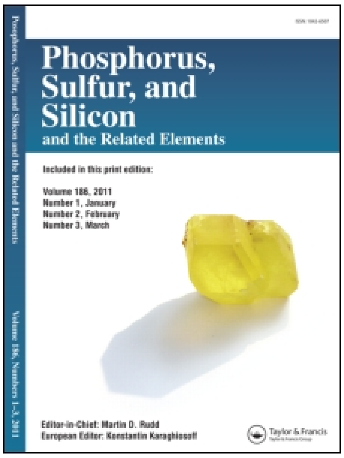

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Chemical Games with Molecular Footballs, Darts and Paddlewheels

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CHEMICAL GAMES WITH MOLECULAR FOOTBALLS, DARTS AND PADDLEWHEELS

(A lecture given in celebration of Professor Alan H. Cowley's sixtieth birthday)

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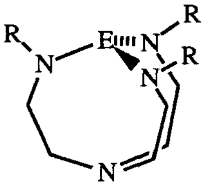
Molecules of the title types take part in a wide variety of chemical and structural games. Some of the more surprising transformations are discussed and rationales for them are put forth.

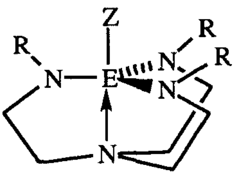
Key Words: Basicity; catalysis; transannulation; synthesis.

INTRODUCTION

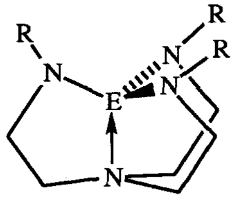
The title molecular shapes discussed in this lecture are represented by **A**, **B** and **C**,



A



B



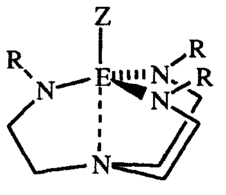
C

respectively, wherein E can be a main group element and Z can be a non-metallic or metallic substituent. While football is a peculiarly American game, darts is rather more British and at least that part of this talk should have some appeal to Alan. For the authors, paddlewheels have been a symbol of substantial significance ever since the record floods of 1993 in the Midwest, which quickly taught Iowans to "paddle" in order to stay afloat.

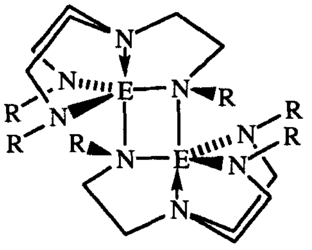
This presentation summarizes some of our recent investigations of the structural and chemical idiosyncracies of these aesthetically pleasing molecular shapes, in which E is, for example, phosphorus in **A**; gallium, silicon, germanium and tin in **B**; and boron, aluminum and gallium in **C**. Some of the surprises we will encounter include the extraordinary and useful basicity and catalytic activity of **A** (E = P, R = Me), some factors governing the intermediate transannular $P \leftarrow N_{ax}$ distances in novel hybrids of footballs and darts which we call "darballs" (**D**), unusual substitution reactions of **B**, interesting associations of darts and paddlewheels into dimers such as **E**, and also some extraordinary reactions of E.

FOOTBALL GAMES

Footballs **1** and **2** were first fabricated in a transamination reaction of $P(NMe_2)_3$ with

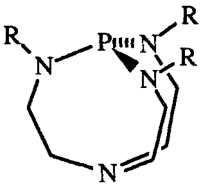


D

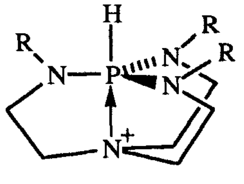


E

the corresponding tetramine $(RHNCH_2CH_2)_3N$.[1] However, this reaction takes weeks,



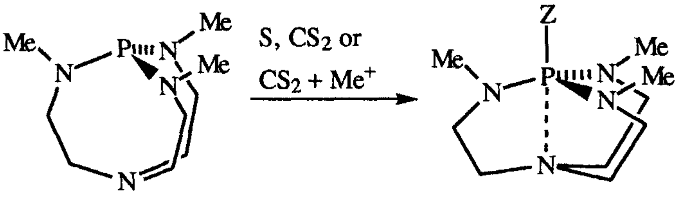
	R	
1	Me	**4**
2	CH_2Ph	**5**
3	H	**6**



and yields are low. In the case of **3**, only polymer formation is observed. Compounds **1** and **2**, as well as **3** are much more efficiently made from darts as we shall see later.

These footballs very readily engage in a game in which they transform themselves quantitatively to trigonal bipyramidal darts **4-6**, respectively, in the presence of even exceedingly weak acids such as protonated proton sponge.[2,3] This is a rather surprising result, in view of the much stronger basicity of the amine lone pair compared with the phosphorus lone pair, which was expected to lead to protonation of one of the nitrogens in **1-3** rather than phosphorus.

Football **1** reacts with other electrophiles such as those shown in equation 1 to give darballs such as **7-9**.[4-7] From the plot of the parameters in Fig. 1 which we obtained



1

	Z
7	S
8	CS_2
9	$C(S)SMe^+$

(1)

from X-ray crystallographic studies,[5,6,8] it is seen that the transannular distance decreases linearly with opening of the N-P-N bond angles ($r^2 = 0.9$). This plot constitutes an excellent example of progression along an S_N2 reaction coordinate involving the formation of a trigonal bipyramidal intermediate. Interesting features of this progression are the inversion of the axial nitrogen with the closing transannular distance and the substantial change in structural parameters (> 1.0 Å transannular closure and ~15° N-P-N expansion).

Football **1** also engages in transient darball formation in the highly efficient catalysis depicted in Scheme 1.[9,10] The six-membered ring **10** formed in quantitative

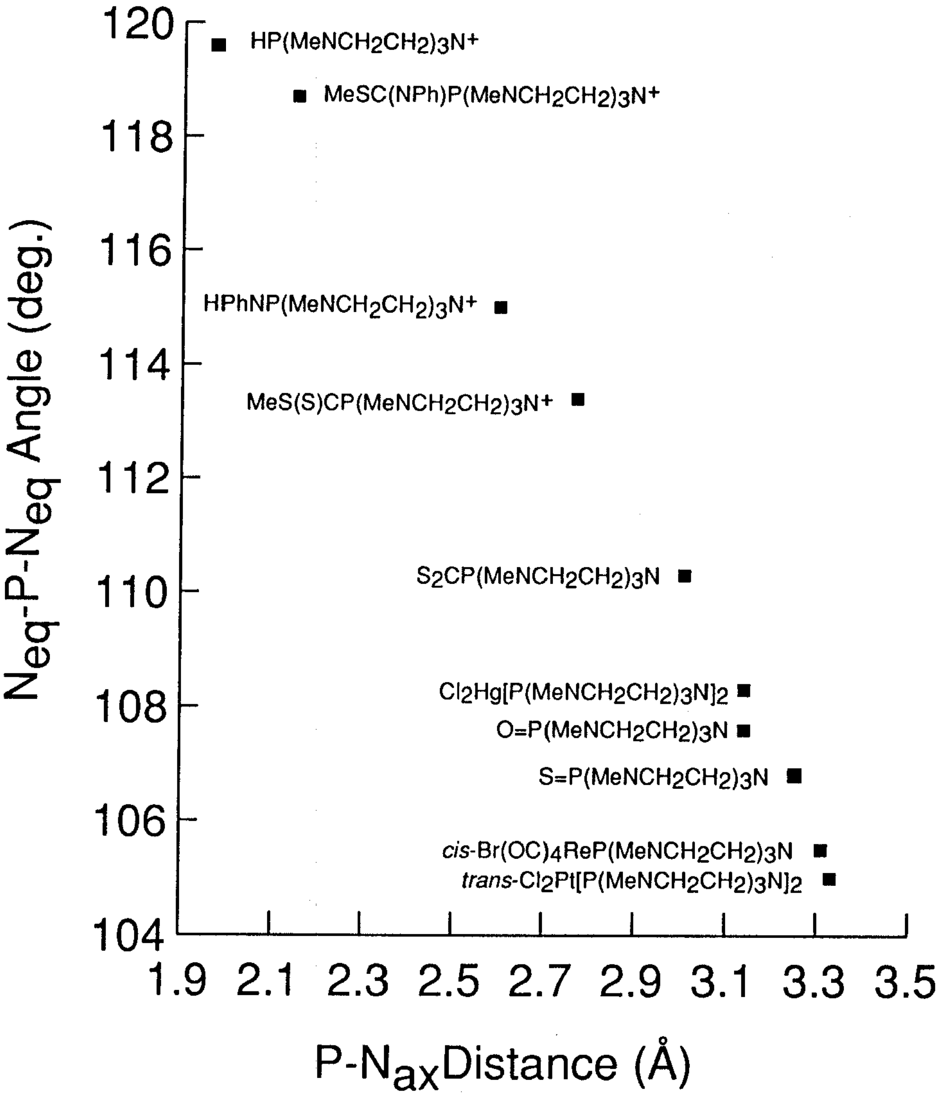
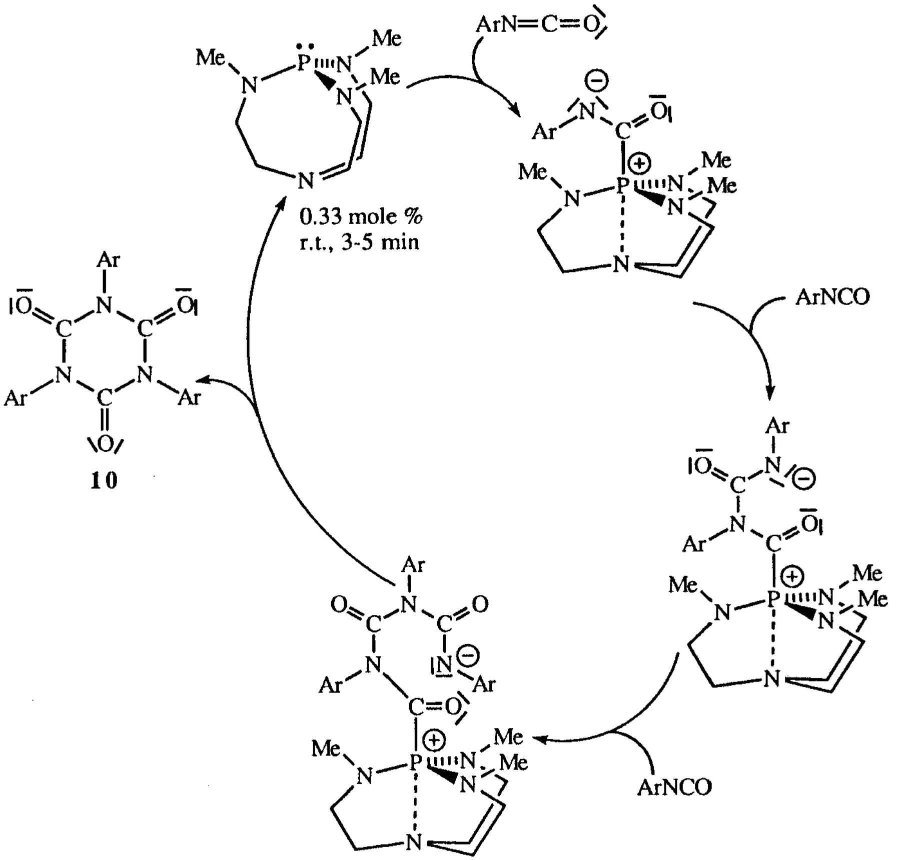


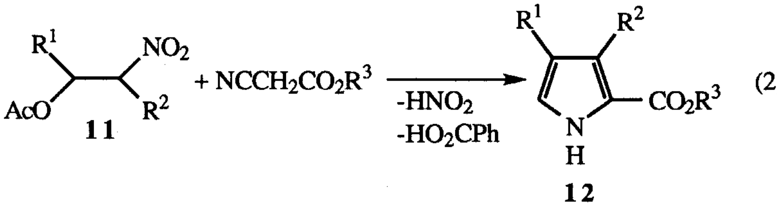
FIGURE 1 Plot of P-N$_{ax}$ distances against MeN-P-NMe angles in ZP(MeNCH$_2$CH$_2$)$_3$N compounds.

yields and in TLC purity in this reaction are important activators for the anionic polymerization of ε-caprolactam to Nylon 6 with a low monomer content and a stable melt viscosity. This structure also lends hydrolytic and thermal stability to isocyanurate-based foams and plastics.

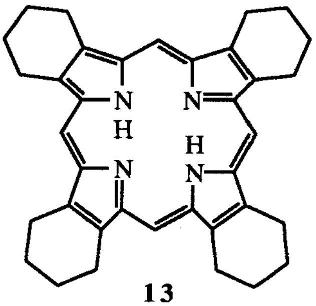
Scheme 1



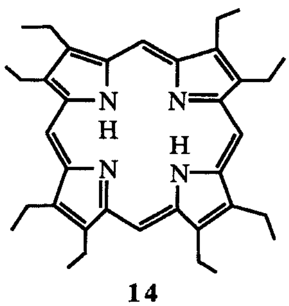
The extraordinary tendency for the football **1** to become dart **4** can be utilized in a variety of useful syntheses involving deprotonation steps. For example the transformation shown in reaction 2 is completely unsuccessful in two hours at low



temperature using the strong organic base DBU. Under the same conditions, **1** effects the formation of **12** in quantitative yield.[8,11] Compounds **11** are important intermediates in the synthesis of porphyrins such as **13** and **14** for which we have developed high-yield (> 60%) one-pot syntheses beginning with R^1CHO and $NO_2CH_2R^2$, the precursors to **11**.[8,11]



13

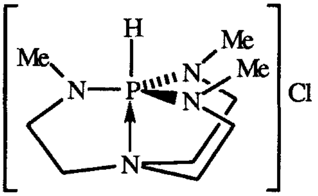


14

DART GAMES

Surprisingly, dart **4**(Cl) can be made in high yield by reaction 3 even in the presence of excess triethyl amine, which was expected to promote the formation of **1** and

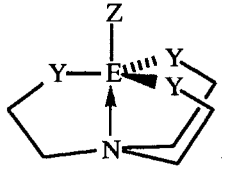
$ClP(NMe_2)_2 + (MeHNCH_2CH_2)_3N \longrightarrow$



4(Cl)

(3)

$[HNEt_3]Cl$.[1,11,12-13] Although the transamination reaction of $P(NMe_2)_3$ with $(MeHNCH_2CH_2)_3N$ is inefficient for synthesizing football **1**, this type of reaction works very well for making darts such as **15-20.**[14-21]

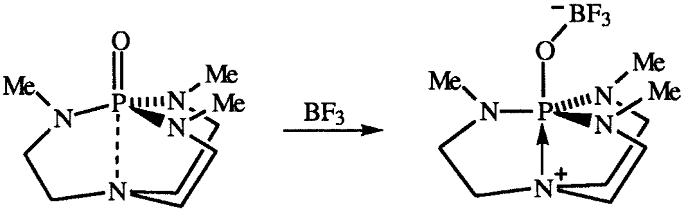


	E	Z	Y		E	Z	Y
15	Si	R	O	**18**	Si	R	NMe
16	Ge	R	O	**19**	Ge	R	NMe
17	Sn	R	O	**20**	Sn	R	NMe

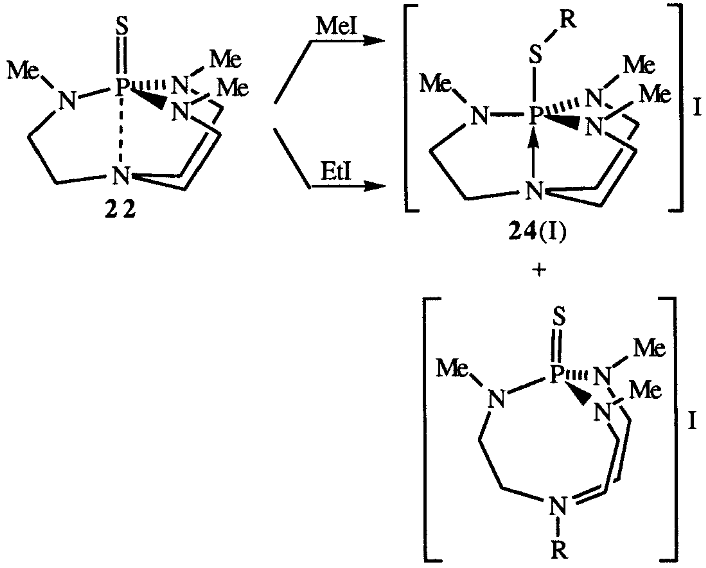
Darballs such as **21** and **22** (see Fig. 1) can also be transformed into darts by adding a Lewis acid to the chalcogen, as in **23**[22] and **24**,[7] respectively. In reactions 5 and 6, however, it was also observed that the regioisomeric compounds **25**(I) formed.[7]

Darts engage in games in which they are transformed to footballs and darballs. The most efficient route to **1**, for example, is to deprotonate dart **4** with a strong anionic base (reaction 7).[1,11,13] In the case of **26**, the stepwise introduction of steric hindrance with Me_3Si groups creates darball **27**, which upon treatment with MeI affords the cationic football **28**.[23]

The tips of darts and darballs are quite basic owing to electron induction from the transannular interaction. Thus these tips can bind robustly in many instances to Lewis acidic "targets". It is clear from reactions 8 and 9 that transannulation is responsible for the enhanced basicity of the axial oxygen which permits isolation of adducts **29** and

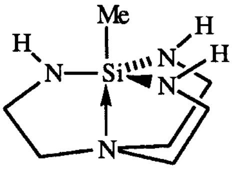


21 **23** (4)

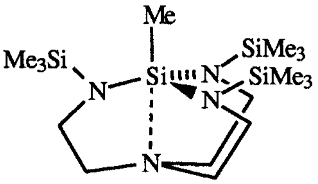


22 **24(I)** + **25(I)** (5) (6)

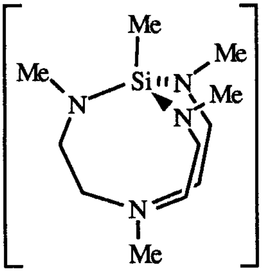
$$\mathbf{4} \xrightarrow[\text{MeCN}]{\text{KO-}t\text{-Bu}} \mathbf{1} \qquad (7)$$



26

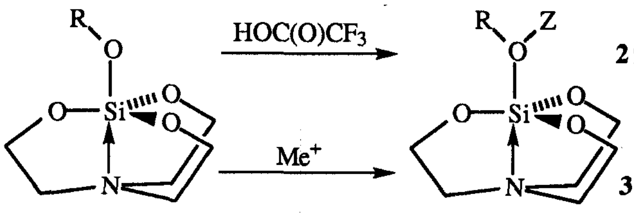


27

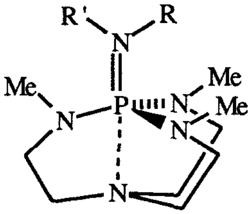


28(I)

30.[15] Interestingly, **29** is a hydrogen bonded adduct, while **30** is a fully alkylated cation. By contrast, **31** (which is probably a darball similar to **21** and **22**) and **32** are fully protonated in **33** and **34**, respectively, both of which are also still darballs, as was shown to be the case for **34** (see Fig. 1).[6] The ranking of basicities toward protons



	Z	R	
29	HOC(O)CF$_3$	Et	(8)
30	Me$^+$	Me	(9)



	R'	R
31	lone pair	Me
32	lone pair	Ph
33	H$^+$	Me
34	H$^+$	Ph

$Me_3CN{=}P[N{=}P(NMe_2)_3]_3$

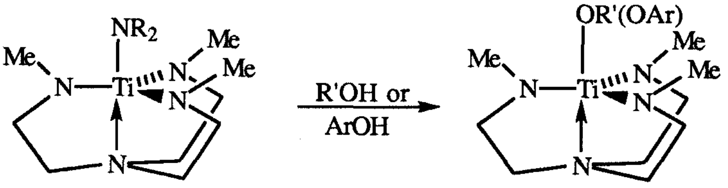
35

shown below reveals that two of our compounds are more basic than DBU, and that

$$\mathbf{1} > \mathbf{31} > (Me_2N)_3P{=}NMe > DBU > \mathbf{32} > (Me_2N)_3P{=}NPh$$

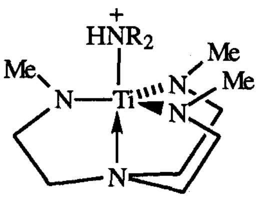
transannulation in **31** and **32** plays an important role in enhancing their basicities over their acyclic analogues.[6] The phosphazene **35**, which like **31** and **32** protonates an imino nitrogen,[24] is somewhat more basic (by one *p*K unit) than **1**, which is the most powerful phosphine base known.[6]

The dart tips and feathers can be replaced by other analogous parts. The peculiar aspect of the displacement shown in reaction 10 is that the reaction is actually faster for **36** when R is the comparatively bulky ethyl group than when R = Me.[25] Our rationale

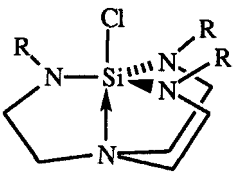


36 **37** (10)

is that protonation of **36** to give intermediate **38** is favored by the more basic NEt$_2$ substituent. Intermediate **38** is then attacked by the nucleophilic anion to give **37**.



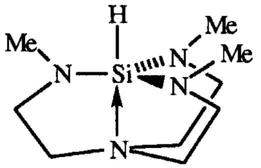
38



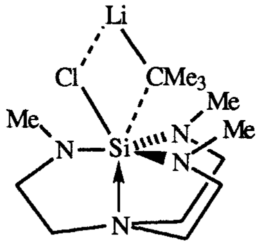
	R
39	H
40	Me

Confirmatory evidence for this rationale is the observation that Et_4NBr, a potential bromide source, does not react with **36** (R = Et) whereas NH_4Br, which also serves as a proton source, does.

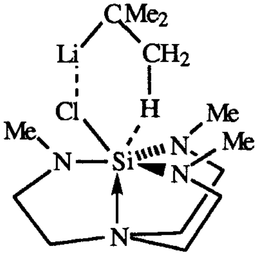
The azasilatrane dart **39** undergoes nucleophilic displacement of the chloride with $LiNR_2$ and LiR, for example, as expected. In contrast, **40** in the presence of such reagents gives varying yields of a second product **41**, which in the case of $LiCMe_3$ is quantitative.[18] We attribute this observation to steric interference of the N-methyl groups with the bulky *t*-butyl moiety in a four-center intermediate **42**, which is reduced in a more sterically favorable hydride transfer pathway facilitated by intermediate **43**.



41

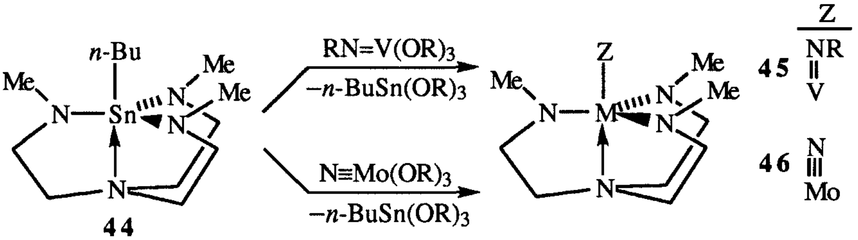


42



43

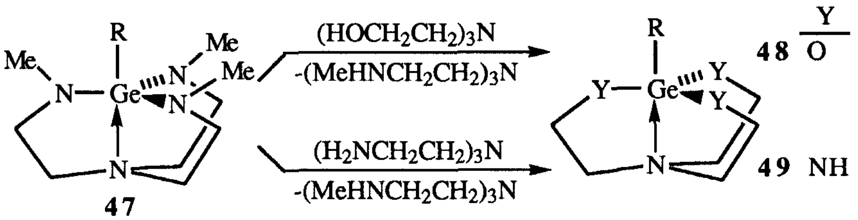
Rather than just the tip, the entire point of a dart is replaced in transmetallation reactions 11 and 12.[26] It is also feasible to replace all the feathers of darts, as in reactions 13-15.[20] The governing influences in reactions 13 and 15 are the formation of stronger E-O bonds accompanied by a reduction in steric hindrance, while the latter is the sole factor driving reaction 14.



(11)

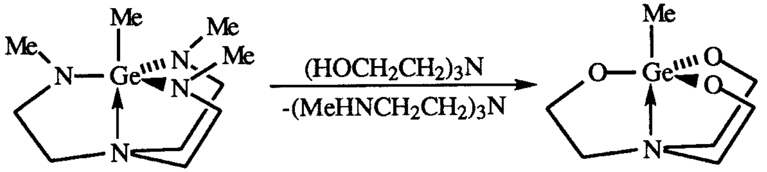
(12)

Although we normally speak of a "friendly game of darts", darts can be very friendly with one another, as in the spontaneous dimerization of the monomeric dart units leading to **52**.[27] With a little thermal encouragement in the presence of a catalytic amount of KH, **53** forms the dimeric structure **54**.[18]

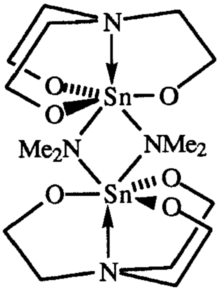


(13)

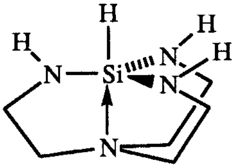
(14)



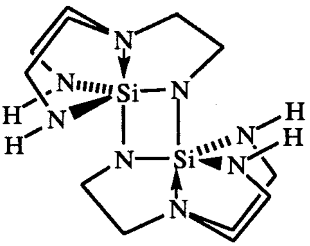
50 **51** (15)



52



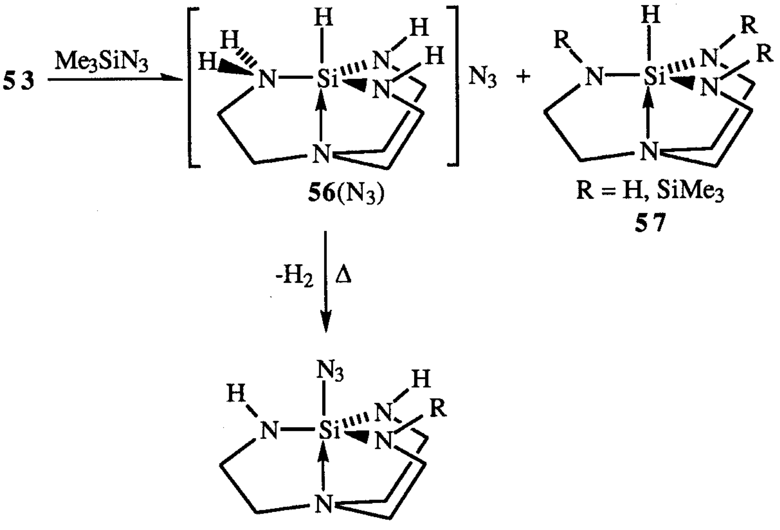
53



54

The feathers on darts can become chemically ruffled. An attempt to use Me_3SiN_3 in Scheme 2 to synthesize **55** from **53** resulted instead in the protonation and trimethyl silylation of **53** to give **56** and **57**, respectively.[28-30] Heating intermediate **56** leads to

Scheme 2



56(N_3)

R = H, $SiMe_3$

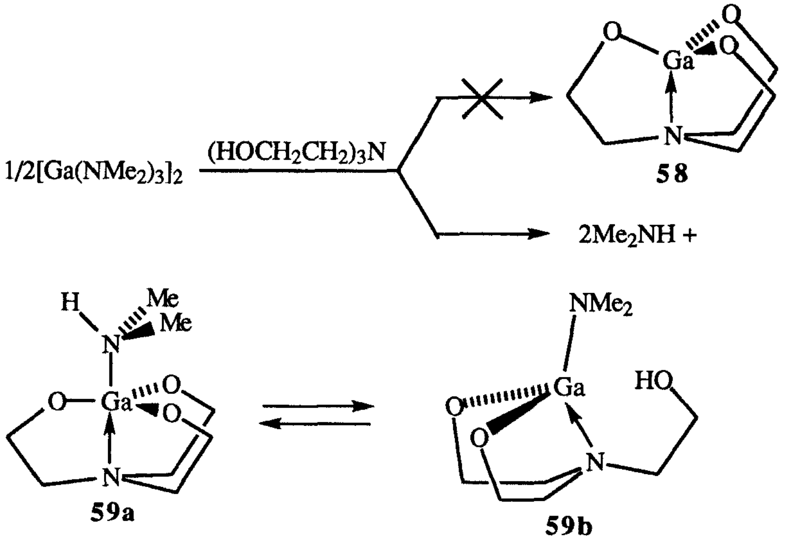
57

55

55, the product sought originally.

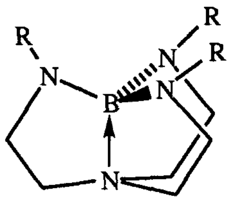
An attempt to synthesize the paddlewheel **58** via Scheme 3, leads instead to the equilibrium shown, in which one of the feathers is partially dislodged in **59b** in solution.[31]

Scheme 3

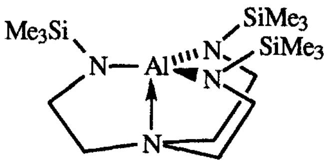


BUT WHAT CAN WE DO WITH PADDLEWHEELS?

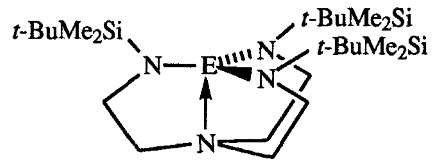
Transamination reactions involving $E(NMe_2)_3$ and $(RHNCH_2CH_2)_3N$ give rise to paddlewheels such as **60**,[32] **61**,[32] and **62**[33]-**64**.[33] Whereas the boron in **60** and **61**



	R
60	Me
61	SiMe$_3$



62



	E
63	Al
64	Ga

appears to be tetrahedral, the metals in **62-64** adopt the rare trigonal monopyramidal coordination geometry.

Paddlewheels play games of their own invention. In **61**, for example, the $SiMe_3$ groups sterically interact sufficiently to slow down the flipping of its paddles[32] as depicted in Figure 2. The substantial and negative $\Delta S^{\ddagger}$ value associated with this process (-36 J•mol^{-1}K^{-1}) indicates that the three rings invert in a concerted manner through the C_{3v} intermediate shown in the figure.

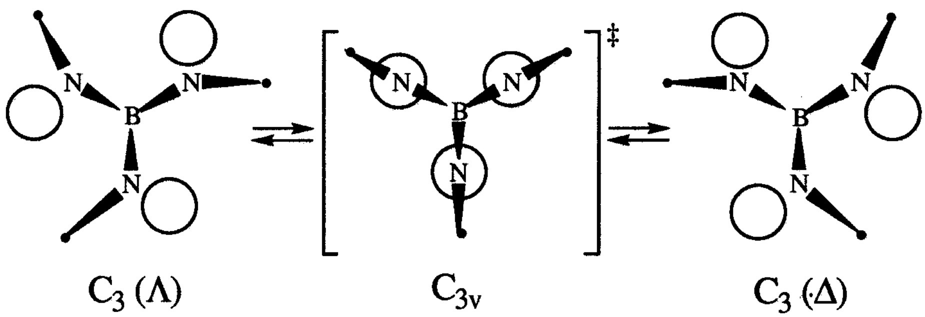
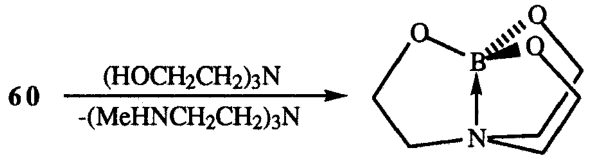


FIGURE 2 View down the B-N transannular bond axis of **61** showing an eclipsed enantiomeric conformation of the bonds on these bridgehead atoms ($C_3(\Lambda)$, $C_3(\Delta)$), and a proposed transition state in which all the atoms in the framework of the five-membered rings are coplanar (C_{3v}).

Paddlewheels can exchange their paddles as shown in reactions 16[33] and 17.[33]

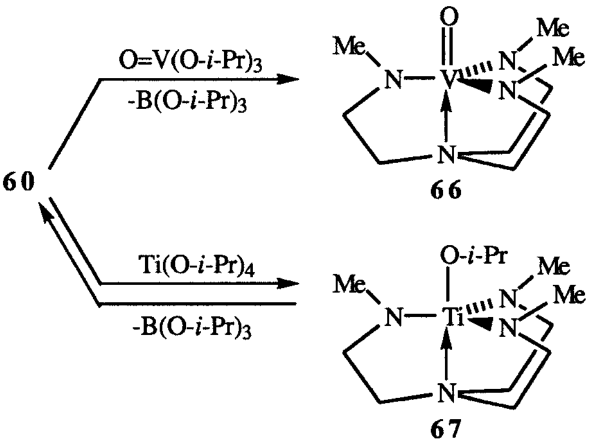


65

(16)

$$\mathbf{63} \xrightarrow[-Al(acac)_3]{Ga(acac)_3} \mathbf{64} \qquad (17)$$

The driving force in these reactions is substantially electronic in origin since stronger E-O bonds are formed. In the similar reactions 18 and 19, it is seen that paddlewheels



66

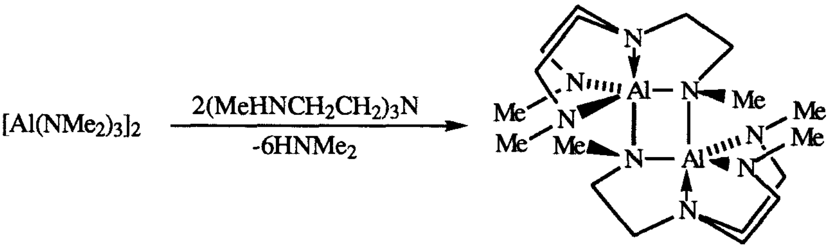
(18)

67

(19)

can also become darts **66** and **67**, respectively.[33]

Paddlewheels can express their friendliness by pairing up as in reaction 20 to form dimeric **68**.[32] This structure somewhat unexpectedly features cis methyl groups on the central four-membered ring.[34] Because of sterically encumbering $SiMe_3$ groups, **62** is reluctant to pair up unless hydrolysis occurs as shown in reaction 21.[33] Noteworthy again is the cis relationship of the hydrogens on the four-membered ring in **69**.

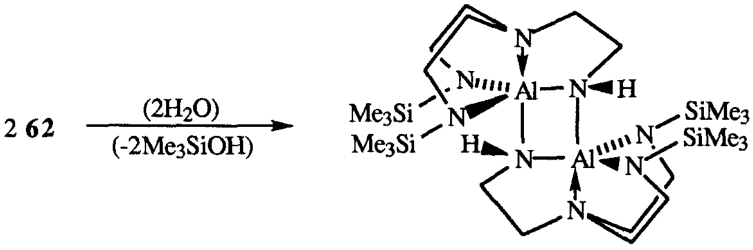


(20)

68

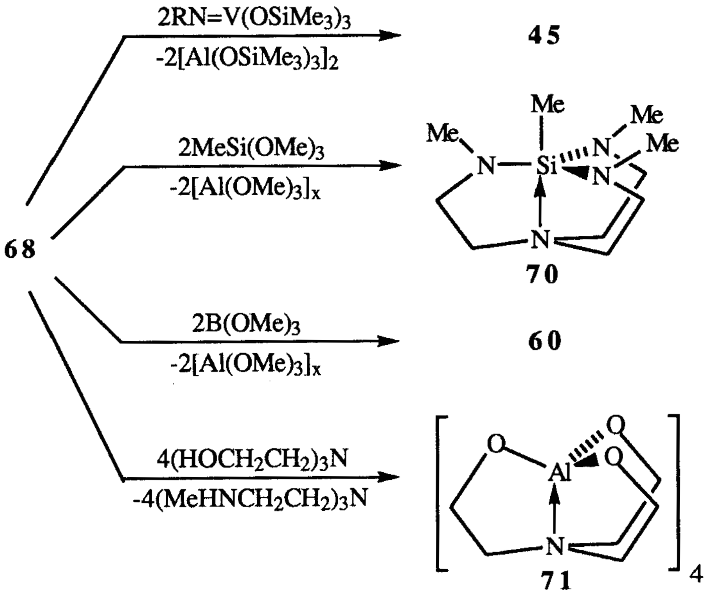
Paired paddlewheels are not "mates for life", however, and they are easily transformed into darts[33] (reactions 22 and 23), single paddlewheels[33] (reaction 24) and also a cluster of three darts and a football[34] (reaction 25) in processes that represent deeply seated molecular reorganizations. We have found that **71**, the structure of which was determined previously by others using X-ray crystallography[35] (Figure 3) displays an interesting fluxionality in solution wherein the two non-bridging five-membered rings of the three dart-like moieties racemize at lower temperatures, while at higher temperatures the darts rotate around their three-fold axes.[34]

Another example of the playfulness of **68** is its willingness to exchange its metal for a smaller one (reaction 26) with compensatory formation of thermodynamically more stable Al-O bonds.[33]



(21)

69

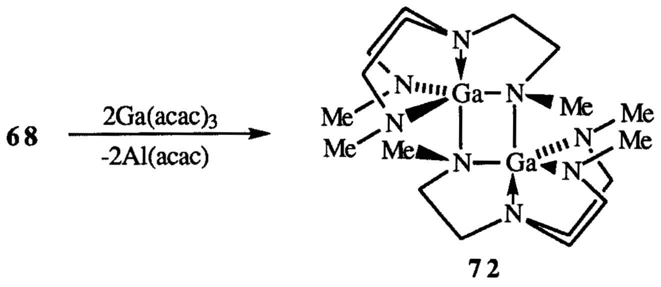

68
$2RN{=}V(OSiMe_3)_3$
$-2[Al(OSiMe_3)_3]_2$
45
$2MeSi(OMe)_3$
$-2[Al(OMe)_3]_x$
70
$2B(OMe)_3$
$-2[Al(OMe)_3]_x$
60
$4(HOCH_2CH_2)_3N$
$-4(MeHNCH_2CH_2)_3N$
71
4

(22)

(23)

(24)

(25)


68
2Ga(acac)$_3$
-2Al(acac)
72

(26)

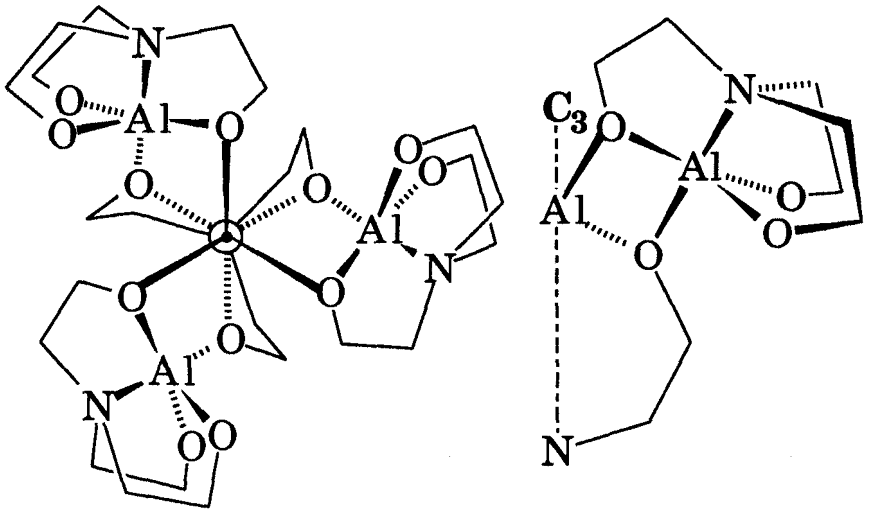


FIGURE 3 Side view of an equivalent one-third of tetrameric alumatrane **71** (right) and a view down the C_3 axis of **71** (left).

CONCLUSION

Even though $(H_2NCH_2CH_2)_3N$ is a very old molecule, it as well as its derivatives $(RHNCH_2CH_2)_3N$ are continuing to provide surprising and utilitarian main-group chemical transformations. New games being discovered in our laboratories with these playful molecules will undoubtedly provide additional insights regarding the pathways of the interesting exchange reactions they undergo.

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