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Preparation of Polyfunctional Olefins and Allenes Using 1,1-Bimetallics of Zinc and Zirconium

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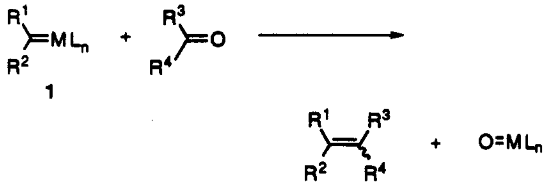
The hydrozirconation of various alkenylzinc halides with $Cp_2Zr(H)Cl$ in dry dichloromethane provides 1,1-dimetalloalkanes of zinc and zirconium which react with aldehydes, providing (*E*)-alkenes with good to excellent stereoselectivity (up to 98% *E*). The reaction tolerates the presence of a wide range of functionalities in the dimetallic species as well as in the aldehyde, allowing the preparation of functionalized olefins. Ketones can also be olefinated by these reagents. However, only a moderate stereoselectivity is observed. The hydrozirconation of alkynylzinc halides with $Cp_2Zr(H)Cl$ gives 1,1-dimetalloalkenes of zinc and zirconium which react with aldehydes, affording allenes. The olefination of α,β-unsaturated aldehydes provides a short access of 1,2,4-trienes.

Introduction



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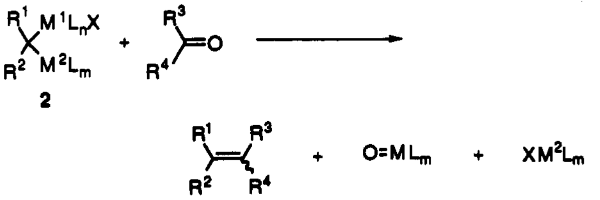
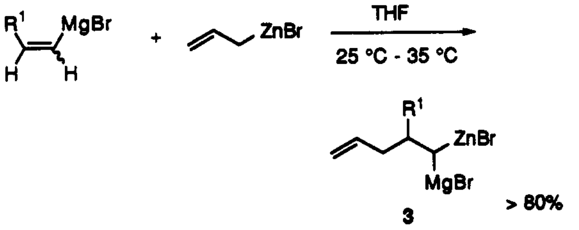


(2)

The methylenation of aldehydes and ketones using transition-metal carbene complexes 1 or related 1,1-bimetallic organometallics 2 (R^1 and R^2 = H) constitutes an excellent preparation of olefins and has found many applications in organic synthesis.[1] The extension of this method to alkylidenation reactions is possible in many cases but is often complicated by the instability of the organometallic reagents 1 and 2 (R^1 and/or $R^2 \neq$ H) and often shows a moderate *E*/*Z* stereoselectivity (eqs 1 and 2).[2] In the course of our studies concerning the reactivity of 1,1-bimetallic reagents of zinc and magnesium 3, we found a need for a more general synthesis of these reagents, which were prepared by allylzincation of alkenylmagnesium halides (eq 3).[3] Inspired by the work of Schwartz,[1e-g,4] who has shown that various alkenyl organometallics can



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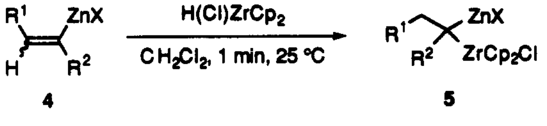

(4)

● Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978,** *100,* 3611. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981,** *103,* 5584. (c) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980,** *102,* 3270. (d) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980,** *102,* 6876. (e) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983,** *105,* 1664. (f) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983,** *55,* 1733. (g) Clawson, L.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* **1984,** *25,* 5733. (h) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986,** *108,* 733. (i) Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem.* **1985,** *50,* 1212. (j) For an excellent review concerning titanium-based olefination reagents: Pine, S. H. *Org. React.* **1993,** *43,* 1. (k) Kauffmann, T.; Fiegenbaum, P.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 531. (l) Kauffmann, T.; Möller, T.; Rennefeld, H.; Welke, S.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 348. (m) Lombardo, L. *Org. Synth.* **1987,** *65,* 81.

(2) (a) Okazoe, T.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1987,** *52,* 4410. (b) Takai, K.; Fujimura, O.; Kataoka, Y.; Utimoto, K. *Tetrahedron Lett.* **1989,** *30,* 211. (c) Takai, K.; Kataoka, Y.; Okazoe, T.; Utimoto, K. *Tetrahedron Lett.* **1988,** *29,* 1065. (d) Takai, K.; Tezuka, M.; Kataoka, Y.; Utimoto, K. *Synlett* **1989,** 27. (e) Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981,** *103,* 4979. (f) Hartner, F. W.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983,** *105,* 640. (g) Clift, S. M.; Schwartz, J. *J. Am. Chem. Soc.* **1984,** *106,* 8300. (h) Schrock, R. R. *J. Am. Chem. Soc.* **1976,** *98,* 5399. (i) Aguero, A.; Kress, J. A.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986,** 531. (j) Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981,** *103,* 1276. (k) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986,** *5,* 721. (l) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986,** *108,* 855. (m) Stille, J. R.; Santarsiero, B. D.; Grubbs, R. H. *J. Org. Chem.* **1990,** *55,* 843. (n) Yoshida, T. *Chem. Lett.* **1982,** 429. (o) Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983,** *105,* 5490. (p) Mortimore, M.; Kocienski, P. *Tetrahedron Lett.* **1988,** *29,* 3357. (q) Doxsee, K. M.; Mouser, J. K. M. *Tetrahedron Lett.* **1991,** *32,* 1687. (r) Doxsee, K. M.; Mouser, J. K. M.; Farahi, J. B. *Synlett.* **1992,** 13. (s) Petasis, N. A.; Akritopoulou, I. *Synlett* **1992,** 665. (t) Petasis, N. A.; Bzowej, E. I. *J. Org. Chem.* **1992,** *57,* 1327.

(3) (a) Gaudemar, M. *C. R. Seances Acad. Sci., Ser. C* **1971,** *273,* 1669. (b) Frangin, Y.; Gaudemar, M. *C. R. Seances Acad. Sci., Ser. C* **1974,** *278,* 885. (c) Bellassoued, M.; Frangin, Y.; Gaudemar, M. *Synthesis* **1977,** 205. (d) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986,** *27,* 1039, 1043, 4427, 4431, 5727. (e) Knochel, P.; Xiao, C.; Yeh, M. C. P. *Tetrahedron Lett.* **1988,** *29,* 6697. (f) Knochel, P.; Yeh, M. C. P.; Xiao, C. *Organometallics* **1989,** *8,* 2831. (g) Tucker, C. E.; Achyutha Rao, S.; Knochel, P. *J. Org. Chem.* **1990,** *55,* 5446. (h) Waas, J. R.; Sidduri, A.; Knochel, P. *Tetrahedron Lett.* **1992,** *33,* 3717. (i) Tucker, C. E.; Knochel, P. *Synthesis* **1993,** 530.

(4) Clift, S. M.; Schwartz, J. *J. Organomet. Chem.* **1985,** *285,* C5.

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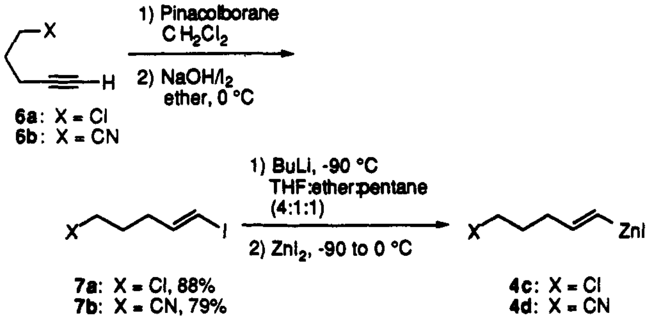
Scheme 1

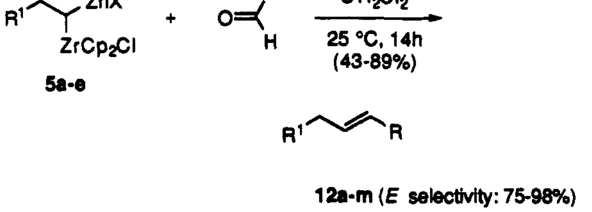


be hydrometalated with $Cp_2Zr(H)Cl$,[5] we found that the hydrozirconation of alkenylzinc halides **4** with $Cp_2Zr(H)Cl$ proceeds smoothly in CH_2Cl_2, leading to 1,1-bimetallic reagents tentatively depicted as **5** (eq 4). These reagents react rapidly with aldehydes and ketones, providing (*E*)-olefins with good to excellent stereoselectivity.[6] We report herein our full results, which demonstrate the excellent functional group tolerance of the reaction and its application to the preparation of alkenes.

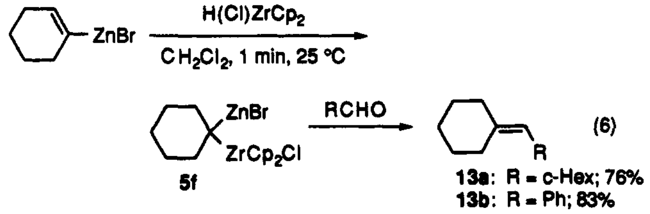
Results and Discussion

The addition of a CH_2Cl_2 suspension of $Cp_2Zr(H)Cl$[5f] to a CH_2Cl_2 solution of an alkenylzinc halide **4** (**4a**, R^1 = Hex, R^2 = H; **4b**, R^1 = Ph, R^2 = H; **4c–e**, see Schemes 1 and 2) affords instantaneously a yellow solution of the relatively unstable 1,1-bimetallics of zinc and zirconium **5a–f**, to which an aldehyde or a ketone must be immediately added. A spectroscopic characterization (NMR or X-ray) of the reactive intermediates failed due to their instability. However, the hydrolysis of **5a** (R^1 = Hex, R^2 = H) affords *n*-octane, as indicated by GLC analysis and by mass spectroscopy. After 10 min at 25 °C, ca. 75% of **5a** has decomposed and the GLC analysis of a hydrolyzed aliquot shows the formation of a mixture of octane and octene (ca. 3:1 ratio). Remarkably, the hydrozirconation can be applied to functionalized alkenylzinc reagents bearing an ester, chloride, or cyano functionality (see Table 1). The preparation of these functionalized alkenylzinc halides **4c,d** was performed using a low-temperature iodine–lithium exchange followed by a transmetalation with a THF solution of ZnI_2.[7] Thus, the commercially available alkyne **6a** was first hydroborated with pinacolborane,[8] leading to a boronic ester, which was then treated without purification with I_2/NaOH (25 °C, 1 h), providing (*E*)-5-chloro-1-iodo-1-pentene (**7a**; 88% overall yield). The reaction of **7a** with BuLi (1.05 equiv, -90 °C, 3 min) in the Trapp mixture,[9] followed by the addition of a THF solution of ZnI_2, provides the zinc reagent **4b** in over 90% yield (estimated by the iodolysis of a reaction aliquot). Similarly, 5-hexynenitrile (**6b**) was converted to (*E*)-6-iodo-5-hexenenitrile (**7b**; 79% overall yield), which after successive treatment with BuLi and ZnI_2 at -90 °C affords the functionalized alkenylzinc iodide **4c** (Scheme 1). The ester-substituted alkenylzinc species **4e** was prepared from 5-iodopentyne (**8**).[10] after hydroboration of **8** using pinacolborane (84% yield), the resulting boronic ester **9** was treated with zinc dust (THF, 25 °C, 4 h),[11] leading to an intermediate zinc species which was transmetalated with the THF-soluble copper salt $CuCN{\cdot}2LiCl$[11] and added to ethyl propiolate, furnishing the functionalized boronic ester **10**. After a Michael addition of $Bu_2Cu(CN)Li_2$[12] (69% yield) and iodolysis of the boronic ester group, the alkenyl iodide **11** was isolated in 77% yield. Its reaction with BuLi (Trapp mixture, −100 °C, 3 min) followed by a transmetalation with ZnI_2 gives the desired ester-substituted alkenylzinc iodide **4e** in ca. 80% yield (by iodolysis of a reaction aliquot; Scheme 2).

All the alkenylzinc halides **4a–e** rapidly react with $Cp_2Zr(H)Cl$[5f] in dry CH_2Cl_2 (0 °C, 1 min). The resulting yellow solution has to be immediately used; otherwise, low yields of the olefination products are obtained. Thus, the addition of a CH_2Cl_2 solution of hexanal (0.9 equiv) leads after 14 h of stirring at 25 °C, usual workup (see Experimental Section), and a short filtration over silica gel to a crude product, which gives a single peak in capillary gas chromatography. The ^{13}C NMR spectrum shows, however, the presence of an impurity which was separated by performing two flash chromatographies,[13] leading to (*E*)-6-tetradecene (**12a**) in 73% isolated yield with an *E*:*Z* ratio >98:2 (determined by ^{13}C NMR spectroscopy; eq 5



(5)



and Table 1, entry 1). It should be noted that the performance of this reaction in other solvents such as THF, ether, and toluene gave only trace amounts of the product. The addition of phosphines such as PPh_3 and Me_2PhP which typically stabilize zirconium bimetallics[2f] completely inhibits the olefination reaction. A variety of unfunctionalized (entries 1, 2, 5, and 10–13) or functionalized (entries 3, 4, and 6–9) aldehydes produce the desired (*E*)-olefins in acceptable yields (43–89%) and satisfactory *E*-stereoselectivity (75–98% *E*). The functionalized bimetallic species **5c–e** react in significantly lower yields (55–64%) but in excellent stereoselectivity (>94% *E*; see entries 11–13). Although the *E*/*Z* ratio was always

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[5] (a) Schwartz, J.; Hart, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 8115. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (c) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (d) Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1976**, *98*, 262. (e) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. (f) Buchwald, S. L.; La Maire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

[6] Tucker, C. E.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 9888.

[7] Tucker, C. E.; Majid, T. N.; Knochel, P. *J. Am. Chem. Soc.* **1992**, *114*, 3983.

[8] Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.

[9] Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *6*, 41.

[10] Knoess, H. P.; Furlong, M. T.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 5974.

[11] Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.

[12] Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

[13] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Scheme 2

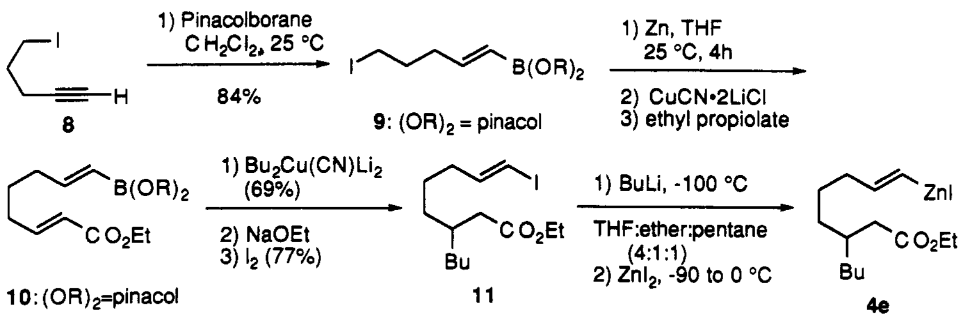
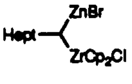
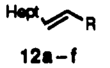
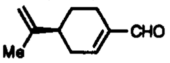
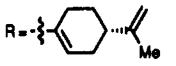
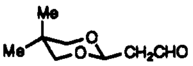
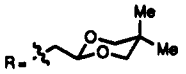
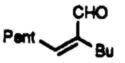
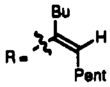
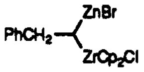
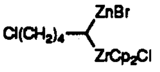
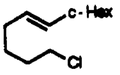
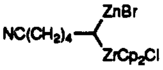
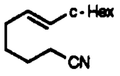
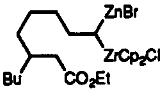
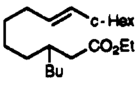


Table 1. Preparation of (*E*)-Polyfunctional Olefins 12 by the Reaction of 1,1-Bimetallic Reagents of Zinc and Zirconium 5a–e with Aldehydes

entry no.	1,1-bimetallic **5**	aldehyde	product **12**	*E*/*Z* ratio	yield (%)[a]
1	 **5a**	Pent-CHO	 **12a–f**	98/2	73
2	**5a**	*c*-HexCHO	**12b**, R = *c*-Hex	98/2	83
3	**5a**	$MeO_2C(CH_2)_4CHO$	**12c**, R = $(CH_2)_4CO_2Me$	98/2	46
4	**5a**	$PivO(CH_2)_3CHO$	**12d**, R = $(CH_2)_3OPiv$	75/25	60
5	**5a**	$Ph(CH_2)_2CHO$	**12e**, R = $(CH_2)_2Ph$	89/11	82
6	**5a**	$MeS(CH_2)_2CHO$	**12f**, R = $(CH_2)_2SMe$	94/6	66
7	**5a**		 **12g**	91/9	70
8	**5a**		 **12h**	89/11	43
9	**5a**		 **12i**	85/15	81
10	 **5b**	Pent-CHO	 **12j**	98/2	89
11	 **5c**	*c*-HexCHO	 **12k**	98/2	64
12	 **5d**	*c*-HexCHO	 **12l**	94/6	55
13	 **5e**	*c*-HexCHO	 **12m**	97/3	58

[a] Isolated yields of products being >95% pure.

reproducible, the yields of the reaction were found to be dependent on the quality of the $Cp_2Zr(H)Cl$ (variations up to 20% were observed) and the preparation method of the Schwartz reagent[5] developed by Buchwald[5f] gave the best results. Interestingly, the reaction could also be extended to the preparation of disubstituted 1,1-dimetallic reagents. Thus, cyclohexenylzinc bromide, prepared by a transmetalation of cyclohexenyllithium[14] with $ZnBr_2$, readily adds $Cp_2Zr(H)Cl$, providing the intermediate bimetallic **5f**, which reacts with aliphatic and aromatic aldehydes, leading to the *exo*-alkylidenecyclohexanes **13a,b** in 76–83% yield (eq 6). Ketones also undergo the olefination reaction, providing trisubstituted olefins **14a–e** in moderate stereoselectivity and 39–87% yields (Table 2). The reaction of **5a** with menthyl glyoxylate[15] gives the α,β-unsaturated menthyl ester **14e** in excellent yield (87%; *E*:*Z* = 14:86; entry 5 of Table 2), showing that ester functions do not react with these bimetallics.[2] Olefination of esters such as ethyl benzoate failed, even when the reaction was performed in the presence of a base such as pyridine or triethylamine.[16] The hydrozirconation of

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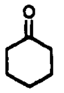
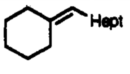
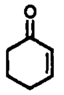
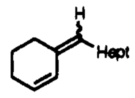
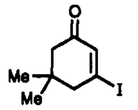
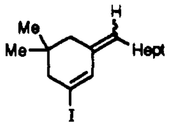
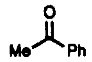
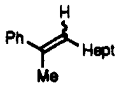
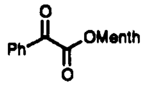
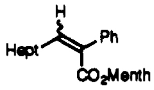
[14] Brandsma, L.; Verkruijsse, H. D. In *Preparative Polar Organometallic Chemistry*; Springer-Verlag: New York, 1987; Vol. 1, p 50.

[15] Boireau, G.; Deberly, A.; Abenhaïm, D. *Tetrahedron Lett.* **1988**, *29*, 2175.

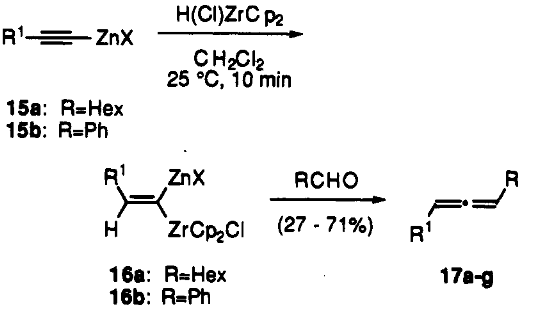
[16] Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

Table 2. Preparation of Trisubstituted Olefins 14a–e by the Reaction of the 1,1-Bimetallic Reagent 5a with Various Ketones

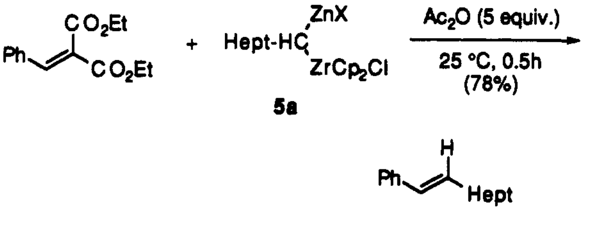
entry no.	ketone	product of type 14	*E*/*Z* ratio	yield (%)[a]
1		 **14a**		85
2		 **14b**	50/50	82
3		 **14c**	33/67	39
4		 **14d**	86/14	70
5		 **14e**	14/86	87

[a] Isolated yields of products being >95% pure.

alkynylzinc halides **15a,b** is also possible and affords 1,1-dimetalloalkenes to type **16**, which react with aldehydes to provide the allenes **17a–g** in moderate yields (Table 3 and eq 7). The method seems to be well suited for the preparation of 1,2,4-trienes (**17c–g**; entries 3–7 of Table 3). Numerous attempts to improve the yields failed. Finally, the olefination of alkylidenemalonates[3g,i] with the 1,1-bimetallic reagents proceeds cleanly in the presence of acetic anhydride (5 equiv, 25 °C, 0.5 h) and allows the conversion of diethyl benzylidenemalonate (0.9 equiv) and **5a** into 1-phenyl-1-octene **18** (78%, *E*/*Z* = 65/35; eq 8). As in the Wittig reaction,[17] we believe that the first step of the reaction of the bimetallic **5** with aldehydes is the formation of a cyclic intermediate of type **19** which eliminates the zirconium moiety, affording the olefin of type **12** (Scheme 3). It is this elimination which seems to be the rate-determining step, since it was observed that the aldehyde disappears immediately after addition (rapid formation of **19**) but the maximum yield is obtained by workup of the reaction mixture after ca. 12 h.



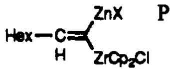
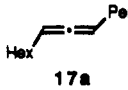
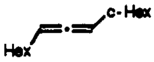
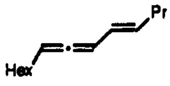
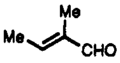
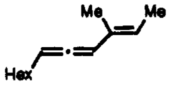
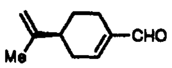
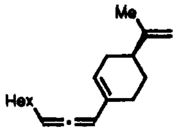
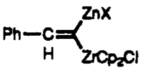
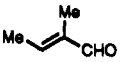
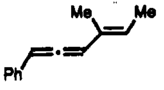
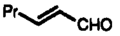
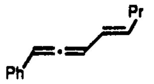
(7)



(8)

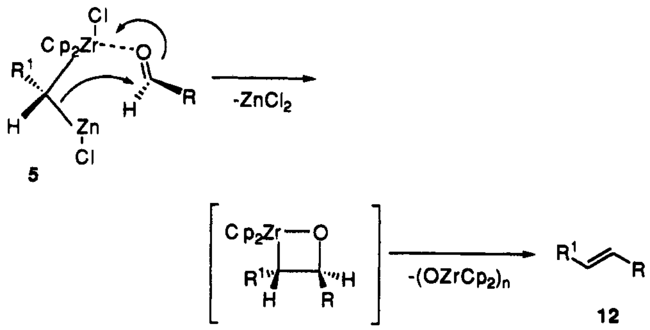
18 (*E*/*Z* = 65/35)

Table 3. Preparation of Allenes 17a–g by the Reaction of 1,1-Bimetallic Alkenes of Zinc and Zirconium with Aldehydes

entry no.	1,1-bimetallic reagent 16	aldehyde	allene product 17	yield (%)[a]
1	 **16a**	Pent-CHO	 **17a**	68
2	**16a**	*c*-HexCHO	 **17b**	71
3	**16a**		 **17c**	45
4	**16a**		 **17d**	49
5	**16a**		 **17e**	29
6	 **16b**		 **17f**	49
7	**16b**		 **17g**	29

[a] Isolated yields of products being >95% pure.

Scheme 3



In summary, we have shown that 1,1-bimetallic species of zinc and zirconium prepared by the hydrozirconation of alkenylzinc halides provide a new access to 1,1-bimetallic compounds of zinc and zirconium **5**. These reagents react with aldehydes with good to excellent *E* selectivity. The reaction constitutes an interesting preparation of functionalized (*E*)-olefins, since various functionalities can be present either in the 1,1-bimetallic or in the aldehyde. The reaction of **5** with ketones proceeds with low stere-

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(17) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

oselectivity. An extension to the preparation of allenes is possible by reacting alkynylzinc iodides with $Cp_2Zr(H)Cl$, which leads to a 1,1-dimetalloalkene of type **16**. Their reaction with aldehydes provides allenes in moderate yields.

Experimental Section

General Considerations. All reactions were carried out under argon. Solvents (ether, THF) were dried over sodium/benzophenone and freshly distilled. The zinc foil was purchased from Alfa (0.62 mm thick, purity m3N). LiCl and ZnI_2 were dried for 1–2 h under vacuum (0.1 mmHg) at 150 °C before use. The reactions were monitored by gas chromatography (GLC) analysis. FT-IR spectra were recorded on sodium chloride plates. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.5 MHz) were measured in $CDCl_3$ on a Bruker WM-300 spectrometer.

Preparation of the Functionalized Alkenylzinc Halides 4c–e. Preparation of (*E*)-5-Chloro-1-iodo-1-pentene (7a). In a three-necked flask equipped with an addition funnel, a nitrogen inlet, and a thermometer, $BH_3 \cdot SMe_2$ (20 mmol, 10.0 M in methyl sulfide) was added to a solution of pinacol (2.36 g, 20 mmol) in CH_2Cl_2 (4 mL) at 0 °C and stirred for 1 h. After the mixture was warmed to 25 °C and stirred until no further evolution of H_2 was observed, the pinacolborane solution[8] was cooled to 0 °C, and 5-chloro-1-pentyne (1.02 g, 10 mmol; Aldrich) was added. After it was warmed to 25 °C and stirred for 8 h, the reaction mixture was washed quickly with two 200-mL portions of saturated aqueous NH_4Cl. The aqueous phase was extracted twice with 50-mL portions of ether, the combined organic phases were dried over $MgSO_4$, and the solvents were removed under reduced pressure. Without further purification, the resulting oil was dissolved in ether (10 mL) and cooled to 0 °C. Aqueous sodium hydroxide (30 mmol, 3.0 M) was added dropwise, and the resulting white reaction mixture was stirred at 0 °C for 10 min. Iodine (5.08 g, 20 mmol, 2.0 M in ether) was then added dropwise, and the reaction mixture was stirred for an additional 1 h. After workup with aqueous $Na_2S_2O_3$, the organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography (solvent hexane), yielding 2.02 g (88%) of (*E*)-5-chloro-1-iodo-1-pentene (**7a**) as a red oil (*E*/*Z* ratio >98/2). IR (neat): 2955 (s), 2948 (m), 2912 (m), 1588 (m), 1442 (s), 1218 (s), 946 (s), 651 (s) cm^{-1}. ^{1}H NMR: δ 6.49 (dt, 1H, *J* = 14.3, 7.2 Hz), 6.10 (d, 1H, *J* = 14.3 Hz), 3.45 (t, 2H, *J* = 6.4 Hz), 2.27–2.20 (m, 2H), 1.91–1.82 (m, 2H). ^{13}C NMR: δ 144.6, 76.0, 43.8, 33.1, 31.1. MS (EI, 70 eV; *m*/*e* (relative intensity)): 232 (8), 230 (25), 167 (26), 127 (12), 103 (26), 67 (74), 41 (100). HRMS: calcd for $C_5H_8{}^{35}ClI$ 230.5126, obsd 230.5121.

Preparation of (*E*)-5-Cyano-1-iodo-1-pentene (7b). The same procedure as described for **7a** was used. A pale yellow oil (1.52 g, 69%) was obtained from 5-hexynenitrile (0.93 g, 10 mmol) after flash chromatography (solvent 5% ether in hexane): *E*/*Z* ratio >98/2. IR (neat): 2936 (s), 2246 (m), 1609 (m), 1424 (s), 1219 (s), 947 (s) 659 (m) cm^{-1}. ^{1}H NMR: δ 6.45 (dt, 1H, *J* = 14.4, 7.2 Hz), 6.16 (d, 1H, *J* = 14.4 Hz), 2.36 (t, 2H, *J* = 7.0 Hz), 2.24 (q, 2H, *J* = 7.2 Hz), 1.76 (p, 2H, *J* = 7.2 Hz). ^{13}C NMR: δ 143.8, 119.1, 76.9, 34.6, 24.1, 16.3. MS (EI, 70 eV; *m*/*e* (relative intensity)): 221 (21), 195 (15), 167 (40), 127 (16), 94 (48), 67 (100). HRMS: calcd for C_6H_8N 221.0691, obsd 221.0687.

Preparation of (*E*)-Pinacol (5-Iodo-1-pentenyl)boronate (9). The same procedure as described for **7a** was used. A clear oil (2.70 g, 84%) was obtained from 5-iodo-1-pentyne (1.94 g, 10 mmol) after flash chromatography (solvent 5% ether in hexane): *E*/*Z* ratio >98/2. IR (neat): 2978 (s), 2932 (m), 1639 (s), 1388 (m), 1368 (s), 1324 (s), 1204 (m), 1165 (s), 1001 (m), 974 (m), 850 (s) cm^{-1}. ^{1}H NMR: δ 6.55 (dt, 1H, *J* = 6.5 Hz), 5.49 (dt, 1H, *J* = 1.5, 18.0 Hz), 3.17 (t, 2H, *J* = 7.0 Hz), 2.26 (dq, 2H, *J* = 1.2, 6.8 Hz), 1.95 (p, 2H, *J* = 7.0 Hz), 1.26 (s, 12H). ^{13}C NMR: δ 151.4, 119.5 (bs), 82.8, 36.0, 31.7, 24.6, 5.8. MS (EI, 70 eV; *m*/*e* (relative intensity)): 322 (48), 307 (41), 236 (31), 223 (18), 195 (46), 153 (61), 109 (71), 101 (66), 83 (57), 67 (100). HRMS: calcd for $C_{11}H_{20}BIO_2$ 322.0601, obsd 322.0602.

Preparation of (1*E*,6*E*)-Pinacol 7-Carboethoxy-1,6-heptadienylboronate (10). To a three-necked flask equipped with an argon inlet, an addition funnel, and a thermometer, charged with a slurry of zinc dust (60 mmol, 3.92 g) activated by the addition of 1,2-dibromoethane (0.19 g, 1.0 mmol) and chlorotrimethylsilane (0.11 g, 1.0 mmol), in THF (5 mL), was added dropwise a solution of pinacol (5-iodo-1-pentenyl)boronate (**9**; 6.44 g, 20 mmol) in THF (7 mL). The resulting slurry was then stirred at 25 °C for 4 h, and the excess zinc dust was allowed to settle. The clear solution was then cannulated to a solution of CuCN (1.79 g, 20 mmol) and LiCl (1.70 g, 40 mmol)[11] in THF (20 mL) cooled to −50 °C. The resulting solution was warmed to 0 °C, stirred for 5 min, and then cooled to −78 °C. A solution of ethyl propiolate (1.96 g, 20 mmol) in THF (5 mL) was then added, and the reaction mixture was warmed to −20 °C and stirred for 14 h. After workup in ether with saturated aqueous NH_4Cl, the organic layer was dried over $MgSO_4$, and the solvents were removed under vacuum. Purification of the residue by flash chromatography (solvent, 10% ether in hexane) yielded 3.70 g (63% yield) of (1*E*,6*E*)-pinacol 7-carboethoxy-1,6-heptadienylboronate (**10**) as a clear oil: *E*,*E* purity >98%. IR (neat): 2979 (s), 2933 (s), 1722 (s), 1654 (2), 1368 (s), 1364 (s), 1321 (s), 1269 (s), 1209 (s), 1096 (s), 996 (s), 849 (s) cm^{-1}. ^{1}H NMR: δ 6.93 (dt, 1H, *J* = 15.6, 6.9 Hz), 6.58 (dt, 1H, *J* = 18.9, 6.4 Hz), 5.80 (d, 1H, *J* = 15.6 Hz), 5.44 (d, 1H, *J* = 18.0 Hz), 4.17 (q, 2H, *J* = 7.1 Hz), 2.24–2.14 (m, 4H), 1.63–1.56 (m, 2H), 1.35–1.13 (m, 15H). ^{13}C NMR: δ 166.6, 153.2, 148.6, 121.7, 83.0, 60.0, 34.9, 31.4, 26.4, 24.7, 14.2. MS (EI, 70 eV; *m*/*e* (relative intensity)): 294 (2), 279 (1), 248 (3), 236 (8), 194 (57), 166 (54), 122 (82), 84 (100), 55 (90), 41 (83). HRMS: calcd for $C_{16}H_{27}{}^{11}BO_4$ 294.2002, obsd 294.2019.

Preparation of (*E*)-Pinacol 6-Butyl-7-carboethoxy-1-heptenylboronate. BuLi (20 mmol, 1.6 M in hexanes) was added to a three-necked flask (equipped with an argon inlet, an addition funnel, and a thermometer) charged with CuCN (0.90 g, 10 mmol) in THF (10 mL) and cooled to −78 °C. After the mixture was warmed to −60 °C, stirred for 5 min, and cooled to −78 °C, a solution of **10** (2.94 g, 10 mmol) in THF (5 mL) was added. The reaction mixture was warmed to −20 °C and stirred for 4 h. After workup in ether with saturated aqueous NH_4Cl, the organic phase was dried over $MgSO_4$ and the solvents were removed under vacuum. Purification of the remaining residue by flash chromatography (solvent, 10% ether in hexane) yielded 3.06 g (87%) of pinacol (6-butyl-7-carboethoxy-1-heptenyl)boronate as an oil. IR (neat): 2977 (s), 1958 (s), 2930 (s), 1714 (s), 1639 (s), 1374 (s), 1320 (s), 1146 (s) cm^{-1}. ^{1}H NMR: δ 6.60 (dt, 1H, *J* = 7.9, 6.0 Hz), 5.41 (d, 1H, *J* = 17.9 Hz), 2.36 (t, 3H, *J* = 7.4 Hz), 2.29 (d, 2H, *J* = 6.6 Hz), 2.14–2.04 (m, 2H), 1.96–1.80 (m, 1H), 1.57–1.43 (m, 4H), 1.43–1.10 (m, 17H), 0.95–0.81 (m, 6H). ^{13}C NMR: δ 168.3, 154.0, 47.5, 42.8, 35.7, 33.5, 28.6, 25.7, 25.1, 24.5, 24.0, 22.6, 22.1, 21.8, 13.7, 13.5. MS (EI, 70 eV; *m*/*e* (relative intensity)): 352 (1), 307 (1), 264 (3), 201 (38), 165 (9), 136 (11), 109 (10), 101 (40), 85 (48). HRMS: calcd for $C_{20}H_{37}{}^{11}BO_4$ 35.2843, obsd 352.2850.

Preparation of (*E*)-Ethyl-3-butyl-8-iodo-7-octenoate (11). The same procedure as described for the preparation of **7a**,**b** was used. However, sodium ethoxide (1.63 g, 24.0 mmol) in ethanol (50 mL) was used instead of sodium hydroxide. A clear oil (1.91 g, 81% yield) was obtained from (*E*)-pinacol (6-butyl-7-carboethoxy-1-heptenyl)boronate (2.35 g, 6.7 mmol) after purification by flash chromatography (solvent 10% ether in hexane). IR (neat): 2957 (s), 2921 (s), 1750 (s), 1452 (s), 1360 (s), 1311 (s), 1047 (s) cm^{-1}. ^{1}H NMR: δ 6.49 (dt, 1H, *J* = 17.2, 6.7 Hz), 6.29 (d, 1H, *J* = 17.2 Hz), 2.40 (t, 3H, *J* = 7.1 Hz), 2.19–2.11 (m, 2H), 2.04–1.96 (m, 1H), 1.66–1.55 (m, 4H), 1.48–1.04 (m, 5H), 0.98–0.82 (m, 6H). ^{13}C NMR: δ 167.3, 122.4, 76.8, 49.1, 44.6, 37.2, 34.0, 28.9, 26.1, 25.9, 22.9, 21.6, 13.9, 13.7. MS (EI, 70 eV; *m*/*e* (relative intensity)): 352 (1), 307 (4), 262 (1), 237 (11), 205 (4), 180 (8), 167 (18), 137 (9), 113 (15), 85 (92). HRMS: calcd for $C_{14}H_{25}O_2I$ 352.2629, obsd 352.2633.

Typical Procedure for the Preparation of Functionalized Alkenylzinc Halides Such as 4c–e. A 100-mL three-necked flask equipped with a thermometer, an argon inlet, and an addition funnel was charged under argon with (*E*)-5-chloro-1-iodo-1-pentene (**7a**; 1.58 g, 2.50 mmol) in a mixture of THF/ether/pentane (4/1/1; 12 mL) and cooled to −100 °C (liquid N_2, ether bath), and *n*-BuLi (2.6 mmol, 1.60 M in hexanes) was added over 4 min. The resulting yellow solution was stirred for 3 min at −100 °C, and a solution of ZnI_2 (0.83 g, 2.60 mmol) in THF (5 mL) was added. After it was stirred for 10 min at −100 °C, the solution was warmed up to 0 °C and was ready for use. Under these conditions **4c** was obtained in >90% yield, **4d** in ca. 85% yield, and **4e** in ca. 80% yield, as determined by performing an iodolysis of a reaction aliquot (analysis by capillary GLC).

Typical Procedure for the Formation of (*E*)-Olefins of Type 12. Preparation of (*E*)-1-Cyclohexyl-1-nonene (12a). A three-necked flask equipped with an argon inlet and a thermometer was charged under argon with dry $ZnBr_2$ (1.13 g, 5 mmol) in dry THF (5 mL). After the flask was cooled to −50 °C, 1-octenyl-1-magnesium bromide (5 mmol, 1.0 M in THF) was added dropwise. After the mixture was warmed to 25 °C, the THF was removed under vacuum and replaced with dry CH_2Cl_2 (10 mL). After dissolution, a slurry of $Cp_2Zr(H)Cl$,[5f] (1.29 g, 5 mmol) in CH_2Cl_2 (8 mL) was added all at once, followed immediately by a solution of cyclohexanecarboxaldehyde (0.50 g, 4.5 mmol) in CH_2Cl_2 (3 mL). The resulting bright yellow solution was stirred for 14 h at 25 °C. After the usual workup and evaporation of the solvents, the residue was purified by flash chromatography (solvent hexane), affording 777 mg (83%) of (*E*)-1-cyclohexyl-1-nonene (**12a**) as a colorless oil (*E*/*Z* >98/2). In some cases, such as **12a**, two successive purifications by flash chromatography were necessary (solvent hexane) to obtain a pure compound.

Typical Procedure for the Preparation of the Functionalized Olefin 12. Preparation of (*E*)-6-Chloro-1-cyclohexyl-1-hexene (12k). To a three-necked flask equipped with an argon inlet and a thermometer, charged under argon with (*E*)-5-chloro-1-iodo-1-pentene (**7a**; 1.15 g, 5 mmol), and cooled to −100 °C was added BuLi (5 mmol, 1.8 M in hexanes). After stirring for 3 min, a solution of dry $ZnBr_2$ (1.13 g, 5 mmol) in THF (5 mL) was added dropwise. After the mixture was stirred at 25 °C, the solvents were removed under vacuum and replaced with dry CH_2Cl_2 (10 mL). After dissolution, a slurry of $Cp_2Zr(H)Cl$[5f] (1.29 g, 5 mmol) in CH_2Cl_2 (8 mL) was added all at once, followed immediately by a solution of cyclohexanecarboxaldehyde (0.50 g, 4.5 mmol) in CH_2Cl_2 (3 mL). The resulting bright yellow solution was stirred for 14 h at 25 °C. After the usual workup and evaporation of the solvents, the residue was purified by flash chromatography (solvent hexane), affording 594 mg (64%) of (*E*)-6-chloro-1-cyclohexyl-1-hexene (**12k**) as a colorless oil (*E*/*Z* 98/2).

Analytical Data for Compounds 12. (*E*)-6-Tetradecene (12a). A clear oil (644 mg, 73%) was obtained from hexanal (4.5 mmol, 450 mg) after two successive flash chromatographies (solvent hexane): *E*/*Z* ratio >98/2. IR (neat): 3003 (s), 2957 (s), 2873 (s), 2855 (s), 1467 (m), 967 (m) cm^{-1}. ^{1}H NMR: δ 5.42–5.33 (m, 2H), 2.01–1.91 (m, 4H), 1.40–1.13 (m, 16H), 0.89 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR: δ 130.3, 32.4, 31.7, 31.3, 29.5, 29.2, 29.1, 29.0, 28.9, 22.5, 22.4, 13.8. MS (EI, 70 eV; *m*/*e* (relative intensity)): 196 (16), 140 (2), 125 (6), 111 (23), 97 (56), 83 (75), 69 (100). HRMS: calcd for $C_{14}H_{28}$ 196.2191, obsd 196.2189.

(*E*)-1-Cyclohexyl-1-nonene (12b).[18] A clear oil (777 mg, 83%) was obtained from 504 mg of cyclohexanecarboxaldehyde (504 mg, 4.5 mmol) after flash chromatography (solvent hexane). The spectral data match those given in ref 18: *E*/*Z* ratio 98/2. IR (neat): 2961 (s), 2915 (s), 2850 (s), 1451 (m) cm^{-1}. ^{1}H NMR: δ 5.38–5.31 (m, 2H), 2.15–1.80 (m, 3H), 1.73–1.56 (m, 5H), 1.39–0.94 (m, 15H), 0.87 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR: δ 136.5, 127.9, 40.8, 33.5, 32.7, 32.0, 29.8, 29.3, 29.2, 26.4, 26.2, 22.7, 14.1. MS (EI, 70 eV; *m*/*e* (relative intensity)): 208 (18), 180 (2), 138 (3), 124 (4), 109 (42). HRMS: calcd for $C_{15}H_{28}$ 208.2191, obsd 208.2186.

(*E*)-Methyl 6-Tetradecenoate (12c). A clear oil (497 mg, 46%) was obtained from methyl 6-oxohexanoate (4.5 mmol, 648 mg) after flash chromatography (solvent hexane): *E*/*Z* ratio 98/2. IR (neat): 2954 (s), 2926 (s), 2856 (s), 1743 (s), 1437 (m), 1172 (m) cm^{-1}. ^{1}H NMR: δ 5.42–5.31 (m, 2H), 3.67 (s, 3H), 2.32 (t, 2H, *J* = 6.1 Hz), 2.05–1.91 (m, 4H), 1.66–1.54 (m, 2H), 1.44–1.28 (m, 12H), 0.87 (t, 3H, *J* = 6.2 Hz). ^{13}C NMR: δ 174.3, 130.6, 129.6, 129.6, 51.4, 34.0, 32.6, 31.9, 29.8, 29.6, 29.2, 24.6, 24.5, 22.7, 14.1. MS (EI, 70 eV; *m*/*e* (relative intensity)): 240 (1), 208 (8), 166 (15), 151 (3), 137 (7), 124 (17), 110 (20), 96 (43). HRMS: calcd for $C_{15}H_{28}O_2$ 240.2089, obsd 240.2081.

(*E*)-4-Dodecenyl 2,2-Dimethylpropionate (12d). A clear oil was obtained after flash chromatography (solvent hexane/ether 90/10): *E*/*Z* ratio 75/25. IR (neat): 2959 (vs), 2927 (vs), 2855 (vs), 1732 (vs), 1480 (m), 1460 (m), 1284 (s), 1261 (s), 1157 (br, s), 968 (s), 771 (br, s) cm^{-1}. ^{1}H NMR: δ 5.39 (m, 2H), 4.04 (t, 2H, *J* = 6.6 Hz), 2.05 (m, 2H), 1.97 (q, 2H, *J* = 7.6 Hz), 1.28 (m, 10H), 1.19 (s, 9H), 0.87 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR: δ 178.5, 131.5, 128.6, 63.7, 38.7, 32.5, 31.8, 29.5, 29.2, 29.1, 28.9, 28.5, 27.2, 23.5, 14.1. MS (NH_3; *m*/*e* (relative intensity)): 286 (98, $[M + NH_4]^+$), 269 (40, $[M + H]^+$), 136 (100). HRMS: calcd for $C_{17}H_{32}O_2H$ 269.2481, obsd 269.2458.

(*E*)-1-Phenyl-3-undecene (12e). A clear oil was obtained after flash chromatography using hexane as solvent: *E*/*Z* ratio 89/11. IR (neat): 3027 (m), 2956 (vs), 2926 (vs), 2871 (vs), 2854 (vs), 1496 (m), 1466 (s), 1455 (s) cm^{-1}. ^{1}H NMR: δ 7.13 (m, 5H), 5.39 (m, 2H), 2.59 (t, 2H, *J* = 7.3 Hz), 2.25 (m, 2H), 1.90 (m, 2H), 1.18 (m, 10H), 0.81 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR: δ 142.2, 131.2, 129.3, 128.4, 128.2, 125.6, 36.2, 34.4, 32.6, 31.9, 29.6, 29.2, 29.1, 22.7, 14.0. MS (EI, 70 eV; *m*/*e* (relative intensity)): 230 (27), 104 (48), 83 (33). HRMS: calcd for $C_{17}H_{26}$ 230.2035, obsd 230.2043.

(*E*)-1-(Methylthio)-3-undecene (12f). A clear oil was obtained after flash chromatography using hexane as solvent: *E*/*Z* ratio 94/6. IR (neat): 3026 (vs), 2925 (vs), 2871 (vs), 2853 (vs), 1485 (s), 1437 (s), 967 (vs) cm^{-1}. ^{1}H NMR: δ 5.49 (m, 2H), 2.53 (t, 2H, *J* = 6.9 Hz), 2.27 (q, 2H, *J* = 6.9 Hz), 1.98 (q, 2H, *J* = 6.6 Hz), 1.27 (m, 10H), 0.88 (t, 3H, *J* = 6.9 Hz), 2.11 (s, 3H). ^{13}C NMR: δ 132.1, 127.9, 34.3, 32.5, 32.4, 31.8, 29.4, 29.1, 29.09, 29.6, 15.5, 14.0. MS (EI, 70 eV; *m*/*e* (relative intensity)): 200 (6), 185 (59), 129 (12), 95 (14), 81 (21), 61 (100), 55 (29). HRMS: calcd for $C_{12}H_{24}S$ 200.1599, obsd 200.1585.

(*E*)-(4*S*)-1-(1-Nonenyl)-4-isopropenylcyclohexene (12g). A clear oil was obtained after flash chromatography using hexane/ether as solvent: *E*/*Z* ratio 91/9. IR (neat): 3022 (w), 2955 (vs), 2926 (vs), 2855 (vs), 1645 (m), 1466 (s), 1437 (m), 1376 (m) 964 (s), 888 (s) cm^{-1}. ^{1}H NMR: δ 6.0 (d, 1H, *J* = 15.9 Hz), 5.65 (m, 1H), 5.57 (dt, 1H, *J* = 15.9, 6.8 Hz), 4.72 (s, 2H), 2.15 (m, 6H), 1.90 (m, 1H), 1.74 (s, 3H), 1.50 (m, 1H), 1.33 (m, 12H), 0.87 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR: δ 149.8, 135.5, 132.9, 127.2, 126.0, 108.6, 41.5, 32.9, 31.9, 31.4, 29.8, 29.3, 27.7, 25.3, 22.7, 20.7, 14.0. MS (*m*/*e* (relative intensity)): 246 (46), 205 (67), 147 (32), 133 (22), 119 (27), 107 (38), 105 (34), 93 (61), 79 (100), 55 (33). HRMS: calcd for $C_{18}H_{30}$ 246.2348, obsd 246.2334.

(*E*)-1-(4,4-Dimethyl-2,6-dioxolan-1-yl)dec-2-ene (12h). A clear oil was obtained after flash chromatography using hexane/ether as a solvent: *E*/*Z* ratio 89/11. IR (neat): 2955 (s), 2925 (s), 2853 (s), 1468 (m), 1391 (m), 1261 (m), 1128 (s), 1095 (s), 1023 (s), 971 (m), 805 (br s) cm^{-1}. ^{1}H NMR: δ 5.53 (dt, 1H, *J* = 15.8, 6.6 Hz), 5.42 (dt, 1H, *J* = 15.8, 6.6 Hz), 4.41 (t, 1H, *J* = 5.1 Hz), 3.62 (d, 2H, *J* = 10.0 Hz), 3.42 (d, 2H, *J* = 10.0 Hz), 2.35 (t, 2H, *J* = 5.2 Hz), 2.00 (q, 2H, *J* = 6.6 Hz), 1.3 (m, 10H), 0.87 (t, 3H, *J* = 6.9 Hz), 0.71 (s, 6H). ^{13}C NMR: δ 133.8, 123.7, 102.0, 77.3, 38.3, 32.6, 29.2, 29.1, 31.4, 31.8, 29.3, 23.0, 22.6, 21.8, 27.4. MS (*m*/*e* (relative intensity)): 272 (24, $[M + NH_4]^+$), 255 (100, $[M + H]^+$), 168 (46), 136 (63), 115 (25). HRMS: calcd for $C_{16}H_{30}O_2H$ 255.2324, obsd 255.2325.

(6*Z*,8*E*)-7-Butyl-6,8-hexadecadiene (12i). A clear oil was obtained after flash chromatography using hexane as solvent: *E*/*Z* ratio 85/15. IR (neat): 3018 (m), 2957 (vs), 2926 (vs), 2872 (vs), 2856 (vs), 1466 (s), 964 (s) cm^{-1}. ^{1}H NMR: δ 5.93 (d, 1H, *J* = 15.8 Hz), 5.56 (dt, 1H, *J* = 15.8, 6.9 Hz), 5.32 (t, 1H, *J* = 7.3 Hz), 2.19 (t, 2H, *J* = 7.4 Hz), 2.07 (q, 4H, *J* = 6.3 Hz), 1.31 (m,

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[18] Pelter, A.; Hutchings, M. G.; Rowe, K.; Smith, K. *J. Chem. Soc., Perkin Trans 1* **1975**, 138.

20H), 0.92 (m, 9H). ^{13}C NMR: δ 138.3, 133.5, 130.5, 127.3, 33.0, 31.9, 31.7, 31.4, 29.7, 29.6, 29.6, 29.2, 28.0, 23.1, 22.7, 22.6, 14.1, 14.0. MS (*m/e* (relative intensity)): 278 (10), 179 (23), 166 (14), 137 (14), 123 (36), 109 (37), 95 (54), 93 (14), 81 (79). HRMS: calcd for $C_{20}H_{37}$ 278.2974, obsd 278.2968.

(*E*)-1-Phenyl-2-octene (12j). A clear oil (754 mg, 89%) was obtained from benzaldehyde (4.5 mmol, 477 mg) after flash chromatography (solvent hexane). IR (neat): 3027 (m), 2958 (s), 2927 (s), 2857 (s), 1454 (m), 737 (m), 697 (s) cm^{-1}. ^{1}H NMR: δ 7.47–7.13 (m, 5H), 5.61–4.97 (m, 2H), 3.43 (d, 2H, J = 6.3 Hz), 2.17 (q, 2H, J = 7.43 Hz), 1.48–1.22 (m, 6H), 0.97–0.85 (m, 3H). ^{13}C NMR: δ 143.7, 140.3, 136.2, 135.1, 127.8, 122.4, 54.6, 44.6, 32.9, 29.6, 27.3, 15.0. MS (EI, 70 eV; *m/e* (relative intensity)): 188 (2), 174 (5), 160 (8), 122 (10), 109 (21), 96 (33). HRMS: calcd for $C_{14}H_{20}$ 188.1565, obsd 188.1567.

(*E*)-6-Chloro-1-cyclohexyl-1-hexene (12k). A clear oil (594 mg, 64%) was obtained from cyclohexanecarboxaldehyde (504 mg, 4.5 mmol) after flash chromatography (solvent hexane): *E*/*Z* ratio 98/2. IR (neat): 2945 (s), 2908 (s), 1748 (s), 948 (m), 736 (s), 703 (m) cm^{-1}. ^{1}H NMR: δ 5.41–5.23 (m, 2H), 2.54 (t, 2H, J = 6.9 Hz), 2.00 (q, 2H, J = 7.1 Hz), 1.96–1.81 (m, 1H), 1.81–1.54 (m, 6H), 1.54–1.43 (m, 2H), 1.42–0.94 (m, 6H). ^{13}C NMR: δ 137.3, 126.9, 44.9, 40.7, 33.3, 32.1, 31.8, 26.9, 26.3, 26.1. MS (EI, 70 eV; *m/e* (relative intensity)): 202 (3), 200 (8), 109 (50), 96 (48). HRMS: calcd for $C_{12}H_{21}{}^{35}Cl$ 206.1643, obsd 200.1655.

(*E*)-6-Cyano-1-cyclohexyl-1-hexene (12l). A clear oil (472 mg, 55%) was obtained from cyclohexanecarboxaldehyde (504 mg, 4.5 mmol) after flash chromatography (solvent 10% ethyl acetate in hexane): *E*/*Z* ratio 94/6. IR (neat): 2951 (s), 2930 (s), 2248 (m), 1466 (m), 980 (m), 745 (s) cm^{-1}. ^{1}H NMR: δ 5.52–5.45 (m, 2H), 2.34 (t, 2H, J = 7.2 Hz), 2.11–1.93 (m, 2H), 1.93–1.58 (m, 7H), 1.58–1.42 (m, 2H), 1.39–0.91 (m, 6H). ^{13}C NMR: δ 135.1, 128.4, 116.2, 39.7, 34.2, 33.4, 31.9, 26.7, 25.8, 25.4, 14.2. MS (EI, 70 eV; *m/e* (relative intensity)): 191 (3), 108 (41), 95 (40), 81 (70), 67 (100). HRMS: calcd for $C_{13}H_{21}N$ 191.1726, obsd 191.1733.

(*E*)-Ethyl-3-Butyl-9-cyclohexyl-8-nonenoate (12m). A clear oil (840 mg, 58%) was obtained from cyclohexanecarboxaldehyde (4.5 mmol, 504 mg) after flash chromatography (solvent 20% ether in hexane): *E*/*Z* ratio 93/7. IR (neat): 2955 (s), 2930 (s), 2892 (s), 1742 (s), 1475 (s), 1063 (s), 991 (m) cm^{-1}. ^{1}H NMR: δ 5.63–5.56 (m, 2H), 2.42 (t, 3H, J = 7.4 Hz), 2.30 (d, 2H, J = 7.7 Hz), 2.18–2.04 (m, 2H), 2.04–1.49 (m, 13H), 1.49–0.89 (m, 16H). ^{13}C NMR: δ 168.2, 139.6, 128.3, 48.2, 40.0, 36.2, 33.5, 33.3, 32.2, 32.1, 29.6, 28.6, 26.3, 26.2, 22.4, 21.9, 13.7, 13.4. MS (EI, 70 eV; *m/e* (relative intensity)): 322 (2), 277 (15), 249 (13), 140 (7), 127 (10), 123 (11), 109 (15), 85 (47). HRMS: calcd for $C_{21}H_{38}O_2$ 322.2948, obsd 322.2951.

Typical Procedure for the Preparation of Alkylidenecyclohexanes 13a,b. Preparation of (Cyclohexylmethylene)cyclohexane (13a). A three-necked flask equipped with an argon inlet and a thermometer was charged under argon with dry $ZnBr_2$ (1.13 g, 5 mmol) in 5 mL of dry THF. After the flask was cooled to –50 °C, 1-cyclohexenyllithium[14] (5 mmol, 1.1 M in ether) was added dropwise. After the mixture was warmed to 25 °C, the THF was removed under vacuum and replaced with 10 mL of dry CH_2Cl_2. After dissolution, a slurry of $Cp_2Zr(H)Cl$ (1.29 g, 5 mmol) in CH_2Cl_2 (3 mL) was added. The resulting bright yellow solution was stirred for 14 h at 25 °C. After the usual workup and evaporation of the solvents, the residue was purified by flash chromatography (solvent hexane), affording 610 mg (76%) of (cyclohexylmethylene)cyclohexane (13a) as a colorless oil. ^{1}H NMR: δ 4.87 (d, 1H, J = 9.1 Hz), 2.57–0.55 (m, 21H). The spectrum matches the literature data.[19]

Benzylidenecyclohexane (13b). A clean oil was obtained after flash chromatography (solvent hexane). ^{1}H NMR: δ 7.41–7.0 (m, 5H), 6.22 (bs, 1H), 2.39–2.30 (m, 2H), 2.25–2.20 (m, 2H), 1.80–1.38 (m, 6H). The ^{1}H spectrum matches the literature data.[20]

Typical Procedure for the Preparation of Trisubstituted Olefins 14a–e by the Reaction of the 1,1-Bimetallic Species 5a with Ketones. Preparation of 1-Octylidenecyclohexane (14a). A three-necked flask equipped with an argon inlet and a thermometer was charged under argon with dry $ZnBr_2$ (1.13 g) in dry THF (5 mmol). After the flask was cooled to –50 °C, 1-octenylmagnesium bromide (5 mmol, 1.0 M in THF) was added dropwise. After the mixture was warmed to 25 °C, the THF was removed under vacuum and replaced with dry CH_2Cl_2 (10 mL). After dissolution, a slurry of $Cp_2Zr(H)Cl$ (1.29 g, 5 mmol) in CH_2Cl_2 (8 mL) was added all at once, followed immediately by a solution of cyclohexanone (477 mg, 4.5 mmol) in CH_2Cl_2 (3 mL). The resulting bright yellow solution was stirred for 14 h at 25 °C. After the usual workup and evaporation of the solvents, the residue was purified by flash chromatography (solvent hexane), affording 726 mg (85%) of 1-octylidenecyclohexane (14a) as a colorless oil.

Analytical Data for 14a–e. 1-Octylidenecyclohexane (14a). A clear oil (726 mg, 85%) was obtained from benzaldehyde (477 mg, 4.5 mmol) after flash chromatography (solvent hexane). IR (neat): 2956 (s), 2925 (s), 2871 (s), 2854 (s), 1466 (m), 1459 (m), 1447 (m) cm^{-1}. ^{1}H NMR: δ 5.09 (t, 1H, J = 7.8 Hz), 2.16–2.04 (m, 4H), 2.04–1.91 (m, 2H), 1.65–1.40 (m, 6H), 1.40–1.14 (m, 10H), 0.89 (t, 3H, J = 7.4 Hz). ^{13}C NMR: δ 139.5, 121.6, 37.3, 32.0, 31.8, 30.3, 29.3, 28.8, 28.7, 27.9, 27.1, 27.08, 22.7, 14.1. MS (EI, 70 eV; *m/e* (relative intensity)): 194 (11), 166 (1), 151 (1), 137 (1), 123 (3), 109 (48), 96 (70). HRMS: calcd for $C_{14}H_{26}$ 194.2035, obsd 194.2034.

1-Octylidene-2-cyclohexene (14b). A clear oil (708 mg, 82%) was obtained from cyclohexenone (4.5 mmol, 432 mg) after flash chromatography (solvent hexane): *cis*/*trans* ratio 1/1. IR (neat): 3030 (s), 3001 (s), 2955 (s), 2924 (s), 2870 (s), 2832 (s), 1466 (m), 1438 (m) cm^{-1}. ^{1}H NMR: δ 6.47–6.36 (m, 0.5H), 6.09–6.03 (m, 0.5H), 5.84–5.63 (m, 1H), 5.28–5.06 (m, 1H), 2.34–2.20 (m, 2H), 2.20–2.02 (m, 4H), 1.73–1.64 (m, 2H), 1.46–1.16 (m, 10H), 0.88 (t, 3H, J = 7.6 Hz). ^{13}C NMR: δ 134.8, 133.3, 131.4, 129.4, 127.6, 127.0, 125.8, 124.6, 32.4, 31.9, 30.1, 29.7, 29.4, 29.3, 29.0, 27.4, 26.9, 26.9, 26.3, 25.7, 25.3, 23.4, 22.7, 22.6, 14.1. MS (EI, 70 eV; *m/e* (relative intensity)): 192 (24), 135 (30), 107 (75), 94 (83). HRMS: calcd for $C_{14}H_{24}$ 192.1878, obsd 192.1876.

5,5-Dimethyl-3-iodo-1-octylidene-2-cyclohexene (14c). A clear, red oil (608 mg, 39%) was obtained from 5,5-dimethyl-3-iodo-2-cyclohexanone (1.13 g, 4.5 mmol) after flash chromatography (solvent hexane): *cis*/*trans* ratio 68/32. IR (neat): 2954 (s), 2925 (s), 2869 (s), 2854 (s), 2829 (s), 1681 (w), 1466 (m), 1366 (w), 1339 (w), 724 (w) cm^{-1}. ^{1}H NMR: δ 7.03 (s, 0.32H), 6.65 (s, 068H), 5.29 (t, 0.32H, J = 7.1 Hz), 5.03 (t, 1H, J = 7.1 Hz), 2.49–2.40 (m, 2H), 2.13–1.96 (m, 4H), 1.46–1.17 (m, 10H), 1.08–0.87 (m, 9H). ^{13}C NMR: δ 140.6, 135.0, 134.4, 133.2, 132.2, 130.1, 128.2, 98.9, 94.7, 54.4, 53.6, 51.9, 44.5, 37.6, 33.7, 33.2, 31.8, 30.0, 29.6, 29.3, 28.2, 27.8, 27.1, 22.6, 14.1. MS (EI, 70 eV; *m/e* (relative intensity)): 346 (32), 331 (2), 261 (85), 247 (93), 233 (9), 219 (15), 204 (28), 163 (14), 149 (12), 134 (92), 119 (81), 105 (59), 91 (88). HRMS: calcd for $C_{16}H_{27}I$ 346.1158, obsd 346.1153.

2-Phenyl-2-decene (14d). A clear oil (680 mg, 70%) was obtained from acetophenone (4.5 mmol, 540 mg) after flash chromatography (solvent hexane): *cis*/*trans* ratio 39/61. IR (neat): 2956 (s), 2924 (s), 2871 (s), 2854 (s), 1494 (m), 1466 (m), 1457 (m), 1444 (m), 757 (s), 698 (s) cm^{-1}. ^{1}H NMR: 7.44–7.26 (m, 5H), 5.77 (t, 0.61H, J = 7.7 Hz), 5.43 (t, 0.39H, J = 7.7 Hz), 2.20 (q, 2H, J = 6.9 Hz), 2.03 (s, 3H), 1.51–1.18 (m, 10H), 0.97–0.83 (m, 3H). ^{13}C NMR: δ 144.0, 142.1, 135.9, 134.2, 128.7, 128.0, 127.9, 126.3, 126.2, 125.5, 31.8, 30.0, 29.5, 29.3, 29.1, 29.0, 28.9, 28.7, 25.4, 22.5, 15.6, 13.9. MS (EI, 70 eV; *m/e* (relative intensity)): 216 (18), 201 (1), 145 (3), 131 (100), 118 (79), 105 (15). HRMS: calcd for $C_{16}H_{24}$ 216.1878, obsd 216.1875.

Menthyl 2-Phenyl-2-decenoate (14e). A clear oil (1.50 g, 87%) was obtained from menthyl phenylglyoxylate (1.22 g, 4.5 mmol) after flash chromatography (solvent 20% ether in hexane): *cis*/*trans* ratio 86/14. IR (neat): 2957 (s), 2928 (s), 2871 (s), 2857 (s), 1721 (s), 1450 (m), 1256 (s), 1181 (m), 1149 (m), 697 (m) cm^{-1}. ^{1}H NMR: δ 7.59–7.40 (m, 2H), 7.38–7.21 (m, 3H), 6.05–5.93 (m, 1H), 4.81–6.62 (m, 1H), 2.18–1.78 (m, 4H), 1.70–1.54 (m, 2H), 1.54–1.38 (m, 3H), 1.38–1.09 (m, 8H), 1.09–0.70 (m,

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(19) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHennry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245.

(20) Shi, M.; Okamoto, Y.; Takamuku, S. *J. Org. Chem.* **1990**, *55*, 3821.

10H), 0.63 (d, 3H, J = 6.1 Hz), 0.51 (d, 3H, J = 6.1 Hz). ^{13}C NMR: δ 174.4, 142.1, 132.7, 132.3, 129.7, 128.3, 128.1, 127.8, 126.5, 126.3, 78.0, 47.1, 40.5, 40.2, 34.2, 32.3, 31.8, 31.5, 29.1, 28.8, 26.2, 25.5, 23.3, 23.1, 22.7, 22.0, 20.8, 20.6, 61.1, 15.7, 14.1. MS (EI, 70 eV; m/e (relative intensity)): 384 (1), 262 (1), 246 (1), 217 (100), 133 (49), 105 (15), 83 (26). HRMS: calcd for $C_{26}H_{40}O_2$ 384.3028, obsd 284.3033.

Typical Procedure for the Preparation of Allenes by the Reaction of the 1,1-Dimetalloalkenes 16a,b with Aldehydes. Preparation of 4,6,7-Tetradecatriene (17c). A three-necked flask equipped with an argon inlet and a thermometer was charged under argon with 1-octyne (0.55 g, 5.00 mmol) in 5 mL of dry THF. After the flask was cooled to −80 °C, *n*-butyllithium (5.00 mmol, 1.6 M in hexanes was added dropwise. After warming to 25 °C a solution of dry $ZnBr_2$ (1.13 g, 5.00 mmol) in THF was added at −60 °C. After the mixture was warmed to 25 °C, the THF was removed under vacuum and replaced by dry CH_2Cl_2 (10 mL). $Cp_2Zr(H)Cl$ (1.16 g, 4.50 mmol) in dry CH_2Cl_2 (8 mL) was added at once, and the mixture was stirred for 10 min. *trans*-2-Hexenal (0.39 g, 4.05 mmol) was added dropwise. The resulting yellow-green solution was stirred for 12 h at 25 °C. After the usual workup and evaporation of the solvents, the resulting residue was purified by flash chromatography (solvent hexane), yielding 0.35 g (45% yield) of pure 4,6,7-tetradecatriene (17c).

Analytical Data for the Allenes 17a–g. 6,7-Tetradecadiene (17a). A clear oil (594 mg, 68%) was obtained from hexanal (450 mg, 4.5 mmol) after flash chromatography (solvent hexane). The spectral data match those given in ref 21. ^{1}H NMR: δ 5.48–5.33 (m, 2H), 1.98–1.64 (m, 4H), 1.47–0.86 (m, 16H), 0.96–0.82 (m, 6H).

1-Cyclohexyl-1,2-nonadiene (17b). A clear oil (658 mg, 71%) was obtained from cyclohexanecarboxaldehyde (504 mg, 4.5 mmol) after flash chromatography (solvent hexane). The spectral data match those given in ref 21. ^{1}H NMR: δ 5.39–5.31 (m, 2H), 1.99–1.79 (m, 1H), 1.78–1.57 (m, 2H), 1.48–1.00 (m, 18H), 1.00–0.75 (m, 3H).

(*E*)-4,6,7-Tetradecatriene (17c).[22] A clear oil (350 mg, 45% yield) was obtained from (*E*)-2-hexenal (390 mg, 4.05 mmol) after flash chromatograhy (solvent hexane): *E*/*Z* ratio >98% *E*. ^{1}H NMR: δ 5.68–5.80 (m, 2H), 5.51–5.60 (m, 1H), 5.21–5.24 (m, 1H), 1.95–2.02 (m, 4H), 1.23–1.40 (m, 10H), 0.81–0.88 (m, 6H). ^{13}C NMR: δ 206.3, 132.2, 126.1, 94.1, 92.3, 34.8, 31.7, 29.1, 29.0, 28.8, 22.7, 22.6, 14.1, 13.7. IR (neat): 2957 (s), 2927 (s), 2856 (s), 1942 (w), 1708 (m), 1627 (w), 1460 (s) cm^{-1}. MS (EI, 70 eV; m/e (relative intensity)): 208 (1), 194 (1), 192 (2), 137 (2), 122 (47), 95 (23), 93 (51), 91 (22), 81 (22), 80 (51), 79 (100).

(*E*)-3-Methyl-2,4,5-dodecatriene (17d).[22] A clear oil (290 mg, 49% yield) was obtained from (*E*)-2-methyl-2-butenal (290 mg, 3.50 mmol) after flash chromatography (solvent hexane): *E*/*Z* ratio >98% *E*. ^{1}H NMR: δ 5.80 (q, 1H, J = 3.1 Hz), 5.45–5.31 (m, 2H), 2.02–1.97 (m, 2H), 1.68–1.64 (m, 4H), 1.39–1.30 (m, 10H), 0.88–0.83 (m, 3H). ^{13}C NMR: δ 204.4, 131.0, 122.3, 99.2, 93.9, 31.6, 29.11, 29.05, 28.7, 22.5, 13.9, 13.7, 13.1. IR (neat): 2955 (s), 2926 (s), 2852 (s), 1942 (w), 1696 (m), 1622 (m), 1455 (m). MS (EI, 70 eV; m/e (relative intensity)): 194 (4), 179 (3), 151 (3), 137 (3), 124 (9), 123 (100), 110 (31), 109 (34), 108 (42), 107 (20), 95 (35), 93 (57), 81 (25), 79 (35).

(*S*)-1-(1,2-Nonadienyl)-4-Isopropenylcyclohexene (17e).[22] A clear oil (290 mg, 29% yield) was obtained after purification by flash chromatography (solvent hexane). ^{1}H NMR: δ 5.82–5.78 (m, 1H), 5.63 (m, 1H), 5.33 (m, 1H), 4.71 (s, 3H), 2.23–1.96 (m, 6H), 1.72 (s, 3H), 1.50–1.20 (m, 10H), 0.87 (t, 3H, J = 6.9 Hz). ^{13}C NMR: δ 204.4, 149.9, 132.3, 124.6, 108.6, 97.2, 94.2, 43.1, 31.8, 31.3, 29.2, 28.9, 27.6, 26.3, 26.2, 22.6, 20.8, 14.0. IR (neat): 2956 (s), 2921 (s), 2857 (s), 1942 (w), 1688 (m), 1639 (m), 1455 (s) cm^{-1}. MS (EI, 70 eV; m/e (relative intensity)): 189 (3), 175 (1), 133 (2), 70 (7), 57 (5), 55 (8), 44 (9), 43 (13), 42 (5), 41 (9), 32 (23), 29 (7), 28 (100), 27 (6).

1-Phenyl-4-methyl-1,2,4-hexatriene (17f). A yellow oil (290 mg, 49% yield) was obtained from (*E*)-2-methyl-2-butenal (290 mg, 3.50 mmol) after flash chromatography (hexane). ^{1}H NMR: δ 7.25–7.30 (m, 5H), 6.40–6.38 (m, 1H), 6.27 (d, 1H, J = 6.4 Hz), 5.57–5.54 (m, 1H), 1.73 (d, 3H, J = 7.2 Hz), 1.70 (s, 3H). ^{13}C NMR: δ 206.5, 134.7, 130.2, 128.5, 126.8, 126.6, 124.3, 103.1, 97.3, 13.8, 13.2. IR (neat): 2977 (m), 2927 (m), 1944 (w), 1699 (s), 1618 (s), 1493 (s), 1448 (s), 1072 (s) cm^{-1}. MS (EI, 70 eV; m/e (relative intensity)): 186 ($M + NH_3$, 10), 171 (M + 1, 19), 170 (M^+, 46), 169 (8), 155 (46), 128 (21), 115 (23), 91 (27), 77 (24), 43 (23), 28 (100). HRMS: calcd for $C_{13}H_{14}$ 170.1096, obsd 170.1094.

(*E*)-1-Phenyl-1,2,4-octatriene (17g). A yellow oil (190 mg, 29% yield) was obtained from (*E*)-hexenal (340 mg, 3.50 mmol) after purification by flash chromatography (solvent hexane). *E*/*Z* ratio >98% *E*. ^{1}H NMR: δ 7.30–7.16 (m, 5H), 6.32–6.19 (m, 2H), 5.91–5.87 (m, 1H), 5.77–5.71 (m, 1H), 2.12–2.05 (m, 2H), 1.51–1.37 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR: δ 208.6, 134.4, 134.3, 128.7, 127.02, 127.0, 124.5, 97.9, 95.9, 34.9, 22.5, 13.8. IR (neat): 2956 (s), 2926 (s), 2870 (m), 1931 (m), 1596 (m), 1494 (m), 1453 (m) cm^{-1}. MS (EI, 70 eV; m/e (relative intensity)): 185 (M + 1, 5), 184 (M^+, 30), 155 (100), 128 (20), 115 (22), 77 (26), 32 (23), 28 (91). HRMS: calcd for $C_{14}H_{16}$ 184.1252, obsd 184.1266.

Reaction of an Alkylidenemalonate with a 1,1-Bimetallic Reagent of Zr and Zn. Preparation of 1-Phenyl-1-nonene (18). A three-necked flask equipped with an argon inlet, an addition funnel, and a thermometer was charged under argon with dry $ZnBr_2$ (5 mmol, 1.13 g) in 5 mL of dry THF. After the flask was cooled to −50 °C, a solution of 1-octen-1-ylmagnesium bromide (5 mmol, 0.63 M in THF) was added dropwise. After the mixture was warmed to 25 °C, the THF was removed under vacuum and replaced with dry CH_2Cl_2 (10 mL). After dissolution, $Cp_2Zr(H)Cl$ (1.29 g, 5 mmol) in CH_2Cl_2 (8 mL) was added all at once, followed immediately by diethyl benzylidenemalonate (1.12 g, 4.5 mmol) in CH_2Cl_2 (3 mL). After the mixture was stirred for 10 min at 25 °C, acetic anhydride (5.10 g, 50 mmol) was added. The yellow solution was stirred for 13 h at 25 °C. After the usual workup and evaporation of solvents the residue was purified by flash chromatography, yielding 0.91 g (70%) of 1-phenyl-1-nonene (18) as a clear oil: *E*/*Z* ratio 60/40. The spectral data match those given in ref 23. IR (neat): 2947 (s), 2936 (s), 1465 (s), 1450 (m), 743 (s), 701 (m) cm^{-1}. ^{1}H NMR: δ 7.49–7.14 (m, 5H), 6.45–6.18 (m, 2H), 2.33 (q, 1.2H, J = 7.6 Hz), 2.21 (q, 0.8H, J = 7.6 Hz), 1.43–1.11 (m, 10H), 0.99–0.84 (m, 3H). ^{13}C NMR: δ 138.1, 138.0, 133.3, 131.3, 129.9, 128.8, 128.5, 128.2, 126.8, 126.5, 126.0, 33.1, 31.9, 29.5, 29.4, 29.3, 28.7, 22.7, 14.1. MS (EI, 70 eV; m/e (relative intensity)): 159 (1), 145 (1), 131 (4), 117 (75), 104 (100), 91 (24).

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(21) Cherkasow, L. N.; Dubrooskaya, N. M.; Krovosheya, A. N. *Fiz. Khim., Khim. Tekhnol.* **1969**, 221; *Chem. Abstr.* **1971**, *75*, 140151y.

(22) The instability of this allene did not allow us to obtain a satisfactory CHN analysis. Also, a HRMS could not be performed due to the low intensity of the molecular peak. However, capillary GC and ^{1}H and ^{13}C NMR showed that the product has a purity >95%.

(23) Tolstikov, G. A.; Dzhemilev, U. M. *J. Organomet. Chem.* **1985**, *292*, 133.