

Titanocene and zirconocene complexes in phosphinine chemistry

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Abstract

The implication of titanocene and zirconocene complexes in phosphinine chemistry is reviewed. Two approaches to polyfunctional phosphinines using dimethyltitanocene as starting precursor have been developed so far. The first one involves the thermal rearrangement of 1-alkynyl-dihydrophosphetes. The second relies on the reactivity towards alkynes of 1,3,2-diazaphosphinines which are obtained by a metal transfer reaction from the corresponding diazatitanacycle. (2-Phosphinyl)-halogenozirconocene complexes, prepared by insertion of zirconocene into the carbon–halogen bond of 2-halogenophosphinines, have found interesting applications in the synthesis of α -functionalized compounds and 2,2'-biphosphinines upon reaction with electrophiles and nickel(0) complexes, respectively. Another important development of their chemistry is provided by the synthesis of monomeric and dimeric phosphabenzynes–zirconocene complexes. Preliminary investigations have shown that their reactivity closely mimics that of their carbon counterparts. Various molecules such as polar alkynes, aldehydes, ketones, nitriles, phosphine sulfides, insert into the carbon–zirconium bond of these complexes to give a wide range of annelated metallacycles which can be subsequently transformed into functional phosphinines upon acidic hydrolysis. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Devising synthetic methodologies in order to derivatize sp^2 hybridized phosphorus compounds is a prerequisite to the design and the elaboration of sophisticated planar delocalized ligands and edifices having unique coordinative properties. Over the last few years, a great deal of effort has been devoted to this aim and recent reports demonstrate that the challenge which would consist of including phosphalkenes [1], phospholide anions [2] or phosphinines [3] as subunits in various types of organic and inorganic structures is now tenable. If in some cases, classical approaches derived from carbon and nitrogen chem-

istry can be duplicated, it is clear that specific strategies taking into account the presence of a highly reactive P=C double bond must be considered. This is particularly valid for phosphinines which functionalization precludes any methods implicating nucleophilic and/or basic reagents that tend to react at phosphorus [4]. This limitation accounts for the attention dealt to neutral methods involving transition metals, which are used as templates for the formation of the ring [5], as part of a C_{ring} -bonded reactive organometallic fragment [6] or as a P-protecting group [7], have attracted so much attention. As part of a continuing program intended to enlarge the diversity of polyfunctional phosphinines, we recently developed several synthetic pathways based on the use of titanocene and zirconocene complexes. In this account, the most significant results of our investigations will be addressed.

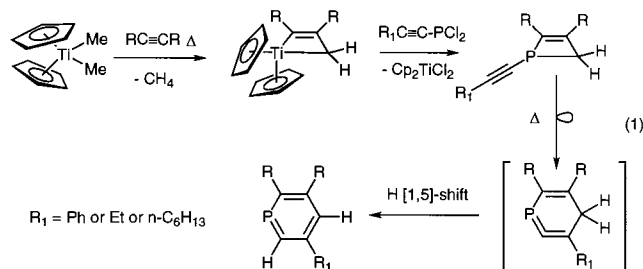
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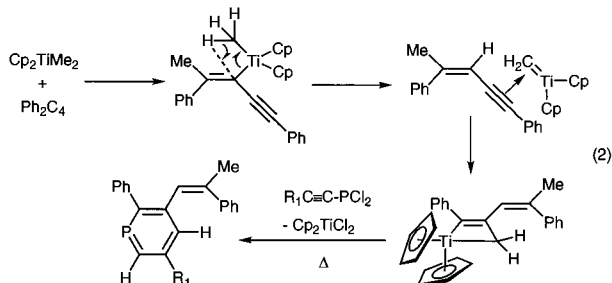
2. Titanocene complexes

2.1. Thermal rearrangement of 1-alkynyl-dihydrophosphetes

Titana- and zirconacycle transfer reactions play an ever increasing role in the synthesis of both new and known group 15 heterocycles. In many instances, they appear to be a facile method where conventional organic approaches fail or do not exist. A number of reports [8] attest that studies have mainly focused on the preparation of four and five membered rings and little attention has been paid to six membered compounds. Two methods, which both rely on the chemistry of the Tebbe's complex $\text{Cp}_2\text{Ti}=\text{CH}_2$ [9], have been developed in our laboratory for the synthesis of poly-functional phosphinines. The first one exploits the transformation of titanacyclobutenes to 1,2-dihydrophosphetes studied by Doxsee ([8]e, f) and Tumas ([8]h) several years ago. In view of their ability to equilibrate with 1,4-phosphadienes under heating, we extended the synthesis of these heterocycles to P-alkynyl derivatives which, as hoped, isomerize to phosphinines via a 4π -cycloreversion followed by a 6π electrocycloisatation and a [1,5] hydrogen shift [10]. Several phosphinines bearing phenyl or alkyl groups have thus been prepared in fair to good yields (Eq. (1)).

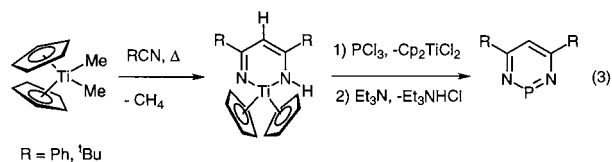


An interesting result has also been obtained when dimethyltitanocene was reacted with 1,4-diphenylbutadiyne. A 3-methylstyryl-1,2-dihydrophosphete is formed. Although no mechanistic studies have been undertaken yet, this mechanism is thought to involve, in a first step, an insertion of one $\text{C}\equiv\text{C}$ triple bond into a $\text{Ti}-\text{Me}$ bond [10]. In the second step, after a classical α -elimination of H, the titanium carbene reacts with the second alkyne function to give the metallacyclobutene skeleton. This process opens the way to 3-vinyl-substituted phosphinines (Eq. (2)).

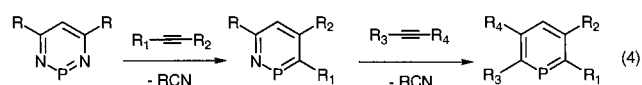


2.2. Synthesis and reactivity of 1,3,2-diazaphosphinines

This second approach which is based upon a $\text{Ti}-\text{N}$, $\text{N}-\text{P}$ bond metathesis is by far the most interesting and rewarding one. In 1996, we found that Doxsee's 1,3,2-diazatitanacycles [11], which are readily formed from the reaction of Cp_2TiMe_2 with nitriles, could be used as precursors in the synthesis of the previously unknown 1,3,2-diazaphosphinines [12] (Eq. (3)). When compared to phosphinines, it appears that the replacement of two carbon atoms by two electronegative nitrogen considerably reduces the aromaticity within the ring thus rendering the $\text{P}=\text{N}$ double bond highly reactive towards protic reagents.



However, as their 1,3-aza and 1,3,5-diaza isomers developed by Märkl a few years ago [13], the most interesting feature of their reactivity lies in their aptitude to give $[4+2]$ cycloadditions with alkynes. Thus, 1,2-azaphosphinines and phosphinines are formed under mild conditions via a thermally promoted cycloaddition/cycloreversion sequence which involves an extrusion of nitrile [12,14] (Eq. (4)).



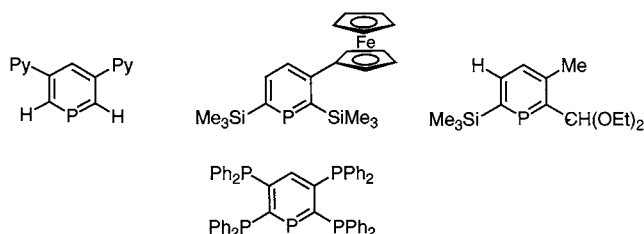
In that way, a number of 1,2-azaphosphinines, tetra-symmetrically and unsymmetrically substituted phosphinines, which were not accessible using conventional methodologies, have been prepared in fair to good yields. Some selected examples are presented in Scheme 1.

Interesting polydentate ligands such as SiMe_2 , PPh and $-(\text{CH}_2)_3-$ linked bis-phosphinines and tris-phosphinines are also accessible via this approach, provided that appropriate 1,3-diynes are used [14] (Scheme 2).

3. Zirconocene complexes

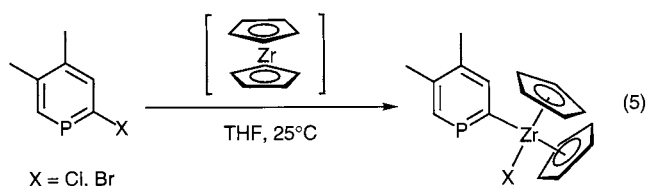
3.1. (2-Phosphinyl)-halogenozirconocene complexes

Alkenyl- and aryl-halogenozirconocene complexes have found a widespread use in several organic transformations either as soft nucleophiles [15] or as precursors for highly reactive species such as alkyne and aryne zirconocene complexes [16]. Usually, they are readily

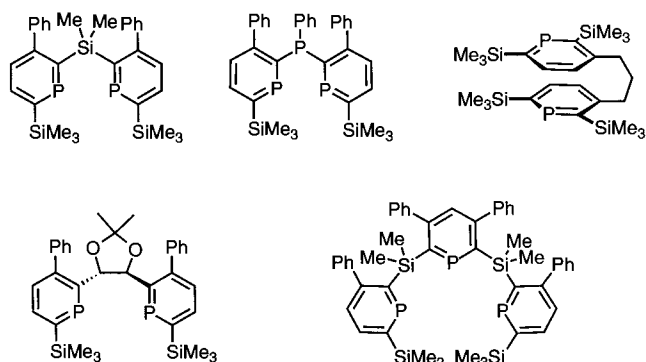


Scheme 1. Some functional phosphinines obtained from 1,3,2-diazaphosphinines.

obtained using conventional transmetalation procedures from Cp_2ZrCl_2 and the corresponding organolithium or organomagnesium salts. Unfortunately, a similar approach is not transposable to phosphinines given the presence of the positively charged phosphorus atom which prevents the formation of highly reactive organometallic derivatives. This limitation prompted us to develop a direct approach relying on the reactivity of the carbon-halogen bond of 2-halogenophosphinines toward electron deficient species, a strategy that had already been used in palladium and nickel catalyzed cross-coupling reactions [6]. As expected, zirconocene quantitatively inserts into this C–X (X = Cl, Br) bond to give (2-phosphininy)-halogenozirconocene complexes as depicted in the Eq. (5). An X-ray structure of the $[\text{ZrCp}_2(\text{C}_7\text{H}_8\text{P})\text{Cl}]$ complex has been recorded.

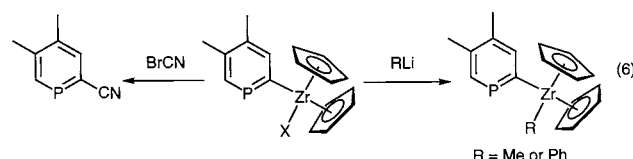


Like classical alkenyl and aryl-(halogeno)zirconocene complexes, the C–Zr bond can be cleaved by various

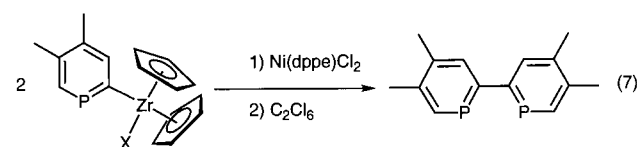


Scheme 2. Some polyphosphinines obtained from 1,3,2-diazaphosphinines.

electrophiles such as D_2O , I_2 , AgCl , and BrCN to give 2-deutero, 2-iodo, 2-silver and 2-cyanophosphinines, respectively [17] (see Eq. (6)). The metal–halogen bond is another important reactive site. Given the strong steric crowding provided by the Cp_2Zr fragment, methyl and phenyllithium specifically react at this bond, without interfering with the reactive $\text{P}=\text{C}$ double bond, to give the corresponding $\text{Zr}-\text{R}$ derivatives (R = Me or Ph) [18]; a class of compounds which, as we will see later, plays a crucial role in the chemistry of phosphabenzynes–zirconocene complexes.

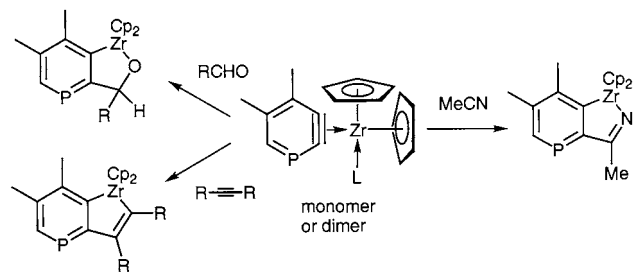


Finally, another important application of these (2-phosphininy)-halogenozirconocene derivatives is provided by their reaction with $\text{Ni}(\text{dppf})\text{Cl}_2$ which leads to $\text{Ni}^{(0)}(\text{dppf})(2,2'\text{-biphosphinine})$ complexes. This homocoupling reaction, which involves a C–Zr to C–Ni bond metathesis, appears to be the most convenient pathway to 2,2'-biphosphinines since free ligands are easily obtained by oxidation of the Ni(0) center with hexachloroethane [19] (Eq. (7)).

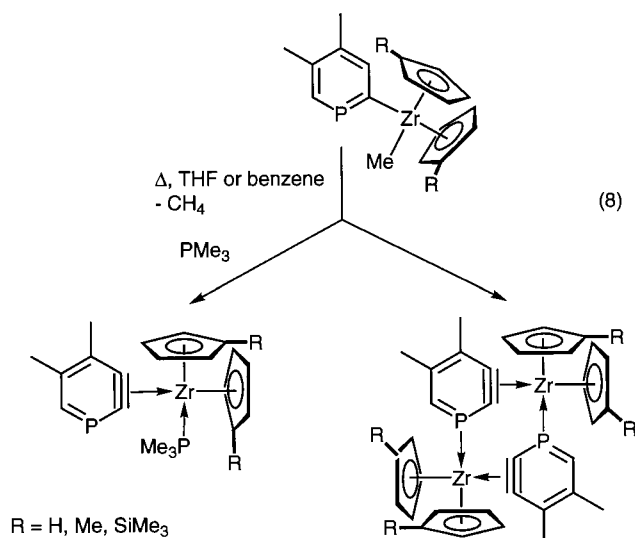


3.2. Synthesis and reactivity of phosphabenzynes–zirconocene complexes

Whereas the synthesis and reactivity of benzyne complexes are well documented [16,20], it appears that no attempts to obtain heteroaryne derivatives have been successfully achieved so far. Thus, in the case of furan– and thiophene–zirconocene complexes, a previous report of Erker et al. has shown that, instead of $\text{C}\equiv\text{C}$ bond complexation, the insertion of zirconocene into the carbon–heteroatom bond was the favoured process [21]. With phosphinines, following a methodology which was developed for benzynes [16]b, we found in 1994 that the thermally promoted β -elimination of methane or benzene from (2-phosphininy)(phenyl or methyl)zirconocene complexes was an efficient approach. Under mild conditions, η^2 -phosphabenzynes–zirconocene complexes are formed and can be isolated either as their PMe_3 adducts [18] or as dimers when the elimination is carried out without added phosphine [22]

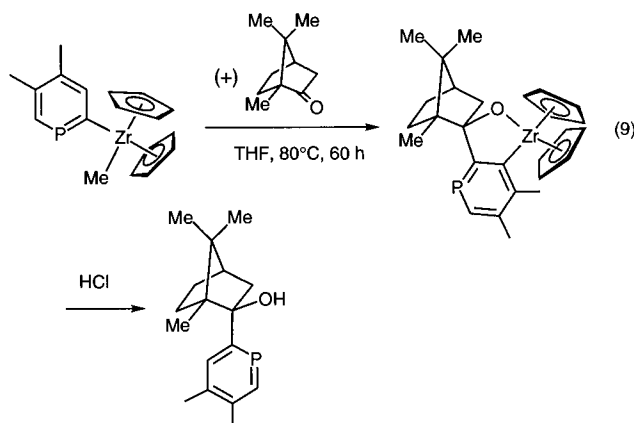
Scheme 3. Chemistry of η^2 -phosphabenzynes-zirconocene complexes.

(Eq. (8)). Besides their interest as reactive species, these dimers constitute the first examples of η^1 -phosphinine-zirconium (II) complexes.

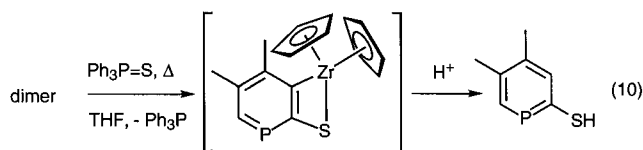


Contrary to PMe_3 complexes, which are not isolable in pure form and were only characterized in solution, an X-ray crystal structure of the very stable dimer ($\text{R} = \text{Me}$) has been recorded. The most interesting feature of this structure is the length of the CC 'pseudo triple bond' (1.361(2) Å) which compares to that of the benzyne complex described by Erker and Buchwald (1.364(8) Å). Other significant information is given by comparison of the two C–Zr bond distances which reveals that the positively charged zirconium atom is closer to C_2 ($\text{Zr}-\text{C}_2$: 2.238(2) Å) than to C_3 ($\text{Zr}-\text{C}_3$: 2.250(2)). This observation suggests that, as in free phosphinines, the C_2 carbon is more negatively charged than C_3 . This particular electronic situation explains why reactions with polar molecules such as aldehydes, alkynes and nitriles exclusively take place at the C_2 -Zr bond. As shown in the following scheme, the reactivity of η^2 -phosphabenzynes complexes closely parallels that of their carbon counterparts. A number of functional phosphinines bearing alcohols and vinyl groups have been obtained after acidic hydrolysis of the corresponding zirconacycles [22] (Scheme 3).

Ketones also insert into the C_2 -Zr bond to give tertiary alcohols after treatment with HCl (Me_3SiCl , MeOH). A straightforward application of this approach was recently provided by the reaction of the dimer or its $\text{Zr}(\text{Me})\text{Cp}_2(\text{phosphinyl})$ precursor with (+)-camphor. Probably due to a strong steric repulsion between the phosphorus lone pair and the dimethylated bridge during the formation of the intermediate zirconacycle, only one diastereomer is formed (Eq. (9)). The absolute configuration of this alcohol has been ascertained by an X-ray crystal structure of the corresponding $\text{P}-\text{W}(\text{CO})_5$ complex.



Finally, to conclude this presentation, it must be pointed out that the affinity of zirconium towards sulfur has been recently utilized for the synthesis of an original 2-phosphininethiol [22]. Reaction of the dimer with triphenylphosphine sulfide results in the formation of a poorly soluble intermediate complex (tentatively formulated as a four membered ZrCp_2SC_2 zirconacycle) and in the concomitant release of free triphenylphosphine. Acidic hydrolysis yields the 2-phosphininethiol.



4. Conclusion

As attested by the results reported here, the contribution of titanocene and zirconocene complexes to phosphinine chemistry is considerable. Thus far, these studies have led to the preparation of a number of functional derivatives which were not accessible using other known methodologies and therefore have revealed new fields of investigations. In many cases they also raised some interesting mechanistic problems. In the near future, new developments might emerge in the elaboration of sophisticated edifices from 1,3,2-diazaphosphinines. Among the possibilities, the synthesis of

phosphinine-based macrocycles constitutes a stimulating challenge. Concerning η^2 -phosphabenzynes-complexes, a first screening of their reactivity has revealed a striking parallel with that of their benzyne counterparts. This observation which emphasizes once more the fascinating analogy between phosphorus and carbon ensures that a continued exploration of this area will be fruitful.

Acknowledgements

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