C–C Bond Formation

DOI: 10.1002/ange.201307493

1,1-Carbozirconation: Unusual Reaction of an Alkyne with a Methyl Zirconocene Cation and Subsequent Frustrated Lewis Pair Like Reactivity**

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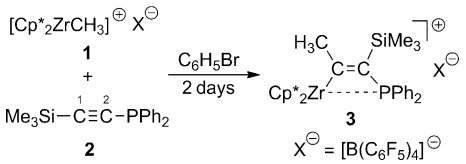
Methylzirconocene cations have been shown to be essential initial catalytic species in homogeneous single-site Ziegler–Natta olefin polymerization catalysis.[1,2] They are often formed in situ by treatment of various zirconocene complexes with methylalumoxane[3] or selectively produced through methyl anion abstraction from dimethylzirconocene by trityl cation[4] or $B(C_6F_5)_3$.[5] The $[^RCp_2ZrCH_3]^+$ cations typically then undergo consecutive olefin insertion reactions into the Zr–carbon σ bond to form a polymeric chain. This insertion reaction is a typical 1,2-addition reaction of the electron-deficient alkyl zirconocene species to the olefinic substrate.[2] The ubiquitous 1,2-insertion of the $[Zr]^+$-CH_3 moiety has also been observed for acetylenes,[6] so that it was considered to be the typical reaction mode of such [Zr]-C electrophiles with unsaturated organic substrates. We have now found a different reaction mode that a $[Zr]^+$-CH_3 species may undergo with an acetylenic substrate under mild reaction conditions, namely a 1,1-carbozirconation reaction.

We observed this prevailing alternative reaction mode when we treated the salt $[Cp^*_2ZrCH_3]^+[B(C_6F_5)_4]^-$ (Cp^* = pentamethylcyclopentadienyl) with diphenylphosphino(trimethylsilyl)acetylene (**2**). The cation **1** (Scheme 1) was



Scheme 1.

generated in situ from $[Cp^*_2Zr(CH_3)_2]$ by methyl abstraction with the corresponding trityl salt.[4] The reaction of **1** with **2** had gone to completion after 2 days at room temperature in bromobenzene and we isolated the unique 1,1-carbozirconation product **3** as a red crystalline solid in more than 80% yield (see Scheme 1).

Compound **3** shows a ^{31}P NMR resonance at $\delta = -6.8$ ppm. It features the typical downfield ^{13}C NMR signal

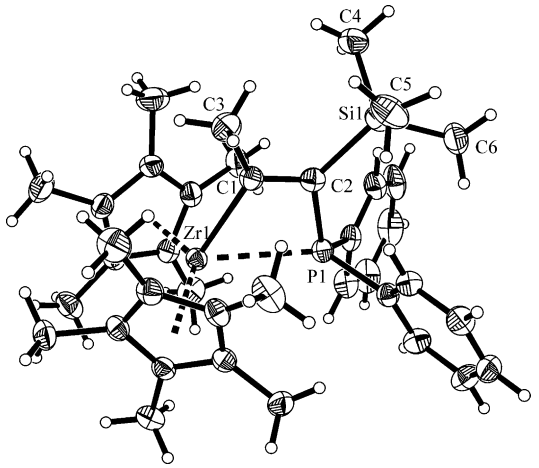


Figure 1. Molecular structure of the 1,1-carbozirconation product **3** (only the cation is depicted). Selected bond lengths [Å] and angles [°]: Zr1–C1 2.282(4), C1–C2 1.363(5), C1–C3 1.505(5), C2–P1 1.824(4), C2–Si1 1.920(4); Zr1-C1-C2 110.7(3), C1-C2-P1 107.9(3), Zr1-C1-C2-P1 −6.7(3).[20]

of the α-carbon atom of a substituted vinyl group at the zirconocene moiety [$\delta = 259.4$ ppm (d, $^2J_{PC} = 15.7$ Hz)][7] and the respective β-carbon atom resonance at $\delta = 122.8$ ppm (d, $^1J_{PC} = 15.5$ Hz). The salt **3** was characterized by X-ray diffraction. The X-ray crystal-structure analysis (Figure 1) confirmed the formation of this product by a unique 1,1-carbozirconation reaction. Apparently, the $[Cp^*_2ZrCH_3]^+$ reagent was added to carbon atom C1 of the acetylene **2**, thus inducing 1,2-migration of the trimethylsilyl group along the acetylene framework concomitant with shifting of the methyl substituent from zirconium to C1. Eventually, both the zirconocene unit and its former methyl substituent are found bonded to the same alkenyl carbon atom (C1) of the former acetylene moiety, and both the PPh_2 and $SiMe_3$ groups are found geminally bonded at C2. We note that the Cp^*_2Zr and PPh_2 substituents are found *cis*-vicinally positioned and there is an interaction between the zirconium Lewis acid and the phosphane Lewis base (P1···Zr1 2.768(1) Å).

This reaction type is often observed in borane chemistry (1,1-carboboration, the "Wrackmeyer reaction").[8] Recently, the use of strongly electrophilic $R-B(C_6F_5)_2$ reagents has markedly extended the scope and synthetic applicability of the conversion of alkynes into substituted alkenylboranes.[9–12] These alkenylboranes have been found to be useful moderated Lewis acids[13] and they have been used in subsequent cross-coupling reactions.[10,11] 1,1-Carboboration reactions of phosphanyl-substituted alkynes gave new vicinal B/P frus-

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[**] Financial support from the Alexander von Humboldt Stiftung (stipend to X.X.) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307493.

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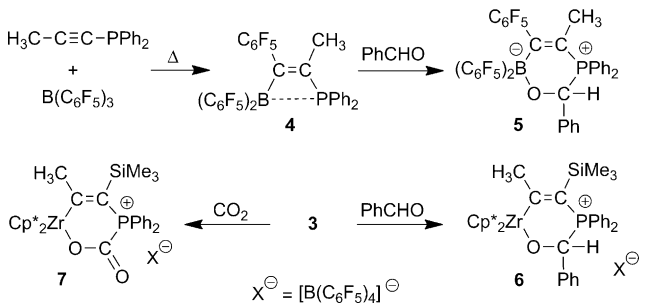


Scheme 2. Top: Typical 1,1-carboboration reaction and reactivity of the resulting FLP.[14] Bottom: Reactions of the 1,1-carbozirconation product **3**.

trated Lewis pairs (FLPs).[14] These typically undergo a variety of addition reactions to unsaturated substrates. Scheme 2 shows a typical example (**4**) that cleanly adds to benzaldehyde to form **5**.[14] This posed the question of whether our new $[Zr]^+$/P product **3** would undergo related FLP reactions. This turned out to be the case.

The zirconocene complex **3** reacted rapidly (1 h, room temperature) with benzaldehyde to give the $[Zr]^+$/P 1,2-addition product **6** (isolated in greater than 90% yield). It shows the typical downfield ^{13}C NMR signal of the Zr–alkenyl moiety [C1: $\delta = 266.2$ ppm, C2: $\delta = 122.9$ ppm (d, $^1J_{PC} = 47.8$ Hz)]. Owing to the newly introduced chiral center, we observed NMR signals for pairs of diastereotopic Cp* ligands at zirconium and phenyl substituents at phosphorus. The X-ray crystal-structure analysis of **6** shows a half-chair shaped six-membered heterocyclic core structure. The zirconium atom of the 1,1-carbozirconation product **3** has added to the carbonyl oxygen atom and the phosphane nucleophile has added to the carbonyl carbon atom of the reagent (for details and a view of the structure of complex **6** in the solid state, see the Supporting Information).

The 1,1-carbozirconation product **3** reacted similarly with carbon dioxide[15] to give the product **7** (see Scheme 2 and Figure 2). This product shows a carbonyl carbon NMR resonance at $\delta = 162.5$ ppm ($^1J_{PC} = 104.1$ Hz) and an IR $\tilde{\nu}$(C=O) band at 1686 cm^{-1}. The Zr-alkenyl C1 ^{13}C NMR signal occurs at $\delta = 268.4$ ppm [C2: $\delta = 126.6$ ppm (d, $^1J_{PC} = 27.8$ Hz)]. The X-ray crystal-structure analysis confirmed the 1,2-addition reaction of the $[Zr]^+$/P FLP to the CO_2 carbonyl group. The resulting product **7** contains an almost planar six-membered heterocyclic framework.

A number of vicinal boron/phosphorus systems have been shown to add to transition-metal complexes,[16] and so does the vicinal $[Zr]^+$/P system **3**. Its reaction with the (norbornadiene)RhCl dimer gave the bimetallic addition product **8**, which was isolated in approximately 65% yield as a yellow solid (Scheme 3). It shows the typical [Zr]-α-alkenyl ^{13}C NMR resonance [C1: $\delta = 242.6$ ppm (d, $^2J_{PC} = 49.1$ Hz); C2: $\delta = 139.7$ ppm (d, $^1J_{PC} = 26.1$ Hz)], a ^{31}P NMR signal at $\delta = 38.1$ ppm that features coupling to rhodium ($^1J_{RhP} = 161.7$ Hz), and a ^{29}Si NMR signal at $\delta = -5.1$ ppm (dd, $^2J_{PSi} = 11.4$ Hz, $^3J_{RhSi} = 1.3$ Hz). The X-ray crystal-structure analysis (Figure 3) revealed that the $[Zr]^+$/P pair of **3** had added across the Rh–Cl bond to give a bimetallic six-

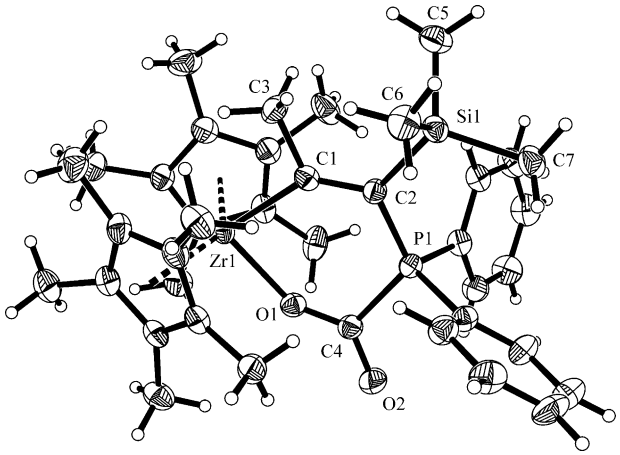
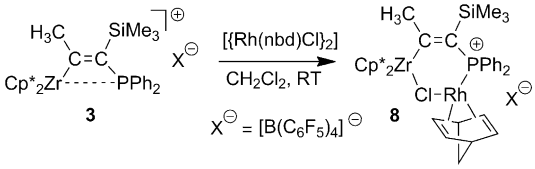


Figure 2. Molecular structure of the CO_2 addition product **7** (only the cation is shown). Selected bond lengths [Å] and angles [°]: Zr1–C1 2.304(5), Zr1–O1 2.081(3), O1–C4 1.278(6), C4–O2 1.205(6), C4–P1 1.885(5), P1–C2 1.787(5), C2–C1 1.369(7); O1-Zr1-C1 86.2(2), O1-C4-P1 117.0(4), C4-P1-C2 117.4(2).[20]



Scheme 3.

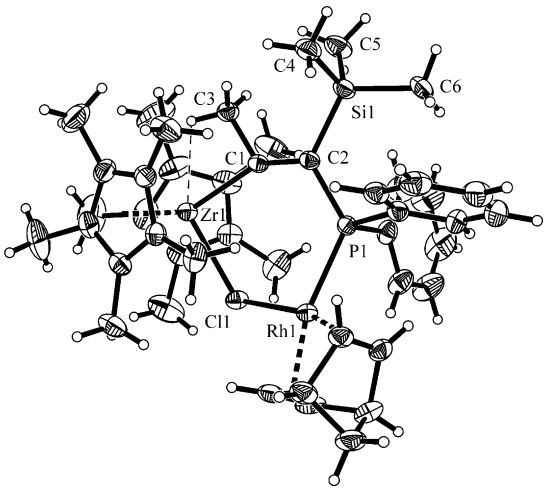


Figure 3. Molecular structure of the heterobimetallic Zr/Rh complex **8** (only the cation is shown). Selected bond lengths [Å] and angles [°]: Zr1–C1 2.258(3), C1–C2 1.362(5), C2–P1 1.831(3), P1–Rh1 2.331(1), Rh1–Cl1 2.363(1), Cl1–Zr1 2.536(1); Zr1-Cl1-Rh1 121.4(4), C1-Zr1-Cl1 91.5(1).[20]

membered heterocyclic core structure. The Rh atom is tetracoordinate and shows bonds to the phosphane of **3**, to the chloride now bridging between the early/late transition-metal pair, and to both norbornadiene C=C bonds.

Finally, we treated the $[Zr]^+$/P Lewis acid/Lewis base pair **3** with carbon monoxide (1.5 bar, CH_2Cl_2, room temperature).

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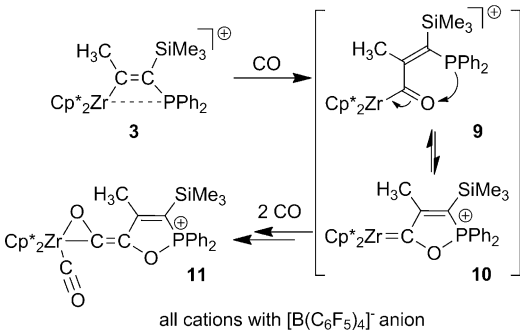

Scheme 4.

Under these conditions, complex **3** took up three molar equivalents of CO to form the product **11** (isolated in 74% yield). The X-ray crystal-structure analysis revealed that a (η^2-ketene)zirconocene complex had been formed. We assume that the reaction is initiated by CO insertion into the zirconium–carbon σ bond of **3** (Scheme 4)[17] followed by activation of the resulting acyl functionality by the zirconium Lewis acid and the phosphane Lewis base. This could lead to a reactive intermediate exhibiting a metallocene carbene complex character. Subsequent coupling with a CO molecule would lead to the observed (η^2-ketene)$ZrCp^*_2$ moiety, which would then be coordinatively stabilized by addition of another CO molecule. The Zr1–O3 bond is short, as is the Zr1–C4 linkage. The C3–C4 bond length in **11** is in the C=C bond range. The framework of compound **11** is close to planar (Figure 4).

Compound **11** shows a IR $\tilde{\nu}$(C≡O) band at 2094 cm^{-1}. The ^{13}C NMR signals of the C≡O and the conjugated η^2-ketene ligand were found at $\delta = 209.9$, 199.6, 163.7, 142.6 and 88.3 ppm (broad, $^1J_{PC} \approx 50$ Hz).

A number and variety of 1,1-carboboration reactions have been reported.[8–12] It is remarkable that there is now an example of a related reaction mode observed for a transition-metal system. The formation of the alkyne 1,1-carbozirconation product **3** probably profits from the strongly electrophilic character of the methyl zirconocene reagent, the migratory aptitude of the trimethylsilyl group, and last but not least the thermodynamically favorable internal PPh_2 coordination to zirconium in the product **3**. We nevertheless regard the formation of **3** by 1,1-carbozirconation as a remarkable reaction. The $[Zr]^+$/P system **3** itself shows reaction behavior similar to that of a variety of recently reported vicinal B/P frustrated Lewis pairs (1,2-addition to unsaturated compounds including CO_2, reaction with metal halides).[18] The CO coupling reaction that we observed at the "$[Zr]^+$/P FLP" framework is different because it probably involves CO insertion into a Zr–C bond, which is a typical transition-metal reaction pattern. The subsequent activation and coupling, however, apparently utilizes the interplay between the phosphane Lewis base and the adjacent zirconium Lewis acid. It remains to be seen whether such metal Lewis acid/main-group element Lewis base combinations[19] might lead to new reactions combining the typical features of both FLP and transition-metal chemistry.

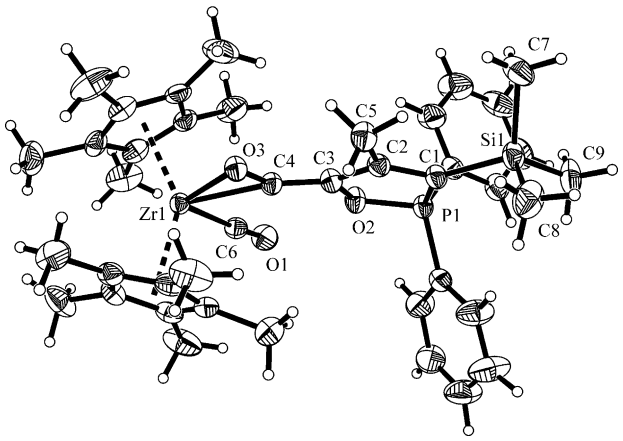

Figure 4. A view of the molecular structure of compound **11** (only the cation is shown). Selected bond lengths [Å] and angles [°]: Zr1–C4 2.207(4), Zr1–O3 2.163(3), Zr1–C6 2.262(5), C6–O1 1.131(6), C3–C4 1.351(6), C3–O2 1.450(5), O2–P1 1.589(3), P1–C1 1.737(5), C1–C2 1.389(6), C2–C3 1.428(6); Zr1-C4-O3 70.9(2), Zr1-C6-O1 175.8(4), Zr1-O3-C4 74.6(2), O3-C4-C3-O2 179.6(4).[20]

Received: August 26, 2013
Published online: November 12, 2013

Keywords: 1,1-carbozirconation · C–C coupling · frustrated Lewis pairs · phosphorus · zirconium

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[20] CCDC 963578 (**3**), 963579 (**6**), 963580 (**7**), 963581 (**8**), 963582 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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