Zirconium Spirophosphanes

Metalla-Azaspirophosphanes: Synthesis, Structure, and Reactivity**

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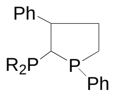
Zirconium derivatives play central roles in a number of technologically important processes including, for example, the Ziegler–Natta-type polymerization of olefins.[1] The group IV metallocene derivatives have been the target of a range of studies directed either at the generation and trapping, or the isolation of a large number of significant species in organic and organometallic chemistry. A number of new methodologies in synthesis has been found that give easy access to useful starting materials, such as various heterocycles, chiral ligands, or more sophisticated molecules. Indeed the success of organozirconium reagents in organic, inorganic, and organometallic chemistry can be explained in terms of chemo-, regio-, diastereo-, and enantioselectivity. These reagents are generally able to discriminate between similar functionalities that differ only slightly in their steric and/or electronic environment.[2] However, studies of interactions between main-group elements and, more precisely, phosphorus derivatives and zirconium compounds have not been so frequently reported.[3,4] We recently reported the formation of mono- or tricyclic diphosphanes by exchange reactions between monochlorophosphanes or dichlorophosphanes and, for example, the zirconaindane phospholane (phospholanozirconaindane) **1** to obtain compounds **2** and **3** in good yields[5,6] and even in an enantiomerically pure form for one of these derivatives.[7] Functionalization of these ligands and their grafting on polymer supports or on dendrimers should open up interesting perspectives in catalysis. At first glance, an easy method of functionalization may involve the direct reaction of **1** with trichlorophosphane oxide or sulfide in order to synthesize monohalogenated tricyclic ligands such as **4**. However treatment of **1** with (S)PCl$_3$ or (O)PCl$_3$ gave numerous phosphorus species, as attested by the complexity of ^{31}P NMR spectra of the resulting mixtures. Unexpectedly, an unprecedented reaction was observed when **1** was treated with the trichloro iminophosphorane **5** leading to the first metallaspirophosphane **6**. We report here the full characterization of this unique compound including X-ray diffraction studies. The extension of this surprising reaction to the synthesis of another metalla-azaspirophosphane is described, as well as details concerning the mechanism of formation of these species and preliminary results concerning their reactivity.



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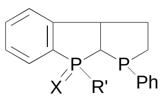
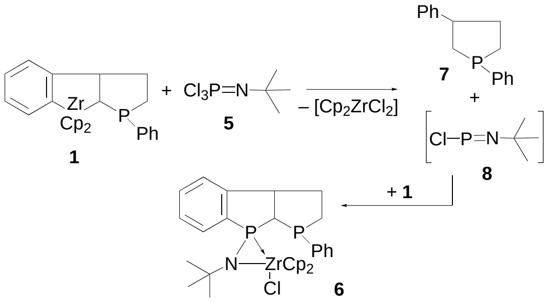


3 X = lone pair; R' = alkyl, NR$_2$, ...
4 X = O, S; R' = Cl

Treatment of the zirconaindane phospholane **1** (2 equiv) with Cl$_3$P=N−*t*Bu (**5**; 1 equiv) in toluene at room temperature resulted in the formation of two phosphorus species **6** and **7** and [Cp$_2$ZrCl$_2$] (Scheme 1, Cp = η^5-C$_5$H$_5$). The ^{31}P {^{1}H} NMR spectrum of **6**, which was isolated in 52 % yield, exhibits two doublets at $\delta = 3.7$ and 1.1 ppm ($^2J_{PP} = 22.4$ Hz), while a signal at $\delta = -10$ ppm is attributed to the phospholane **7**.[8] In addition to the signals from the carbon–phosphorus tricyclic



Scheme 1. Synthesis of the zircona–azaspirophosphane **6.** Solvent and conditions: toluene, 0 °C, 30 min.

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backbone and from the *tert*-butyl group linked to the nitrogen atom, two doublets are detected at $\delta = 6.05$ ($J_{HP} = 1.7$ Hz) and 6.09 ppm ($J_{HP} = 1.7$ Hz) in the ^{1}H NMR spectrum of **6**, which are characteristic of coupling of the cyclopentadienyl protons with a phosphorus atom when a direct phosphorus–zirconium bond is formed.[9,10] Other ^{1}H NMR data as well as ^{13}C NMR data are in agreement with the proposed structure for **6**, the first metalla-azaspirophosphane derivative reported to date. The solid-state structure of **6** has been corroborated by a single-crystal X-ray diffraction study.[11] An ORTEP diagram of **6** is shown in Figure 1 with selected bond lengths and angles.

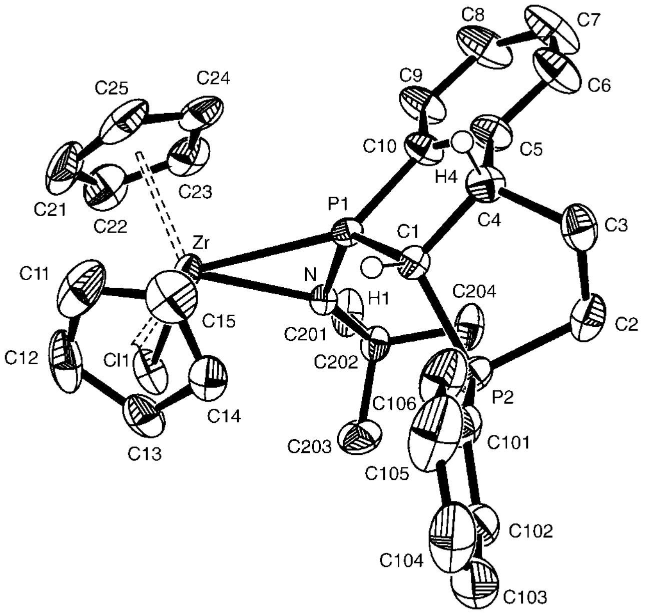
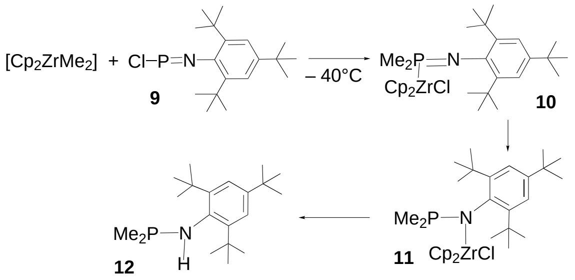


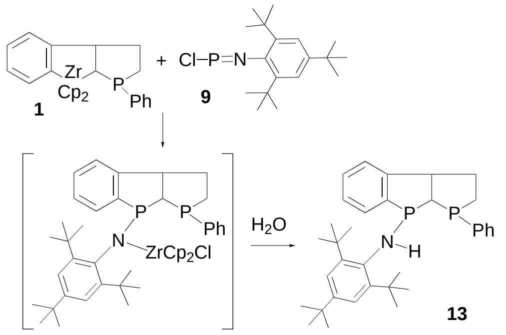
Figure 1. ORTEP drawing of complex **6**. Selected bond lengths [Å] and angles [°]: Zr-N 2.204(2), Zr-P(1) 2.5805(9), P1-N 1.615(2), P1-C1 1.865(2), P1-C10 1.807(3); N-Zr-P1 38.44(5), N-P1-Zr 58.05(7), P1-N-Zr 83.51(9), C10-P1-C1 92.9(12), N-P1-C1 123.54(11).

As a first approach, one can postulate that the trichloro iminophosphorane **5** reacts with the first equivalent of **1** (with removal of [Cp_2ZrCl_2]) to form the transient chlorophospha-imine Cl−P=N−*t*Bu (**8**), which reacts further with the second equivalent of **1** by insertion into an intracyclic Zr−C bond with concomitant migration of the chlorine atom from the phosphorus to the zirconium center. Rearrangement then leads to the stable 18 electron metalla-species **6**. Such an assumption is supported by previous work[10] in which the reaction of an analogous chlorophospha-imine **9** with [Cp_2ZrMe_2] was reported. In this latter experiment the reaction proceeded by insertion of **9** into a Zr−Me bond followed by migration of the chlorine atom from the phosphorus to zirconium center and concomitant migration of the second methyl group in the opposite direction to give the kinetic product **10**, with the reaction observed only at −40 °C. Migration of a {Cp_2ZrCl} fragment to nitrogen occurred, which led to the thermodynamic product **11** which is extremely water-sensitive and gave the final amino phosphane **12** through cleavage of the nitrogen–zirconium bond (Scheme 2).



Scheme 2. Addition of the chloro iminophosphane **9** to [Cp_2ZrMe_2].

In order to provide additional arguments in favor of the mechanism involving **1** and **5**, **1** was reacted with the stable chlorophospha-imine **9** in a 1:1 ratio in toluene at 0 °C. Such a reaction allowed the isolation of the bisphosphane **13**, obtained as only one isomer, and arising from the insertion of **9** into a zirconium–carbon bond of **1** with release of a {Cp_2ZrCl} fragment after mild hydrolysis of the nitrogen–zirconium bond (Scheme 3). Indeed, this experiment corroborates the proposed mechanism for the formation of **6** in which the trapping of an analogous chlorophospha-imine is postulated.

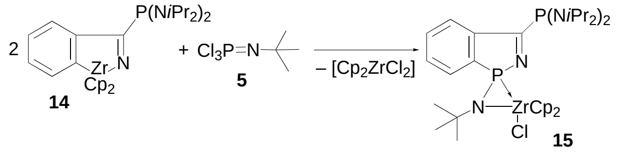


Scheme 3. Addition of the chloro iminophosphane **9** to the tricyclic system **1**.

As well as representing the preparation of an unique metalla-azaspirophosphane, these preliminary experiments show that in the presence of **1**, the trichloro iminophosphorane **5** can be regarded as a precursor of the unstable chlorophospha-imine **8**, a potentially useful new reagent in organophosphorus chemistry.

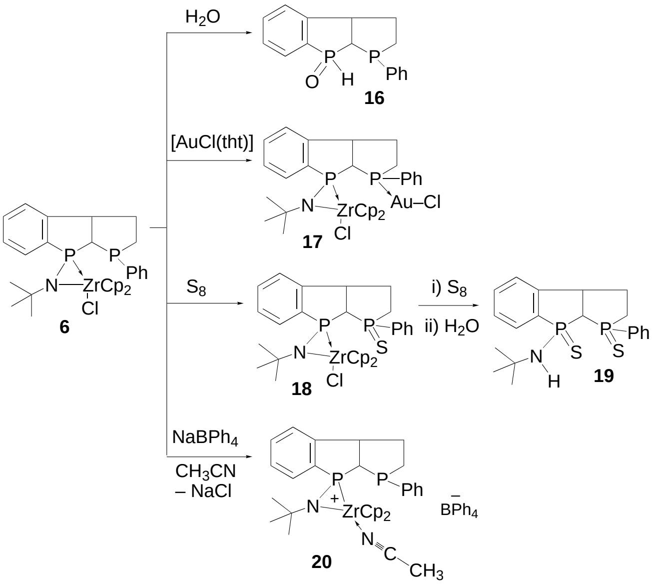
A question remains: Is it possible to generalize such a reaction? In other words, can other zircona complexes act in a similar fashion to **5**? To answer this question, the azazirconacyclopentene **14**[12] (2 equiv) was heated at 50 °C for 2 h in the presence of **5** (1 equiv); in these conditions the expected metalla-bisazaspirophosphane **15** was isolated in 49 % yield (Scheme 4). Therefore, the presence of a N-Zr-C linkage in the starting reagent **14**, instead of the C-Zr-C unit in **1**, does not prevent the reaction from taking place.

Such unusual complexes offer the opportunity to study their versatile behavior since several possible reactions can be



Scheme 4. Synthesis of the zircona-bisazaspirophosphane **15**.

envisaged, including regiospecific reactions on one or both of the phosphorus atoms, selective cleavage of P–N or P–Zr bonds, and specific reactions at the zirconium center. Preliminary results obtained from experiments conducted with the metalla-azaspirophosphane **6** are shown in Scheme 5.



Scheme 5. Reactivity of the zircona-azaspirophosphane **6**.

Indeed, several observations can be made. Hydrolysis occurred, as expected, at the "central" phosphorus moiety with concomitant P–N and P–Zr bond cleavage that led to a new tricyclic ligand **16**, obtained as two isomers (*cis* and *trans* with respect to the position of the substituents on phosphorus atoms, that is, the proton and the phenyl group) in a 9:1 ratio and characterized by ^{31}P NMR (major product: $\delta = 3.4$ (br d, $^2J_{PP} = 143$ Hz, PPh) and 51.3 ppm (d of br d, $^2J_{PP} = 143$ Hz, $^1J_{PH} = 488$ Hz, PN); minor product: $\delta = -7.9$ (br d, $^2J_{PP} = 53$ Hz, PPh) and 37.4 ppm (d of br d, $^2J_{PP} = 53$ Hz, $^1J_{PH} = 488$ Hz, PN)), ^{1}H and ^{13}C NMR spectroscopy, as well as by mass spectrometry. Addition of [AuCl(tht)] (tht = tetrahydrothiophene) to **6** occurred at the phospholane ring, that is, on the external trivalent phosphorus atom, to form a unique bimetallic complex **17**. Treatment of **6** with two equivalents of sulfur initially afforded the derivative **18** resulting from sulfuration of the "external" phosphorus atom. The reaction can be monitored by ^{31}P NMR (doublets at $\delta = 60.3$ (P(S)Ph) and -0.5 ppm (PN) with $^2J_{PP} = 26$ Hz). Sulfuration of the central phosphorus moiety then occurred with cleavage of the dative P–Zr bond followed by mild hydrolysis of the N–Zr bond to form the disulfide adduct **19**, which was obtained as two isomers in a 9:1 ratio (major product: $\delta = 57.9$ (d, PPh) and 67.8 ppm (d, PN) with $^2J_{PP} = 7.8$ Hz; minor product: 57.5 (d, PPh) and 65.5 ppm (d, PN) with $^2J_{PP} = 4.4$ Hz). Dissociation of the strong zirconium–chlorine bond and retention of the ring system was observed when NaBPh$_4$ was added to a solution of **6** in acetonitrile. ^{31}P NMR spectra show the disappearance of the two doublets that arise from complex **6**, and two new doublets at $\delta = 4.4$ (PN) and 6.3 ppm (PPh) with $^2J_{PP} = 32$ Hz. Proof of ring retention is given by a small coupling constant ($J_{HP} = 1.5$ Hz) in the ^{1}H NMR spectrum that results from interactions between cyclopentadienyl protons and the phosphorus center. However, the resulting new cationic zirconium azaspirophosphane **20** is highly unstable and decomposes to several unidentified products. Indeed, the presence of P–Zr and N–Zr bonds does not significantly help in the stabilization of **20**. Nevertheless a specific reaction at the zirconium center can be emphasized at this stage.

In conclusion, the reaction of a trichloro iminophosphorane with two different zirconaindane complexes led to unique metallaspirophosphanes. The extension of such a methodology to other trichloro iminophosphoranes and to other zirconium complexes should provide a range of new metallaspirophosphanes; their versatile behavior would allow the preparation of useful reagents for organometallic chemistry and catalysis.

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[8] The phospholane **7** was isolated and characterized as its sulfide adduct. Main characteristic data: $^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz): $\delta = 55.1$ ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.6 MHz): $\delta =$ 29.8 (d, $^{1}J_{CP} = 66.8$ Hz; CH_2P), 32.7 (d, $^{2}J_{CP} = 3.7$ Hz; CH_2), 37.5 (d, $^{1}J_{CP} = 66.5$ Hz; CH_2P), 45.3 (d, $^{2}J_{CP} = 11.6$ Hz; CH), 126.7 (s), 127.0 (s), 128.8 (s), 128.9 (d, $J_{CP} = 11.1$ Hz; *o*-Ph or *m*-Ph), 129.9 (d, $J_{CP} = 9.8$ Hz; *m*-Ph or *o*-Ph), 131.9 ppm (s, *p*-Ph).

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