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Organolanthanide-Centered Hydroamination/Cyclization of Aminoolefins. Expedient Oxidative Access to Catalytic Cycles

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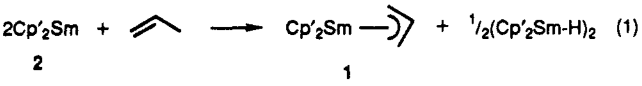
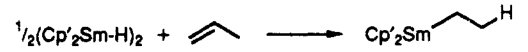
Summary: The readily accessible $(Me_5C_5)_2Sm$ and $(Me_5C_5)_2Sm(THF)_2$ catalyze the hydroamination/cyclization of a variety of aminoolefins. Mechanistic observations suggest that the active catalysts are trivalent organosamarium complexes.

We recently reported[1] that the marked facility with which olefin insertion occurs at Cp'_2Ln-X centers ($Cp' = \eta^5-Me_5C_5$; Ln = lanthanide)[2,3] can be coupled to the protonolytic reactivity of Ln–C σ bonds[2,4] to effect the efficient catalytic hydroamination/cyclization of a variety of aminoolefins (Scheme I). The precatalysts employed were Cp'_2LnR and $(Cp'_2LnH)_2$ compounds, which are accessible only via nontrivial, multistep syntheses.[2,3] In the course of recent organosamarium thermochemical studies,[5a,b] we learned that binuclear, oxidative allylic C–H activation and coupled follow up processes[5c] (e.g., eq 1–3 can be highly exothermic and rapid.[5d] These results combined with the observation that the η^3-allyl complex **1** is also a precatalyst for hydroamination (eq 4)[5,6] raise the intriguing question of whether Cp'_2Sm (**2**)[7] or its even more easily prepared (in one step from SmI_2 + KCp′) precursor, $Cp'_2Sm(THF)_2$ (**3**),[8] might serve as convenient precatalysts for hydroamination/cyclization. We report that this is indeed the case and relate initial mechanistic observations concerning the reaction pathway.



(1)

$\Delta H_{calcd} \approx -6$ kcal / mol of Sm



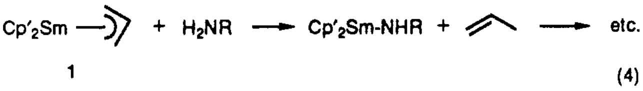
(2)

$\Delta H_{calcd} \approx -29$ kcal / mol of Sm

(3)

$\Delta H_{calcd} \approx -10$ kcal / mol of Sm

overall $\Delta H_{calcd} \approx -39$ kcal / mol of Sm



(4)

$\Delta H_{calcd} \approx -5$ kcal / mol of Sm

Anaerobic reaction of **2** or **3** with a variety of dry, degassed aminoolefins (typically in 20–100-fold molar excess) proceeds to completion at 60 °C in hydrocarbon solvents to afford the cyclization products shown in Table I.[9] Reactions are conveniently monitored by ^1H NMR spectroscopy and products identified by comparison with literature spectral data[10] and/or those of authentic samples. Products of all reactions in Table I were shown to be >95% pure by ^1H NMR and GC/MS studies. The scope of the cyclization process includes pyrrolidine, *N*-methylpyrrolidine, piperidine, and indoline products. That rates of Cp'_2Sm- and $Cp'_2Sm(THF)_2$-catalyzed reactions are indistinguishable is consistent with the lability of THF coordination[7] and the observation that competitive inhibition of catalysis occurs only at very high THF concentrations.[1]

Preliminary observations suggest that the present catalytic chemistry involves initial oxidation of **2**/**3** to trivalent Cp′Sm– species (cf. eq 1–3), which then function as do other Cp'_2LnR catalysts.[1] Thus, in situ ^1H NMR spectroscopy reveals the diminution of characteristic divalent $Cp'_2Sm(base)_n$ signatures (broad Cp′ signals at $\delta \approx$

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[1] (a) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109. (b) Gagné, M. R.; Marks, T. J. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14; American Chemical Society: Washington, DC, 1989; INOR 32.

[2] (a) Mauermann, H.; Marks, T. J. *Organometallics* **1985**, *4*, 200–202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (c) Jeske, C.; Schock, L. E.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118.

[3] Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–55.

[4] (a) Schumann, H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J. Fragalà, I., Eds.; D. Reidel: Dordrecht, Holland, 1985; Chapter 1. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131–177. (c) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50. (d) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry*; Moeller, T., Kmerke, Y., Schleitzer-Rust, E., Eds.; Springer-Verlag: Berlin, 1983; pp 137–303. (e) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 21.

[5] (a) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. *ACS Symp. Ser.*, in press. (b) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853. (c) For another example, see: Evans, W. J. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987; American Chemical Society; Washington, DC, 1987; INOR 315. (d) Equation 1 is not intended to portray an exact reaction mechanism.

[6] Nolan, S. P.; Marks, T. J. Unpublished results.

[7] Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928–3936.

[8] Evans, W. J.; Grate, J. W.; Chei, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

[9] Preparative-scale reactions have been performed with 1-amino-4-pentene and 2,2-dimethyl-1-amino-4-pentene by using 0.5–1.0 mL of the aminoolefin in pentane at 60 °C. Typical reaction conditions are as follows: Under an Ar atmosphere, 20 mg of $Cp'_2Sm(THF)_2$ (0.035 mmol) was stirred in 2 mL of pentane with 0.40 g of 1-amino-4-pentene (4.7 mmol, 134-fold excess). Upon addition of amine, the reaction solution gradually changed from the characteristic purple of the divalent complex to dark orange-red. The mixture was next heated in a tube sealed with a Teflon needle valve at 60 °C until the solution became yellow-orange, indicating completion of the reaction (48 h). Volatiles were then vacuum-transferred, and residual pentane was removed from the distillate by rotary evaporation at 0 °C to give an 85% isolated yield (0.34 g) of 2-methylpyrrolidine.[10a] An alternative to vacuum transfer is to filter the reaction solution through a short column of Florisil under an inert atmosphere (to remove the catalyst) and to then work up as above. In both workup procedures, the product was >95% pure by ^1H NMR and GC/MS.

[10] (a) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Consiglio, C.; Bachech, B.; Zambonelli, L. *J. Organomet. Chem.* **1979**, *181*, 255–269. (b) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Ughetto, G.; Zambonelli, L. *J. Organomet. Chem.* **1978**, *160*, 329–335. (c) Harding, K. E.; Burks, S. R. *J. Org. Chem.* **1981**, *46*, 3920–3922. (d) 1,4-Dimethylpyrrolidine[10c] is obtained as a 2:3 trans–cis mixture (60 °C). (e) Perie, J. J.; Laval, J. P.; Roussel, J.; Lattes, A. *Tetrahedron* **1972**, *28*, 675–699. (f) Pugin, B.; Venanzi, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6877–6881. (g) Tamaru, Y.; Hojo, M.; Higashima, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1988**, *110*, 3994–4002. (h) Confirmed with spectroscopic data from an authentic sample (Aldrich Chemical Co.). (i) Prepared by the $BF_3 \cdot Et_2O$-catalyzed rearrangement of *N*-allylaniline. We thank Prof. A. G. M. Barrett for suggesting this procedure.

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Scheme I

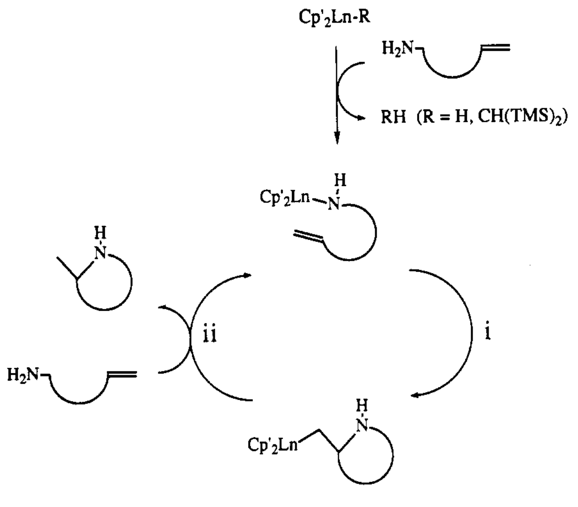
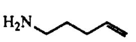
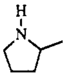
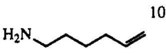
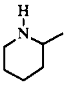
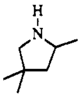
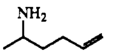
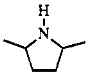
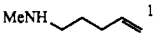
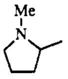
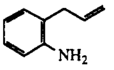
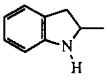
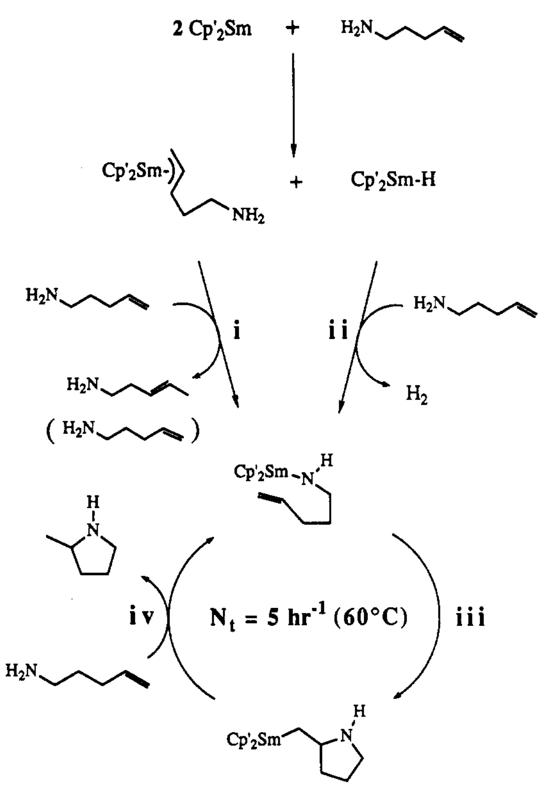


Table I. Organosamarium-Catalyzed Hydroamination[a]

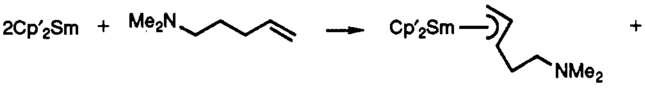
Substrate (ref)		Product (ref)		N_t (hr^{-1})[b]
	10a,b		10a,b	5
	10a,b		10a,b,h	1
	10g		10a,b	50
	10a,b,c		10a,b,c,d	40
	10e		10f	0.5
	10i		10h,i	1

[a] Catalyst: $Cp'_2Sm(THF)_2$. [b] Approximate turnover frequency at 60 °C.

Scheme II



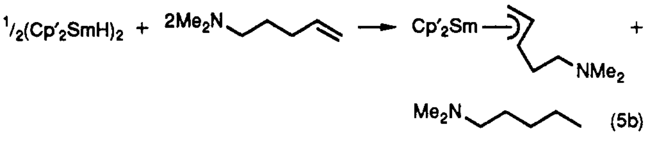
2.0–4.0)[11,12] and the concurrent growth of trivalent features (sharper Cp′ resonances at $\delta \approx 1.0$–1.5)[5b,13] as turnover begins. Concomitant color changes are also in accord with these observations.[9] That the major oxidative pathway is probably allylic C–H attack is suggested by rapid stoichiometric reaction of 2 with 1-(dimethylamino)-4-pentene to yield an η^3-allyl species (**4**, eq 5).[14]



4

$^1/_2(Cp'_2Sm\text{-}H)_2$ (5a)

$\Delta H_{calcd} \approx -6$ kcal / mol of olefin



(5b)

$\Delta H_{calcd} \approx -39$ kcal / mol of olefin

In contrast, reaction of 2 with saturated primary amines yields only divalent base adducts (eq 6)[11,12] and no NMR evidence for (yel-

$$Cp'_2Sm + xH_2N^nPr \rightleftharpoons Cp'_2Sm(H_2N^nPr)_x \qquad (6)$$

low-orange) trivalent $Cp'_2SmNHR(H_2NR)$ complexes (accessible independently via $Cp'_2SmCH(TMS)_2 + H_2NR$).[5b,15–17] Further support for the catalytic agency

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(11) Typical Cp′ ^{1}H NMR data (400 MHz, 25 °C, toluene-d_8, in excess amine) for nitrogen base adducts: $Cp'_2Sm(H_2N^nPr)_x$, δ 3.7 ($\Delta\nu_{1/2}$ = 5 Hz); $Cp'_2Sm(HNEt_2)_x$, δ 4.0 ($\Delta\nu_{1/2}$ = 5 Hz); $Cp'_2Sm[H_2N(4\text{-pentenyl})]_x$, δ 3.9 ($\Delta\nu_{1/2}$ = 11 Hz); $Cp'_2Sm[H_2N(2,2\text{-dimethyl-4-pentenyl})]_x$, δ 3.9 ($\Delta\nu_{1/2}$ = 11 Hz); $Cp'_2Sm(THF)_2$, δ 2.1 ($\Delta\nu_{1/2}$ = 8 Hz).

(12) For additional examples of Cp'_2Ln^{II} amine complexes see: (a) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* 1982, *21*, 2647–2649. (b) Wayda, A. L.; Dye, J. L.; Rogers, R. D. *Organometallics* 1984, *3*, 1605–1610.

(13) (a) Cp′ ^{1}H NMR data (400 MHz, 25 °C, toluene-d_8) in excess amine: $Cp'_2Sm\text{-}N(H)(4\text{-pentenyl})[H_2N(4\text{-pentenyl})]_x$, δ 1.5 ($\Delta\nu_{1/2}$ = 1 Hz); $Cp'_2Sm\text{-}N(H)(2,2\text{-dimethyl-4-pentenyl})[H_2N(2,2\text{-dimethyl-4-pentenyl})]_x$, δ 1.5 ($\Delta\nu_{1/2}$ = 1 Hz). (b) Doublets at δ 1.3–1.4 are also noted and are suggestive of the magnetically nonequivalent Cp′ signals of a $Cp'_2Sm(\eta^3\text{-allyl})$ species:[2b,5b,13c] δ(Cp′) 1.1, 1.3 ($\Delta\nu_{1/2}$ = 1 Hz). (c) For 1, δ(Cp′) 1.01, 1.20 ($\Delta\nu_{1/2}$ = 5 Hz).

(14) In a preparative reaction, 0.50 g (1.2 mmol) of Cp'_2Sm was stirred in 20 mL of toluene with 0.21 g (1.8 mmol) of 1-(dimethylamino)-4-pentene for 24 h. The toluene was then removed under vacuum and 20 mL pentane added. Subsequent filtration, slow cooling to −78 °C, decantation of the pentane, and drying in vacuo afforded an isolated yield of ca. 0.49 g (76.9%) of a red oily solid. ^{1}H NMR (benzene-d_6, 25 °C, tentative assignments); δ 7.20 (br s, 1 H, $\mathrm{CH_2C}\mathit{H}\mathrm{CHCH_2CH_2NMe_2}$), 5.30 (br s, 1 H, $\mathrm{C}\mathit{H}\mathrm{HCHCHCH_2CH_2NMe_2}$), 16.23 (br s, 1 H, $\mathrm{CH_2CHC}\mathit{H}\mathrm{CH_2CH_2NMe_2}$), 10.27 (br s, 1 H, $\mathrm{CH}\mathit{H}\mathrm{CHCHCH_2CH_2NMe_2}$), −2.41 (br s, 2 H, $\mathrm{CH_2CHCHC}\mathit{H_2}\mathrm{CH_2NMe_2}$), −2.19 (br s, 2 H, $\mathrm{CH_2CHCHCH_2C}\mathit{H_2}\mathrm{NMe_2}$), 2.68 (s, NMe_2, 6 H), 1.42 (s, 15 H, Me_5C_5, $\Delta\nu_{1/2}$ = 5 Hz), 1.31 (s, 15 H, Me_5C_5, $\Delta\nu_{1/2}$ = 5 Hz). Anal. Calcd for $C_{27}H_{44}NSm$: Sm, 28.1; mol wt, 534. Found: Sm, 28.3; mol wt, 534 (direct-injection MS).

(15) (a) Hedden, D.; Nolan, S. P.; Marks, T. J. Unpublished results. (b) ^{1}H NMR for $Cp'_2Sm(NH^nPr)(H_2N^nPr)$ (C_6D_6, 25 °C): Cp′ resonance at δ 1.51; rapid exchange observed between bound ^{n}Pr functionalities and free H_2N^nPr.[16] Anal. Calcd for $C_{26}H_{47}N_2Sm$: Sm, 27.95; mol wt, 539. Found: Sm, 27.25; mol wt, 535 (direct-injection MS).

of Sm(III) species is provided by the observation that the relative rates of the present reactions are consistent with general Cp'_2LnR ionic radius–rate correlations (La > Sm > Lu)[1] and that the present reactions are zero-order in substrate (Scheme I, $k_{ii}[\text{substrate}] \gg k_i$) as for other Cp'_2LnR catalysts.[1] The unimportance of divalent species in the catalytic cycle is also argued by the observation that Cp'_2Eu[18] is catalytically inactive under the present conditions. From thermochemical data[5a] we estimate that ΔH is approximately 22 kcal/mol of propylene more endothermic for the europium analogue of eq 1 and that binuclear reductive-elimination reactions (eq 7) are invariably exothermic (in contrast to the case for samarium).

$$Cp'_2EuR + Cp'_2EuR' \rightarrow 2Cp'_2Eu + RR' \qquad (7)$$

$$\Delta H_{\text{calcd}} \approx -8 \text{ to } -12 \text{ kcal/mol of Eu}$$

ably exothermic (in contrast to the case for samarium). Scheme II illustrates a representative, minimum catalytic cycle that accounts for the above observations.[19]

In summary, these results offer an expedient access to organolanthanide-catalyzed hydroamination/cyclization chemistry. They also underscore the diversity that the varying redox characteristics of 4f ions can introduce in lanthanide-centered catalytic chemistry.

Acknowledgment. We are grateful to the NSF for support of this research under Grant CHE-8800813. M.R.G. thanks Rhône-Poulenc for a graduate fellowship.

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(16) For analogous amine–amido complexes and/or similar exchange processes, see: (a) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495–2502. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443–450 (footnote 14). (c) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472–5478.

(17) (a) The oxidation of Cp'_2Sm to $Cp'_2SmNHR + {}^1/_2H_2$ is estimated from existing data[5b,17b] to be slightly exothermic ($\Delta H_{\text{calcd}} \approx -7$ kcal/mol of Sm) but may well be endergonic. To date, we have observed neither this reaction nor the microscopic reverse. (b) McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(18) (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. J. *Organometallics* **1986**, *5*, 1285–1291. (b) Tilley, T. D.; Andersen, R. A.; Spender, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999–3003.

(19) (a) We are unable to detect internal olefins or their cyclization products in low substrate/catalyst ratio experiments, suggesting that proton transfer in step i (Scheme II) is to the substituted allyl carbon atom or that internal olefins are subsequently isomerized. (b) Reaction of Sm alkyls (subsequent to step iii, Scheme II) with olefin could also yield η^3-allyls[2b,5b,13b] and the corresponding heterocyclic product (an alternative to step iv). The η^3-allyl would presumably then reenter the cycle at step i.

Ring-Opening Reactions of Strained-Ring Thioethers in Metal Cluster Complexes. Photoinduced Transformation of Thietane to 2-Propenethiolate in a Triosmium Cluster Complex

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Received February 26, 1990

Summary: $Os_3(CO)_{11}[S(CH_2)_3]$ undergoes photoassisted ring opening, CH activation, and decarbonylation to yield $Os_3(CO)_{10}[\mu\text{-}SCH_2C(H){=}CH_2](\mu\text{-}H)$ (**2**). **2** engages in a phosphine-assisted insertion reaction between the allyl group and the hydride ligand to yield $Os_3(CO)_{10}(PMe_2Ph)[\mu\text{-}S(CH_2)_3]$ (**3**), which contains a novel thiametallacyclic ring. **3** is decarbonylated at 97 °C to yield the PMe_2Ph derivative of **2**.

The ring-opening reaction is believed to be an integral step in the desulfurization of cyclic thioethers, the principal sulfur-containing contaminants of fossil fuels.[1] Metal complexes[2] have been shown to promote this process, and it is also known to occur readily on molybdenum surfaces.[3] Due to their intrinsic strain, small-ring thioethers, such as thiiranes[4] and thietanes,[5] exhibit a greater tendency to undergo ring opening and desulfurization. Thiiranes usually undergo complete desulfurization upon reaction with metal complexes.[4] The chemistry of thietane, $S(CH_2)_3$, in metal complexes has been studied very little.[6] On metal surfaces, thietane is readily desulfurized.[5] In this report, the preliminary results of our study of the coordination and transformation of thietane by a triosmium cluster is described.

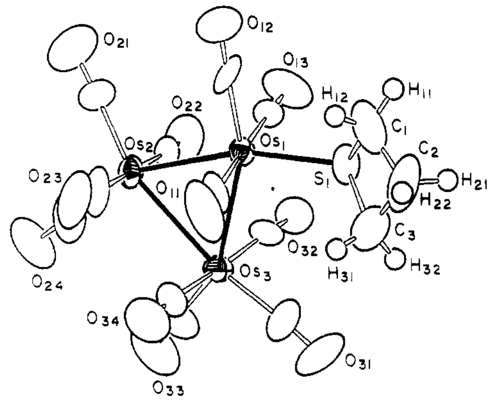

Figure 1. ORTEP diagram of $Os_3(CO)_{11}[S(CH_2)_3]$ (**1**) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are as follows: Os(1)–Os(2) = 2.850 (1), Os(1)–Os(3) = 2.887 (1), Os(2)–Os(3) = 2.887 (1), Os(1)–S(1) = 2.375 (5), S(1)–C(1) = 1.85 (2), S(1)–C(3) = 1.83 (2).

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(1) (a) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (b) Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295. (c) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (d) Curtis, M. D.; Penner-Hahn, J. E.; Schwank, J.; Beralt, O.; McCabe, D. J.; Thompson, L.; Waldo, G. *Polyhedron* **1988**, *7*, 2411.

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