CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201001143

A Selective Ru-Catalyzed Semireduction of Alkynes to *Z* Olefins under Transfer-Hydrogenation Conditions

Christian Belger, N. Matthias Neisius, and Bernd Plietker*[a]

Dedicated to Professor Franz Effenberger on the occasion of his 80th birthday

Abstract: By using a readily available, air- and moisture-stable dihydrido–Ru complex, a variety of *Z* olefins are accessible under transfer-hydrogenation conditions with formic acid as the hydrogen source in excellent yields and *Z*/*E* selectivities.

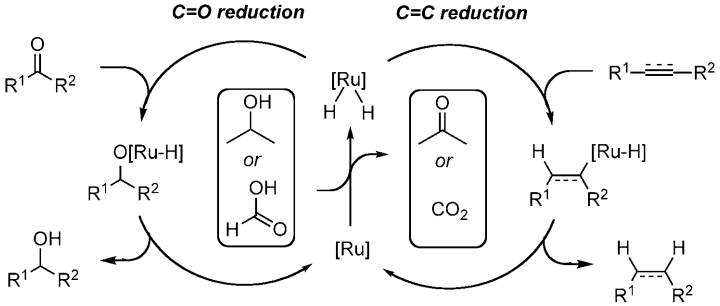
Keywords: alkenes · alkynes · catalysis · ruthenium · transfer hydrogenation

Introduction

Olefins are important functional units within molecular frameworks that allow a selective transformation of two planar sp^2-hybridized carbon atoms into defined three-dimensional structural architectures by a variety of methods. Most of these methods rely on direct translation of the π-bond geometry of the olefin into a defined relative configuration of the two adjacent stereogenic centers formed. Hence, the problems that arise in stereoselective synthesis can in part be attributed to the selective formation of either *E*- or *Z*-configured olefins. Although many methods for the selective formation of the thermodynamically favorable *E* olefins that start from different substrates (e.g., carbonyl compounds,[1] olefins,[2] alkynes[3–7]) have been developed, *Z*-configured olefins are somewhat more difficult to obtain.[8] Apart from the classical alkyne reduction by using stoichiometric amounts of reductants,[9] the heterogeneous Pd-catalyzed semireduction of alkynes, namely, the Lindlar reduction,[10] has proved to be the most reliable method so far. Recently research in this field focused on the development of catalytic systems that allow the semireduction of alkynes under transfer-hydrogenation conditions.[11] In particular, the latter aspect appears to be of significant importance because the use of a hydrogen atmosphere is avoided. Herein, we present a Ru-catalyzed semireduction of alkynes[12] by using formic acid as the hydrogen source, thus adding to the Pd-catalyzed methods developed most recently.[11]

The addition of a Ru–H species to a C=O bond certainly represents one of the best investigated methods.[13] In-depth studies on the reaction mechanism and scope have led to the development of powerful catalytic transformations. Further to the initial reports on Ru-catalyzed C=O reduction with hydrogen as a stoichiometric reductant, transfer-hydrogenation conditions involving nonvolatile and hazardous reductants, such as alcohols or formic acid, have been developed.[13] In a similar manner, one might envision a Ru-catalyzed C=C reduction in alkenes or alkynes to be of comparable importance (Scheme 1).[12]

Recently we have shown that Ru–hydride complexes are active catalysts in the hydrovinylation of a variety of terminal and internal alkynes.[14] From our mechanistic point of



Scheme 1. Mechanistic relationship between C=O and alkene/alkyne reduction.

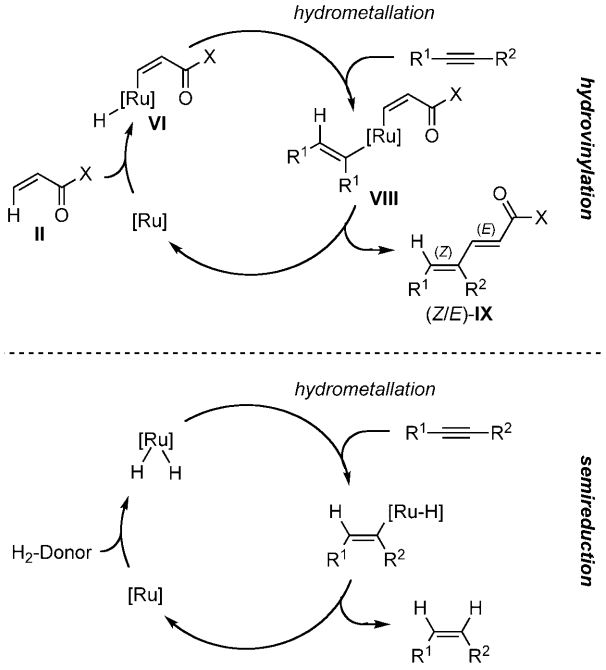
[a] Dipl.-Chem. C. Belger, Dipl.-Chem. N. M. Neisius, Prof. Dr. B. Plietker
Institut für Organische Chemie
Universität Stuttgart, Pfaffenwaldring 55
70569 Stuttgart (Germany)
Fax: (+49) 711-685
E-mail: bernd.plietker@oc.uni-stuttgart.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001143.

View this journal online at wileyonlinelibrary.com

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

view, hydrometallation of an alkyne was proposed to be a crucial intermediate step (Scheme 2). On the basis of these results, we envisioned a similar mechanism that probably



Scheme 2. The role of hydrometallation in the mechanism of hydrovinylation and semireduction reactions.

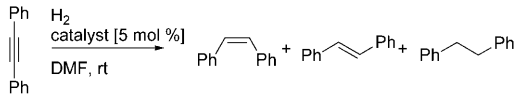
leads to the corresponding *Z*-configured olefins instead (Scheme 2). Different from the hydrovinylation mechanism in which the active Ru–hydride species is formed through oxidative insertion into a vinylic C–H bond, the metal hydride in the semireduction is derived from a suitable H_2 surrogate. The active species subsequently reacts with the alkyne in a hydrometallation/reductive elimination sequence to give the corresponding alkene (Scheme 2).

Although this reaction appears to be a solved problem at first sight (see above),[3–12] we were surprised to find that in contrast to the Ru-catalyzed reduction of a C=O bond the reduction of an alkene/alkyne under transfer-hydrogenation conditions remained to be an unexplored field in Ru catalysis. This finding was even more surprising if one considers this transformation to provide access to *Z*-configured alkenes that possess two prostereogenic carbon atoms that represent suitable starting points for further synthetic elaborations. Herein, we present an in-depth study that leads to a broadly applicable Ru-catalyzed semireduction of alkynes to *Z* olefins in the presence of only 1.25 mol% $[RuH_2(Ph_3P)_4]$ in high yields under transfer-hydrogenation conditions at room temperature.

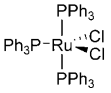
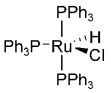
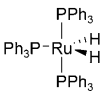
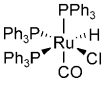
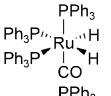
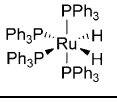
Results and Discussion

One the basis of our investigations into Ru-catalyzed hydrovinylation reactions[14] (see above), we initially wondered whether the same or a similar catalytic system, in which a second hydride ligand is bound to the metal center, would allow the stereoselective semireduction of alkynes in a hydrogen atmosphere. In this respect, the above –outlined mechanism would differ significantly from the groundbreaking investigation by Shvo and co-workers on the use of redox-active cyclopentadienyl Ru complexes,[12] in which the hydride is bound to the metal center and a proton is transferred from the ligand. Hence at the outset of our investigations different Ru catalysts were tested for their reduction potency under hydrovinylation conditions in DMF at room temperature as a starting point in a hydrogen gas atmosphere (Table 1).

Table 1. The influence of the catalyst in H_2-mediated Ru-catalyzed semireduction reactions of alkyne **1**.[a]



1 (*Z*)-**2** (*E*)-**2** **3**

Entry	Catalyst		(*Z*)-**2**[b]	(*E*)-**2**[b]	**3**[b]	Conv. [%][c]
1		**4**	87	13	–	76
2		**5**	77	23	–	32
3		**6**	64	36	–	17
4		**7**	72	28	–	12
5		**8**	64	36	–	13
6		**9**	63	37	–	38

[a] The reactions were performed in a H_2 atmosphere (1 bar) on a 1 mmol scale with 5 mol% catalyst in dry DMF (1 mL) at room temperature for 14 h. [b] Determined by integration of the GC and ^1H NMR spectroscopic analyses of the crude products. [c] Determined by GC integration with undecane as an internal standard.

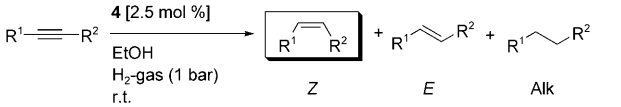
Different Ru complexes can catalyze this transformation. Amongst them, $[RuCl_2(Ph_3P)_3]$ (**4**) gave the best result (Table 1, entry 1). The reaction took place at room temperature without formation of the overreduction product **3**. Furthermore, $[RuH_2(Ph_3P)_4]$ (**9**) proved to be suitable by giving rise to the desired *Z*-configured olefin **2**, albeit in moderate yield and selectivity (Table 1, entry 6). However, catalyst **8**,

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

which was successfully employed in the hydrovinylation protocol, delivered the product in low yields and moderate *E*/*Z* selectivity (Table 1, entry 5).

Further optimization of the solvent led to an improved protocol in which the semireduction of 1,2-diphenylacetylene (**1**) was achieved in almost quantitative yield and perfect stereoselectivity in the presence of only 2.5 mol% **4** at room temperature. No traces of the overreduction product **3** were observed, even after prolonged reaction times. Furthermore, the H_2 atmosphere proved to be necessary, thus excluding reduction under transfer-hydrogenation conditions at this point. Different alkynes were subjected to the reaction conditions to explore the scope of the H_2-mediated Ru-catalyzed semireduction (Table 2). We were pleased to find the catalytic process to be applicable to a range of different alkynes and provided the desired olefins in good-to-excellent yields and *E*/*Z* selectivities. Different functional groups were compatible with the reductive conditions. Compared to the Lindlar reduction, no overreduction took place because the reaction stops at the olefin stage.

Table 2. Scope and limitations of the Ru-catalyzed semireduction reaction.[a]



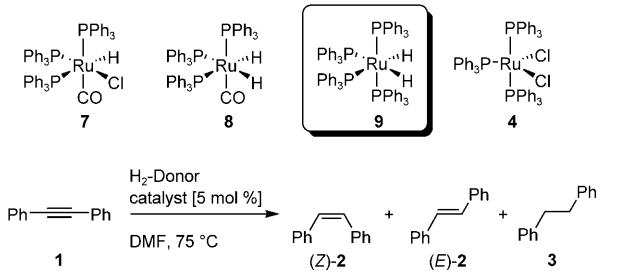
Entry	Alkyne	*t* [h]	Product	*Z*/*E*/alkane[b]	Yield [%][c]
1[d]	Ph—≡—Ph	12	**2**	99:1:0	97
2[d]	C_4H_9—≡—C_4H_9	12	**10**	98:2:0	93
3[d]	Ph—≡—C_3H_7	12	**11**	93:7:0	95
4	C_2H_5—≡—$C_6H_{12}Cl$	12	**12**	98:2:0	92
5	C_2H_5—≡—$C_6H_{13}CN$	12	**13**	–	<10
6	C_2H_5—≡—$C_6H_{13}NPhtal$	12	**14**	81:19:0	89
7	C_4H_9—≡—C_4H_9OH	12	**15**	99:1:0	91
8	C_4H_9—≡—$C_2H_4C(O)CH_3$	12	**16**	91:9:0	23

[a] The reactions were performed on a 1 mmol scale with 2.5 mol% **4** and 1 atm H_2. [b] Determined by integration of the GC and ^{1}H NMR spectroscopic analyses of the crude products. [c] Yield of the isolated products. [d] Catalyst loading = 1.25 mol% **4**. alk = alkane.

With these encouraging results in hand, we subsequently turned our attention toward the development of a transfer-hydrogenation protocol in which common H_2 surrogates were employed in the presence of potential Ru–H complexes. However, amongst the various Ru complexes tested only **9** gave promising conversions and selectivities in the presence of formic acid as the H_2 surrogate (Table 3, entry 7).

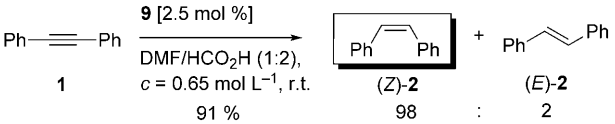
Further optimizations indicated that the *Z*/*E* selectivity significantly increased upon decreasing the reaction temperature. Finally, changing the concentration and solvent/formic acid stoichiometry resulted in a protocol that allowed for the *Z*-selective semireduction of **1** in the presence of only 1.25 mol% **9** in excellent yield at room temperature (Scheme 3).

Table 3. Influence of the solvent and temperature on the Ru-catalyzed semireduction reaction.



Entry	H_2 donor	Catalyst	(*Z*)-**2**/(*E*)-**2**/**3**[b]	Conv. [%][c]
1	*i*PrOH	**7**	87:13:0	25
2	*i*PrOH	**8**[d]	79:21:0	59
3	*i*PrOH	**9**	67:33:0	53
4	*i*PrOH	**4**	100:0:0	2
5	HCO_2H	**7**	33:67:0	90
6	HCO_2H	**8**[d]	50:50:0	94
7	HCO_2H	**9**	70:30:0	100
8	HCO_2H	**4**	6:94:0	100
9	HCO_2H/NEt_3	**7**	61:39:0	63
10	HCO_2H/NEt_3	**8**[d]	61:39:0	85
11	HCO_2H/NEt_3	**9**	40:60:0	100
12	HCO_2H/NEt_3	**4**	63:37:0	81
13	$[NH_4][HCO_2]$	**7**	75:25:0	22
14	$[NH_4][HCO_2]$	**8**[d]	62:38:0	23
15	$[NH_4][HCO_2]$	**9**	77:23:0	29
16	$[NH_4][HCO_2]$	**4**	87:13:0	25
17	HCO_2Et/H_2O	**7**	71:29:0	33
18	HCO_2Et/H_2O	**8**[d]	64:36:0	22
19	HCO_2Et/H_2O	**9**	60:40:0	29
20	HCO_2Et/H_2O	**4**	100:0:0	3

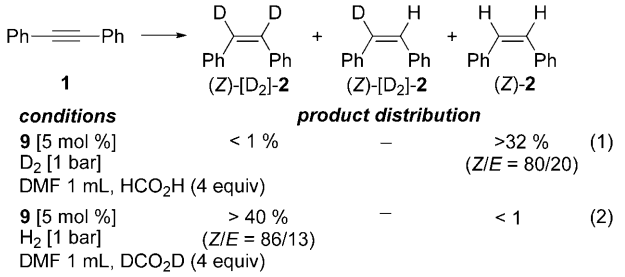
[a] The reactions were performed in a N_2 atmosphere on a 1 mmol scale with 5 mol% catalyst and H_2 donor (4 equiv) in dry DMF (1 mL) at 75 °C for 12 h. [b] Determined by integration of the GC and ^{1}H NMR spectroscopic analyses of the crude products. [c] Determined by GC integration with undecane as an internal standard. [d] Prepared in situ from **1** by addition of 10 mol% NaOMe to the reaction mixture prior to the addition of the H_2 donor.



Scheme 3. The *Z*-selective Ru-catalyzed semireduction of alkynes.

Ru complexes are known to catalyze the decomposition of formic acid into CO_2 and H_2.[15] Because both hydrogen and formic acid might serve as suitable reductants in this semireduction reaction, the question arose whether this transformation follows a transfer-hydrogenation mechanism or whether formic acid decomposes to CO_2 and hydrogen in the presence of **9** prior to the reduction reaction. Subsequent re-coordination of H_2 to the metal center would lead to a Ru–H complex that might catalyze the semireduction reaction. Two competition experiments were performed to shed light on the role of the reductant (Scheme 4). The semireduction of alkyne **1** was performed under standard conditions either in the presence of formic acid [Eq. (1) and

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 4. The use of formic acid as the H_2 source.

Scheme 4] or deuterated formic acid [Eq. (2) and Scheme 4]. Furthermore, the nitrogen atmosphere was exchanged for a deuterium or hydrogen atmosphere [Eqs (1) and (2), respectively; Scheme 4].

The competition between these two reductants in the semireduction reaction was followed by GC–MS analysis. In either case, the hydrogenated or deuterated product was formed exclusively in the presence of HCO_2H or DCO_2D. Hydrogen or deuterium incorporation from the gas atmosphere was not observed. Furthermore, the conversion of the reaction was significantly decreased, thus leading to product formation in lower yields and significantly lower *Z*/*E* selectivity. On the basis of these results, we propose that formic acid acts as a transfer-hydrogenation reagent and follows the mechanistic scenario outlined in Scheme 2.

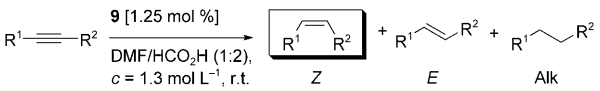
With these results in hand, we turned our attention toward an investigation into the scope and limitation of this transformation (Table 4).

We were pleased to find the reaction to be applicable to various substituted alkynes. The corresponding *Z*-configured olefins were obtained in good-to-excellent selectivities and yields. However, alkyne-bound carboxyl groups led to an erosion in *Z*/*E* selectivity due to a fast acid-mediated isomerization (Table 4, entries 12 and 13). The corresponding formate compounds were isolated in good yields by using unprotected alcohols (Table 4, entries 14). The alkynes were subjected to standard conditions for the Lindlar reduction to compare the present catalytic system with established heterogeneous catalysts. In the presence of 5 mol% of the catalyst, efficient and fast conversions into the corresponding *Z* alkenes were observed; however, in some cases a fast overreduction to the corresponding alkane occurred. Furthermore, a decrease in the catalyst loading down to 1.25 mol% led to an erosion in the conversion.

The first indication of the chemoselectivity of the transfer-hydrogenation protocol (Table 4) suggested that the carbonyl groups were unreactive under the reaction conditions. Ynone **25** was subjected to the three hydrogenation protocols used in this investigation to finalize this statement (Scheme 5).

The Ru-catalyzed transfer hydrogenation is highly chemoselective. Neither enol **26** nor the corresponding alkanol or alkinol were observed. The *Z*-configured alkene (*Z*)-**16** was obtained as a single product in high yield [Eq. (2) and Scheme 5]. The corresponding hydrogen-mediated protocols

Table 4. Scope and limitations of the Ru-catalyzed semireduction reaction.[a]



Entry	Alkyne	*t* [h]	Product	*Z*/*E*/alkane[b]	Yield [%][c]
1[e,f]	Ph—≡—Ph	36 (2)	**2**	98:2:0 (99:1:0)	91 (98)
2	C_4H_9—≡—C_4H_9	36 (2.5)	**10**	91:9:0 (97:3:0)	96 (97)
3	C_3H_7—≡—C_5H_{11}	36 (2.5)	**17**	90:10:0 (99:1:0)	96 (96)
4	C_2H_5—≡—C_6H_{13}	36 (2.5)	**18**	91:9:0 (99:1:0)	95 (97)
5	H_3C—≡—C_7H_{15}	36 (7.5)	**19**	90:10:0 (99:1:0)	96 (98)
6[e]	Ph—≡—CH_3	36 (0.5)	**20**	92:8:0 (68:1:31)	94 (99)
7[e]	Ph—≡—C_3H_7	36 (0.75)	**11**	92:8:0 (67:1:32)	93 (97)
8	C_2H_5—≡—$C_6H_{12}Cl$	36 (3)	**12**	96:4:0 (99:1:0)	90 (99)
9	C_2H_5—≡—$C_6H_{13}CN$	36 (2)	**13**	n.b. (99:1:0)	<10 (98)
10[f]	C_2H_5—≡—$C_6H_{13}NPhtal$	36 (3)	**14**	90:10:0 (99:1:0)	90 (96)
11[g]	C_4H_9—≡—C_4H_9OH	36 (3)	**15**	87:13:0 (99:1:0)	91 (98)
12[e]	Ph—≡—CO_2Me	48 (2.25)	**21**	80:20:0 (88:1:11)	89 (98)
13[e]	MeO_2C—≡—CO_2Me	48 (1.25)	**22**	25:75:0 (71:1:28)	91 (98)
14[e,f]	$BzOH_2C$—≡—CH_2OBz	48 (3)	**23**	98:2:0 (99:1:0)	96 (99)
15[e,h]	$TBSOH_2C$—≡—CH_2OTBS	48 (1)	**24**	99:1:0 (99:1:0)	91 (98)

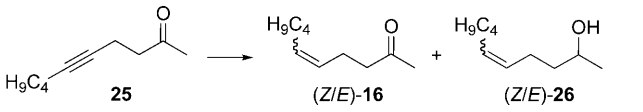
[a] The reactions were performed under N_2 on a 1 mmol scale with 1.25 mol% **9** and HCO_2H (500 μL) in dry DMF (250 μL) at room temperature. [b] The numbers in parentheses refer to the Lindlar reduction reaction, which used 5 mol% Lindlar catalyst, quinoline (30 mol%), and alkyne (1.0 mmol) in toluene (7.5 mL) at room temperature. H_2 uptake was measured with a gas burette. [c] Determined by integration of the GC and ^{1}H NMR spectroscopic analyses of the crude products. The numbers in parentheses refer to the ratio of the products when the Lindlar reduction was used. [d] Yield of the isolated products. The numbers in parentheses refer to conversion when the Lindlar reduction was used. [e] Catalyst loading: 2.5 mol% **9**. [f] H_2 source: HCO_2H (1000 μL), solvent: dry DMF (500 μL). [g] The product was isolated as the formate compound. [h] The product was isolated as the bis-formate compound.

that employed either Ru catalyst **4** or the heterogeneous Lindlar system [Eqs (1) and (3), respectively; Scheme 5] possess some disadvantages. Although in the former system both the *Z*/*E* selectivity and yield were lower, the latter system required higher catalyst loading and careful control of H_2 uptake to minimize the formation of overreduction products.

Conclusion

Herein, we have reported a broadly applicable, scalable, H_2-free Ru-catalyzed stereoselective semireduction of internal

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



conditions	product distribution			
4 [2.5 mol %] H_2 [1 bar] EtOH 1.5 mL	23 % (*Z*/*E* = 91/9)	–	0 %	(1)
9 [2.5 mol %] HCO_2H 0.5 mL DMF 0.25 mL	81 % (*Z*/*E* = 99/1)	–	0 %	(2)
Lindlar catalyst [5 mol %] H_2 [1 bar] toluene 7.5 mL	93 % (*Z*/*E* = 99/1)	–	0 %	(3)

Scheme 5. Chemoselecitvity in Ru- or Pd-catalyzed semireduction of alkynones.

alkynes. The catalyst employed in this study is derived as an air-stable complex within one step that starts from inexpensive [$RuCl_3$]. To the best of our knowledge, this is the first report of a Ru-catalyzed reduction of alkynes to alkenes under transfer-hydrogenation conditions. No problems with overreduction to the corresponding alkanes or functional group reductions were observed in any of the cases investigated. The overall operational simplicity, functional-group tolerance, and chemoselectivities are characteristic of this process, which represents a good alternative to the methods developed so far. Future study will concentrate on an expansion of the reaction scope by employing alcohols as H_2 donors.

Experimental Section

General: Dry DMF was purchased from Acros and used without further purification. The [$RuH_2(PPH_3)_4$],[16] [$RuCl_2(PPh_3)_3$], [17] and [$RuCl(CO)(H)(PPh_3)_3$][18] complexes were prepared according to reported procedures.

General procedure for the preparation of *Z* alkenes by hydrogenation: A 10 mL Schlenk tube was charged with [$RuCl_2(PPH_3)_3$] (28.8 mg, 0.025 mmol, 2.5 mol %) and the solid alkyne (1.0 mmol) in a N_2 atmosphere. Ethanol (1.5 mL) was added to the reaction mixture. If the alkyne was a liquid (1.0 mmol), it was added at this point. The reaction mixture was deaereated, flushed with hydrogen gas from a balloon, and the reaction was carried out for the appropriate time. The crude product was directly purified by flash chromatography on silica gel with pentane as the eluent for nonpolar products. For polar products, the reaction mixture was diluted with diethyl ether, washed with water then brine, dried (Na_2SO_4), and gently evaporated. Purification was performed by column chromatography on silica gel with petroleumeum ether/ethyl acetate as the eluent.

General procedure for the preparation of *Z* alkenes by transfer hydrogenation: A 2 mL Wheaton vial was charged with [$RuH_2(PPH_3)_4$] (14.4 mg, 0.0125 mmol, 1.25 mol %) and the solid alkyne (1.0 mmol) in a N_2 atmosphere. The vial was sealed, evacuated, and vented with nitrogen gas. Dry DMF (0.25 mL) was added to the reaction mixture. If the alkyne was a liquid (1.0 mmol), it was added at this point. Formic acid (0.5 mL) was added and the reaction was carried out in the sealed vessel for the appropriate time. The workup was performed as described above.

General procedure for the preparation of *Z* alkenes through the Lindlar reduction: A 50 mL two-necked round-bottom flask was charged with the Lindlar catalyst (106.2 mg, 0.05 mmol, 5 mol %), absolute toluene (7.5 mL), quinoline (38.8 mg, 0.3 mmol, 30 mol %), and alkyne (1.0 mmol) in a N_2 atmosphere. The reaction mixture was deaereated and flooded with hydrogen gas. The reaction vessel was attached to a gas burette to monitor H_2 consumption and the reaction was stopped when 1.0 mmol of H_2 had been consumed. Purification was performed as described above. (**Caution**: Heterogeneous active metal catalysts have to be handled with care!)

(*Z*)-Stilbene [(*Z*)-2]:[19] Yield: 164 mg (0.91 mmol, 91 %). R_f = 0.90 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.14 (m, 10H), 6.60 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 130.3, 128.9, 128.2, 127.1 ppm; IR (film): $\tilde{\nu}$ = 2978 (m), 2872 (m), 1111 (m), 905 (s), 726 cm^{-1} (s); MS (EI): *m*/*z* (%): 180 (100) [*M*]$^+$, 165 (50), 152 (15), 102 (11), 89 (20), 76 (17), 51 (15).

(*Z*)-[D_2]Stilbene [(*Z*)-[D_2]-2]:[20] Yield: 59.6 mg (0.33 mmol, 33 %). R_f = 0.90 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.07 (m, 10H), 6.59–6.56 ppm (m, 0.1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 131.8 129.0, 128.3, 127.2 ppm; IR (film): $\tilde{\nu}$ = 3054 (m), 3021 (m), 2240 (w), 1951 (w), 1493 (m), 1442 (m), 918 (m), 742 (s), 691 cm^{-1} (s); MS (EI): *m*/*z* (%): 182 (100) [*M*]$^+$, 167 (31), 153 (10), 103 (6), 90 (17), 77 (14), 63 (6), 51 (10).

(*Z*)-5-Decene [(*Z*)-10]:[21] Yield: 135 mg (0.96 mmol, 96 %). R_f = 0.95 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.38–5.29 (m, 2H), 2.11–1.92 (m, 4H), 1.42–1.24 (m, 8H), 0.95–0.84 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.8, 32.0, 27.0, 22.4, 14.0 ppm; IR (film): $\tilde{\nu}$ = 2977 (m,), 2931 (w), 2872 (m), 1111 (m), 907 (s), 728 cm^{-1} (s); MS (EI): *m*/*z* (%): 140 (17) [*M*]$^+$, 95 (19), 81 (33), 70 (30), 67 (89), 55 (100).

(*Z*)-1-Phenyl-1-pentene [(*Z*)-11]:[22] Yield: 136 mg (0.93 mmol, 93 %). R_f = 0.90 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.14 (m, 5H), 6.41 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.67 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.31 (dq, *J* = 7.4, 1.9 Hz, 2H), 1.57–1.40 (m, 2H), 0.94 ppm (t, *J* = 7.37 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.9, 133.1, 128.8, 128.7, 128.1, 126.4, 30.7, 23.2, 13.9 ppm; IR (film): $\tilde{\nu}$ = 2978 (m), 2935 (w), 2872 (m), 961 (s), 728 cm^{-1} (s); MS (EI): *m*/*z* (%): 146 (33) [*M*]$^+$, 128 (4), 117 (100), 104 (34), 91 (31), 77 (7).

(*Z*)-1-Chloro-7-decene [(*Z*)-12]: Yield: 157 mg (0.90 mmol, 90 %). R_f = 0.90 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39–5.18 (m, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.04–1.85 (m, 4H), 1.76–1.64 (m, 2H), 1.42–1.12 (m, 6H), 0.88 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 131.8, 129.0, 45.2, 32.7, 29.6, 28.6, 26.9, 26.8, 20.5, 14.4 ppm; IR (film): $\tilde{\nu}$ = 2959 (m), 2930 (s), 2856 (m), 1461 (m), 1304 (w), 966 (w), 726 cm^{-1} (s); MS (EI): *m*/*z* (%): 174 (57) [*M*]$^+$, 118 (15), 104 (34), 83 (34), 69 (64), 55 (100), 41 (78); HRMS (ESI+HR) calcd for $C_{10}H_{19}Cl$: 174.1175; found: 174.1172.

(*Z*)-1-Cyano-7-decene [(*Z*)-13]: Yield: 155 mg (0.94 mmol, 94 %). R_f = 0.75 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.43–5.25 (m, 2H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.09–1.95 (m, 4H), 1.71–1.60 (m, 2H), 1.51–1.30 (m, 6H), 0.96 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.9, 128.8, 119.8, 29.4, 28.6, 28.3, 26.9, 25.4, 20.5, 17.1, 14.4 ppm; IR (film): $\tilde{\nu}$ = 3004 (m), 2930 (s), 2857 (m), 2246 (w), 1462 (m), 1069 (w), 729 cm^{-1} (m); MS (EI): *m*/*z* (%): 164 (6) [*M*]$^+$, 150 (8), 136 (74), 122 (100), 108 (19), 94 (33), 80 (31), 69 (61), 55 (94); HRMS (ESI+HR): calcd for $C_{11}H_{19}N$: 165.1517; found: 165.1501.

(*Z*)-1-Phthalimido-7-decene [(*Z*)-14]: Yield: 256 mg (0.90 mmol, 90 %). R_f = 0.75 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.79–7.70 (m, 2H), 7.66–7.57 (m, 2H), 5.41–5.14 (m, 2H), 3.59 (t, *J* = 7.4 Hz, 2H), 2.02–1.78 (m, 4H), 1.67–1.52 (m, 2H), 1.32–1.11 (m, 8H), 0.85 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.4, 133.8,132.2, 131.6, 129.0, 123.1, 38.0, 29.5, 28.8, 28.5, 26.9, 26.7, 20.5, 14.3 ppm; IR (film): $\tilde{\nu}$ = 2929 (m), 2856 (w), 1707 (s), 1393 (s), 1366 (m), 1187 (w), 1048 (m), 715 cm^{-1} (s); MS (EI): *m*/*z* (%): 285 (2) [*M*]$^+$, 186 (4), 160 (100), 148 (32), 130 (13), 104 (6), 77 (11), 55 (6); HRMS (ESI$^+$HR) calcd for $C_{18}H_{23}NO_2$+Na: 308.1626; found: 306.1611.

(*Z*)-1-Hydroxy-5-decene [(*Z*)-15]:[23] Yield: 142 mg (0.91 mmol, 91 %); R_f = 0.30 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.47–5.29 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 2.12–1.95 (m, 2H), 1.65–1.59 (m, 2H), 1.49–1.39 (m, 2H), 1.38–1.24 (m, 6H), 0.95–0.85 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 130.4, 129.3, 63.0,

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

32.4, 31.9, 27.0, 26.9, 25.9, 22.4, 14.0 ppm; IR (film): $\tilde{\nu}$ = 3331 (b), 2954 (m), 2926 (s), 2858 (m), 1965 (w), 1456 (m), 1060 (m), 713 cm^{-1} (w); MS (EI): *m*/*z* (%): 138 (6) $[M-H_2O]^+$, 110 (15), 95 (44), 81 (66), 67 (100), 55 (76).

(*Z*)-5-decen-2-one [(*Z*)-16]:[24] Yield: 125 mg (0.81 mmol, 81%). R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.44–5.24 (m, 2H), 2.51–2.43 (m, 2H), 2.35–2.23 (m, 2H), 2.14 (s, 3H), 2.09–1.95 (m, 2H), 1.38–1.23 (m, 4H), 0.94–0.8 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.6, 131.3, 127.6, 43.7, 31.8, 30.0, 26.9, 22.4, 21.7, 14.0 ppm; IR (film): $\tilde{\nu}$ = 2957 (m), 2926 (m), 2858 (w), 1966 (m), 1715 (s), 1359 (m), 1160 (m), 1014 (w), 795 cm^{-1} (m); MS (EI): *m*/*z* (%): 154 (9) $[M]^+$, 136 (4), 125 (12), 111 (22), 96 (69), 81 (100), 67 (58), 54 (81).

(*Z*)-4-Decene [(*Z*)-17]:[25] Yield: 135 mg (0.96 mmol, 96%). R_f = 0.95 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37–5.22 (m, 2H), 2.04–1.84 (m, 4H), 1.37–1.12 (m, 8H), 0.90–0.77 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.1, 129.6, 31.6, 29.5, 29.4, 27.3, 23.0, 22.6, 14.1, 13.9 ppm; IR (film): $\tilde{\nu}$ = 2945 (w), 2928 (m), 2895 (w), 1465 (w), 903 (s), 724 cm^{-1} (s); MS (EI): *m*/*z* (%): 140 (100) $[M]^+$, 125 (5), 111 (16), 97 (52), 83 (75), 69 (45), 55 (28).

(*Z*)-3-Decene [(*Z*)-18]:[26] Yield: 133 mg (0.95 mmol, 96%). R_f = 0.95 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.37–5.19 (m, 2H), 2.04–1.84 (m, 4H), 1.34–1.12 (m, 8H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.81 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.5, 129.4, 31.8, 29.8, 29.0, 27.1, 22.7, 20.6, 14.4, 14.1 ppm; IR (film): $\tilde{\nu}$ = 2959 (m,), 2924 (s), 2855 (m), 1459 (w), 1210 (w), 906 (s), 730 cm^{-1} (s); MS (EI): *m*/*z* (%): 140 (21) $[M]^+$, 111 (6), 97 (15), 83 (13), 69 (45), 55 (100).

(*Z*)-2-Decene [(*Z*)-19]:[27] Yield: 135 mg (0.96 mmol, 96%). R_f = 0.95 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.44–5.26 (m, 2H), 2.05–1.91 (m, 4H), 1.56–1.52 (m, 3H), 1.32–1.13 (m, 8H), 0.88–0.72 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.9, 123.6, 31.9, 29.6, 29.3, 29.2, 26.9, 22.7, 14.0, 12.7 ppm; IR (film): $\tilde{\nu}$ = 2957 (m,), 2925 (s), 2855 (m), 1464 (w), 1377 (w), 907 (m), 732 cm^{-1} (m); MS (EI): *m*/*z* (%): 140 (22) $[M]^+$, 111 (7), 97 (16), 83 (15), 69 (54), 55 (100).

(*Z*)-1-Phenyl-1-propene [(*Z*)-20]:[28] Yield: 111 mg (0.94 mmol, 94%). R_f = 0.90 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.06 (m, 5H), 6.37 (dq, *J* = 11.6, 1.8 Hz, 1H), 5.72 (dq, *J* = 11.6, 7.2 Hz, 1H), 1.83 ppm (dd, *J* = 7.2, 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 129.9, 128.8, 128.1, 126.8, 126.4, 14.6 ppm; IR (film): $\tilde{\nu}$ = 3020 (m), 2937 (w), 1494 (m), 1443 (m), 962 (w), 912 (w), 764 (m), 692 cm^{-1} (s); MS (EI): *m*/*z* (%): 117 (100) $[M-H]^+$, 103 (11), 91 (40), 77 (11), 63 (13), 51 (17).

(*Z*)-1-Formyl-5-decene [(*Z*)-21]: Yield: 168 mg (0.91 mmol, 91%). R_f = 0.75 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 5.43–5.19 (m, 2H), 4.15–4.05 (m, 2H), 2.08–1.84 (m, 4H), 1.71–1.51 (m, 2H), 1.43–1.14 (m, 6H), 0.90–0.77 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 129.7, 127.8, 62.9, 30.9, 27.1, 25.9, 25.6, 24.9, 21.3, 13.0 ppm; IR (film): $\tilde{\nu}$ = 2927 (m), 2859 (w), 1728 (s), 1465 (w), 1165 cm^{-1} (s); MS (EI): *m*/*z* (%): 184 (1) $[M]^+$, 138 (44), 110 (44), 95 (70), 81 (74), 67 (100), 55 (82), 41 (77), 29 (28); HRMS (ESI+ HR) calcd for $C_{11}H_{20}O_2$: 184.1463; found: 184.1432.

(*Z*)-Methyl cinnamate [(*Z*)-21]:[29] Yield: 115 mg (0.71 mmol, 71%). R_f = 0.40 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 2H), 7.35–7.24 (m, 3H), 6.89 (d, *J* = 12.4 Hz, 1H), 5.89 (d, *J* = 12.4 Hz, 1H), 3.64 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 143.4, 134.8, 129.7, 129.1, 128.1, 119.3, 51.4 ppm; IR (film): $\tilde{\nu}$ = 2950 (w), 1723 (s), 1631 (m), 1436 (m), 1198 (s), 1167 (s), 827 (m), 696 cm^{-1} (m); MS (EI): *m*/*z* (%): 163 (36) $[M-H]^+$, 131 (100), 121 (6), 103 (10), 77 (4), 51 (2).

(*E*)-Methyl cinnamate [(*E*)-21]:[29] R_f = 0.40 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 16.1 Hz, 1H), 7.49–7.42 (m, 2H), 7.35–7.29 (m, 3H), 6.37 (d, *J* = 16.1 Hz, 1H), 3.74 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7 ppm; IR (film): $\tilde{\nu}$ = 2950 (w), 1723 (s), 1631 (m), 1436 (m), 1198 (s), 1167 (s), 827 (m), 696 cm^{-1} (m); MS (EI): *m*/*z* (%): 163 (84) $[M-H]^+$, 131 (100), 121 (16), 103 (22), 77 (11), 51 (7).

Dimethyl maleate (22):[30] Yield: 33 mg (0.23 mmol, 23%). R_f = 0.40 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.28 (s, 2H), 3.82 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 129.8, 52.2 ppm; IR (film): $\tilde{\nu}$ = 2956 (w), 1722 (s), 1437 (m), 1389 (m), 1215 (m), 1157 (s), 990 (w), 817 cm^{-1} (m); MS (EI): *m*/*z* (%): 144 (3) $[M]^+$, 113 (100), 85 (20), 59 (27).

Dimethyl fumarate (22):[30] R_f = 0.50 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.88 (s, 2H), 3.82 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 133.4, 52.3 ppm; IR (film): $\tilde{\nu}$ = 2963 (w), 1710 (s), 1437 (m), 1302 (m), 1155 (m), 987 (s), 880 cm^{-1} (m); MS (EI): *m*/*z* (%): 144 (3) $[M]^+$, 113 (100), 85 (70), 59 (36), 53 (23).

(*Z*)-1,4-*bis*-Benzoyl-2-butene [(*Z*)-23]:[31] Yield: 284 mg (0.96 mmol, 96%). R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13–8.00 (m, 4H), 7.62–7.38 (m, 6H), 6.02–5.89 (m, 2H), 5.06–4.99 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 133.1, 129.9, 129.7, 128.4, 128.3, 60.6 ppm; IR (film): $\tilde{\nu}$ = 1720 (s), 1266 (s), 1097 (m), 709 cm^{-1} (m); MS (EI): *m*/*z* (%): 296 (1) $[M]^+$, 175 (5), 105 (100), 77 (29).

(*Z*)-1,4-*bis*-Formyl-2-butene [(*Z*)-24]:[32] Yield: 131 mg (0.91 mmol, 91%). R_f = 0.5 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (s, 2H), 5.77–5.65 (m, 2H), 4.70 ppm (d, *J* = 4.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 127.9, 59.4 ppm; IR (film): $\tilde{\nu}$ = 2977 (m), 2864 (s), 1716 (s), 1120 (s), 934 (s), 845 cm^{-1} (s); MS (EI): *m*/*z* (%): 98 (6) $[M-CO_2]^+$, 70 (100), 57 (26).

Acknowledgements

Financial support by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (SFB 706), Landesgraduiertenförderung Baden-Württemberg (PhD grant for C.B.) ,and the Dr-Otto-Röhm-Gedächtnisstiftung is gratefully acknowledged.

[1] For an excellent review on the Wittig olefination, see:B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863.

[2] I. S. Kim, G. R. Dong, Y. H. Jung, *J. Org. Chem.* **2007**, *72*, 5424.

[3] For a general review on the semireduction of alkynes, see: I. J. Munslow in *Modern Reduction Methods* (Eds.: P. G. Andersson, I. J. Munslow), Wiley-VCH, Weinheim, **2008**, p. 363.

[4] Metal/NH_3: a) L. Brandsma, W. F. Nieuwenhuizen, J. W. Zwikker, U. Maeorg, *Eur. J. Org. Chem.* **1999**, 5; b) K. K. Chan, N. Cohen, J. P. Denoble, A. C. Specian, G. J. Saucy, *J. Org. Chem.* **1976**, *41*, 3497.

[5] Metal hydrides: a) T. Tsuda, T. Yoshida, T. Kawamoto, T. J. Saegusa, *J. Org. Chem.* **1987**, *52*, 1624; b) T. K. Jones, S. E. Denmark in *Organic Syntheses, Vol. 7*, Wiley, New York, **1985**, p. 524.

[6] Ru-catalyzed: B. M. Trost, Z. T. Ball, T. Jöge, *J. Am. Chem. Soc.* **2002**, *124*, 7922.

[7] Enzyme-catalyzed: A. Müller, R. Stürmer, B. Hauer, B. Rosche, *Angew. Chem.* **2007**, *119*, 3380; *Angew. Chem. Int. Ed.* **2007**, *46*, 3316.

[8] a) J. W. Sprengers, J. Wassenaar, N. D. Clement, K. J. Cavell, C. J. Elsevier, *Angew. Chem.* **2005**, *117*, 2062; *Angew. Chem. Int. Ed.* **2005**, *44*, 2026; b) K. R. Campos, D. Cai, M. Journet, J. J. Kowal, R. D. Larsen, R. J. Reider, *J. Org. Chem.* **2001**, *66*, 3634; c) M. Gruttadauria, R. Noto, G. Deganello, L. F. Liotta, *Tetrahedron Lett.* **1999**, *40*, 2857; d) M. W. Van Laren, C. J. Elsevier, *Angew. Chem.* **1999**, *111*, 3926; *Angew. Chem. Int. Ed.* **1999**, *38*, 3715; e) n. M. Yoon, K. B. Park, H. J. Lee, J. Choi, *Tetrahedron Lett.* **1996**, *37*, 8527; f) J. Choi, N. M. Yoon, *Tetrahedron Lett.* **1996**, *37*, 1057; g) B. M. Choudary, G. V. M. Sharma, P. Bharath, *Angew. Chem.* **1989**, *101*, 506; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 465; h) D. Savoia, E. Tagliavini, C. Trombini, A. Umani-Ronchi, *J. Org. Chem.* **1981**, *46*, 5340; i) J.-J. Brunet, P. Caubere, *J. Org. Chem.* **1984**, *49*, 4058; j) P. Gallois, J.-J. Brunet, P. Caubere, *J. Org. Chem.* **1980**, *45*, 1946; k) N. A. Cortese, R. F. Heck, *J. Org. Chem.* **1978**, *43*, 3985.

[9] a) E. J. Corey, D. J. Pasto, W. L. Mock, *J. Am. Chem. Soc.* **1961**, *83*, 2957; b) E. J. Corey, W. L. Mock, D. J. Pasto, *Tetrahedron Lett.* **1961**, *2*, 347; c) S. Hünig, H.-R. Müller, W. Their, *Tetrahedron Lett.* **1961**,

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2, 353; d) F. Alonso, I. Osante, M. Yus, *Adv. Synth. Catal.* **2006**, *348*, 305.
[10] H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446.
[11] Pd-catalyzed *cis*-hydrogenation: a) B. T. Khai, A. Arcelli, *Chem. Ber.* **1993**, *126*, 2265; b) L.-L. Wie, L.-M. Wie, W.-B. Pan, S.-P. Leou, M.-J. Wu, *Tetrahedron Lett.* **2003**, *44*, 1979; c) P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani, C. J. Elsevier, *Angew. Chem.* **2008**, *120*, 3267; *Angew. Chem. Int. Ed.* **2008**, *47*, 3223.
[12] For Ru-catalyzed semireduction in the presence of hydrogen, see: a) Y. Blum, D. Czarkie, Y. Shvo, *Organometallics* **1985**, *4*, 1459; b) Y. Shvo, I. Goldberg, D. Czerkie, D. Reshef, Z. Stein, *Organometallics* **1997**, *16*, 133.
[13] M. Kitamura, R. Noyori in *Ruthenium in Organic Synthesis* (Eds.: S.-I- Murahashi), Wiley-VCH, Weinheim, **2004**, pp. 3–52.
[14] N. M. Neisius, B. Plietker, *Angew. Chem.* **2009**, *121*, 5863; *Angew. Chem. Int. Ed.* **2009**, *48*, 5752.
[15] a) B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962; b) C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem.* **2008**, *120*, 4030; *Angew. Chem. Int. Ed.* **2008**, *47*, 3966.
[16] A. Yamamoto, S. Kitazume, S. Ikeda, *J. Am. Chem. Soc.* **1968**, *90*, 1089.
[17] P. S. Hallman, T. A. Stephenson, G. Wilkinson, *Inorg. Synth.* **1970**, *12*, 237.
[18] S. Komiya, M. Hurano in *Synthesis of Organometallic Compounds* (Eds.: S. Komiya), Wiley-VCH, Weinheim, **1997**, pp. 196–197.
[19] K. J. Kolonko, R. H. Shapiro, *J. Org. Chem.* **1978**, *43*, 1404.
[20] L. P. Olson, S. Niwayama, H.-Y. Yoo, K. H. Houk, N. J. Harris, J. J. Gajewski, *J. Am. Chem. Soc.* **1996**, *118*, 886.
[21] E.-I. Negishi, K.-W. Chiu, *J. Org. Chem.* **1976**, *41*, 3484.
[22] H. L. Goering, E. P. Seitz, C. C. Tseng, *J. Org. Chem.* **1981**, *46*, 5304.
[23] A. G. M. Barrett, J. A. Flygare, *J. Org. Chem.* **1991**, *56*, 638.
[24] W. Giersch, F. Naef, *Helv. Chim. Acta* **2004**, *87*, 1704.
[25] A. Zhang, S. Wang, *Org. Prep. Proced. Int.* **2008**, *40*, 293.
[26] J. M. Concellón, H. Rodriguez-Solla, C. Simal, M. Huerta, *Org. Lett.* **2005**, *7*, 5833.
[27] A. Alexakis, G. Cahiez, J. F. Normant, *Synthesis* **1979**, 826.
[28] M. Delmas, Y. Le Bigot, A. Gaset, J. P. Gorrichon, *Synth. Commun.* **1981**, *11*, 125.
[29] F. D. Lewis, J. D. Oxman, L. L. Gibson, H. L. Hampsch, *J. Am. Chem. Soc.* **1986**, *108*, 3005.
[30] O. Ceder, B. Beuer, *Tetrahedron* **1972**, *28*, 4341.
[31] J. Ramnauth, E. Lee-Ralf, *Can. J. Chem.* **1997**, *75*, 518.
[32] A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433.

Received: April 29, 2010
Published online: September 16, 2010

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim