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Hydroalumination

Titanium-Catalyzed Hydroalumination of Conjugated Dienes: Access to Fulvene-Derived Allylaluminium Reagents and Their Diastereoselective Reactions with Carbonyl Compounds

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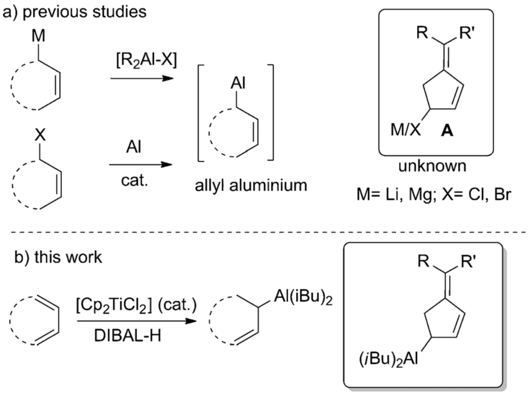
Abstract: The described titanium-catalyzed hydroalumination of conjugated dienes opens up a new way to allylaluminium reagents. The reaction is carried out by using diisobutylaluminium hydride (DIBAL-H) and a catalytic amount of [Cp_2TiCl_2] (Cp = cyclopentadienyl). When applied to mono- and disubstitued pentafulvenes, this reaction proceeds in a highly endocyclic manner. The formed allylaluminium compounds react regio- and stereoselectively with both aldehydes and ketones to afford homoallylic alcohols that are suitable synthons for functionalized cyclopentanones. An extension of this methodology to simple dienes was also investigated. In the proposed mechanism, the initially formed bimetallic species (Ti/Al) are involved in the two possible catalytic cycles with a direct hydroalumination or/and a hydrotitanation followed by a titanium to aluminium transmetallation.

Introduction

Transition-metal-catalyzed hydroalumination of unsaturated carbon–carbon bonds has gained wide interest for selective access to reactive aluminium reagents under mild conditions.[1,2] Numerous substrates, including internal and terminal alkenes and alkynes, as well as nonconjugated dienes have been investigated. In contrast, examples using conjugated dienes are scarce and no reactivity studies towards electrophiles other than protolysis have been reported.[3] The controlled hydroalumination of such substrates would open up a new pathway to allylicaluminium reagents, which are interesting nucleophiles for a number of stereoselective transformations.[4]

To date, allylic aluminium compounds have mainly been synthesized by direct metal insertion into allylic halides or by salt metathesis using Grignard or lithium reagents (Scheme 1a).[4] However, for certain substrates no allylic halide or metal precursors can be accessed. Among those, fulvenes are prominent examples as the corresponding 3-halo-5-methylenecyclopent-1-enes or their metalated analogues have not been reported (Scheme 1a). Fulvenes have found widespread use in cycloaddition reactions in which they can act as 2-, 4- or 6-π-electron components.[5,6] However, the selective transformation of the endocyclic diene system by methods other than cycloaddition reactions is largely unexplored.[7] Such methods would potentially launch fulvene as a suitable synthon for functionalized cyclopentanones.



Scheme 1. Access to allylaluminium reagents.

We recently reported a new titanium-mediated activation of the endocyclic diene moiety in pentafulvenes.[8] The initial approach involved the well-known formation of η^3-allyltitanocenes from dienes following the sequence shown in Scheme 2.[9]

We noticed, however, that the classical reaction conditions (2 RMgCl + [Cp_2TiCl_2]) (Cp = cyclopentadienyl) did not apply to fulvenes. In this case, no allyltitanocene intermediate was

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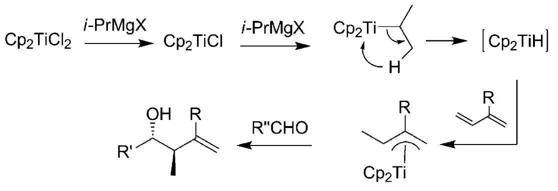
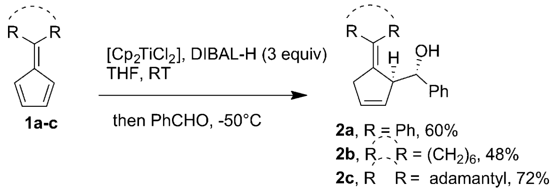


Scheme 2. Formation of η^3-allyltitanocenes from pentafulvenes and their addition to aldehydes.

formed as confirmed by quenching the reaction with PhCHO. We therefore used diisobutylaluminium hydride (DIBAL-H) (2 equivalents) instead of RMgCl. Firstly, DIBAL-H was already associated with [Cp_2TiCl_2] in some cases to give an efficient allylmetalation reaction.[10] Second, we demonstrated that DIBAL-H alone reacted very slowly towards fulvenes at room temperature. Initial experiments performed under rigorously stoichiometric conditions, by using benzaldehyde as the electrophile, afforded the corresponding homoallylic alcohol **2a** in 10 to 30% yields. Performing the reaction at −50 °C, increased the yield to 40%. Finally, the use of an excess of DIBAL-H (3 equivalents) provided **2a** in 60% isolated yield, without competitive reduction of the aldehyde. Cycloheptyl- and adamantyl-derived fulvenes and other aromatic and aliphatic aldehydes were tested to afford the homoallylic alcohols with total regio- and stereoselectivity, up to 72% isolated yields (Scheme 3).[8]



Scheme 3. Synthesis of homoallylic alcohols from pentafulvenes.

The significant increase of the yield upon addition of 3 versus 2 equivalents of DIBAL-H, indicates that an excess of DIBAL-H is crucial for promoting an efficient allylmetallation. At this stage, one may assume that an allylaluminium intermediate could be generated under these reaction conditions.

A plausible mechanistic rationale for this reaction involves the formation of the bimetallic species **I**,[8]which would act as the hydrotitanation agent to form an allyltitanium intermediate (path a). The transmetallation from titanium to aluminium could afford the allylaluminium species (path b). A third pathway, which would involve a direct hydroalumination could also operate (path c) (Figure 1).

The aforementioned mechanistic scenarios led us to the assumption that a titanium-catalyzed hydroalumination of conjugated dienes might be possible.

In this paper, we would like to disclose the development of a new catalytic system based on [Cp_2TiCl_2] and DIBAL-H that allows the highly selective endocyclic hydroalumination of pentafulvenes (Scheme 1b). The successive allylalumination of carbonyl compounds is high yielding and displays very good regio- and stereoselectivities. We have demonstrated that this new approach also applies to simple dienes.

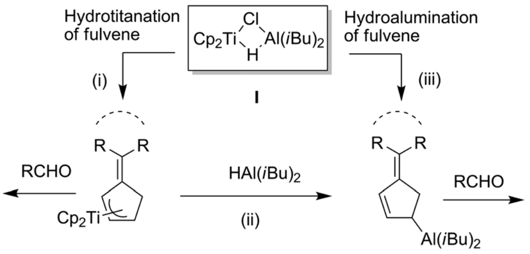
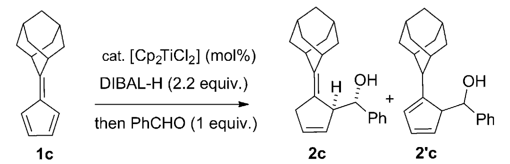


Figure 1. Plausible pathways for the stoichiometric allylmetalation.

Results and Discussion

In the first experiments, DIBAL-H (1.1 mmol) was added to a THF solution of fulvene (0.5 mmol) and [Cp_2TiCl_2] (1 mol%) at room temperature. After stirring for 16 h at the same temperature, benzaldehyde (0.5 mmol) was added at −60 °C and the reaction was continued for 1 h. Basic workup (aqueous $NaHCO_3$) resulted in the exclusive formation of cyclopentadienyl homoallylic alcohol **2′c** related to the exocyclic attack of the hydride (Table 1, entry 1). By increasing the catalyst loading to 10 mol%, the *endo* addition product **2c** also started to form and the ratio of *exo*/*endo* products turned to be nearly 1:1 with a total yield of 51% (entry 2). With a catalyst loading of 20 mol%, exocyclic attack was almost suppressed but the yield remained moderate (entry 3). A rise in temperature proved to be beneficial and at 50 °C the homoallylic alcohol was obtained in 99% yield, with total *endo* selectivity and an exclusive *anti* stereoselectivity with respect to the vicinal protons (entry 4). Further, at this temperature the catalyst loading was reduced to 10 mol% and reaction time to 4 h without having any detrimental effect on the yield and regio- or diastereoselectivities (entry 5). However, a further decrease of the catalyst loading to 5 mol% led again to the formation of some **2′c**, albeit in low

Table 1. Optimization studies.



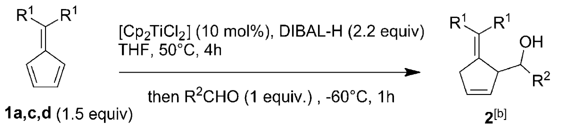
	[Cp_2TiCl_2][a] [mol%]	1c [equiv]	t [h]	T	2c [%][b]	2′c[b]
1	1	1.0	16	RT	–	52
2	10	1.0	16	RT	28	23
3	20	1.0	16	RT	55	<5
4	20	1.5	16	50 °C	99	–
5	10	1.5	4	50 °C	99	–
6	5	1.5	4	50 °C	72	5
7	–	1.5	4	50 °C	–	91

[a] Based on amount of aldehyde used. [b] NMR spectroscopic yields.

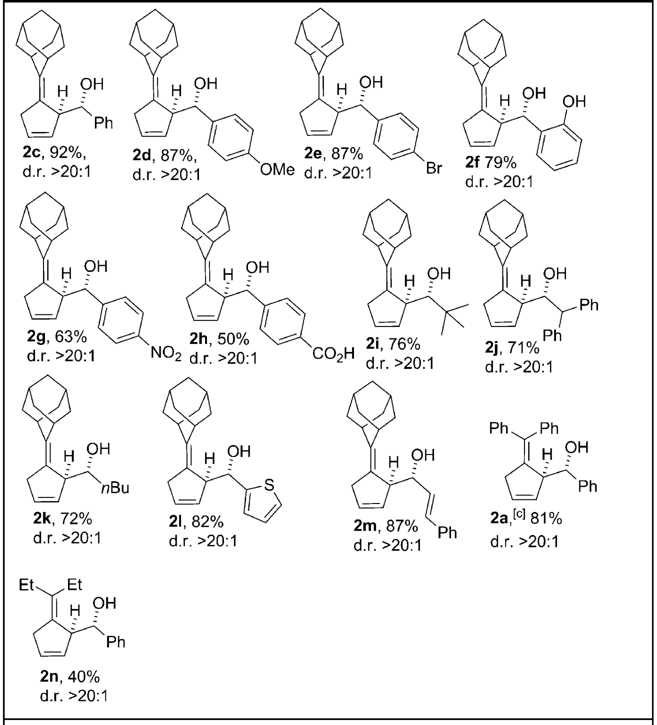
quantities (entry 6). In the absence of titanium complex under the optimised conditions exclusive formation of **2′c** was observed in high yield (entry 7). Small amounts of fulvene reduced products are also formed in all the cases. It is important to note that other aluminium hydrides (Red-Al, Lithium tri-*tert*-butoxyaluminium hydride), boron hydride (L-selectride) and Grignard reagents failed to produce this novel titanium-catalysed hydrometallation.

With the optimized conditions in hand, the substrate scope of this new catalytic reaction was further explored. Aliphatic, aromatic, α,β-unsaturated and heteroaromatic aldehydes showed excellent reactivity and afforded the corresponding homoallylic alcohols in good yields and with total diastereoselectivity according to ^{1}H NMR spectroscopy (Table 2). In the case of cinnamaldehyde, the 1,2-addition product **2m** was formed exclusively. It is noteworthy that compounds with reactive functional groups, for example −OH, $-NO_2$, and even −COOH, were also tolerated under the reaction conditions (Table 2, **2f**–**h**.) When the adamantyl group in fulvene was replaced with two phenyl or two ethyl groups (fulvenes **1a**, **d**) still high selectivity could be achieved (**2a**, **n**).

Table 2. Reactions of disubstituted pentafulvenes with aldehydes.[a]



1a,c,d (1.5 equiv) → **2**[b]

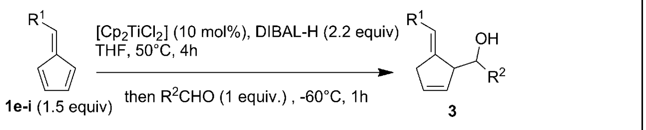


2c, 92%, d.r. >20:1; **2d**, 87%, d.r. >20:1; **2e**, 87%, d.r. >20:1; **2f** 79% d.r. >20:1; **2g**, 63% d.r. >20:1; **2h**, 50% d.r. >20:1; **2i**, 76% d.r. >20:1; **2j**, 71% d.r. >20:1; **2k**, 72% d.r. >20:1; **2l**, 82% d.r. >20:1; **2m**, 87% d.r. >20:1; **2a**,[c] 81% d.r. >20:1; **2n**, 40% d.r. >20:1

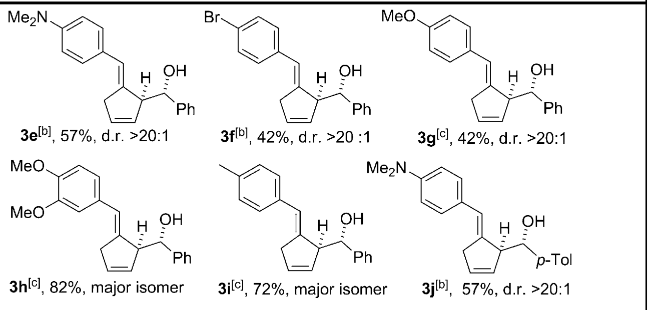
[a] Reaction conditions: Fulvene (0.75 mmol), $[Cp_2TiCl_2]$ (0.05 mmol), DIBAL-H (1.1 mmol), THF, 50 °C, 4 h, then aldehyde (0.5 mmol), −60 °C, 1 h. [b] Isolated yields. [c] Reaction time before adding electrophile is 12 h.

The very good results obtained with the new catalytic system and disubstituted pentafulvenes, led us next to the investigation of monosubstituted pentafulvenes. These are more challenging substrates in terms of achieving endocyclic selectivity because the highly reactive exocyclic C-6 position is readily exposed. Indeed, under stoichiometric hydrotitanation conditions, only reduction products of fulvene were observed. However, under catalytic conditions, we were pleased to find that the endocyclic positions were again the preferred site of reactivity. A variety of monosubstituted fulvenes carrying 4-*N,N′*-dimethylamino-, 4-bromo-, 4-methyl-, and 4-methoxyphenyl substituents **1e**–**i** were studied and the resulting homoallylic alcohols **3e**–**i** were obtained in moderate to good yields with high regio- and diastereoselectivity (Table 3).

Table 3. Reactions of monosubstituted pentafulvenes with aldehydes.[a]



1e-i (1.5 equiv) → **3**



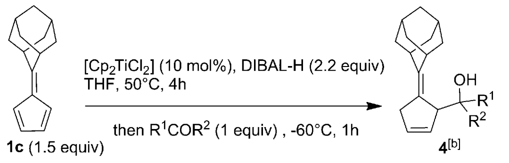
3e[b], 57%, d.r. >20:1; **3f**[b], 42%, d.r. >20 :1; **3g**[c], 42%, d.r. >20:1; **3h**[c], 82%, major isomer; **3i**[c], 72%, major isomer; **3j**[b], 57%, d.r. >20:1

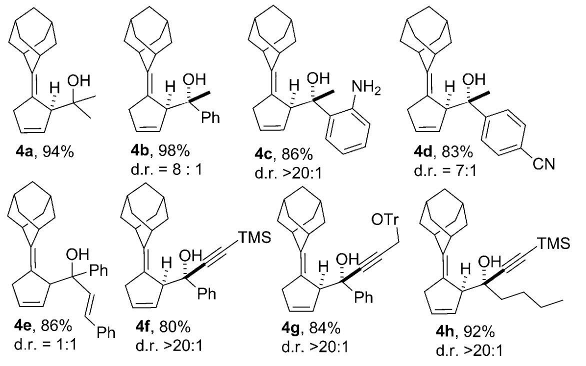
[a] Reaction conditions: Fulvene (0.75 mmol), $[Cp_2TiCl_2]$ (0.05 mmol), DIBAL-H (1.1 mmol), THF 50 °C, 4 h, then aldehyde (0.5 mmol), −60 °C, 1 h. [b] Isolated yields. [c] NMR spectroscopic yields calculated by using 1,2-tetrachloroethane as the internal standard.

Through selective endocyclic dihydroxylation followed by oxidative cleavage of the exocyclic double bond, the relative configuration of these new homoallylic alcohols was established and it was again found to be *anti* with respect to vicinal protons.

Allylation of aldehydes is known to proceed in a highly diastereoselective manner with several allylic metal reagents.[11] In contrast, achieving such a level of selectivity with ketones is rare.[12] Recently, the highly diastereoselective addition of cyclic allylalanes onto methylketones was described.[4a] We thus decided to investigate ketones in our catalytic conditions (Table 4). At first, acetone was employed, affording the corresponding alcohol **4a** in 94 % yield. A series of unsymmetrical ketones were used next. Acetophenone derivatives provided good to excellent diastereoselectivities (**4b**–**d**), probably due to a different steric demand within the ketone. In contrast, chalcone led to a 1:1 mixture of diastereomers **4e** along with a 1,4-addition product. To maintain a significant size differentiation between the two branches of the electrophile, ketones containing an alkynyl substituent, which constitutes an alkyl

Table 4. Reactions of adamantyl-derived pentafulvene**1 c** with ketones.[a]





4a, 94%

4b, 98%
d.r. = 8 : 1

4c, 86%
d.r. >20:1

4d, 83%
d.r. = 7:1

4e, 86%
d.r. = 1:1

4f, 80%
d.r. >20:1

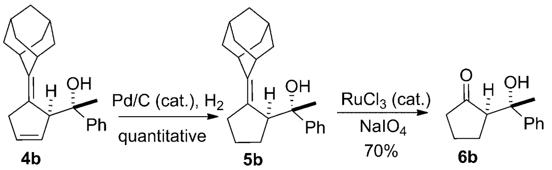
4g, 84%
d.r. >20:1

4h, 92%
d.r. >20:1

[a] Reaction conditions: **1 a** (0.75 mmol), [Cp$_2$TiCl$_2$] (0.05 mmol), DIBAL-H (1.1 mmol), THF, 50 °C, 4 h, then ketone (0.5 mmol). [b] Isolated yields.

chain precursor, were tested. In these cases, alcohols **4 f**–**h** were obtained in a diastereoselectively pure form. Interestingly, functional groups could be incorporated to the alkynyl chain, for example, a protected alcohol in **4g**. The use of a ketone containing a linear alkyl and an alkynyl chain opens up the way to diastereoselective access to tertiary alcohol **4h** bearing two comparable alkyl chains.

This approach, involving fulvene-derived allylaluminium species, is of particular interest since it constitutes an alternative to cyclopentanone–ketone cross-aldol reactions.[13] The corresponding products can be readily obtained in two steps from the homoallylic alcohol: hydrogenation of the endocyclic double bond followed by oxidative cleavage of the exocyclic double bond (Scheme 4). After the oxidation step, adamantanone can be fully recovered and reused in the formation of starting fulvene.



Scheme 4. Transformation of homoallylic alcohols to cross-aldol products.

Mechanistic studies of this new titanium-catalyzed hydroalumination reaction were hampered by the fact, that the initial reaction between titanocene dichloride and DIBAL-H yielded paramagnetic Ti^{III} species.[8] Hence, the reaction could not be followed by NMR spectroscopy.[14] We therefore attempted to detect intermediate species by ESI-MS studies. Whereas the catalytic species remained elusive, we were able to confirm the formation of allylicalumininum species in the case of the *p*-*N*,*N*′-dimethylaminophenylfulvene (**1 e**) by HRMS (**B**, Figure 2).

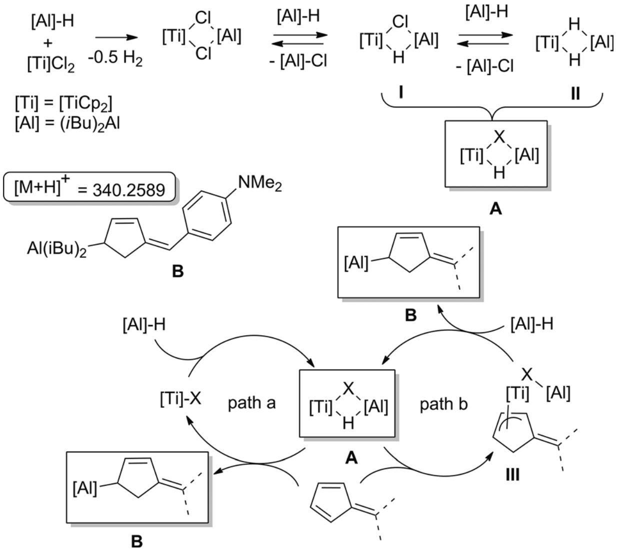


Figure 2. Proposed reaction mechanism.

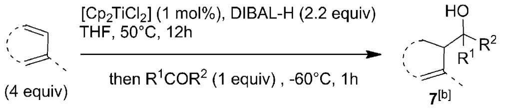
We also noticed that for the hydrotitanation, the classical [Cp$_2$TiCl$_2$]/*i*PrMgX system or any other transition-metal/DIBAL-H combination ([Cp$_2$ZrCl$_2$], NiCl$_2$, CuCl$_2$) cannot be applied to fulvenes.[8] This may indicate that the catalytically active hydride involves a cooperative Al/Ti association.

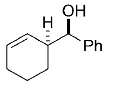
Based on these results and on our previous mechanistic studies for the stoichiometric reaction,[8] a plausible mechanism is shown in Figure 2. Starting from the initially formed trivalent complex [Cp$_2$Ti(μ-Cl)$_2$Al(*i*Bu)$_2$], chloride for hydride exchanges could generate two bimetallic hydride intermediates **I** and **II**(**A**).

Two reaction pathways could then operate. In the first, the bimetallic species **A** could give direct hydroalumination to yield the allylaluminium **B** (path a). Alternatively, the bimetallic species could act as a fulvene hydrotitanation agent to give the π-allyltitanocene **III**, which transmetallates to **B** and regenerates the catalytically active hydride (path b). Path a is possibly favoured under the catalytic conditions, as referred to the stoichiometric variant, (see Figure 1), however, path b cannot be ruled out at this stage. To date we cannot exclude that even more complex species are involved in this transformation.

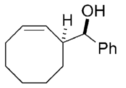
To examine the generality of this new catalytic system, the optimized reaction conditions were applied to simple dienes, that is, cyclohexadiene, cyclooctadiene, and isoprene. In these cases, a longer reaction time (12 h) was necessary to obtain the corresponding homoallylic alcohols in good yields (Table 5). Cyclic dienes reacted with higher diastereoselectivity, whereas in the case of isoprene complete loss of diastereoselectivity was observed. With simple dienes, the catalyst loading can even be reduced to 1 mol %, probably due to the relatively decreased competition from other reactive sites.

Table 5. Generalisation to simple dienes.[a]

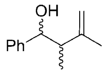




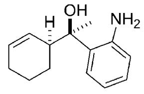
7a, 70%, d.r. >20:1



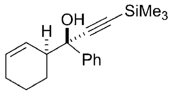
7b, 74%, d.r. = 8:1



7c, 60%, d.r. = 1:1



7d, 94%, d.r. >20:1



7e, 92%, d.r. = 3:1

[a] Reaction conditions: Diene (2 mmol), [Cp$_2$TiCl$_2$] (0.05 mmol), DIBAL-H (1.1 mmol), THF, 50 °C, 12 h, then electrophile (0.5 mmol), −60 °C, 1 h. [b] Isolated yields.

Conclusion

In summary, we have developed a new titanium-catalyzed hydroalumination that allows the formation of allylaluminium reagents from conjugated dienic systems. With mono and disubsituted pentafulvenes, hydroalumination took place in a highly endoselective manner. The formed allylaluminium reagents are excellent nucleophiles for aldehydes and ketones and allowed the diastereoselective formation of homoallylic alcohols. The easy accessibility of cross-aldol products from these homoallylic alcohols emphasizes the potential of the present methodology. Simple dienes also form allylaluminium reagents under the reaction conditions thereby making this novel catalytic system suitable for broad applicability. Investigations regarding the basis of site selectivity, exact nature of catalytic species, and applications to other classes of electrophiles are currently underway.

Experimental Section

General remarks

All reactions involving organometallics were conducted under an atmosphere of argon. Prior to use, THF was distilled over sodium-benzophenoneketyl. [Cp$_2$TiCl$_2$], DIBAL-H, and aldehydes were purchased from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$on a Bruker AC-250 spectrometer. Mass spectra were recorded on a Micromass Q-TOF micro MS spectrometer. All fulvenes (**1c**–**j**) except diphenylfulvene **1a** were prepared by the procedure reported by Little.[15] Purification of the compounds was done through flash column chromatography on silica gel.

General procedure for homoallylic alcohols derived from fulvenes and aldehydes/ketones

A standard Schlenk tube with magnetic stir bar was charged with fulvene (0.75 mmol) and [Cp$_2$TiCl$_2$] (12.5 mg, 0.05 mmol). The system was evacuated and back filled with argon (three times). Dry THF was added (5 mL) followed by slow addition of DIBAL-H (1 M in THF, 1.1 mL) at room temperature. When the addition of DIBAL-H was completed, the reaction vessel was inserted into a preheated oil bath at 50 °C. After 4 h at the same temperature, the mixture was cooled to −50 °C and aldehyde or ketone (0.5 mmol) was added. The reaction was continued for 1 h at the same temperature and then quenched by adding a saturated aqueous solution of NaHCO$_3$. The mixture was further diluted with ether (25 mL) and stirred for another 2 h. The organic phase was separated and concentrated under reduced pressure. The residue was purified by column chromatography to give the corresponding homoallylic alcohol.

General procedure for homoallylic alcohols derived from simple dienes and benzaldehyde/ketones

A standard Schlenk tube with magnetic stir bar was charged with [Cp$_2$TiCl$_2$] (2.5 mg, 0.01 mmol). The system was evacuated and back-filled with argon (3 times). Dry THF (5 mL) was added followed by the diene (1 mmol). DIBAL-H (1 M in THF, 1.1 mL) was added over 2 min at room temperature. When the addition of DIBAL-H was completed the reaction vessel was inserted into a preheated oil bath at 50 °C. After 12 h at the same temperature, the mixture was cooled to −50 °C. Then, benzaldehyde or ketone (0.5 mmol) was added. The stirring was continued for 1 h at the same temperature. The reaction was quenched by adding a saturated aqueous solution of NaHCO$_3$, and the mixture was further diluted with Et$_2$O (25 mL) and stirred for another 2 h. The organic phase was separated and concentrated under reduced pressure. The residue was purified by column chromatography to give the corresponding homoallylic alcohol.

Synthesis of 2-(1′-hydroxy-1′-methyl)benzylcyclopentanone (6b)

A mixture of **4b** (1 mmol) and Pd/C (10%, 100 mg, 0.1 mmol) in MeOH (5 mL) was stirred under an atmosphere of hydrogen for 1 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (10 mL) and filtered through a pad of Celite. The filtrate was evaporated to dryness and the crude product of **5b** was directly used without purification.

The crude mixture **5b** was dissolved in a 1:1 mixture of CH_3CN:CCl_4 (20 mL). NaIO$_4$ (1.278 g, 6 mmol) was added with stirring. Then a solution of $RuCl_3 \cdot H_2O$ (22.5 mg, 0.1 mmol) in water (10 mL) was added in one portion. The reaction was continued for 5 h. The reaction mixture was diluted with water (10 mL) and extracted with CH$_2$Cl$_2$ (3×15 mL). The organic layer was evaporated to dryness and the residue was purified by column chromatography to give the ketone **6b** (142 mg, 70%) as a colourless oil.[13] ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.46$ (m, 2H), 7.34 (m, 2H), 7.25 (m, 1H), 4.58 (brs, 1H),2.44 (m, 2H), 2.16 (m, 1H), 1.82 (m, 1H), 1.67 (m, 2H),1.58 ppm (s, 3H); ^{13}C NMR (62.5 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 222.41$, 145.9, 128.10, 127.00, 125.16, 74.97, 59.90, 39.89, 27.13, 23.54, 20.00 ppm; HRMS-ESI: m/z: elemental analysis calcd (%) for $C_{13}H_{16}NaO_2$: 227.1048; found: 227.1050 $[M+Na]^+$.

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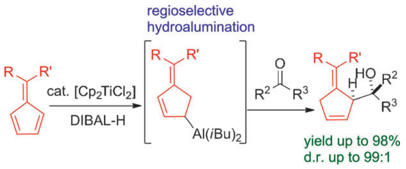
FULL PAPER

Aluminate your chemistry! The described titanium-catalyzed hydroalumination of conjugated dienes opens up a new way to allylaluminum reagents. When applied to mono- and disubstitued pentafulvenes, this reaction proceeds in a highly endocyclic manner producing allylaluminium compounds that react with aldehydes and ketones to afford homoallylic alcohols (see scheme; DIBAL-H = diisobutylaluminium hydride, Cp = cyclopentadienyl).



Hydroalumination

*J. Joseph, F. Jaroschik, D. Harakat, K. V. Radhakrishnan, J.-L. Vasse, J. Szymoniak**

■■ – ■■

Titanium-Catalyzed Hydroalumination of Conjugated Dienes: Access to Fulvene-Derived Allylaluminium Reagents and Their Diastereoselective Reactions with Carbonyl Compounds