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Zirconate complexes: multifaceted reagents

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Zirconium compounds play an important role in a large number of synthetic methods leading to simple or complex molecules for which straightforward preparations are not well-defined or appeared difficult to handle. Such a versatile behaviour of zirconium reagents can be explained by the fact that they can exhibit a metal centre with 14 to 18 electrons and a valence coordination number from 3 to 5. Among organozirconium species, zirconate complexes, not extensively studied up to now, seem very attractive species to deal with since convenient methods of preparation of these complexes are now available. The design, preparation, characterization and properties of these compounds are presented and discussed in this review.

Introduction

Over the past 20 years, interest in organozirconium chemistry has been rapidly increasing and a tremendous number of applications in synthetic chemistry starting from zirconocene complexes have been found.[1] Recent contributions were highlighted in a special volume[2] demonstrating the usefulness of such complexes for the development of modern synthetic methodologies.

Special attention has been paid to the preparation and the properties of group 4 d° bis(cyclopentadienyl) complexes Cp_2ZrX_n (**A**, n = 1; **B**, n = 2; **C**, n = 3) with Zr–X bonds. They can exhibit metal centres with 14 to 18 electrons and valence coordination numbers from 3 to 5 (Fig. 1). Bent cationic bis(cyclopentadienyl) complexes **A** have received considerable attention as they have been identified as the active catalytic species in the homogeneous metallocene Ziegler–Natta process for the polymerization of olefins.[3] The chemistry of **B** complexes has been also extensively explored, these compounds being used as reagents for the preparation of various new organic and organometallic compounds.

An examination of the known chemistry of anionic **C** metallocenes shows that these five-coordinated derivatives are postulated as intermediates in a number of stoichiometric and catalytic reactions. However, only a very few of these zirconates **C** have been spectroscopically and structurally characterized. Such realistic assumptions concerning the transient generation of complexes of type **C** are, of course, very important because they offer plausible mechanistic explanations concerning the preparation of various organic derivatives, as it was demonstrated in a large number of papers. Despite this, there is always a need to have "in bottle" stable reagents, fully characterized, for use in a more comfortable way as starting materials for a diversified chemistry.

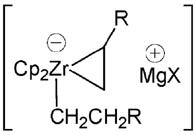
In order to take further steps towards these goals it is mandatory to have a rational view of the general principles governing the formation and the stabilization of such anionic metallocene derivatives **C** since no attempt has been made to provide a picture of the scope and limitations, characterization and properties of zirconate complexes.

It is not the purpose of this paper to review all the investigations done on this topic. Through selected examples we wish to show how it is possible to generate transient "ate" complexes or to form stable "ate" or zwitterionic "ate" complexes, thus providing the readers with tools for future developments in the field of the use of zirconium reagents in organic and heteroatomic chemistry, as well as in organometallic chemistry.

Anionic zirconocene complexes $Cp_2Zr(R)(R^1)(R^2)$.

As previously mentioned such zirconate complexes were found as key intermediates in a number of reactions.

In 1989, Negishi and colleagues reported, in a pioneering work, the insertion of α-haloorganolithium reagents into acyclic zirconocene chlorides.[4] Such a methodology is particularly useful as most organozirconocene complexes are electronically unsaturated (16 electrons), therefore the reaction may occur by formation and 1,2 -rearrangement of an 18-electron ate complex **1** (Scheme 1). The transient formation of an anionic zirconocene complex **2** was evoked to explain the "pair" selective and regioselective carbon–carbon bond forming reaction of zirconacyclopentane derivatives with Grignard reagents.[5] It was shown that the Zr-catalyzed carbomagnesation of alkenes likely proceeds with formation of zirconacyclopentanes (Scheme 2). The anionic cyclic complex **3** was also implicated as an intermediate in similar reactions and in hydrogenation reactions.[6,7]



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Whitby *et al.* proposed the generation, as intermediates, of zirconates **4** and **5** to explain the formation of complexes **6** and **7** arising in a first step from coordination of a lithiated reagent on zirconium (Scheme 3).[8,9] This group has developed the insertion of a wide range of carbenoïds into organozirconocene chlorides derived by hydrozirconation to provide useful multi-

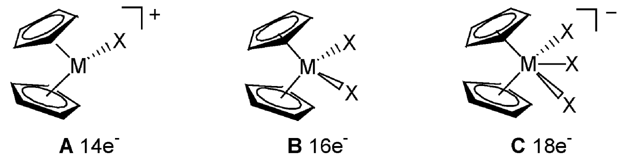
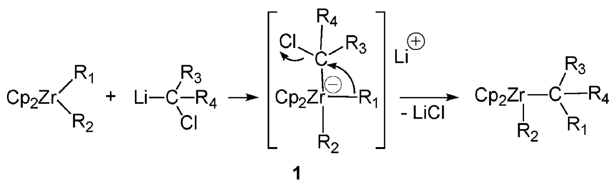


Fig. 1 Group 4 d° metallocene complexes Cp_2ZrX_n (**A**, n = 1, **B**, n = 2; **C**, n = 3).



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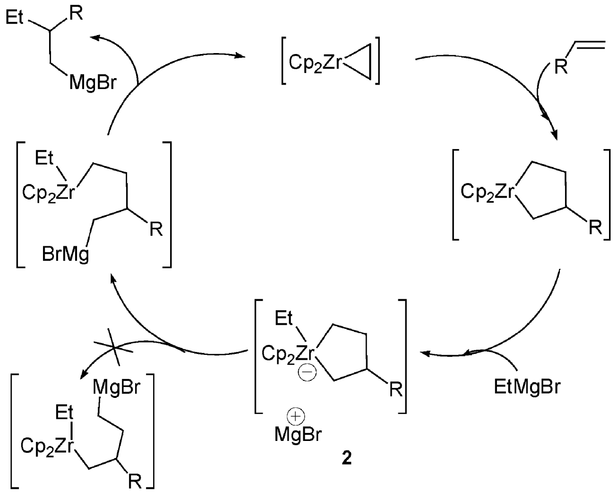
Scheme 1 Transient formation of the 18-electron "ate" complex **1**.



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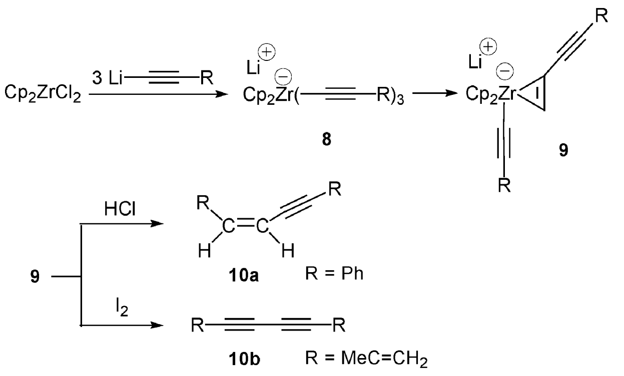
Scheme 2 Zr-catalyzed carbomagnesation of alkenes.

component coupling methods.[10,11] Ring expansion of zirconacyclo-pentanes and pentenes to afford 6-membered zirconacycles by insertion of a range of carbenoïds was also extensively reported.[2,9]

The zirconocene-promoted carbon-carbon bond formation *via* a 1,2-migration reaction of alkynylzirconium derivatives was proposed using the zirconate complex Li[$Cp_2Zr(C{\equiv}C–Ph)_3$] **8** (Scheme 4).[12] Complex **8** was prepared by treatment of Cp_2ZrCl_2 with 3 equiv. of Li–C≡C–Ph in THF at −78 °C. Reaction of **9** with HCl produced (*Z*)-1,4-diphenyl-1-buten-3-yne, **10a**, as a >96% isomerically pure compound. Similarly, the reaction of Cp_2ZrCl_2 with 3 equiv. of Li–C≡C–C(Me)=CH_2 followed by iodinolysis produced **10b** in almost quantitatively yield. Zirconocene derivatives containing both alkynyl and aryl groups also undergo a similar reaction. Pre-formed $Cp_2Zr(C{\equiv}C–Ph)_2$ reacted with PhLi, providing upon quenching with HCl, (*Z*)-stilbene. Contrary to the previous zirconate complexes reported above, **8** was stable enough to be fully characterized by NMR. However, it appears that in the very large majority of cases the anionic zirconocene complexes are not stable enough to be characterized.



Scheme 4 Carbon-carbon bond formation promoted by zirconate complexes.

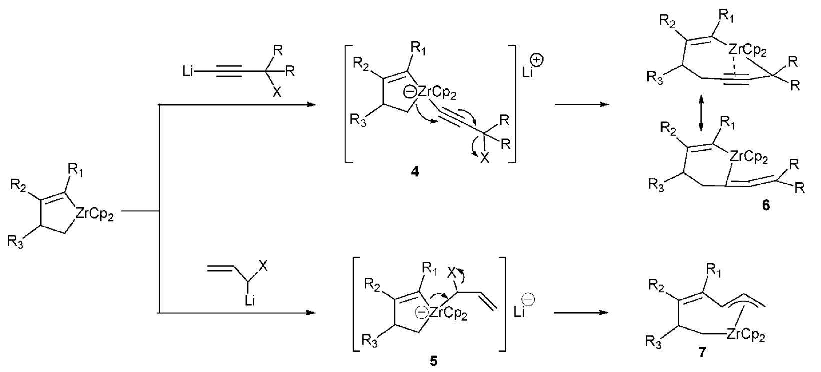
A remarkable exception to this behaviour was furnished by Stephan *et al.* who proposed synthetic pathways to several salts of the anion $[Cp^*_2ZrH_3]^-X^+$, **11**.[13] It should be noted that early metal-based hydride anions analogous to the main group hydrides were unknown until this work.

Reactions of $Cp^*_2ZrH_2$, prepared from $[Cp^*_2Zr(N_2)]_2(\mu\text{-}N_2)$, with KH in THF afforded **11a** (X = K). In a similar manner, addition of LiH gave $[Cp^*_2ZrH_3]Li$, **11b**. Another preparation involving the reaction of $Cp^*_2ZrCl_2$ with 3 equiv. of *n*-BuLi under H_2 affords $[Cp^*_2ZrH_3]Li\cdot0.5LiCl–THF$, **12**. Alternatively, reaction of $Cp^*_2ZrCl_2$ with $LiAlH_4$ gave the species $Cp^*_2ZrH(\mu^2\text{-}H_2AlH_2)$, which reacts with *n*-BuLi to give **11b** in high yield (Scheme 5). Crystallographic studies of **11b** and **12** confirm cation-anion pairing. Further NMR data affirm the formulation of the anion as a classical Zr(IV) trihydride formulation.

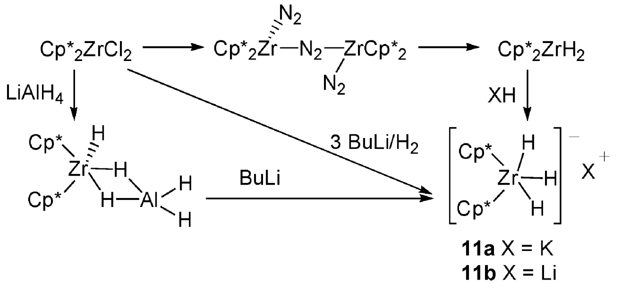
The catalytic dehydro-oligomerization of 1,2-$C_6H_4(PH_2)_2$ with $[Cp^*_2ZrH_3][K(THF)_2]$ results in deposition of the octamer (1,2-$C_6H_4P_2)_8$, **13**, an unprecedented 16-membered ring of contiguous P atoms.[14] In an effort to understand the process of formation of the macrocycle **13**, the dimeric organophosphane species $[C_6H_4(PH_2)_2]$, **14**, was isolated, suggesting that **14** subsequently undergoes dehydro coupling to afford **13**.

Zwitterionic (anionic zirconocene) complexes

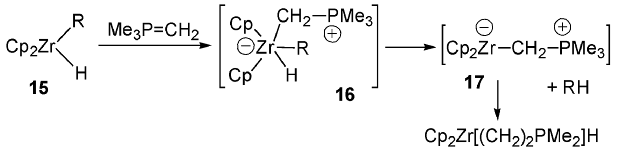
Gell and Schwartz, in pioneering work, postulated the transient formation of a acyclic zwitterionic (phosphonium anionic



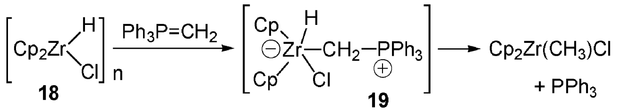
Scheme 3 Transient generation of zirconocene-ate complexes **4** and **5**.



Scheme 5 Synthesis of the anion $Cp^*_2ZrH_3^-$.



Scheme 6 Synthesis of zirconium(IV) ylide hydride *via* generation of acyclic zwitterionic (phosphonium anionic zirconocene) complexes.



Scheme 7 Methylene transfer reaction involving transient zwitterion **19**.

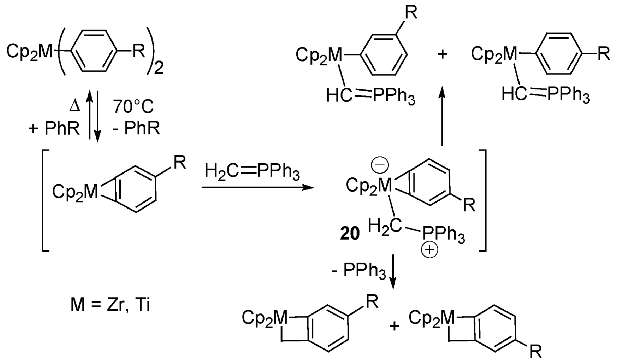
zirconocene) complex during the synthesis of zirconium(IV) ylide hydride species as shown in Scheme 6.[15] The strong nucleophile $Me_3P{=}CH_2$ attacks the unsaturated zirconium(IV) alkyl hydride **15**, producing an unstable 18-electron Zr(IV) species **16**, which collapses to a Zr(II) intermediate **17** by reductive elimination of methylcyclohexane.[15]

A clean methylene-transfer reaction was observed when hydridozirconocene chloride **18** (Schwartz reagent) was treated with $Ph_3P{=}CH_2$, leading to $Cp_2Zr(CH_3)Cl$ and $P(Ph)_3$ *via* a 1,2-hydrogen migration from zirconium to carbon with transient generation of the zwitterion **19**[16] (Scheme 7). Later on the transient formation of another zwitterionic complex **20** was proposed in order to explain the formation of metallacyclic four-membered ring systems[17] (Scheme 8).

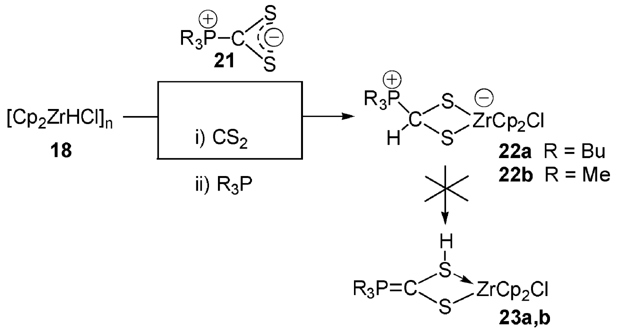
However, even if the claims concerning the generation of highly unstable phosphonium anionic zirconocene complexes appeared to be reasonable, no real proof was furnished until the mid-nineties concerning the existence of such complexes.

Indeed, in 1996 two reactions allowed to isolate the fully characterized zirconated phosphonio dithiolate complexes **22**[18] (Scheme 9). The first one consists in the treatment of the adduct R_3PCS_2 **21** (R = Bu, Me), obtained from carbon disulfide and the corresponding phosphine R_3P, with the Schwartz reagent **18**. Alternatively, carbon disulfide can be added first to the Schwartz reagent, the resulting mixture being treated with R_3P. The complex **22a** was isolated in high yield as a yellowish crystalline product. The nature of the substituents on phosphorus strongly affects the stability of these complexes: **22a** decomposes in solution over 1 day but is stable as a powder for several weeks at −25 °C, while **22b** has to be used as generated *in situ*. It should be noted that no 1,2-hydrogen shift, which would have resulted in the formation of complexes **23a** or **23b**, has been detected.

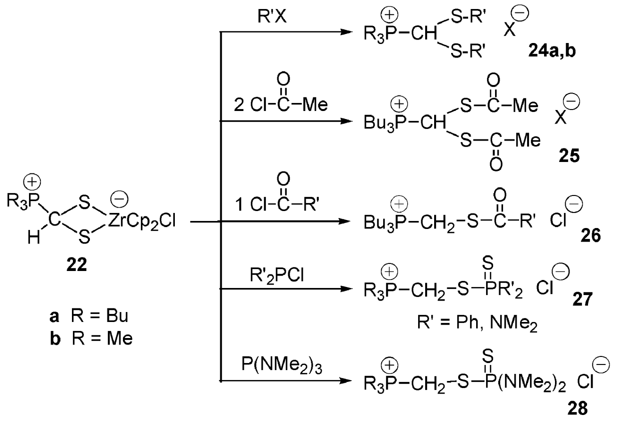
Complexes **22** present a diversified reactivity. **22a** easily reacts with methyl iodide and benzyl bromide with formation in high yield of *S*,*S*′-dialkylated phosphonium salts **24a,b**. Similarly, addition of 2 equiv. of acetylchloride to **22a** affords the bisthioacylated phosphonium salt **25**, while treatment of **22a** with only 1 equiv. of acetylchloride gives rise to the other new methylene phosphonium salt **26** (Scheme 10).



Scheme 8 Formation of metallacyclic four-membered ring systems.



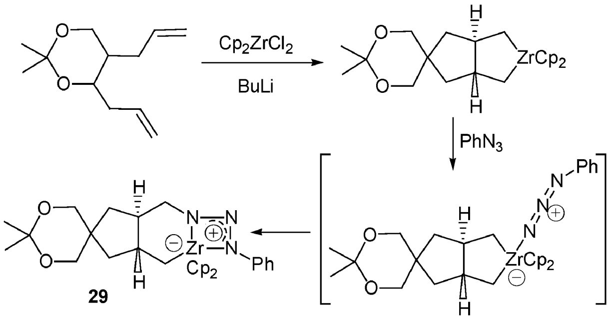
Scheme 9 Synthesis of phosphonio dithiolate zirconate complexes **22**.



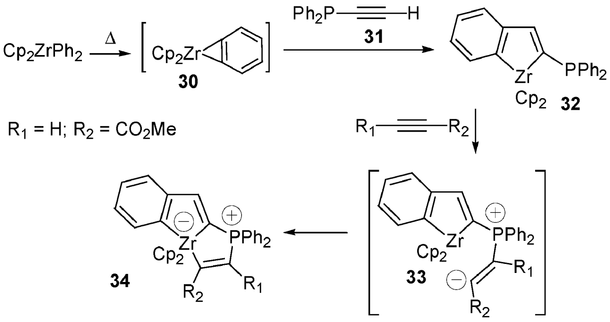
Scheme 10 Reactivity of complexes **22**.

Remarkably, the reaction of **22a** or **22b** with chlorophosphines or aminophosphines led to the unprecedented methylene thiophosphorylated phosphonium salts **27** and **28**. The mechanism of this unusual reaction has not been unequivocally established but can be regarded as a three-step process: (i) nucleophilic substitution at sulfur in **22a** or **22b**, (ii) then sulfurization on the tricoordinated phosphorus atom and (iii) hydrogen transfer in order to form the PCH_2SR sequence.

A few other zwitterionic complexes bearing an anionic zirconocene moiety and a nitrogen cationic part were also reported. In an elegant work Whitby *et al.* described the synthesis of the triazenidoalkylzirconocene **29** (Scheme 11),[19] which was found to be stable to air and water, surviving in aqueous workup intact and no change being observed after exposure of the crystals of **29** to light and air for 2 weeks. An explanation for this nonreactivity is that a bidendate coordination mode of the triazenido moiety gives an electronically saturated (18 electrons) zirconium centre.[19] An X-ray structure



Scheme 11 Synthesis of triazenidoalkylzirconocene **29**.



Scheme 12 Synthesis of the zwitterion **34** *via* treatment of the zirconaindene complex **32** with methyl propiolate.

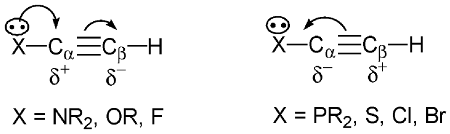
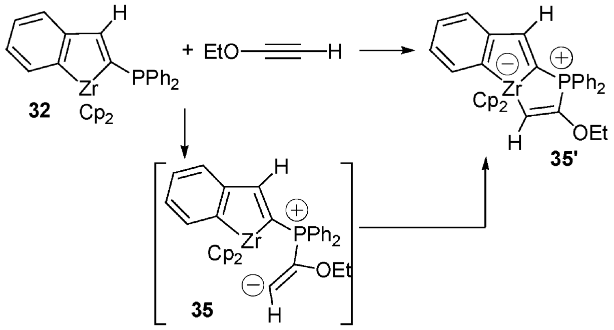
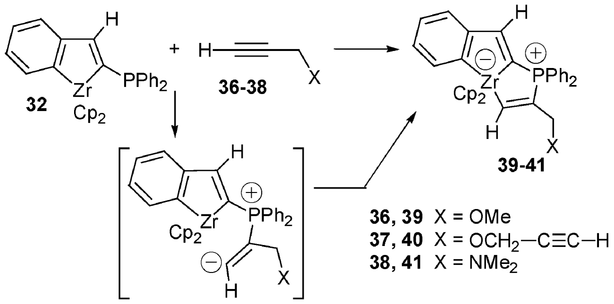


Chart 1



Scheme 13 Synthesis of zwitterion **36** *via* a [3 + 2] cycloaddition reaction.



Scheme 14 Reaction of propargylic systems with the zirconaindene **32**.

determination of **29** confirmed the bidendate nature of the triazo ligand-metal interaction.

[3 + 2] cycloaddition reactions

X-Ray structure determinations of various zwitterionic (phosphonium anionic zirconocene) complexes appeared a little later, these unprecedented zwitterions being prepared *via* formal [3 + 2] cycloaddition reactions. Treatment of benzyne-zirconocene **30**, generated by heating Cp$_2$ZrPh$_2$ in refluxing toluene, with alkynylphosphines **31** led to 2-phosphinozirconaindenes **32**. Addition of methyl propiolate, for example, to **32** in toluene at room temperature afforded the complex **34** fully characterized by X-ray diffraction studies[20] (Scheme 12). It was reasonably postulated that the first step of the reaction is the nucleophilic attack of phosphorus(III) on the unsubstituted acetylenic carbon with formation of the corresponding transient zwitterion **33**. In the second step an intramolecular cyclization of the carbanionic centre of the betaïne species **33** on the zirconium metal fragment occurs to form the stable zirconate product **34**.

No reaction occurred on **32** with nonactivated terminal acetylenic systems such as *tert*-butyl, phenyl, and trimethylacetylene. Thus, zwitterionic organozirconocene-ate complexes are obtained with **32** when functional groups linked to the acetylenic moiety provide sufficient activation by conjugation with the carbon-carbon triple bond.

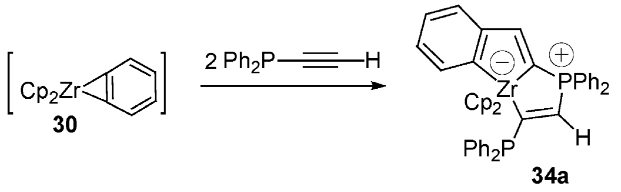
To expand the scope of the formation of anionic organozirconocene-ate complexes obtained from acetylenic compounds, investigations concerning the reaction of **32** with heteroacetylene reagents were performed. It is known through calculations and experimental studies that the regioselectivity of nucleophilic additions of tertiary phosphines on terminal heteroacetylene derivatives depends on the nature of the heteroatom directly bonded to the unsaturated system (Chart 1). The regioselective formation of **36** is in agreement with the nucleophilic attack of the phosphine moiety in **32** on the acetylenic carbon atom linked to the methoxy group to form the intermediate **35**, which gives, after cyclization, complex **35'** (Scheme 13). The reaction of **32** with an acetylenic system directly substituted with a second-row element such as the phosphorus atom proceeds similarly but in much more drastic conditions (110 °C, 16 h, instead of room temperature, 3 h).[21]

Coupling reactions involving zirconocene complexes and propargylic systems lead generally to mixtures of products with low yields. In marked contrast, addition of heterosubstituted propargyl derivatives **36–38** to **32** gave regioselectively and quantitatively the anionic zirconocene complexes **39–41** (Scheme 14).

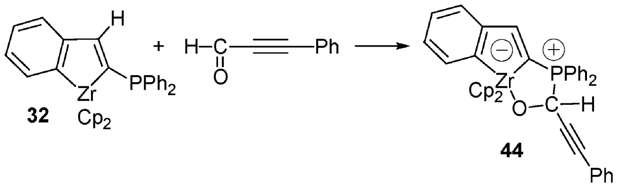
To summarize, [3 + 2] cycloadditions involving **32** and acetylenic systems lead to a large variety of stable anionic five-coordinate zirconocene-ate complexes. Nucleophilic reaction of the phosphine moiety **32** follows the proposed rule that a heteroelement in conjugation with the triple bond of a terminal acetylene orientates nucleophilic attack on C$_\alpha$ for first-row elements and on C$_\beta$ for elements of the second period (Chart 1).

To end up with such [3 + 2] cycloadditions using acetylenic systems it must be emphasized that the one-pot reaction of 1 equiv. of **30** with 2 equiv. of the acetylenic phosphine Ph$_2$P–C≡C–H leads directly to the zwitterionic (phosphonium anionic zirconocene) complex **34a** (Scheme 15).

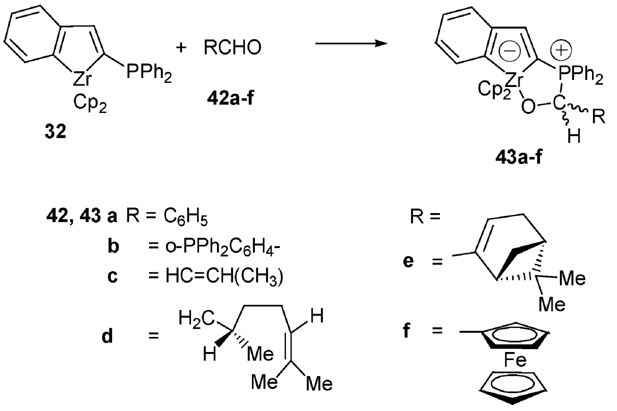
Such formal [3 + 2] cycloadditions reactions can be performed also with various aldehydes **42a–f**[22] (Scheme 16). Reactions are conducted in toluene for 1 h at either −78 °C or room temperature, depending on the aldehyde, and afforded the desired stable zwitterionic 18-electron d° anionic zirconocenes



Scheme 15 One-pot formation of the zwitterionic complex **34a**.



Scheme 17 Reactivity of the zirconaindene **32** with Ph–C≡C–CHO.



Scheme 16 Reactivity of the zirconaindene **32** with aldehydes.

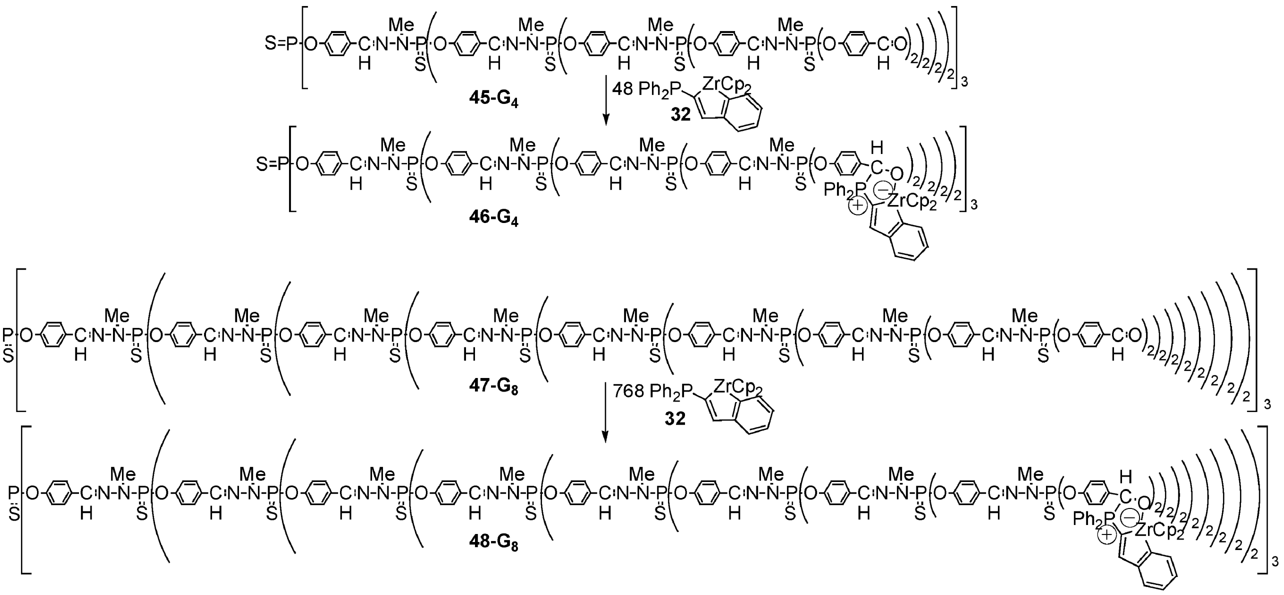
43a–f in 53–73% yield after workup. It can be emphasized that these cycloadditions occur selectively on the carbonyl group, allowing therefore the preparation of diversely functionalized zwitterionic zirconocene complexes possessing either a free phosphino group (**43b**) or free alkenyl group (**43c–e**). NMR data of these complexes fit well with the proposed structures; one of them (**43e**) was fully identified by X-ray crystallographic studies, which confirm the formation of the suggested cycloadduct. Interestingly, the nucleophilic attack of the phosphine unit in **32** on Ph–C≡C–C(O)H took place selectively at the carbon atom of the aldehyde function to give quantitatively the zwitterion **44** after cyclization (Scheme 17).[21]

The ability of **32** to react with polyaldehydes was investigated: the same strategy was used to decorate the surface of a dendrimer of generation 4 (48 terminal aldehyde groups) and the surface of a dendrimer of generation 8 (768 aldehyde end groups) with respectively 48 and 768 anionic zirconocene moieties. These first zwitterionic metalladendrimers **46-G$_4$** and **48-G$_8$** with anionic early transition metal units grafted on the periphery were isolated in 70 and 76% yield, respectively (Scheme 18).

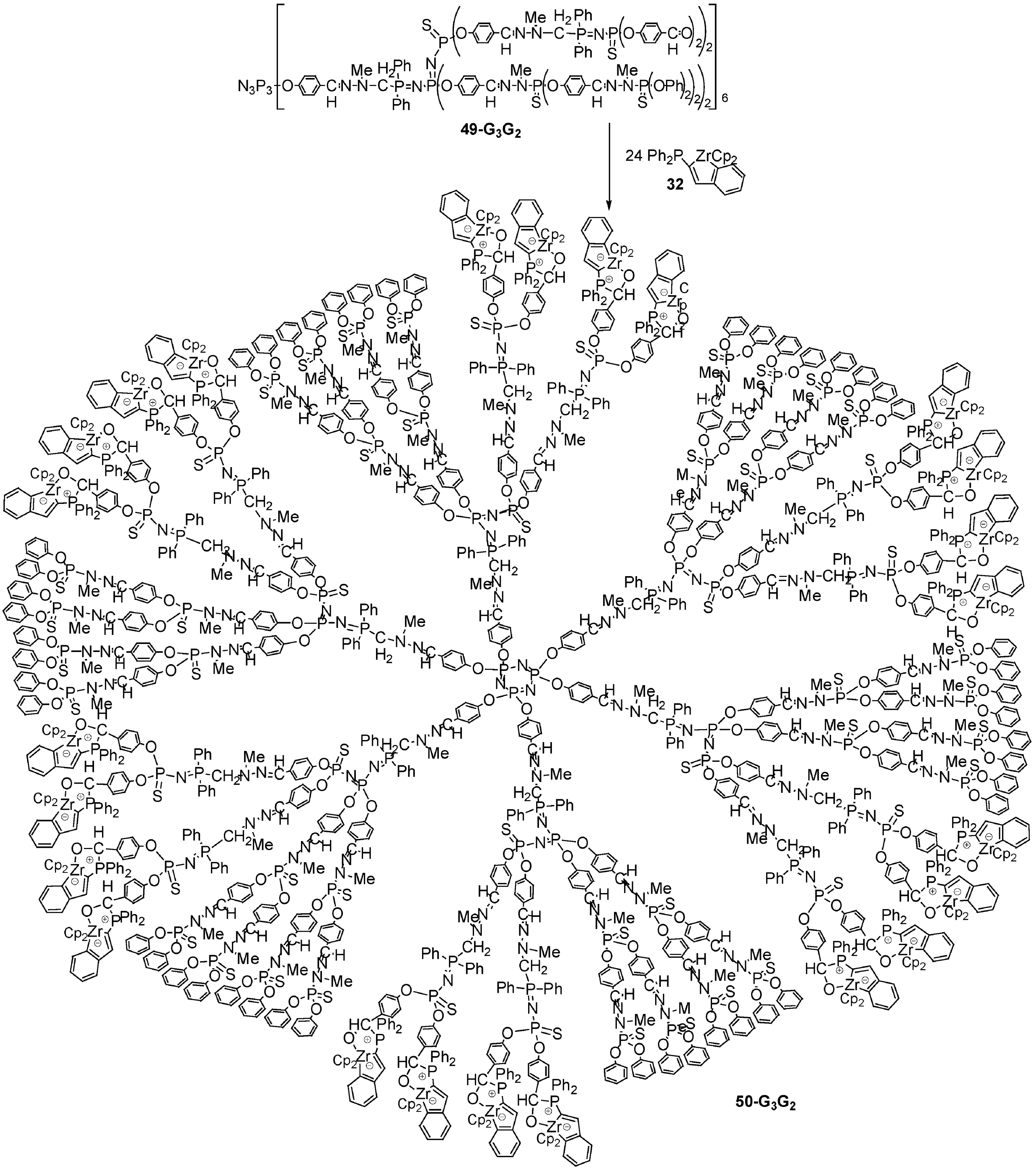
Remarkably, a controlled number of anionic zirconocene units can be selectively introduced into the internal layers of a polydendritic macromolecule. Indeed, treatment of the multi-dendritic system **49-G$_3$-G$_2$** constituted by a central dendrimer of generation 3 and by six internal dendrimers of generation 2 possessing 24 internal aldehyde groups, with **32** (excess) clearly leads to the polyzwitterionic zirconocene polydendritic structure **50-G$_3$-G$_2$** (88% yield),[22] in which all the early transition metal anions are located within the cascade structure (Scheme 19).

Such chemio- and regioselective cycloadditions were extended to the formation of complexes bearing zirconium–sulfur or zirconium–nitrogen bonds (Scheme 20).[23] Indeed, the metallocene species **51–55** were isolated in good to excellent yields (53%–84%) by treatment of **32** with an equimolecular amount of the corresponding heterocumulene: CO_2, CS_2, Cy–N=C=N–Cy, R–N=C=S, R–N=C=O. Several X-ray diffraction studies were carried out to confirm the proposed zwitterionic structures. With isocyanates and isothiocyanates, the anionic charge is delocalized over the carbamoyl skeleton in **I**, but the preferred coordination site in these systems is the nitrogen atom. The η^1-bonding mode of the carbamoyl group in complexes **54** and **55** is very strong since no competition between nitrogen and oxygen or between nitrogen and sulfur was observed either in the solid state or in solution.

Such a methodology leading to a large number of stable and well-characterized zwitterionic 18-electron d° anionic metallocene complexes can be illustrated with the reactivity of other 16-electron metallocene species, such as **56**. Addition of phenyl isothiocyanate to **56** in toluene at −40 °C leads to the expected



Scheme 18 Synthesis of phosphorus dendrimers decorated with zwitterionic zirconate complexes.

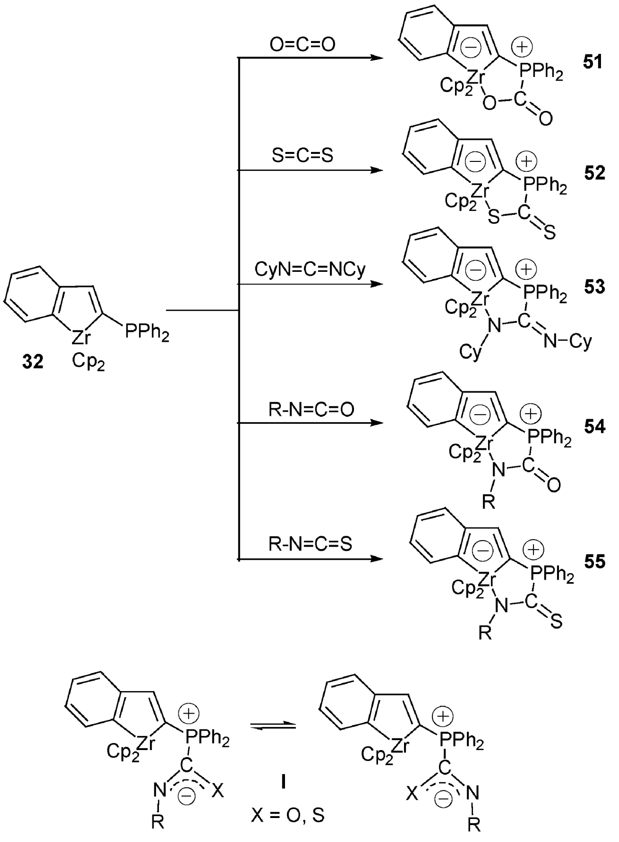


Scheme 19 Incorporation of zwitterionic zirconate complexes within a multidendritic macromolecule.

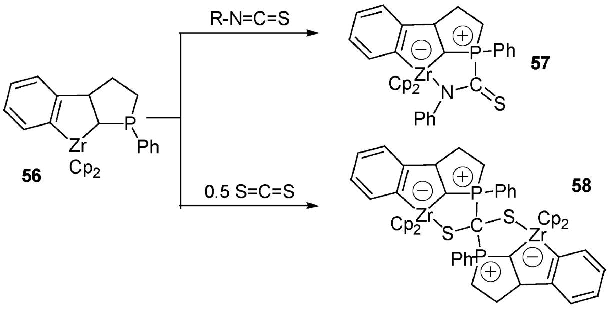
complex **57** isolated in 91% yield after workup. Surprisingly, the same reaction performed with **56** (1 equiv.) and carbon disulfide (0.5 equiv.) affords the unique "dimeric" species **58** arising from successive (or concomitant) cycloaddition reactions on the two carbon–sulfur double bonds of CS_2. Under stoichiometric conditions, only half of the neutral complex **56** is transformed into the bis(zwitterionic) complex **58** (Scheme 21).[23]

[3 + 1] cycloaddition reactions

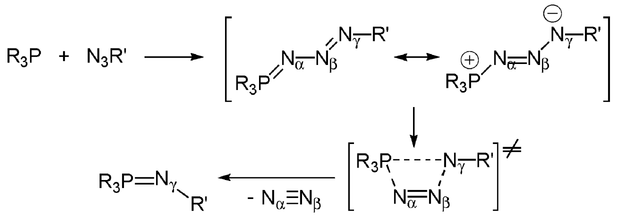
The chemistry of iminophosphorane compounds of general structure $R_3P{=}N{-}R'$, which incorporate a four-coordinate phosphorus and a formal double bond between the phosphorus and the nitrogen, is very well documented. Iminophosphoranes are employed in a number of useful reactions in organic chemistry, such as Aza-Wittig reactions[24] or as very strong neutral bases.[25] The Staudinger reaction of azides with tertiary phosphines is one of the two major routes in the preparation of iminophosphoranes.[26] Such a reaction proceeds by nucleophilic attack of the phosphine on the terminal α-nitrogen atom of the azide to afford a linear phosphazide, rarely stable,[27] which then dissociates to the iminophosphorane with elimination of dinitrogen (Scheme 22). Iminophosphoranes form complexes with a variety of metals by *N*-imino complexation (covalent or dative bonds).[24] In marked contrast, only a few phosphazide complexes have been prepared.[28] The unique seven-coordinate complex $[WBr_2(CO)_3(Ar{-}N{=}$



Scheme 20 Formation of zwitterionic zirconate complexes bearing Zr–O, Zr–S or Zr–N bonds.

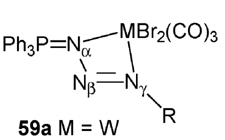


Scheme 21 Reactivity of tricyclic zirconocene complexes with R–N=C=S and CS_2.

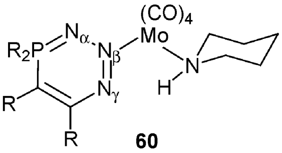


Scheme 22 Mechanism of the Staudinger reaction between phosphines and azides.

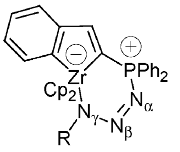
N–N=PPh_3)], **59a**, was characterized by X-ray diffraction studies: the phosphazide ligand is bound to the tungsten metal fragment in a bidentate fashion through the α- and γ-nitrogen atoms.[28b] More recently, the cyclic (*Z*)-phosphazide **60** was found to act as a monodentate two-electron donor through the less sterically hindered β-nitrogen atom.[28c] Since in all the previous reactions involving [3 + 2] cycloaddition reactions and leading to zwitterionic phosphonium anionic zirconocene complexes the first step consists of a nucleophilic attack of the phosphine moiety, it was of interest to see if such a reaction can be observed with various azides and, for example, complexes **32** and **56**. One can expect that a Staudinger reaction will take place with the formation of a transient phosphazide or the formation of the more stable iminophosphorane. The trapping of phosphazide through complexation of the γ-nitrogen atom to the zirconium centre may be anticipated because of the well-established zwitterionic character of the PN_3R fragment (P^+–N_α=N_β–$N^-{}_\gamma$–R)[27] with formation of the zirconate species **D**. Complexation of phosphazide through the less-hindered nitrogen atom N_β, which would lead to complexes of type **E** can be also envisaged. Otherwise, chelation of the iminophosphorane would lead to complexes of type **F**, whereby the zirconium counterpart plays the role of a Lewis acid in each case. Lastly, insertion of the azide into a Zr–C bond cannot be totally ruled out.[29]



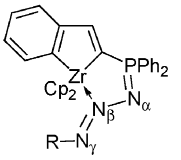
59a M = W
59b M = Mo



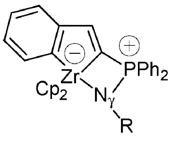
60



D



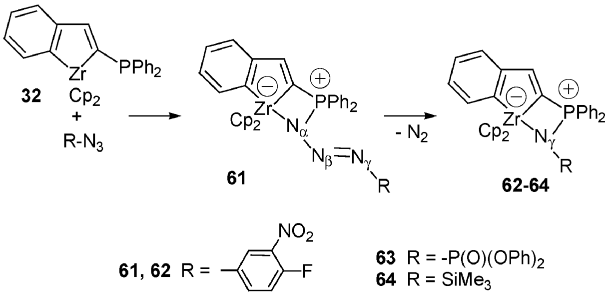
E



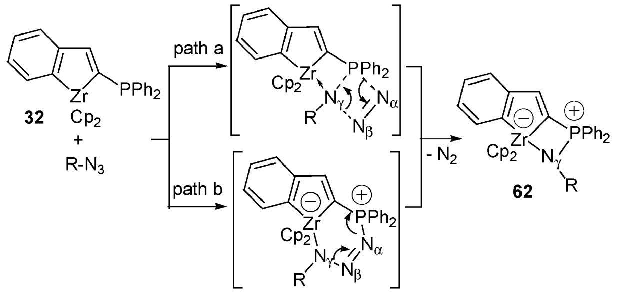
F

Indeed, an unprecedented chelation of phosphazides, which involves a formal [3 + 1] cycloaddition that occurs exclusively with the α-nitrogen atom of the phosphazide moiety, was found with formation of a variety of new stable, polycyclic zwitterionic complexes.[30] This was first observed when the α-phosphinozirconaindene **32** was reacted with a 4-fluoro-3-nitrophenyl azide (Scheme 23). No evolution of dinitrogen was detected and the structure of the resulting complex **61** was established by X-ray diffraction studies. Therefore, in marked contrast to the situation encountered for compounds **59** and **60**, intramolecular donor-acceptor interactions only occur with the α-nitrogen atom, which suggests that this nitrogen atom is a better donor than N_γ and that the polarization of the phosphazide moiety is more correctly represented as –P^+–N^-–N=N–R rather than P^+–N=N–N^-–R, at least for the structure reported above.

The zwitterionic zirconocene-ate complex **61** is stable at room temperature and dinitrogen is only liberated on heating under reflux in toluene for 2 h to give rise to the new complex **62** (Scheme 23). This evolution of molecular nitrogen may imply a dissociation of the Zr–N_α bond. Two possible path-



Scheme 23 Synthesis of zwitterionic complexes **61** and **62–64** by [3 + 1] cycloaddition.



Scheme 24 Proposed mechanism for the formation of complex **62**.

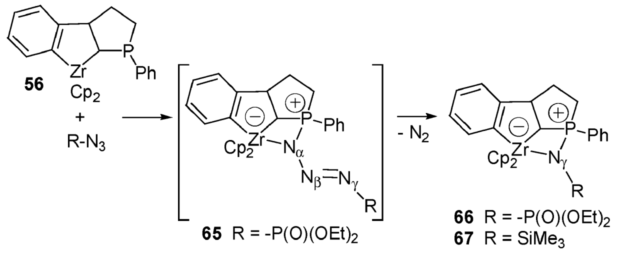
ways to rationalize the formation of **62** may be proposed (Scheme 24). The first path involves the mechanism demonstrated for the Staudinger reaction with transient formation of a four-centred transition state, coordination of the γ-nitrogen atom to phosphorus, and elimination of the α- and β-nitrogen atoms (path a) to give compound **62**. However, the transient formation of a six-membered ring (path b) cannot be totally ruled out. The X-ray structure analysis of **62** shows that the nitrogen atom is connected to zirconium [d(Zr–N) = 2.426(2) Å] and the phosphorus–nitrogen bond length [1.620 (2) Å] is in the normal range for such a bond. No structural change is observed for this derivative in comparison with **32**; the fused tricyclic system is still planar (maximum deviation 0.062 Å).

Interestingly, the reaction of **32** with the azide $N_3P(O)(OPh)_2$ in toluene at room temperature for 1 h gave the zwitterionic derivative **63** directly (Scheme 23); the transient formation of a phosphazide complex was not detected in this case. A similar result was observed when a toluene solution of **32** was treated for 1 h with trimethylsilylazide: the complex **64** was the only product formed and was isolated in 61% yield (Scheme 23). However, this reaction did not proceed at room temperature; it was necessary to reflux for 1 h in order for the reaction to go to completion.

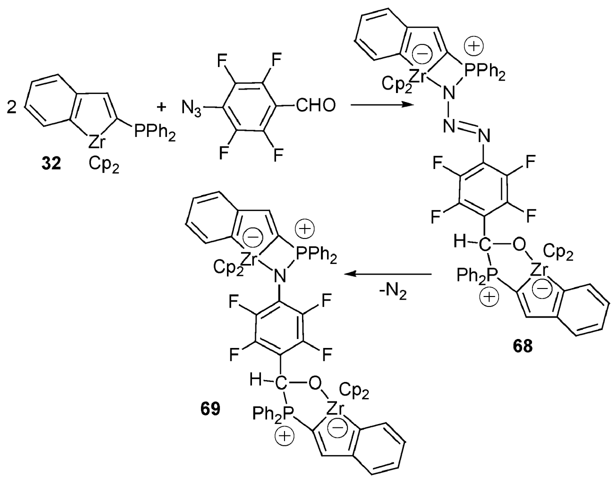
Such a formal [3 + 1] cycloaddition involving azides and α-zirconated phosphines can be extended to tricyclic systems such as **56** (Scheme 25). Indeed, when a solution of **56** and $N_3P(O)(OPh_2)_2$ in toluene was stirred at room temperature for 1 h, in contrast to the reaction that led to **63**, the formation of a transient phosphazide complex **65** was detected by ^{31}P NMR spectroscopy.

Lastly, as in the reaction of trimethylsilylazide with **32**, the iminophosphorane complex **67** was directly formed when the tricyclic system **56** was treated with trimethylsilylazide at room temperature. Remarkably, only one isomer of each complex **66** and **67** was formed, as indicated by NMR spectroscopy.

Therefore, it appears that the lifetime of transient phosphazide complexes is greatly dependent on the nature of both the starting α-zirconated phosphine and the azide used. As previously shown,[24] phosphazides are thermodynamically stabilized by the presence of electron-withdrawing groups on nitrogen and of electron-donating groups on phosphorus. This was also demonstrated in this work. Concomitant [3 + 1] and [3 + 2] cycloaddition reactions were observed when α-phosphinozirconaindene **32** was treated with difunctional reagents such as 4-azidotetrafluorobenzaldehyde.[30] The bisphosphonium species **68** was isolated and fully characterized when the reaction is performed at room temperature for 30 min. When **68** was heated in refluxing toluene, dinitrogen was liberated and adduct **69** was formed (Scheme 26). A similar reactivity was found when compound **32** was treated with 4-azidophenyl isocyanate at room temperature: the stable polycyclic bis(zwitterionic) adduct **70** containing four- and five-membered rings with Zr–C–P–N and Zr–N–C–P–C backbones is formed in near quantitative yield. As for all the reactions reported above, the phosphazide complex can be easily transformed into an iminophosphorane-like complex **71** by heating in refluxing toluene (Scheme 27).



Scheme 25 Synthesis of zwitterionic zirconaphosphazide complexes **66** and **67**.

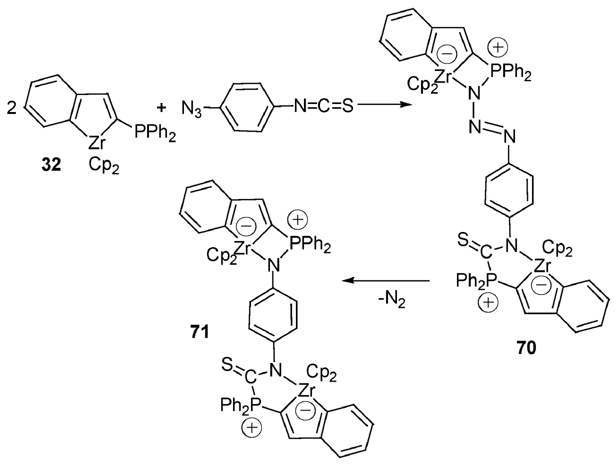


Scheme 26 The [3 + 1] and [3 + 2] cycloadditions between 4-azidotetrafluorobenzaldehyde and **32**.

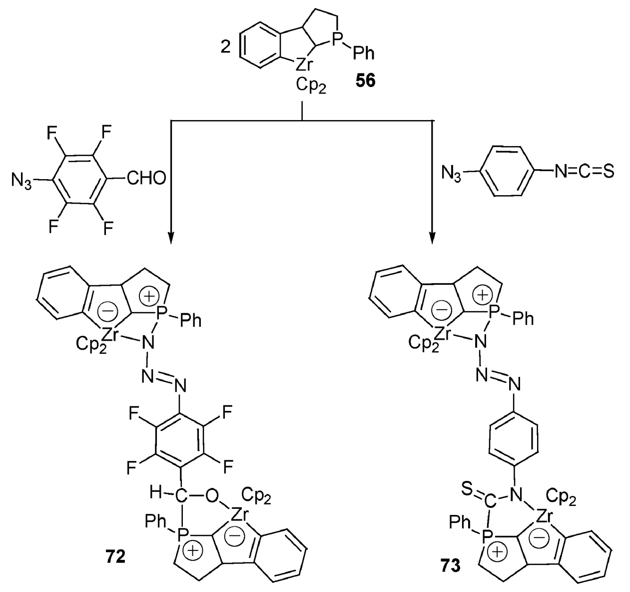
Analogous reactions conducted with the tricyclic system **56** instead of **32** and with 4-azidotetrafluorobenzaldehyde or with 4-azidophenyl isocyanate allowed the formation of the bis (zwitterionic) complexes **72** and **73** (Scheme 28). Contrary to what was seen with the other phosphazide complexes, **72** and **73** do not cleanly lose dinitrogen when refluxed in toluene; decomposition of these complexes occurs with formation of numerous unidentified derivatives.

Miscellaneous ways of synthesis of zwitterionic complexes

To finish up with the formation of zwitterionic (phosphonium anionic zirconocene) complexes, two other ways of formally



Scheme 27 The [3 + 1] and [3 + 2] cycloadditions between 4-azidophenyl isothiocyanate and **32**.

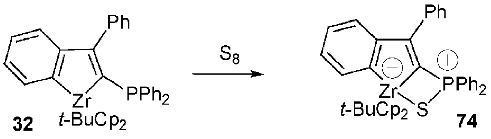


Scheme 28 The [3 + 1] and [3 + 2] cycloadditions between **56** and 4-azidotetrafluorobenzaldehyde or 4-azidodiphenyl isothiocyanate.

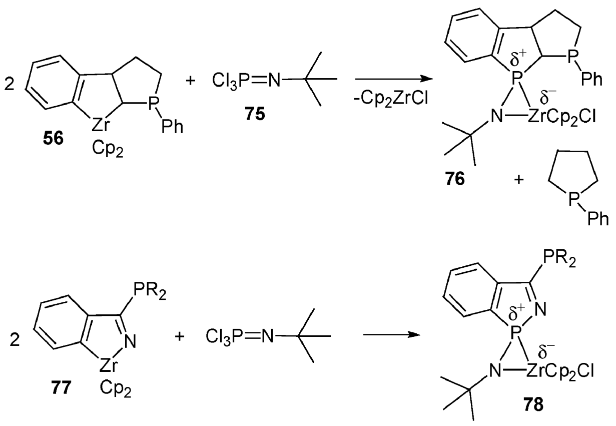
obtaining these species can be emphasized: the first one involves the sulfuration of **32** leading to the complex **74**. X-Ray structure analysis of **74** revealed an interaction between zirconium and sulfur: the P–S bond length was found to be slightly longer [2.005 (1) Å] than those generally observed for thiophosphoryl groups (1.93–1.95 Å). Indeed the P–S bond length lies in between those of single and double bonds, suggesting a zwitterionic character for **74**[31] (Scheme 29). The second method deals with an exchange reaction between the zircona complex **56** and trichlorophosphineimine **75**, leading to a metallaazaspirophosphane **76** (Scheme 30). The solid state structure of **76** has been corroborated by a single-crystal X-ray diffraction study[32] showing a slight zwitterionic character for this complex, the P–N bond length [1.615(2) Å] being in between that of single and double bonds. A similar reaction performed with the complex **77** and $Cl_3P{=}N$–*t*-Bu affords the zirconabisazaspirophosphane **78**.

If the synthesis of zwitterionic (phosphonium anionic zirconocene) complexes is now well-documented, that of the corresponding ammonium species is quite rare[19] and it is only very recently that the preparation and X-ray characterization of a bis-sulfonium zirconocene-ate dimer was proposed.[33] A toluene solution of diphenylphosphinoacetylene and a zirconocene thioaldehyde equivalent, $Cp_2Zr(Me)SCH_2Ph$, prepared from dimethylzirconocene and phenylmethanethiol, led to such a complex isolated as dimer **79**. Remarkably, the cleavage of such a binuclear thiazirconacycle with borane afforded the monomeric thiazirconacyclic complexes **80**, thus pointing out a weak association through bridging sulfur atoms in dimer **79** (Scheme 31).

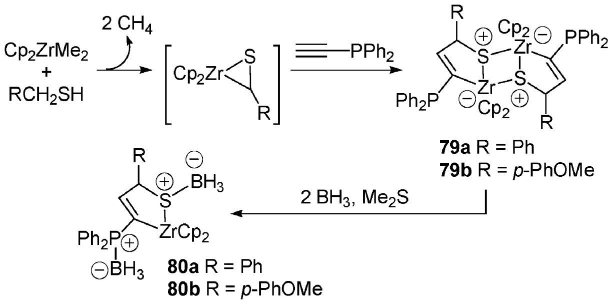
Reactivity of zwitterionic (phosphonium anionic zirconocene) complexes



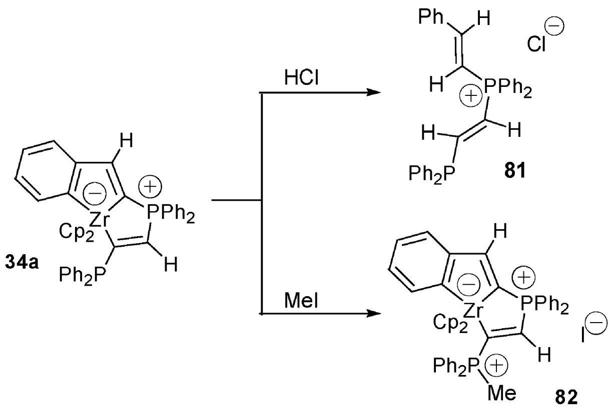
Scheme 29 Synthesis of a zwitterionic complex *via* sulfuration of the phosphinozirconaindene **32**.



Scheme 30 Synthesis of zirconabisazaspirophosphanes **76** and **78**.



Scheme 31 Preparation of bis-sulfonium zirconocene-ate dimer.



Scheme 32 Reactivity of the anionic five-coordinate zirconocene complex **34a**.

In marked contrast with the work done with unstable zirconate complexes such as those mentioned in the first part of this report, a few reactions were described dealing with the corresponding stable zwitterionic complexes. Addition of HCl to **34a** leads to the cleavage of the three Zr–C bonds to give the divinyl phosphonium compound **81** as the major product. Addition of MeI to the same zwitterionic complex affords the bisphosphonium zirconate **82** (Scheme 32). Even in the presence of an excess of MeI no electrophilic cleavage of one of the three Zr–C bonds was observed.

Concluding remarks

Throughout this manuscript is reported either the transient generation of anionic zirconocene complexes or the isolation and full characterization of stable zwitterionic [phosphonium (sulfonium or "ammonium") anionic zirconocene] complexes. Transient zirconate complexes were postulated in a number of reactions leading to the formation of linear, cyclic or polycyclic derivatives, but because of their "inherent" instability, it is often difficult to orientate the reactions that they are initiating. Indeed, their role and behaviour are often explained *a posteriori*. In marked contrast the corresponding zwitterionic species are remarkably stable and they can be easily manipulated, but the major drawback of these complexes is their lack of reactivity. However, the zirconated phosphino dithiolate complexes **22**, owing to their Zr–S bonds, represent a good compromise between reactivity and stability since they easily offer the possibility to prepare a variety of phosphonium salts, for example, difficult or even impossible to prepare *via* classical methods. Similarly, bis-sulfonium zirconocene-ate dimers seems to be also versatile reagents.

It is clear that studies concerning the design of new zirconates with controllable activity is highly desirable not only for creating new and efficient tools in organic and organometallic chemistry but also for expanding the number of useful applications that were already proposed with complexes of type **A** and **B**. As an example the fascinating potential of both zirconium on the one hand and phosphorus sulfur or nitrogen chemistries on the another hand will help chemists to further develop this stimulating and still lively field of challenging research.

References

1 (*a*) For recent reviews, see: H. G. Alt and A. Köppl, *Chem. Rev*., 2000, **100**, 1205; (*b*) G. Erker, *Acc. Chem. Res*., 2001, **34**, 309; (*c*) E.-I. Negishi, *Pure Appl. Chem*., 2001, **73**, 239; (*d*) P. Wipf and C. Kendall, *Chem.-Eur. J*., 2002, **8**, 1778.

2 K. Suzuki and P. Wipf, *Tetrahedron*, 2004, **60**, 1267.

3 (*a*) R. F. Jordan, *J. Mol. Catal. A: Chem*., 1998, **128**, 1; (*b*) W. E. Piers, *Chem.-Eur. J*., 1998, **4**, 13 and references therein.

4 E.-I. Negishi, K. Akiyoshi, B. O'Connor, K. Takagi and G. Wu, *J. Am. Chem. Soc*., 1989, **111**, 3089.

5 T. Takahashi, T. Seki, Y. Nitto, M. Sabura, C. J. Rousset and E.-I. Negishi, *J. Am. Chem. Soc*., 1991, **113**, 6266.

6 (*a*) A. H. Hoveyda, J. P. Morken, A. F. Houri and Z. Hu, *J. Am. Chem. Soc*., 1992, **114**, 6692 and references therein; (*b*) T. Takahashi, N. Suzuki, M. Kageyana, Y. Nitto, M. Saburi and E.-I. Negishi, *Chem. Lett*., 1991, 1579.

7 (*a*) K. S. Knight and R. M. Waymouth, *J. Am. Chem. Soc*., 1991, **113**, 6268; (*b*) D. P. Lewis, P. M. Muller, R. J. Whitby and R. U. H. Jones, *Tetrahedron Lett*., 1991, **32**, 6797; (*c*) C. J. Rousset, E.-I. Negishi, N. Suzuki and T. Takahashi, *Tetrahedron Lett*., 1992, **33**, 1965.

8 G. J. Gordon and R. J. Whitby, *Chem. Commun*., 1997, 1321.

9 S. F. Fillery, G. J. Gordon, T. Luker and R. J. Whitby, *Pure Appl. Chem*., 1997, **69**, 633.

10 (*a*) A. N. Kasatkin and R. J. Whitby, *Tetrahedron Lett*., 1997, **38**, 4857; (*b*) A. Kasatkin and R. J. Whitby, *J. Am. Chem. Soc*., 1999, **121**, 7039.

11 (*a*) A. N. Kasatkin and R. J. Whitby, *Tetrahedron Lett*., 1999, **40**, 9353; (*b*) A. N. Kasatkin and R. J. Whitby, *Tetrahedron Lett*., 2000, **41**, 6211; (*c*) A. N. Kasatkin and R. J. Whitby, *Tetrahedron Lett*., 2000, **41**, 6201; (*d*) A. N. Kasatkin and R. J. Whitby, *Tetrahedron*, 2003, **59**, 9857.

12 (*a*) K. Takagi, C. J. Rousset and E.-I. Negishi, *J. Am. Chem. Soc*., 1991, **113**, 1440; (*b*) Complex **9** has been characterized by X-ray diffraction: R. Choukroun, J. Zhao, C. Lorber, P. Cassoux and B. Donnadieu, *Chem. Commun*., 2000, 1511.

13 N. Etkin, A. J. Hoskin and D. W. Stephan, *J. Am. Chem. Soc*., 1997, **119**, 11420.

14 N. Etkin, M. C. Fermin and D. W. Stephan, *J. Am. Chem. Soc*., 1997, **119**, 2954.

15 K. I. Gell and J. Schwartz, *Inorg. Chem*., 1980, **19**, 3206.

16 G. Erker, P. Czisch, R. Mynott, Y. H. Tsay and C. Krüger, *Organometallics*, 1985, **4**, 1310.

17 H. J. R. de Boer, O. S. Akkermann, F. Bickelhaupt, G. Erker, P. C. Czisch, R. Mynott, J. M. Wallis and C. Krüger, *Angew. Chem., Int. Ed. Engl*., 1986, **25**, 639.

18 A. Gudina, A. Igau, B. Donnadieu and J. P. Majoral, *J. Org. Chem*., 1996, **61**, 9585.

19 T. Luker, R. J. Whitby and M. Webster, *J. Organomet. Chem*., 1995, **492**, 53.

20 Y. Miquel, A. Igau, B. Donnadieu, J. P. Majoral, N. Pirio and P. Meunier, *J. Am. Chem. Soc*., 1998, **120**, 3504.

21 Y. Miquel, V. Cadierno, B. Donnadieu, A. Igau and J. P. Majoral, *Organometallics*, 2000, **19**, 54.

22 V. Cadierno, A. Igau, B. Donnadieu, A. M. Caminade and J. P. Majoral, *Organometallics*, 1999, **18**, 1580.

23 V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau and J. P. Majoral, *Organometallics*, 1999, **18**, 1882.

24 For a review, see: (*a*) A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993; (*b*) For recent examples, see: M. T. Reetz, E. Bohres and R. Goddard, *Chem. Commun*., 1998, 935; (*c*) R. W. Reed, B. Santarsiero and R. G. Cavell, *Inorg. Chem*., 1996, **35**, 4292.

25 See, for example: (*a*) R. Schwesinger and H. Schlemper, *Angew. Chem., Int. Ed. Engl*., 1987, **26**, 1167; (*b*) R. Link and R. Schwesinger, *Angew. Chem., Int. Ed. Engl*., 1992, **31**, 850 and references therein.

26 The second major route to the iminophosphoranes is the Kirsanov reaction; see ref. 24.

27 For X-ray structures of phosphazides see: (*a*) M. Alajarin, P. Molina, A. Lopez-Lazaro, C. Foces-Foces and C. Fernandez-Castano, *Tetrahedron*, 1996, **52**, 9629; (*b*) J. R. Goerlich, M. Farkens, A. Fischer, P. G. Jones and R. Schmutzler, *Z. Anorg. Allg. Chem*., 1994, **620**, 707; (*c*) A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, M. P. Ponomarchuk, L. F. Kasukhin and V. P. Kukhar, *Zh. Obshch. Khim*., 1992, **62**, 2675; (*d*) C. G. Ghidester, J. Smuszkovicz, D. J. Duchamp, L. G. Laurian and J. P. Freeman, *Acta Crystallogr., Sect. C*, 1988, **44**, 1080; (*e*) A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, I. E. Boldeskul, M. P. Ponomarchuk, L. F. Kasukhin and V. P. Kukhar, *Zh. Obshch. Khim*., 1984, **54**, 1979.

28 (*a*) G. L. Hilhouse and B. L. Haymore, *J. Organomet. Chem*., 1978, **162**, C23; (*b*) G. L. Hilhouse, G. V. Goeden and B. L. Haymore, *Inorg. Chem*., 1982, **21**, 2064; (*c*) K. Bieger, G. Bouhadir, R. Réau, F. Dahan and G. Bertrand, *J. Am. Chem. Soc*., 1996, **118**, 1038.

29 (*a*) K. W. Chiu, G. Wilkinson, M. Thornton-Pett and M. Hursthouse, *Polyhedron*, 1984, **3**, 79; (*b*) T. Luker, R. J. Whitby and M. Webster, *J. Organomet. Chem*., 1995, **492**, 53; (*c*) Recently, it was also demonstrated that azides add smoothly, and without loss of N_2, to a polarized metal–metal bond in an early/late heterobinuclear complex, with formation of a bridging imido complex: T. A. Hanna, A. M. Baranger and R. G. Bergman, *Angew. Chem., Int. Ed. Engl*., 1996, **35**, 653.

30 V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J. P. Majoral and A. Skowronska, *Chem.-Eur. J*., 2000, **6**, 346.

31 Y. Miquel, A. Igau, B. Donnadieu, J. P. Majoral, L. Dupuis, N. Pirio and P. Meunier, *Chem. Commun*., 1997, 279.

32 K. Owsianik, M. Zablocka, B. Donnadieu and J. P. Majoral, *Angew. Chem., Int. Ed*., 2003, **42**, 2176.

33 E. Ortega, N. Pirio, P. Meunier and B. Donnadieu, *Chem. Commun*., 2004, 678.