Phosphorus Ligands

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Access to Phosphorus-Rich Zirconium Complexes**

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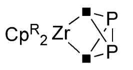
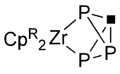
Dedicated to Professor John F. Nixon on the occasion of his 75th birthday

Activation and transfer of small molecules is a current research area in chemistry. Among the numerous target molecules, the interest in those containing phosphorus is substantial.[1] Recent developments of transfer reagents make use of Nb and to some extent W complexes to transfer P_2, P_3, and $P_n(CR)_m$ moieties to other transition metals or to generate novel phosphorus-rich cage compounds.[2]



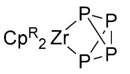
A

Cp^R = Cp



B

■ = C*t*Bu

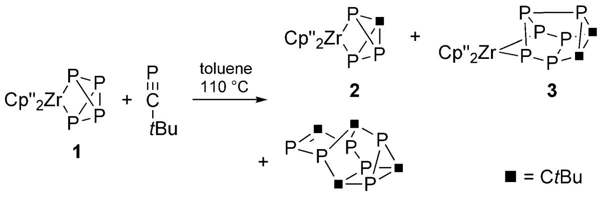


C

Cp^R = Cp''

Looking closer in this field, the roots of phosphorus-containing transfer reagents go back to early developments of Binger and Regitz, who obtained the diphosphabicyclobutane zirconium complex **A** in 1987 by reaction of "Cp_2Zr" with *t*BuC≡P.[3] They demonstrated the use of **A** as a starting material for the synthesis of unprecedented molecules such as tetraphosphacubane[4] and numerous P,C cage compounds[5,6] under halogenation conditions. Later, Francis et al. contributed by showing that this starting material is useful for creating nido-type cage compounds of main-group elements.[7] Recently, Russell et al. used **A** as a starting material by reacting with element halides of Group 15 elements to form square-pyramidal cationic $[EP_2(CtBu)_2]^+$ (E = P, As) moieties,[8–10] and unexpected neutral P,C[11] and P,C heteroelement cages,[12] to find unusual pathways to triphospholyl anions.[13,14] In contrast, the all-phosphorus analogue of **A**, the tetraphosphacyclobutane complex **C**, which was synthesized in 1988 by Scherer et al.,[15] has to date not been used for subsequent reactions. One reason might be its limited stability; it is only stable if Cp'' (Cp'' = η^5-$C_5H_3tBu_2$-1,3) is present as auxiliary ligand. Even for Cp* ligands, this compound decomposes at room temperature. In contrast, no evidence has yet been reported on the existence of the corresponding triphospha derivative **B**. However, by using **C** as starting material in the reaction with *t*BuC≡P, we found a straightforward synthesis to this triphosphabicyclobutane derivative **B** and other phosphorus-rich organic molecules, which will in future be new synthetic tools for Zr-mediated transfer reactions.

When **1** and *tert*-butylphosphaalkyne are allowed to react in boiling toluene for four days, the ^{31}P NMR spectrum of the reaction mixture shows an absence of the two triplets of **1**, whereas the triplet and the doublet of the major product $[Cp''_2Zr(\eta^2\text{-}P_3CtBu)]$ (**2**) emerge among the signals of the cage compounds **3** and **4** [Equation (1)].



1 **2** **3** **4**

(1)

The brown compound **3** crystallizes from the reaction mixture in moderate yields. Compound **2** can be separated from **3** by column chromatography, which however leads to a decrease of its yield. Compound **4** crystallizes as single crystals from this fraction and the residue contains almost pure **2**. Unfortunately, numerous attempts to obtain single crystals of **2** that were suitable for X-ray structural analysis failed as yet. However, the red, crystalline bis(di-tert-butylcyclopentadienyl)-1,2,4-triphospha-bicyclo[1.1.0]butane-2,4-diylzirconium complex **2** could be characterized without doubt by ^{31}P NMR spectroscopy and mass spectrometry.[16] In the ^{31}P NMR spectrum of **2**, an A_2X spin system is evident with one doublet at 179.7 ppm and a triplet at −236.5 ppm in an integration ratio of 2:1; both signals show a ^1J(P,P)

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Supporting information for this article, including complete synthesis and spectroscopic details for **2**–**4** and **6**, crystallographic details and complete details and references for the DFT calculations, is available on the WWW under http://dx.doi.org/10.1002/anie.201103634.

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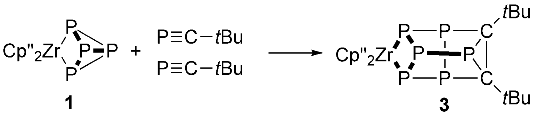
coupling of 185 Hz. As the ^{31}P NMR spectroscopic data of **2** are very similar to those of **1** (A_2X_2 spin system with two triplets at 173.7 and −205.1 ppm, with a coupling constant of ^1J(P,P) = 203 Hz)[15] as well as [$Cp_2Zr\{P_2(CtBu)_2\}$] (singlet at −247 ppm),[3] it can be concluded that **2** possesses the structure of isomer **B**. Furthermore, FD mass spectroscopy shows the molecular ion peak of **2** at *m/z* 606 with the correct isotope pattern. Transition metal complexes containing a triphosphabicyclo[1.1.0]butane ligand such as in **2** have not been reported; however, a few uncoordinated triphosphabicyclo[1.1.0]butanes with organic substituents $RP_3CR'_2$ (R = $tBu_3C_6H_2$, $(Me_3Si)_2CH$, $(Me_3Si)_2NN(SiMe_3)$; R′ = Me_3Si)[17] are known.

The formation pathway for **2** is not clear, but it is possible that **1** eliminates a P_2 unit and the formed unsaturated zirconium complex reacts with *t*BuC≡P to give **2**. The eliminated P_2 units react with *t*BuC≡P to give carbon–phosphorus cage compounds such as **4**, which represents a tetramer of *t*BuC≡P extended by one P_2 moiety. Interestingly, all of the isolated products are formed in an almost equimolar ratio as found in the ^{31}P NMR of the crude reaction mixture. Moreover, **3** can be viewed as an addition product of two molecules of phosphaalkyne to the starting material **1** (Scheme 1). To shed light into the reaction pathway, the arsenic complex [$Cp''_2Zr(\eta^2\text{-}As_4)$] was reacted with *t*BuC≡P to give a mixture of products. To date, crystals of an arsenic analogue of **3** could be isolated, and its X-ray structure shows clearly the occupancy of phosphorus in striking distance to the carbon atoms. This result shows that insertion of the phosphaalkyne occurs in a P–P and As–As bond, respectively, of the bridge-head atoms not bound to Zr.



Scheme 1. Proposed formation of **3** by addition of two phosphaalkyne units to **1**.

The brown crystals of [$Cp''_2Zr\{\eta^2\text{-}P_6(CtBu)_2\}$] (**3**) are readily soluble in common organic solvents, such as *n*-hexane and toluene. The ^{1}H NMR spectrum of **3** at room temperature shows four signals for the CH protons of the Cp″ ring and three signals for the *t*Bu groups. This inequivalence of the signals, combined with large differences in the chemical shifts of the Cp″ ring protons (5.50 and 7.29 or 5.32 and 7.95 ppm), lead to the assumption that Cp″ ring rotation is hindered. A similar behavior with an inequivalence of the protons of the Cp^R ring is observed in [$\{\eta^5\text{-}P_2(CtBu)_3\}CpZrCl_2$] as well as in [$\{\eta^5\text{-}P_3(CtBu)_2\}CpZrCl_2$].[18] The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a higher-order spectrum that could be simulated as an AA′MM′XY spin system.[16]

The main feature of the molecular structure of **3** is a ZrP_6C_2 core, which displays a cuneane-like structural motif (Figure 1).[16] This motif is sometimes found in polyphosphorus compounds, for example in Hittorf's phosphorus allotrope and some polyphosphorus complexes and compounds.[19] The cuneane structure is also calculated to be the minimum structure of a hypothetical P_8 molecule.[20] In **3**, the cuneane core is made up by six phosphorus atoms and two carbon atoms with the $ZrCp''_2$ fragment inserted into one P–P bond of the cuneane core; this core has bond lengths in the usual range of P–P, C–P, and C–C single bonds. The P–P bond lengths vary between 2.181(2) and 2.225(3) Å and are in the same range as the P–P bonds in the P_8 core of $(1,2\text{-}C_6H_4)_2P_8$[19d] or in the tricyclic compound [$(1,2\text{-}C_6H_4)_2H_2P_6\{W(CO)_5\}_4$].[21] The Cp″ ligands around the zirconium atom are in an antiparallel arrangement and face in different directions. That might explain the extreme differences in the chemical shifts for the CH protons attached to the Cp″ rings. The CH group of the top ring faces towards the P_6C_2 cage and is strongly influenced by the lone pair of the phosphorus atom P2 (Figure 1), whereas the HCCH unit of the Cp ring faces in a different direction. For the bottom ring, the situation is the other way round, but it does not interact with the lone pair of the phosphorus atoms. If the rings cannot rotate freely, which is more likely due to the steric repulsion of the bulky *t*Bu substituents, the protons are fixed in very different magnetic environments, and thus show large differences in their chemical shifts.

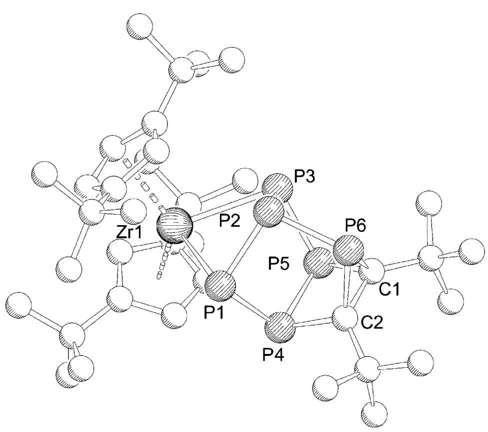
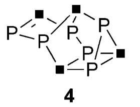
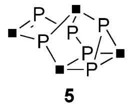


Figure 1. Molecular structure of **3** in the solid state (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Zr1–P1 2.6911(19), Zr1–P3 2.699(2), P1–P4 2.193(2), P1–P2 2.210(3), P2–P6 2.211(3), P2–P3 2.219(2), P3–P5 2.181(2), P4–C2 1.876(7), P4–P5 2.225(3), P5–C1 1.872(6), P6–C2 1.890(6), P6–C1 1.871(5), C1–C2 1.567(9); P1-Zr1-P3 76.85(6), Zr1-P1-P2 81.79(7), Zr1-P1-P4 97.66(8).

Like **2**, the yellow plates of **4** show high solubility in all common organic solvents. The ^{31}P NMR of **4** exhibits a higher-order spectrum that could be simulated as an ADEFPQ spin system.[16]



4



5

■ = C*t*Bu

The molecular structure of **4** (Figure 2)[16] shows a framework that is similar to the carbon–phosphorus cage **3** with one *t*BuCP unit replacing the Cp''_2Zr fragment. However, the molecule contains four C*t*Bu groups instead of only two in **3**, and there are no vicinal C*t*Bu groups. Overall seven isomers

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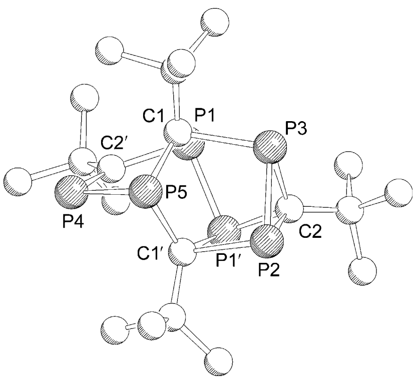
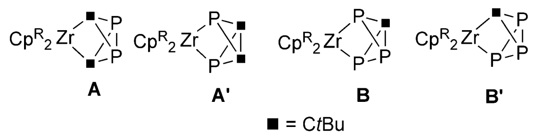


Figure 2. Molecular structure **4** in the solid state (hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: C2′–P4 1.713(5), P4–P5 2.235(3), P5–C1′ 1.849(5), C1′–P2 2.188(7), P2–C2 1.842(5), C2–P1′ 1.842(5), P2–P3 2.192(4), P3–C2 1.857(5), P1–P1′ 2.192(2), C1–P5 1.713(6), C1–P1 1.866(5).

of the formula $P_6(CtBu)_4$ have been described;[22] one of them (**5**) is closely related to the isomer **4**, which has now been discovered; both compounds differ in the position of the atoms P4 and C2′ in the C=P bond.[23] In **4**, the position of the *t*BuC group and phosphorus atom in the *t*BuC=P unit are interchanged with respect to **5**. As a result, **4** contains three P–P units, whereas **5** features only one P–P unit, one P–P–P chain, and an isolated P atom. Thus, the chemical shifts in the ^{31}P NMR spectrum differ slightly in **4** and **5**.[23] The P–P and P–C bonds in **4** are all within the range of normal single bonds, except for the P4–C2′ bond, which corresponds to a P=C bond (1.713(5) Å). In the solid state structure of **4**, an interesting disordering of the molecules is observed.[16] The molecule possesses a crystallographic twofold axis which goes through the P1–P1′ bond. Therefore, the phosphorus atoms P2, P3, P4, P5, the carbon atom C2, and two *t*Bu groups are disordered over two positions with occupation factors of 50%. Cages containing only phosphorus and C*t*Bu groups, such as the tetraphosphacubane $(PCtBu)_4$,[4] can also be obtained by oligomerization of neat *t*BuCP at higher temperatures[24] or by cyclooligomerization mediated by transition-metal complexes[25] as well as by CuI.[26]

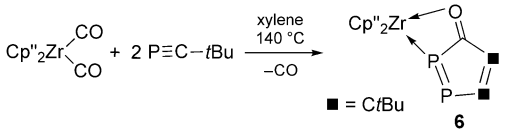
Moreover, it is very astonishing that so far only isomer **A** and not **A′** has been synthesized, and that we succeeded in synthesizing **B** and not **B′**. To shed light onto this problem, DFT calculations were carried out (Scheme 2).[16]



	A	A'	B	B'
Cp^R = Cp	0	7.1	0.03	0
Cp^R = Cp"	72.2	0	0	45.5

Scheme 2. Relative energies of the isomers in kJ mol^{-1}, depending on the Cp^R ligand at the Zr atom (B3LYP/pVDZ level of theory; ECP on Zr).

Whereas the formation of **B** and **B′** is almost energetically equivalent for the case of the Cp ligand (the energy difference between isomers is only a minuscule 0.03 kJ mol^{-1}), for the Cp″ ligand isomer **B** is more stable by 45 kJ mol^{-1} (in agreement with experimental isolation of **B** and not **B′**). Isomer **A** is slightly (by 7 kJ mol^{-1}) favored by the Cp ligand; however, if the Cp″ ligand is present at the Zr atom, the formation of the unknown isomer **A′** is strongly favored over isomer **A** (by 72 kJ mol^{-1}). To investigate this result, we treated $[Cp''_2ZrCl_2]$ with *t*BuC≡P after reducing the Zr complex. Indeed it was possible to detect the expected compound **A′** by NMR spectroscopy. The ^{31}P NMR chemical shift is found at 185.5 ppm, which corresponds well to those of **1** (+173.7 ppm) and **2** (+179.1 ppm) for the Zr bound P atoms. Although **A′** was one of the major products out of numerous formed products in this reaction, its isolation failed.[27] An interesting hint for the possibility of its formation was found when $[Cp''_2Zr(CO)_2]$ was reacted with *t*BuC≡P [Equation (2)]. The blue-green product **6** has a diphosphacyclopentadienone ligand, which is bound by P and O at the Zr moiety as a consequence of head-to-head coupling of the phosphaalkyne in which a CO molecule is inserted into a P–C bond of the phosphaalkyne. Also in this case, the zirconium-bound P atom shows a ^{31}P NMR chemical shift at 153.8 ppm, with a large P,P coupling constant of 430 Hz, which is in accordance with the P=P bond found in the X-ray structure analysis.



(2)

In the molecular structure of **6** (Figure 3),[16] the five-membered ring of the novel ligand shows bonds in the usual range of P=P, C=P, and C=C double bonds, which indicates a delocalized π system over the five-membered ring. Both the

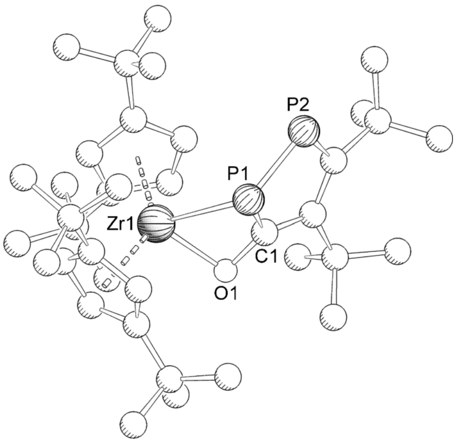


Figure 3. Molecular structure of **6** in the solid state (hydrogen atoms omitted for clarity). Selected bond lengths [Å]: Zr1–P1 2.6525(13), Zr1–O1 2.066(3), Zr1–C1 2.568(4), P1–P2 2.1139(16), P1–C1 1.785(4), P2–C3 1.769(4), O1–C1 1.364(5), C1–C2 1.418(5), C2–C3 1.436(6).

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oxygen outside of the ring as well as the P1 atom within the ring are coordinated by the Zr atom, with bond lengths in the expected range.[28] Owing to the coordination of the O atom, the C$=$O double bond is slightly elongated.

In summary, we have shown that the tetraphosphazirconocene derivative $[\mathrm{Cp''_2Zr(\eta^2\text{-}P_4)}]$ (**1**) and tBuC$\equiv$P are useful starting materials for the synthesis of novel phosphorus–carbon cage compounds. In contrast to known concepts, phosphorus-rich derivatives of these classes of compounds are obtained by this method. Based on this reaction, the novel complex $[\mathrm{Cp''_2Zr(\eta^2\text{-}P_3C}t\mathrm{Bu})]$ (**2**) as well as the cuneane-like complex $[\mathrm{Cp''_2Zr\{\eta^2\text{-}P_6(C}t\mathrm{Bu)_2\}}]$ (**3**) were synthesized; the latter can be regarded as an addition product of two tBuC$\equiv$P units at **1**. Compound **2** is the missing member **B** of the bicyclobutane zirconium complex family **A**–**C**. Moreover, synthetic evidence of another as yet unknown isomer **A′** by using $\mathrm{Cp''_2Zr}$ moieties hints at the possibility of tuning the steric influence of adjacent complex fragments to form previously unknown isomers. In light of the rich chemistry of **A** in the past, the novel phosphorus-rich zirconium derivatives **2** (type **B**) and **3** will no doubt play a decisive role in the future for zirconium-mediated transfer reactions to obtain novel P-rich complexes and main-group-element cages.

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