Iron Catalysis

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A General and Selective Iron-Catalyzed Aminocarbonylation of Alkynes: Synthesis of Acryl- and Cinnamides**

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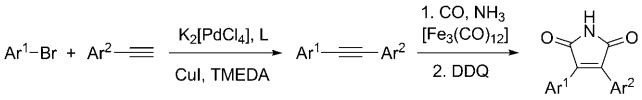
Dedicated to Professor Karlheinz Drauz on the occasion of his 60th birthday

Carbonylation reactions rank among the most important examples of industrially applied homogeneous catalytic reactions. In addition to hydroformylation, the synthesis of carboxylic acid derivatives from unsaturated hydrocarbons has in particular attracted considerable industrial and academic interest.[1] Since the pioneering work of Reppe,[2] various organometallic catalysts and synthetic procedures have been explored for the carbonylation of alkynes.[3] Initially, nickel-based catalysts prevailed in industry. In fact, the carbonylation of acetylene to acrylic acid was one of the first large-scale industrial applications of organometallic complexes.[4]

After the important development by Drent et al. in the 1980s,[5] cationic palladium complexes became the catalysts of choice for the carbonylation of alkynes to substituted acrylic acid derivatives. Thus, Shell developed a palladium-catalyzed process for the production of methyl methacrylate from propyne.[6] Since then, mainly noble-metal catalysts have been investigated for such transformations.[7] However, the high cost, limited availability, and sometimes sensitivity as well as toxicity of precious-metal complexes means there is increasing interest to substitute them by more easily available biorelevant metals. In this respect, homogeneous catalysis with iron complexes offers a highly attractive replacement. Without doubt, this area has become one of the "hot topics" in organometallic catalysis.[8–10] Although a number of stoichiometric iron-mediated carbonylation reactions are known,[11] catalytic processes have been only scarcely investigated. One of the exceptions is our synthesis of 3-(hetero)-aryl-4-arylsuccinimides and -maleimides. Here, the key step was the selective double aminocarbonylation of an internal alkyne in the presence of $[Fe_3(CO)_{12}]$ (Scheme 1).[12] This work awoke our interest in the selective monocarbonylation of alkynes to give the corresponding α,β-unsaturated amides.[13] To the best of our knowledge no such general iron-catalyzed method is known. Notably, the resulting acryl- or cinnamides are present in the structure of numerous natural products[16] which show considerable biological and insecticidal activity.[17] In addition, acrylamides are employed in a wide range of organic reactions,[18] including polymerizations.[19]



Scheme 1. Iron-catalyzed double carbonylation to 3,4-bisaryl maleimides. Ar^1 = (hetero)aryl, Ar^2 = (hetero)aryl, aryl, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, L = 2-(di-*tert*-butylphosphino)-*N*-phenylindole, TMEDA = *N*,*N*,*N*′,*N*′-tetramethethylenediamine.

At the start of our investigations we studied the influence of different parameters (ligands, pressure, temperature, and solvents) on the reaction of phenylacetylene with carbon monoxide and cyclohexylamine in the presence of various iron salts and complexes. Selected results are shown in Table 1. Iron(II) and iron(III) chloride were completely inactive (Table 1, entries 1 and 2), whereas iron carbonyl complexes in general showed high activity (Table 1, entries 3–9). However, in addition to the desired monocarbonylation product **1**, the double carbonylation product *N*-cyclohexyl-2-phenylsuccinimide was observed. The chemoselectivity for **1** is significantly increased by using $[(cot)Fe(CO)_3]$ (cot = cyclooctatetraene) as the catalyst precursor (Table 1, entry 8) compared to reactions with $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, or $[Fe_3(CO)_{12}]$ as catalyst precursors (Table 1, entries 3–5). Interestingly, in the latter cases no significant differences were observed, thus making a similar active species likely. To prove that the observed catalyst activity does not depend on other metal impurities, we investigated possible contaminations and analyzed $[Fe_3(CO)_{12}]$ by atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP). However, all other metals were below the detection limits of these methods (see the Supporting Information).[20] Furthermore, catalytic experiments were carried out using 5 mol% $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$, and with 100 ppm $[Ru_3CO_{12}]$, $[Pd(dba)_2]$ (dba = *trans*,*trans*-dibenzylideneacetone), $[Ni(acac)_2]$ (acac = acetylacetanoate), as well as six different copper salts. In no case was the carbonylation product obtained, which clearly proves that the reaction is catalyzed by iron.

Next, we tested different solvents (diglyme, NMP, THF, and cyclohexylamine) in the benchmark reaction (Table 1, entries 5, 11–13). Performing the reaction in neat amine

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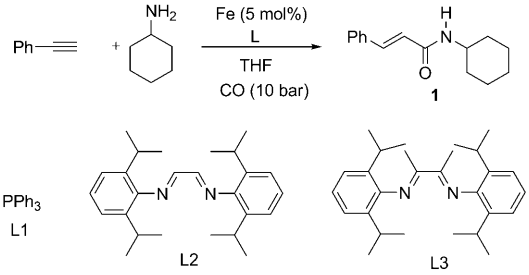
Table 1: Iron-catalyzed mono carbonylation of phenylacetylene: catalysts, ligands, and conditions.[a]



Entry	Iron catalyst	L[e]	Solvent	Yield [%][b]
1	$Fe^{II}Cl_2$	–	THF	0
2	$Fe^{III}Cl_3$	–	THF	0
3	$[Fe(CO)_5]$	–	THF	58
4	$[Fe_2(CO)_9]$	–	THF	59
5	$[Fe_3CO_{12}]$	–	THF	60
6[c]	$[Fe_3CO_{12}]$	–	THF	59
7[d]	$Na_2[Fe(CO)_4]$	–	THF	49
8	$[COTFe(CO)_3]$	–	THF	74
9	$[HNEt_3][HFe_3(CO)_{11}]$[14]	–	THF	63
10	$[NEt_4][Fe(NO)(CO)_3]$[15]	–	THF	1
11	$[Fe_3CO_{12}]$	–	diglyme	53
12[f]	$[Fe_3CO_{12}]$	–	NMP	1
13	$[Fe_3CO_{12}]$	–	$CyNH_2$	17
14[g]	$[Fe_3CO_{12}]$	–	THF	72
15	$[Fe_3CO_{12}]$	**L1**	THF	51
16	$[Fe_3CO_{12}]$	**L2**	THF	66
17	$[Fe_3CO_{12}]$	**L3**	THF	77

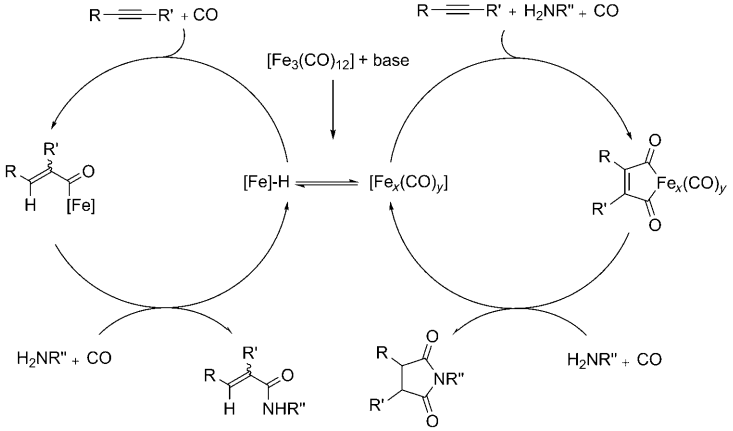
[a] Reaction conditions: 20 mL THF, 2 mmol phenylacetylene, 30 mmol cyclohexylamine ($CyNH_2$), 5 mol% Fe, 10 bar CO, 120°C, 16 h. [b] Determined by HPLC with *o*-xylene (0.5 mL) as internal standard. [c] Only 2 mol% Fe. [d] Collmann's reagent 94% purity; addition of 200 μL degassed H_2O. [e] Fe/L = 3:1. [f] *N*-Methyl-2-pyrrolidine (NMP). [g] Reaction with 10 equiv amine and 5 equiv NEt_3.

resulted in the catalyst activity and product yield decreasing (Table 1, entry 13). The best result was obtained using THF as the solvent. Nevertheless, the amine concentration has an important influence on the product yield (Table 1, entries 5, 13, and 14). The addition of triphenylphosphine somewhat decreased the selectivity of the catalyst (Table 1, entry 15). However, the chemoselectivity for **1** was improved in the presence of 1,4-diazabutadiene ligands[21] (Table 1, entries 16 and 17), and the best result was achieved using L3 as the ligand. The optimum catalytic activity was observed at 120°C, with full conversion of the alkyne achieved. Furthermore, the CO pressure has a major influence on the catalysis. The best selectivity for the monocarbonylation product **1** was observed at 10 bar CO pressure; higher pressure resulted in the double carbonylation increasing.

We propose two independent reaction pathways to give either mono- or double carbonylation products since it is impossible to generate *N*-cyclohexyl-2-phenylsuccinimide from **1** under the typical reaction conditions. On the basis of previous stoichiometric studies we assume that succinimide formation proceeds by a concerted double insertion of CO,[22] whereas the monocarbonylation would take place by a stepwise mechanism (Scheme 2). For this latter process we propose that an iron hydride carbonyl cluster reacts with the alkyne. It is well known that $[HNEt_3][HFe_3(CO)_{11}]$ is formed easily by addition of the amine to various iron carbonyl species.[22] Indeed, the use of $[HNEt_3][HFe_3(CO)_{11}]$ as the precatalyst gave similar product yields and selectivities as $[Fe_3(CO)_{12}]$, $[Fe_2(CO)_9]$, and $[Fe(CO)_5]$ (Table 1, entries 3–5 and 9). Subsequent formation of an acylcarbonyliron complex and nucleophilic attack by the amine should lead to an acrylamide and regenerate the active iron species. It is important to note that the observed anti-Markovnikov regioselectivity is in contrast to most known palladium-catalyzed carbonylations of alkynes.[23]

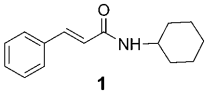
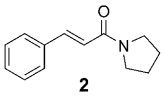
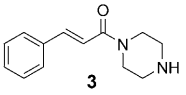
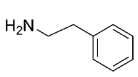
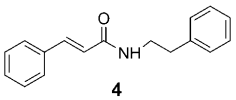
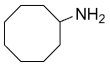
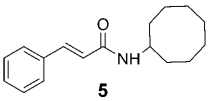
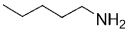
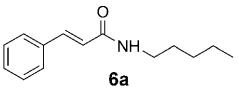
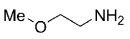
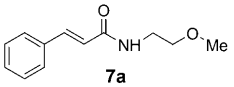
Next, the scope of the optimized iron catalyst system was demonstrated in the carbonylation of phenylacetylene with various primary and secondary amines (Table 2). In most cases the corresponding *N*-substituted cinnamides were obtained in good to very good yields. It is important to note that in all cases the linear, *E*-configured products were formed as the main product (>90% selectivity) with complete conversion. Bulky primary amines provided the desired monocarbonylation product in higher yields, and no double carbonylation product was detectable. However, in the case of linear pentylamine and 2-methoxyethylamine the corresponding succinimides were also isolated as side products (Table 2, entries 6 and 7) in 20 and 32% yield, respectively. The use of secondary amines as substrates results in only monocarbonylation taking place, since double carbonylation is not possible, and the corresponding *N*-substituted cinnamides are formed in excellent yields (Table 2, entries 2 and 3).

Finally, various alkynes were also applied in the standard reaction (Table 3). The synthesis of substituted cinnamides proceeded smoothly in good yields (Table 3, entries 1–8). Comparison of the reactions of different phenylacetylenes shows that electron-donating substituents (Table 3, entries 2, 3, and 6–8) seem to have no or little influence on the product yield, whereas electron-withdrawing substituents such as the CF_3 group lead to lower yields (Table 3, entry 4). The reason for this might be the lower nucleophilicity of the acceptor-



Scheme 2. Proposed mechanism for the iron-catalyzed carbonylation of alkynes.

Table 2: Carbonylation of phenylacetylene with different amines.[a]

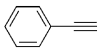
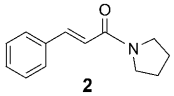
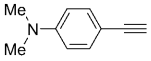
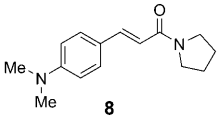
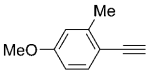
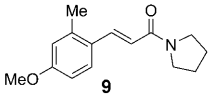
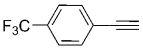
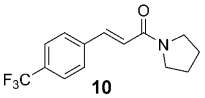
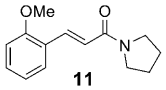
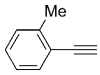
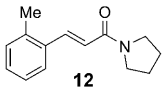
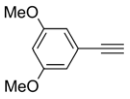
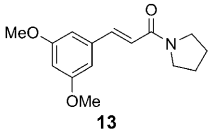
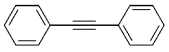
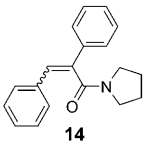
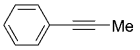
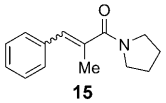
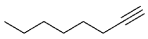
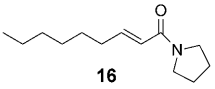
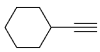
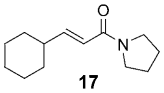
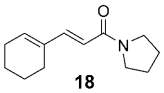
Entry	Amine	Product	Yield[b] [%]
1		 **1**	60 (77)
2		 **2**	78 (87)
3		 **3**	80
4		 **4**	78
5		 **5**	96
6		 **6a**	58
7		 **7a**	60

[a] Reaction conditions: 20 mL THF, 2 mmol phenylacetylene, 20 mmol amine, 10 mmol NEt_3, 5 mol% Fe ($[Fe_3CO_{12}]$), 1:1 Fe/L2, 10 bar CO, 120°C, 16 h. [b] Yields of isolated product. Yields from HPLC in parenthesis; determined with *o*-xylene (0.5 mL) as internal standard.

substituted alkynes. To our delight, symmetric and nonsymmetric internal alkynes are also aminocarbonylated in good to excellent yields (Table 3, entries 9 and 10). In the case of diphenylacetylene, both *E* and *Z* isomers were isolated (Table 3, entry 9). The configuration was determined by NOE measurements (see the Supporting Information). Up to four isomers can be formed in the case of 1-phenyl-1-propyne. However, (*E*)-cinnamide **15** was isolated as the main product in a 10:1 ratio of the anti-Markovnikov to Markovnikov product (see the Supporting Information). Furthermore, challenging terminal aliphatic alkynes such as 1-octyne, cyclohexylacetylene, and 1-ethynylcyclohexene provided the corresponding acrylamides in moderate to almost quantitative yields (Table 3, entries 11–13).

In conclusion, we have developed the first general iron-catalyzed aminocarbonylation of alkynes. Starting from commercially available amines and alkynes, a range of structurally diverse cinnamides and acrylamides are obtained smoothly in the presence of catalytic amounts of $[Fe_3(CO)_{12}]$ and L3. Notably, the method is highly chemo- and regioselective, and no expensive catalyst is required for this novel environmentally friendly reaction.

Table 3: Reaction of various substituted alkynes with pyrrolidine.[a]

Entry	Alkyne	Product	Yield[b, c] [%]
1		 **2**	78 (87)
2		 **8**	74
3		 **9**	59
4		 **10**	47
6		 **11**	82
7		 **12**	71
8		 **13**	72
9		 **14**	68[d]
10[c]		 **15**	91
11		 **16**	58
12		 **17**	58
13		 **18**	95

[a] Reaction conditions: 20 mL THF, 2 mmol alkyne, 20 mmol pyrrolidine, 10 mmol NEt_3, 5 mol% Fe ($[Fe_3CO_{12}]$), 1:1 Fe/L2, 10 bar CO, 120°C, 16 h. [b] Yields of isolated product. Yields from HPLC in parenthesis; determined with *o*-xylene (0.5 mL) as internal standard. [c] Product ratio determined by ^1H NMR spectroscopy. [d] $Z/E = 1.2:1$.

Experimental Section

General procedure: A mixture of alkyne (2 mmol), amine (20 mmol), triethylamine (10 mmol) and $[Fe_3(CO)_{12}]$ (5 mol% Fe) and L3 (0.1 mmol) was dissolved in THF (20 mL) in a 50 mL Schlenk flask under argon before being transferred into an autoclave. The autoclave was then pressurized with 10 bar CO and heated to 120°C for 16 h before the contents were cooled to room temperature. The pressure was then released, and the reaction mixture was transferred to a 50 mL Schlenk flask and *o*-xylene (0.5 mL, internal standard) added. A sample was taken to determine the yield by

HPLC. QuadraSil TA (0.5–1 g) was added and the reaction mixture stirred at room temperature for 30 min. After filtration of the QuadraSil TA and removal of the solvent in vacuo, the crude reaction mixture was purified by column chromatography on silica gel. The yield of the amide was measured by HPLC.

Synthesis of **1** (Table 2, entry 1): Following the general procedure, amide **1** was prepared from $[Fe_3(CO)_{12}]$ (17.7 mg, 0.033 mmol, 5 mol% Fe), L3 (40.4 mg, 0.1 mmol), THF (20 mL), cyclohexylamine (2.3 mL, 20 mmol), triethylamine (1.4 mL, 10 mmol), and phenylacetylene (220 μL, 2 mmol). The crude product was purified by column chromatography (heptane/ethyl acetate 10:1→3:1) to give **1** in 60% yield as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.61$ (d, $^3J_{CH,CH} = 15.9$ Hz, 1H, CH), 7.50–7.47 (m, 2H, CH_{aryl}), 7.37–7.33 (m, 3H, CH_{aryl}), 6.37 (d, $^3J_{CH,CH} = 15.9$ Hz, 1H, CH), 5.53 (br s, 1H, NH), 3.96–3.87 (m, 1H, CH), 2.02–1.97 (m, 2H, CH_2), 1.76–1.63 (m, 3H, CH_2), 1.47–1.36 (m, 2H, CH_2), 1.24–1.14 ppm (m, 3H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 164.9$ (s, CO), 140.7 (s, CH), 135.0 (C_{qu}), 129.5, 128.8, 127.8 (3 s, C_{aryl}), 121.1 (s, CH), 48.3 (s, CH), 33.2, 25.6, 24.9 (3 s, 3 × CH_2). MS (EI): m/z (I_{rel}) 230 (7), 229 (48), 148 (32), 146 (36), 132 (10), 131 (100), 103 (30), 102 (4), 98 (10), 77 (13). HRMS (ESI): calcd for $C_{15}H_{20}NO$: $[M+H]^+$ 230.15394, found: 230.15374. IR (ATR): 3272 (m), 3080 (w), 3030 (w), 2915 (m), 2851 (m), 1652 (s), 1615 (s), 1577 (w), 1550 (s), 1496 (w), 1446 (m), 1370 (w), 1342 (s), 1284 (w), 1259 (w), 1243 (m), 1219 (s), 1153 (w), 1096 (w), 1073 (w), 1027 (w), 997 (m), 989 (m), 980 (m), 966 (m), 893 (w), 869 (w), 841 (w), 803 (w), 762 (m), 724 (s), 692 (m), 673 (s).

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[1] a) *Modern Carbonylation Methods* (Ed.: L. Kollár), Wiley-VCH, **2008**; b) *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Berlin, **2006**; c) *Carbonylation Direct Synthesis of Carbonyl Compounds* (Eds.: H. M. Colquhoun, D. J. Thompson, M. V. Twigg), Plenum, New York, **1991**; d) *New Syntheses with carbon monoxide* (Ed.: J. Falbe), Springer, Berlin, **1980**.

[2] W. Reppe, *Justus Liebigs Ann. Chem.* **1953**, *582*, 1–37.

[3] For selected recent examples, see a) R. Suleiman, J. Tijani, B. El Ali, *Appl. Organomet. Chem.* **2010**, *24*, 38–46; b) B. Qu, N. Haddad, Z. S. Han, S. Rodriguez, J. C. Lorenz, N. Grinberg, H. Lee, C. A. Busacca, D. K. Krishnamurthy, C. H. Senanayake, *Tetrahedron Lett.* **2009**, *50*, 6126–6129; c) A. Takács, R. Farkas, L. Kollár, *Tetrahedron* **2008**, *64*, 61–66; d) Y. Li, H. Alper, Z. Yu, *Org. Lett.* **2006**, *8*, 5199–5201; e) X. Wu, J. Wannberg, M. Larhed, *Tetrahedron* **2006**, *62*, 4665–4670; f) Y. Uenoyama, T. Fukuyama, O. Nobuta, H. Matsubara, I. Ryu, *Angew. Chem.* **2005**, *117*, 1099–1102; *Angew. Chem. Int. Ed.* **2005**, *44*, 1075–1078; g) U. Matteoli, A. Scrivanti, V. Beghetto, *J. Mol. Catal. A* **2004**, *213*, 183–186; h) B. El Ali, J. Tijani, *Appl. Organomet. Chem.* **2003**, *17*, 921–931; i) J. Wannberg, M. Larhed, *J. Org. Chem.* **2003**, *68*, 5750–5753; j) B. El Ali, J. Tijani, A. M. El-Ghanam, *J. Mol. Catal. A* **2002**, *187*, 17–33; k) B. Gabriele, G. Salerno, L. Veltri, M. Costa, *J. Organomet. Chem.* **2001**, *622*, 84–88.

[4] J. Henkelmann, J.-D. Arndt, R. Kessinger in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), 2nd ed., Wiley-VCH, Weinheim, **2002**, pp. 274–285.

[5] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1984**, *475*, 57–63.

[6] a) G. Kiss, *Chem. Rev.* **2001**, *101*, 3435–3456; b) E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247–253.

[7] For reviews, see a) A. Brennführer, H. Neumann, M. Beller, *ChemCatChem* **2009**, *1*, 28–41; b) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176–4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114–4133.

[8] For recent reviews and highlights on iron catalysis, see a) *Iron Catalysis in Organic Chemistry* (Ed: B. Plietker), Wiley-VCH, Weinheim, **2008**; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363–3367; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; c) S. Gaillard, J.- L. Renaud, *ChemSusChem* **2008**, *1*, 505–509; d) C. Bolm, J. Legros, J. L. Paith, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; e) A. Correa, O. G. Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108–1117; f) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500–1511; g) A. Fürstner, *Angew. Chem.* **2009**, *121*, 1390–1393; *Angew. Chem. Int. Ed.* **2009**, *48*, 1364–1367; h) R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504–7507; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360–7363.

[9] For selected recent iron-catalyzed reactions, see a) A. Rudolph, M. Lautens, *Angew. Chem.* **2009**, *121*, 2694–2708; *Angew. Chem. Int. Ed.* **2009**, *48*, 2656–2670; b) N. Meyer, A. J. Lough, R. H. Morris, *Chem. Eur. J.* **2009**, *15*, 5605–5610; c) M. Jegelka, B. Plietker, *Org. Lett.* **2009**, *11*, 3462–3465; d) M. Holzwarth, A. Dieskau, M. Tabassam, B. Plietker, *Angew. Chem.* **2009**, *121*, 7387–7391; *Angew. Chem. Int. Ed.* **2009**, *48*, 7251–7255; e) S. H. Wunderlich, P. Knochel, *Angew. Chem.* **2009**, *121*, 9897–9900; *Angew. Chem. Int. Ed.* **2009**, *48*, 9717–9720; f) R. B. Bedford, M. A. Hall, G. R. Hodges, M. Huwe, M. C. Wilkinson, *Chem. Commun.* **2009**, 6430–6432; g) B. D. Sherry, A. Fürstner, *Chem. Commun.* **2009**, 7116–7118; h) T. Hatakeyama, S. Hashimoto, K. Ishizuka, M. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 11949–11963; i) J. Y. Wu, B. Moreau, T. Ritter, *J. Am. Chem. Soc.* **2009**, *131*, 12915–12917; j) B.-J. Li, L. Xu, Z.-H. Wu, B.-T. Guan, C.-L. Sun, B.-Q. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2009**, *131*, 14656–14657; k) A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, *J. Am. Chem. Soc.* **2008**, *130*, 8773–8787; l) A. Fürstner, K. Majima, R. Martin, H. Krause, E. Kattnig, R. Goddard, C. W. Lehmann, *J. Am. Chem. Soc.* **2008**, *130*, 1992–2004; m) C. Bolm, *Nat. Chem.* **2009**, *1*, 420.

[10] Selected reports on iron catalysis from our group: Reductions: a) S. Enthaler, G. Erre, M. K. Tse, K. Junge, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8095–8099; hydrogenations: b) D. Addis, N. Shaikh, S. Zhou, S. Das, K. Junge, M. Beller, *Chem. Asian J.* **2010**, *5*, 1687–1691; c) K. Junge, B. Wendt, N. Shaikh, M. Beller, *Chem. Commun.* **2010**, *46*, 1769–1771; oxidations: d) F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M. K. Tse, M. Beller, *Angew. Chem.* **2007**, *119*, 7431–7435; *Angew. Chem. Int. Ed.* **2007**, *46*, 7293–7296; e) K. Möller, G. Wienhöfer, K. Schröder, B. Join, K. Junge, M. Beller, *Chem. Eur. J.* **2010**, *16*, 10300–10303; f) K. Schröder, S. Enthaler, B. Join, K. Junge, M. Beller, *Adv. Synth. Catal.* **2010**, *352*, 1771–1778; g) A. Boddien, B. Loges, F. Gärtner, C. Torborg, A.-E. Surkus, K. Fumino, H. Junge, R. Ludwig, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 8924–8934; C–H functionalizations: h) I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem.* **2005**, *117*, 3981–3985; *Angew. Chem. Int. Ed.* **2005**, *44*, 3913–3917.

[11] For stoichiometric studies of this double carbonylation, see a) M. Periasamy, A. Mukkanti, D. S. Raj, *Organometallics* **2004**, *23*, 6323–6326; b) M. Periasamy, A. Mukkanti, D. S. Raj, *Organometallics* **2004**, *23*, 619–621; c) C. Rameshkumar, M. Periasamy, *Synlett* **2000**, 1619–1621; d) C. Rameshkumar, M. Periasamy, *Tetrahedron Lett.* **2000**, *41*, 2719–2722; e) C. Rameshkumar, M. Periasamy, *Organometallics* **2000**, *19*, 2400–2402; f) M. Periasamy, C. Rameshkumar, U. Rhadhakrishnan, J.- J. Brunet, *J. Org. Chem.* **1998**, *63*, 4930–4935; g) M. Periasamy, C. Rameshkumar, U. Rhadhakrishnan, *Tetrahedron Lett.* **1997**, *38*, 7229–7232.

[12] a) S. Prateeptongkum, K. M. Driller, R. Jackstell, A. Spannenberg, M. Beller, *Chem. Eur. J.* **2010**, *16*, 9606 – 9615; b) S. Prateeptongkum, K. M. Driller, R. Jackstell, M. Beller, *Chem. Asian J.* **2010**, *5*, 2173 – 2176; c) K. M. Driller, H. Klein, R. Jackstell, M. Beller, *Angew. Chem.* **2009**, *121*, 6157 – 6160; *Angew. Chem. Int. Ed.* **2009**, *48*, 6041 – 6044.

[13] For other preparations of α,β-unsaturated amides, see a) E. Hernández-Fernández, M. Fernández-Zertuche, O. García-Barradas, O. Muñoz-Muñiz, M. Ordóñez, *Synlett* **2006**, 440 – 445; b) F. J. P. Feuillet, M. Cheeseman, M. F. Mahon, S. D. Bull, *Org. Biomol. Chem.* **2005**, *3*, 2976 – 2989; c) S. Kim, C. J. Lim, W. Xue, *Angew. Chem.* **2004**, *116*, 5492 – 5494; *Angew. Chem. Int. Ed.* **2004**, *43*, 5378 – 5380; d) J. M. Concellón, E. Bardales, *Eur. J. Org. Chem.* **2004**, 1523 – 1526.

[14] W. McFarlane, G. Wilkinson, W. Hübel, *Inorg. Synth.* **1966**, *8*, 181 – 183.

[15] B. Plietker, A. Dieskau, *Eur. J. Inorg. Chem.* **2009**, 775 – 787.

[16] a) I. R. Davies, M. Cheeseman, D. G. Niyadurupola, S. D. Bull, *Tetrahedron Lett.* **2005**, *46*, 5547 – 5549; b) K. Wei, W. Li, K. Koike, Y. Pei, Y. Chen, T. Nikaido, *J. Nat. Prod.* **2004**, *67*, 1005 – 1009; c) B. Riemer, O. Hofer, H. Greger, *Phytochemistry* **1997**, *45*, 337 – 341.

[17] For activities of α,β-unsaturated amides, see a) J. C. Bressi, R. de Jong, Y. Wu, A. J. Jennings, J. W. Brown, S. O'Connell, L. W. Tari, R. J. Skene, P. Vu, M. Navre, X. Cao, A. R. Gangloff, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 3138 – 3141; b) N. Zhou, W. Zeller, J. Zhang, E. Onua, A. S. Kiselyov, J. Ramirez, G. Palsdottir, G. Halldorsdottir, P. Andrésson, M. E. Gurney, J. Singh, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 1528 – 1531; c) S. Mahboobi, A. Sellmer, H. Höcher, C. Garhammer, H. Pongratz, T. Maier, T. Ciossek, T. Beckers, *J. Med. Chem.* **2007**, *50*, 4405 – 4418; d) T. W. Schultz, J. W. Yarbrough, S. K. Koss, *Cell Biol. Toxicol.* **2006**, *22*, 339 – 349; e) K. S. Putt, V. Nesterenko, R. S. Dothager, P. J. Hergenrother, *ChemBioChem* **2006**, *7*, 1916 – 1922; activities of cinnamides: f) A. Kamal, G. Balakishan, G. Ramakrishna, T. B. Shaik, K. Sreekanth, M. Balakrishna, Rajender, D. Dastagiri, S. V. Kalivendi, *Eur. J. Med. Chem.* **2010**, *45*, 3870 – 3884; g) B. J. Leslie, C. R. Holaday, T. Nguyen, P. J. Hergenrother, *J. Med. Chem.* **2010**, *53*, 3964 – 3972; h) G. Giannini, M. Marzi, R. Pezzi, T. Brunetti, G. Battistuzzi, M. Di Marzo, W. Cabri, L. Vesci, C. Pisano, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2346 – 2349; i) B. Debnath, S. Samanta, K. Roy, T. Jha, *Bioorg. Med. Chem.* **2003**, *11*, 1615 – 1619; j) M. Winn, E. B. Reilly, G. Liu, J. R. Huth, H.-S. Jae, J. Freeman, Z. Pei, Z. Xin, J. Lynch, J. Kester, T. W. von Geldern, S. Leitza, P. DeVries, R. Dickinson, D. Mussatto, G. F. Okasinski, *J. Med. Chem.* **2001**, *44*, 4393 – 4403.

[18] a) M. Kissane, A. R. Maguire, *Chem. Soc. Rev.* **2010**, *39*, 845 – 883; b) R. Suleiman, B. El Ali, *Tetrahedron Lett.* **2010**, *51*, 3211 – 3215; c) V. Verdolinoa, A. Forbesa, P. Helquista, P.-O. Norrbyb, O. Wiesta, *J. Mol. Catal. A* **2010**, *324*, 9 – 14; d) Y. Shibata, K. Tanaka, *J. Am. Chem. Soc.* **2009**, *131*, 12552 – 12553; e) Y.-C. Wong, K. Parthasarathy, C.-H. Cheng, *J. Am. Chem. Soc.* **2009**, *131*, 18252 – 18253; f) R. H. Taaning, K. B. Lindsay, T. Skrydstrup, *Tetrahedron* **2009**, *65*, 10908 – 10916; g) M. R. Nahm, J. R. Potnick, P. S. White, J. S. Johnson, *J. Am. Chem. Soc.* **2006**, *128*, 2751 – 2756; h) D. Riber, T. Skrydstrup, *Org. Lett.* **2003**, *5*, 229 – 231.

[19] a) E. S. Read, K. L. Thompson, S. P. Armes, *Polym. Chem.* **2010**, *1*, 221 – 230; b) M. J. Caulfield, G. G. Qiao, D. H. Solomon, *Chem. Rev.* **2002**, *102*, 3067 – 3083.

[20] a) S. L. Buchwald, C. Bolm, *Angew. Chem.* **2009**, *121*, 5694 – 5695; *Angew. Chem. Int. Ed.* **2009**, *48*, 5586 – 5587; b) the following metals were analyzed by AAS: Co, Mn, Ni, Pd, Pt, Rh, Ru, and Cu; the following metals were analyzed by ICP: Sb, Pb, Cr, Ir, Co, Mn, Mo, Ni, Pd, Pt, Re, Rh, Ru, V, W, Zn, and Sn. All metal concentrations were below the detection limit. The detection limits for both methods are given in the Supporting Information.

[21] a) M. M. Khusniyarov, T. Weyhermüller, E. Bill, K. Wieghardt, *J. Am. Chem. Soc.* **2009**, *131*, 1208 – 1221; b) K. Kaleta, J. Fleischhauer, H. Görls, R. Beckert, W. Imhof, *J. Organomet. Chem.* **2009**, *694*, 3800 – 3805; c) W. Imhof, A. Göbel, *J. Organomet. Chem.* **2005**, *690*, 1092 – 1099; d) W. Imhof, E. Anders, *Chem. Eur. J.* **2004**, *10*, 5717 – 5729; e) W. Imhof, E. Anders, A. Göbel, H. Görls, *Chem. Eur. J.* **2003**, *9*, 1166 – 1181; f) J. Breuer, H.-W. Frühauf, W. J. J. Smeets, A. L. Spek, *Inorg. Chim. Acta* **1999**, *291*, 438 – 447; g) F. Muller, G. van Koten, K. Vrieze, *Organometallics* **1989**, *8*, 33 – 40; h) H. tom Dieck, R. Diercks, L. Stamp, H. Bruder, T. Schuld, *Chem. Ber.* **1987**, *120*, 1943 – 1950; i) H. tom Dieck, R. Diercks, *Angew. Chem.* **1983**, *95*, 1138 – 1446; *Angew. Chem. Int. Ed.* **1983**, *22*, 1138 – 1146; j) H. tom Dieck, A. Orlopp, *Angew. Chem.* **1975**, *87*, 246 – 247; *Angew. Chem. Int. Ed.* **1975**, *14*, 251 – 252.

[22] F. Gärtner, B. Sundararaju, A.-E. Surkus, A. Boddien, B. Loges, H. Junge, P. H. Dixneuf, M. Beller, *Angew. Chem.* **2009**, *121*, 10147 – 10150; *Angew. Chem. Int. Ed.* **2009**, *48*, 9962 – 9965.

[23] M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem.* **2004**, *116*, 3448 – 3479; *Angew. Chem. Int. Ed.* **2004**, *43*, 3368 – 3398.

