Synthesis of Enamines

Highly Selective Synthesis of Enamines from Olefins**

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Dedicated to Professor Manfred T. Reetz on the occasion of his 60th birthday

A major challenge for synthetic chemists constitutes the development of cleaner (green) and practical catalytic technologies for organic synthesis. In this respect, we have been interested for some years in the development of novel methods for the synthesis of nitrogen-containing compounds, for example, amines,[1] enamines,[2] and imines.[3] Members of this class of compounds are useful as dyes, fine chemicals, and biologically active substances for pharmaceuticals. An ideal chemical synthesis of amines and their derivatives should make use of easily available raw materials and produce a minimum of waste.[4] On the one hand, atom economy[5] or atom efficiency[6] of the reaction should be as high as possible, on the other hand, a minimum amount of reaction steps should be performed to avoid tedious workup procedures and to save solvents and energy. These latter points are especially important for large-scale synthesis. Hence, the use of multicomponent coupling reactions[7] or domino reactions[8] is highly desirable compared to classic multistep procedures.

An environmentally benign synthesis of amines constitutes the so-called hydroaminomethylation[9] of olefins. This catalytic domino reaction starting from readily available olefins and consists of an initial hydroformylation step, to give aldehydes, and a subsequent reductive amination (Scheme 1).

Since the discovery of this reaction by Reppe and Vetter at BASF,[10] the hydroaminomethylation reaction has been considered mainly in industry.[11] Notable advances in the last decade have been especially reported by Eilbracht and coworkers, who developed elegant domino variants of hydroaminomethylation reactions.[12] More recently, we presented a rhodium catalyst based on the xantphos ligand (**3**; Scheme 2),[13] which allowed for the first general, efficient, and highly regioselective (typically n/iso > 98:2) hydroaminomethylation of simple as well as of functionalized

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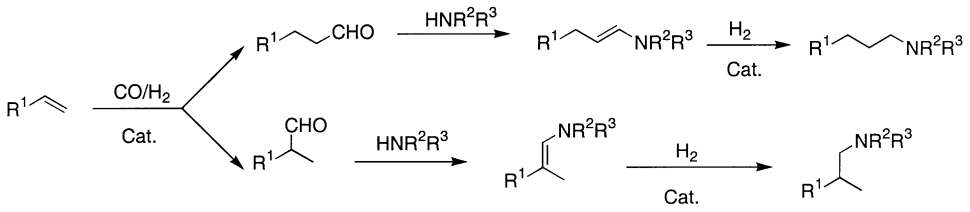
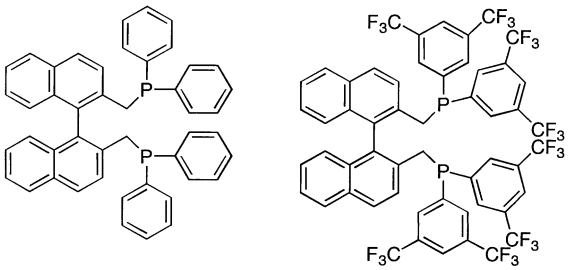
[**] The authors thank Dr. Holger Klein (IfOK) for help with the preparation of the ligand iphos and for his work on the high-pressure infrastructure, Susann Buchholz for GC analyses, and Hannelore Baudisch for GC–MS experiments. Financial support from the BMBF (Bundesministerium für Bildung und Forschung), the Ministry of Education, Science, and Cultural Affairs of Mecklenburg-Vorpommern and the Fonds der Chemischen Industrie (FCI) is gratefully acknowledged.

 DOI: 10.1002/ange.200352320

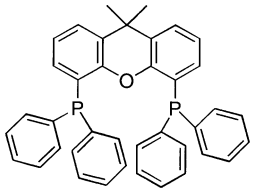


Scheme 1. Hydroaminomethylation of alkenes.



1 naphos

2 iphos



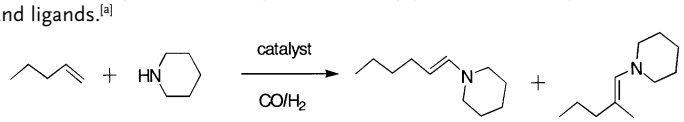
3 xantphos

Scheme 2. Ligands used in the hydroaminomethylenation of 1-pentene with piperidine (Table 1).

α-olefins.[14] During our studies on the improvement of tailor-made catalyst systems for hydroaminomethylations,[15] we noted that the reaction steps of the sequence (1. hydroformylation, 2. imine/enamine formation, 3. hydrogenation) are influenced by the ligand in different ways. Among the ligands tested in the model reaction of 1-pentene with piperidine, 2,2′-bis(diphenylphosphanylmethyl)-1,1′-binaphthyl (naphos (**1**); Scheme 2)[16] and its derivatives provided relatively large amounts of the corresponding enamine (*N*-1-hexenylpiperidine). After studying the literature, we were surprised to find that there was no general protocol for the direct and highly selective synthesis of enamines from olefins.[17] Clearly, such a domino reaction has advantages over the stepwise procedure of hydroformylation and amination, but also over other catalytic syntheses of enamines.[18] Furthermore, this transformation is interesting because it allows the synthesis of unsaturated products in the presence of hydrogen. Therefore, we investigated this new hydroaminomethylenation reaction in more detail. In general the reaction was carried out in the presence of $[Rh(CO)_2(acac)]$ (0.1 mol%), ligand (0.2 mol%), and a 1:1 mixture of synthesis gas. Ligands such as triphenylphosphane and bidentate phosphanes such as naphos, xantphos, or their derivatives were used.

Examination of different solvents, temperatures, time, pressure, and concentration of starting materials in the presence of naphos led to highly selective reaction under remarkably mild conditions (Table 1, entries 1–9). At 65 °C and under 10 bar pressure of synthesis gas ($CO/H_2 = 1:1$), good conversion (90%) and excellent chemoselectivity (>97%) as well as regioselectivity (>99:1) are observed. The high chemoselectivity is noteworthy because of the relatively easy hydrogenation of the produced enamines. We thought that the ligand controls this unusual selectivity to a

Table 1: Hydroaminomethylenation of 1-pentene with piperidine in the presence of different Rh complexes and ligands.[a]



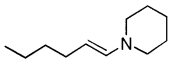
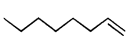
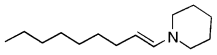
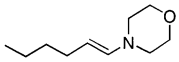
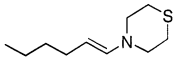
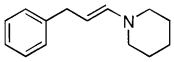
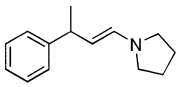
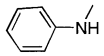
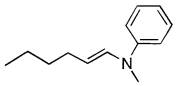
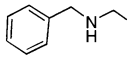
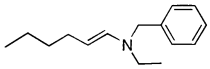
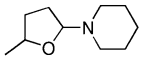
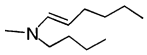
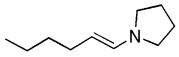
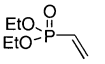
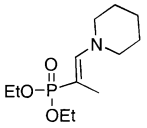
n iso

Entry	Ligand	*T* [°C]	CO/H_2 [bar]	Conv. [%]	Yield [%] *n*-enamine	Selectivity [%][b] *n*-enamine	iso enamine	*n* amine	aldol product	*n*/iso
1	**1**	65	20	69	50	72	8	5	11	90:10
2	**1**	85	20	85	76	89	1	1	3	99:1
3	**1**	100	20	83	75	90	1	2	3	99:1
4	**1**	120	20	80	70	87	5	–	4	95:5
5	**1**	75	10	95	85	89[c]	–	–	1	>99:1
6	**1**	65	40	42	41	98	–	–	–	>99:1
7[d]	**1**	**65**	**10**	**90**	**87**	**97**	**–**	**–**	**–**	**>99:1**
8[e]	**1**	65	20	92	44	48	29	23	–	62:38
9[f]	**1**	65	20	99	15	15	1	76[g]	2	94:6
10[i,j]	**1**	125	40	100	–	–	–	89	–	94:6
11	–	65	10	57	–	–	–	35[h]	18	–
12	PPh_3	65	10	76	37	49	20	13	17	71:29
13	**2**	65	10	79	61	77	–	–	23	99:1
14	**3**	65	10	39	39	39	–	–	–	99:1
15[i,j]	**3**	125	40	100	–	–	–	97	–	98:2

[a] Reaction conditions: 1-pentene (15 mmol), piperidine (15 mmol), $[Rh(CO)_2(acac)]$ (0.1 mol%), ligand (0.2 mol%), toluene (30 mL), 12 h. [b] Selectivities were determined by GC analysis with bis(methoxyethyl) ether as an internal standard. [c] Linear aldehyde (5%), iso-aldehyde (4%). [d] 16 h. [e] THF (30 mL). [f] MeOH (30 mL). [g] Iso-amine (6%). [h] Iso-amine (48%). [i] Alkene (10 mmol), amine (10 mmol), methanol (15 mL), (toluene) 15 mL, CO (7 bar), H_2 (33 bar), 125 °C, 5 h. [j] $[Rh(cod)_2]BF_4$. cod = cycloocta-1,5-diene.

large extent. Indeed, as shown in Table 1 (entries 7, 11–14), both the chemoselectivity and the regioselectivity (*n*/iso)[19] of the reaction are controlled by the added ligand. Whereas in the absence of any phosphane ligand essentially no enamine and a nearly 1:1 mixture of linear and iso-amine is formed, the use of the "standard ligand" triphenylphosphane leads to lower conversion (76%), chemoselectivity (69%), and regioselectivity (*n*/iso = 71:29). Furthermore, it is shown that rhodium catalysts based on xantphos or iphos (**3**)[20] also gave significantly lower conversion and selectivities. Apart from the ligand, the solvent appeared to be important for preventing hydrogenation of the enamine. In this case, aromatic solvents, which are known to coordinate to the rhodium center and thus slow down hydrogenation reactions,[21] seem to be especially suitable. Interestingly, at higher temperature (125 °C) and slightly higher pressure (40 bar), high selectivity to the corresponding amine is observed (Table 1, entries 10 and 15).[14]

Table 2: General synthesis of enamines.[a]

Entry	Alkene	Amine	Major product	Conv. [%]	Selec. [%][b]	*n*/iso
1				100	97	99:1
2				95	95	99:1
3				90	>99	99:1
4[c]				80	>99	99:1
5[d]				100	90	73:27
6[d]				75	>99	99:1
7				40	>99	99:1
8				98	85[d]	89:11
9				100	98	99:1
10				98	>98	99:1
11				100	>98	99:1
12[e]				95	86	99:1

[a] Reaction conditions: substrate (1:1, 15 mmol), [$Rh(CO)_2(acac)$] (0.1 mol%), naphos (0.2 mol%), toluene (30 mL), P_{CO/H_2} (1:1, 10 bar), 65 °C, 16 h. [b] Selectivities were determined by GC analysis with bis(methoxyethyl) ether as an internal standard. [c] Thiomorpholine (30 mmol). [d] 20 h. [e] THF (30 mL).

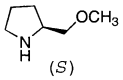
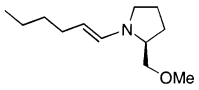
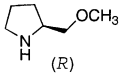
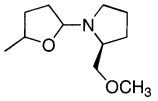
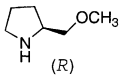
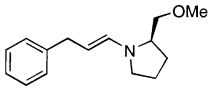
Evidently, the new procedure for enamine synthesis is only of significant importance to synthetic organic chemists if different aliphatic and aromatic olefins with various functional groups as well as various amines can be applied with success. Therefore, we were interested in the scope and limitations of our new reaction (Table 2).

We were pleased to find that not only lower but also higher aliphatic as well as aromatic olefins react well with piperidine to give the linear products with good to excellent selectivity (Table 2, entries 1–8). *N*-Methylaniline, *N*-ethylbenzylamine, and other aliphatic secondary amines (morpholine, thiomorpholine, pyrrolidine, *N*-methyl-*N*-butylamine) react well to give the corresponding enamine in high yield and selectivity. Notably, an unprotected allylic alcohol is efficiently converted into the corresponding N,O acetal, which is the cyclization product of the 4-hydroxyenamine, with high *n*/iso ratio (99:1) (Table 2, entry 9). In most cases, the reaction proceeds with an extremely high degree of chemo- (typically >95%) and regioselectivity (>99:1) towards the linear enamines. In case of aliphatic olefins, only the *E* enamine is detected. This is of special importance because the separation of mixtures of the branched and the linear enamine products is often very tedious owing to similar physical properties of both compounds. Hence, regioselectivities >98% are an important factor for the application of the method. Among the different reactions studied, the hydroaminomethylenation of α-methylstyrene with pyrrolidine and of 1-pentene with *N*-methylaniline needed longer reaction time and/or higher reaction temperature for complete conversion.

Notably, chiral secondary amines such as 2-methoxymethylpyrrolidine also produce the chiral aliphatic enamines in excellent yields and selectivities (chemoselectivity >98%; *n*/iso >98:2; Table 3, entry 1). In the case of styrene, the regioselectivity is somewhat lower. It is evident that these chiral enamines are useful building blocks for asymmetric synthesis.[22]

In conclusion, we have shown the first direct synthesis of enamines from olefins. Remarkably, excellent selectivities are observed under mild reaction conditions. Aliphatic olefins give the corresponding linear products in general with regioselectivities of 99:1, which allows easy isolation of the product. Key to the success of the reaction is the use of a catalyst system consisting of a neutral rhodium precursor together with naphos as ligand. The reported catalyst system is tolerant to a variety of potentially reactive functional groups, making the procedure valuable for the synthesis of interesting organic building blocks, including chiral enamines.

Table 3: Synthesis of various enamines using chiral amines.[a]

Entry	Alkene	Amine	Major product	Conv. [%]	Selec. [%][b]	*n*/iso
1		 (*S*)		100	98	98:2
2		 (*R*)		100	98	99:1
3[c]		 (*R*)		90	82[d]	63:37

[a] Reaction conditions: substrate (1:1, 10 mmol), $[Rh(CO)_2(acac)]$ (0.1 mol%), naphos (0.2 mol%), toluene (30 mL), P_{CO/H_2} (1:1, 10 bar), 65 °C, 16 h. [b] Selectivities were determined by GC analysis with bis(methoxyethyl) ether as an internal standard. [c] 20 h. [d] Major side product is amine (15%, 80:20).

Clearly, this new synthesis of enamines is atom-economic and environmentally friendly (i.e., water is the only by-product), and the starting materials are both inexpensive and readily available.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (^{1}H: 400.1, ^{13}C: 100.6 MHz). Chemical shifts (δ) are given in ppm relative to residual solvent as internal standard. Gas chromatographic analyses were performed on a Hewlett Packard HP 5890 chromatograph with flame-ionization detector and an HP5 column (cross-linked 5% PH ME siloxane). Mass spectra (GC–MS) experiments were conducted on an Agilent-6890. The products were isolated from the reaction mixture by evaporation of the solvent and/or further purified by vacuum distillation wherever necessary. All yields reported in Tables 1–3 refer to GC yields using bis(methoxyethyl) ether as an internal standard. All yields of isolated compounds (which vary by 5–10% from those determined by GC) were estimated to be >95% pure as determined by GC and NMR. All new compounds were further characterized by HRMS. Linear/branched ratios were determined by GC analysis of the crude reaction mixtures. Compounds known in the literature were characterized by comparing their ^{1}H NMR, ^{13}C NMR, and GC–MS data with the previously reported data. The purity of known compounds was confirmed by GC.

General procedure: All hydroaminomethylenation experiments were carried out in a Parr stainless-steel autoclave (100 mL). In a typical experiment, the autoclave was charged with $[Rh(CO)_2(acac)]$ (0.1 mol%), naphos (0.2 mol%), olefin (15.0 mmol), amine (15.0 mmol), and toluene (30 mL) under argon. The autoclave was pressurized with CO (5 bar) and hydrogen (5 bar), and the reaction was carried out at 65 °C for 16 h. The autoclave was then cooled to room temperature and depressurized. The reaction mixture was transferred to a Schlenk flask under an argon atmosphere, dried over $MgSO_4$, and analyzed by GC with bis(methoxyethyl) ether as internal standard.

N-1-Hexenylpiperidine: Yield: 99% (GC); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.79$ (d, $J = 14$ Hz, 1H), 4.36 (quint, $J = 14$ Hz, $J = 7$ Hz, 1H), 2.78–2.69 (m, 4H), 1.95–1.90 (m, 2H), 1.58-1.46 (br m, 4H), 1.29–1.26 (m, 6H), 0.86 ppm (t, $J = 7$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 140.1$, 101.4, 50.1, 33.5, 30.2, 25.4, 24.3, 22.0, 13.9 ppm; MS (EI, 70 eV): *m*/*z* (%): 167 [M^+], 152, 138, 124, 110, 96, 80, 68, 55, 41, 27; HRMS: calcd for $C_{11}H_{21}N$ [M^+]: 167.16795; found: 167.16740.

2-Methyl-5-piperidinyltetrahydrofuran: Yield: 99% (GC); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.54$ and 4.51 (t, $J = 6.4$ Hz and dd, $J = 6.4$ Hz, 4.0 Hz, 1H of the two isomers), 3.98–3.90 and 3.81–3.73 (m, 1H of the two isomers), 2.71–2.40 (br m, 4H), 1.98–1.78 (m, 4H), 1.53–1.36 (m, 6H), 1.16 and 1.11 ppm (d, $J = 6.0$ Hz and d, $J = 6.0$ Hz, 3H of the two isomers); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 95.9$, 95.7, 74.3, 73.4, 48.3, 47.8, 32.9, 32.1, 28.2, 25.5, 24.0, 20.7, 19.8 ppm; MS (EI, 70 eV): *m*/*z* (%): 169 [M^+], 154, 140, 125, 114, 98, 84, 69, 55, 41, 29; HRMS: calcd for $C_{10}H_{19}NO$ [M^+]: 169.14443; found: 169.1466.

N-(1-Hexenyl)-2-methoxymethylpyrrolidine: Yield: 98% (GC); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.21$ (d, $J = 14$ Hz, 1H), 4.16 (quint, $J = 14$ Hz, $J = 7$ Hz, 1H), 3.36 (d, $J = 3$ Hz, 2H), 3.34 (s, 3H), 3.22–3.17 (m, 1H), 2.82 (t, $J = 8.12$ Hz, 2H), 1.98–1.93 (m, 2H), 1.89–1.79 (m, 2H), 1.73–1.69 (m, 2H), 1.31–1.27 (m, 4H), 0.87 ppm (t, $J = 7$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.4$, 99.0, 75.7, 60.2, 59.0, 49.0, 33.9, 30.3, 28.4, 23.5, 22.1, 14.0 ppm; MS (EI, 70 eV): *m*/*z* (%):197 [M^+], 182, 166, 152, 122, 108, 94, 81, 70, 54, 41, 27; HRMS: calcd for $C_{12}H_{23}NO$ [M^+]: 197.15984. found: 197.16231.

Received: July 7, 2003 [Z52320]

Keywords: amines · enamines · homogeneous catalysis · rhodium · synthetic methods

[1] M. Beller, C. Breindl, T. H. Riermeier, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1998**, *110*, 3571–3573; *Angew. Chem. Int. Ed.* **1998**, *37*, 3389–3391.
[2] M. Beller, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1997**, *109*, 2306–2308; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2225–2227.
[3] a) A. Tillack, I. Garcia Castro, C. G. Hartung, M. Beller, *Angew. Chem.* **2002**, *114*, 2646–2648; *Angew. Chem. Int. Ed.* **2002**, *41*, 2541–2543; b) C. G. Hartung, H. Trauthwein, A. Tillack, M. Beller, *J. Org. Chem.* **2001**, *66*, 6339–6343.
[4] For reviews, see: a) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703; b) Y. Yamamoto, U. Radhakrishnan, *Chem. Soc. Rev.* **1999**, *28*, 199–207; c) M. Nobis, B. Driessen-Hölscher, *Angew. Chem.* **2001**, *113*, 4105–4108; *Angew. Chem. Int. Ed.* **2001**, *40*, 3983–3986; d) M. Beller, C. Breindl, M. Eichberger, C. G. Hartung, J. Seayad, O. R. Thiel, A. Tillack, H. Trauthwein, *Synlett* **2002**, *10*, 1579–1594; e) J. Seayad, A. Tillack, C. G. Hartung, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 795–813.
[5] a) B. M. Trost, *Science* **1991**, *254*, 1471–1477; b) B. M. Trost, *Angew. Chem.* **1995**, *107*, 285–307; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259–281.
[6] R. A. Sheldon, *Pure Appl. Chem.* **2000**, *72*, 1233–1246.
[7] a) H. Bienaymé, C. Hulme, G. Oddon, P. Schmitt, *Chem. Eur. J.* **2000**, *6*, 3321–3329; b) G. H. Posner, *Chem. Rev.* **1986**, *86*, 831–844; c) R. W. Armstrong, A. P. Combs, P. A. Tempest, S. D. Brown, T. A. Keating, *Acc. Chem. Res.* **1996**, *29*, 123–131.
[8] a) L. F. Tietze, F. Haunert in *Stimulating Concepts in Chemistry* (Eds.: M. Shibasaki, J. F. Stoddart, F. Vögtle), Wiley-VCH, Weinheim, **2000**, pp. 39–64; b) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136; c) L. F. Tietze, A. Modi, *Med. Res. Rev.* **2000**, *20*, 304–322.
[9] For a review, see: P. Eilbracht, L. Bärfacker, C. Buss, C. Hollmann, B. E. Kitsos-Rzychon, C. L. Kranemann, T. Rische, R. Roggenbuck, A. Schmidt, *Chem. Rev.* **1999**, *99*, 3329–3365.
[10] W. Reppe, H. Vetter, *Justus Liebigs Ann. Chem.* **1953**, *582*, 133–163.

[11] a) B. Zimmermann, J. Herwig, M. Beller, *Angew. Chem.* **1999**, *111*, 2515 – 2518; *Angew. Chem. Int. Ed.* **1999**, *38*, 2372 – 2375; b) A. F. M. Iqbal, *Chem. Acta* **1971**, *54*, 1440; b) F. Jachimowicz, J. W. Raksis, *J. Org. Chem.* **1982**, *47*, 445 – 447; c) E. MacEntire, J. F. Knifton (Texaco Inc.), EP-B 241093, **1987** [*Chem. Abstr.* **1989**, *110*, 134785h]; d) J. J. Brunet, D. Neibecker, F. Agbossou, R. S. J. Srivastav, *J. Mol. Catal.* **1994**, *87*, 223 – 230; e) E. Drent, A. J. M. Breed (Shell Int. Res.M.), EP-B 457386, **1992** [*Chem. Abstr.* **1992**, *116*, 83212h]; f) S. Törös, I. Gemes-Pesci, B. Heil, S. Maho, Z. Tubar, *J. Chem. Soc. Chem. Commun.* **1992**, 585 – 589; g) T. Baig, P. Kalck, *J. Chem. Soc. Chem. Commun.* **1992**, 1373 – 1374; h) T. Baig, J. Molinier, P. Kalck, *J. Organomet. Chem.*. **1993**, *455*, 219 – 224; i) M. D. Jones, *J. Organomet. Chem.* **1989**, *366*, 403 – 408; j) G. Diekhaus, D. Kampmann, C. Kniep, T. Müller, J. Walter, J. Weber (Hoechst AG), DE-B 4334809, **1993** [*Chem. Abstr.* **1995**, *122*, 314160g]; k) H. Schaffrath, W. Keim, *J. Mol. Catal. A* **1999**, *140*, 107 – 113.

[12] a) T. Rische, L. Bärfacker, P. Eilbracht, *Eur. J. Org. Chem.* **1999**, *3*, 653 – 660; b) T. Rische, B. Kitsos-Rzychon, P. Eilbracht, *Tetrahedron* **1998**, *54*, 2723 – 2742; c) C. L. Kranemann, P. Eilbracht, *Synthesis* **1998**, *1*, 71; d) T. Rische, P. Eilbracht, *Synthesis* **1997**, *11*, 1331 – 1337; e) B. Breit, *Tetrahedron Lett.* **1998**, *39*, 5163 – 5166.

[13] For a review, see: a) P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895 – 904; b) M. Kranenburg, Y. E. M. van der Bugt, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1995**, *14*, 3081 – 3083; c) L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem.* **1999**, *111*, 349 – 351; *Angew. Chem. Int. Ed.* **1999**, *38*, 336 – 338; d) L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1999**, *18*, 4765 – 4777; e) L. A. van - der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 872 – 883; f) J. M. Fox, X. H. Huang, A. Chieffi, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 1360 – 1370; g) P. W. N. M. van Leeuwen, A. J. Sandee, J. N. H. Reek, P. C. J. Kamer, *J. Mol. Catal. A* **2002**, *182*, 107 – 123; h) C. R. Landis, J. Uddin, *J. Chem. Soc. Dalton Trans.* **2002**, 729 – 742; i) C. Botteghi, M. Marchetti, S. Paganelli, S. Scognamillo, *J. Mol. Catal. A* **2002**, *179*, 79 – 86; j) W. Goertz, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Chem. Eur. J.* **2001**, *7*, 1614 – 1618.

[14] M. Ahmed, A. M. Seayad, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2003**, *125*, 10311–10318.

[15] a) A. Seayad, M. Ahmed, H. Klein, R. Jackstell, T. Gross, M. Beller, *Science* **2002**, *297*, 1676 – 1678; b) for a commentary on this work, see: J. F. Hartwig, *Science* **2002**, *297*, 1653 – 1654.

[16] a) T. J. Devon, G. W. Philips, T. A. Puckette, J. L. Satvinoha, J. J. Vanderbilt, (Eastman Kodak), WO 87/07600, **1987**; b) M. Beller, J. G. E. Krauter, *J. Mol. Catal. A* **1999**, *143*, 31 – 39; c) W. A. Herrmann, R. Schmid, C. W. Kohlpaintner, T. Priermeier, *Organometallics* **1995**, *14*, 1961 – 1968; d) H. B. Bahrmann, K. Bergrath, H.-J. Kleiner, P. Lapper, C. Naumann, D. Peters, D. Regnat, *J. Organomet. Chem.* **1996**, *520*, 97 – 100; e) F. A. Rampf, M. Spiegler, W. A. Herrmann, *J. Organomet. Chem.* **1999**, *582*, 204 – 210; f) R. W. Eckl, T. Priermeier, W. A. Herrmann, *J. Organomet. Chem.* **1997**, *532*, 243 – 249; g) M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A* **1995**, *104*, 17 – 85; h) S. Okucu, A. Karacar, M. Freytag, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1339 – 1345; f) A. C. Da Silva, K. C. B. De Oliveira, E. V. Gusevskaya, E. N. Dos Santos, *J. Mol. Catal. A* **2002**, *179*, 133 – 141.

[17] a) Y.-S. Lin, B. E. Ali, H. Alper, *J. Am. Chem. Soc.* **2001**, *123*, 7719 – 7720; b) C. A. Busaca, Y. Dong, *J. Org. Chem.* **1997**, *62*, 6464 – 6465.

[18] a) X. Zhang, A. Fried, S. Knapp, A. S. Goldman, *Chem. Commun.* **2003**, 2060 – 2061; b) M. C. Willis, G. N. Brace, *Tetrahedron Lett.* **2002**, *43*, 9085 – 9088; c) N. Fujiwara, Y. Yamamoto, *Tetrahedron Lett.* **1998**, *39*, 4729 – 4732; d) P. W. Hickmott, *Tetrahedron* **1982**, *38*, 1975 – 2050; e) P. W. Hickmott, *Tetrahedron* **1982**, *38*, 3363 – 3446.

[19] The *n*/iso ratios were determined by GC analysis of the crude reaction mixture.

[20] H. Klein, R. Jackstell, K.-D. Wiese, C. Borgmann, M. Beller, *Angew. Chem.* **2001**, *113*, 3505 – 3508; *Angew. Chem. Int. Ed.* **2001**, *40*, 3408 – 3411.

[21] D. Heller, H.-J. Drexler, A. Spannenberg, B. Heller, J. S. You, W. Baumann, *Angew. Chem.* **2002**, *114*, 814 – 817; *Angew. Chem. Int. Ed.* **2002**, *41*, 777 – 780.

[22] a) C. Agami, L. Dechoux, C. Menard, S. Hebbe, *J. Org. Chem.* **2002**, *67*, 7573 – 7576; b) B. Jiang, F. Zhang, W. Xiong, *Tetrahedron*, **2002**, *58*, 261 – 264; c) V. I. Tararov, R. Kadyrow, T. H. Riermeier, J. Holz, A. Börner, *Tetrahedron Lett.* **2000**, *41*, 2351 – 2355; d) M. Nour, K. Tan, C. Cave, D. Villeneuve, D. Desmale, J. D'Angelo, C. Riche, *Tetrahedron: Asymmetry* **2000**, *11*, 995 – 1002; e) E. Caballero, P. Puela, M. Sanchez, M. Medarde, L. M. del Prado, A. San Feliciano, *Tetrahedron: Asymmetry* **1995**, *6*, 1985 – 1994; f) R. C. F. Jones, I. Turner, K. J. Howard, *Tetrahedron Lett.* **1993**, *34*, 6329 – 6332; g) W. S. Saari, T. E. Fischer, *Synthesis* **1990**, 6, 453 – 454; h) W. Keim, A. Koehnes, T. Roethel, D. Enders, *J. Organomet. Chem.* **1990**, *382*, 295 – 301.

