(10)	8.5029(12)	10.4943(10)
b (Å)	15.6390(10)	9.027(2)	10.6518(12)
c (Å)	15.0070(10)	17.722(2)	14.9495(14)
α (deg)	90	77.226(11)	110.175(6)
β (deg)	103.31	81.737(9)	97.651(5)
γ (deg)	90	65.183(12)	98.927(7)
V (Å^3)	2230.2	1202.1(3)	1517.8(3)
Z	4	2	2
D_{calcd} (Mg/m^3)	1.507	1.486	1.387
diffractometer	Siemens P4	Siemens P4	Siemens P4
μ (mm^{-1})	2.648	2.622	1.961
refinement[b] w$R2$ (all data)	0.0651	0.1066	0.0802

[a] Radiation: Mo Kα (μ = 0.710 730 Å). Monochromator: highly oriented graphite. [b] $R1 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(w(F_o^2)^2]]^{1/2}$.

$[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2$, 4. Intensity data were collected at 153 K from a yellow parallelepiped-shaped crystal of approximate dimensions 0.33 × 0.20 × 0.20 mm. The 2/*m* diffraction symmetry and the systematic absences $h + l \neq 2n$ for the $h0l$ reflections and $k \neq 2n$ for the $0k0$ reflections uniquely defined the monoclinic space group $P2_1/n$. Refinement of 279 variables against 6508 unique data converged to a final value of w$R2$ (all data) of 0.0651 and a conventional R (based on F for 5593 data with $F > 4(\sigma(F))$ of 0.0252.

$(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, 8. Data were collected at 153 K from a yellow crystal of approximate dimensions 0.17 × 0.16 × 0.14 mm. The $\bar{1}$ diffraction symmetry and the lack of systematic absences indicated the triclinic crystal system; refinement was successfully carried out in the centrosymmetric space group $P\bar{1}$. The pentamethylcyclopentadienyl ring defined by atoms C(11)−C(20) is disordered. In the final refinement model, each atom was included with two equally weighted components. Disorder was also observed for the sulfur atom and carbon atoms C(21)−C(24) and was treated in the same manner. Refinement of 388 variables against 5485 unique data converged to a final value of w$R2$ (all data) of 0.1066 and a conventional R (based on F for 4762 data with $F > 4(\sigma(F))$ of 0.0370.

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(22) *XSCANS Software Users' Guide*, version 2.1; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

(23) Broach, R. W. *CARESS*; Argonne National Laboratory: Argonne, IL 1978.

(24) Sheldrick, G. M. *SHELXTL*, Version 5.03; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

(25) *International Tables for Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

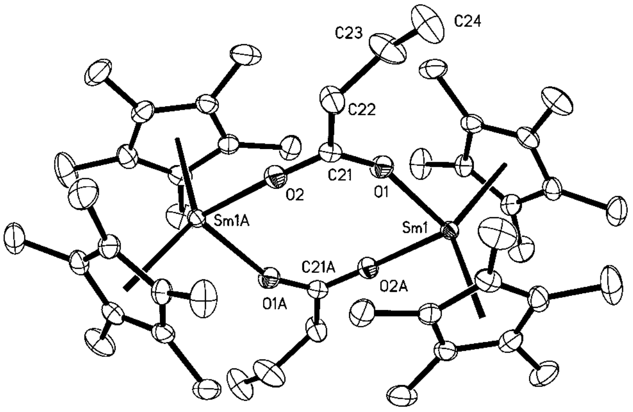

Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2$, **4**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

$[(C_5Me_5)_2Sm(\eta^2\text{-}O_2CC_6H_5)]_2$, 10. Data were collected at 293 K from a yellow platelike crystal of approximate dimensions 0.42 × 0.20 × 0.11 mm. The $\bar{1}$ diffraction symmetry and the lack of systematic absences indicated the triclinic crystal system; refinement was successfully carried out in the centrosymmetric space group $P\bar{1}$. Refinement of 343 variables against 3887 unique data converged to a final value of w$R2$ (all data) of 0.0802 and a conventional R (based on F for 3372 data with $F > 4(\sigma(F))$ of 0.0316.

$[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}(O_2C)_2C_6H_4]$, 11. The data on crystals of **11** were sufficient to provide atom connectivity but not high precision metrical information due to the poor quality of data collected. Cell constants for the triclinic crystals at 153 K follow: $P\bar{1}$, a = 10.135(3) Å, b = 10.322(2) Å, c = 15.784(6) Å, α = 74.02(2)°, β = 80.45(2)°, γ = 87.42(2)°, V = 1565.5(8) Å^3, Z = 1, D_{calcd} = 1.415 Mg/m^3.

Results

CO_2 Reactions with $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$. $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, **1**, reacts instantly with CO_2 in toluene at room temperature to form **4** as a light orange solid in quantitative yield. Complex **4** was characterized by elemental analysis, mass spectrometry, solution molecular weight, IR and NMR spectroscopy, and X-ray crystallography. The X-ray study (Table 3) showed that crystals of **4** grown from hexanes exist in the solid state as the bimetallic complex $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2$ (Figure 1); i.e., the reaction occurs as shown in eq 7. When the reaction was repeated in THF, **4** was again produced as the major product, but the ^1H NMR spectrum contained other C_5Me_5 resonances as well as signals for C_5Me_5H and $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$.[26] The syntheses in THF gave mixtures from which **4** could not be easily separated.

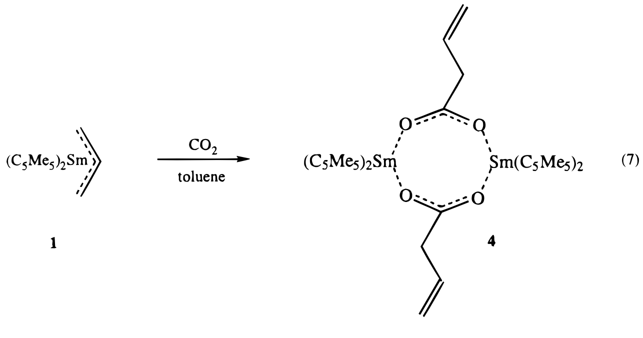

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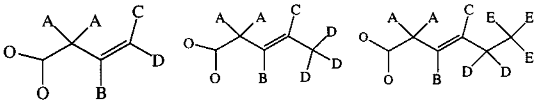
Table 2. ^1H NMR Chemical Shifts (δ) for $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CHCHR)]_2$, (R = H (4), Me (5), Et (6)) in C_6D_6 and THF-d_8



Proton(s)	**4**		**5**		**6**	
	C_6D_6	THF-d_8	C_6D_6	THF-d_8	C_6D_6	THF-d_8
C_5Me_5	1.58	1.31	1.60	1.19	1.61	1.20
A	-1.58	3.27	-1.53	3.10	-1.53	3.10
B	0.48	6.09	0.20	5.60	0.28	5.66
C	2.35	5.24	2.71	5.60	2.86	5.66
D	2.71	5.15	-0.12	1.73	0.26	2.09
E	-	-	-	-	-0.28	1.06

Data obtained in solution indicate that **4** is not always in a bimetallic form. The solution molecular weight of **4** was measured in both arenes and THF. In toluene the molecular weight was found to be 1020 g/mol, which is consistent within experimental error with the molecular weight calculated for the dimer observed by X-ray crystallography, 1011 g/mol. However, in THF, a solution molecular weight of 590 g/mol was observed. This is consistent with a monometallic species, but is closer to the 578 g/mol calculated for the monometallic THF solvate, $(C_5Me_5)_2Sm(\eta^2\text{-}O_2CCH_2CH{=}CH_2)(THF)$, than to the 506 g/mol calculated for a solvent free monomer, $(C_5Me_5)_2Sm(\eta^2\text{-}O_2CCH_2CH{=}CH_2)$. Equilibrium data presented below were also consistent with the presence of a solvated monomer.

The infrared spectrum of neat **4** contained absorptions at 1571 and 1415 cm^{-1}, which are in the frequency range for OCO asymmetric and symmetric stretches, respectively, in metal carboxylate complexes.[27,28] These absorptions match those observed in benzene, 1576 and 1412 cm^{-1}, which suggests that the structure of **4** in benzene is the same as the solid-state structure in Figure 1. In THF, however, additional absorptions are seen. The two major absorptions in THF are found at 1542 and 1436 cm^{-1}. Minor absorptions at 1575 and a low-frequency shoulder on the absorptions at 1436 cm^{-1} are similar to the bands in the benzene and neat spectra.

Both the ^1H and ^{13}C NMR spectra of **4** contained resonances for a $CH_2CH{=}CH_2$ unit in both benzene-d_6 and THF-d_8, but the NMR spectra differed in other respects in the two solvents. The room-temperature ^1H NMR chemical shift assignments are shown in Table 2. In benzene-d_6, a single set of signals is observed, while in THF-d_8 two sets of signals are found. The minor set of signals in THF-d_8 is only slightly shifted

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from the positions observed in the benzene-d_6 spectrum, and this set is likely to correspond to the bimetallic form of **4** observed exclusively in benzene. This is consistent with the solution IR spectra. The splitting and coupling constants for the major set of signals in THF-d_8 are identical to the minor set. Only the chemical shifts differ. These data and their solvent dependencies are consistent with the existence of a bimetallic species in benzene and an equilibrium between monometallic and bimetallic species in THF.

An NMR solvent dependence for **4** was also observed in the ^{13}C NMR spectra. As observed in the ^{1}H NMR spectra, the ^{13}C NMR spectrum of **4** contains one set of signals in benzene-d_8 and two sets of signals in THF-d_8.

To examine the equilibrium in THF-d_8, variable-temperature ^{1}H NMR experiments were conducted on **4** from −50 to 55 °C. At temperatures below −30 °C, only the set of resonances assigned to the monometallic form was observed. From −30 to 55 °C, the ratio of the monometallic to the bimetallic forms of **4** decreased. The fact that increased temperature favored the bimetallic species is not what is expected thermodynamically for a conversion of two monomers to one dimer. However, it is reasonable if the monometallic species exists as a solvate which loses THF when it forms a bimetallic species, eq 8.

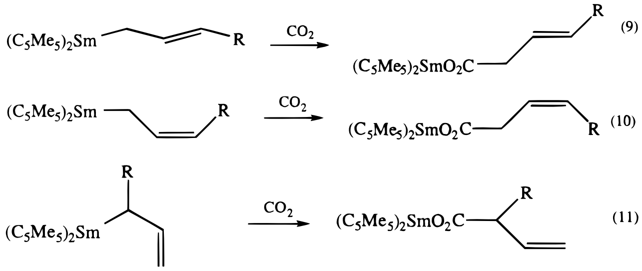
$$2\,(C_5Me_5)_2Sm(\eta^2\text{-}O_2CCH_2CH{=}CH_2)(THF) \rightleftharpoons [(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2 + 2\,THF \quad (8)$$

To examine this equilibrium starting with a predominance of dimer, a variable temperature NMR experiment was conducted in benzene-d_6 in the presence of THF-d_8. A plot of ln K vs $1/T$ over a range of temperatures from 295 to 340 K gave $\Delta H° = 17.6$ kJ/mol and $\Delta S° = 8.7$ J/(mol K) on the basis of the equilibrium shown in eq 8. The positive $\Delta S°$ is consistent with the equilibrium proposed in eq 8.

Attempts to grow crystals of the monometallic form of **4** have been unsuccessful, in part due to the high solubility of **4** in coordinating solvents. Recrystallization from a hexanes/THF mixture produced crystals, which in benzene-d_6 contained no signals for THF by ^{1}H NMR spectroscopy. These crystals had unit cell constants identical to those of the bimetallic form of **4**. Even in the presence of stronger coordinating bases, such as pyridine or phthalan, **4** crystallizes as an unsolvated bimetallic compound as determined by ^{1}H NMR spectroscopy and unit cell determinations.

CO_2 Reactivity with $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = Me, Et). To further investigate the reactivity of CO_2 with organosamarium allyl complexes, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$, **2**, and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHEt)$, **3**, were treated with CO_2 under the same conditions as **1**. At room temperature in toluene, both **2** and **3** reacted with CO_2 to produce orange oils. A characteristic C_5Me_5 singlet was observed for both reactions at ca. δ 1.60 in benzene-d_6. However, in both cases the singlet was broad ($\nu_{1/2}$ ca. 30 Hz) compared to that of **4**, which suggested the presence of several C_5Me_5 environments. Consistent with this, a number of smaller multiplets were observed downfield. These observations suggest that several products were formed in each reaction.

The formation of several products in these reactions was reasonable since the η^3-allyl ligands in **2** and **3**, unlike that in **1**, are asymmetrical and could adopt three η^1-forms leading to three different insertion products, eqs 9−11.



However, at −78 °C, CO_2 cleanly reacts with **2** and **3** in toluene to produce single isomers of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CHR)]_2$ (R = Me (**5**), Et (**6**)). The neat and solution IR spectra of **5** and **6** in the ν_{CO} stretching regions were also similar to those for **4**: neat samples had ν_{CO} absorptions (**5**, 1574, 1419 cm^{-1}; **6**, 1572, 1419 cm^{-1}) with peak positions close to those observed for solid **4**, while solution absorptions for **5** [benzene, 1574, 1419 cm^{-1}; THF, 1573, 1540, 1424 (with a low-frequency shoulder) cm^{-1}] and **6** [benzene, 1572, 1419 cm^{-1}; THF, 1570, 1544, 1435 (with a low-frequency shoulder) cm^{-1}] were close to those observed for **4** in benzene and THF, respectively. Solution molecular weight data on **5** and **6** indicated monometallic species in THF and bimetallic species in benzene, which again was similar to the behavior of **4**. As in **4**, the solution molecular weights determined for **5** and **6** were closer to the weights calculated for THF-solvated species than to the weights of the unsolvated monomers.

The ^{1}H NMR spectra of **5** and **6** in benzene-d_6 and THF-d_8 are listed in Table 2. The resonances for the olefinic signals shifted between benzene-d_6 and THF-d_8 in a manner similar to that observed for **4**. However, unlike **4**, only signals relating to the monometallic species were observed in THF-d_8 at room temperature. The trans nature of the double bond in **5** could be unequivocally determined by ^{1}H NMR spectroscopy, whereas overlap in the ^{1}H NMR spectrum of **6** interfered with isomer determination.

COS and CS_2 Reactions with $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$. CS_2 reacts with **1** in hexanes to produce $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH_2CH{=}CH_2)$, **7**, which was characterized by spectroscopic and analytical methods. In solution, **7** slowly isomerizes to $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, **8**, eq 12. The initial NMR spectra of **7** in benzene-d_6 and THF-d_8 plainly show the $-CH_2CH{=}CH_2$ substructure of the olefin, which is identical to that of **4**, Table 4. The chemical shifts of **7** in benzene-d_6 and THF-d_8 initially suggested a solvent dependence similar to that of **4**−**6**, but molecular weight

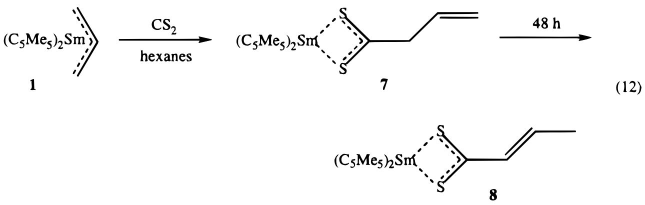
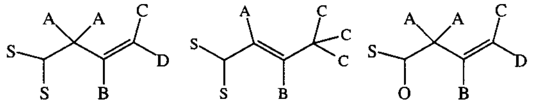


Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2$, 4

$Sm(1)-C(C_5Me_5)$[a]	2.729(3)	C(21)−O(2)	1.257(3)
Sm(1)−O(1)	2.327(2)	C(21)−C(22)	1.518(3)
Sm(1)−O(2a)	2.307(2)	C(22)−C(23)	1.487(4)
C(21)−O(1)	1.252(3)	C(23)−C(24)	1.288(4)
Cnt(1)−Sm(1)−Cnt(2)	133.4	O(1)−C(21)−O(2)	124.5(2)
Cnt(1)−Sm(1)−O(1)	104.0	O(1)−C(21)−C(22)	118.8(2)
Cnt(1)−Sm(1)−O(2a)	104.9	O(2)−C(21)−C(22)	116.7(2)
Cnt(2)−Sm(1)−O(1)	107.6	C(21)−C(22)−C(23)	116.0(2)
Cnt(2)−Sm(1)−O(2a)	108.0	C(22)−C(23)−C(24)	125.7(2)
O(1)−Sm(1)−O(2a)	90.85(7)		

[a] $Sm(1)-C(C_5Me_5)$ is the average bond distance between Sm(1) and C(1) to C(5) and C(11) to C(15).

Table 4. ^1H NMR Chemical Shifts for $(C_5Me_5)_2Sm(\mu\text{-}S_2CCH_2CH{=}CH_2)$, 7, $(C_5Me_5)_2Sm(\mu\text{-}S_2CCH{=}CHCH_3)$, 8, and $(C_5Me_5)_2Sm[\eta^2\text{-}(OCS)CH_2CH{=}CH_2]$, 9, in C_6D_6 and THF-d_8



	7		8		9	
Proton(s)	C_6D_6	THF-d_8	C_6D_6	THF-d_8	C_6D_6	THF-d_8
C_5Me_5	0.83	1.15	0.90	1.14	0.78	1.18
A	4.78	1.79	7.78	6.39	5.32	3.0
B	7.15	5.40	7.78	6.82	7.15	5.79
C	5.64	5.20	1.87	1.93	5.83	4.98
D	5.55	5.20	-	-	5.59	4.98

Table 5. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, 8

$Sm(1)-C(C_5Me_5)$[a]	2.66(2)	C(22)−C(23)	1.33(2)
Sm(1)−S(1)	2.849(3)	C(23)−C(24)	1.49(3)
Sm(1)−S(2)	2.857(3)	S(1b)−C(21b)	1.679(14)
Sm(1)−S(1b)	2.790(3)	S(2b)−C(21b)	1.720(13)
Sm(1)−S(2b)	2.857(3)	C(21b)−C(22b)	1.47(2)
S(1)−C(21)	1.693(13)	C(22b)−C(23b)	1.31(2)
S(2)−C(21)	1.703(12)	C(23b)−C(24b)	1.50(3)
C(21)−C(22)	1.45(2)		
Cnt(1)−Sm(1)−Cnt(2)	140.3	S(1)−C(21)−C(22)	116.0(9)
Cnt(1)−Sm(1)−S(1)	104.4	S(2)−C(21)−C(22)	120.6(9)
Cnt(1)−Sm(1)−S(2)	110.6	C(21)−C(22)−C(23)	125.1(12)
Cnt(2)−Sm(1)−S(1)	105.2	C(22)−C(23)−C(24)	123(2)
Cnt(2)−Sm(1)−S(2)	106.1	S(1b)−C(21b)−S(2b)	123.5(7)
Cnt(1)−Sm(1)−S(1b)	107.2	S(1b)−C(21b)−C(22b)	121.4(9)
Cnt(1)−Sm(1)−S(2b)	98.4	S(2b)−C(21b)−C(22b)	115.1(10)
Cnt(2)−Sm(1)−S(1b)	107.9	C(21b)−C(22b)−C(23b)	124.4(13)
Cnt(2)−Sm(1)−S(2b)	112.9	C(22b)−C(23b−C(24b)	126(2)
S(1)−C(21)−S(2)	123.4(6)		

[a] $Sm(1)-C(C_5Me_5)$ is the average bond distance between Sm(1) and C(1) to C(5) and C(11) to C(15).

analysis was impossible because **7** isomerizes during the course of the analysis (see below).

The ^1H NMR spectrum of **7** changes over a 48 h period with signals of a new species, **8**, growing in while signals for **7** diminished. Complex **8** was characterized by spectroscopic and analytical methods as well as by X-ray crystallography (Table 5) and found to be $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, Figure 2. The crystals, grown from a mixture of hexanes and phthalan, revealed a monometallic structure with an η^2-CS_2 group attached via a four-membered $\overline{\text{SmSCS}}$ ring with no coordination of phthalan. Also shown in the X-ray study was the position of the double bond which exists between the carbons α and β to the CS_2 unit instead of the carbons β and γ as observed for **4** and **5**. Solution molecular weight determinations on **8** indicated that a monometallic species existed in both THF and toluene. Solution IR spectra obtained for **8** in THF and benzene were similar to each other and to the spectrum of a neat sample indicating no change in the bonding mode of the SCS group as a function of solvent.

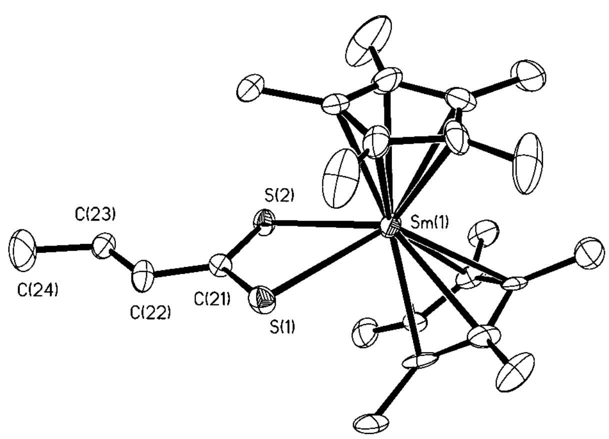
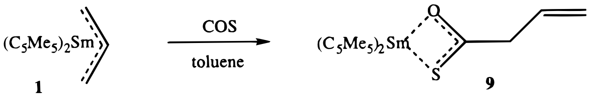


Figure 2. Thermal ellipsoid plot of $(C_2Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, **8**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms as well as the disordered carbons atoms have been excluded for clarity.

In an attempt to further study the isomerization, CS_2 was reacted with **2** at −78 °C in toluene. The ^1H NMR spectrum of the dark red oil isolated after removal of solvent contained multiple signals in the C_5Me_5 and olefinic regions. Attempts to isolate a single product via solvent extraction or crystallization were unsuccessful. The formation of an oil and the multiple NMR signals were analogous to reactions of **2** and **3** with CO_2 at room temperature and indicate that a number of insertion products may have been formed.

COS reacts with **1** in toluene to produce a viscous orange oil, **9**, which is formulated as $(C_5Me_5)_2Sm[\eta^2\text{-}(OCS)CH_2CH{=}CH_2]$, eq 13. The ^1H and ^{13}C NMR spectra of **9** had chemical shifts in benzene-d_6 and THF-d_8 closely related to those of **7**, Table 4. Unlike **7**, isomerization was not observed for **9** even at 70 °C over a 48 h period. Solution molecular weight determinations on **9** indicated a monometallic species in both THF and benzene, as was observed for **8**. Solution IR spectroscopy also indicated no change from THF to benzene, and the spectra were similar to the neat spectrum as in the case of **8**.



1 9 (13)

Syntheses of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CC_6H_5)]_2$. CO_2 reacts with $(C_5Me_5)_2Sm(C_6H_5)$ in toluene at room temperature to form $[(C_5Me_5)_2Sm(\mu\text{-}O_2CC_6H_5)]_2$, **10**, as a light orange solid in quantitative yield, eq 14. **10** can also be prepared from the direct reduction of benzoic acid with $(C_5Me_5)_2Sm(THF)_2$ in yields around 80% after purification, eq 15. Solution molecular weight data and IR and NMR spectroscopy indicated that the solution behavior of **10** is similar to that of **4**−**6**: in noncoordinating solvents, **10** exists as a bimetallic compound,

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(\mu\text{-}O_2CC_6H_5)]_2$, 10

Sm(1)−C(C$_5$Me$_5$)[a]	2.720(6)	C(21)−O(1)	1.252(6)
Sm(1)−O(1)	2.303(4)	C(21)−O(2a)	1.265(6)
Sm(1)−O(2)	2.317(4)	C(21)−C(22)	1.492(7)
Cnt(1)-Sm(1)−Cnt(2)	133.1	O(1)−Sm(1)-O(2)	87.36(13)
Cnt(1)-Sm(1)−O(1)	109.0	O(1)−C(21)-O(2a)	124.4(5)
Cnt(1)-Sm(1)−O(2)	107.8	O(1)−C(21)-C(22)	117.9(5)
Cnt(2)-Sm(1)−O(1)	105.9	O(2)−C(21)-C(22)	117.7(5)
Cnt(2)-Sm(1)−O(2)	104.1		

[a] Sm(1)−C(C$_5$Me$_5$) is the average bond distance between Sm(1) and C(1) to C(5) and C(11) to C(15).

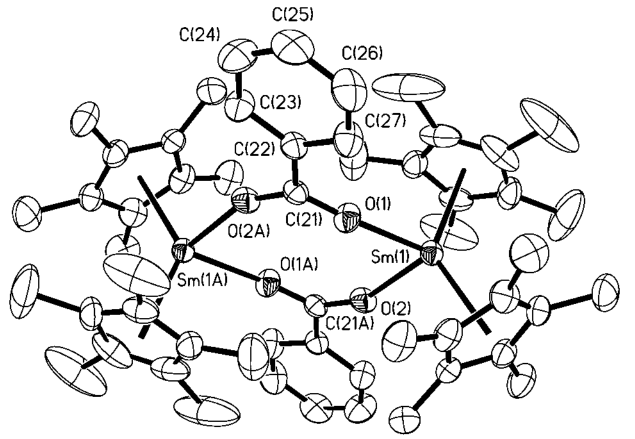
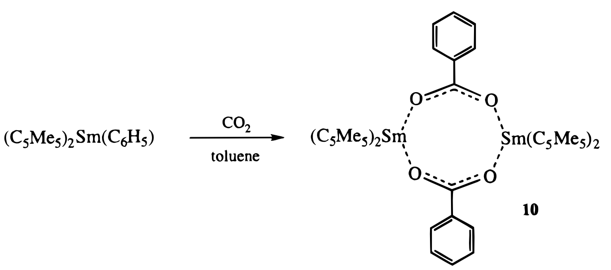


Figure 3. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(\eta^2\text{-}O_2CC_6H_5)]_2$, **10**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms and the cocrystallized toluene molecule have been excluded for clarity.

while, in THF, a monometallic species is present. An X-ray structure determination of crystals of **10** obtained from hexanes (Table 6) confirmed the bimetallic bridging structure seen for **4** in the solid state, Figure 3. Once again, attempts to obtain crystals of a monometallic THF solvate were unsuccessful.



(14)

10

$$2\,(C_5Me_5)_2Sm(THF)_2 + 2\,C_6H_5CO_2H \xrightarrow{THF} \textbf{10} \qquad (15)$$

Synthesis of $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}1,4\text{-}(O_2C)_2C_6H_4]$. Although it was not possible to obtain X-ray crystallographic data on monometallic η^2-OCO chelated forms of **4**−**6** or **10**, crystallographic evidence for this structural type was obtainable from the reduction of terephthalic acid with 2 equiv of $(C_5Me_5)_2Sm(THF)_2$ in THF. This reaction produced $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}1,4\text{-}(O_2C)_2C_6H_4]$, **11**, in approximately 80% yield after purification, eq 16. Crystals of **11** grown from THF were initially soluble in toluene, but yellow precipitates formed in less than 1 h. These solids would slowly dissolve in THF over several hours to produce a yellow solution with a ^{1}H NMR spectrum identical to that of the crystals. Consistent with this apparent loss of solvent, crystals of **11** grown from THF would quickly degrade when transferred from solvent to the diffractometer. This limited the quality of the crystallographic data obtainable, and bond distances and angles for **11** cannot be discussed. However, the overall structure of **11** was determined, Figure 4, and shown to be a symmetrical structure in which each $(C_5Me_5)_2Sm$ unit is solvated by THF and chelated by a carboxylate group. The infrared spectrum of neat **11** contained two strong absorptions in the OCO stretching range at 1573 and 1384 cm^{-1}. Surprisingly, the solution IR spectrum of **10** in THF had absorptions at different frequencies, 1550 and 1402 cm^{-1}.

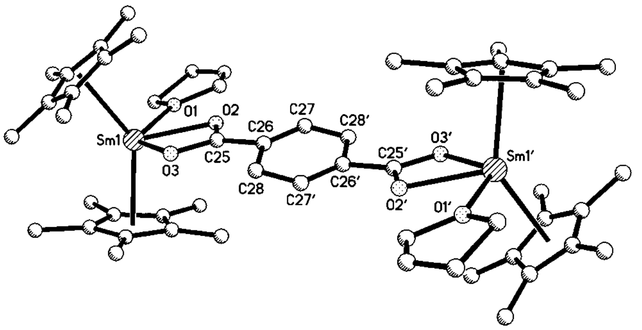
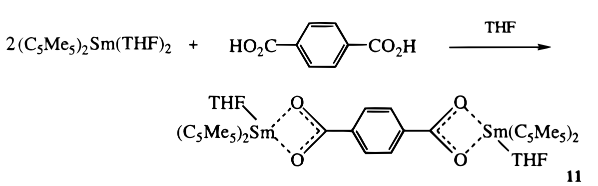


Figure 4. Ball and stick plot of $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}1,4\text{-}(O_2C)_2C_6H_4]$, **11**. Hydrogen atoms and the cocrystallized toluene molecules have been excluded for clarity.



(16)

11

Structural Studies of 4, 8, and 10. Detailed structural data were obtainable on complexes $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CH_2)]_2$, **4**, $(C_2Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, **8**, and $[(C_5Me_5)_2Sm(\eta^2\text{-}O_2CC_6H_5)]_2$, **10**. These compounds are similar in that in each case the $(C_5Me_5)_2Sm$ bent metallocene unit is coordinated to two additional ligands to give formally eight coordinate complexes. This is the most common coordination geometry for $(C_5Me_5)_2Sm$-containing compounds, and these compounds have metrical parameters that are normal for this type of complex.[29] The carboxylate complexes, **4** and **10**, are quite similar. Hence, the respective average Sm−C(C$_5$Me$_5$) distances, 2.730(2) and 2.753(6) Å, ring centroid−Sm−ring centroid angles, 133.4, and 133.1°, and average Sm−O distances, 2.317(2) and 2.310(4) Å, are indistinguishable within the error limits. The 90.85(7) and 87.36(13)° O−Sm−O angles differ only slightly. Both complexes also have a staggered arrangement of their C$_5$Me$_5$ rings. Hence, phenyl and allyl substituents on the bridging carboxylate ligand affect the coordination geometry around the metal in the same way. The two C−O bond lengths in each structure are also indistinguishable, and they are equal in the two structures, as are the O−C−O angles. The eight atoms of the $\overline{\text{SmOCOSmOCO}}$ ring are coplanar to within 0.10 Å in **4** and 0.09 Å in **10**, and in both structures these planes are nearly perpendicular to the

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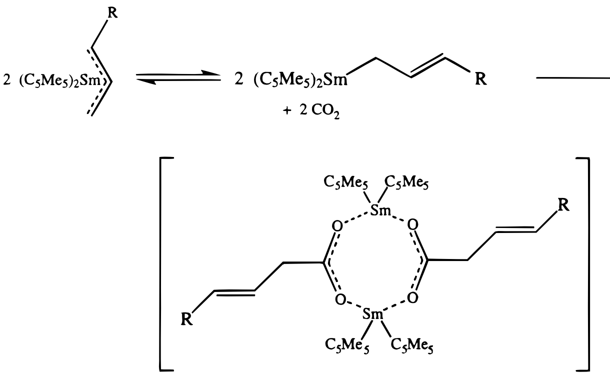
(29) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.

plane defined by the Sm and the two ring centroids (90.3° in **4**; 89.7° in **10**). In **10**, the best plane of the phenyl ring carbon atoms makes a 17.6° dihedral angle with the plane of the SmOCOSmOCO ring. In **4**, the 1.288(4) Å C(23)−C(24) bond clearly identifies the double bond as being terminal. The allyl group is not coplanar with the SmOCOSmOCO ring.

$(C_5Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, **8**, displayed disorder not only in the $S_2CCHCHCH_3$ unit but also in one of the C_5Me_5 rings which led to larger estimated standard deviations on the metrical data. Accordingly, no conclusions can be drawn from the fact that the 2.69(2) Å average $Sm{-}C(C_5Me_5)$ distance is in the low end of the range of typical values for eight coordinate $(C_5Me_5)_2Sm$-containing complexes and the 140.3° ring centroid−Sm−ring centroid angle is on the high end of the range.[29] As expected the larger sulfur donor atoms are further away from the metal than the carboxylate oxygens with 2.790(3)−2.857(3) Å Sm−S bonds. This apparently fills the coordination environment around the metal to the extent that the $S_2CCHCHCH_3$ ligand prefers to chelate rather than bridge. Since the $S_2CCHCHCH_3$ unit is chelating instead of bridging the S(1)−Sm−S(2) angle, 63.23(10)°, is much smaller than the O−Sm−O angles in **4** and **10**. In addition, the 2.991 Å S(1)···S(2) nonbonding distance is smaller than the analogous distances in **4** (O(1)···O(2′) = 3.299 Å) and **10** (O(1)···O(2) = 3.191 Å). In contrast to **4**, the allyl group in **8** is coplanar with the CS_2 unit to within 0.13 Å. Since in this case the double bond is internal rather than terminal, resonance structures involving conjugation between a C═S bond and the C═C bond can be written. This could explain the planar (vs perpendicular) orientation of the double bond with respect to the CS_2 unit. Unfortunately, the bond distances have error limits too large to confirm this. If such conjugation is occurring, the disorder in the allyl unit in the solid state is equivalent to having cocrystallized cis and trans diene structures.

Discussion

CO_2 Insertion Reactions. CO_2 reacts rapidly with the red allyl complexes $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = H (**1**), Me (**2**), Et (**3**)) to form the yellow insertion products $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2CH{=}CHR)]_2$, **4**−**6**, as shown in eq 17. These reactions provide a convenient route to oxo-ligated organosamarium complexes containing a pendent olefinic group. Such compounds are potentially useful in the formation of lanthanide-doped polyolefins.

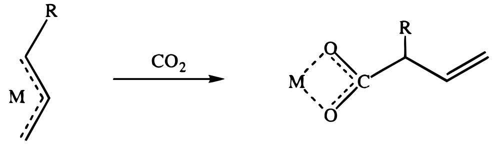


(17)

Although these insertion reactions were facile as expected, precise selection of reaction conditions was crucial for isolation of a pure product in high yield. This is consistent with earlier organosamarium CO_2 chemistry.[9] In each case, arene solvents rather than THF give quantitative yields of product. For R = H, temperature is less crucial than for R = alkyl. The latter cases require lower temperatures in order to obtain single crystalline products **5** and **6**. This suggests that several η^1 isomers are accessible at room temperature for **2** and **3**.

The isolation of the carboxylate products **4**−**6** does not provide details of the insertion reaction, but these reactions confirm that the η^3-allyl unit can be converted to an $\eta^1\text{-}CH_2CH{=}CHR$ substituent attached to an inserted substrate. These results are consistent with the sequence shown in eq 17. Equation 17 is further supported by examples of CO_2 insertion reactions with transition metal allyl compounds which contained both η^1 and η^3 bonds. In these cases it was shown that CO_2 inserted only into the metal η^1-allyl bonds.[13b,d,h,i,l]

The insertion of CO_2 into the least substituted carbon in **2** and **3** to produce **5** and **6** is interesting in that most CO_2 insertion studies on substituted allyl transition metal complexes resulted in branched products,[13a,b,f,g,i,l] eq 18. Very few examples of linear insertion products analogous to **5** and **6** have been reported.[13d,h]



(18)

The observed organosamarium CO_2 insertion reactions are not limited only to allyl complexes as demonstrated by insertion into the Sm−phenyl bond of $(C_5Me_5)_2Sm(C_6H_5)$ to make $[(C_5Me_5)_2Sm(\mu\text{-}O_2CC_6H_5)]_2$, **10**, eq 14, in high yield. CO_2 insertion into other $(C_5Me_5)_2Sm{-}R$ bonds is likely to be facile as well.

Reduction of Carboxylic Acids. Organosamarium carboxylates can also be obtained from the related carboxylic acids by reduction with the divalent $(C_5Me_5)_2Sm(THF)_2$. The direct reduction of benzoic and terephthalic acid by $(C_5Me_5)_2Sm(THF)_2$ to generate **10** and **11** in good yield provides an alternative general route for the preparation of metallocene lanthanide carboxylates, which have usually been prepared by metathesis[30] or insertion of CO_2.[9,11,12] Since a wider variety of carboxylic acids are available than well-characterized $(C_5Me_5)_2SmR$ complexes, this is a broadly applicable route to organosamarium carboxylate products.

Monometallic/Bimetallic Equilibria. All of the spectroscopic and molecular weight data on these car-

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(30) (a) Schumann, H.; Zietzke, K.; Weiman, R. *Eur. J. Solid State Inorg. Chem.* **1996**, 121. (b) Schumann, H.; Zietzke, K.; Erbstein, F.; Weimann, R. *J. Organomet. Chem.* **1996**, *520*, 265. (c) Deacon, G. B.; Fallon, G. D.; Gatehouse, B. M.; Rabinovich, A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *501*, 23. (d) Deacon, G. B.; Fallon, G. D.; Fallon, P. I.; MacKinnon, R. H.; Newham, G. N.; Pain, T. D.; Tuong, D. L.; Wilkinson, D. L. *J. Organomet. Chem.* **1984**, *277*, C21. (e) Tilley, T. D.; Anderson, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1982**, *21*, 2644. (f) Coutts, R. S. P.; Wailes, P. C. *J. Organomet. Chem.* **1970**, *25*, 117. (g) Maginn, R. E.; Manastyrsyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.

boxylate complexes indicate that their specific structures depend on the solvent. In noncoordinating solvents such as benzene and toluene, complexes **4**−**6** and **10** appear to have dimeric structures such as those determined crystallographically for **4** and **10**. In the X-ray crystal structures of **4** and **10,** the formally eight-coordinate coordination environment commonly observed in $(C_5Me_5)_2Sm$-containing complexes is found.[29] In coordinating solvents such as THF, the data are consistent with an equilibrium between the dimeric form and a solvated monometallic compound. Although the monometallic solvate cannot be definitively identified spectroscopically in solution, the thermodynamic data obtained from the temperature dependence of the equilibrium is reasonable only if a solvated monometallic complex is formed. In addition, X-ray crystallographic data obtained on $[(C_5Me_5)_2Sm(THF)]_2[\mu\text{-}\eta^2,\eta^2\text{-}1,4\text{-}(O_2C)_2C_6H_4]$, **11**, show that η^2-O_2CR units can attach to a $(C_5Me_5)_2Sm$ moiety with one THF of solvation. These solvated monometallic species are formally nine coordinate, but since a nonbridging η^2-carboxylate group is a small bite chelate, they are not that sterically different from the eight coordinate structures of **4** and **10**. Recently, it was found that $(C_5Me_4{}^tBu)_2Lu(\eta^2\text{-}O_2CCH_3)$ crystallizes with a nonbridging η^2-OC_2R unit in the absence of coordinated solvent.[30b] With this smaller metal, steric saturation apparently can be achieved without THF of solvation.

CS_2 and COS Insertion Reactivity. CS_2 and COS also participate in insertion reactions with $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, eqs 12 and 13, to form $(C_2Me_5)_2Sm(\eta^2\text{-}S_2CCH_2CH{=}CH_2)$, **7**, and $(C_5Me_5)_2Sm[\eta^2\text{-}(OCS)CH_2CH{=}CH_2]$, **9**. In contrast to the allyl carboxylates, complex **7** undergoes a double bond isomerization to form $(C_2Me_5)_2Sm(\eta^2\text{-}S_2CCH{=}CHCH_3)$, **8**. Complexes **8** and **9** also differ from **4**−**6** and **10** in that they do not participate in monometallic/bimetallic equilibria. Apparently, the larger S_2CR unit is sterically sufficient as a nonbridging η^2 ligand to stablize the $(C_5Me_5)_2Sm$ moiety. This has also been observed and reported in the solid-state structures of $(C_5Me_5)_2Sm(\eta^2\text{-}S_2CNMe_2)$[31] and $(C_5Me_5)_2Yb(\eta^2\text{-}S_2CNEt_2)$[32] and has been suggested for $(C_5Me_5)_2Y(S_2CR)$ complexes in which R is $CH(SiMe_3)_2$ and $CH_2(C_6H_3Me_2\text{-}3,5)$.[33]

Conclusion

CO_2, CS_2, and COS react under the proper precise conditions with $(C_5Me_5)_2Sm(\eta^3\text{-allyl})$ complexes to form carboxylate products consistent with the insertion of these reagents into an η^1-allyl moiety. Accordingly, CO_2, CS_2, and COS are useful insertion reagents with which to probe access to reactive intermediates in organolanthanide chemistry. These reactions also demonstrate a general synthetic route to a series of organosamarium complexes which have a pendent olefin unit. Similar organosamarium carboxylates can also be obtained by insertion of CO_2 into Sm−phenyl bonds and by Sm(II) reduction of carboxylic acids. The carboxylate products of the reactions participate in monometallic/bimetallic interconversions which demonstrate that the carboxylate unit is flexible both thermodynamically and kinetically as a bidentate ligand. This flexibility is more than might be expected for an oxygen-based small bite chelating group with these oxophilic metals and could be advantageous in reactions for which variable coordination numbers are desirable. Since, in contrast to the carboxylates, the CS_2 and COS insertion products form only monometallic species, it appears that preference for monomers or dimers can be controlled by increasing the size of just one donor atom in these systems.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compounds **4**, **8**, **10**, and **11** (48 pages). Ordering information is given on any current masthead page.

OM9710428

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[31] Edelmann, F. T.; Recknagel, A.; Noltemeyer, M.; Stalke, D.; Pieper, U.; Schmidt H. *J. Organomet. Chem.* **1991**, *411*, 347.

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