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Catalytic reaction of methyl formate with amines to formamides

Jens Deutsch *, Reinhard Eckelt, Angela Köckritz, Andreas Martin

Leibniz Institute for Catalysis at University Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

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ABSTRACT

A feasible procedure of using methyl formate as cheap reagent for the conversion of aliphatic and aromatic amines into formamides with high yields is reported. The improved amine formylation method proceeds mainly at room temperature and in presence of bicyclic guanidines as catalysts. A verifiable key intermediate of outstanding formylating activity is generated from methyl formate and the catalyst in the reaction mixture.

1. Introduction

The transformation of primary or secondary amines into formamides is an important chemical reaction. The reaction products are used as polar solvents or as intermediates for the production of pharmaceuticals.[1] In synthetic organic chemistry, the *N*-bonded formyl group is introduced commonly as a temporary protection group[2] or reduced to a methyl group.[3] The formamides, which derived from primary amines grant easy access to isocyanides.[4]

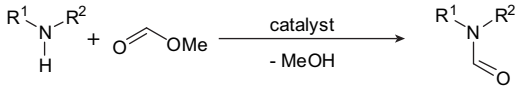
Various *N*-formylating reagents have already been reported in the literature. The most conventional of them are formic acid,[1,5] formamide,[6] acetic formic anhydride,[7] chloral,[8] trialkyl orthoformates,[9] enol formates,[10] cyanomethyl formate,[11] 2,2,2-trifluoroethyl formate,[12] pentafluorophenyl formate,[13] diformamide,[14] *N*-formylimidazole,[15] *N*-formylbenzotriazole,[16] and potassium cyanide/dimethyl malonate.[17] Formic acid and formamide are inexpensive formylating compounds. Regrettably, their only moderate reactivity demands increased reaction temperatures, especially for the formylation of sterically hindered and aromatic amines. In contrast, the mentioned activated formic acid esters and amides show a considerably higher formylating power and can be used under milder reaction conditions. Nevertheless, their practical application seems to be limited to laboratory use only. The main disadvantages of these reagents are their accessibility, poor atom economy and, for some of them, the stoichiometric liberation of toxic byproducts.

Carbon monoxide[18] or carbon dioxide in combination with hydrogen[18,19] were developed as alternative and clean reagents for the synthesis of formamides from amines during the last decades. The weak carbonyl activity of the carbon oxides requires harsh reaction conditions, a considerable technical expenditure, the addition of homogeneous or heterogenised ruthenium or platinum catalysts to the reaction mixture, and impedes the synthesis of formanilides from aromatic amines.

Besides the formylating agents listed above, methyl formate can be utilised for the synthesis of formamides. However, its reaction with amines has only been reported for single examples and has not yet been investigated systematically. The literature indicates that long reaction times and/or a large excess of the ester are required to achieve acceptable product yields, even for aliphatic formamides.[20]

2. Results and discussion

The aim of the investigations was to establish a practicable and improved method of using methyl formate for amine formylations



Scheme 1. Catalytic formylation of various amines with methyl formate. Amines: Piperidine: R^1–R^2=$(CH_2)_5$; morpholine: R^1–R^2=$(CH_2)_2$-O-$(CH_2)_2$; *n*-hexylamine: R^1=*n*-Hex, R^2=H; benzylamine: R^1=Ph–CH_2, R^2=H; cyclohexylamine: R^1=*c*-Hex, R^2=H; 1-phenylethylamine: R^1=Ph–CH(Me), R^2=H; *t*-butylamine: R^1=*t*-Bu, R^2=H; 4-methoxyaniline: R^1=4-MeO–C_6H_4, R^2=H; 4-methylaniline: R^1=4-Me-C_6H_4, R^2=H; *N*-methylaniline: R^1=Ph, R^2=CH_3; aniline: R^1=Ph, R^2=H; 4-chloroaniline: R^1=4-Cl–C_6H_4, R^2=H; ethyl-*i*-propylamine: R^1=Et, R^2=*i*-Pr; 4-amino methyl benzoate: R^1=4-MeO_2C–C_6H_4, R^2=H; 4-nitroaniline: R^1=4-O_2N–C_6H_4, R^2=H.

* Corresponding author. Tel.: +49 3811281266; fax: +49 381128151266.
E-mail address: jens.deutsch@catalysis.de (J. Deutsch).

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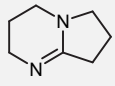
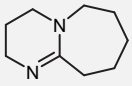
(Scheme 1). The main aspects were i) the exploration of suitable catalysts for the reaction, ii) the optimisation of the reaction conditions according to the reactivity of the amine to be converted into a formamide, and iii) studies on the catalytic cycle. Methyl formate might become a useful future platform chemical as it is available from methanol, hydrogen and the exhaust gas carbon dioxide in the presence of ruthenium catalysts.[19b,19d,21]

An initial model experiment revealed that morpholine is able to react slowly at room temperature in the absence of a catalyst with methyl formate to *N*-formylmorpholine (Table 1 entry 1a). Remarkably, the known N-acylation catalysts 4-dimethylaminopyridine[22], 1-methylimidazole,[23] imidazole,[11] and 1,2,4-triazole[24] were inactive and did not accelerate this reaction. For that reason, the considerably stronger bases 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) were evaluated as possible alternatives (Table 1). DBN and DBU have been reported as stoichiometrically usable dehydrohalogenating agents for the transformation of alkyl halogenides into alkenes.[25] Furthermore, DBN was applied as catalyst for Michael additions.[26] The present experiments have shown that the three bases have noticeable catalytic influences on the formylation of morpholine (Table 1, entries 1b–d). Consequently, the structurally related bicyclic guanidine bases 1,4,6-triazabicyclo[3.3.0]oct-4-ene (TBO), 1,4,6-triazabicyclo[3.4.0]non-4-ene (TBN), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD-1), 1,4,6-triazabicyclo[3.5.0]dec-4-ene (TBD-2) and 1,5,6-triazabicyclo[4.5.0]undec-5-ene (TBU) (Table 1) were included additionally into the investigations. It is known from the literature that TBD-1 can be applied in a semicatalytic amount of 30 mol % as activating additive in the aminolysis of alkanoic and benzoic acid esters. These reactions were performed for 12 h at 75 °C.[27] Surprisingly it was found out that TBO, TBN, TBD-1, TBD-2 and TBU effected a nearly complete reaction between methyl formate and morpholine within 30 min at room temperature (Table 1, entries 1e–i). Thus, the

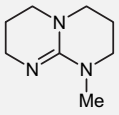
Table 1
Evaluation of amidine and guanidine catalysts in the reactions of morpholine and *t*-butylamine with methyl formate at room temperature according to Scheme 1[a]



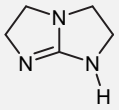
1,5-Diazabicyclo[4.3.0]non-5-ene
DBN



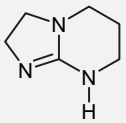
1,8-Diazabicyclo[5.4.0]undec-7-ene
DBU



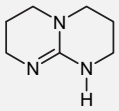
7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
MTBD



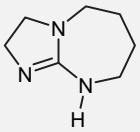
1,4,6-Triazabicyclo[3.3.0]oct-4-ene
TBO



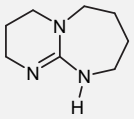
1,4,6-Triazabicyclo[3.4.0]non-4-ene
TBN



1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TBD-1



1,4,6-Triazabicyclo[3.5.0]dec-4-ene
TBD-2



1,5,6-Triazabicyclo[4.5.0]undec-5-ene
TBU

Amine	Reaction time [h]	Entry	Catalyst	Product yield [%]
Morpholine	0.5	1a	Blank test	2
		1b	DBN	6
		1c	DBU	14
		1d	MTBD	9
		1e	TBO	89
		1f	TBN	87
		1g	TBD-1	90
		1h	TBD-2	88
		1i	TBU	87
t-Butylamine	7	2a	Blank test	0
		2b	DBN	0
		2c	DBU	0
		2d	MTBD	0
		2e	TBO	9
		2f	TBN	38
		2g	TBD-1	70
		2h	TBD-2	57
		2i	TBU	24

[a] All the reactions were carried out using 10 mmol morpholine or *t*-butylamine, 12 mmol methyl formate, 120 mmol toluene as solvent, and 0.5 mmol (5 mol %) catalyst.

Table 2
Reaction of amines with methyl formate at room temperature over various catalysts[a]

Entry	Amine	Product yield according to GC analysis [%]					
		Reaction time [h]	Blank test	Catalyst			
				DBN	DBU	MTBD	TBD-1
1	Piperidine	0.5	13	14	22	20	98
2	Morpholine	0.5	2	6	14	9	90
3	*n*-Hexylamine	0.5	2	2	3	2	95
4	Benzylamine	1	3	7	7	4	98
5	Cyclohexylamine	2	3	2	2	3	93
6	1-Phenylethylamine	4	0	3	n.d.[b]	n.d.[b]	94
7	*t*-Butylamine	24	0	1	1	0	90
8	4-Methylaniline	48	0	2	n.d.[b]	n.d.[b]	72
9	*N*-Methylaniline	240	1	2	2	1	74

[a] All the reactions were carried out at room temperature using 10 mmol of amine, 12 mmol of methyl formate, 120 mmol of toluene as solvent, and 0.5 mmol (5 mol %) of the catalyst.
[b] Not determined, exact GC separation of target product and catalyst not possible.

guanidine bases exhibited by far higher activities than DBN, DBU and MTBD and proved to be excellent catalysts for amine formylations with methyl formate. It has to be noted that a real catalytic amount of 5 mol % guanidine base was sufficient for the reaction.

The superior formylating activities of TBO, TBN, TBD-1, TBD-2 and TBU to DBN, DBU and MTBD that were found lead to the assumption that their guanidine function with one NH group is the essential structural moiety of the catalyst molecule. For verification of this hypothesis, the formylation of *t*-butylamine was used as a second, and more challenging test reaction. Indeed, Table 1 shows that only TBO, TBN, TBD-1, TBD-2 and TBU are actually able to catalyse the formation of *t*-butyl formamide (entries 2a–i). Their performances were found to increase in the order TBO<TBU<TBN<TBD-2<TBD-1. In accordance with these results, the symmetric ten-membered bicyclic structure of TBD-1 proved as optimal catalyst property.

In continuation of the experiments reported above, the investigations were extended to reactions of methyl formate with amines of differing nucleophilic power. As given in Table 2, DBN, DBU, MTBD and TBD-1 were chosen as catalysts for the formylations. Additionally, every reaction was performed without catalyst for comparison. It was observed that relevant catalytic influences of DBN, DBU and MTBD were limited to the formylations of the very reactive amines piperidine, morpholine and benzylamine (Table 2, entries 1,2,4). In contrast, TBD-1 was catalytically effective for the formylation of various secondary, primary and even of aromatic amines (Table 2, entries 1–9). As an exception, the sterically hindered amine diisopropylamine could not be formylated with methyl formate in presence of TBD-1 (not given in Table 2).

To develop a convenient synthetic method for the preparation of formamides with methyl formate, the TBD-1 catalysed experiments reported above were repeated under optimised reaction conditions (Table 3). For formylations of reactive amines, a catalyst amount of 2.5 mol % was sufficient (Table 3, entries 1–6). The reactions of aromatic amines and ethyl-i-propylamine were done with 5 mol % TBD-1, an increased amount of methyl formate and in the absence of solvent (Table 3, entries 7–15). Compared to previously reported amine formylations with methyl formate,[28] 4-methylformanilide and 4-methoxyformanilide were synthesised in the presence of TBD-1 much faster, under milder conditions and with higher yields. Formylations of aromatic amines with electron withdrawing groups like 4-amino methyl benzoate and 4-nitroaniline were run above the boiling point of methyl formate in an autoclave. As expected, the weak nucleophilic compound 4-nitroaniline gave the lowest product yield (Table 3, entry 15).

Some of the formamides to be isolated from the organic reaction mixture are water soluble compounds. By the neutralisation with the solid acid $KHSO_4$ followed by filtration product loss, caused by an extractive removal of unreacted amine and catalyst with water, was avoided.

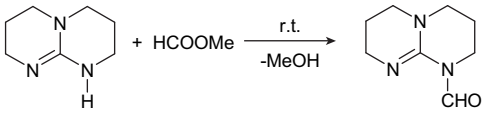
On the whole, the amines were converted without any side products into the desired formamides with high purities and yields.

To identify the active formylating species in the reaction, an equimolar mixture of methyl formate and TBD-1 was prepared. The signals in the ^{1}H NMR spectrum of the obtained oil could be assigned without any doubt to 7-formyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (FTBD-1) formed according to Scheme 2 with an NMR yield of 65%. Moreover, its IR spectrum shows typical bands for a formamide carbonyl group (1668 cm^{-1}) and a C=N bond (1626 cm^{-1}). FTBD-1 proved to have a limited thermal stability because of a probable propensity for decarbonylation into TBD-1 and carbon monoxide. Consequently, neither a sure GC–MS identification nor the separation of FTBD-1 from unreacted TBD-1 by distillation or flash chromatography was successful.

Table 3
TBD-1 catalysed formylation of amines according to Scheme 1 under optimised conditions[a]

Entry	Amine	Molar ratio methyl formate/amine	Catalyst amount [mol %]	Reaction temperature [°C]	Reaction time [h]	Product yield [%][b]
1	Piperidine	1.2	2.5	25	1	98
2	Morpholine	1.2	2.5	25	1	97
3	*n*-Hexylamine	1.2	2.5	25	1	96
4	Benzylamine	1.2	2.5	25	2	94
5	Cyclohexylamine	1.2	2.5	25	8	87
6	1-Phenylethylamine	1.2	2.5	25	16	93
7	*t*-Butylamine	1.2	5	25	24	86
8	4-Methoxyaniline[c]	2.4	5	25	8	88
9	4-Methylaniline[c]	2.4	5	25	16	87
10	*N*-Methylaniline[c]	2.4	5	25	48	91
11	Aniline[c]	2.4	5	25	48	85
12	4-Chloroaniline[c]	2.4	5	25	96	95
13	Ethyl-i-propylamine[c]	2.4	5	25	96	71
14	4-Amino methyl benzoate[c]	2.4	5	70	96	65
15	4-Nitroaniline[c]	2.4	5	70	96	~30[d]

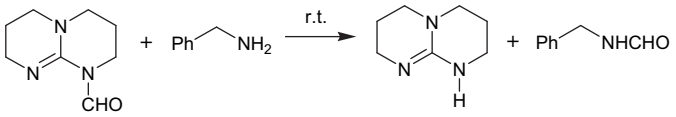
[a] All the reactions were carried out using 30 mmol of amine, 36 or 72 mmol of methyl formate, 360 mmol of toluene as solvent, and 0.75 or 1.5 mmol (2.5 or 5 mol %) catalyst.
[b] After isolation and purification (entries 1–13: Kugelrohr distillation, entry 14: flash chromatography).
[c] Reaction in absence of solvent.
[d] According to GC analysis.



Scheme 2. Generation of 7-formyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (FTBD-1) from TBD-1 and methyl formate.

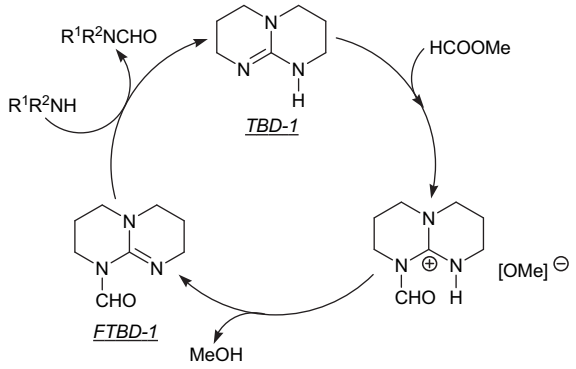
The equimolar mixture of methyl formate with MTBD, the *N*-methyl derivative of TBD-1, shows both the ^{1}H NMR and IR spectrum as sum of the single compound spectra. Hence, MTBD cannot be converted into detectable amounts of a reactive formyl compound, evidently because of its methylated nitrogen atom. This may explain the usually low catalytic activity or inactivity of MTBD in the amine formylations listed in Tables 1 and 2.

The ability of FTBD-1 to transmit its formyl group onto amines was confirmed with the formylation of benzylamine (Scheme 3). We noticed that the stoichiometric addition of the amine to a toluene solution of FTBD-1 (the obtainable crude product) resulted in an immediate and exothermic reaction within few minutes. Benzyl formamide and TBD-1 were identified as formed products with GC–MS and by comparison with authentic samples.



Scheme 3. The formyl group transfer reagent FTBD-1 in the stoichiometric reaction with benzylamine.

The results of the reported studies may be summarised to a three-step reaction cycle for TBD-1-catalysed reactions of amines with methyl formate (Scheme 4). Methyl formate and TBD-1 react within the initial step of giving '*N*-formyl guanidinium methoxide' as hypothetic intermediate of short life time and/or low concentration, which cannot be ascertained by common spectroscopic methods. An elimination of methanol yields FTBD-1 as an identifiable molecule in the second step. The third and final step should be the evidenced transfer of the formyl group from FTBD-1 to the amine under formation of the desired formamide and back-formation of the catalyst TBD-1.



Scheme 4. The assumed catalytic cycle for the reaction of amines with methyl formate in presence of TBD-1.

3. Conclusion

In conclusion it can be announced that methyl formate is usable as a cheep and clean reagent for the conversion of amines into formamides, when the reaction is catalysed by bicyclic guanidines containing a free NH group, such as 1,4,6-triazabicyclo[3.3.0]oct-4-ene (TBO), 1,4,6-triazabicyclo[3.4.0]non-4-ene (TBN), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD-1), 1,4,6-triazabicyclo[3.5.0]dec-4-ene (TBD-2), or 1,5,6-triazabicyclo[4.5.0]undec-5-ene (TBU). A preliminary formyl group transfer from methyl formate to the NH function of the guanidines generates their *N*-formyl derivatives as intrinsic and powerful formylating intermediates. The catalytic performances of TBO, TBN, TBD-1, TBD-2 and TBU depend on their molecular structure. TBD-1, the catalytically most active of the five bicyclic guanidines that were checked, is best suited to synthesise conveniently a wide spectrum of formamides from methyl formate and amines with high yields.

4. Experimental

4.1. General

Chemicals and solvents were purchased commercially from Aldrich, Fluka and Acros and used without further purification. Exceptionally, *n*-hexylformamide, 1-phenylethylformamide, ethyl-i-propylformamide, TBO, TBN, TBD-2 and TBU were synthesised according to the procedures published in the literature.[11,29] GC experiments were performed using a Hewlett Packard 5890 chromatograph with an HP-5 column (30 m×25 mm×0.25 μm). ^{1}H NMR spectra were recorded in $CD_3C_6D_5$ at 500 MHz.

4.2. General procedure for the catalytic experiments

In all catalytic experiments, the amine formylation was carried out at room temperature and monitored with GC. For a typical example, a mixture of amine (10 mmol), toluene as solvent (120 mmol), internal standard (diethylene glycol dimethyl ether, *n*-nonane, *n*-decane, *n*-dodecane, or *n*-tetradecane) and catalyst (0.5 mmol) was prepared. The reaction was started by the addition of methyl formate (12 mmol) and the progressing product formation was analysed periodically.

4.3. General procedure for the preparation of aliphatic formamides

A mixture of amine (30 mmol), methyl formate (36 mmol), toluene as solvent (360 mmol) and the catalyst TBD-1 (0.75–1.5 mmol) was stored in a closed flask at room temperature for 1–24 h. The reaction was quenched by adding finely powdered $KHSO_4$ and subsequent stirring of the resulting slurry for 1 h. After filtration of the solid, the remaining clear solution was concentrated in vacuum and the obtained crude formamides were purified by Kugelrohr distillation. The identity of all synthesised products as known compounds was ensured with GC–MS and ^{1}H NMR and by analytic comparison with authentic samples.

4.4. General procedure for the preparation of aromatic formamides and ethyl *i*-propylformamide

A mixture of amine (30 mmol), methyl formate (72 mmol) and catalyst TBD-1 (1.5 mmol) was stored in a closed flask at room temperature for 8–96 h. Because of their lower solubility and reactivity, 4-amino methyl benzoate and 4-nitroaniline were reacted at 70 °C under stirring in an autoclave for 96 h. The reaction was quenched by adding 20 ml toluene (50 ml acetonitrile for the formylation of 4-amino methyl benzoate; see Table 3, entry 14), finely powdered $KHSO_4$ and stirring of the resulting slurry for 1 h. With exception of the not isolated 4-nitroformanilide, the target products were purified and identified as given for the aliphatic formamides. The compound 4-formylamino methyl benzoate (Table 3, entry 14) was purified by flash chromatography (Kieselgel 60, eluent 3:1 ethyl acetate/*n*-hexane mixture). All synthesised formamides are known compounds. Their identity was ensured by analytic comparison (GC–MS and ^{1}H NMR) with authentic samples.

4.5. Synthesis and identification of FTBD-1 as intermediate formylating agent

A mixture of TBD-1 (20 mmol) and methyl formate (20 mmol) was stored overnight at room temperature in a closed flask. Subsequently, unreacted methyl formate and formed methanol were removed at room temperature under vacuum. The resulting colourless oil was analysed spectroscopically and contained FTBD-1 as the main component (65% NMR yield, see data) along with unreacted TBD-1.

Colourless oil; IR ($CHCl_3$): ν=1668, 1626 cm^{-1}; ^1H NMR (500 MHz, $CD_3C_6D_5$): δ=1.23–1.25 (m, 2H), 1.43–1.45 (m, 2H), 2.38–2.40 (m, 2H), 2.60–2.62 (m, 2H), 3.21–3.24 (m, 2H), 3.27–3.29 (m, 2H), 9.60 ppm (s, 1H).

Acknowledgements

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References and notes

1. Hosseini-Sarvari, M.; Sharghi, H. *J. Org. Chem.* **2006**, *71*, 6652–6654.
2. Seebach, D.; Aebi, J. D. *Tetrahedron Lett.* **1984**, *25*, 2545–2548.
3. (a) Wessely, F.; Swoboda, W. *Monatsh. Chem.* **1951**, *82*, 621–627; (b) Akabori, S.; Takanohashi, Y.; Aoki, S.; Sato, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3121–3125.
4. (a) Bestmann, H. J.; Lienert, J.; Mott, L. *Justus Liebigs Ann. Chem.* **1968**, *718*, 24–32; (b) Bonin, M.-A.; Giguere, D.; Roy, R. *Tetrahedron* **2007**, *63*, 4912–4917.
5. (a) Clark, V. M.; Kalckar, H. M. *J. Chem. Soc.* **1950**, 1029–1030; (b) De Luca, L.; Giacomelli, G.; Porcheddu, A.; Salaris, M. *Synlett* **2004**, 2570–2572.
6. Lachowicz, B. *Monatsh. Chem.* **1888**, *9*, 695–700.
7. Huffman, C. W. *J. Org. Chem.* **1958**, *23*, 727–729.
8. Smith, G. B. L.; Silver, M.; Becker, E. I. *J. Am. Chem. Soc.* **1948**, *70*, 4254.
9. Swaringen, R. A.; Eaddy, J. F.; Henderson, T. R. *J. Org. Chem.* **1980**, *45*, 3986–3989.
10. Neveux, M.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1197–1199.
11. Deutsch, J.; Niclas, H.-J. *Synth. Commun.* **1993**, *23*, 1561–1568.
12. Hill, D. R.; Hsiao, C.-N.; Kurukulasuriya, R.; Wittenberger, S. *J. Org. Lett.* **2002**, *4*, 111–113.
13. Kisfaludy, L.; Ötvös, L. *Synthesis* **1987**, 510.
14. Allenstein, E.; Beyl, V. *Chem. Ber.* **1967**, *100*, 3551–3563.
15. Staab, H. A.; Polenski, B. *Justus Liebigs Ann. Chem.* **1962**, *655*, 95–102.
16. Katritzky, A. R.; Chang, H.-X.; Yang, B. *Synthesis* **1995**, 503–505.
17. Bao, K.; Zhang, W.; Bu, X.; Song, Z.; Zhang, L.; Cheng, M. *Chem. Commun.* **2008**, 5429–5431.
18. Süss-Fink, G.; Langenbahn, M.; Jenke, T. *J. Organomet. Chem.* **1989**, *368*, 103–109.
19. (a) Schreiner, S.; Yu, J. Y.; Vaska, L. *J. Chem. Soc., Chem. Commun.* **1988**, 602–603; (b) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344–355; (c) Kroecher, O.; Koeppel, R. A.; Baiker, A. *Chem. Commun.* **1996**, 1497–1498; (d) Kroecher, O.; Koeppel, R. A.; Baiker, A. *Chem. Commun.* **1997**, 453–454; (e) Kroecher, O.; Koeppel, R. A.; Fröba, M.; Baiker, A. *J. Catal.* **1998**, *178*, 284–298; (f) Kayaki, Y.; Shimokawatoko, Y.; Ikariya, T. *Adv. Synth. Catal.* **2003**, *345*, 175–179; (g) Schmid, L.; Canonica, A.; Baiker, A. *Appl. Catal. A: Gen.* **2003**, *255*, 23–33; (h) Rohr, M.; Grunwaldt, J.-D.; Baiker, A. *J. Mol. Catal. A: Chem.* **2005**, *226*, 253–257; (i) Rohr, M.; Grunwaldt, J.-D.; Baiker, A. *J. Catal.* **2005**, *229*, 144–153; (j) Rohr, M.; Günther, M.; Jutz, F.; Grunwaldt, J.-D.; Emerich, H.; van Beek, W.; Baiker, A. *Appl. Catal. A: Gen.* **2005**, *296*, 238–250.
20. (a) Lunazzi, L.; Macciantelli, D. *Tetrahedron* **1985**, *41*, 1991–1998; (b) Stingl, K.; Martens, J. *Synth. Commun.* **1992**, *22*, 2745–2756; (c) Burns, D. H.; Jabara, C. S.; Burden, M. W. *Synth. Commun.* **1995**, *25*, 379–387; (d) Reimann, E.; Grasberger, F. *Monatsh. Chem.* **2005**, *136*, 193–209.
21. (a) Darensbourg, D. J.; Ovalles, C.; Pala, M. *J. Am. Chem. Soc.* **1983**, *105*, 5937–5939; (b) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Chem. Soc., Chem. Commun.* **1995**, 707–708; (c) Ng, S. M.; Yin, C.; Yeung, C. H.; Chan, T. C.; Lau, C. P. *Eur. J. Inorg. Chem.* **2004**, 1788–1793.
22. (a) Litvinenko, L. M.; Kirichenko, A. I. *Dokl. Akad. Nauk SSSR Ser. Khim.* **1967**, *176*, 97–100; (b) Steglich, W.; Höfle, G. *Angew. Chem.* **1969**, *81*, 1001; (c) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem.* **1978**, *90*, 602–615; (d) Murugan, R.; Scriven, E. F. V. *Aldrichimica Acta* **2003**, *36*, 21–27.
23. Guibe-Jampel, E.; Bram, G.; Vilkas, M. *Bull. Soc. Chim. Fr.* **1973**, 1021–1027.
24. Openshaw, H. T.; Whittaker, N. *J. Chem. Soc. C* **1969**, 89–91.
25. (a) Oediger, H.; Kabbe, H.-J.; Möller, F.; Eiter, K. *Chem. Ber.* **1966**, *99*, 2012–2016; (b) Oediger, H.; Möller, F. *Angew. Chem.* **1967**, *79*, 53; (c) Wolkoff, P. *J. Org. Chem.* **1982**, *47*, 1944–1948.
26. Dauben, W. G.; Gerdes, J. M. *Tetrahedron Lett.* **1983**, *24*, 3841–3844.
27. Sabot, C.; Kumar, K. A.; Meunier, S.; Mioskowski, C. *Tetrahedron Lett.* **2007**, *48*, 3863–3866.
28. Janza, B.; Studer, A. *Org. Lett.* **2006**, *8*, 1875–1878.
29. (a) Cotton, F. A.; Murillo, C. A.; Wang, X.; Wilkinson, C. C. *Inorg. Chem.* **2006**, *45*, 5493–5500; (b) Cotton, F. A.; Murillo, C. A.; Wang, X.; Wilkinson, C. C. *Dalton Trans.* **2006**, 4623–4631.