

Lanthanide organometallic chemistry springs a surprise: A serendipitous route to a 'nonclassical' carbocation

S. S. Krishnamurthy

There are many instances in science where breathtaking new discoveries are made by serendipity. Oftentimes, breakthrough in a particular field is achieved by scientist(s) working in an entirely different area. A striking example of this facet of scientific research is the recent report by Evans and coworkers¹ on the synthesis and structure of a thermally stable 'nonclassical' 7-norbornadienyl carbocation intramolecularly stabilized by an anionic organosamarium(III) moiety. The unusual reaction leading to the unexpected product is shown in Scheme 1.

Evans and coworkers had no intention of making a carbocation but were only interested in studying the reactivity of samarium tris(pentamethylcyclopentadienyl) which they had earlier synthesized and structurally characterized². To their great surprise, the reaction of **1** with carbon monoxide in toluene gave **2** as a yellow solid in >90% yield. The structure **2** has been determined by single crystal X-ray diffraction. Although only extremely tiny crystals of **2** could be obtained, the determination of its structure was made possible by the use of a rotating anode system. The novel reaction depicted in Scheme 1 may be formally considered as cycloaddition of two molecules of a heteroene (such as CO) to a diene with concomitant formation of a carbon-carbon bond between the heteroynes. It is interesting to note that the reaction of CO with the divalent samarium complex $(C_5H_5)_2Sm(thf)_2$ leads to homologation of

CO to give a ketene carboxylate $(O_2C-C=C=O)$ derivative³.

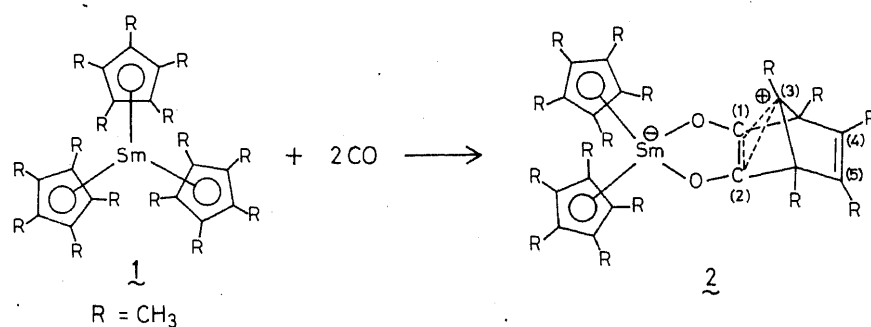
At this point, a bit of background on 'nonclassical' carbocations may be appropriate. Carbocations are reactive intermediates encountered in organic chemistry and possess three coordinated carbon centres with a positive charge on carbon. Two examples are shown in Figure 1; of these the *t*-butyl carbocation (**a**) is regarded as 'classical' while the 7-norbornenyl cation (**b**) is often cited as representing an archetypal 'nonclassical' carbocation. The central idea behind the 'nonclassical' bonding hypothesis is that the positive charge is dispersed over several carbon atoms (see Figure 1 *b*). The nonclassical hypothesis evoked a fierce controversy among many scientists including Nobel laureates H. C. Brown and G. A. Olah⁴⁻⁶. NMR spectroscopic^{5,7,8} and X-ray diffraction studies⁹ have confirmed 'nonclassical' structures for norbornyl and norbornenyl carbocations. These carbocations are generally thermally unstable and it is difficult to obtain single crystals of these compounds. The crystal structures of only a few aliphatic carbocations have been reported and in all these instances, invariably there is an anion such as $(BX_4)^-$ ($X = F$ or Cl) or $(SbF_6)^-$ whose halogen atoms show weak interactions with the carbocation⁹. The successful synthesis of a thermally stable carbocationic derivative **2** by Evans and coworkers represents a significant breakthrough in this field as they have

uncovered an entirely new way of stabilizing a carbocationic centre.

The X-ray crystallographic data for **2** clearly support the presence of a 'nonclassical' carbocationic centre. The carbon atom C(3) is closer to the C(1)-C(2) double bond [1.876(4) Å] than to the C(4)-C(5) double bond (2.406 Å). As a result, the C(1)-C(2) distance [1.426(4) Å] is longer compared to C(4)-C(5) distance [1.328(5) Å] which is close to a normal C-C double bond distance. These structural features are similar to those observed for 2,3-dimethyl-7-phenyl-2-norbornen-7-ylum carbocation in the crystal structure of its $(SbF_6)^-$ derivative⁹. The absence of a proton on C(3) in **2** is supported by ¹³C NMR studies¹.

In recent years there has been an upsurge in organolanthanide chemistry¹⁰. Some of the exciting developments in this area are: (a) the synthesis of the first stable lanthanide(II)-carbene complexes using the nucleophilic imidazol-2-ylidene type carbenes first reported by Arduengo and coworkers¹¹; (b) cyclooctatetraenyl complexes¹² of cerium(IV); (c) the versatile reactivity of $(C_5Me_5)_2Sm$ towards unsaturated species such as N_2 , alkynes and olefins^{2,13,14} and (d) synthesis and structural characterization of a metal ketyl complex derived from the samarium(II) aryloxide derivative¹⁵ $Sm(OR)_2(thf)_3$ ($R = C_6H_2(tBu)_2-2,4,Me-6$). The present report on the unusual reaction of $Sm(C_5Me_5)_3$ with CO to give an intramolecularly stabilized 'nonclassical' carbocation is yet another surprise to spring from organolanthanide chemistry.

Further studies on the mechanism of formation of **2**, its reactivity and also synthesis and structures of various deriva-



Scheme 1.

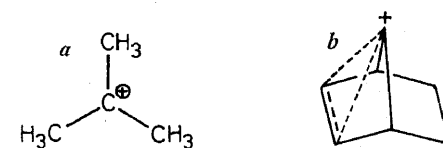


Figure 1. Structures of **a**, *t*-butyl carbocation and **b**, 'nonclassical' 7-norbornenyl carbocation.

RESEARCH NEWS

tives related to **2** by varying the lanthanide metal and the substituents on the cyclopentadienyl ring would enrich the organometallic chemistry of lanthanides as well as the chemistry of carbocations.

1. Evans, W. J., Forrestal, K. J. and Ziller, J. W., *J. Am. Chem. Soc.*, 1995, **117**, 12635–12636.
2. Evans, W. J., Gonzales, S. L. and Ziller, J. W., *J. Am. Chem. Soc.*, 1991, **113**, 7423–7424.
3. Evans, W. J., Grate, J. W., Hughes, L. A., Zhand, H. and Atwood, J. L., *J. Am. Chem. Soc.*, 1985, **107**, 3728–3730.
4. Brown, H. C., *Acc. Chem. Res.*, 1983, **16**, 432–440.
5. Olah, G. A., Suryaprakash, G. K. and Saunders, M., *Acc. Chem. Res.*, 1983, **16**, 440–448.
6. Walling, C., *Acc. Chem. Res.*, 1983, **16**, 448–454.
7. Olah, G. A., Suryaprakash, G. K., Williams, R. E., Field, L. E. and Wade, K., *Hypercarbon Chemistry*, 1987, Ch. 5, pp. 139–189.
8. Myhre, P. C., Webb, G. G. and Yannoni, C. S., *J. Am. Chem. Soc.*, 1990, **112**, 8991–8952.
9. Laube, T., *Acc. Chem. Res.*, 1995, **28**, 399–405.
10. Fischer, R. D., *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 2165–2168.
11. (a) Arduengo III, A. J., Tamm, M., McLain, S. J., Calabrese, J. C., Davidson, F. and Marshall, W. J., *J. Am. Chem. Soc.*, 1994, **116**, 7927–7928; (b) Schumann, H., Glanz, M., Winterfeld, J., Hemling, H., Kuhn, N. and Kratz, T., *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1733–1734.
12. Edelmann, F. T., *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2466–2488.
13. Evans, W. J., *Polyhedron*, 1987, **6**, 803–835.
14. Evans, W. J., Ulibarri, T. A. and Ziller, J. W., *J. Am. Chem. Soc.*, 1988, **110**, 6877–6879; 1990, **112**, 2314–2324.
15. Hou, Z., Miyano, T., Yamazaki, H. and Wakatsuki, Y., *J. Am. Chem. Soc.*, 1995, **117**, 4421–4422.

S. S. Krishnamurthy is in the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India.

COMMENTARY

The Exponential Law of Academic Decay

G. Prathap and U. N. Sinha

Preamble

The National Aerospace Laboratories run a very vibrant programme using students on its various projects and missions. This student strength has grown rapidly and currently as many as 650 students (BE, M Sc, MCA, ME, Ph D) work on various assignments of relevance to NAL and at the same time meet the requirements of excellence demanded for submission of dissertations to their respective university departments. Many on completion of their student training programmes join in various temporary capacities in NAL, e.g. as Graduate Trainees, Post-graduate Trainees, JRFs, SRFs, Fellows, etc.

Over the last few years, we (GP and UNS) have been able to closely interact with a sample size of about 150 students on some major developmental projects in NAL which for various logistical reasons were dependent not insignificantly on 'student-power'. This has allowed us also to observe them closely in a sociologically significant manner, both as mentors in providing them informal on-the-job train-

ing and on dissertation preparation and also as task-givers in assigning tasks and monitoring their completion and delivery in keeping with the project and mission requirements. Thus, a continuous chain of work definition, performance management, training and development, and appraisal and reward is involved in our interaction with the students. Also, in view of the difficulties in absorbing these young talent in permanent positions in NAL due to current hiring restrictions, it is necessary for us to humanely manage their 'organizational exit' from NAL after they have completed their temporary assignments.

Formulation of 'The law of exponential decay'

A rapid turnover of students is involved and many have been observed carefully. Often we (GP and UNS) have compared notes on our experiences using these students and from time to time, we have appeared jointly or separately before com-

mittees seeking views on how to formulate postgraduate education and research programmes for the future. One underlying theme that we have discerned and conceptualized and that we feel must be taken care of by any planner/policy maker/administrator who wants to design a framework for PG education and research or even a Human Resources Management Policy is what we call 'The exponential law of academic decay'. Note that our formulation is particularly inspired by Andre Weil's famous law—'A first rate man will hire a first rate man; a second rate man will hire a fourth rate man; etc.', although the contexts are slightly different.

Figure 1 captures the spirit of the law. We have assumed that the *y*-axis shows some kind of ability (IQ, achievement indicator, etc.) rating while the *x*-axis shows the career path. The exponentially decaying solid line shows how and when the transition is made from academic career to professional career. What we find is that undergraduate students, especially if they are from elitist institutions