Communications to the Editor

Synthesis and Structure of a Thermally Stable, Nonclassical, 7-Norbornadienyl Carbocation Obtained from $(C_5Me_5)_3Sm$ and CO

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Cationic norbornenyl compounds have played a prominent role in developing the chemistry of positively-charged reactive intermediates in organic chemistry. Extensive solvolytic, NMR, and theoretical studies of the 7-norbornenyl cation, **1**, Figure 1, and its derivatives have been conducted over a 40 year period to evaluate the existence of nonclassical bonding in these systems.[1] Despite the enormous interest in nonclassical carbonium ions, to date only one X-ray crystallographic study of a 7-norbornenyl carbocation has been reported, namely, that of 2,3-dimethyl-7-phenyl-2-norbornen-7-ylium hexafluoroantimonate-(V), **2**, Figure 1.[2] Few X-ray crystallographic studies have been carried out due to the difficulty in preparing and isolating single crystals of such species, which often require low-temperature methods. Indeed, to our knowledge only six crystal structures of aliphatic carbocations of any kind have been reported.[3] These are all isolated with either $(BCl_4)^-$, $(BF_4)^-$, $(SbF_6)^-$, or $(Sb_2F_{11})^-$ counterions. In each case, the halide ions are located within 2.88(2)–3.451(4) Å of the cation in the solid state, distances which are less than the sum of the van der Waals radii of carbon and the corresponding halide.

We report here a new method to form, stabilize, and provide structural information on carbocations exemplified by the 7-norbornadienyl system. The precursor to this chemistry, $(C_5Me_5)_3Sm$,[4] was the first fully characterized tris(pentamethylcyclopentadienyl) metal complex of any kind. Since such $(C_5Me_5)_3M$ complexes were originally thought to be too sterically crowded to exist, it was possible that $(C_5Me_5)_3Sm$ would have a limited chemistry due to steric inhibition of reactions. However, $(C_5Me_5)_3Sm$ is reactive and provides a product with CO not seen with other C_5Me_5 metal compounds.

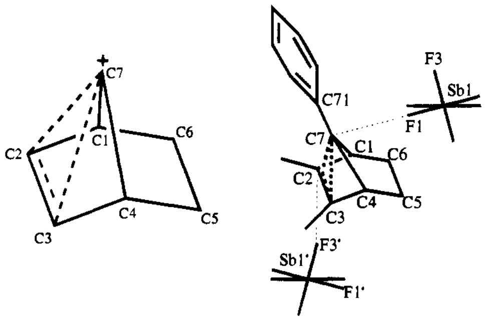

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Figure 1. Structure of the 7-norbornenyl cation, **1**, and 2,3-dimethyl-7-phenyl-2-norbornen-7-ylium hexafluoroantimonate, **2**, showing one cation and the positions of two symmetry-equivalent anions.

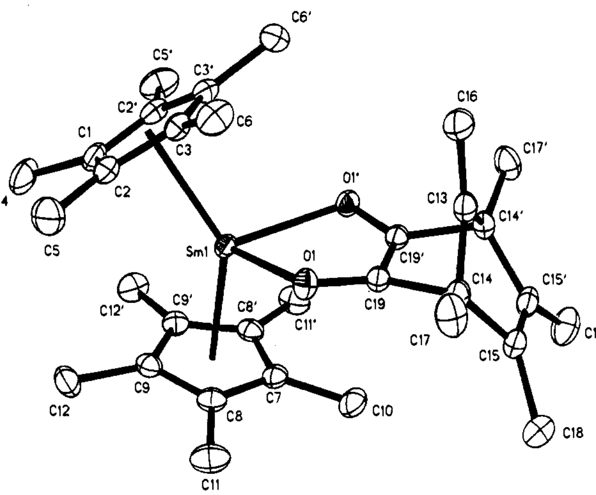

Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(O_2C_7Me_5)$, **3**. Ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

$(C_5Me_5)_3Sm$ reacts in toluene with CO at 1 atm in 5 min to form a hexane-soluble yellow compound, **3**, which can be isolated in >90% yield.[5] The ^1H NMR spectrum of **3** in C_6D_6 contains five signals in the C_5Me_5 region (intensity ratio15:15:6:6:3) which are consistent with two inequivalent C_5Me_5 rings attached to samarium and a C_5Me_5 unit of another kind. The $^{13}C\{^1H\}$ NMR spectrum displays 11 peaks and indicates that this is a Sm(III) complex.[6] DEPT[7] and decoupling experiments reveal that five of these 11 resonances are due to methyl carbon atoms and none of the remaining six carbon atoms are attached to hydrogen. The ^1H and ^{13}C NMR spectra of the product of the reaction between $(C_5Me_5)_3Sm$ and ^{13}CO are identical to those of **3** except for a dramatic enhancement of the peak resonating at 165.5 ppm, which is not a methyl resonance.

Since the NMR data were not structurally definitive, an X-ray diffraction study was attempted. Although only very small crystals were obtainable, by using a Siemens rotating anode system, a high-quality structure (R_f = 2.9%) was obtained[8] and **3** was identified as $(C_5Me_5)_2Sm(O_2C_7Me_5)$, Figure 2. The structure of **3** has a mirror plane which contains Sm, C(13),

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[1] (a) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183. (b) Winstein, S.; Ordronneau, C. *J. Am. Chem. Soc.* **1960**, *82*, 2084. (c) Story, P. R.; Saunders, M. *J. Am. Chem. Soc.* **1962**, *84*, 4876. (d) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3954. (e) Brown, H. C. *Acc. Chem. Res.* **1973**, *6*, 377. (f) Story, P. R.; Clark, B. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Chapter 23.

[2] Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224.

[3] (a) Laube, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 349. (b) Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 560. (c) Montgomery, L. K.; Grendze, M. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749. (d) Reference 2. (e) Laube, T.; Hollenstein, S. *J. Am. Chem. Soc.* **1993**, *115*, 7240. (f) Laube, T.; Lohse, C. *J. Am. Chem. Soc.* **1994**, *116*, 9001.

[4] Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

[5] In the glove box, $(C_5Me_5)_3Sm^4$ (400 mg, 0.720 mmol) was dissolved in toluene (10 mL) and placed in a Schlenk flask equipped with a stir bar. The flask was attached to a Schlenk double manifold and evacuated. CO at 1 atm was introduced to the flask, and the brown solution turned yellow-orange within 5 min. The solvent was removed in vacuo, leaving $(C_5Me_5)_2Sm(O_2C_7Me_5)$, **3** (392 mg, 98%), as a yellow powder. IR (KBr): 2966 s, 2930 s, 2857 s, 1688 m, 1546 s, 1443 s, 1402 m, 1377 s, 1112 s, 1070 s, 1017 m, 977 w, 798 s cm^{-1}. Anal. Calcd for $SmC_{32}H_{45}O_2$: Sm, 24.60; C, 62.81; H, 7.36. Found: Sm, 24.35; C, 62.53; H, 7.46. Magnetic susceptibility: $\chi_M{}^{294K} = 4.5 \times 10^{-4}$ (cgs); $\mu_{eff} = 1.0\mu_B$. ^1H NMR (C_6D_6): δ 3.65 (3H), 2.32 (6H), 1.29 (6H), 1.07 (15H), 0.991 (15H). ^{13}C NMR (C_6D_6): δ 165.5 (*C*O), 135.7, 117.4 (C_5Me_5), 116.9(C_5Me_5), 78.63, 59.42, 17.20 (Me), 16.84 (Me), 12.11 (Me), 8.34 (Me), 6.66 (Me).

[6] Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292.

[7] Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.

[8] **3** crystallizes from hexane in space group *Pnma* with a = 11.2516(12) Å, b = 14.995(2) Å, c = 17.250(3) Å, V = 2910.3(7) Å^3, and D_{calc} = 1.397 mg/m^3 for Z = 2. Least-squares refinement of the model based on 3701 reflections ($F > 3.0\sigma(F)$) converged to a final R_F = 2.9%.

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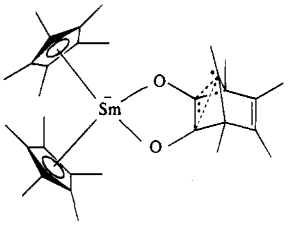
and C(16). The seven non-methyl carbon atoms of the $O_2C_7Me_5$ ligand, which originate from the five ring carbon atoms of a C_5Me_5 group and the carbon atoms of two CO molecules, adopt a norbornadiene structure. Equation 1 shows the stoichiometry involved in the formation of **3**. The NMR data fit this static structure exactly.

$$(C_5Me_5)_3Sm + 2CO \rightarrow (C_5Me_5)_2Sm(OC)_2(C_5Me_5) \quad (1)$$

The most unusual atom in the $O_2C_7Me_5$ ligand is C(13). It is within classical single-bonding distances of only three atoms, and these atoms are arranged in a planar fashion around C(13). The sum of the three C−C−C angles around C(13) is 359.8(1)°. No hydrogen atoms were observed on C(13) by X-ray crystallography, and this is fully consistent with the complete DEPT and ^{13}C NMR data on the complex.

These data and other structural features of **3** indicate that C(13) can be formally viewed as a carbocationic center (as shown below). C(13) is not symmetrically located between the C(19)−C(19′) and C(15)−C(15′) double bonds of the norbornadienyl skeleton. The C(13)−C(19) distance is 1.876(4) Å, compared to a C(13)−C(15) distance of 2.406 Å. This is consistent with nonclassical carbonium ion stabilization.[1] Such an interaction would be expected to lengthen C(19)−C(19′), and this is indeed found. The C(19)−C(19′) distance is 1.426(4) Å, compared to the 1.328(5) Å distance of C(15)−C(15′), which is normal compared to the standard value of 1.33(1) Å for a tetraalkyl-substituted double bond.[9] It is possible that C(19)−C(19′) is longer due to the $(C_5Me_5)_2SmO$ substituents. However, examination of the closest structurally related organosamarium complex, $(C_5Me_5)_2(Ph_3PO)Sm(OCH{=}CHO)Sm(OPPh_3)(C_5Me_5)_2$, **4**,[10] suggests that this is not the case: the C=C double bond in **4** is 1.324(22) Å.



The formal positive charge on C(13) is charge stabilized within the molecule by an organosamarium moiety of the general type $[(C_5Me_5)_2Sm(OR)_2]^-$ in which the oxygen atoms are those furnished by CO and the two R groups are carbon atoms C(19) and C(19′). The structural parameters around samarium (2.73(1) Å Sm−C(C_5Me_5) average distance; 139.0° ring centroid−Sm−ring centroid angle) are consistent with a formally eight-coordinate[11] trivalent samarium metallocene complex.[12] The symmetry-equivalent 2.347(2) Å Sm−O bonds are within the 2.08(1)−2.39(1) Å range observed for $(C_5Me_5)_2Sm{-}OR$ bonds and are shorter than the 2.44(2)−2.72(2) Å range of $(C_5Me_5)_2ZSm{-}(OR_2)$ bonds (Z = monoanionic ligand).[8] However, the Sm−O distance in **3** is in the long end of the Sm−OR bond distance range and is longer than the analogous 2.147(10) and 2.179(10) Å bond distances in **4**.

Table 1. Selected Bond Lengths for $(C_5Me_5)_2Sm(O_2C_7Me_5)$, **3**, and $[C_7H_6(Me)_2Ph]^+[SbF_6]^-$, **2**, Aligned To Compare Analogous Distances

3		2	
C19−C19′	1.426(4)	C2−C3	1.38(1)
C13−C19	1.876(4)	C2−C7	1.86(1)
C13−C19′	1.876(4)	C3−C7	1.86(1)
C13−C16	1.486(5)	C7−C71	1.48(1)
C15−C15′	1.328(5)		
Sm−O1	2.347(2)		
C19−O1	1.293(3)		
C14−C17	1.514(4)		
C15−C18	1.494(4)		
C13−C14	1.513(3)		
C14−C15	1.520(3)		
C14−C19	1.523(3)		

The structural arrangement of **3** is suitable for delocalized overlap of a p orbital on C(13) with the π orbitals of C(19) and C(19′) and the p orbitals on O(1) and O(1′). The fact that the 1.293(3) Å C(19)−O(1) distance is slightly shorter than typical C−O single bonds,[13] which vary from 1.36(1) Å (ArOH, RC(O)−OR′) to 1.430(3) Å (ROH, ROR), is consistent with some delocalization in the $O_2C_7Me_5$ ligand. However, this C−O distance is equivalent within error limits to the 1.319(19) and 1.352(18) Å distances in **4**.[10]

Comparison of the crystallographic data obtained on **3** with that of 2,3-dimethyl-7-phenyl-2-norbornen-7-ylium hexafluoroantimonate(V)[2] (Table 1) shows that the two structures are similar. Stabilization of the carbocation by the formally anionic organosamarium unit apparently is quite effective, since **3** is stable at 60 °C in C_6D_6 for several weeks. Studies of the mode of formation of **3**, its reactivity, and the synthesis and structure of derivatives are in progress.

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Supporting Information Available: Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[9] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

[10] Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671.

[11] The three electron pairs of the $(C_5Me_5)^-$ ligand are counted as occupying three coordination positions.

[12] Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.

[13] *Spec. Publ. Chem. Soc.* **1965**, *18*, M665. Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197 and references therein.