The ion undergoes condensation reactions, as well as hydride transfer, with alkyl benzenes and condensation reactions (with and without loss of H_2 from the product ion) with olefins.

Even though cyclopropenium ions [i.e., $(C_3H_3^+)$] are unreactive with the propargyl halides, acetylene, and benzene, these ions are observed to react with a variety of compounds, although usually at a much lower rate than the corresponding reactions of CH_2CCH^+. For instance, c-$C_3H_3^+$ reacts with unsaturated molecules having four or more carbon atoms by condensation. This ion also reacts with aldehydes by hydride transfer and with amines through several mechanisms including hydride transfer and condensation [$k \sim (1-10) \times 10^{-10}$ cm^3/molecule·s]. The cyclic ions do not react with linear or branched alkanes (C_4–C_{10}), even though reactions which are exothermic by as much as 10 or 15 kcal/mol can be written for these systems.

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Synthesis and X-ray Crystal Structure of a Soluble Divalent Organosamarium Complex

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For many years, the organometallic chemistry of the lanthanide elements has centered primarily on the 3+ oxidation state.[2] During the past few years, we have investigated the low valent chemistry of the lanthanide elements in an effort to develop a more extensive chemistry for these metals than is found for their trivalent complexes,[3–8] and recently, interest in this area has increased considerably.[9–11] As part of our research program, we have used the metal vaporization technique[12–18] to examine the reactivity

(1) Camille and Henry Dreyfus Teacher–Scholar. Address correspondence to the University of Chicago.
(2) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51–107.
(3) Evans, W. J.; Engerer, S. C.; Neville, A. C. *J. Am. Chem. Soc.* **1978**, *100*, 331–333.
(4) Evans, W. J.; Wayda, A. L.; Chang, C. W.; Cwirla, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 333–334.
(5) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007–1008.
(6) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. "Fundamentals of Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, pp 941–952.
(7) Evans, W. J.; Zinnen, H. A.; Pluth, J. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810–812.
(8) Evans, W. J.; Coleson, K. M.; Engerer, S. C.; Wayda, A. L.; Zinnen, H. A. Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980; INOR 297.
(9) Watson, P. L. *J. Chem. Soc., Chem. Commun.*, **1980**, 652–653.
(10) Tilley, D. T.; Anderson, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999–3003.
(11) Lappert, M. F.; Yarrow, P. I. W.; Atwood, J. L.; Shakir, R.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1980**, 987–988.
(12) Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195–199.
(13) Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53–112.
(14) Klabunde, K. J. "Chemistry of Free Atoms and Particles"; Academic Press: New York, 1980.
(15) Blackborow, J. R.; Young, D. "Metal Vapor Synthesis in Organometallic Chemistry"; Springer Verlag: Berlin, West Germany, 1979.
(16) Moskovits, M.; Ozin, G. A. "Cryochemistry"; Wiley: New York, 1976.
(17) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625–631.
(18) Blackborow, J. R.; Eady, C. R.; Koerner Von Gustorf, E. A.; Scrivanti, A.; Wolfbeis, O. *J. Organomet. Chem.* **1976**, *108*, C32–C34.
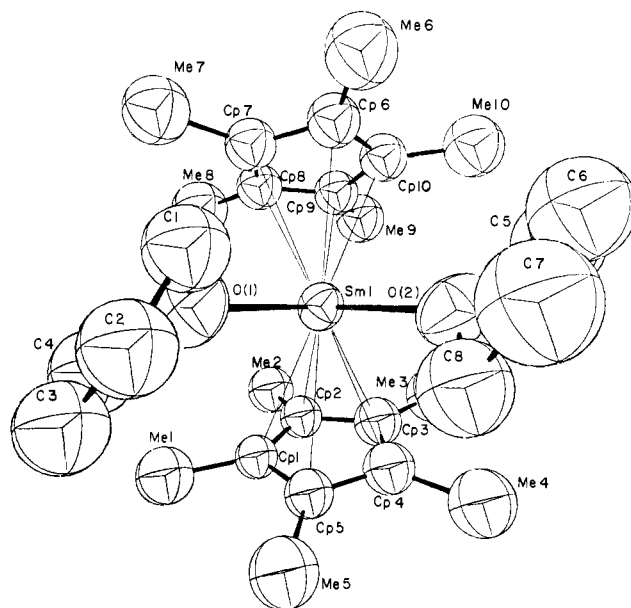

Figure 1. ORTEP plot of the molecular structure of $(C_5Me_5)_2Sm(THF)_2$.

of the zero-valent lanthanides with neutral unsaturated hydrocarbons. These reactions have provided a variety of new classes of organolanthanide complexes,[3,5,6,8] including some which display catalytic activity.[5,6] We report here the utility of this low valent approach to lanthanide chemistry in providing access to soluble divalent organosamarium complexes. These complexes are especially significant in light of recent interest in applying divalent lanthanide chemistry to organic synthesis[19,20] and catalytic reactions involving the Ln(III)/Ln(II) couple.[7,9] Sm(II) is the most reactive of the readily accessible divalent lanthanides [Sm(III) + e → Sm(II):–1.50 V[21]], but the only previously synthesized Sm(II) organometallics, $(C_5H_5)_2Sm^{22}$ and $(CH_3C_5H_4)_2Sm,^{23}$ are insoluble and hence of limited utility.

Vaporization of samarium metal into a mixture of pentamethylcyclopentadiene in hexane in a rotary metal vaporization reactor[24] cooled by a petroleum ether slush bath kept at ca. –120 °C generates a yellow, then green, and finally black solution over a period of 40 min. Filtration of the green-black reaction mixture at room temperature in an inert atmosphere glove box separates a solid, which, after washing with hexane and toluene, can be extracted with tetrahydrofuran (THF) to form a purple-brown solution. Removal of THF from this solution gives a product which contains Sm(II) and hydride ligands based on complete elemental analysis, magnetic susceptibility, and deuteriolytic decomposition which forms HD and D_2 in a 1.9:1 ratio.[25] Attempts to obtain crystals of this reactive hydride from THF at low temperature result in decomposition and/or ligand redistribution reactions

(19) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2703.
(20) White, J. D.; Larson, G. L. *J. Org. Chem.* **1978**, *43*, 4555–4556.
(21) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827–841.
(22) Watt, G. W.; Gillow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 775–776.
(23) Evans, W. J.; Zinnen, H. A., unpublished results.
(24) Constructed by adaptation of a Buchi rotary evaporator using plans kindly supplied by P. L. Timms. The reactor flask was a 2-L round bottom flask attached to a 200 × 45-mm glass tube. The metal was vaporized from a three strand 0.025-in. tungsten wire crucible coated with alumdum cement.
(25) Complete elemental analysis (Bernhardt) of this product is consistent with the formula $C_5Me_5SmH(THF)_2$, the product expected from simple oxidative addition of C_5Me_5H to samarium. Anal. Calcd for $SmC_{18}H_{32}O_2$: Sm, 34.98; C, 50.30; H, 7.26; O, 7.44. Found: Sm, 35.09; C, 50.28; H, 7.37 (by difference). However, the magnetic susceptibility of the sample, χ_M^{296} = 3400 × 10^{-6} was less than that expected for a pure Sm(II) complex [4800 × 10^{-6} (μ = 3.4) to 5400 × 10^{-6} (μ = 3.6)] and deuteriolysis gave less than the quantitative amount of gas expected (0.85 mol/mol of Sm). These data could arise from a divalent hydride (which does not quantitatively hydrolyze and which has a low magnetic susceptibility at room temperature) or from a product containing a 2:1 mixture of a divalent hydride plus a trivalent hydride such as $(C_5Me_5)_2SmH$. If the latter product is present, its decomposition to I has precedent in organoytterbium chemistry.[7]

which form a second divalent complex which contains much less hydride (by deuteriolysis) and a smaller percentage of samarium.[26] This latter divalent product can be purified, however, by a subsequent low temperature THF recrystallization to provide purple, crystalline $(C_5Me_5)_2Sm(THF)_2$ (I), identified by analytical,[27] magnetic,[27] infrared,[27] and X-ray diffraction methods. Since this reaction can be conveniently run to provide a recrystallized yield of 0.5 g of I,[28] this metal vapor synthesis provides the first preparative scale route to a soluble divalent organosamarium complex.[29]

I is not only the first soluble divalent organosamarium complex but also the first structurally characterized divalent organosamarium system. Two crystallographically independent molecules are found in the unit cell[30] and do not differ significantly in bonding parameters. Figure 1 presents a view of one of the molecules. Average $Sm-C(\eta^5)$ and $Sm-O$ bond lengths are 2.86 (3) and 2.63 (1) Å, respectively. In comparison, $(C_5Me_5)_2Yb(THF)(C_7H_8)_{0.5}$[10] has $Yb-C(\eta^5)$ and $Yb-O$ distances of 2.66 and 2.41 Å, respectively. The differences in these distances, 0.20 and 0.22 Å, are only slightly larger than the difference in ionic radii of Sm(II) and Yb(II), 0.18[31]-0.19.[32] The small lengthening can be attributed to the more crowded coordination environment in the disolvated 8-coordinate samarium case.

The ^1H NMR spectrum of I[33] in C_6D_6, the first reported NMR spectrum of a divalent samarium complex, exhibited relatively sharp singlets at δ 2.45 (30 H, $\Delta\nu_{1/2}$ = 8 Hz) and 4.43 (7 H, $\Delta\nu_{1/2}$ = 33 Hz) and a broad absorption at δ 17.99 ($\Delta\nu_{1/2}$ = 92 Hz). Exchange of the solvated THF in I with THF-d_8 gave a complex which displayed only the δ 2.45 absorption. Hence, we assign this absorption to C_5Me_5, the δ 4.32 absorption to the β-CH_2 group most distant from the Sm(II) center, and the broad resonance to the α-CH_2 group. The ^{13}C NMR spectrum of I[34] in C_6D_6 exhibited a pattern of absorptions just the opposite of that found in other pentamethylcyclopentadienyl lanthanide complexes:[35] δ

-73.7 (s, $C_5(CH_3)_5$), 33.4 (t, J = 125 Hz, $\overline{OCH_2CH_2CH_2CH_2}$),

94.62 (q, J = 117 Hz, $C_5(CH_3)_5$), 149.5 ($\overline{OCH_2CH_2CH_2CH_2}$).[36]

Given the large radial size and large reduction potential of Sm(II) compared to the other accessible divalent lanthanides, the

soluble divalent products of this reaction would be expected to be highly reactive. A preliminary survey of reactivity supports this contention. The crystallized product reacts rapidly with CO, NO, 3-hexyne, HgR_2, and $Co(PR_3)_4$ to form trivalent products. It is also observed to polymerize ethene and functions as a catalyst precursor for catalytic hydrogenation of 3-hexyne to >99% *cis*-3-hexene under mild conditions.[37] These reaction products, as well as the interesting byproducts of this metal vapor reaction, are currently under investigation. On the basis of these results, we anticipate a rich and varied reaction chemistry for divalent organosamarium complexes now that a preparative scale synthesis of a soluble derivative is available.

Supplementary Material Available: Tables of bond distances, bond angles, final fractional coordinates, and thermal parameters and the ORTEP plot of the other crystallographically independent molecule of $(C_5Me_5)_2Sm(THF)_2$ in the unit cell (31 pages). Ordering information is given on any current masthead page.

(37) At 25 °C and 1 atm of H_2, the rate was 0.85 × 10^{-3} turnovers/min based on H_2 uptake.

A Novel Catalytic System for Homogeneous Hydrogenation of Carbon Monoxide: Ruthenium Complexes in the Presence of Iodide Promoters

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Homogeneous catalysts for CO hydrogenation[1-5] and systems modeling their behavior[6,7] have been the subject of much recent research because such catalytic systems offer the potential of selectively converting synthesis gas to chemicals now derived from petroleum. Various metal complexes have been investigated as potential catalysts for synthesis gas conversion in the homogeneous phase. The highest activity has been observed with rhodium catalysts[8] which produce mainly ethylene glycol and methanol, along with smaller amounts of other oxygenates. Cobalt and ruthenium catalysts also produce oxygenates, and complexes of other metals have been found to exhibit only very low or insignificant catalytic activity.[1] Reported here are initial studies of a novel ruthenium-containing catalytic system which hydrogenates

(26) Crystallization from THF at -78 °C gives purple crystals which contain ca. 29% Sm rather than the 35% found in the original THF extract. Deuteriolysis gives HD to D_2 ratios of 1:1 rather than 2:1. If this product is dissolved in THF and subsequently reanalyzed, the % Sm drops to ca. 27 [cf. $(C_5Me_5)_2Sm(THF)_2$, 26.61%] and the HD to D_2 ratio falls to <0.25 (<17% hydride). The red-brown mother liquor remaining after crystallization of I contains divalent samarium hydride complexes based on deuteriolysis, but attempts to isolate crystals from this fraction have not yet been successful.

(27) Recrystallization from THF at -50 °C gives purple crystals which contain 26.1% Sm and have χ_M^{296} = 5490 × 10^{-6}, μ_{eff} = 3.6 μ_B. IR (KBr, cm^{-1}): 3100-2725 s, 2705 w, 1440 s, 1370 w, 1240 m, 1210 w, 1080 s, 1040 s, 950 w, 895 s, 795 m. The charge-transfer absorption in the near-infrared–visible spectrum has no maxima in the visible region.

(28) Vaporization of 3-4 g of Sm into a 0.246 M solution of C_5Me_5H in hexane (3.5-4.5 g in 100-140 mL) provides 0.9-1.2 g of crystalline product after a single crystallization.[26] Yields of a twice crystallized product are ca. 0.5 g.[27]

(29) Solution syntheses of I from halide precursors are conceivable,[9-11,22,23] but given the high reactivity of I, the large size of Sm(II), and the propensity of organolanthanide complexes to form alkali metal halide adducts,[9] it may be difficult to obtain halide free products by solution methods.

(30) The space group is the triclinic $P\overline{1}$ with a = 15.155 (6) Å, b = 16.141 (6) Å, c = 16.179 (6) Å, α = 55.92 (3)°, β = 65.13 (3)°, γ = 62.18 (3)°, and D_C = 1.33 g cm^{-3} for Z = 4. Least-squares refinement on the basis of 3949 observed reflections led to a final R = $\sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.061. Hydrogen atoms have not been included, and the ring carbon atoms were refined with isotropic temperature factors. The thermal motion of all other atoms was dealt with anisotropically.

(31) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1002.

(32) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751-767.

(33) 18.8 mg/mL at 23 °C. The spectrum is temperature and concentration dependent, see ref 10.

(34) 30.3 mg/0.3 mL at 38 °C.[33]

(35) Cf. $(C_5Me_5)_2SmCl_2Li(THF)_2$: ^{13}C NMR (C_6D_6) δ 116.3 (s, C_5Me_5), 68.6 (t, J = 166 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 25.7 (q, J = 167 Hz, $C_5(CH_3)_5$), 18.2 (t, J = 133 Hz, $\overline{OCH_2CH_2CH_2CH_2}$). Evans, W. J.; Bloom, I., unpublished results.

(36) Signal too weak to observe in undecoupled spectrum.

(1) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136-141 and references therein.

(2) Paxson, T. E.; Reilly, C. A.; Holocek, D. R. *J. Chem. Soc., Chem. Commun.* **1981**, 618-619 and references therein.

(3) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419-7421.

(4) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855-6857. See also: Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 188-189.

(5) King, R. B.; King, A. D., Jr.; Tanaka, K. *J. Mol. Catal.* **1981**, *10*, 75-83.

(6) (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479-490. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121-127. (c) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7-C10.

(7) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466-6468.

(8) For example, rates (mmol products per mmol metal per unit time) reported in ref 1 (at 1973 atm, 230 °C) are 1.2 × 10^{-1} s^{-1} for rhodium catalysis and 1.2 × 10^{-2} s^{-1} for cobalt catalysis. Another source[9] includes a rate for rhodium catalysis (to the major products) at 1020 atm, 270 °C, of 1.2 × 10^{-1} s^{-1}. The reported[3] rate for ruthenium catalysis at 1300 atm, 268 °C, is 8.5 × 10^{-3} s^{-1}.

(9) Kaplan, L.; Walker, W. E. German Offen. 2643971 (to Union Carbide Corp.), 1977. U.S. Patent Application 618021, 1975.