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## MAIN-GROUP CHEMISTRY WITHIN MACROCYCLIC RINGS AND BASKETS

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 HONGMING ZHANG, and MICHAEL LATTMAN\*

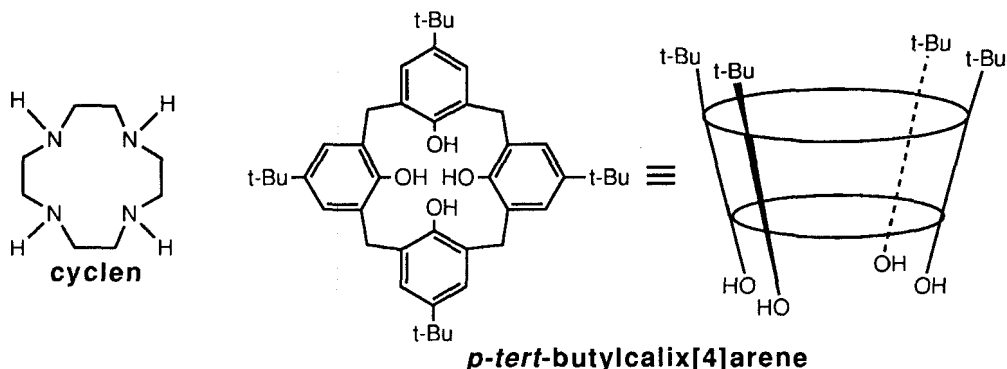
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The incorporation of main-group elements into macrocycles leads to stabilization of novel structures and control of reactivity. The tetraamino macrocycle cyclen appears to favor a pentacoordinate trigonal bipyramidal (tbp) geometry about phosphorus, even when phosphorus is bonded to transition-metals. The tbp geometry is also favored for arsenic. The tetraphenol macrocycle *p*-*tert*-butylcalix[4]arene appears to stabilize a hexacoordinate phosphorus geometry under certain conditions; however, pentacoordinate and tricoordinate structures are also found.

**Key Words:** cyclen, calix[4]arene, hypervalent, macrocycle, phosphorane, phosphoranide

### INTRODUCTION

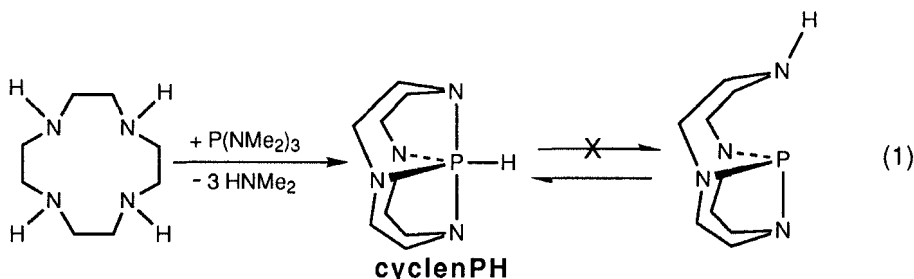
We have been interested in the incorporation of main-group elements, mostly phosphorus, into macrocycles in order to (1) stabilize novel, usually high-coordinate or "hypervalent" geometries around the main-group atom and (2) study the reactivities of these species. In particular, we are concerned with how the different constraints of the macrocycles cyclen and *p*-*tert*-butylcalix[4]arene control structure and reactivity about the main-group element.



### RESULTS AND DISCUSSION

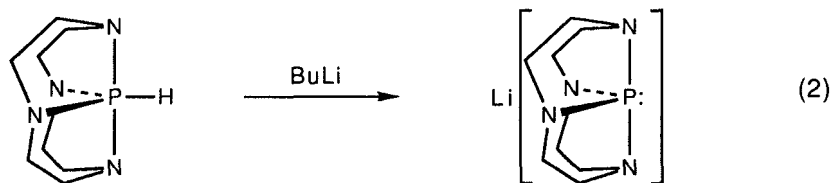
#### *Derivatives of cyclen*

Several years ago, Richman and Atkins<sup>1</sup> reported the synthesis of cyclenphosphorane (cyclenPH) by the treatment of cyclen with hexamethylphosphorous triamide (equation 1). With this particular



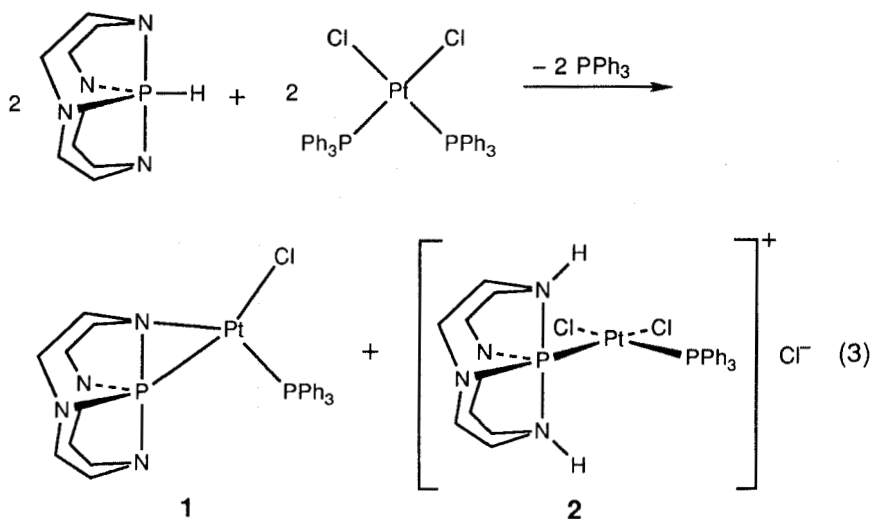
macrocycle (all ethylene bridges between nitrogens), no evidence for any "open" phosphine tautomer was found. When larger macrocycles were used in the reaction, the open form was also observed. When all of the nitrogen bridges were trimethylene groups, only the open form was observed.

Since the constraint of the smaller macrocycle cyclen appears to stabilize a pentacoordinate geometry around phosphorus in cyclenPH, we felt that this geometry might be maintained in derivatives of cyclenPH. Simple deprotonation of cyclenPH with butyllithium (equation 2) leads to lithium cyclenphosphorane<sup>2</sup> in



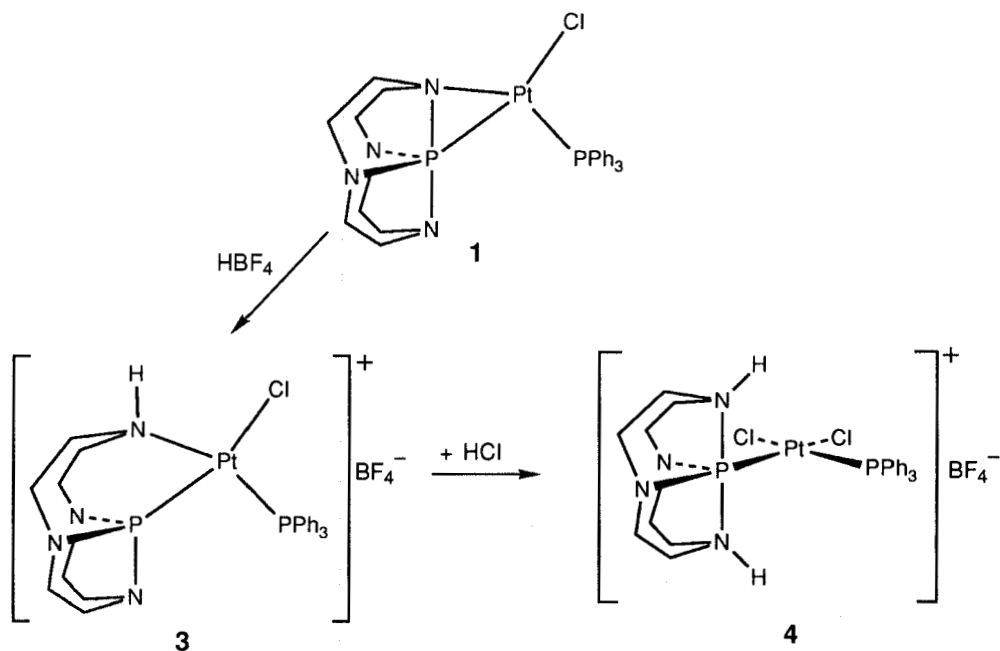
which the phosphorus now has a pseudo-trigonal bipyramidal ( $\psi$ -tbp) geometry with two nitrogens occupying axial positions and two at equatorial sites. The third equatorial site has a lone-pair of electrons.

cyclenPH can also be used to synthesize novel phosphoranide-substituted transition-metal complexes (or, alternatively, transition-metal-substituted phosphoranes). For example, treatment of cis-dichlorobis(triphenylphosphine)platinum with cyclenPH yields two complexes, **1** and **2**, both of which feature a pentacoordinate phosphorus (equation 3).<sup>3</sup> Complex **1** is covalent and has a bidentate cyclenP ligand with a P-N-Pt triangular bonding array, a common geometry found for metallated derivatives of cyclenP. Complex **2** is ionic and features a monodentate cyclenP ligand which can clearly be described as a phosphoranide. Such a simple description for cyclenP in **1** is questionable due to the unusual triangular bonding geometry with the metal. The platinum-bound nitrogen in **1** is almost in the plane of the metal and two carbons bonded to it. Thus, the nitrogen-metal interaction may be more "amide-like" and the phosphorus-metal bond more "phosphine-like". Partial donation of the amide lone-pair of electrons to phosphorus completes the fifth coordination site around the group 15 atom. This is obviously a simplistic view of the bonding in **1** and detailed molecular orbital calculations are



needed to elucidate a more accurate description of the electronic structure. However, the unusual geometry of the platinum-bound nitrogen atom in **1** suggests that there may be significant electron density "above" the nitrogen (i. e., trans to phosphorus). In fact, treatment of **1** with tetrafluoroboric acid leads to **3**, in which the nitrogen is protonated and the P-N bond is cleaved (Scheme 1).<sup>4</sup>

**Scheme 1**

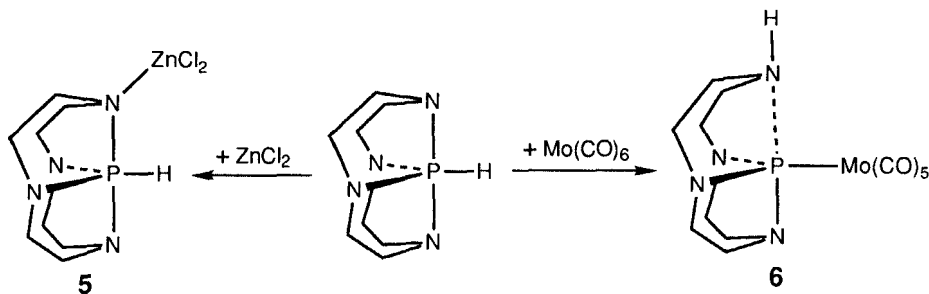


Although direct protonation at nitrogen could account for the formation of **3**, other mechanisms, such as protonation at the metal or non-coordinated nitrogen followed by rearrangement, could also lead to the observed product. Further treatment of **3** with HCl leads to **4** which contains the same cation as **2**. An acid with a non-coordinating anion is needed to isolate the cation in **3**, since treatment of **1** with HCl leads directly to **2**; with less than two equivalents of HCl, only **2** and unreacted **1** are observed.

The platinum reactions illustrate important aspects in the chemistry of cyclenP. First of all, the pentacoordinate tbp geometry is favored in metallated derivatives of cyclenP. Only under forcing conditions (i. e., treatment of **1** with an acid containing a non-coordinating anion) can the open form be observed. Secondly, the axial nitrogens of the tbp are basic; one or both of these are usually either protonated or involved in coordination to a metal. Moreover, the constraint of the cyclen macrocycle prevents rupture of the P-N bond, the usual fate of such a linkage when the nitrogen is protonated.

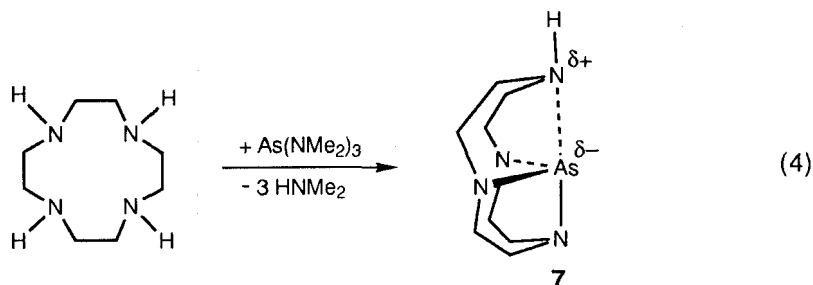
When the metal uses only one of its coordination sites, the complexation of cyclenP appears to follow the hard and soft acid/base rules. Scheme 2 illustrates this for the reaction of cyclenPH with

**Scheme 2**



zinc (II) chloride and molybdenum hexacarbonyl. The harder zinc acid prefers the nitrogen base,<sup>5</sup> while the softer molybdenum prefers phosphorus.<sup>6</sup> The tbp-constraint of the cyclen macrocycle is even evident in **6**: a transannular N...P interaction of 234 pm is found between the secondary amine nitrogen and the phosphorus.

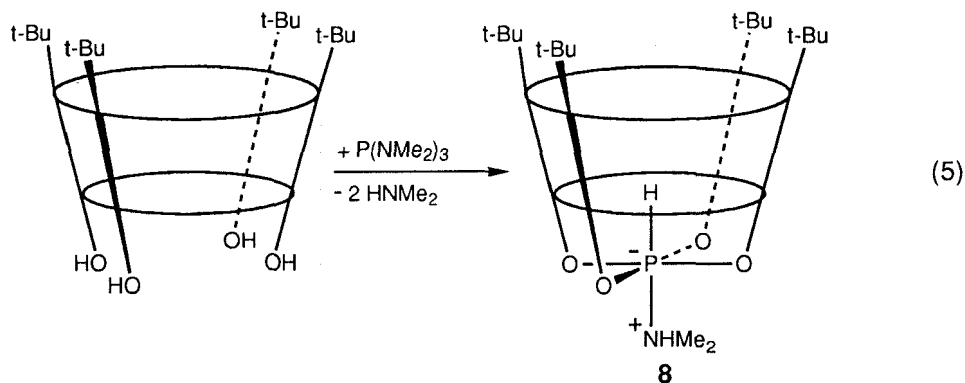
The tbp-constraint of cyclen is even observed with larger main-group elements. Introduction of arsenic (equation 4)<sup>7</sup> leads to **7** which contains a N-H rather than an As-H bond. However, there is still a transannular interaction between the secondary amine nitrogen and the arsenic leading to what can be considered a zwitterionic arsorane species. In fact, the transannular N...As interaction is 240 pm, quite similar to the N...P interaction in **6**. The fact that the hydrogen is bound to nitrogen rather than arsenic is most likely due to the much weaker bond energy of the As-H bond compared to N-H (or even P-H).



#### Derivatives of calix[4]arene

Our initial expectation when we started using calix[4]arene macrocycles was that the four hydroxyl protons in these species might react similarly to the four amine protons of the cyclen ring and lead to similar products. While high-coordinate products are obtained with calix[4]arenes, the constraint of the oxygen macrocycle is significantly different than the nitrogen system.

Treatment of *p*-*tert*-butylcalix[4]arene with hexamethylphosphorous triamide leads to loss of only two moles of dimethylamine (equation 5).<sup>8</sup> The product obtained, **8**, is a zwitterionic molecule that contains

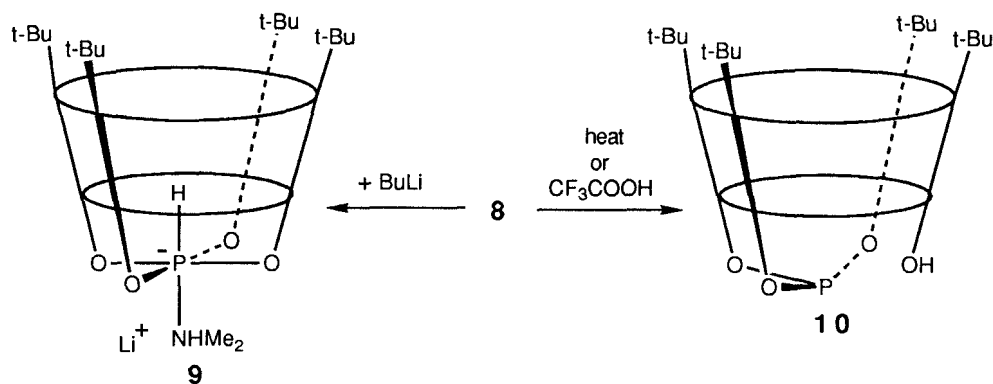


a hexacoordinate phosphorus bonded to all four oxygens of the calix[4]arene. The other two phosphorus coordination sites are occupied by a molecule of dimethylamine and a hydrogen, the latter of which is bound to the phosphorus inside the basket.

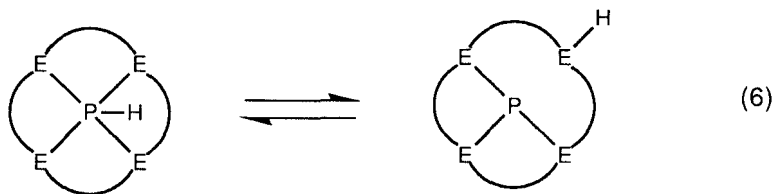
Treatment of **8** with butyllithium deprotonates the amine to give **9**, while either reaction with trifluoroacetic acid in solution or simply heating in the solid-state leads to **10** (Scheme 3).<sup>9</sup>

The fact that no pentacoordinate phosphorus is observed when the last mole of dimethylamine is lost indicates that the constraints of the two macrocycles are significantly different. Thus, equilibrium 6 is shifted to the left when the macrocycle is cyclen ( $\text{E} = \text{N}$ ) and to the right when it is calix[4]arene ( $\text{E} = \text{O}$ ). Only when another base is present, such as dimethylamine, does the calix[4]arene stabilize a

## Scheme 3



high-coordinate structure. However, in this case, a hexacoordinate, not a pentacoordinate, geometry is found.

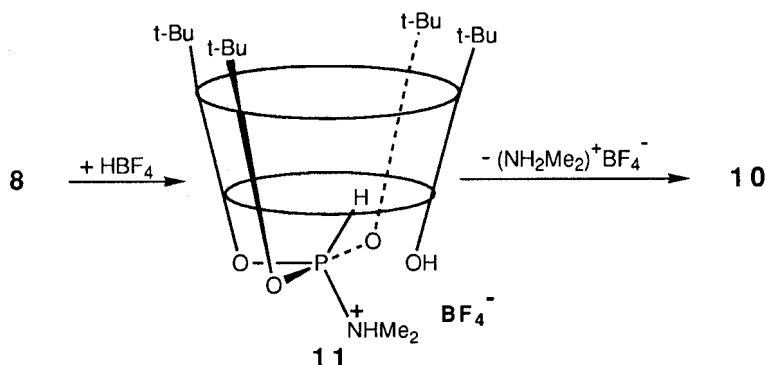


The X-ray crystal structure of **9**<sup>9</sup> yields insight into why the hexacoordinate phosphorus geometry is stabilized and not the pentacoordinate one. The P-O bonds in **9** are long which is common for high-coordinate species. In addition, the P-O-C bond angles are well within the usual range for these linkages.<sup>10</sup> Thus, the phosphorus atom may be a perfect size to fit into the oxygen plane of the calix[4]arene. However, for a pentacoordinate structure with four P-O bonds and one P-H bond, the ligand backbone may be too strained. The most likely structure of such a species should be a square-pyramid with ideal *trans* basal angles of  $150^\circ$ <sup>11</sup> where the phosphorus lies "below" the oxygen plane and the hydrogen occupies the unique axial site. This might elongate the P-O bonds and alter the P-O-C angles to such an extent as the rupture the P-O bond. For a *tbp* geometry, too much strain would be introduced to accommodate the equatorial O-P-O angle (ideally  $120^\circ$ ).

The acid reaction in Scheme 3 most likely proceeds via initial protonation of one oxygen leading to P-O bond cleavage. However, no intermediate corresponding to such a structure could be observed in the case of trifluoroacetic acid. On the other hand, if tetrafluoroboric acid is used, an intermediate, **11**, is found with a  $^{31}\text{P}$  chemical shift at  $-21$  ppm; this is  $99$  ppm downfield of **8**, indicating a lower coordination for phosphorus. Moreover, a large P-H coupling of  $706$  Hz is observed, indicative of a direct P-H bond. In addition,

the  $^1\text{H}$  NMR spectrum shows three *tert*-butyl resonances (2:1:1 ratio) as well as peaks due to  $\text{Me}_2\text{NH}$  bonded to phosphorus. These data strongly suggest that the acid reaction goes through an intermediate with a pentacoordinate phosphorane geometry (Scheme 4). Such an intermediate is consistent with the constraint of the ligand backbone which appears to support geometries with  $90^\circ$  O-P-O angles. Signals for **11** disappear within 24 h and are replaced by those due to **10**, accompanied by precipitation of  $(\text{Me}_2\text{NH}_2)\text{BF}_4$ .

#### Scheme 4



#### CONCLUSION

The constraints of the two macrocycles control the structure and reactivity of the resulting main-group element derivatives. In addition, thermodynamics is also important when the central element is changed.

#### ACKNOWLEDGMENT

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