# 最先端有機元素化学①:最新論文からのトピックス

Phosphorus as a Lewis Acid: CO<sub>2</sub> Sequestration with Amidophosphoranes Lindsay J. Hounjet, Christopher B. Caputo, Douglas W. Stephan\* Angew. Chem. Int. Ed. 2012, 51, 4714.



**CO<sub>2</sub>snapper**: Compounds containing both acidic and basic RN functionalities have been prepared. Of these, two amidophosphoranes containing highly reactive PN bonds within four-membered rings react rapidly with CO<sub>2</sub>, resulting in relief of ring strain. These compounds demonstrate the utility of phosphorus as a Lewis acid for small-molecule



Prof. Stephan University of Toronto

タイトルとTOCグラフィックから読み取れること

・リン原子がルイス酸になる

・五配位のリン化合物(phosphorane)の話

Introductionから読み取れること

・二酸化炭素の話、特に貯留の話:例としてMOF, FLP

FLP: frustrated Lewis pair

Reviews:





北川進 (京都大学) Omar Yaghi (UCLA)

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#### MOF: metal organic framework



## Introduction: Frustrated Lewis Pair (FLP)



ACIE 2009, 48, 9839.

# **Introduction 2: modified FLP**



## Introduction 3: FLP other than Group 13/15

Group 14 Lewis Base



#### Lewis酸としてのphosphonium salt



**Scheme 2.** Hypervalent interaction between a phosphonium salt and a Lewis base.





**Scheme 11.** Formation and coordination mode of the DMF/ phosphonium salt **11** complex.

この論文を読む上での鍵

# This Work 1: Synthesis of Amidophosphorane



## This Work 2: Crystal Structure of 3 and 4

Crystal Structure of 3



Figure 1. POV-ray depiction of 3.

two crystallographically independent molecules



Figure 2. POV-ray depiction of 4.



X線で得られる結合距離・角度は 末尾の桁の後ろに括弧書きで 標準偏差が記されている



### This Work 3: Double Insertion of CO<sub>2</sub>



## **Consideration about FLP Reactivity**





What can we do next?.....



Scheme 3. Resonance forms of 3. It can be considered that **3** is in resonance with ring-opening and charge-separated form

amidophosphorane showed FLP property



#### 次週の宿題

Fukazawa, A.; Li, Y.; Yamaguchi, S.; Tsuji, H.; Tamao, K.

"Coplanar Oligo(p-phenylenedisilenylene)s Based on the Octaethyl-Substituted s-Hydrindacenyl Groups" *J. Am. Chem. Soc.* **2007**, *129*, 14164.

Supporting Informationにも目を通して光学特性の評価などを学びましょう