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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Fan, Maomian , Zhang, Hongming and Lattman, Michael(1999) 'Variable Coordination of Phosphorus within Calixarenes and Complexing Abilities of Phosphorus-Based Calixarenes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 144: 1, 257 – 260

**To link to this Article:** DOI: 10.1080/10426509908546230

**URL:** <http://dx.doi.org/10.1080/10426509908546230>

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# Variable Coordination of Phosphorus within Calixarenes and Complexing Abilities of Phosphorus-Based Calixarenes

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Solvent-dependent coordination of phosphorus within a calix[4]arene cavity is shown and the differences in the abilities of a ligand to bind to a metal within calix[4]arenes and calix[5]arenes is demonstrated.

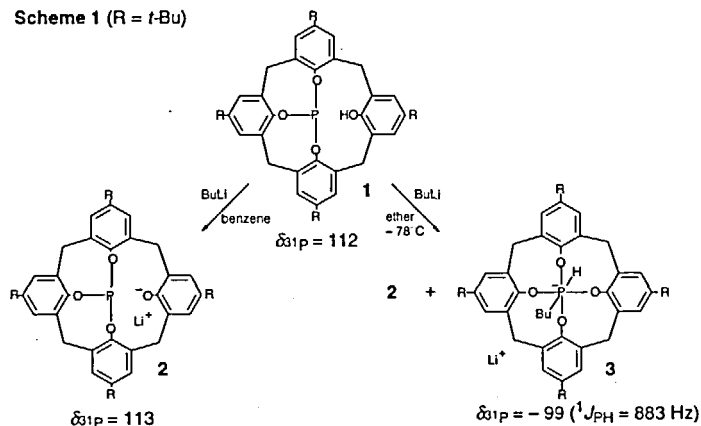
**Keywords:** calixarenes; phosphorus ligands

## INTRODUCTION

The cavities of calixarenes<sup>[1]</sup> can vary from very small to very large. We herein report the use of two smaller members of the series, *p-t*-butylcalix[4]arene and *p-t*-butylcalix[5]arene, to demonstrate variable coordination of phosphorus and novel phosphorus-metal binding within the cavities.

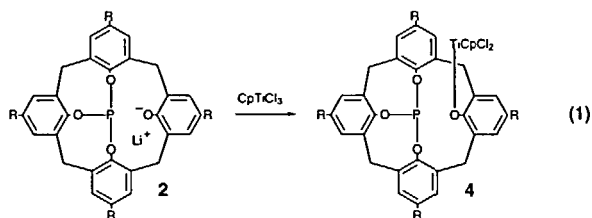
## RESULTS AND DISCUSSION

We have previously demonstrated that six-, five-, four-, and three-coordinate phosphorus can be accommodated within the calix[4]arene cavity.<sup>[2]</sup> We have now found that solvent plays an important role in determining the coordination number of phosphorus within the calix[4]arene cavity. Treatment of the phosphite **1** ( $R = t\text{-Bu}$ ) with butyllithium in benzene results in simple deprotonation of the phenolic proton without a coordination change at the phosphorus (Scheme 1). The lack of any coordination change is supported by the almost identical <sup>31</sup>P chemical shift values of both **1** and **2**. However, if the reaction is carried out in ether at low temperature, a mixture of both **2** and the hexacoordinate phosphorus species **3** is formed in an approximate 1:1 ratio. The formation of **3** results from nucleophilic attack of Bu<sup>-</sup> at the phosphorus. The upfield <sup>31</sup>P

**Scheme 1** ( $R = t\text{-Bu}$ )

chemical shift of  $-99$  and the large P-H coupling constant supports the formation of the hexacoordinate anion.

In addition to providing a cavity in which a central main-group atom may easily undergo coordination changes, it might be possible to bind both a ligand (i.e., phosphorus) and a metal at the base of a calixarene in order to stabilize a ligand-metal interaction. In an effort to achieve this, we treated the anion **2** with  $\text{CpTiCl}_3$ . The reaction proceeds smoothly to give the complex **4** (Eq. 1). However, x-ray crystal



structural analysis of **4** showed that the calix[4]arene backbone is in an approximate partial cone conformation in which the phosphorus lone pair and titanium are on opposite sides of the calix[4]arene (Fig. 1). The cavity of the calix[4]arene appears to be too small to accommodate both the ligand and metal on the same side.

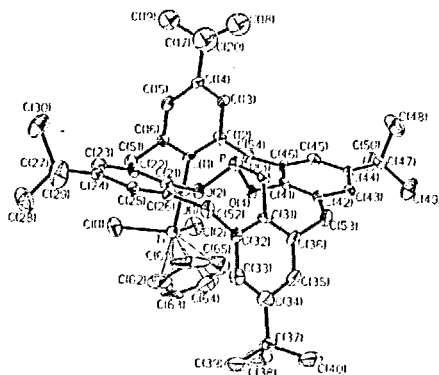
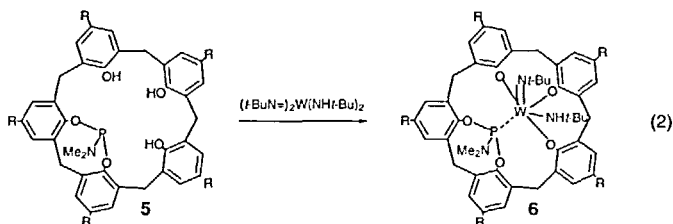


FIGURE 1 Computer-generated drawing of the x-ray structure of 4.

The cavity of calix[5]arene is larger than calix[4]arene and may be large enough for the ligand to bind directly to the metal. Treatment of *p*-*t*-butylcalix[5]arene<sup>[3]</sup> with tris(dimethylamino)phosphine leads to **5** (Eq. 2). Insertion of a tungsten can then be accomplished via the mixed imido/amido reagent (*t*-BuN=)<sub>2</sub>W(NH*t*-Bu)<sub>2</sub>.<sup>[4]</sup> The x-ray structure of **6** shows a very long P---W distance of 3.148(3) Å. However, there is a small P-W coupling constant (43 Hz) observed in the <sup>31</sup>P NMR spectrum indicating that there is at least some interaction between the two atoms.



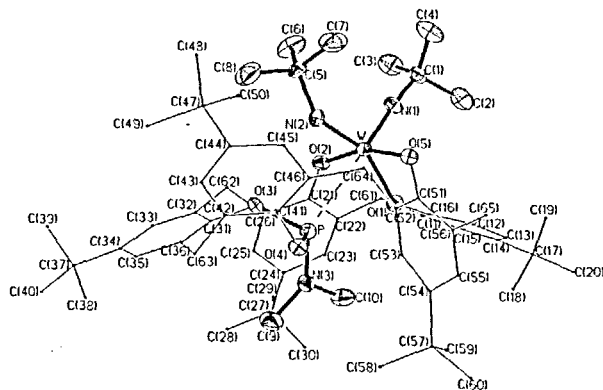


FIGURE 2 Computer-generated drawing of the x-ray structure of 6.

Thus, the size of the calix[5]arene cavity appears to be able to accommodate at least weak interactions between a ligand and metal. We are currently investigating further examples of this type of weak binding in these systems.

### Acknowledgments

Acknowledgment is made to the National Science Foundation (CHE-9522606), Robert A. Welch Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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