

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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

Online publication date: 27 October 2010

To cite this Article Fan, Maomian , Zhang, Hongming and Lattman, Michael(2010) 'Phosphorus-Based Calix[4]arene Ligands Bound to Metals through Oxygen', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 177: 6, 1549 – 1551

To link to this Article: DOI: 10.1080/10426500212257

URL: <http://dx.doi.org/10.1080/10426500212257>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

(Received; accepted)

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.

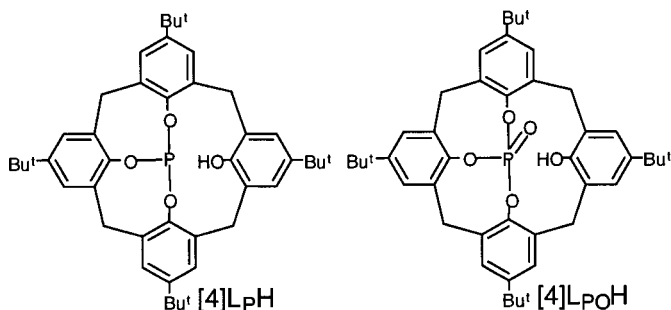


FIGURE 1

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.

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

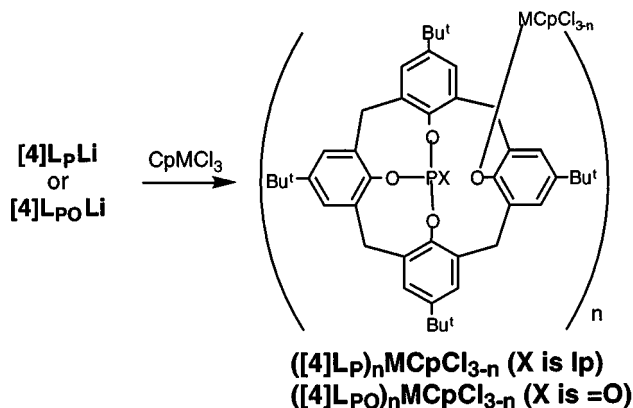


FIGURE 2

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 $([4]L_{pO})_2ZrCpCl$ was obtained and is illustrated in Figure 3. Proton NMR spectra indicate a mirror

TABLE I $([4]L_p)_nMCPCl_{3-n}$ and $([4]L_{pO})_nMCPCl_{3-n}$ 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

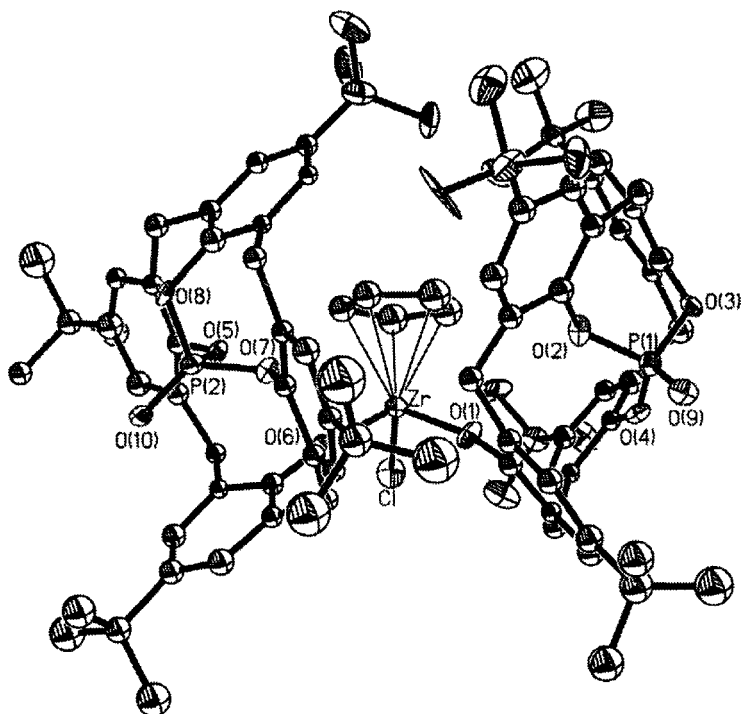


FIGURE 3 X-ray crystal structure of $([4]L_{pO})_2ZrCpCl$.

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°.

REFERENCES

- [1] C. J. Colbey, D. D. Ellis, A. G. Orpen, and P. G. Pringle, *J. Chem. Soc. Dalton Trans.*, 1101–1109 (2000).
- [2] F. J. Parlevliet, C. Kiener, J. Fraanje, M. Lutz, A. L. Spek, P. C. Kamer, and P. W. N. M. van Leuwen, *J. Chem. Soc. Dalton Trans.*, 1113 (2000).
- [3] (a) D. V. Khasnis, M. Lattman, and D. Gutsche, *J. Am. Chem. Soc.*, **112**, 9422 (1990);
(b) D. V. Khasnis, J. M. Burton, J. D. McNeil, C. J. Santini, H. Zhang, and M. Lattman, *Inorg. Chem.*, **33**, 2657 (1994).