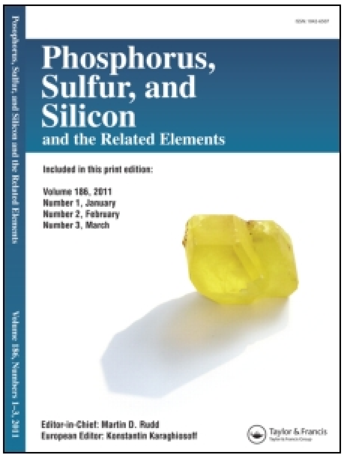


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Functionalised Phosphorus-Based Ligands in Early Transition Metal Chemistry

Ulrike Segerer; Reinhard Felsberg; Steffen Blaurock; Ghasan A. Hadi; Evamarie Hey-Hawkins

To cite this Article Segerer, Ulrike , Felsberg, Reinhard , Blaurock, Steffen , Hadi, Ghasan A. and Hey-Hawkins, Evamarie(1999) 'Functionalised Phosphorus-Based Ligands in Early Transition Metal Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 477 — 480

To link to this Article: DOI: 10.1080/10426509908546285

URL: http://dx.doi.org/10.1080/10426509908546285

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 477-480
Reprints available directly from the publisher
Photocopying permitted by license only

Functionalised Phosphorus-Based Ligands in Early Transition Metal Chemistry

ULRIKE SEGERER, REINHARD FELSBERG, STEFFEN BLAUROCK, GHASAN A. HADI and EVAMARIE HEY-HAWKINS

Universität Leipzig, Institut für Anorganische Chemie, Talstr. 35, 04103 Leipzig, Germany

When the transition metal halides $Cp^x{}_2ZrCl_2$, Cp^xZrCl_3, Cp^xMoCl_2(Cp^x = C_5H_5, C_5H_4Me, C_5Me_4Et), or Cp^xMCl_4 (Cp^x = C_5H_5, C_5H_4Me, C_5Me_4Et, C_5Me_5; M = Nb, Ta, or Mo) are treated with functionalised phosphorus-based ligands (functional group = P-H; P-$SiMe_3$ or P-H for $Cp^x{}_2ZrCl_2$), reduction of the transition metal or substitution of chloro by phosphorus ligands occurs. With primary phosphines or lithium phosphanides, various phosphorus ligands are formed, depending on the steric bulk of the ligands on M and P, the reaction conditions, and solvent. Thus, complexes exhibiting phosphine, phosphanido, phosphinidene, triphospha-1,3-diyl, diphosphene, or diphosphanyl ligands are formed.

The reactions of these early transition metal complexes include substitution of the P-based ligand by polar or protic reagents, insertion of multiply bonded inorganic or organic systems (CS_2, diazoalkanes, diaryl- or dialkylcarbodiimide, phenylacetylene, isonitriles, isothiocyanates, nitriles, ketones etc.) into the metal-phosphorus bond, as well as insertion followed by elimination of PHR or PR fragments.

Keywords: zirconium; tantalum; molybdenum complexes; phosphine; phosphanido; phosphinidene ligands; insertion reactions

INTRODUCTION

For some time we have been interested in the preparation of complexes in which a P ligand that bears functional groups besides alkyl or aryl ligands is coordinated to an early transition metal. Thus, we study the formation of phosphine complexes with primary phosphines and of phosphanido complexes in which the P atom bears $SiMe_3$ groups or H atoms and in which the P-ligand bond should be reactive. Most of our studies so far have been concerned with the latter type of compounds. Furthermore, we have shown that the complexes with reactive P-H bonds can be employed in the synthesis of transition metal complexes with phosphinidene groups.

The synthetic potential of some of the products obtained is reported.

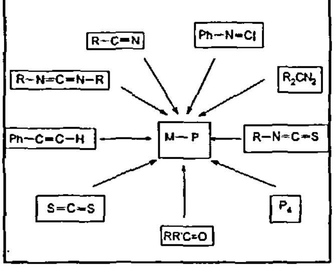
Zirconium

While zirconocene complexes with terminal $P(SiMe_3)_2$ ligands are easily accessible[1], zirconocene complexes with primary phosphanido ligands are only obtained with certain combinations of substituted cyclopentadienyl ligand and P-R substituent[2]. Thus, P-H functionalised zirconocene complexes $[Cp^x{}_2ZrCl(PHR)]$ are only obtained from reactions of $[Cp^x{}_2ZrCl_2]$ with LiPHR where Cp^x = Cp, R = 2,4,6-$R'_3C_6H_2$ [R' = Me (Mes), Pr^i (Tipp), Bu^t (Mes*)]; Cp^x = C_5H_4Me (Cp'), R = Tipp; or Cp^x = C_5Me_4Et (Cp°), R = Ph, Bu^t, Cy, Tipp. Metallacyclic systems with a ZrP_3 or ZrP_2 arrangement, dimeric phosphanido-bridged Zr(III), as well as Zr(IV) complexes with terminal or bridging phosphinidene ligands are obtained, depending on the starting materials employed[1,3].

Insertion reactions

The insertion of polar multiple-bond systems into the Zr-P bond of $[Cp^x{}_2ZrCl\{P(SiMe_3)_2\}]$ or $[Cp^x{}_2ZrCl(PHR)]$ (Scheme 1) allows the synthesis of novel P-functionalised ligands within the coordination sphere of Zr which are either difficult to synthesise or inaccessible by other routes[1,2].

Scheme 1



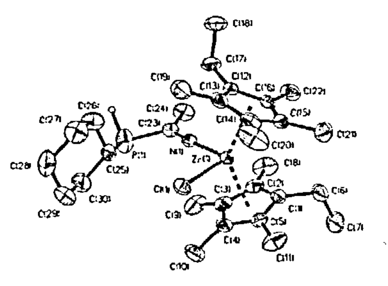


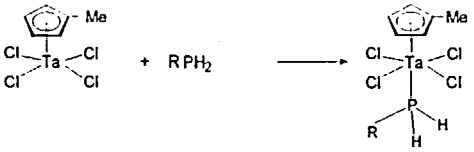
Fig. 1 $[Cp°_2Zr(Cl)\{NC(Me)PHCy\}]$

A different course of reaction is observed when [Cp°$_2$ZrCl(PHCy)] is reacted with diisopropylcarbodiimide or CH$_3$CN. Again, insertion products are obtained (e.g., Fig. 1); however, these slowly convert into [Cp°$_2$Zr(η^2-NPr^{i}CHNPr^i)(Cl)] or [Cp°$_2$(Cl)Zr(μ-N=CMe-CMe=N)Zr(Cl)Cp°$_2$], respectively.

Tantalum

[Cp^{x}TaCl$_4$] readily reacts with primary phosphines PH$_2$R to form the adduct [Cp^{x}TaCl$_4$(PH$_2$R)] (Cp^x = Cp', R = Tipp, eq. 1; Cp^x = C$_5$Me$_5$ (Cp*), R = Cy, Bu^t, Ph, Tipp).

(1)



Attempts to eliminate HCl from [Cp'TaCl$_4$(PH$_2$Tipp)] with DBU gave the phosphinidene-bridged Ta(IV) complex [Cp'TaCl(μ-PTipp)]$_2$[4], while [Cp*TaCl$_4$(PH$_2$Cy)] reacts with DBU yielding the Ta(IV) complex [Cp*TaCl$_4$]$^-$[(DBU)H]$^+$. In the solid state, the (DBU)H$^+$ cation interacts with the [Cp*TaCl$_4$]$^-$ anion via a hydrogen bond.

Finally, the reaction of [Cp*TaCl$_4$(PH$_2$Tipp)] with DBU gives the terminal Ta(V) phosphinidene complex [Cp*TaCl$_2$(PTipp)] (Fig. 2).

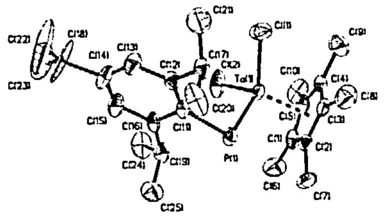


Fig. 2

Another synthetic route to phosphinidene-bridged Ta(IV) complexes [Cp*TaCl(μ-PR)]$_2$ is the reaction of [Cp*TaCl$_4$] with LiPHR (R = Ph, Cy, ^{t}Bu). Crystal structure analyses showed that the central Ta$_2$P$_2$ rings of these complexes are planar.

Insertion reaction

While the phosphinidene-bridged Ta(IV) complexes [Cp*TaCl(μ-PR)]$_2$ (R = Ph, Cy, ^{t}Bu) do not react with Et$_2$AlCl, acetaldehyde or acetone, the terminal Ta(V) phosphinidene complex [Cp*TaCl$_2$(PTipp)] readily reacts with acetone with insertion into the Ta=P bond to give [Cp*TaCl$_2${(OCMe$_2$)$_2$PTipp}] (Fig. 3).

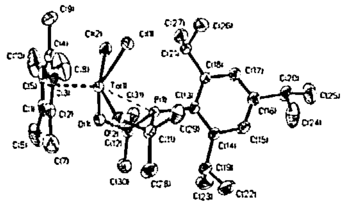


Fig. 3

Molybdenum

The reaction of [Cp°MoCl$_2$(PMe$_3$)$_2$] with LiPHMes* yielded the terminal Mo(II) phosphanido complex [Cp°Mo(PMe$_3$)$_2$(PHMes*)], while the reaction with LiPHMes gave the Mo(II) diphosphanyl complex [Cp°Mo(PMe$_3$)$_2$-(PMesPHMes)]. In both complexes, the phosphorus ligand acts as a 3-electron donor (Mo-P 2.250(3) and 2.253(2) Å). In contrast, [Cp'MoCl$_2$(PMe$_3$)$_2$] reacts with LiPHMes yielding the Mo diphosphene complex [Cp'Mo(PMe$_3$)$_2$-(η^2-PMesPMes)] (Mo-P 2.512(2), 2.624(2) Å)[5].

Adducts with primary phosphines, [Cp'MoCl$_4$(PH$_2$R)], were obtained from [Cp'MoCl$_4$(CH$_3$CN)] and PH$_2$R (R = Cy, Tipp). These compounds are paramagnetic d^1 systems and have a characteristic EPR spectrum which shows P and Mo coupling. Crystal structure determinations showed a trans arrangement of the Cp' and the primary phosphine ligand[6]. Preliminary reactions of these adducts with the base DBU indicate that HCl elimination is possible. However, up to now, we were unable to isolate and characterise the products.

Acknowledgments

We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and thank the company Chemetall for a generous donation of lithium alkyls and H. C. Starck AG for a generous donation of TaCl$_5$ and MoCl$_5$.

References

[1] E Hey-Hawkins, *Chem. Rev.*, **94**, 1661 (1994) and ref. cited therein.

[2] U. Segerer and E. Hey-Hawkins, *Polyhedron*, **16**, 2537 (1997) and ref. cited therein.

[3] C. Frenzel and E. Hey-Hawkins, *Z. anorg. allg. Chem.*, **623**, 277 (1997) and ref. cited therein.

[4] G. A. A. Hadi, K. Fromm, S. Blaurock, S. Jelonek, and E. Hey-Hawkins, *Polyhedron*, **16**, 721 (1997).

[5] E. Hey-Hawkins and K. Fromm, *Polyhedron*, **14**, 2825 (1995).

[6] R. Felsberg, S. Blaurock, S. Jelonek, T. Gelbrich, R. Kirmse, A. Voigt, and E. Hey-Hawkins, *Chem. Ber./Recueil*, **130**, 807 (1997).