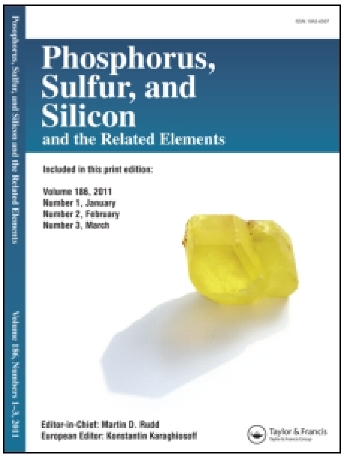

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Blaurock, Steffen , Koch, Thomas , Kühl, Olaf , Lönnecke, Peter , Majoumo, Felicite , Sommer, René , Sterzik, Anke and Hey-Hawkins, Evamarie(2002) 'Early/Late Heteronuclear Complexes Bridged by Bifunctional Phosphorus-Based Ligands', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1451 — 1456

To link to this Article: DOI: 10.1080/10426500212271

URL: http://dx.doi.org/10.1080/10426500212271

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1451–1456
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1042-6507/02 \$12.00 + .00
DOI: 10.1080/10426500290093441

EARLY/LATE HETERONUCLEAR COMPLEXES BRIDGED BY BIFUNCTIONAL PHOSPHORUS-BASED LIGANDS

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(Received August 31, 2001; accepted December 25, 2001)

Substituted bifunctional phosphorus-based ligands $HX(CRR')_nPR''H$ *(or* $-PR''_2$*) [where* $X = O, S, NR'$*, (substituted) cyclopentadienyl;* $n = 1, 2, 3$*;* $R, R', R'' =$ *alkyl, aryl, H] were employed as bridging ligands in the synthesis of early/late bridged transition metal complexes. Synthetic routes to the bifunctional ligands were also developed. First, mononuclear complexes, such as* $[TpZr(OCH_2PPh_2)_3]$ *(Tp = trispyrazolylborato),* $[Cp_2Zr(1\text{-}O\text{-}2\text{-}PHR\text{-}C_6H_{10})(Me)]$ *(R = 2,4,6-*$Pr^i{}_3C_6H_2$ *(Tipp)),* $[Cp_2Zr(SCH_2CH_2PHR)_2]$ *(R = Ph, Mes, Tipp), and phosphinoferrocene derivatives, were prepared. These complexes are suitable precursors for the introduction of a second metal (as in, for example,* $[TpZr(\mu\text{-}OCH_2PPh_2)_3Mo(CO)_3]$*).*

Keywords: Iron; molybdenum; nickel; PH-functionalized phosphinoalcohols; phosphinoalkylcyclopentadienyl ligands; phosphinoamine ligands; phosphinothiols; polymerization catalysts; tantalum; zinc complexes; zirconium

INTRODUCTION

For some time we have been interested in the preparation of heteronuclear complexes in which a P-based bifunctional ligand bridges two metal centers. In heterogeneous catalysis it is often observed that a combination of two or more different metals enhances the catalytic properties. Thus, we expect that in heteronuclear complexes, each metal

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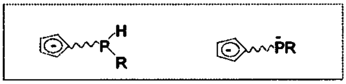
TABLE I

HX⌒YH (or R)

X	Y	Spacer
O	PR',NR',S	= (CR''R''')$_n$ with n = 0, 1, 2, 3
S	PR',NR'	
NR'	PR'	

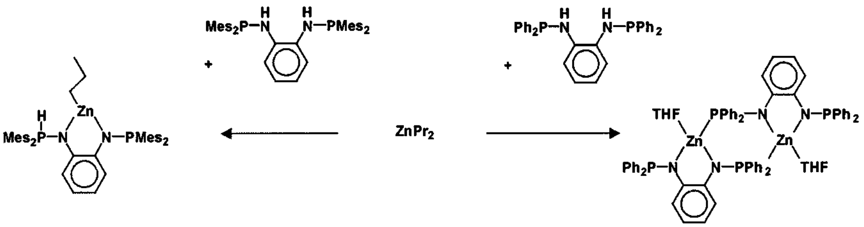


center should exhibit its specific reactivity, as well as being influenced by the second metal.[1]

Up to now we have studied several different combinations (Table I) with phosphorus and nitrogen, oxygen, or sulfur as donor atoms. In general, the two donor atoms are linked by a C_1–C_3 spacer.[2–4] We are also interested in bifunctional ligands in which a cyclopentadienyl ring and a PH-functionalized phosphino group are separated by a spacer consisting of one or two C atoms or in which the phosphino group is directly bonded to the cyclopentadienyl ring.[5]

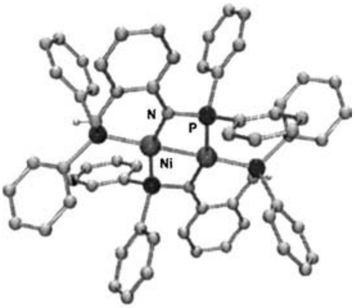
PHOSPHINOAMINE LIGANDS

Phosphinoamines without a spacer and different steric demand can easily be prepared by a salt-elimination reaction beween a dialkyl- or diarylchlorophosphine and a lithium amide. Disubstituted benzene derivatives, such as 1,2-$(PR_2NH)_2C_6H_4$ (R = Ph, Mes), react with $ZnPr_2$ with formation of the dinuclear complex **1** or the zwitterionic complex **2**, depending on the substituents R at phosphorus.



2 **1**

Unexpectedly, 1,2-$(PPh_2NH)_2C_6H_4$ reacts with BuLi and $NiCl_2$ (1:1:1) with formation of the unusual dimeric Ni^I complex **3**, in which the P and N atoms of each of the two monoanionic ligands chelate one Ni atom, whereas the second phosphino group is coordinated to the second Ni atom. The NH group is uncoordinated.



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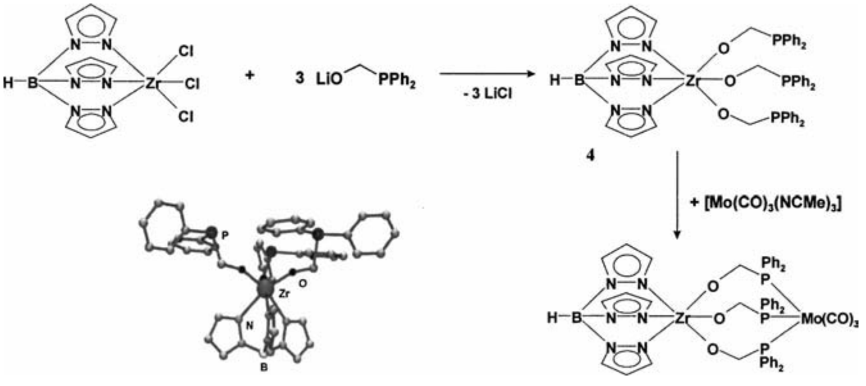
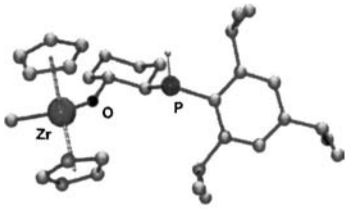
PHOSPHINOALCOHOL LIGANDS

We have prepared a range of phosphinoalcohols with one to three C atoms as spacer and with or without chiral centers.[3] The phosphinoalcohols are readily deprotonated by BuLi, and the resulting alkoxides react readily with transition metal chloro complexes, such as $[TpZrCl_3]$.[3c] The three phosphorus atoms in **4** are suitably arranged for coordination of a 12-electron fragment, such as a $Mo(CO)_3$ moiety.[3c]



Dimethylzirconocene reacts with 1-HO-2-PHTipp C_6H_{10} in refluxing toluene with elimination of methane to give the zirconocene alkoxide **5**. Only monosubstitution is observed. The phosphino group can be employed in the coordination of $Mo(CO)_5$. In the presence of MAO, both zirconocene complexes are active catalysts for the polymerization of α-olefins.[3b]



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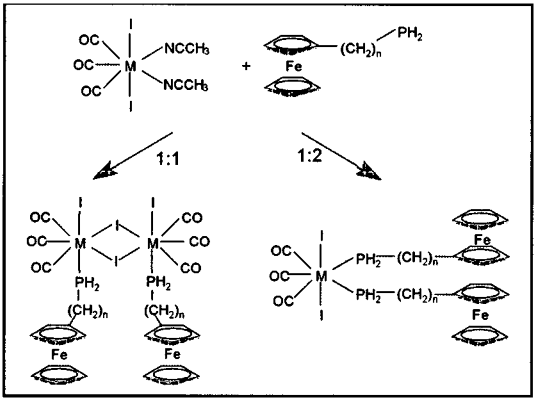
PHOSPHINOTHIOL LIGANDS

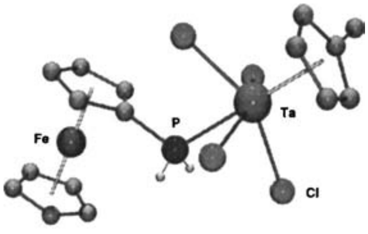
Thiirane and LiPHR yield phosphinothiols as colorless liquids after hydrolytic workup. $[Cp_2TiCl_2]$ reacts with $HSCH_2CH_2PHR$ in the presence of NEt_3 to yield *rac*- and *meso*-$[Cp_2Ti(SCH_2CH_2PHR)_2]$ (R = Ph (**6**), Mes (**7**), Tipp (**8**)). **6** reacts with $[Cu(CH_3CN)_4]BF_4$ to give the Cu^I complex **9**, which has six chiral centres; however, only one pair of enantiomers is observed in the solid state.[4]

PHOSPHINOALKYLCYCLOPENTADIENYL LIGANDS

While the phosphinocyclopentadienyl ligand is unstable, the corresponding mono-[6a] (**10**) and bis(phosphino)ferrocene[6b] (**11**) are known. Also, $[Fe(C_5H_4CH_2PH_2)_2]$ (**12**) was reported in 1999.[6c]

The reaction of **10** and **12** with 7-coordinate Mo and W complexes gives tri- and tetranuclear complexes.[5c] **10** reacts with $[Cp'TaCl_4]$ to give the dinuclear complex **13**. A mixture of **10**, **11** and $AlBu^{i}_{3}$ (1:1:3) gives the pentanuclear complex **14**.





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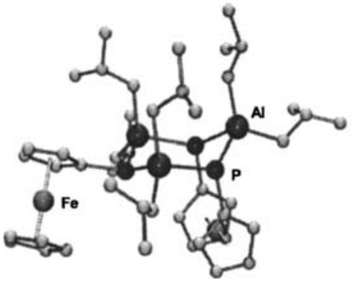

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ACKNOWLEDGMENTS

We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and thank the company H. C. Starck Berlin GmbH & Co. KG for a generous donation of $TaCl_5$.

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