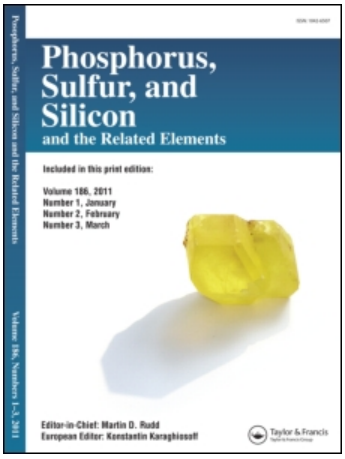

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Phosphorus-Based Calix[4]arene Ligands Bound to Metals through Oxygen

Maomian Fan[a]; Hongming Zhang[a]; Michael Lattman[a]
[a] Department of Chemistry, Southern Methodist University, Dallas, Texas, USA

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PHOSPHORUS-BASED CALIX[4]ARENE LIGANDS BOUND TO METALS THROUGH OXYGEN

Maomian Fan, Hongming Zhang, and Michael Lattman
Department of Chemistry, Southern Methodist University, Dallas, Texas, USA

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Calixarenes containing phosphorus are useful ligands toward transition metals. We report complexes of calix[4]arenes in which metal binding is through one of the oxygens of the calixarene backbone.

Keywords: Calixarenes; phosphorus ligands

INTRODUCTION

Recently, there have been several investigations[1,2] into metal complexes of the calix[4]arene phosphorus ligand [4]L_PH that we previously reported.[3] We herein describe the preparation of metal complexes of phosphorus-containing calix[4]arenes in which the binding to the metal is through the oxygen of the calixarene backbone.

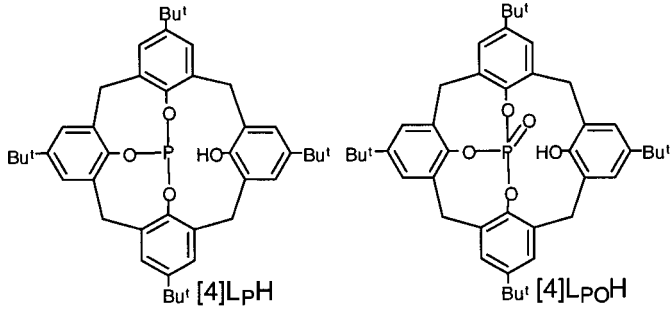

FIGURE 1

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Address correspondence to Maomian Fan, Department of Chemistry, Southern Methodist University, Dallas, TX 75275-0314, USA. E-mail:

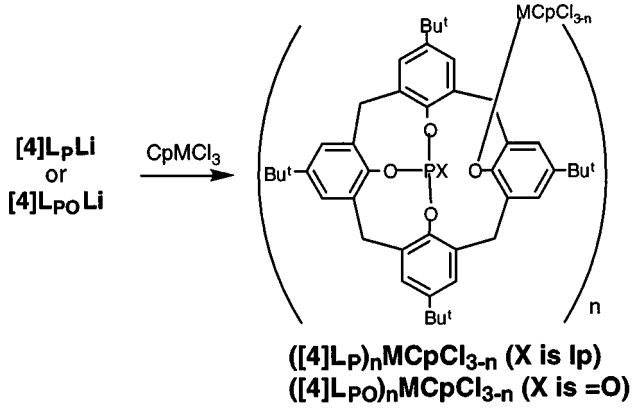

FIGURE 2

RESULTS AND DISCUSSION

The phosphite [4]L_PH can be oxidized to the phosphoryl [4]L_{PO}H via treatment with *tert*-butylhydroperoxide.[3] Both can be deprotonated with butyllithium in benzene. The resulting lithium salts, [4]L_PLi and [4]L_{PO}Li, form precipitates which are isolated. Treatment of these salts with $MCpCl_3$ (M = Ti, Zr) leads to complexes in which the ligand is bound to the metal through the oxygen of the calixarene according to Figure 2.

[4]L_P and [4]L_{PO} form 1:1 complexes with titanium which can be isolated and purified. However, greater substitution is difficult, even with excess lithium salt. With zirconium, greater substitution is observed and, in fact, no 1:1 complexes can be isolated. These results are summarized in Table I. Thus, the degree of substitution appears more dependent on the size of the metal than any other factor, with the larger zirconium leading to greater substitution.

The x-ray crystal structure of ([4]L_{PO})$_2$ZrCpCl was obtained and is illustrated in Figure 3. Proton NMR spectra indicate a mirror

TABLE I ([4]L_P)$_n$$MCpCl_{3-n}$ and ([4]L_{PO})$_n$$MCpCl_{3-n}$ Complexes

L	M	n = 1	n = 2	n = 3
[4]L_P	Ti	Isolated	Observed	Not observed
[4]L_P	Zr	Not observed	Not observed	Isolated
[4]L_{PO}	Ti	Isolated	Not observed	Not observed
[4]L_{PO}	Zr	Observed	Isolated	Observed

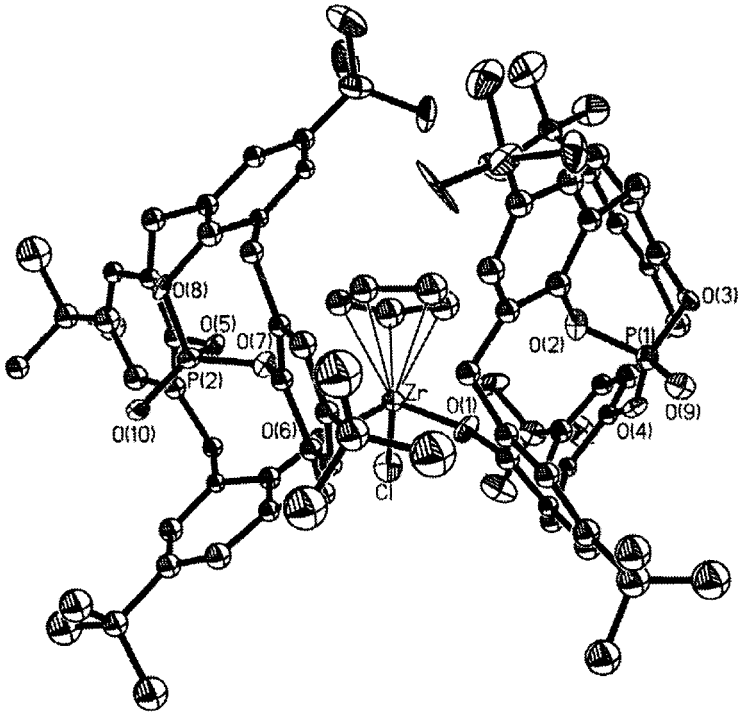

FIGURE 3 X-ray crystal structure of $([4]L_{PO})_2ZrCpCl$.

plane in this compound. The two Zr—O bond lengths are 1.941(13) and 1.910(11) Å, and the Zr—O—C bond angles are 164 and 167°.

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