Angewandte Chemie International Edition

Allylzinc Monocation

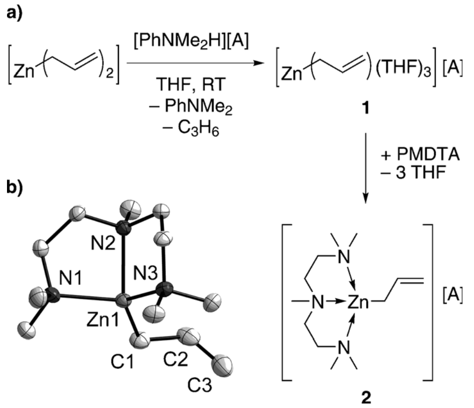
DOI: 10.1002/anie.201203698

Dimerization of the Allylzinc Cation: Selective Coupling of Allyl Anions in a Metallo-Ene Reaction**

*Crispin Lichtenberg, Thomas P. Spaniol, and Jun Okuda**

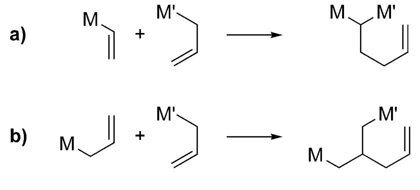
Cationic organometallic compounds of electropositive metals have been identified as key intermediates in important catalytic processes, such as (stereo)selective olefin oligomerization and (co)polymerization.[1] They also show unique reactivity patterns in stoichiometric reactions.[2] Thus, cationization as a means of controlling reactivity is well established for compounds of Lewis acidic tri- and tetravalent Group 3, 4, and 13 metals, and the lanthanoids.[1–3] In contrast, cationic organometallic complexes of nontoxic and abundant divalent Group 2 and 12 metals have only recently been described.[4–7] In the case of organozinc compounds, few monocations have been applied as selective catalysts in lactide,[6a,e,7b,d] lactone,[6d] and epoxide polymerization,[6d] as well as in hydrosilylations[6f] and hydroaminations.[6f] We report herein the isolation and full characterization of the allylzinc monocation, which—in contrast to its neutral parent compound bis(allyl)zinc—allows for efficient coupling of allyl anions in a highly selective metallo-ene reaction.

Reaction of bis(allyl)zinc with one equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ gave the allylzinc monocation $[Zn(C_3H_5)(THF)_3][B(C_6F_5)_4]$ (**1**) in quantitative yield (Scheme 1 a).[8] The colorless compound can be stored under inert gas atmosphere over months without decomposition. In the ^1H NMR spectrum of **1** in $[D_8]THF$ at ambient temperature, the allyl ligand gives rise to an A_2MNX pattern, which corresponds to an η^1 bonding mode. For the neutral parent compound bis(allyl)zinc, the η^1 bonding mode of the allyl ligands can only be detected at temperatures below −60 °C in THF solution.[9] Thus, the allyl exchange rate in cationic **1** is significantly decreased compared to bis(allyl)zinc. The allyl exchange in **1** is expected to proceed intermolecularly.[9,10] Notably, transformation of bis(allyl)zinc to **1** did not induce a change in the bonding mode of the allyl ligand from η^1 to η^3 which is in good agreement with the current understanding of zinc–allyl interactions.[10] The THF ligands in **1** are labile and reaction of **1** with pentamethyldiethylenetriamine (PMDTA) gave $[Zn(C_3H_5)(PMDTA)][B(C_6F_5)_4]$ (**2**) in 99 % yield (Scheme 1 a). The solid-state structure of **2** was investigated by single-crystal X-ray analysis. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The zinc center is found in a distorted tetrahedral coordination geometry without any direct interactions with the counterion (Scheme 1 b). The allyl ligand coordinates to the metal center in an η^1 bonding mode with the Zn−C bond being slightly shortened compared to the corresponding value in neutral allylzinc complexes, which is ascribed to the higher Lewis acidity of cationic **2**.[11]



Scheme 1. a) Synthesis of allylzinc monocations **1** and **2**; [A] = $[B(C_6F_5)_4]$. b) Molecular structure of cationic part of **2**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–C1 1.982(3), Zn1–N1 2.113(3), Zn1–N2 2.118(3), Zn1–N3 2.118(3), C1–C2 1.469(5), C2–C3 1.316(5); C1-Zn1-N1 116.13(13), C1-Zn1-N2 120.12(13), C1-Zn1-N3 125.90(13), N1-Zn1-N2 86.91(10), N1-Zn1-N3 111.53(11), N2-Zn1-N3 85.74(10), C1-C2-C3 127.5(4).

Neutral allylzinc species are key components in metallo-ene reactions between allyl and a vinyl anions (Gaudemar/Normant (G/N) coupling, Scheme 2 a).[12–15] This reaction combines a selective C−C bond formation with the formation of two synthetically useful metal–carbon bonds in the coupling product. The isolation and characterization of the dimetalated products or detailed experimental investigations of kinetic and thermodynamic parameters of this reaction have not been reported to date. In addition, the scope of the reaction concerning the metalated ene component is still limited to vinyl and allenyl metal compounds.



Scheme 2. General addition a) of an allyl metal compound to a vinyl metal compound and b) of an allyl metal compound to an allyl metal compound.

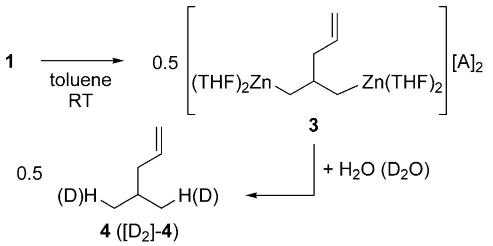
---

[*] Dipl.-Chem. C. Lichtenberg, Dr. T. P. Spaniol, Prof. Dr. J. Okuda
Institut für Anorganische Chemie, RWTH Aachen
Landoltweg 1, 52056 Aachen (Germany)
E-mail: jun.okuda@ac.rwth-aachen.de

[**] Generous financial support by Fonds der Chemischen Industrie (Kekulé scholarship to C.L.) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203698.

An exception to this are neutral allylzinc reagents, which have been reported to dimerize in extremely sluggish (108 days reaction time) or unselective (10 % dimer formation) reactions (Scheme 2 b),[16] the major side reaction being radical coupling of the allyl ligands with concomitant formation of Zn^0. The products of this reaction have never been isolated. We therefore set out to investigate the characteristics of the Lewis acidic allylzinc monocation **1** in metallo-ene reactions. Compound **1** is stable in THF solutions at ambient temperature. Addition of an aromatic hydrocarbon, such as toluene or benzene, to neat **1** gave an emulsion, from which the dimerization product **3** slowly precipitated as a colorless solid (Scheme 3). Quenching with H_2O or D_2O gave the expected (deuterated) 4-methyl-1-pentene **4** and 5,5′-$[D_2]$-**4**, respectively, which were identified by NMR spectroscopy and GC/MS. Notably, the dimerization of **1** proceeds with 100 % Markovnikov selectivity and the dimetalated product **3** was isolated in quantitative yield. This is the first well-defined metallo-ene reaction in which the metalated ene is not a vinyl or allenyl metal compound. The bis(PMDTA) derivative of compound **3**, $[\{Zn(PMDTA)CH_2)\}_2CHCH_2CH{=}CH_2][B(C_6F_5)_4]_2$ (**5**), was synthesized to obtain single-crystals for X-ray analysis (Figure 1). Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and both zinc centers adopt a distorted tetrahedral coordination geometry without any direct interactions with the counterions. Zn−C bonds in **5** are slightly shorter than that in **2** which was ascribed to the stronger electron-donating character of the alkyl ligands in **5** compared to the allyl group in **2**. Consequently, Zn−N bonds in **5** are slightly elongated compared to those in **2**. Compound **5** is the first product of a metallo-ene reaction between two metalated reagents that has been isolated and fully characterized.



Scheme 3. Dimerization of **1** in a metallo-ene reaction to give **3** and quenching of the dianionic hydrocarbon fragment with H_2O (D_2O) to give **4** (5,5′-$[D_2]$-**4**).

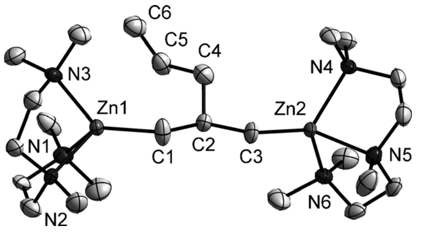


Figure 1. Molecular structure of dicationic part of **5**. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms are omitted for clarity. 1.5 equivalents of CH_2Cl_2 and 0.5 equivalents of pentane, that are present per formula unit, show no direct interactions with **5** and are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–C1 1.964(4), Zn1–N1 2.133(3), Zn1–N2 2.183(3), Zn1–N3 2.152(3), Zn2–C3 1.961(4), Zn2–N4 2.117(3), Zn2–N5 2.143(3), Zn2–N6 2.120(3), C1–C2 1.506(6), C2–C3 1.541(6), C2–C4 1.527(6), C4–C5 1.500(7), C5–C6 1.311(7); C1-Zn1-N1 128.64(17), C1-Zn1-N2 113.74(16), C1-Zn1-N3 118.90(18), N1-Zn1-N2 82.63(13), N1-Zn1-N3 110.67(14), N2-Zn1-N3 84.32(12), C3-Zn2-N4 122.42(16), C3-Zn2-N5 121.13(16), C3-Zn2-N6 120.68(17), N4-Zn2-N5 84.03(14), N4-Zn2-N6 111.50(13), N5-Zn2-N6 85.30(13).

To better understand the dimerization of **1**, the reaction was monitored by NMR spectroscopy under homogeneous conditions using CD_2Cl_2 as a weakly coordinating solvent. In an overall slow reaction, 50 % conversion was observed after 1 day and equilibrium conditions were reached after 9 days with 88 % conversion (Figure 2, left). This situation suggests the dimerization of **1** is reversible. The monomer/dimer ratio was increased at elevated temperature (50 °C) and reached the initially observed value again after few days at room temperature. This process was reversible (Figure 2, right). The reversibility of the dimerization of **1** was also observed in THF as a polar solvent at elevated temperatures.[17] Analysis of the kinetic data of the reaction in CD_2Cl_2 revealed the monomer/dimer equilibrium to be a second-order forward reaction (dimerization) opposed by a second-order reverse reaction (monomer formation). Rate constants of $k_f = (4.1 \times 10^{-4} \pm 1.7 \times 10^{-6})\ L\,mol^{-1}\,s^{-1}$ and $k_r = (8.7 \times 10^{-6} \pm 3.6 \times 10^{-8})\ L\,mol^{-1}\,s^{-1}$ were determined for these processes (see the Supporting Information).[18] The reversibility of metallo-ene reactions plays a crucial role for the α/γ-selectivity of such reactions.[12e] The thermodynamic parameters of this reaction are $\Delta H^{\ominus} = -(49.3 \pm 2.0)\ kJ\,mol^{-1}$ and $\Delta S^{\ominus} = -(103 \pm 7)\ J\,mol^{-1}\,K^{-1}$ as calculated from a van't Hoff plot in the range of 23 to 40 °C (see the Supporting Information).[19]

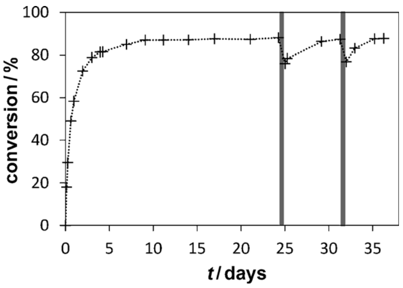
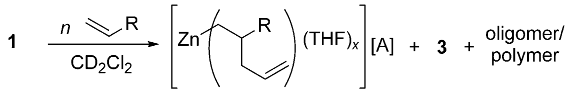


Figure 2. Time conversion plot for the reversible dimerization of **1** to give **3** in CD_2Cl_2 at room temperature; gray bars indicate periods of heating to 50 °C.

The methallylzinc monocation, $[Zn(\eta^1\text{-}CH_2(CMe)CH_2)(THF)_3]\ [B(C_6F_5)_4]$ (**6**), was synthesized to investigate whether the dimerization of allylzinc monocations is limited to parent compound **1**. Compound **6** dimerized smoothly upon addition of toluene in a slow reaction with 100 % Markovnikov selectivity. The dimer $[Zn_2(C_4H_7\text{-}2\text{-}C_4H_7)(THF)_6][B(C_6F_5)_4]_2$ (**7**) was isolated in 94 % yield. In contrast to the monomer/dimer pair **1**/**3**, **6** decomposes in CH_2Cl_2 and **7** can quantitatively be split into monomeric **6** under harsh conditions in THF. Thus, the dimerization of allylzinc monocations seems to be a general reaction pathway. Small alterations in the substitution pattern of the allyl ligand significantly affect the monomer/dimer equilibrium.

To compare the reactivity of **1** in the addition to a metalated hydrocarbon (dimerization of **1**) with that in the addition to non-metalated hydrocarbons, reactions of **1** with olefins were studied (Table 1). Reaction of **1** with an equimolar amount of styrene as an activated olefin gave a mixture of **1**, **3**, and **8**-Ph after equilibrium had been reached (entry 1). Using excess olefin led to formation of **8**-Ph with a selectivity of over 96% (entry 2). Reaction of **1** with excess styrene at elevated temperature gave polystyrene in quantitative yield (entry 3, blank run: entry 4). Reaction of **1** with excess propene as a non-activated olefin gave a mixture of **3** and **8**-Me at room temperature and **8**-Me exclusively at 50 °C (entries 5, 6).

Table 1: Reaction of **1** with olefins.



8-R

x = 2-3; [A] = [B(C$_6$F$_5$)$_4$]

Entry	R	Conditions			Product distribution [%]			
		n	*T* [°C]	*t* [d]	**1**	**3**	**8**-R	Other
1	Ph	1	23	5	11	60	29	n.d.[e]
2	Ph	100	23	0.2	n.d.[e]	< 4[a]	> 96[a]	n.d.[e]
3	Ph	100	50	4.5	n.d.[e]	n.d.[e]	n.d.[e]	> 99 (PS)[b]
4	Ph	–	50	4.5	–	–	–	n.d.[e]
5	Me	50	23	0.1	n.d.[e]	17[a]	83[a]	n.d.[e]
6	Me	50	50	0.6	n.d.[e]	n.d.[e]	> 99[a]	n.d.[e]
7	Me	1000	80	5.0	n.d.[e]	< 0.01	n.d.[e]	1 (OP)[c]
8	Me	1500	80	5.0	n.d.[e]	< 0.01	n.d.[e]	4 (OP)[d]
9	*n*Bu	100	80	5.0	n.d.[e]	n.d.[e]	> 99[a]	n.d.[e]

[a] Conversion based on amount of **1** used. [b] PS = polystyrene, $M_n = 2.23\times10^3$ g mol^{-1}, polydispersity index (PDI) = 3.30. [c] OP = oligopropene, $M_n = 3.26\times10^2$ g mol^{-1}, $M_w/M_n = 2.05$. [d] OP = oligopropene, $M_n = 4.14\times10^2$ g mol^{-1}, $M_w/M_n = 14.7$. [e] n.d. = not detected.

When the reaction temperature was raised to 80 °C, oligopropene was obtained in low yield after long reaction times (entries 7, 8). Using 1-hexene, no oligomerization was observed, but the remarkably stable addition product **8**-*n*Bu is formed exclusively (entry 9). Overall, dimerization of **1** is favored over addition of **1** to olefins, but the addition reaction can be enforced by using excess olefin. Cationic **1** with its higher Lewis acidity proved superior to neutral bis(allyl)zinc in reactions with non-activated olefins.[20,21] All the addition reactions proceed with 100% Markovnikov selectivity, in good agreement with the literature.[20]

The dimerization of **1** is related to the production of 4-methylpentene (**4**), which is used as a monomer for the synthesis of (co)polymers with excellent optical, thermal, and electrical properties.[22] Compound **4** is currently synthesized on industrial scale by the alkali-metal-catalyzed dimerization of propene under heterogeneous conditions.[23] Little is known about the mechanism of this industrially relevant reaction. Allyl alkali-metal species, isoelectronic with **1**, are believed to play a key role.[23] Thus, the dimerization of **1** is a suitable model reaction for the C–C bond forming step in the alkali-metal-catalyzed synthesis of 4-methylpentene. It shows that a metallo-ene type mechanism is feasible and that the presence of radical intermediates[23b] is not necessary. Although dimerizations of $[M(C_3H_5)]^z$ (M = alkali metal, $z = 0$; M = Zn, $z = +1$) proceed more readily, the reaction of **1** with olefins suggest that under the conditions of the alkali-metal-catalyzed propene dimerization, carbometalation of propene by $[M(C_3H_5)]^z$ should be the more probable C–C bond forming step.

In conclusion, we have shown using thermodynamic and kinetic data that allylzinc cations allow for an efficient and highly selective metal-assisted coupling of allyl anions. The dimerization of the allylzinc monocation **1** and reactions of **1** with olefins can serve as model systems for the C–C bond forming step in the alkali-metal-catalyzed synthesis of 4-methylpentene.

Experimental Section

1: A solution of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (200 mg, 0.25 mmol) in THF (1.0 mL) was added to a solution of bis(allyl)zinc (37 mg, 0.25 mmol) in THF (0.5 mL) to give a colorless solution. The volume of the reaction mixture was reduced in vacuo to 0.5 mL. Addition of pentane (4.0 mL) led to precipitation of a colorless solid, which was collected by filtration, washed with pentane (3 × 2.0 mL), and dried in vacuo. Yield: 251 mg, 0.25 mmol, quantitative.

^{1}H NMR (400.1 MHz, [D$_8$]THF): $\delta = 1.46$ (ddd, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 0.8$ Hz, $^4J_{HH} = 1.3$ Hz, 2H, CH_2-CH=CH$_2$) 1.76–1.79 (m, 12H, β-THF), 3.60–3.63 (m, 12H, α-THF), 4.45 (ddt, $^2J_{HH} = 2.3$ Hz, $^3J_{HH} = 9.8$ Hz, $^4J_{HH} = 0.8$ Hz, 1H, CH_2-CH=CH^{cis}H^{trans}), 4.69 (ddt, $^2J_{HH} = 2.3$ Hz, $^3J_{HH} = 16.8$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, CH_2-CH=CH$^{cis}\mathit{H}^{trans}$), 6.12 ppm (ddt, $^3J_{HH} = 8.8$ Hz, $^3J_{HH} = 9.8$ Hz, $^3J_{HH} = 16.8$ Hz, 1H, CH$_2$-CH=CH$_2$). ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta =$ 1.47 (br s, 2H, CH_2-CH=CH$_2$) 2.03–2.07 (m, 12H, β-THF), 3.93–3.97 (m, 12H, α-THF), 4.52 (br s, 1H, CH_2-CH=CH^{cis}H^{trans}), 4.73 (br d, $^3J_{HH} = 15.6$ Hz, 1H, CH_2-CH=CH$^{cis}\mathit{H}^{trans}$), 6.03–6.14 ppm (m, 1H, CH$_2$-CH=CH$_2$). ^{1}H NMR (400.1 MHz, [D$_5$]pyridine/[H$_5$]pyridine (1:1)): $\delta = 1.60$–1.63 (m, 12H, β-THF), 1.96 (br d, $^3J_{HH} = 8.5$ Hz, 2H, CH_2-CH=CH$_2$) 3.63–3.67 (m, 12H, α-THF), 4.60 (br d, $^3J_{HH} = 9.3$ Hz, 1H, CH_2-CH=CH^{cis}H^{trans}), 4.88 (br d, $^3J_{HH} = 17.1$ Hz, 1H, CH_2-CH=CH$^{cis}\mathit{H}^{trans}$), 6.50 ppm (m, 1H, CH$_2$-CH=CH$_2$). ^{13}C NMR (100.6 MHz, [D$_8$]THF): $\delta = 13.35$ (s, CH$_2$-CH=CH$_2$), 26.48 (s, β-THF), 68.37 (s, α-THF), 106.12 (s, CH$_2$-CH=CH$_2$), 125.31 (br s, *ipso*-C$_6$F$_5$), 137.25 (dm, $^1J_{CF} = 248.0$ Hz, *m*-C$_6$F$_5$), 139.26 (dm, $^1J_{CF} = 243.6$ Hz, *p*-C$_6$F$_5$), 142.25 (s, CH$_2$-CH=CH$_2$), 149.29 ppm (dm, $^1J_{CF} = 242.8$ Hz, *o*-C$_6$F$_5$). ^{11}B NMR (128.4 MHz, [D$_8$]THF): $\delta = -16.59$ (s) ppm. Elemental analysis (%) calcd for C$_{39}$H$_{29}$BF$_{20}$O$_3$Zn (1001.80 g mol^{-1}): Zn 6.53; found: Zn 6.42.

3: Toluene (0.60 mL) was added to **1** (50 mg, 50 μmol) to give an emulsion. After stirring for 36 h a colorless suspension was obtained. The volume of the liquid phase was reduced to half under reduced pressure. After addition of pentane (3.0 mL) the colorless solid was collected by filration, washed with pentane (3 × 1.5 mL), and dried in vacuo. Yield: 47 mg, 25 μmol, quantitative.

^{1}H NMR (400.1 MHz, [D$_8$]THF): $\delta = 0.51$ (dd, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 8.0$ Hz, 2H, CH^1H^2(CHR)CH^1H^2), 0.66 (dd, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 4.5$ Hz, 2H, CH$^1\mathit{H}^2$(CHR)CH$^1\mathit{H}^2$), 1.76–1.79 (m, 16H, β-THF), 1.93 (dd, $^3J_{HH} = 6.5$ Hz, $^3J_{HH} = 6.8$ Hz, 2H, CH_2-CH=CH$_2$), 2.12 (m, 1 H, $\mathrm{CH_2(C\mathit{H}R)CH_2}$), 3.60–3.63 (m, 16 H, α-THF), 4.94–5.01 (m, 2 H, $\mathrm{CH_2\text{-}CH{=}C\mathit{H}_2}$), 5.83 ppm (ddt, $^3J_{\mathrm{HH}} = 6.8$ Hz, $^3J_{\mathrm{HH}} = 10.2$ Hz, $^3J_{\mathrm{HH}} = 16.9$ Hz, 1 H, $\mathrm{CH_2\text{-}C\mathit{H}{=}CH_2}$). ^{1}H NMR (400.1 MHz, $\mathrm{CD_2Cl_2}$): $\delta = 0.27$ (dd, $^2J_{\mathrm{HH}} = 12.9$ Hz, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2 H, $\mathrm{C\mathit{H}^1H^2\text{-}(CHR)C\mathit{H}^1H^2}$), 0.58 (dd, $^2J_{\mathrm{HH}} = 12.9$ Hz, $^3J_{\mathrm{HH}} = 6.3$ Hz, 2 H, $\mathrm{CH^1\mathit{H}^2\text{-}(CHR)CH^1\mathit{H}^2}$), 1.86–1.97 (m, 1 H, $\mathrm{CH_2(C\mathit{H}R)CH_2}$), 2.03 (dd, $^3J_{\mathrm{HH}} = 5.5$ Hz, $^3J_{\mathrm{HH}} = 7.5$ Hz, 2 H, $\mathrm{C\mathit{H}_2\text{-}CH{=}CH_2}$), 2.06–2.09 (m, 16 H, β-THF), 3.97–4.01 (m, 16 H, α-THF), 5.18 (ddt, $^2J_{\mathrm{HH}} = 2.8$ Hz, $^3J_{\mathrm{HH}}$ 17.8 Hz, $^4J_{\mathrm{HH}} = 1.3$ Hz, 1 H, $\mathrm{CH_2\text{-}CH{=}CH^{cis}\mathit{H}^{trans}}$), 5.55 (br dd, $^2J_{\mathrm{HH}} = 2.8$ Hz, $^3J_{\mathrm{HH}} = 9.8$ Hz, 1 H, $\mathrm{CH_2\text{-}CH{=}C\mathit{H}^{cis}H^{trans}}$), 5.84 ppm (ddt, $^3J_{\mathrm{HH}} = 7.5$ Hz, $^3J_{\mathrm{HH}} = 9.8$ Hz, $^3J_{\mathrm{HH}} = 17.8$ Hz, 1 H, $\mathrm{CH_2\text{-}C\mathit{H}{=}CH_2}$). ^{13}C NMR (100.6 MHz, $[\mathrm{D_8}]$THF): $\delta = 21.66$ (s, $\mathrm{\mathit{C}H_2(CHR)\mathit{C}H_2}$), 26.49 (s, β-THF), 37.29 (s, $\mathrm{CH_2(\mathit{C}HR)CH_2}$), 51.05 (s, $\mathrm{\mathit{C}H_2\text{-}CH{=}CH_2}$), 68.38 (s, α-THF), 115.87 (s, $\mathrm{CH_2\text{-}CH{=}\mathit{C}H_2}$), 125.35 (br s, *ipso*-$\mathrm{C_6F_5}$), 137.20 (dm, $^1J_{\mathrm{CF}} = 241.0$ Hz, *m*-$\mathrm{C_6F_5}$), 139.28 (dm, $^1J_{\mathrm{CF}} = 245.4$ Hz, *p*-$\mathrm{C_6F_5}$), 139.87 (s, $\mathrm{CH_2\text{-}\mathit{C}H{=}CH_2}$), 149.28 (dm, $^1J_{\mathrm{CF}} = 239.3$ Hz, *o*-$\mathrm{C_6F_5}$) ppm. ^{13}C NMR (100.6 MHz, $\mathrm{CD_2Cl_2}$): $\delta = 18.85$ (s, $\mathrm{\mathit{C}H_2(CHR)\mathit{C}H_2}$), 25.85 (s, β-THF), 37.31 (s, $\mathrm{CH_2(\mathit{C}HR)CH_2}$), 51.17 (s, $\mathrm{\mathit{C}H_2\text{-}CH{=}CH_2}$), 72.47 (s, α-THF), 117.76 (s, $\mathrm{CH_2\text{-}CH{=}\mathit{C}H_2}$), 125.43 (br s, *ipso*-$\mathrm{C_6F_5}$), 136.87 (dm, $^1J_{\mathrm{CF}} = 239.3$ Hz, *m*-$\mathrm{C_6F_5}$), 138.80 (dm, $^1J_{\mathrm{CF}} = 248.8$ Hz, *p*-$\mathrm{C_6F_5}$), 148.71 (dm, $^1J_{\mathrm{CF}} = 237.6$ Hz, *o*-$\mathrm{C_6F_5}$), 151.60 ppm (s, $\mathrm{CH_2\text{-}\mathit{C}H{=}CH_2}$). ^{11}B NMR (128.4 MHz, $[\mathrm{D_8}]$THF): $\delta = -13.00$ ppm (s). ^{11}B NMR (128.4 MHz, $\mathrm{CD_2Cl_2}$): $\delta = -16.67$ ppm (s). Elemental analysis (%) calcd for $\mathrm{C_{70}H_{42}B_2F_{40}O_4Zn_2}$ (1859.40 g mol^{-1}): Zn 7.03; found: Zn 6.96.

CCDC 880470 (**2**) and 880471 (**5**) contains 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.

Received: May 13, 2012
Published online: July 3, 2012

Keywords: 4-methylpentene · allylzinc monocation · carbometalation · Lewis acids · metallo-ene reaction

---

[1] For Reviews see: a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255–1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170; b) G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223–1252; c) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315; d) G. W. Coates, P. D. Hustad, S. Reinartz, *Angew. Chem.* **2002**, *114*, 2340–2361; *Angew. Chem. Int. Ed.* **2002**, *41*, 2236–2257; e) R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325–387; f) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404–2433.

[2] a) M. B. Harney, R. J. Keaton, J. C. Fettinger, L. R. Sita, *J. Am. Chem. Soc.* **2006**, *128*, 3420–3432; b) M. U. Kramer, D. Robert, S. Arndt, P. M. Zeimentz, T. P. Spaniol, A. Yahia, L. Maron, O. Eisenstein, J. Okuda, *Inorg. Chem.* **2008**, *47*, 9265–9278; c) A. Yahia, M. U. Kramer, J. Okuda, L. Maron, *J. Organomet. Chem.* **2010**, *695*, 2789–2793; d) C. Lichtenberg, D. Robert, T. P. Spaniol, J. Okuda, *Organometallics* **2010**, *29*, 5714–5721; e) T. Klis, D. R. Powell, L. Wojtas, R. J. Wehmschulte, *Organometallics* **2011**, *30*, 2563–2570; f) C. Lichtenberg, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2012**, *51*, 2254–2262.

[3] a) D. A. Atwood, *Coord. Chem. Rev.* **1998**, *176*, 407–430; b) S. Dagorne, D. A. Atwood, *Chem. Rev.* **2008**, *108*, 4037–4071.

[4] Selected examples of organomagnesium monocations: a) A. D. Pajerski, M. Parvez, H. G. Richey, Jr., *J. Am. Chem. Soc.* **1988**, *110*, 2660–2662; b) R. M. Fabicon, A. D. Pajerski, H. G. Richey, Jr., *J. Am. Chem. Soc.* **1993**, *115*, 9333–9334; c) H. Viebrock, U. Behrens, E. Weiss, *Angew. Chem.* **1994**, *106*, 1364–1365; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1257–1259; d) B. J. Ireland, C. A. Wheaton, P. G. Hayes, *Organometallics* **2010**, *29*, 1079–1084; e) A. Jaenschke, J. Paap, U. Behrens, *Z. Anorg. Allg. Chem.* **2008**, *634*, 461–469.

[5] Fully characterized organocalcium monocations: a) K. C. Jayaratne, L. S. Fitts, T. P. Hanusa, V. G. Young, *Organometallics* **2001**, *20*, 3638–3640; b) K. Yan, B. M. Upton, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* **2009**, *131*, 15110–15111; c) C. Lichtenberg, P. Jochmann, T. P. Spaniol, J. Okuda, *Angew. Chem.* **2011**, *123*, 5872–5875; *Angew. Chem. Int. Ed.* **2011**, *50*, 5753–5756.

[6] Fully characterized organozinc monocations: a) C. A. Wheaton, P. G. Hayes, *Chem. Commun.* **2010**, *46*, 8404–8406; b) D. A. Walker, T. J. Woodman, D. L. Hughes, M. Bochmann, *Organometallics* **2001**, *20*, 3772–3776; c) M. A. Chilleck, T. Braun, B. Braun, *Chem. Eur. J.* **2011**, *17*, 12902–12905; d) M. D. Hannant, M. Schormann, M. Bochmann, *J. Chem. Soc. Dalton Trans.* **2002**, 4071–4073; e) C. A. Wheaton, P. G. Hayes, *Dalton Trans.* **2010**, *39*, 3861–3869; f) R. J. Wehmschulte, L. Wojtas, *Inorg. Chem.* **2011**, *50*, 11300–11302; g) M. Haufe, R. D. Köhn, G. Kociok-Köhn, A. C. Filippou, *Inorg. Chem. Commun.* **1998**, *1*, 263–266.

[7] Organozinc monocations or organozinc cations in contact ion pairs: a) H. Tang, M. Parvez, H. G. Richey, Jr., *Organometallics* **2000**, *19*, 4810–4819; b) C. A. Wheaton, B. J. Ireland, P. G. Hayes, *Organometallics* **2009**, *28*, 1282–1285; c) R. M. Fabicon, A. D. Pajerski, H. G. Richey, Jr., *J. Am. Chem. Soc.* **1991**, *113*, 6680–6681; d) H. Sun, J. S. Ritch, P. G. Hayes, *Inorg. Chem.* **2011**, *50*, 8063–8072; e) E. Wissing, M. Kaupp, J. Boersma, A. L. Spek, G. van Koten, *Organometallics* **1994**, *13*, 2349–2356.

[8] Reactions of bis(allyl)zinc with Lewis acids such as $\mathrm{BPh_3}$ or $[\mathrm{Al(C_3H_5)_3(THF)}]$ (see Ref. [2d]) or weaker Brønsted acids, such as $[\mathrm{NEt_3H}][\mathrm{BPh_4}]$, did not give the desired allylzinc monocation irrespective of the presence of neutral chelating ligands, such as diglyme. Disproportionation of bis(allyl)zinc in the presence of neutral chelating ligands to give an ion pair (as reported for an equimolar mixture of $\mathrm{ZnEt_2}$ and $\mathrm{ZnPh_2}$ (see Ref. [7c])) was also not observed.

[9] E. G. Hoffmann, H. Nehl, H. Lehmkuhl, K. Seevogel, W. Stempfle, *Chem. Ber.* **1984**, *117*, 1364–1377.

[10] C. Lichtenberg, J. Engel, T. P. Spaniol, U. Englert, G. Raabe, J. Okuda, *J. Am. Chem. Soc.* **2012**, DOI: 10.1021/ja303480a.

[11] H. Yasuda, Y. Ohnuma, A. Nakamura, Y. Kai, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1101–1111.

[12] Selected examples: a) M. Gaudemar, *C. R. Seances Acad. Sci. Ser. C* **1971**, *273*, 1669–1673; b) Y. Frangin, M. Gaudemar, *C. R. Seances Acad. Sci. Ser. C* **1974**, 278, 885–887; c) M. Bellassoued, Y. Frangin, M. Gaudemar, *Synthesis* **1977**, 205–208; d) P. Knochel, J. F. Normant, *Tetrahedron Lett.* **1986**, *27*, 1039–1042; e) K. Suzuki, T. Imai, S. Yamanoi, M. Chino, T. Matsumoto, *Angew. Chem.* **1997**, *109*, 2578–2580; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2469–2471; f) M. Nakamura, K. Hara, T. Hatakeyama, E. Nakamura, *Org. Lett.* **2001**, *3*, 3137–3140; g) N. Bernard, F. Chemla, F. Ferreira, N. Mostefai, J.-F. Normant, *Chem. Eur. J.* **2002**, *8*, 3139–3147; h) A. Levin, I. Marek, *Chem. Commun.* **2008**, 4300–4302; i) L. Labaudinière, J. Hanaizi, J.-F. Normant, *J. Org. Chem.* **1992**, *57*, 6903–6908; j) J.-F. Normant, J. C. Quirion, *Tetrahedron Lett.* **1989**, *30*, 3959–3962; k) J.-F. Normant, J. C. Quirion, A. Alexakis, Y. Masuda, *Tetrahedron Lett.* **1989**, *30*, 3955–3958.

[13] For Reviews see: a) J.-F. Normant, I. Marek, J.-M. Lefrançois, *Pure Appl. Chem.* **1992**, *64*, 1857–1864; b) I. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3241–3267; c) I. Marek, J.-F. Normant in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: P. J. Stang, J. Diederich), Wiley-VCH, Weinheim, **1998**, pp. 271–337; d) J. F. Normant, *Acc. Chem. Res.* **2001**, *34*, 640–644.

[14] a) I. Marek, P. R. Schreiner, J. F. Normant, *Org. Lett.* **1999**, *1*, 929–931; b) A. Hirai, M. Nakamura, *J. Am. Chem. Soc.* **1999**, *121*, 8665–8666; c) A. Hirai, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 11791–11798.

[15] E. Nakamura, K. Kubota, G. Sakata, *J. Am. Chem. Soc.* **1997**, *119*, 5457–5458.

[16] a) H. Lehmkuhl, I. Döring, R. McLane, H. Nehl, *J. Organomet. Chem.* **1981**, *221*, 1–6; b) H. Lehmkuhl, I. Döring, H. Nehl, *J. Organomet. Chem.* **1981**, *221*, 7–11.

[17] Heating a 0.02 molar sample of **3** in [D$_8$]THF to 70 °C (19 h), 100 °C (19 h) or 140 °C (22 h) in a sealed NMR tube gave molar ratios **3**/**1** of 1.0:0.1, 1.0:8.7, and 1.0:22.1, respectively (Supporting Information).

[18] Second-order rate constants between 1.3×10^{-4} L mol^{-1} s^{-1} and 1.7×10^{-3} L mol^{-1} s^{-1} have been reported for metallo-ene reactions of allyl metal compounds with non-metalated enes depending on the nature of the metal center. No equilibria were detected: W. J. Kinart, E. Śineć, I. Tylak, C. M. Kinart, *Phys. Chem. Liq.* **2000**, *38*, 193–201.

[19] A reaction energy of -25.9 kJ mol^{-1} was calculated for the G/N coupling between allylzinc chloride and vinylzinc chloride (Ref. [14c]).

[20] H. Lehmkuhl, I. Döring, H. Nehl, *J. Organomet. Chem.* **1981**, *221*, 123–130.

[21] For allylzincation of olefins also see: K. Kubota, S. Mori, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 13334–133341.

[22] a) TPX, Mitsui Chemicals, Inc. http://www.mitsuichemicals.com/tpx.htm; b) G. Xu, D. Cheng, *Macromolecules* **2001**, *34*, 2040–2047; c) L. J. Irwin, J. H. Reibenspies, S. A. Miller, *J. Am. Chem. Soc.* **2004**, *126*, 16716–16717; d) S. Gendler, S. Groysman, Z. Goldschmidt, M. Shuster, M. Kol, *J. Polym. Sci. Part A* **2005**, *44*, 1136–1146; e) Y. Suzuki, T. Yasumoto, K. Mashima, J. Okuda, *J. Am. Chem. Soc.* **2006**, *128*, 13017–13025.

[23] a) K. Weissermel, H.-J. Arpe in *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, New York, **2003**; b) A. W. Shaw, C. W. Bittner, W. V. Bush, G. Holzman, *J. Org. Chem.* **1965**, *30*, 3286–3289.