(1)

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-91-J-1934

R&T Code 4132060

Tert-butylalumoxanes: synthetic analogs for methylalumoxane (MAO) and new catalytic routes to polyolefins and polyketones

Andrew R. Barron

Harvard University

Department of Chemistry
12 Oxford Street
Cambridge, Massachusetts 02138

Date Submitted:
June 15, 1994

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4132060
Contract/Grant Number: N00014-91-J-1934
Contract/Grant Title: Tert-Butylalumoxanes: synthetic analogs for methylalumoxane (MAO) and new catalytic routes to polyolefins and polyketones
Principal Investigator: A. R. Barron
Mailing Address: Dept. of Chemistry
Harvard University, 12 Oxford Street, Cambridge, MA 02138
Phone Number: (617) 495-5008/495-9364 Fax Number: (617) 496-7402
E-mail Address: Barron@chemistry.harvard.edu

a. Number of papers submitted to refereed journals, but not published: 0
b. * Number of papers published in refereed journals (**for each, provide a complete citation**): 4
c. Number of books or chapters submitted, but not yet published: 0
d. * Number of books or chapters published (**for each, provide a complete citation**): 0
e. * Number of printed technical reports/non-refereed papers (**for each, provide a complete citation**): 0
f. Number of patents filed: 0
g. * Number of patents granted (**for each, provide a complete citation**): 0
h. * Number of invited presentations (**for each, provide a complete citation**): 3
i. * Number of submitted presentations (**for each, provide a complete citation**): 0
j. * Honors/Awards/Prizes for contract/grant employees (list attached): 2
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
k. Total number of **Full-time equivalent** Graduate Students and Post-Doctoral associates supported durin this period, under this R&T project number:
Graduate Students: 1
Post-Doctoral Associates: 3
including the number of,
Female Graduate Students: 0
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 1
l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published
Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

* Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

b. Papers Published in Refereed Journals

1. Hydrolysis of tri-*tert*-butyl aluminum: the first structural characterization of alkylalumoxanes, $[(R_2Al)_2O]_n$ and $[RAlO]_n$.
   M.R. Mason, J.M. Smith, S.G. Bott, and A.R. Barron, *J. Am. Chem. Soc.*, 1993, **115**, 4971.

2. Oxides, chalcogenides, and related clusters of aluminum, gallium, and indium.
   A.R. Barron, *Comments Inorg. Chem.*, 1993, **14**, 123.

3. Molecular structure of Tris (tri-methyl aluminum) (diglyme)
   J.T. Leman, C.C. Landry, and A.R. Barron, *Main Group Met. Chem.*, 1993, **16**, 193.

4. *Tert*-butylaluminum hydroxides and oxides: structural relationship between alkyl alumoxanes and alumina gels
   C.J. Harlan, M.R. Mason, and A.R. Barron, *Organometallics*, 1994, (July issue).

h. Invited Presentations

1. University of California: Berkeley campus,
2. Davis campus,
3. Irvine campus.

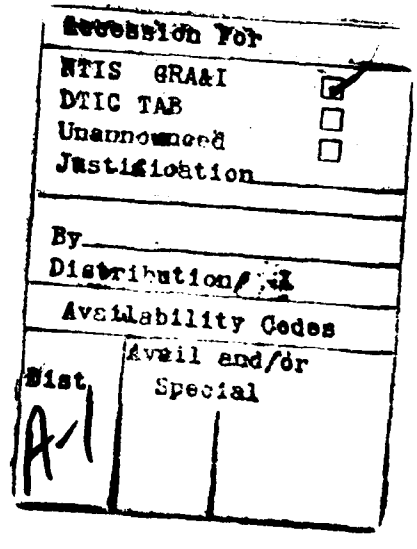
j. Honors/Awards/Prizes

1. Alcoa Foundation Fellowship, 1993.
2. Editorial Board, Main Group Metal Chemistry.

l. Other Funding

1. National Science Foundation
   Group 13 Chalcogenides
   Amount received this year: $110K
   Total: $265K
   April 1993 - March 1996 No relationship.

2. Office of Naval Research
   Group 13 Chalcogenides
   Amount received this year; grant started 1/1/94
   Total: $300K
   January 1994 - December 1996 No relationship.



OFFICE OF NAVAL RESEARCH

END OF YEAR REPORT

PART II

a) Principal Investigator: Andrew R. Barron

b) Current telephone number: (617) 495-5008; FAX (617) 496-7402

c) Cognizant ONR Scientific Officer: Dr. K. Wynne

d) Description of project:

Alkyl alumoxanes, the roducts from the partial hydrolysis of aluminum trialkyls, have been shown to be active catalysts and co-catalysts for a variety of polymerization processes. Despite industrial useage, no one has been able to isolate individual compounds and demonstrate a structure activity correllation. The purpose of this study is to: (a) isolate single alumoxane species, (b) determine the function of alumoxanes in Ziegler Natta Catalysis, and (c) develop new polymers, employing these catalysts.

e) Significant Results

Methylalumoxane, (MeAlO)n or MAO, has been proposed to exist as cyclic or linear structures. We have been the first to show that, by the synthetic analogue approach, alkyl alumoxanes are three-dimensional clusters, thus confirming our previous proposal that all alumoxanes are cluster species. X-ray crystallographic evidence for the hexameric, octameric, and nonameric forms of *tert*-butyl alumoxane, $[(^tBu)AlO]_n$, have been obtained. In addition, we have isolated the first example of an alkyl alumoxane containing a highly Lewis acidic three-coordinate aluminum center.

We have isolated a full range of alumoxanes and determined specific synthesis to allow large quantities of several of the compounds to be prepared at high yield.

Our most important result is the demonstration that the popular concept of alumoxanes as Lewis acids is false. Conventional wisdom suggests that to be active, an alumoxane needs to have a three-coordinate aluminum center. We have shown that $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$, which does have a three-coordinate Al, **is not** an active catalyst. However, $[(^tBu)AlO]_6$, which has no three-coordinate Al, **is** an active co-catalyst for olefin polymerization. Furthermore, we have isolated the first Zr/Al catalyst complex, $[Cp_2Zr(Me)]\ [(^tBu)_6Al_6(O)_6(Me)]$.

Our studies with Pd/alumoxane polyketone synthesis have now demonstrated that high molecular weight-crystalline $[CH_2CH_2C(O)]_n$ may be prepared at modest temperatures and pressures. We have determined the steps in the polymerization initiation reaction, including the crystallographic characterization of the catalyst precursor.

We have initiated work on polyester and polyether synthesis.

f) Summary for Next Year's Work

In the next week we propose to capitalize on our new synthetic routes to siloxy and carboxy alumoxanes.

With our isolation of a well-defined Zr/alumoxane catalyst, we can now investigate the full reaction steps of Ziegler-type olefin polymerization. Furthermore, we proposed to develop a comparison for the activity of each of our isolated clusters.

We will attempt to optimize our polyketone synthesis, as well as further our work with biodegradable polymers.

g) Student Researchers

Candice Lowe (Undergraduate)
Chloë Zubieta (Undergraduate)

Christopher Landry (Graduate)

C. Jeff Harlan (Post-Doctoral)
Yoshihiro Koide (Post-Doctoral)
Mark Mason (Post-Doctoral)

Explanatory Paragraph

Alumoxanes are known to be co-catalysts for the zirconium-catalyzed polymerization of olefins. While the general function of methyl alumoxane MAO is known (SLIDE 1, upper), there has been much speculation as to the actual identity of the Al species (SLIDE 1, lower). We have isolated compounds both with and without the three-coordinate Al center, proposed to be the active species. However, the species proposed to be active (SLIDE 2, left hand-side) is not, and the cage compounds we have demonstrated to be the major component of alumoxanes are active (SLIDE 2, right hand-side). The reason for the activity of the cages is due to the *Latent Lewis acidity* of the alumoxane. We have propsed this new term (SLIDE 3). The activity of the cage compound is shown to be only slightly lower than that of commercial MAO.

The Facts

proposed reaction of Cp_2ZrX_2 with methyl alumoxane (MAO)

$$Cp_2Zr(Cl)Me + MAO \longrightarrow [Cp_2ZrMe]^+ + [MAO(Cl)]^-$$

$$Cp_2ZrCl_2 + MAO \longrightarrow Cp_2Zr(Cl)Me + [MAO(Cl)]$$

$$Cp_2ZrMe_2 + MAO \longrightarrow [Cp_2ZrMe]^+ + [MAO(Me)]^-$$

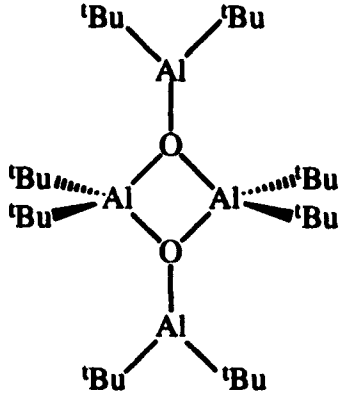
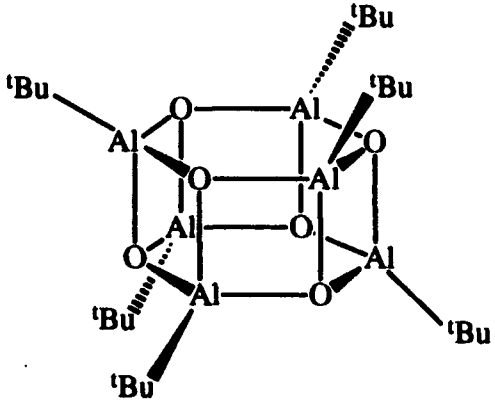
The Myth

For catalytic activity alumoxanes

MUST

contain a three coordinate Lewis acidic aluminum center

Destroying the Myth

Proposed to be active	Proposed to be inactive
	
No reaction with Cp_2ZrMe_2	Reaction with Cp_2ZrMe_2
No catalysis	Catalysis

$$Cp_2ZrMe_2 + [(^tBu)AlO]_6 \rightleftharpoons [Cp_2ZrMe][[(^tBu)_6Al_6O_6(Me)]$$

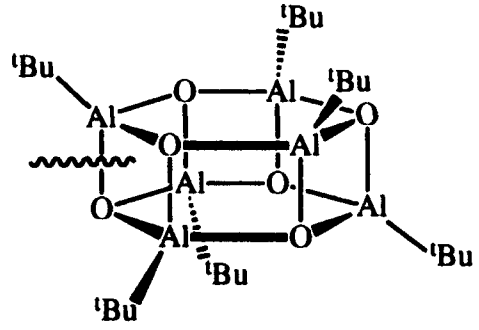
$$K_{eq} = 0.05\ mol^{-1}dm^3$$

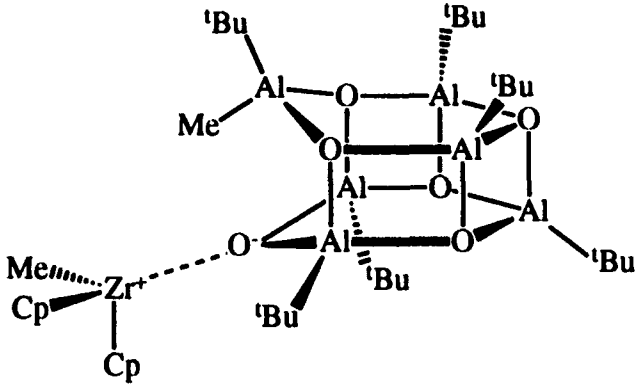
Destroying the Myth

Three-coordinate aluminum is NOT required for catalysis

"Latent Lewis Acidity"

ring strain





"active complex"

alumoxane co-catalyst	Al:Zr ratio	catalytic activity
$[(^tBu)AlO]_n$	6	10 kg/mol Zr/h
$[(^tBu)AlO]_6$	6	17 kg/mol Zr/h
MAO	200	160 kg/mol Zr/h