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Rhodium-Catalyzed Deallylation of Allylmalonates and Related Compounds

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Various allylmalonates and other related compounds were selectively deallylated in the presence of a catalytic amount of a rhodium complex and an excess of triethylaluminum. Comparison of several phosphane (PPh_3) and BIAP (bis(imidazolonyl)pyridine) rhodium complexes showed that the latter are more active and general with respect to the structural diversity of the substrate then the former. It was shown that the role of triethylaluminum is not only to generate in situ a rhodium hydride, which is assumed to be the catalytically active species, but also to act as a Lewis acid to activate the carbonyl group of the substrate. Thus, the proposed mechanism of deallylation involves hydrorhodation of the double bond along with activation of the carbonyl group of the substrate by triethylaluminum followed by a sequence of bond formations and cleavages, furnishing an enolate and an alkene. The methodology provides an efficient and selective route to deallylation of allylmalonates under mild reaction conditions.

Introduction

Rhodium belongs to the group of transition metals (Ru, Os, Pd, etc.) that has caused a real revolution in synthetic organic chemistry in the past 30 years. Although its utilization has been overshadowed by the use of more successful (cheaper) metals, e.g. Pd, there has been recently renewed focus on rhodium catalysis within the context of the C−C bond forming reactions. In this regard it has been used as a catalyst in 1,4-conjugate additions, 1,2-additions to C═X bonds, cross-coupling reactions, cycloisomerizations, cyclotrimerizations, carbometalations of double and triple bonds, carbene chemistry, aldol condenzation, etc.[1,2] On the other hand, rhodium complexes are also effective catalysts for the reverse process—C−C bond cleavage.[3,4] They proved to be excellent catalysts for the cleavage of strained cyclic systems such as cyclopropane rings,[5] cubane,[6] the cyclobutane ring of biphenylene,[7] and rings of cyclobutanones[8,9] and larger cycloalkanones.[9] Similarly, it has been shown that Rh catalysts are suitable also for the cleavage of acyclic C−C bonds. Typical examples are the cleavage of the sp^2-sp^3 bond of alkylbenzenes[10] and the activation of the sp^3-sp^3 bond in ketones[11] and ketimines[12] and of the sp−sp bond of alkynes.[13] It is also worth mentioning that the C−C bond cleavage of cyclopropane and cyclobutane rings is crucial for rhodium-catalyzed higher order [5 + 2][14] and [6 + 2][15] cycloaddition reactions.

Recently, we have described an iron phosphane complex catalyzed alkylative cyclization of α,ω-2-chlorodienes with trimethyl- and triethylaluminum, giving 1-methylidene-2-alkylcyclopentanes. During the course of the study we observed that the reaction of allyl(2-chloroallyl)malonate proceeds anoma-

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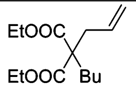
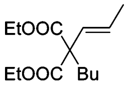
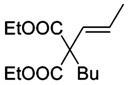
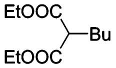
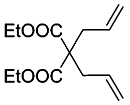
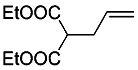
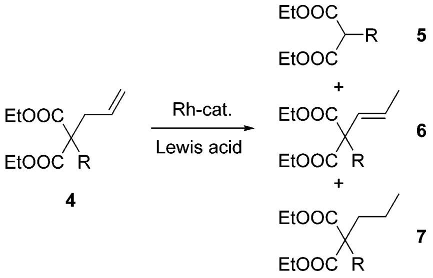
Table 1. Deallylation of Allylmalonates by Rh(PPh$_3$)$_4$H (1)

Entry	Substrate	Cat. (%)	Additive[a]	T (°C)	t (h)	Product	Yield (%)[b]
1	 (**4a**)	5		60	48		n. r.
2		100		60	48	 (**6a**)	93 (7)
3		5	NaH	20	3		n. r.
4		25	$(C_6F_5)_3B$	60	5		n. r.
5		12	$AlCl_3$	60	10		n. r.
6		12	$ZnBr_2$	60	10		n. r.
7		5	Et_2Zn	20	5		n. r.
8		12	Et_3B	20	5	 (**6a**)	24 (76)[c]
9		4	Et_3Al	20	19	 (**5a**)	84[d,e]
10	 (**4b**)	5	Et_3Al	20	19	 (**5b**)	25 (14)[f]

[a] Usually 2 equiv. [b] GC or ^{1}H NMR yield. In parentheses is given the amount of the unreacted starting material, if present (GC or ^{1}H NMR analysis). n.r. = no reaction. [c] At 60 °C isomerized product 30%, starting material 70%. [d] Butylpropylmalonate formed in 16% yield. [e] In the presence of 25 mol % of the catalyst the deallylation was 100% complete. [f] Allylpropenylmalonate **6b** formed in 55% yield.

lously: instead of alkylative cyclization, C−C bond cleavage (deallylation) took place to furnish (2-chloroallyl)malonate.[16] Additionally, we have reported that this reaction—deallylation—can be catalyzed by a number of other transition-metal phosphane complexes (Ru, Co, Rh, Ni, and Pd) as well. Although the deallylation products were obtained in all cases, a detailed comparison of the Ni- and Ru-catalyzed reactions indicated a distinct difference between the individual catalysts as far as the selectivity for various substrates is concerned.[17] The preliminary results also showed that Rh(PPh$_3$)$_3$Cl—Wilkinson's catalyst—could be the best choice of an catalyst for the allylbutylmalonate deallylation in comparison with other complexes under the standard conditions.

Scheme 1. Dealyllation by Rh Complexes



Further interest in Rh-catalyzed deallylation was based on conclusions made from the proposed reaction mechanism.[17] It was reasonable to expect that the natures of the catalytically active species generated from Ni and Rh complexes should be different. Since it has been known that cationic Ni species are formed by the reaction of Ni(II) compounds with alkylaluminums,[18] we assumed that a cationic Ni(II) hydride was the catalytically active species. On the other hand, the formation of similar cationic species from a Rh(I) complex is unlikely under the same reaction conditions, because the reaction of $Rh^{I}-X$ with triethylaluminum should result in the formation of a Rh^{I}−alkyl species that undergoes β-hydrogen elimination to give a neutral Rh^{I}−hydride. This is supported by the reported formation of Rh−hydride complexes upon reaction with alkylmetals (Et_2Zn,[19] Et_3Al,[20] BuLi[21]), metal hydrides (Et_3SiH,[22] catecholborane,[23] BH_3[24]), or hydrogen in the presence of a base.[25] The aforementioned applications, along with an interest

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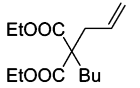
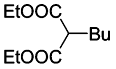
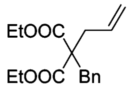
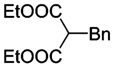
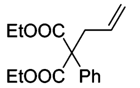
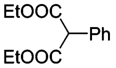
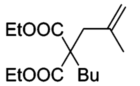
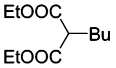
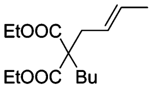
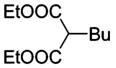
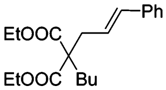
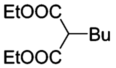
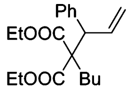
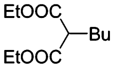
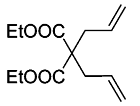
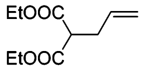
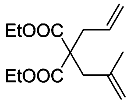
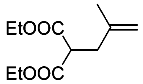
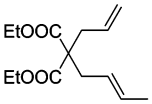
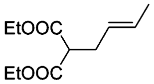
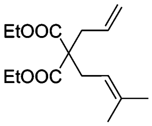
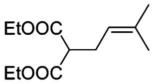
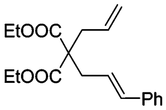
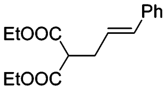
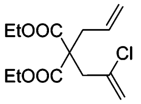
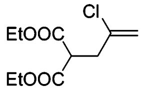
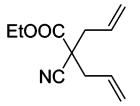
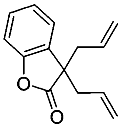
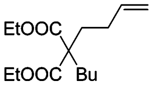
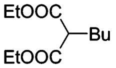
Table 2. Deallylation with Complexes 2 and 3a[a]

Entry	Substrate		Product		t (h)	Yield (%)[b] (cat. **2**)	t (h)	Yield (%)[b] (cat. **3a**)
1		(**4a**)		(**5a**)	6	65[c]	3	100
2		(**4c**)		(**5c**)	3	77[d]	3	100
3		(**4d**)		(**5d**)	24	0 (13)[d]	3	100
4		(**4e**)		(**5a**)	24	28 (72)	24	39 (48)
5		(**4f**)		(**5a**)	24	6 (92)	24	77 (23)
6		(**4g**)		(**5a**)		-[f]	24	29 (71)
7		(**4h**)		(**5a**)		-[f]	3	100
8		(**4b**)		(**5b**)	3	100	3	100
9		(**4i**)		(**5i**)	3	82[g]	3	100
10		(**4j**)		(**5j**)	3	93[h]	3	100
11		(**4k**)		(**5k**)	3	78[i]	3	100
12		(**4l**)		(**5l**)	3	(42)[j]	3	100
13		(**4m**)		(**5m**)	24	41[k]	3	20[l]
14		(**4n**)				-[m]	24	n.r.
15		(**4o**)				-[m]	24	n. r.
16		(**4p**)		(**5a**)	24	31[m]	24	30[m]

[a] Reaction conditions: catalyst (5 mol %), Et_3Al (2 equiv). [b] GC or ^1H NMR yields. In parentheses is given the amount of the unreacted starting material, if present (GC or ^1H NMR analysis). n.r. = no reaction. [c] Butylpropylmalonate 35%. [d] Cyclopentanone **8a** was formed in 23% yield. [e] Isomerized product **6d** was formed in 73% yield. [f] Reaction was not carried out. [g] Unidentified products 11% and 7%. [h] Butylpropylmalonate 7%. [i] Cyclopentanone **8b** was formed in 22% yield. [j] Unidentified products (19, 25, and 12%) could not be separated into individual substances. [k] Allylmalonate **5b** in 23% yield. [l] Diallylmalonate **4b** 45%, allylmalonate **5b** 26%. [m] Contains a mixture of unidentified compounds.

in revealing the scope of the reaction with respect to other transition metals, provided a strong impetus to study the suitability of rhodium complexes for the catalytic deallylation reaction. Herein we to report a detailed study on Rh complex (P or N ligated) catalyzed C−C bond cleavage (deallylation) of allylmalonates.

Results and Discussion

For our study we chose three typical representatives of rhodium complexes: the stable hydride $Rh(PPh_3)_4H$ (**1**), $Rh(PPh_3)_3Cl$ (**2**; Wilkinson's catalyst), and the new class of nitrogen-ligated complexes $Rh(BIAP)Cl_3$ (**3**; BIAP = bis(imidazolonyl)pyridine).[26] The catalytic activities of these complexes were tested by themselves or in the presence of triethylaluminum or other additives.

Reactions Catalyzed by $Rh(PPh_3)_4H$. The possibility of catalytic deallylation with a neutral Rh(I) hydride was especially attractive from a synthetic point of view. To carry out the reaction under neutral conditions would mean broadening of the scope of the reaction to substrates bearing functional groups sensitive to alkylmetals. In view of the foregoing, the use of the stable rhodium hydride ($Rh(PPh_3)_4H$) (**1**) as a catalyst seemed to be inevitable.

The reaction with **1** was carried out under various conditions in toluene (Table 1). Treatment of the allylbutylmalonate **4a** with a catalytic amount of **1** (5 mol %) at 20 or 60 °C for 48 h did not result in any visible reaction (entry 1). Similarly, the deallylation did not proceed with a stoichiometric amount of **1** at 20 °C, but heating of the reaction mixture to 60 °C for 48 h resulted in the double-bond shift and the formation of the butylpropenylmalonate **6a** in 93% yield (entry 2). The next experiment was executed in the presence of NaH to promote the formation of the enolate (at 20 and 60 °C); however, again no reaction was observed (entry 3). Although these results were disappointing, they gave us two hints: first, the hydrometalation of the double bond proceeded (otherwise the isomerization would not occur), and second, the function of triethylaluminum was more than just to generate rhodium hydride or to transmetalate rhodium from the enolate.

Since triethylaluminum is a Lewis acid, it might coordinate to the lone electron pair on the carbonyl oxygen and thus activate bonds in the vicinity of the carbonyl group. We reasoned that adding another Lewis acid into the reaction mixture might induce the deallylation. Unfortunately, our expectations were not met: the presence of $B(C_6F_5)_3$, $AlCl_3$, and $ZnBr_2$ (entries 4−6) or Lewis acids with reductive properties such as $ZnEt_2$ and BEt_3 (entries 7 and 8) did not result in any deallylation. However, in the last case a partial isomerization of the double bond to **6a** (24%) was observed (entry 8). The deallylation of the allylbutylmalonate **4a** to the butylmalonate **5a** proceeded smoothly in good yield (84%) only after addition of Et_3Al into the reaction mixture (entry 9). Along with **5a** the butylpropylmalonate **7a** (16%) was formed by the hydrogenation of the double bond. However, the catalytic activity of **1** in the deallylation of the diallylmalonate **4b** to the allylmalonate **5b** (24%) was rather low and was accompanied by a double-bond shift to the allylpropenylmalonate **6b** in 55% yield (entry 10).

Scheme 2. Formation of Cyclopentanones 8 from 4

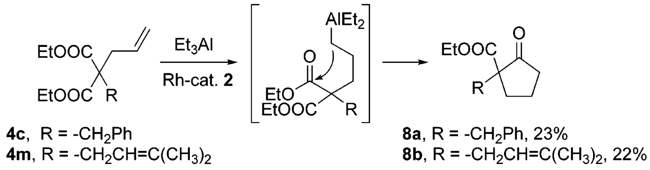
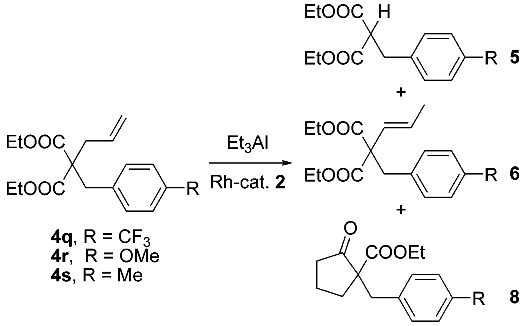


Table 3. Deallylation of Substituted Allylbenzylmalonates[a]



entry	benzylmalonate	product yield (%)[b] 5	6	8
1	**4q**	42 (**5q**)	32 (**6q**)	
2	**4r**	88 (**5r**)		
3	**4s**	66 (**5s**)		25 (**8c**)

[a] Reaction conditions: catalyst (5 mol %), Et_3Al (2 equiv). [b] ^1H NMR or GC yield.

Reactions Catalyzed by $Rh(PPh_3)_3Cl$ (2) and the Rh−BIAP Complex 3a. Better deallylation results were obtained with catalytic systems composed of $Rh(PPh_3)_3Cl$ (**2**) and the Rh−BIAP complex (**3a**) in the presence of Et_3Al. Results are summarized in Table 2. Deallylations by $Rh(PPh_3)_3Cl$ (**2**) and Et_3Al proceeded in good yields with the alkyl(allyl)malonates **4a**,**c** to give **5a**,**c** in 65 and 77% yields, respectively (entries 1 and 2). In the former case a considerable amount (35%) of the allylbutylmalonate **4a** underwent hydrogenation to the butylpropylmalonate **7a**, and in the latter, cyclopentanone **8a** was formed as a side product.

In the case of the allylphenylmalonate **4d** the deallylation did not proceed; only a migration of the double bond to give the phenylpropenylmalonate **6d** in 73% yield was observed (entry 3). Reactions of malonates bearing a methyl substituent on the double bond, **4e**,**f**, resulted in low yields (28 and 6%) of the deallylated products **5e**,**f** (entries 4 and 5). The deallylation of the diallylmalonate **4b** and the unsymmetrically substituted diallylmalonates **4i**−**k** gave rise to **5b**,**i**−**k** in 100, 82, 93, and 77% yields, respectively (entries 8−11). During deallylation of **4k** the formation of cyclopentanone **8b** as a side product in 22% yield was observed. The reaction of the allylcinnamylmalonate **4l** resulted in the formation of an inseparable mixture of unidentified compounds along with the unreacted starting material (42%) (entry 12). Unlike the deallylation of the allyl(chloroallyl)malonate **4m** catalyzed by Ru and Fe complexes, the use of the rhodium catalytic system gave the (chloroallyl)malonate **5m** in 41% yield and the allylmalonate **5b** (23%) along with other unidentified products (entry 13). The reaction of the diallylcyanoacetate **4n** and the diallylcoumaranone **4o** afforded complex reaction mixtures, which did not contain any traces of deallylated products (entries 14 and 15). The butenyl(butyl)malonate **4p** underwent deallylation in low yield after migration of the double bond (entry 16).

The formation of cyclopentanones **8a**,**b** during deallylation of **4c**,**k** indicated that the hydrometalation of the double bond must have proceeded with the reverse regioselectivity, resulting in the formation of an organoaluminum intermediate that underwent intramolecular nucleophilic addition to the carbonyl group (Scheme 2). Cyclization to the cyclopentanone derivatives

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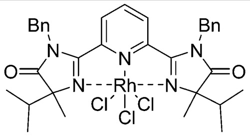
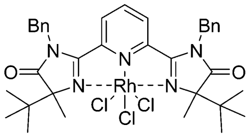
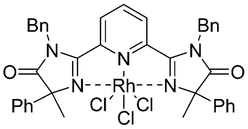
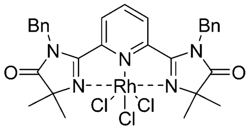
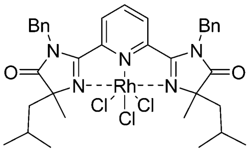
[26] Sedlák, M.; Drabina, P.; Císařová, I.; Růžička, A.; Hanusek, J.; Macháček, V. *Tetrahedron Lett.* **2004**, *45*, 7723−7726.

Table 4. Deallylation of 4a,b with Rh(BIAP)Cl$_3$ Complexes 3a−e[a]

Entry	Catalyst	Malonate	t (h)	**5**, Yield (%)[b]	**9**, Yield (%)[b]
1	 (**3a**)	**4a**	3	**5a**, 100	
		4b	3	**5b**, 100	
		4b	24	**5b**, 70	20
2	 (**3b**)	**4a**	3	**5a**, 100	
		4b	3	**5b**, 100	
		4b	24	**5b**, 56	44
3	 (**3c**)	**4a**	3	**5a**, 100	
		4b	3	**5b**, 100	
		4b	24	**5b**, 35	11[c]
4	 (**3d**)	**4a**	3	**5a**, 100	
		4b	3	**5b**, 100	
		4b	24	**5b**, 33	15[d]
5	 (**3e**)	**4a**	3	**5a**, 100	
		4b	3	**5b**, 100	
		4b	24	**5b**, 73	23

[a] Reaction conditions: catalyst (5 mol %), Et$_3$Al (2 equiv), 3 h. [b] ^{1}H NMR or GC yield. [c] Unidentified products 54%. [d] Unidentified products 51%.

or any other reaction did not proceed in the absence of Wilkinson's catalyst. This assumption is supported by the report of hydroalumination of terminal alkenes with triisobutylaluminum to *n*-alkylaluminums under catalysis of Pd, Co, and Rh complexes.[27] To shed light on the possible effect of the neighboring benzylic group on the course of hydrometalation of the double bond, substituted allylbenzylmalonates **4q−s** were prepared and subjected to deallylation conditions. Surprisingly, in each case a different set of products was obtained (Table 3). Thus, **4q** was partially deallylated to **5q** (42%) and partially isomerized to the propenyl derivative **6q** (35%). On the other hand, **4r** underwent deallylation to the monosubstituted malonate **5r** in high yield (88%). In the case of **4s** the deallylation to the monosubstituted malonate **5s** (66%) was again accompanied by the formation of the cyclopentanone derivative **8c** (25%) (unreacted starting material 6%). The results obtained with **4c**,**q−s** indicate that the aromatic ring of the benzyl group might act as a pendant ligand that coordinates to the rhodium atom, thus affecting its reactivity.[28]

Much better selectivity for deallylation was obtained with a catalytic system composed of the bis(imidazolonyl)pyridine rhodium complex **3a** in the presence of Et$_3$Al. Its use enabled us to deallylate different malonates quantitatively in most cases (entries 1−3 and 7−12). Slightly lower efficiency was observed in deallylation of the butylcrotylmalonate **4f** (77%, entry 5), and low yields were obtained with the methallylmalonate **4e** and the butylcinnamylmalonate **4g** (entries 4 and 6). The allyl(chloroallyl)malonate **4m** was deallylated to the (chloroallyl)malonate **5m** in 20% yield; the major part of the starting material was reductively dehalogenated to the diallylmalonate **4b**, which was probably partially deallylated to **5b** (entry 13). Of course, the possible reductive dehalogenation of **5m** to **5b** cannot be excluded. In the cases of the diallylcyanoacetate **4n** and the diallylcoumaranone **4o** the deallylation did not proceed. The butenyl derivative **4p** was probably deallylated in two steps: (i) the rhodium hydride catalyzed migration of the double bond to give the propenyl derivative **4f** and (ii) its deallylation to give **5f** in 30% yield (entry 16) along with the formation of unidentified compounds. The deallylation of the propenyl derivative **4f** under these conditions proceeded in fair yield (entry 5).

Reactions Catalyzed by Rh(BIAP)Cl$_3$ (3). Since the Rh−BIAP complex **3a** proved to be a good catalyst for the deallylation in the presence of triethylaluminum, we decided to compare its catalytic activity with other four differently substituted Rh−(BIAP) complexes, **3b−e**. The catalytic activity of these complexes was studied in the reaction with the allylbutylmalonate **4a** and the diallylmalonate **4b** in the presence of Et$_3$Al and Et$_2$Zn. The intention was to study the possible effect of the imidazolone ring substituent on the course of the reaction (Table 4). The catalytic activities of all five complexes **3a−e** in the presence of Et$_3$Al were the same. The deallylations of the allylbutylmalonate **4a** and the diallylmalonate **4b** in all of the cases were quantitative within 3 h. The use of Et$_2$Zn as the reductant and Lewis acid for the deallylation of **4a** proved to be totally ineffective; therefore, this combination was no longer checked.

Although the deallylation of the diallylmalonate **4b** was quantitative within 3 h, stirring of the reaction mixture for 24 h resulted in further transformation of the deallylated product

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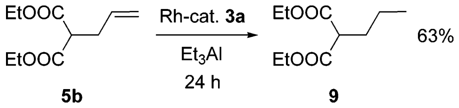
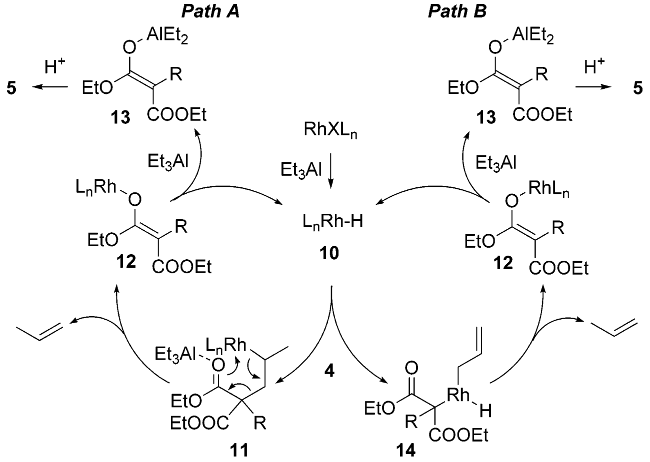
(27) Gagneur, S.; Makabe, H.; Negishi, E. *Tetrahedron Lett.* **2001**, *42*, 785−787.

(28) For typical examples of Rh−arene complexes, see: (a) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191−198. (b) Singewald, E. T.; Slone, C. S.; Stern, C. L.; Mirkin, C. A.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 3048−3056. (c) Huck, S.; Ginsberg, A.; Pritzkow, H.; Siebert, W. *J. Organomet. Chem.* **1998**, *571*, 107−113. (d) Herberich, G. E.; Eckenrath, H. J.; Englert, U. *Organometallics* **1998**, *17*, 519−523.

Scheme 3. Hydrogenation of 5b under the Deallylation Reaction Conditions



Scheme 4. Proposed Reaction Mechanisms for the Deallylation Reaction

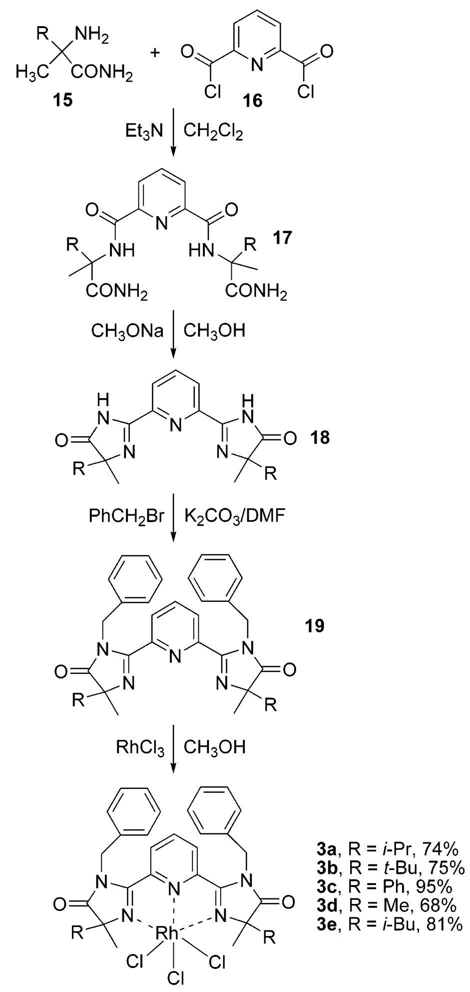


5b into other products. The major byproduct was the product of hydrogenation of the double bond of the deallylated product **5b**—the propylmalonate **9**. An independent experiment showed that subjecting allylmalonate **5b** to the aforementioned conditions resulted in the formation of propylmalonate **9** in 63% yield after 24 h at room temperature (Scheme 3).

Revised Reaction Mechanism. Although the reaction mechanism of the deallylation had been proposed earlier,[17] new results led to its revision in order to include information concerning the role of triethylaluminum and to fit the obtained experimental data. Thus, the revised reaction mechanism for the rhodium complex catalyzed process can be summarized as follows (Scheme 4). In the first step the Rh(I) complex is alkylated to alkylrhodium species that undergo β-hydrogen elimination to give the Rh−hydride **10**. As for Rh^{III}−BIAP complex catalyzed deallylation, it is reasonable to assume that it is reduced to Rh(I) species prior to the hydrometalation of the double bond.

Then two scenarios can be envisioned (paths A and B). We think that the most probable scenario (path A) proceeds via the following steps. First, the hydride **10** hydrometalates the double bond of an allylmalonate to form the *sec*-alkylrhodium species **11** with triethylaluminum (Lewis acid) coordinated to the carbonyl group (Lewis base). Then follows a sequence of C−C, C−O, C−Rh, and Rh−O bond formation and cleavage in **11** through a six-membered transition state promoted by coordination of Et_3Al to the carbonyl group, resulting in the formation of the rhodium enolate **12**.[29] During this process also the allyl moiety is released as an alkene. Finally, the transmetalation of the rhodium enolate **12** with Et_3Al gives the aluminum enolate **13** and the ethylrhodium species, which after β-hydrogen elimination goes back into the catalytic cycle as the hydride **10**. Another possibility is that the shift of the ethyl group from aluminum to rhodium accompanied by the concomitant C−C, C−O, C−Rh, and Rh−O bond formation and cleavage processes in **11** results in the direct formation of the aluminum enolate **13**, the alkylrhodium species, and an alkene. However, in that case eight electrons would have to be moved, and that is not probable.

Scheme 5. Synthesis of Complexes 3



An alternative reaction mechanism of deallylation could be envisioned as well. It was reported that the allylic C−C bond could oxidatively add to an electron-rich Pd(0) complex, forming a π-allyl−Pd^{II} complex.[30] Thus, the second scenario (path B) is based on the oxidative addition of the allylic C−C bond to the hydride **10**, giving the allyl−Rh^{III} complex **14**.[31] The ensuing reductive elimination of propene would afford the rhodium enolate **12**. However, since the addition of rhodium hydrides to the C−C double bond (hydrorhodation) is a well-established reaction, we think that path A should be preferred over path B. On the other hand, the possibility of the coexistence of both reaction pathways cannot be excluded.

Preparation of Rh−BIAP Complexes. The synthesis of rhodium−BIAP complexes followed the protocol recently reported for the preparation of similar iron complexes.[26] The BIAP ligands were synthesized in three steps (Scheme 5): (a) formation of the amide **17** by the reaction of racemic amide **15** and pyridine-2,6-dicarboxylic acid dichloride **16**, (b) intramolecular cyclization to **18**, and (c) benzylation of **18** to ligands

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(29) For leading references concerning the structure of rhodium−enolates, see: (a) Slough, G. A.; Bergman, R. G.; Heathcock, C. K. *J. Am. Chem. Soc.* **1989**, *111*, 938−949. (b) Slough, G. A.; Hayashi, R.; Ashbaugh, J. R.; Shamblin, S. L.; Aukamp, A. M. *Organometallics* **1994**, *13*, 890−898. (c) Hayashi, R.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052−5058.

(30) Nilsson, Y. I. M.; Andersson, P. G.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1993**, *115*, 6609−6613.

(31) For discussions of π-allyl− and σ-allyl−rhodium complexes, see: (a) Evans, P. A.; Nelson, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 5581−5582. (b) Reference 1, pp 193−194.

19. Finally, the complexes **3** were prepared by refluxing of ligands **19** with $RhCl_3 \cdot nH_2O$ in MeOH.

Comparison of Rh-Catalyzed Deallylation with Other Catalytic Systems. In a comparison of the deallylation results under Rh catalysis with the results obtained with other transition-metal complexes (e.g. Ni, Ru),[17] it can be concluded that the same principles should apply for them as well, at least in general terms. The multiple role of Et_3Al as a reducing agent, a Lewis acid, and a transmetalating agent during deallylation seems to be apparent. Furthermore, the effect of the ligation around the central metal atom on the deallylation selectivity and the course of the reaction is important (e.g. compare results obtained with phosphane and BIAP Rh complexes in Table 2, entries 2 and 11). Last but not least, also the nature of the transition metal considerably influences the course of the deallylation: Ni complexes usually deallylate all kinds of allylic compounds, whereas Ru complexes deallylate the unsubstituted ones only. On the other hand, substrates bearing reactive functional groups (CN, halides, etc.) seem to be sensitive to Rh-catalyzed reaction conditions. Typical examples are given by comparisons of deallylations of **4f** and **5a** (Rh−BIAP, 77% (Table 2, entry 5); Ni−phosphane, 86%; Ru−phosphane, 0%[17]) and of **4n** and **5n** (Rh−BIAP, 0% (Table 2, entry 14); Ni−phosphane, 60%; Ru−phosphane, 59%[17]).

Conclusion

We have found that the catalytic system composed of rhodium complexes and triethylaluminum can be successfully used for the deallylation of malonates via allyllic C−C bond cleavage. In particular, deallylation selectivity of the Rh−BIAP complexes, e.g. **3a**, can be in many instances as high as that obtained with the nickel-based systems. Furthermore, the results provide reasonable evidence for a triple role of triethylaluminum: (a) it generates the rhodium hydride, (b) it activates the carbonyl group via the Lewis acid−Lewis base principle, which enhances the formation of enolate and helps to promote the C−C bond cleavage, and probably also (c) it transmetalates the rhodium enolate to release rhodium into the catalytic cycle. As far as the rhodium complexes are concerned, the ligation around the central atom plays a crucial role in the selectivity of the deallylation. In this regard the best results with respect to selectivity and activity were obtained for the reactions of Rh(BIAP)Cl_3 complexes with tridentate N ligands. Also worthy of mention is the formation of cyclopentanone derivatives in three cases of reactions catalyzed by $Rh(PPh_3)_3Cl$ (**2**), which probably proceeds by anti-Markovnikov hydrometalation of the double bond.

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Supporting Information Available: All experimental details and conditions for all starting materials, deallylation reactions, synthesis of ligands **18a**−**e**, and complexes **3a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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