770 *Inorg. Chem.* **1998,** *37,* 770−776

Organosamarium-Mediated Transformations of CO_2 and COS: Monoinsertion and Disproportionation Reactions and the Reductive Coupling of CO_2 to $[O_2CCO_2]^{2-}$

William J. Evans,* Christopher A. Seibel, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, Irvine, California 92697

Received October 31, 1997

The reactivity of CO_2 and COS with divalent and trivalent organosamarium complexes has been investigated. $(C_5Me_5)_2Sm(THF)_2$ reductively couples CO_2 in THF at room temperature to form the oxalate complex, $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2CCO_2)$, **1**, in >90% yield. The metal centers in **1** are formally eight-coordinate. The reaction of COS with $(C_5Me_5)_2Sm(THF)_2$ is more complicated and generates a disproportionation product, $(C_5Me_5)_2Sm(\mu\text{-}\eta^2{:}\eta^1\text{-}S_2CO)Sm(C_5Me_5)_2(THF)$, **2**, which has one $(C_5Me_5)_2Sm$ unit involved in a four-membered $\text{Sm}\overline{\text{SCS}}$ ring, while the other $(C_5Me_5)_2Sm$ unit is bound to THF and the oxygen of the S_2CO ligand. CO_2 reacts with $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2Ph_2)$ in >90% yield to form the asymmetrical monoinsertion product, $(C_5Me_5)_2Sm[\mu\text{-}\eta^2{:}\eta^1\text{-}PhNN(CO_2)Ph]Sm(C_5Me_5)_2(THF)$, **3**. One $(C_5Me_5)_2Sm$ unit is involved in a five-membered $\text{Sm}\overline{\text{NNCO}}$ ring, and the other is attached to THF and the other oxygen originating from CO_2. **1**−**3** were characterized by analytical methods, X-ray diffraction, and NMR and IR spectroscopy.

Introduction

Carbon dioxide is an attractive raw material for the synthesis of carbon-containing compounds.[1−4] Not only is it abundant, but it is actually overabundant. Furthermore, Nature has demonstrated that it can be used on a large scale as a source of carbon: it is efficiently converted to carbohydrates via photosynthesis.

Despite its availability and proven utility as a natural C_1 building block, carbon dioxide is underutilized in industrial chemical processes. This is due in part to its thermodynamic stability, which makes it a challenging material to use as a substrate, and in part to our current inability to develop processes as efficient as those found in nature. Accordingly, CO_2 reduction and activation have been actively studied for years, and the primary and review literature are extensive.[1−4] Chemical, photochemical, and electrochemical transformations of CO_2 have been reported to form a variety of products including CO, carbonate, methanol, formate, oxalate, and alkanes, and a wide range of insertion reactions involving CO_2 have also been reported.

Although most of these reactions are metal-based processes and numerous transition metal complexes have been reported to react with CO_2, the use of the lanthanide metals to manipulate this substrate has not been extensively explored.[5,6] Few reactions which form crystallographically characterizable lan-

---

(1) (a) Halmann, M. M. *Chemical Fixation of Carbon Dioxide*; CRC Press: Boca Raton, FL 1993. (b) Ayers, W. M., Ed. *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. (c) Aresta, M., Forti, G., Eds. *Carbon Dioxide as a Source of Carbon*; D. Reidel: Dordrecht, 1987. (d) Inoue, S., Yamazaki, N., Eds. *Organic and Bio-organic Chemistry of Carbon Dioxide*; John Wiley: New York, 1982. (e) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155. (f) Leitner, W. *Coord. Chem. Rev.* **1996**, *155*, 247. (g) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063. (h) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259. (i) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207. (j) Aresta, M.; Quaranta, E.; Tommasi, I. *New. J. Chem.* **1994,** *18*, 133. (k) Willner, I.; Willner, B. *Top. Curr. Chem.* **1991**, *159*, 157. (l) Collin, J. P.; Sauvage, J. P. *Coord. Chem. Rev.* **1989**, *93*, 245. (m) (m) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (n) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (o) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (p) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (q) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Chapter 50.4. (r) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79.

(2) (a) Hutschka, F.; Dedieu, A.; Eichberger, M.; Fornika, R.; Leitner, W. *J. Am. Chem. Soc.* **1997**, *119*, 4432. (b) Gennaro, A.; Isse, A. A.; Savéant, J.-M.; Severin, M.-G.; Vianello, E. *J. Am. Chem. Soc.* **1996**, *118*, 7190. (c) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 1769. (d) Gassner, F.; Dinjus, E.; Görls, H.; Leitner, W. *Organometallics*, **1996**, 15, 2078. (e) Nagao, H.; Mizukawa, T.; Tanaka, K. *Inorg. Chem.* **1994**, *33*, 3415. (f) Tsai, J.-C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. (g) Hori, Y.; Murata, A.; Takahashi, R.; Suzuki, S. *J. Chem. Soc., Chem. Commun.* **1988**, 17. (h) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105. (i) Ogura, K.; Uchida, H. *J. Chem. Soc., Dalton Trans.* **1987**, 1377. (j) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (k) O'Toole, T. R.; Margerum, L. D.; Westmoreland, T. D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1416. (l) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033. (m) Stalder, C. J.; Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 3673. (n) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082. (o) Amatore, C.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 5021.

(3) (a) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Phys. Chem.* **1996**, *100*, 19981. (b) Gennaro, A.; Isse, A. A.; Severin, M.-G.; Vianello, E.; Bhugun, I.; Savéant, J.-M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3963. (c) Kushi, Y.; Nagao, H.; Nishioka, T.; Isobe, K.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1223. (d) Komeda, N.; Nagao, H.; Matsui, T.; Adachi, G.; Tanaka, K. *J. Am. Chem. Soc.* **1992**, *114*, 3625. (e) Hammouche, M.; Lexa, D.; Momenteau, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 8455. (f) Hawecker, J.; Lehn, J.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328. (g) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. (h) Gressin, J. C.; Michelet, D.; Nadjo, L.; Savéant, J.-M. *Nou. V. J. Chim.* **1979**, *3*, 545. (i) Lamy, E.; Nadjo, L. Savéant, J.-M. *J. Electroanal. Chem.* **1977**, *78*, 403.

(4) (a) Kushi, Y.; Nagao, H.; Nishioka, T.; Isobe, K.; Tanaka, K. *Chem. Lett.* **1994**, 2175. (b) Becker, J. Y.; Vainas, B.; Eger, R.; Kaufman, L. *J. Chem. Soc., Chem. Commun.* **1985**, 1471. (c) Fischer, J.; Lehmann, Th.; Heitz, E. *J. Appl. Electrochem.* **1981**, *11*, 743.

(5) (a) Schumann, H.; Messe-Marktscheffel, J.; Dietrich, A.; Gorlitz, H. *J. Organomet. Chem.* **1992**, *430*, 299. (b) Tilley, T. D. *Inorg. Chem.* **1990**, *22*, 4356. (c) Clair, M.; Santarsiero, B. *Acta Crystallogr.* **1989**, C45, 850.

S0020-1669(97)01381-5 CCC: $15.00

thanide/CO_2 reaction products in high yield have been identified.[5] Since the $(C_5Me_5)_2Sm$ unit has been shown to be effective in obtaining fully characterizable complexes with difficult substrates (e.g. dinitrogen[7] and nonclassical carbonium ions[8]) and in generating unusual reaction chemistry,[9−11] we examined the chemistry of divalent and trivalent $(C_5Me_5)_2Sm$-containing complexes with CO_2. Reactions with the unsymmetrical analogue, COS,[11] were also studied.

Reactivity between CO_2 and the organosamarium reagents was expected. On the basis of previous electrochemical studies of CO_2,[1,3] the strong reduction potential of $(C_5Me_5)_2Sm(THF)_2$,[12] and its propensity to make oxygen-ligated trivalent complexes from oxygen-containing substrates,[13] it was anticipated that $(C_5Me_5)_2Sm(THF)_2$ would reduce CO_2. With trivalent $(C_5Me_5)_2$Sm-containing complexes, CO_2 insertion was probable on the basis of previously observed organosamarium CO insertion chemistry.[9] However, it was uncertain if these reactions could be accomplished cleanly to give fully characterizable products.

We report here that $(C_5Me_5)_2Sm(THF)_2$ reduces CO_2 selectively to oxalate and that COS disproportionates to $(S_2CO)^{2-}$. We find that with a trivalent organosamarium compound of the common formula, $[(C_5Me_5)_2Sm]_2$(substrate), insertion chemistry is observed, but in contrast to CO insertions, which typically form symmetrical double insertion products,[9] *monoinsertion* occurs. This demonstrates a facile route to asymmetrically derivatized substrates using organosamarium chemistry. Finally, we report that these reactions are unusually dependent on reactions conditions and solvent, a factor which may have limited the investigations of lanthanides with CO_2 in the past.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, the syntheses and manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The preparation of $(C_5Me_5)_2Sm(THF)_2$[14] and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2Ph_2)$[15] and methods for drying solvents and taking physical measurements have been described previously.[16] CO_2 (99.995% purity) and COS (96+% purity) were purchased from Matheson and further purified by three freeze−pump−thaw cycles immediately prior to use. ^{13}C and ^{1}H NMR analyses were carried out on a GN 500 NMR spectrometer. Infrared analyses were carried out on a Perkin-Elmer 1600 series FTIR spectrometer by evaporation of THF solutions on NaCl plates.

$[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2CCO_2)$, 1. In a nitrogen-filled glovebox, a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (141 mg, 0.250 mmol) in ca. 15 mL of THF 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 light orange in less than 1 min. After the solution had been stirred for 5 min, the flask was degassed and transferred to a glovebox where solvent was removed, leaving **1** as a light orange solid (107 mg, 92%). ^{1}H NMR (C_6D_6): δ 1.49(s). ^{13}C NMR (C_6D_6): δ 200 ($O_2\mathit{C}CO_2$), 113 (C_5Me_5), 18 ($C_5\mathit{Me}_5$). $^{13}CO_2$ was used to identify the oxalate carbons in the ^{13}C NMR spectrum. IR: 2905 s, 1640 s, 1589 s, 1443 m, 1377 m, 1022 m, 866 m cm^{-1}. IR of sample prepared from $^{13}CO_2$: 2910 s, 1599 vs, 1550 s, 1442 m, 1376 m, 1070 m, 1026 m, 773 m cm^{-1}. Anal. Calcd for $Sm_2C_{42}H_{60}O_4$: Sm, 32.35; C, 54.26; H, 6.50. Found: Sm, 35.0; C, 55.01; H, 6.72. Crystals of **1** suitable for X-ray diffraction were grown from hot toluene as orange plates.

$(C_5Me_5)_2Sm(\mu\text{-}\eta^2{:}\eta^1\text{-}S_2CO)Sm(C_5Me_5)_2(THF)$, 2. Following the procedure described for **1**, $(C_5Me_5)_2Sm(THF)_2$ (90 mg, 0.16 mmol) in ca. 15 mL of THF was treated with excess COS at 1 atm. The solution turned orange in less than 1 min. After the solution had been stirred for 5 min, the flask was degassed and transferred to the glovebox where solvent was removed, leaving dark orange solids. The solids were extracted with hexanes, the remaining orange solids were separated by centrifugation, and the hexanes solution was concentrated and cooled to −30 °C, producing crystals of **2** suitable for X-ray diffraction (42 mg, 52%). ^{1}H NMR (C_6D_6): δ 1.69 (s, $C_5\mathit{Me}_5$, 30H), 1.26 (s, $C_5\mathit{Me}_5$, 30H), −0.55 (br, $\Delta\nu_{1/2} = 40$ Hz, THF, 4H), −0.75 (br, $\Delta\nu_{1/2} = 20$ Hz, THF, 4H). ^{13}C NMR (C_6D_6): δ 118 (C_5Me_5), 117 (C_5Me_5), 18.6 (q, $C_5\mathit{Me}_5$), 18.3 (q, $C_5\mathit{Me}_5$). Neither the S_2CO nor the C_4H_8O carbons were located. IR: 2903 s, 1439 m, 1357 s, 1018 w, 922 m, 864 s cm^{-1}. Anal. Calcd for unsolvated $Sm_2C_{41}H_{60}OS_2$: Sm, 32.21; C, 52.73; H, 6.48. Found: Sm 32.5; C, 52.26; H, 6.31. The ^{1}H NMR spectrum of the hexanes-insoluble solids in C_6D_6 contained one singlet (δ 1.19), while the ^{13}C NMR spectrum contained two signals [δ 118(s), 19.3(q)]. Reaction of a 200 mg sample of $(C_5Me_5)_2Sm(THF)_2$ (0.354 mmol) in ca. 20 mL of THF, following the procedure stated above, produced **2** in over 90% yield with no trace of a second compound.

$(C_5Me_5)_2Sm[\mu\text{-}\eta^2{:}\eta^1\text{-}PhNN(CO_2)Ph]Sm(C_5Me_5)_2(THF)$, 3. In a nitrogen-filled glovebox, a red solution of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2Ph_2)$ (51 mg, 0.05 mmol) in ca. 15 mL of THF 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. The flask was cooled to −78 °C, excess CO_2 at 1 atm was admitted, and the solution turned light orange in less than 1 min. After stirring for 5 min, the flask was degassed and transferred to the glovebox where solvent was removed, leaving **3** as a light orange solid (52 mg, 91%). Crystals of **3** suitable for X-ray diffraction were grown from hot toluene as orange plates. ^{1}H NMR (C_6D_6): δ 6.15 (m, $C_6\mathit{H}_5$, 2H), 5.98 (m, $C_6\mathit{H}_5$, 4H), 5.52 (m, THF, 4H), 4.11 (m, $C_6\mathit{H}_5$, 4H)**,** 1.62 (s, $\Delta\nu_{1/2} = 12$ Hz, $C_5\mathit{Me}_5$, 30H), 1.32 (s, $\Delta\nu_{1/2} = 24$ Hz, $C_5\mathit{Me}_5$, 30H), −0.20 (m, THF, 4H). ^{13}C NMR (C_6D_6): δ 178 ($\mathit{C}O_2$), 124, 123, 117, 116, 109, 51.8, 23.0, 19.2, 18.3. $^{13}CO_2$ was used to identify the carboxylate carbons in the ^{13}C NMR spectrum. IR: 2919 s, 1599 m, 1495 w, 1440 w, 1372 m, 1082 w cm^{-1}. Anal. Calcd for $Sm_2C_{57}H_{78}N_2O_3$: Sm, 26.38; C, 60.05; H, 6.90; N 2.46. Found: Sm, 25.9; C, 59.45; H, 6.88; N, 2.30.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2CCO_2)$, 1. A yellow crystal of approximate dimensions 0.17 × 0.26 × 0.53 mm was mounted on a glass fiber and transferred to the Siemens P4 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.[17] Intensity data were collected at 158 K using the $2\theta/\omega$ scan technique with Mo Kα radiation. The raw data were processed

---

(6) (a) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y. F.; Zakharov, L. N. *J. Organomet. Chem.* **1992**, *429*, 27. (b) Bochkarev, M. N.; Trifonov, A. A.; Fedorova, E. A.; Emelyanova, N. S.; Basalgina, G. S.; Kalinina, G. A.; Razuvaev, G. A. *J. Organomet. Chem.* **1989**, *372*, 217.

(7) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.

(8) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 12635.

(9) (a) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772. (b) Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1722. (c) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1986**, *108*, 7440.

(10) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728.

(11) (a) Pandey, K. *Coord. Chem. Rev.* **1995**, *140*, 37. (b) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661.

(12) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600.

(13) (a) Evans, W. J. *Polyhedron* **1987**, *6*, 803−835. (b) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (c) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

(14) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.

(15) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389.

(16) (a) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671. (b) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.

(17) *XSCANS Software Users Guide*, Version 2.1; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

Table 1. Experimental Data for the X-ray Diffraction Studies of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)$, **1**, $(C_5Me_5)_2Sm(\mu\text{-}\eta^2:\eta^1\text{-}S_2CO)Sm(C_5Me_5)_2(THF)\cdot C_6H_{14}$, **2**, and $(C_5Me_5)_2Sm[\mu\text{-}\eta^2:\eta^1\text{-}PhNN(CO_2)Ph]Sm(C_5Me_5)_2(THF)\cdot C_7H_8$, **3**

compd	**1**	**2**	**3**
empirical formula	$C_{42}H_{60}O_4Sm_2$	$C_{45}H_{68}O_2S_2Sm_2\cdot C_6H_{14}$	$C_{57}H_{78}N_2O_3Sm_2\cdot C_7H_8$
fw	929.60	1091.99	1232.05
temp (K)	158	163	163
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1$
a (Å)	8.6120(7)	36.744(3)	10.764(5)
b (Å)	20.862(2)	17.2090(14)	23.047(5)
c (Å)	11.6768(8)	18.751(2)	11.804(2)
β (deg)	101.564(6)	120.059(6)	102.32(3)
V (Å^3)	2055.3(3)	10262(2)	2860.8(14)
Z	2	8	2
D_{calcd} (Mg/m^3)	1.502	1.414	1.430
diffractometer	Siemens P4	Siemens P4	Siemens P4
m (mm^{-1})	2.866	2.383	2.078
refinement^b	R1, 5.51%	R1, 3.78%	R1, 3.233%
wR2 [$I > 2\sigma(I)$]	wR2, 15.3%	wR2, 8.09%	wR2, 7.87%

[a] Radiation: Mo Kα (μ = 0.710 730 Å). Monochromator: highly oriented graphite. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_c|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

with a local version of CARESS[18] 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 using the SHELXTL program.[19] All 6365 data were corrected for absorption,[19] Lorentz, and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/*m* with systematic absences 0*k*0 for $k = 2n + 1$ and $h0l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ is therefore uniquely defined.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.[20] The molecule is a dimer and is located about an inversion center. The pentamethylcyclopentadienyl ligands are disordered. Two components were included for each of the 10 atoms which define the ligands. The ligands were refined as idealized groups.[19] Hydrogen atoms were not included in the refinement due to the disorder. The poor quality of the refinement is attributed to the disordered pentamethylcyclopentadienyl ligands; however, the molecular connectivity has been established. At convergence, wR2 = 0.1858 and GOF = 1.050 for 107 variables refined against all 5991 unique data (as a comparison for refinement on F, R1 = 0.0551 for those 3960 data with $F > 4.0\sigma(F)$). See Table 1.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\mu\text{-}\eta^2:\eta^1\text{-}S_2CO)Sm(THF)(C_5Me_5)_2\cdot C_6H_{14}$, 2. An orange crystal of approximate dimensions 0.33 × 0.33 × 0.27 mm was handled as described above for **1**. All 6761 data were corrected for absorption,[19] Lorentz, and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/*m* with systematic absences *hkl*, for $h + k = 2n + 1$ and h0*l* for $l = 2n + 1$. The two possible monoclinic space groups are *Cc* and *C*2/*c*. The centrosymmetric space group *C*2/*c* was determined to be correct and is consistent with $Z = 8$.

The structure was solved as described for **1**. Hydrogen atoms were included using a riding model. There is one molecule of hexane present per formula unit. The solvent exists as two C_3H_7 units each located about a 2-fold rotational axis. The half-molecule defined by C(49)–C(51) is disordered. Three components were included for C(49), each with a site-occupancy of $^1/_3$. C(50) was included with two components, each assigned a site-occupancy of $^1/_2$. Hydrogen atoms associated with the solvent molecules were not included in the refinement. At convergence, wR2 = 0.0925 and GOF = 1.050 for 496 variables refined against all 6638 unique data (as a comparison for refinement on F, R1 = 0.0378 for those 4947 data with $F > 4.0\sigma(F)$). See Tables 1 and 2.

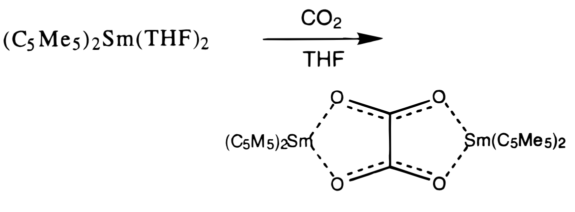
X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm[\mu\text{-}\eta^2:\eta^1\text{-}PhNN(CO_2)Ph]Sm(C_5Me_5)_2(THF)\cdot C_7H_8$, 3. A yellow crystal of approximate dimensions 0.10 × 0.27 × 0.30 mm was handled as described above for **1**. All 5446 data were corrected for absorption, Lorentz, and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/*m* with systematic absences 0*k*0 for $k = 2n + 1$. The two possible monoclinic space groups are $P2_1$ and $P2_1/m$. The noncentrosymmetric space group $P2_1$ was determined to be correct and is consistent with $Z = 2$.

All calculations were carried out as described above for **2**. There is one molecule of toluene solvent present per formula unit. At convergence, wR2 = 0.0787 and GOF = 1.064 for 640 variables refined against all 5159 unique data (as a comparison for refinement on F, R1 = 0.0323 for those 4682 data with F > 4.0σ(F)). The absolute structure was established by refinement of the Flack parameter.[21] See Tables 1 and 2.

Results

Reductive Coupling. $(C_5Me_5)_2Sm(THF)_2$ reacts with CO_2 in toluene and in hexanes both at room temperature and at −78 °C, but only a mixture of products is observed by ^{1}H NMR spectroscopy. From at least four to as many as *fifteen* resonances were observed in the C_5Me_5 region in the spectra of these $CO_2/(C_5Me_5)_2Sm(THF)_2$ reaction products. Some of these signals appeared to be rather broad, but this may be due to overlap of several signals.

However, in THF at room temperature, a clean reaction is observed between $(C_5Me_5)_2Sm(THF)_2$ and CO_2 to form the light orange oxalate complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)$, **1** (eq 1). Complex **1** was obtained in >90% yield using a 6 min reaction period. The ^{1}H NMR shift of **1** was among those observed in the reactions described above in toluene or hexanes, but no evidence for other C_5Me_5-containing products was observed in the reaction in THF at room temperature. The ^{13}C



(1)

---

[18] Broach, R. W. *CARESS*; Argonne National Laboratory: Illinois, 1978.

[19] Sheldrick, G. M. *SHELXTL/PC User's Manual*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

[20] *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

[21] Flack, H. D. *Acta Crystallogr.* **1983**, *39A*, 876.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(\mu\text{-}\eta^2{:}\eta^1\text{-}S_2CO)Sm(C_5Me_5)_2(THF)\cdot C_6H_{14}$, **2**, and $(C_5Me_5)_2Sm[\mu\text{-}\eta^2{:}\eta^1\text{-}PhNN(CO_2)Ph]Sm(C_5Me_5)_2(THF)\cdot C_7H_8$, **3**

2		3	
Sm(1)−Cnt(1)[a]	2.434	Sm(1)−Cnt(1)[a]	2.451
Sm(1)−Cnt(2)[b]	2.425	Sm(1)−Cnt(2)[b]	2.463
Sm(2)−Cnt(3)[c]	2.434	Sm(2)−Cnt(3)[c]	2.449
Sm(2)−Cnt(4)[d]	2.424	Sm(2)−Cnt(4)[d]	2.448
Sm(1)−S(1)	2.773(2)	Sm(1)−N(1)	2.384(7)
Sm(1)−S(2)	2.821(2)	Sm(1)−O(1)	2.342(6)
Sm(2)−O(1)	2.270(5)	Sm(2)−O(2)	2.265(6)
Sm(2)−O(2)	2.459(5)	Sm(2)−O(3)	2.481(6)
C45−O(1)	1.265(8)	C(53)−O(1)	1.264(10)
C45−S(1)	1.717(7)	C(53)−O(2)	1.277(10)
C45−S(2)	1.742(7)	C(53)−N(2)	1.369(11)
Cnt(1)−Sm(1)−Cnt(2)	138.3	N(1)−N(2)	1.439(9)
Cnt(1)−Sm(1)−S(1)	107.7	N(1)−C(41)	1.362(12)
Cnt(1)−Sm(1)−S(2)	105.3	N(2)−C(47)	1.445(10)
Cnt(2)−Sm(1)−S(1)	106.1	Cnt(1)−Sm(1)−Cnt(2)	133.7
Cnt(2)−Sm(1)−S(2)	110.8	Cnt(1)−Sm(1)−O(1)	105.3
S(1)−Sm(1)−S(2)	64.89(6)	Cnt(2)−Sm(1)−O(1)	105.0
Cnt(3)−Sm(2)−Cnt(4)	135.7	Cnt(1)−Sm(1)−N(1)	104.9
Cnt(3)−Sm(2)−O(1)	104.7	Cnt(2)−Sm(1)−N(1)	119.0
Cnt(4)−Sm(2)−O(1)	106.0	Cnt(3)−Sm(2)−Cnt(4)	137.0
O(1)−Sm(2)−O(2)	91.9(2)	Cnt(3)−Sm(2)−O(2)	106.0
O(1)−C(45)−S(1)	119.8(5)	Cnt(4)−Sm(2)−O(2)	105.7
O(1)−C(45)−S(2)	119.8(6)	Sm(1)−O(1)−C(53)	121.9(5)
S(1)−C(45)−S(2)	120.4(4)	Sm(1)−N(1)−C(41)	117.8(5)
		Sm(1)−N(1)−N(2)	116.5(5)
		Sm(2)−O(2)−C(53)	132.2(6)
		O(1)−C(53)−O(2)	121.9(8)
		O(1)−C(53)−N(2)	118.9(7)
		O(2)−C(53)−N(2)	119.2(7)
		C(47)−N(2)−C(53)	122.9(7)
		N(1)−N(2)−C(47)	117.6(6)
		N(1)−N(2)−C(53)	114.4(6)
		C(41)−N(1)−N(2)	114.1(7)

[a] Cnt(1) is the centroid of the C(1)−C(5) ring. [b] Cnt(2) is the centroid of the C(11)−C(15) ring. [c] Cnt(3) is the centroid of the C(21)−C(25) ring. [d] Cnt(4) is the centroid of the C(31)−C(35) ring.

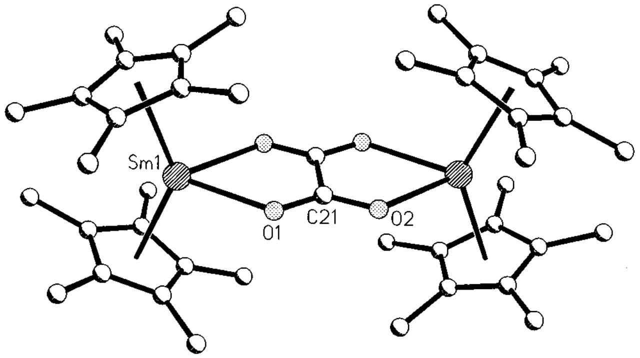
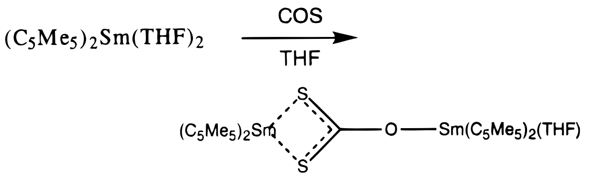


Figure 1. Ball and stick plot of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2CCO_2)$, **1**.

NMR shifts of the C_5Me_5 carbon atoms of **1** were consistent with the presence of Sm(III),[22] and, using $^{13}CO_2$, a resonance attributable to a carboxylate carbon was observed at 200 ppm which is in the range typical for organic carboxylic acids and their salts.[23] Elemental analysis was consistent with the formula, but definitive identification was accomplished by X-ray crystallography, Figure 1.

Although the overall structure of the complex was unequivocally established, the quality of the X-ray data was insufficient to allow a detailed discussion of the bond distance and angles. Each symmetry-equivalent samarium atom in **1** adopts a formally eight-coordinate geometry typical of trivalent $(C_5Me_5)_2$-Sm compounds.[24] Each oxalate ligand coordinates as a bidentate ligand to both metals such that five-membered $\overline{\mathrm{SmOCCO}}$ rather than four-membered $\overline{\mathrm{SmOCO}}$ rings are formed. To our knowledge, all structural examples of lanthanide oxalate compounds contain five-membered rings of this type.[25]

Disproportionation. In contrast to the C−C coupling reaction observed with CO_2, $(C_5Me_5)_2Sm(THF)_2$ reacts with COS under identical conditions to give the disproportionation product, $(C_5Me_5)_2Sm(\mu\text{-}\eta^2{:}\eta^1\text{-}S_2CO)Sm(C_5Me_5)_2(THF)$, **2**, shown in eq 2. Disproportionation products of this type are common for COS.[11,26,27] A second organosamarium complex is formed in this reaction but has not been definitively identified by X-ray crystallography. No evidence was observed for $[(C_5Me_5)_2Sm]_2$-$(\mu\text{-}O)$[28] which is a byproduct usually formed in organosamarium reactions when oxygen-containing substrates are present. By using a high concentration of $(C_5Me_5)_2Sm(THF)_2$ in reaction 2, complex **2** can be made in over 90% yield.



(2)

Since neither the NMR nor the IR data on **2** were structurally definitive, a single-crystal X-ray diffraction study was carried out which revealed the structure shown in Figure 2. Consistent with the solid-state structure, the ^1H NMR spectrum of **2** contains two separate resonances in the C_5Me_5 region. The ^{13}C NMR spectrum also contains two sets of C_5Me_5 resonances, and they occur in the region typical of Sm(III) compounds.[22] Neither the dithiocarbonate carbon nor the THF carbon resonances were located. The fact that the dithiocarbonate carbon

---

(22) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292.

(23) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991.

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

(25) (a) Guillou, O.; Bergerat, P.; Kahn, O.; Bakalbassis, E.; Boubekeur, P.; Batail, P.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 110. (b) Huang, S.; Zhou, G.; Mak, T. C. W. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 127. (c) Baker, P.; Smith, A. J. *Acta Crystallogr., Sect. C* **1990**, *46*, 984. (d) Gorbunov, D. K.; Kizhlo, M. R.; Pushkina, G. Y.; Spridonov, F. M.; Shatskii, V. M. *Kristallografiya* **1988**, *33*, 618. (e) Kahwa, I. A.; Fronczerk, F. R.; Selbin, J. *Inorg. Chim. Acta* **1984**, *82*, 161. (f) Hansson, E. *Acta Chem. Scand.* **1973**, *27*, 2851. (g) Steinfink, H.; Brunton, G. D. *Inorg. Chem.* **1970**, *9*, 2122. (h) Ollendorf, W.; Weigel, F. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 263. (i) Hanson, E.; Albertsson, J. *Acta Chem. Scand.* **1968**, *27*, 1682.

(26) (a) Alvarez, R.; Carmona, E.; Poveda, M. L.; Delgado, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2731. (b) Alverez, R.; Carmona, E.; Puebla, E. G.; Marin, J. M.; Monge, A.; Poveda, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1326. (c) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2851. (d) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2860. (e) Burke, J. M.; Fackler, J. P. *Inorg. Chem.* **1972**, *11*, 2744. (f) Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5873.

(27) (a) Rossi, R.; Marchi, A.; Magon, L.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1990**, 2923. (b) Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. (c) Jones, P. G.; Sheldrick, G. M.; Uson, R.; Fornies, J.; Uson, M. A. *Z. Naturforsch.* **1983**, *38B*, 449. (d) Bianchini, C.; Meli, A.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 197. (e) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4166. (f) Werner, H.; Bertleff, W.; Zimmer-Gasser, B.; Schubert, U. *Chem. Ber.* **1982**, *115*, 1004. (g) Lin, I. J. B.; Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394. (h) Gould, R. O.; Gunn, A. M.; van den Hark, T. E. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1713.

(28) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405.

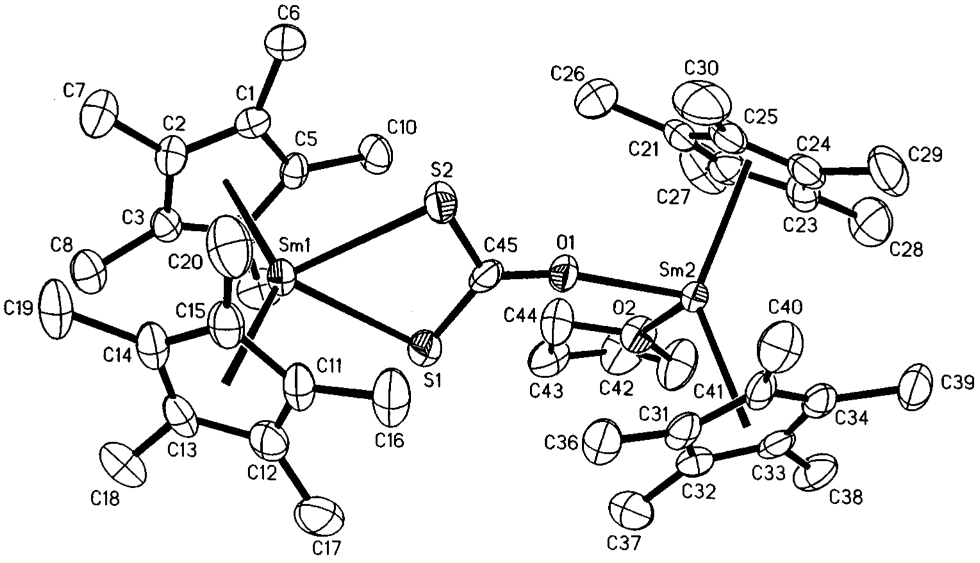


Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(\mu\text{-}\eta^2\text{:}\eta^1\text{-}S_2CO)Sm(C_2Me_5)_2(THF)$, **2**, with the probability ellipsoids drawn at the 50% level.

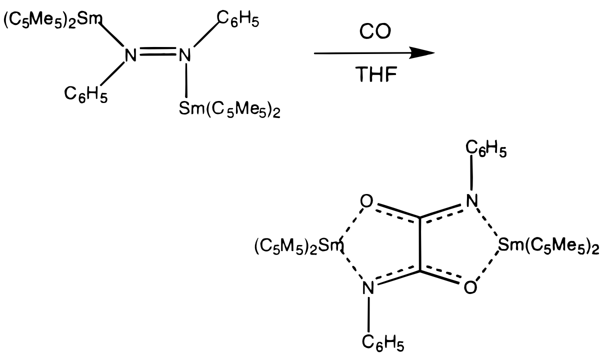
resonance could not be observed was not surprising considering that $^{13}CO_2$ was necessary to observe the oxalate and carboxylate carbons in **1** and **3**, respectively. Consistent with the bimetallic solid-state structure, the infrared spectrum of **2** contained no absorptions in the 1600−1688 cm^{-1} region where C=O stretches in *monometallic* S_2CO transition metal complexes absorb.[26e,f] The bimetallic complex $\{[(C_5H_5)_2V]_2(CS_2O)\}\cdot C_6H_6$, which contains a similarly bound $(S_2CO)^{2-}$ ligand also has no IR signals above 1600 cm^{-1}.[29]

The samarium centers in complex **2**, like those in **1** have the eight coordinate geometry typical of these bent metallocene complexes.[24] The average $Sm-C(C_5Me_5)$ distances for the two metals are 2.715(7) and 2.705(7) Å for Sm(1) and 2.711(7) and 2.706(7) Å for Sm(2). The 138.3° Sm(1) and 135.7° Sm(2) ring centroid−Sm−ring centroid angles are also similar despite the difference in the donor atom−Sm−donor atom angles: 64.89(6)° for the bidentate ligand attached to Sm(1) and 91.9(2)° for the two monodentate attachments to Sm(2).

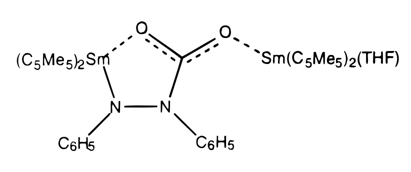
The $(S_2CO)^{2-}$ fragment is planar to within 0.003 Å. The three donor atom−C(45)−donor atom angles are all close to 120°. The bond distances suggest that there is little localization of a C=S bond in the $(S_2CO)^{2-}$ ligand: the 1.717(7) and 1.742(7) Å C(45)−S bond distances are equivalent within experimental error and are between the normal ranges for C−S and C=S bonds.[30] A similar situation was found with the 1.704(8) and 1.708(8) Å C−S bonds in $\{[(C_5H_5)_2V]_2(S_2CO)\}\cdot C_6H_6$[29] as well as with monometallic $(S_2CO)^{2-}$-containing compounds.[27] The C(45)−O(1) bond distance, 1.265(8) Å, is also identical to the C−O bond distance in $\{[(C_5H_5)_2V]_2(S_2CO)\}\cdot C_6H_6$ [1.262(9) Å]. Interestingly, these values also fall into the range found in monometallic $(S_2CO)^{2-}$-containing compounds.[27]

The 2.773(2) Å Sm−S(1) and 2.821(2) Å Sm−S(2) distances are also similar. As expected, these distances are longer than those involving the bonds in $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}S)$, 2.664(1) Å.[31] The 2.270(5) Å Sm(2)−O(1) distance is much shorter than the Sm−O bond to the neutral donor THF, 2.459(5) Å. Both of these Sm−O distances are typical compared to Sm−O distances in eight-coordinate $(C_5Me_5)_2Sm$-containing complexes.[24]

Insertion Chemistry. Since CO has been found to give unusual products from reactions with $[(C_5Me_5)_2Sm]_2$(substrate) complexes derived from $(C_5Me_5)_2Sm(THF)_2$ and unsaturated substrates,[9] e.g. eq 3, analogous CO_2 reaction chemistry was examined. The reaction of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2Ph_2)$ with CO_2 run in toluene at either room temperature or −78 °C gave a mixture of products as did reactions run in THF at room temperature. However, by running the reaction with excess CO_2 at −78 °C in THF a single product, $(C_5Me_5)_2Sm[\mu\text{-}\eta^2\text{:}\eta^1\text{-}PhNN(CO_2)Ph]Sm(THF)(C_5Me_5)_2$, **3**, could be isolated in >90% yield as shown in eq 4. In comparison, reaction 3 proceeds in 80% yield in THF at room temperature.[9c]



(3)



(4)

The IR spectrum of **3** indicated the presence of a CO_2-containing functional group with absorptions at 1521 and 1369 cm^{-1}.[23] The ^1H NMR spectrum contained two singlets of equal

---

(29) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1980**, *19*, 3847.

(30) Allan, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.

(31) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doeden, R. J. *Inorg. Chem.* **1994**, *33*, 2719.

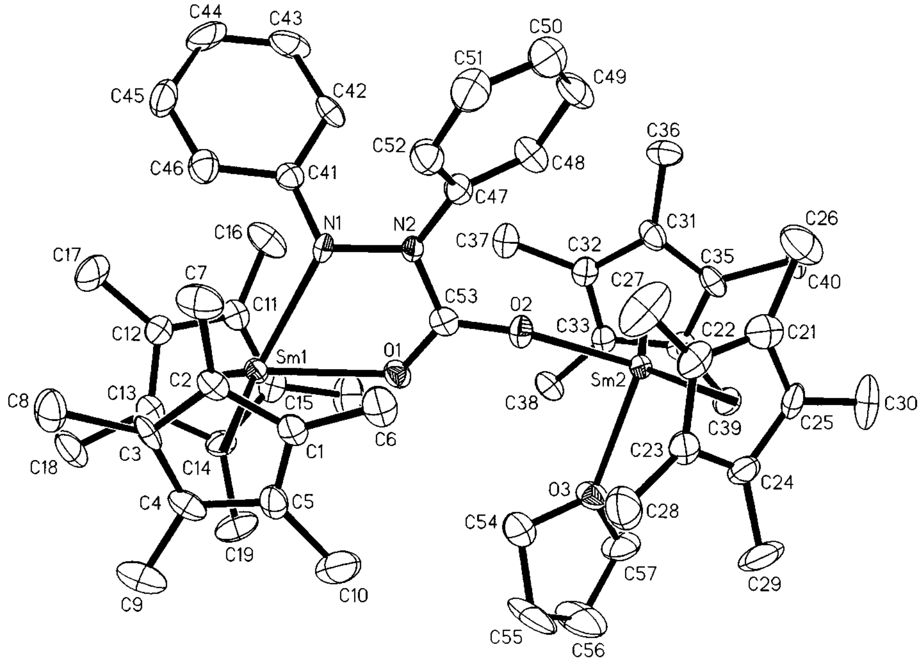


Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Sm[\mu\text{-}\eta^2:\eta^1\text{-}PhNN(CO_2)Ph]Sm(C_5Me_5)_2(THF)$, **3**, with the probability ellipsoids drawn at the 50% level.

intensity in the C_5Me_5 region, but their line widths differed: δ 1.32 ($\Delta\nu_{1/2} = 24$ Hz) and 1.62 ($\Delta\nu_{1/2} = 12$ Hz) ppm. The ^{13}C NMR spectrum contained resonances typical of trivalent products,[22] and again two sets of C_5Me_5 signals were present. To determine if the NMR data arose from two different compounds or a bimetallic product with two different samarium environments, an X-ray diffraction study was performed. As shown in Figure 3, an asymmetrical bimetallic product was formed due to insertion of a single equivalent of CO_2. Attempts to convert any of the products from the mixture obtained in toluene to **3** by addition of THF were unsuccessful. Attempts to further react **3** with CO_2 under pressure (80 psi) or with CO_2 in the presence of Lewis acids such as Al_2Me_6 or $AlPh_3$ did not lead to a second CO_2 insertion.

The structure of **3** also contains formally eight-coordinate samarium centers. The coordination of THF to just the Sm(2) center to achieve the eight-coordination is typical. The bond distances in the ligand reveal both delocalization and asymmetry. The 1.264(10) and 1.277(10) Å bond distances between C(53) and O(1) and O(2) are within experimental error of each other and indicate that there is no localized C=O bond in this CO_2 moiety. The 2.342(6) Å Sm(1)−O(1) bond distance is longer than the Sm(2)−O(2) 2.265(6) Å bond, as expected, but it is much shorter that the 2.481(6) Å Sm(2)−O(3) bond to the neutral donor THF. The 2.384(7) Å bond between Sm(1) and N(1) is the same as in the starting compound $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2Ph_2)$,[15] while the N(1)−N(2) bond distance has increased from 1.247 to 1.439(9) Å. The bonding between the nitrogen and the phenyl carbons is different for each nitrogen. The 1.362(12) Å N(1)−C(41) bond is shorter than the 1.445(10) Å N(2)−(C47) distance, and both of these distances are shorter than the 1.56(2) and 1.61(1) Å distances in the starting material.

Discussion

CO_2 can be reduced by series of electron and proton transfers to a variety of products whose distribution depends on the absence or presence of water, the pH, the electrode, the presence of electron-transfer mediating metal complexes, etc.[1−4] In nonaqueous media, CO_2 reduction is usually described by eqs 5−8.

$$CO_2 + e^- \rightarrow [CO_2]^{\bullet -} \quad (5)$$

$$2[CO_2]^{\bullet -} \rightarrow [O_2C-CO_2]^{2-} \quad (6)$$

$$[CO_2]^{\bullet -} + CO_2 \rightarrow {}^{\bullet}C(O)-O-C(O)O^- \quad (7)$$

$$^{\bullet}C(O)-O-C(O)O^- + [CO_2]^{\bullet -} \rightarrow CO + [CO_3]^{2-} + CO_2 \quad (8)$$

Formate ion is commonly observed and can result from adventitious water according to eqs 9 and 10. The distribution of products in these nonaqueous reductions between formate, oxalate, and CO and carbonate depends on the solvent, the electrode, the presence of metal complexes, the amount of water present, etc., and the potential for these transformations also varies according to conditions. Reduction potentials as negative as −2.21 V vs SCE in dimethylformamide have been reported to be necessary to effect reduction,[1,3] and this is commensurate with the reduction potential of divalent organosamarium complexes.[12] For example, $(C_5Me_5)_2Sm$ has been shown to reduce stilbene[32] which has a reduction potential of −2.22 V vs SCE.

$$[CO_2]^{\bullet -} + H^+ \rightarrow [HCO_2]^{\bullet} \quad (9)$$

$$[HCO_2]^{\bullet} + [CO_2]^{\bullet -} \rightarrow [HCO_2]^- + CO_2 \quad (10)$$

In the reduction of CO_2 by $(C_5Me_5)_2Sm(THF)_2$ to form $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)$, **1**, eq 1, the main reactions which are apparently occurring are eqs 5 and 6. Although oxalate can be selectively formed from CO_2 under the proper electrochemical reduction conditions,[1,4] reductions by metal complexes which give crystallographically characterizable oxalate products are rare. To our knowledge, the only other case involves the

---

(32) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219.

reaction of CO_2 with the cyclopentadienyl Ti(III) alkyl dimer, $Cp_2Ti[\mu\text{-}(CH_2)_3N(^iPr)(CH_2)_2N(^iPr)(CH_2)_3]TiCp_2$, which is reported to make the Ti(IV) product $Cp_2Ti[(O_2C)(CH_2)_3N(^iPr)(CH_2)_2N(^iPr)(CH_2)_3(CO_2)]$ in 80% yield along with $[Cp_2Ti]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2CCO_2)$, which, as a byproduct, must form in low yield.[33,34]

The formation of a C−C bond by reductive dimerization of CO_2 using $(C_5Me_5)_2Sm(THF)_2$ is typical of the reactivity of this divalent species.[13] $(C_5Me_5)_2Sm(THF)_2$ often reacts with substrates in a 2:1 stoichiometry to achieve two electron reduction of the substrate. The initially formed substrate radical can either be reduced by another equivalent of $(C_5Me_5)_2Sm(THF)_2$ to form a $[(C_5Me_5)_2Sm]_2$(substrate) complex or it can couple to form a $(C_5Me_5)_2$Sm(substrate−substrate)$Sm(C_5Me_5)_2$ product.[10,13,35] The reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1,2-bis(2-pyridyl)ethene is a case in which two-electron reductions occur to form *either* the doubly reduced substrate, $[pyCHCHpy]^{2-}$ in $[(C_5Me_5)_2Sm](pyCHCHpy])_2$ *or* the C−C coupled product, $[pyCHC(H)(py)CHpyCHpy]^{2-}$ in $(C_5Me_5)_2Sm[pyCHC(H)(py)CHpyCHpy]Sm(C_5Me_5)_2$, depending on the stoichiometry of the reaction.[35]

In the high-yield formation of oxalate from CO_2 and $(C_5Me_5)_2Sm(THF)_2$, coupling of the initially formed radical must be the favored process. Since the lanthanides are highly oxophilic, the initially formed radical anion, $[CO_2]^{\bullet-}$ is likely to be coordinated to the oxidized $[(C_5Me_5)_2Sm(THF)_x]^+$ unit. Two of these "$[(C_5Me_5)_2Sm(THF)_x]^+[CO_2]^{\bullet-}$" species must couple faster than this species can be reduced by additional $(C_5Me_5)_2Sm(THF)_2$ to form a complex such as $[(C_5Me_5)_2Sm(THF)_x]_2[CO_2]$. The coupling process must also be faster than the reaction of "$[(C_5Me_5)_2Sm(THF)_x]^+[CO_2]^{\bullet-}$" with additional CO_2 to form a complex such as $[(C_5Me_5)_2Sm(THF)_x][{}^{\bullet}C(O){-}O{-}C(O)O]$ in analogy to eq 7. Since several products form in toluene, these other pathways may be competitive with coupling in less polar solvents. The fact that the reduction is highly dependent on the solvent is consistent with previously reported CO_2 reduction chemistry,[1−4] although in most of these systems the difference in the solvents is much greater than the toluene/THF difference studied here. Unfortunately, the high reactivity of $(C_5Me_5)_2Sm(THF)_x$ limits the range of acceptable solvents for this reagent.

The reaction of $(C_5Me_5)_2Sm(THF)_2$ with COS, eq 2, differs markedly from the CO_2 reaction in that the common disproportionation product, $(S_2CO)^{2-}$, is formed in $(C_5Me_5)_2Sm(\mu\text{-}\eta^2{:}\eta^1\text{-}S_2CO)Sm(C_5Me_5)_2(THF)$, **2**. Since this reaction can be run to 90% yield in THF under the same conditions as reaction 1, this difference is not a solvent effect. As expected for Sm(II), this again is a two-electron reduction process. Reaction 2 could occur according to eqs 5, 7, and 8, and, consistent with this, none of the common $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[28] often found in organosamarium reactions with oxygen containing substrates is observed. The oxophilic samarium center could have directed the COS disproportionation to form the all-oxygen ligand, $(CO_3)^{2-}$, with concomitant generation of CS, but apparently the formation of $(S_2CO)^{2-}$ and CO is preferred.

The insertion reaction, eq 4, has considerable precedent. Insertion reactivity is a well-studied branch of CO_2 chemistry, and a large number of transition metal CO_2 insertion products have been fully characterized.[1] There are many examples of insertions of CO_2 into transition metal−amide bonds which result in the formation of metal carbaminato complexes.[36,37] The few lanthanide/CO_2 studies which are reported involve CO_2 insertion. Insertions into Lu−N,[5a] Sc−(Si,C),[5b,c] and Yb−C[6] bonds have been described.

Equation 4 is unusual, however, in that it provides a route to asymmetric insertion products. As described above, organometallic transformations using $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ often involve complexes of general formula $[(C_5Me_5)_2Sm]_2$(substrate). Further derivatization of $[(C_5Me_5)_2Sm]_2$(substrate) complexes by insertion has generally been done with CO.[9] However, as exemplified in eq 3, these reactions generate symmetrical products; it has not been possible to stop the CO insertion reaction at the monoinsertion stage. Hence, CO_2 provides a route to add just one carbon center to a $[(C_5Me_5)_2Sm]_2$(substrate) complex. In the case studied here, the second insertion could not be achieved even under forcing conditions. This may be due to delocalization of charge in the extended bridging ligand system, although attempts to alter this charge distribution with Lewis acids were unsuccessful. It is clear that with the proper substrate/insertion reagent combination, monoinsertion to unsymmetrical products will be possible in $(C_5Me_5)_2$Sm-based transformations.

Conclusion

The reactions of divalent and trivalent organosamarium compounds with CO_2 can provide inseparable mixtures of products, but if done under the proper specific conditions they can provide single products in high yield. The $(C_5Me_5)Sm$ unit is apparently quite efficient in directing the reduction of CO_2 to $(O_2CCO_2)^{2-}$, but it can be equally selective to the alternative carbonate product when COS is employed, in this case forming $(S_2CO)^{2-}$. The monoinsertion of CO_2 into a bimetallic azobenzene complex suggests that CO_2 reactivity is a good route to make unsymmetrical derivatives from symmetrical bis(organosamarium) systems. These reactions show that under the right conditions the lanthanides are viable metals with which to study the activation and derivatization of CO_2.

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

Supporting Information Available: Tables of atomic coordinates, thermal parameters, and complete bond distance and angles for compounds **1**−**3** (46 pages). Ordering information is given on any current masthead page.

IC971381T

---

(33) Frohlich, H. J.; Heike, S. *Z. Chem.* **1983**, *23*, 348.

(34) A crystallographically characterized complex involving a C-O coupling has also been reported: Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(35) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. *Organometallics* **1993**, *12*, 4664.

(36) (a) Hursthouse, M. B.; Malik, M. A.; Motevalli, M.; O'Brien, P. *J. Chem. Soc., Chem. Commun.* **1991**, 1690. (b) Belforte, A.; Dell'Amico, B.; Calderazzo, F. *Chem. Ber.* **1988**, *121*, 1891. (c) Dell'Amico, B.; Calderazzo, F.; Giurlani, U.; Pelizzi, G. *Chem. Ber.* **1987**, *120*, 955.

(37) References 113, 121, and 124−142 in Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 661.