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

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There are many instances in science where breathtaking new discoveries are made by serendipity. Oftentimes, breakthroughs in a particular field are achieved by scientists working in an entirely different area. A striking example of this facet of scientific research is the recent report by Evans and coworkers 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(pentamethylecyclopentadienyl) which they had earlier synthesized and structurally characterized. To their great surprise, the reaction of 1 with carbon monoxide in toluene gave 2 as a yellow solid in > 90% yield. The structure of 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 heteroenes. It is interesting to note that the reaction of CO with the divalent samarium complex \((\text{C}_5\text{H}_5)_2\text{Sm(thf)}_3\) leads to homologation of CO to give a ketene carboxylate \((\text{O}_2\text{C}=\text{C}=\text{C}=\text{O})\) derivative.

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 1b). The nonclassical hypothesis evoked a fierce controversy among many scientists, including Nobel laureates H. C. Brown and G. A. Olah. NMR spectroscopic and X-ray diffraction studies of some of these '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 \((\text{B}X_2)^+\) \((X = \text{F} \text{ or Cl})\), or \((\text{SbF}_5)^-\) whose halogen atoms show weak interactions with the carbocation. 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 \([1.876(4) \text{ Å}]\) than to the C(4)–C(5) double bond \([2.406(6) \text{ Å}]\). As a result, the C(1)–C(2) distance \([1.426(4) \text{ Å}]\) is longer compared to C(4)–C(5) distance \([1.328(5) \text{ Å}]\) 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-yl)carbocation in the crystal structure of its \((\text{SbF}_5)^-\) derivative. The absence of a proton on C(3) in 2 is supported by \(^{13}\text{C}\) NMR studies.

In recent years there has been an upsurge in organolanthane chemistry. Some of the exciting developments in this area are: (a) the synthesis of the first stable lanthanide(II)–carbone complexes using the nucleophilic imidazol-2-ylidene type carbenes first reported by Arduengo and coworkers; (b) cyclooctatetraenyl complexes of cerium(IV); (c) the versatile reactivity of \((\text{C}_6\text{Me}_5)_2\text{Sm}\) towards unsaturated species such as \(\text{N}_2\), alkynes and olefins and (d) synthesis and structural characterization of a metal ketyl complex derived from the samarium(II) aryl oxide derivative. The present report on the unusual reaction of \((\text{C}_6\text{Me}_5)_2\text{Sm}\) with CO to give an intramolecularly stabilized 'nonclassical' carbocation is yet another surprise to spring from organolanthane chemistry.

Further studies on the mechanism of formation of 2, its reactivity and also synthesis and structures of various derivat-
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tives related to 2 by varying the lanthanide metal and the substituents on the
cyclepentadienyl ring would enrich the
golden metallic chemistry of lanthanides
as well as the chemistry of carboxations.

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COMMENTARY

The Exponential Law of Academic Decay

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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,
MSc, 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 ‘stu-
dent-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 manage-
ment, training and development, and appra-
raisal 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 humbly manage
their ‘organizational exit’ from NAL after
they have completed their temporary as-
signments.

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 stu-
dents 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 underly-
ing 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 re-
search or even a Human Resources
Management Policy is what we call ‘The
exponential law of academic decay’. Note
that our formulation is particularly in-
spired 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, espe-
cially if they are from elitist institutions