Homoleptic Lanthanide Amides as Homogeneous Catalysts for Alkyne Hydroamination and the Tishchenko Reaction**

Markus R. Bürgstein, Helga Berberich, and Peter W. Roesky*[a]

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Abstract: The homoleptic bis(trimethylsilyl)amides of Group 3 metals and lanthanides of the general type $[Ln\{N(SiMe_3)_2\}_3]$ (**1**) (Ln = Y, lanthanide) represent a new class of Tishchenko precatalysts and, to a limited extent, precatalysts for the hydroamination/cyclization of aminoalkynes. It is shown that **1** is the most active catalyst for the Tishchenko reaction. This contribution presents investigations on the scope of the reaction, substrate selectivity, lanthanide-ion size-effect, and kinetic/mechanistic aspects of the Tishchenko reaction catalyzed by **1**. The turnover frequency is increased by the use of large-center metals and electron-withdrawing substrates. The reaction rate is second order with respect to the substrate. While donor atoms, such as nitrogen, oxygen, or sulfur, on the substrate decrease the turnover frequency, **1** shows a tolerance for a large number of functional groups. For the hydroamination/cyclization of aminoalkynes, **1** is less active than the well-known metallocene catalysts. On the other hand, **1** is much more readily accessible (one-step synthesis or commercially available), than the metallocenes and might therefore be an attractive alternative catalyst.

Keywords: aldehydes · dimerization · homogeneous catalysis · lanthanides · N ligands · rare-earth compounds

Introduction

Recently, there has been a significant research effort to establish lanthanide(III) compounds as catalysts for various organic transformations. Lanthanide catalysts are active in two fields of application. One involves organolanthanide compounds as catalysts for the transformation of olefins, dienes, and, to a lesser extent, alkynes. Especially, metallocenes, such as $[(C_5Me_5)_2LnR]$ (R = $CH(SiMe_3)_2$, $N(SiMe_3)_2$, H) have proven to be highly efficient catalysts[2] for a variety of olefin transformations, including hydrogenation,[3] polymerization,[4] hydroamination,[5] hydrosilylation,[6] hydroboration,[7] and hydrophosphination.[8] Unfortunately, the metallocenes are not readily accessible. On the other hand, lanthanide alkoxides, triflates, and halogenides were used for Lewis acid catalyzed organic reactions.[9] Thus, lanthanide triflates $[Ln(OTf)_3]$ are very active catalysts for the aldol,[10] Michael,[11] allylation,[12] Diels–Alder,[13] and glycosylation reactions[14] as well as for Friedel–Crafts acylations.[15, 16] Lanthanide alkoxides $[Ln(OR)_3]$ have proven to be useful catalysts for the Meerwein–Ponndorf–Verley reduction[17] and the hydrocyanation,[18] whereas lanthanide shift-reagents, such as $[Eu(fod)_3]$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) can be used as a catalyst for the Diels–Alder[19] and hetero-Diels–Alder reactions.[20]

In contrast to these well-established catalysts, homoleptic lanthanide(III) amides were not expected to be active as homogeneous catalysts. Recently, we communicated that the homoleptic bis(trimethylsilyl)amides of Group 3 metals and lanthanides, ($[Ln\{N(SiMe_3)_2\}_3]$, **1**)[21] (Ln = Y, lanthanide), are the most active catalysts for the Tishchenko reaction.[22] Meanwhile, other groups reported the use of **1** for the ring-opening polymerization of ε-caprolactone and δ-valerolactone.[23] The ternary system $[Nd\{N(SiMe_3)_2\}_3]/(iBu)_3Al/Et_2AlCl$ was used to polymerize butadiene to highly *cis*-1,4-polybutadiene.[24] Compound **1** belongs to a class of materials that has been known for the last 25 years. Recently, in particular, it has proven to be a valuable starting material in lanthanide chemistry because of the facile cleavage of the silylamide group.[25] Compound **1** is very readily accessible. It can either be prepared from a simple one-step synthesis or it can be bought (Ln = Y). Therefore, it is even more surprising that, prior to our investigations, there are almost no reports of **1** as a catalyst.

The Tishchenko reaction (or Claisen–Tishchenko reaction), which is the dimerization of aldehydes to form the

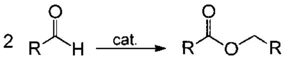
---

[a] Priv.-Doz. Dr. P. W. Roesky, Dr. M. R. Bürgstein, H. Berberich
Institut für Anorganische Chemie der Universität Karlsruhe
Engesserstrasse 15, 76128 Karlsruhe (Germany)
Fax: (+49) 721-661921
E-mail: roesky@achibm6.chemie.uni-karlsruhe.de

[**] Already communicated in part. See Ref. [1].

0947-6539/01/0714-3078 $ 17.50+.50/0

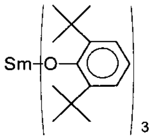
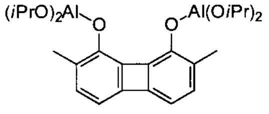
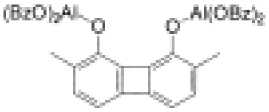
corresponding carboxylic ester [Eq. (1)], has been known for about a century.[26]



(1)

Its industrial importance is reflected in the great number of patents. Thus, the Tishchenko ester of 3-cyclohexenecarbaldehyde is the precursor for the formation of epoxy resins, which are durable against environmental influences. Benzylbenzoate is used as a dye carrier. Other uses include solvents for cellulose derivatives, plasticizers, and the food industry.[27] Traditionally, aluminum alkoxides[28, 29, 30] have been used as homogeneous catalysts for the Tishchenko reaction. More recently, other catalysts, such as boric acid[31] and a few transition metal complexes, have been used. However, these alternative catalysts are either only reactive under extreme reaction conditions (e.g., boric acid), are difficult to prepare (e.g., [$(C_5Me_5)_2LaCH(SiMe_3)_2$]),[32] slow (e.g., [$(C_5H_5)_2ZrH_2$]),[33] expensive (e.g., [$H_2Ru(PPh_3)_2$]),[34] or give small yields (e.g., $K_2[Fe(CO)_4]$).[35] In this contribution, we present a full account of the reaction scope, substrate selectivity, lanthanide-ion size-effect, and kinetic/mechanistic aspects of the Tishchenko reaction catalyzed by **1**. Furthermore, we report that **1** can be used to a limited extent as a precatalyst for the hydroamination/cyclization of aminoalkynes.

Table 1. Tishchenko reaction of benzaldehyde to benzyl benzoate with different catalysts.

Entry	Catalyst	N_t[$^{-1}$]	Yield[%]	T[°C]	Ref.
1	**1a**	63	70	21[a]	
2	**1b**	87	98	21[a]	
3	**1c**	80	98	21[a]	
4	[$(C_5Me_5)_2LaCH(SiMe_3)_2$]		88	RT	[32]
5	SmI_2	–	no reaction	21[a]	
6	$La(OiPr)_3$	–	no reaction	21[a]	[32]
7		1.9	70	21[a]	
8	$Al(OiPr)_3$	8	51	21[a]	
9			67	21[a]	[40]
10			76	21[a]	[40]
11	[$(C_5H_5)_2ZrH_2$]		7	17	[33]
12	[$(C_5H_5)_2HfH_2$]		9	17	[33]
13	[$H_2Ru(PPh_3)_2$]		23	20	[34]
14	$K_2[Fe(CO)_4]$		71	60	[35]
15	$B(OH)_3$		34	250	[31]

[a] Reaction conditions (this work): 1 mol% catalyst in C_6D_6.

Results and Discussion

The goal of this study was to explore the scope of **1** for its use in two areas of lanthanide-catalyzed reactions: C–C multiple bond transformations and organic reactions catalyzed by Lewis acids. This section begins with the discussion of the Tishchenko reaction, for which **1** is a very active catalyst, followed by a short examination of **1** as a precatalyst for the hydroamination/cyclization of aminoalkynes. In the case of the latter reaction, **1** is less effective than the known systems.

The Tishchenko reaction: To compare the reaction rates of **1** with other catalysts, the standard reaction of benzaldehyde to benzyl benzoate was chosen. Benzyl benzoate is used, among others, as solvent for artificial musk, as a perfume fixative, in confectionery, and in chewing-gum flavors. For these uses, it is necessary to prepare the benzoate without any contamination by irritants and or odoriferous materials, such as benzyl chlorides or acids.[27, 35] The reaction rate and the yield were determined by NMR spectroscopy in C_6D_6 with ≈1 mol% catalyst at 21 °C (Table 1). The turnover frequencies (TOFs) were determined from a turnover of 50%.[36] The kinetic data obtained in this study were acquired by ^1H NMR spectroscopic monitoring of the reactions. The decrease of the characteristic aldehyde proton signal, concomitant with the increase in the proton signal of the benzyl group, was normalized to the proton resonances of the stoichiometrically generated $R{-}N(SiMe_3)_2$ reaction byproducts. Tetramethylbenzene was used as an independent standard in a test reaction to show that $R{-}N(SiMe_3)_2$ is formed in a stoichiometric ratio. A comparison of [$Y\{N(SiMe_3)_2\}_3$] (**1a**), [$La\{N(SiMe_3)_2\}_3$] (**1b**), and [$Sm\{N(SiMe_3)_2\}_3$] (**1c**) (entries 1–3) shows that, for an almost quantitative turnover, **1b** has a higher activity than the corresponding Sm catalyst **1c**, whereas the Y catalyst **1a** produces smaller yields and is less active. The dependence of the TOF on the ionic radius of the central metal atom has already been observed.[32] A comparison with other readily accessible lanthanide compounds, such as SmI_2[37] or [$La(OiPr)_3$][32] (entries 5 and 6), which are used as Tishchenko catalysts, showed that these are inactive for the case of benzaldehyde. In contrast, the homoleptic alkoxide [$Sm\{O\text{-}2,6\text{-}(tBu)_2\text{-}C_6H_3\}_3$], which was recently introduced as a catalyst, shows some activity (entry 7).[38] However, the TOFs and the yields are significantly lower than those observed for **1b** and **1c**. From the reaction with the standard aluminum catalyst $Al(OiPr)_3$[29, 30] under the reaction conditions described above, the yield was not quantitative. The reaction rate observed with $Al(OiPr)_3$, which agrees with earlier measured values,[29, 39] is roughly an order of magnitude smaller than that observed with **1b** (entry 8). Even the recently reported high-speed Tishchenko catalyst, (2,7-dimethyl-1,8-biphenylenedioxy)bis(diisopropoxyaluminum) (entry 9) and (2,7-dimethyl-1,8-biphenylenedioxy)bis(dibenzoyloxyaluminum) (entry 10), do not reach the activity of **1b**.[40] Although we do not know of a more active catalyst for the Tishchenko reaction, two compounds are described in the literature ([$(C_5Me_5)_2LaCH(SiMe_3)_2$] (entry 4),[32] and [$Al(OCH_2Ph)_3$]) that could compete with **1b**. [$(C_5Me_5)_2LaCH(SiMe_3)_2$] would probably form the same catalytically active species as **1b** (see below); however, it is evidently more difficult to prepare. [Al(OCH$_2$Ph)$_3$] reaches almost the same TOF as **1b**, but is exclusively optimized for the dimerization of benzaldehyde[39] (Table 1).

The absence of a useful transition metal catalyst for the Tishchenko reaction is demonstrated by a comparison of **1b** and K$_2$[Fe(CO)$_4$], which in the presence of crown ethers is one of the fastest known transition metal catalysts. The yields and activities were compared for two selected substrates (Table 2). With **1b**, benzaldehyde is dimerized in almost quantitative yields, whereas the iron(II) catalyst gives only 46 % conversion (entries 1 and 2). Furthermore, the suitability of **1b** for the dimerization of furfural should be emphasized, because when this reaction is carried out with aluminum alkoxide catalysts or K$_2$[Fe(CO)$_4$]/crown ether catalysts, very low yields are observed.[29, 35, 41] Thus, only 3.4 % yield was obtained by the use of the transition metal catalyst (entry 3), which is in contrast to 40 % conversion for the lanthanide-catalyzed reaction (entry 4).

To investigate the tolerance of **1b** for functional groups, various substituted benzaldehydes were used as substrates (Table 3). To avoid a significant steric influence of the functional group, only *para*-substituted benzaldehydes were used. The reactions were carried out at 21 °C in C$_6$D$_6$, with $\approx$5 mol % of catalyst in order to determine the TOF. All the reactions were repeated on a preparative scale (5 g reactant) without solvent or in hydrocarbons in order to determine the isolated yields. The products were characterized by elemental analysis as well as by ^{1}H and ^{13}C NMR spectroscopy. The workup of the reaction was very simple: in the case of the solvent-free reaction, the product can usually be easily transferred by vacuum. In the case of the reaction with *o*-phthalaldehyde, the ester precipitates cleanly out of the solution (entry 9).

Most of the *para*-substituted benzaldehydes are converted to the corresponding carboxylic esters in quantitative or almost quantitative yields. The only exception is 4-(dimethylamino)benzaldehyde. Thus can it be shown, that a large number of functional groups are tolerated by **1b**. These results are remarkable, since functional groups often show the tendency to block lanthanide catalysts. As seen by the TOFs, the Tishchenko process is faster when the aromatic ring has an electron-withdrawing group. A slight exception are 4-fluoro- and 4-chlorobenzaldehyde (entries 1 and 2), which are a bit slower than one would expect from the electronic influence of the substituents. A similar dependence has been observed with other catalysts, such as K$_2$[Fe(CO)$_4$]/crown ether[35] and KO$_2$/crown ether.[42] Therefore, substrates that contain electron-releasing groups on the aromatic ring have significantly lower TOFs. The lowest TOFs were observed if the substrate has an electron-releasing group with a donor atom, such as nitrogen, oxygen, or sulfur (entries 6–8). These atoms form hemilabile Lewis acid/base adducts with the catalyst and thus

Table 2. A Comparison of **1b** and K$_2$[Fe(CO)$_4$]/crown ether[35] as catalysts for the Tishchenko reaction.

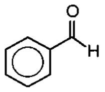
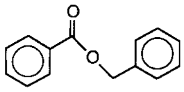
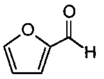
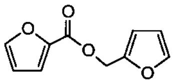
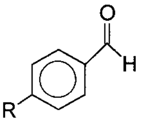
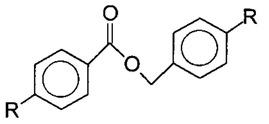
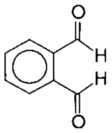
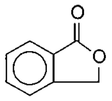
Entry	Substrate	Product	Catalyst	Mol % of catalyst	N_t [h^{-1}]	Yield [%]	T [°C]
1			**1b**	1	87	98	21
2			K$_2$[Fe(CO)$_4$]/crown ether	20	$\ll$1	46	20
3			**1b**	1	2	40	21
4			K$_2$[Fe(CO)$_4$]/crown ether	33	$\ll$1	3.4	33

Table 3. Results for the **1b**-catalyzed dimerization of aromatic aldehydes.[a]

Entry	Substrate	Product	N_t [h^{-1}]	Yield NMR-scale[b, c] [%]	Isolated yield[b,d] [%]
					
1	R =	F	44	87	66
2		Cl	38	98	47
3		Br	106	quant.	71
4		CN	94	quant.	80
5		CH$_3$	11	quant.	78
6		SCH$_3$	2	97	84
7		OCH$_3$	2.1	quant.	86
8		N(CH$_3$)$_2$	–	26	35
9			> 1500	90[e]	85[e, f]

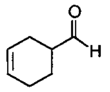
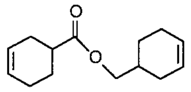
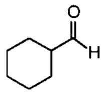
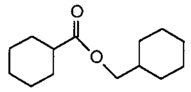
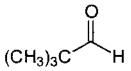
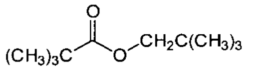
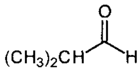
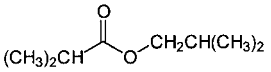
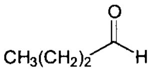
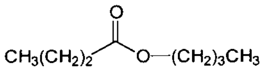
[a] Reaction temperature: 21 °C. [b] 5 mol % catalyst. [c] Solvent C$_6$D$_6$. [d] No solvent, 5 g reactant. [e] 1 mol % catalyst. [f] 50 mL pentane/hexane.

0947-6539/01/0714-3080 $ 17.50+.50/0

hamper the Tishchenko process. This effect is best seen in the case of 4-(dimethylamino)benzaldehyde (entry 8). Not surprisingly, the intramolecular Tishchenko reaction of *o*-phthalaldehyde to the corresponding lactone gives high yields and is very fast (TOF > 1500 h^{-1}) (entry 9).

In addition to aromatic aldehydes as substrates for the Tishchenko reaction, we also investigated the use of aliphatic aldehydes (Table 4). We were interested in cyclic and noncyclic reactants. Again, the reactions were carried out at 21 °C in C_6D_6 with ≈1 mol% of catalyst in the first step in order to determine the TOF. Subsequently, all the reactions were repeated on a preparative scale (5 g reactant) without solvent. The extremely high TOFs for all substrates should be noted. The reactions are usually so rapid, that the product can be only detected in NMR-scale reactions. Thus, on the NMR timescale, quantitative yields were observed for all substrates. Moreover, the catalyst in the reaction solution is still active after several days so that a reaction which has been completed for some time can be restarted by the addition of new reactant. Although **1b** catalyzes the dimerization of aldehydes, with or without one α-H atom, quickly and in high yields, the reaction of butanal at 21 °C only gives higher coupling products (entry 5).[30, 43, 44] If the reaction is started at −78 °C, then butyl butyrate and 2-ethyl-1,3-hexanediol monobutyrate are produced as dimeric and trimeric products in almost the same ratio.[44] The trimeric product is formed by a tandem aldol-Tishchenko reaction.[45]

Table 4. Results for the **1b**-catalyzed dimerization of aliphatic aldehydes.

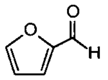
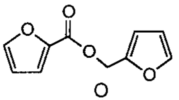
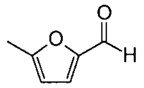
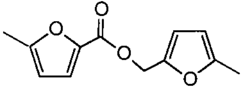
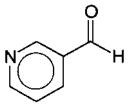
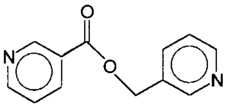
Entry	Substrate	Product	N_t [h^{-1}]	Yield NMR-scale[a] [%]	Isolated yield[b] [%]
1			> 1500	quant.	75
2			> 1500	quant.	80
3			> 1500	quant.	80
4			> 1500	quant.	84
5			–	50[c]	45[c]

[a] Reaction conditions: 21 °C; 1 mol% catalyst in C_6D_6. [b] Reaction conditions: 21 °C; 1 mol% catalyst, no solvent, 5 g reactant. [c] Reaction temperature: −78 °C → RT; the trimer 2-ethyl-1,3-hexanediol monobutyrate was found as a byproduct.

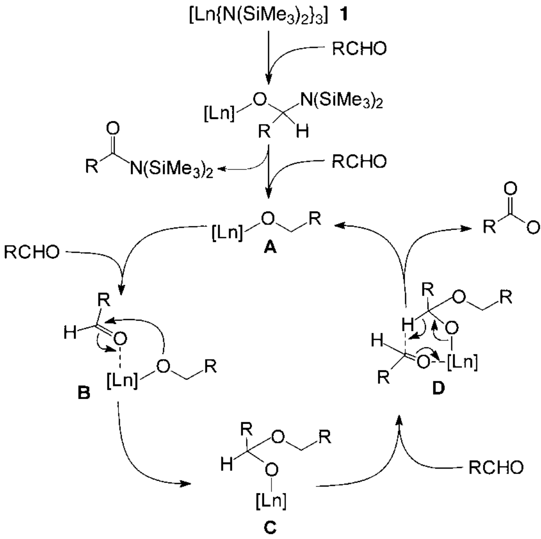
We were also interested in the reactivity of heterocyclic substrates in the Tishchenko reaction catalyzed by **1b**. For this, we choose a few heterocyclic aldehydes (that contain oxygen and nitrogen as substrates, Table 5). Compared to all other substrates, furfural and methylfurfural react very slowly and the turnovers are low (entries 1 and 2). Furthermore, methylfurfural does not give a clean conversion and no clean product could be isolated. The rate for furfural is more than an order of magnitude lower than that with benzaldehyde. Nevertheless, in comparison to aluminum alkoxide or $K_2[Fe(CO)_4]$/crown ether catalysts, much higher turnovers are obtained by the use of **1b** as the catalyst (see above; Table 2). The low turnovers for furfural and methylfurfural compared with benzaldehyde and even pyridine-3-carbaldehyde can be explained by the nature of the substrate. Upon reaction, furfural and methylfurfural can coordinate in a chelating fashion through the carboxylic group and the ether oxygen atom. Thus, a five-membered metallacycle is formed that partly blocks the catalyst.

Kinetics and reaction mechanism of the Tishchenko reaction: In order to elucidate a provisional reaction mechanism, the dimerization of benzaldehyde was studied in more detail. ^1H NMR spectroscopy and GC/MS studies show that, at the beginning of the reaction, bis(trimethylsilyl)amine and benzylic acid bis(trimethylsilyl)amide are cleaved off from **1** to give a lanthanide alkoxide **A** that is, most probably, the catalytically active species (Scheme 1). Investigations of the paramagnetic compound **1c** on catalytic and stoichiometric scales show that all three amide groups are cleaved without a significant induction time. Signals appear in the ^1H NMR spectra that may be attributed to $SmOCH_2$ groups. It can be assumed that the catalytically active species is either the same or very similar to the compound that is formed

Table 5. Results for the **1b**-catalyzed dimerization of heterocyclic aldehydes.

Entry	Substrate	Product	N_t [h^{-1}]	Yield NMR-scale[a] [%]	Isolated yield[b] [%]
1			2	40[b]	36[b]
2			–	28[c,d]	–
3			–	68[c]	37[c]

[a] 21 °C; 1 mol% catalyst in C_6D_6. [b] 21 °C; 1 mol% catalyst, no solvent, 5 g reactant. [c] 5 mol% catalyst. [d] Unknown sideproduct.



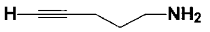
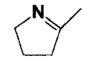
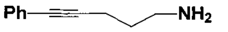
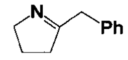
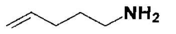
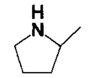
Scheme 1. Proposed mechanism for the catalysis of the Tishchenko reaction by **1**.

in the Tishchenko reaction with $[(C_5Me_5)_2LaCH(SiMe_3)_2]$.[32] This hypothesis is supported by the following observations: i) with **1b** similar yields are obtained as for $[(C_5Me_5)_2LaCH(SiMe_3)_2]$, and ii) during the reaction, both catalysts can completely interchange the whole of their original ligand shells. ^{1}H NMR spectroscopic investigations of the reaction of **1c** with stoichiometric amounts of benzyl alcohol or benzaldehyde show that different compounds are formed. Kinetic investigations indicate that 1/[reactant] is related linearly to the reaction time; that is, there is a second-order reaction with respect to the reactant. Such reaction kinetics have already been established for the aluminum-catalyzed reaction for the dimerization of benzaldehyde[39] and the aldol-Tishchenko reaction catalyzed by the lithium enolate of *p*-(phenyl-sulfonyl)isobutyrophenone.[45a] Presumably, a molecule of the reactant coordinates to **A** (→**B**), which in turn undergoes an alkoxide transfer (→**C**; Scheme 1). A second molecule of the reactant attaches itself to **C** followed by a hydride transfer, which is probably the rate-determining step (→**D**).[39]

Hydroamination/cyclization of aminoalkynes: Organolanthanide complexes exhibit unique reactivity characteristics for the activation of unsaturated organic substrates. This is a result of the high electrophilicity of f-element centers, relatively large ionic radii, an absence of conventional oxidative-addition/reductive-elimination mechanistic pathways, and high kinetic lability.[46] In order to understand the catalytic activity of **1** compared with the well-established metallocenes, such as $[(C_5Me_5)_2LnR]$ ($R = N(SiMe_3)_2$, $CH(SiMe_3)_2$), in C–C multiple-bond transformations, the catalytic hydroamination/cyclization[5, 46] of aminoolefins and aminoalkynes was investigated. The rigorously anaerobic reaction of the catalysts with dry, degassed aminoolefin and aminoalkynes (3–5 mol% catalyst) proceeds regiospecifically in toluene as shown in Table 6. The TOFs obtained in this study were acquired by ^{1}H NMR monitoring of the reactions. The decrease of the substrate proton signal concomitant with the increase of product proton signal was normalized to the proton resonances of the stoichiometrically generated $NH(SiMe_3)_2$ reaction byproducts.

The catalytic activity of **1a** and **1b** for the catalytic hydroamination/cyclization of aminoalkynes at 60 °C is lower than that of the established metallocene $[(C_5Me_5)_2YCH(SiMe_3)_2]$ (**2**) (entries 1–6) at 21 °C. Since it was shown previously that the hydroamination of aminoalkynes is faster than that of aminoolefins,[5] it might be expected that no conversion is observed for aminoolefins with **1a** and **1b** as catalysts (entries 8 and 9). The low TOFs and yields of **1a** and **1b** relative to **2** can be explained by the absence of any ancillary ligands in the homoleptic amines. As seen in the ^{1}H NMR spectra of catalytic reactions, all $N(SiMe_3)_2$ groups are cleaved off from the central metal because of the large excess of substrate. Thus, for each substrate a very different ligand environment is generated on the metal center. This might be an explanation for the differences in the observed rates.

Table 6. Catalytic hydroamination/cyclization results.[a]

Entry	Substrate	Product	Catalyst	N_t [h^{-1}]	Yield NMR-scale[a] [%]
1			**2**[b]	3.3	quant.
2			**1a**	0.3	71
3			**1b**	–	–
4			**2**[b]	8.6	quant.
5			**1a**	0.1	75
6			**1b**	0.09	quant.
7			**2**[b]	0.5	quant.
8			**1a**	–	–
9			**1b**	–	–

[a] 60 °C; 3–5 mol% catalyst in [D$_8$]toluene. [b] 21 °C.

Even **1** is less active for the hydroamination/cyclization of aminoalkynes then the metallocenes, the persuasive argument for **1** is its ready accessibility. For the metallocenes, even access to C_5Me_5H is laborious or expensive. In contrast, **1** can either be prepared from a simple one-step synthesis or it can be bought (Ln = Y). In certain cases it might be advantageous to spend more time on the catalytic experiments by the use of a commercially available catalyst instead of spending time and money on the synthesis of the catalyst.

Conclusion

In summary, it should be emphasized that the bis(trimethylsilyl)amide compounds of the lanthanides represent a new class of Tishchenko catalysts and, to a limited extent, precatalysts for the hydroamination/cyclization of aminoalkynes. The catalytic activity is a result of the high Lewis acidity and the facile interchangeability of the ligand sphere. These compounds are distinguished by a number of practical advantages, such as the ease of accessibility, inexpensive metals, extremely high activities for the Tishchenko reaction (to our knowledge there are no catalysts that are more active), and a high durability of the catalysts. These advantages lead us to hope that **1**, which is already a standard reagent in organolanthanide chemistry, will find further application in catalysis.

Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware either on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled Braun glove box (Uni-Lab 1200/780). Hydrocarbon solvents were distilled under nitrogen from Na wire, prior to use. Deuterated solvents were obtained from Aldrich (all 99 atom% D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on Bruker AC250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry in Karlsruhe (Germany). All aldehydes were obtained from Aldrich and were degassed, dried over $LiAlH_4$, and stored under nitrogen in resealable flasks. 5-Phenyl-4-pentyne-1-amine,[5d] 4-pentyne-1-amine,[5d] and 4-pentene-1-amine[5b] were prepared by literature procedures.

General procedure for the Tishchenko reaction (NMR scale): Compound **1** was weighed under argon into an NMR tube. C_6D_6 ($\approx$0.7 mL) was condensed into the tube and the mixture was frozen to -196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant (product) and the catalyst was exactly calculated by comparison of the integration of all CHO (CH_2O) signals with the $N(SiMe_3)_2$ signals. The latter were used as an internal standard for the kinetic measurements. Tetramethylbenzene was used as an independent standard in a test reaction to show that $R{-}N(SiMe_3)_2$ is formed in a stoichiometric ratio.

General procedure for the Tishchenko reaction (preparative scale)

Method A, without solvent: Under protective gas, the catalyst was stirred in a tempered reaction flask. The reactant (5 g) was added directly to the catalyst. An exothermic reaction was generally observed. After 1 d, the product was isolated by distillation. (The products with high TOFs can be worked up after 1 h (see Tables 3 and 4)).

Method B, in solution: The catalyst and the reactant (5 g) were each dissolved in pentane/hexane (1:1; 25 mL). The solution of the reactant was added to the catalyst solution in a tempered flask. After 1 d, the product was isolated by distillation or filtration.

Benzyl benzoate:[33] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 5.21$ (s, 2H; CH_2O), 6.98–7.27 (m, 7H; aromatic), 7.67–7.71 (m, 1H; aromatic), 8.13–8.18 (m, 2H; aromatic); elemental analysis calcd (%) for $C_{14}H_{12}O_2$: C 79.23, H 5.70; found C 78.93, H 5.72.

4-Fluorobenzyl 4-fluorobenzoate:[32] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta =$ 4.95 (s, 2H; CH_2O), 6.57–7.08 (m, 4H; aromatic), 7.49 (m, 2H; aromatic), 7.85 (m, 2H; aromatic); elemental analysis calcd (%) for $C_{14}H_{10}F_2O_2$: C 67.74, H 4.06; found C 67.52, H 3.98.

4-Chlorobenzyl 4-chlorobenzoate:[32] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 4.89$ (s, 2H; CH_2O), 6.81–7.14 (m, 4H; aromatic), 7.39 (d, J(H,H) = 8.6 Hz, 2H; aromatic), 7.76 (d, J(H,H) = 8.6 Hz, 2H; aromatic); elemental analysis calcd (%) for $C_{14}H_{10}Cl_2O_2$: C 59.81, H 3.59; found C 58.10, H 3.25.

4-Bromobenzyl 4-bromobenzoate:[32] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 4.84$ (s, 2H; CH_2O), 6.74 (d, J(H,H) = 8.5 Hz, 2H; aromatic), 7.15 (d, J(H,H) = 6.5 Hz, 2H; aromatic), 7.31 (d, J(H,H) = 6.6 Hz, 2H; aromatic), 7.67 (d, J(H,H) = 8.7 Hz, 2H; aromatic); elemental analysis calcd (%) for $C_{14}H_{10}Br_2O_2$: C 45.44, H 2.72; found C 45.01, H 2.90.

4-Cyanobenzyl 4-cyanobenzoate:[32] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta =$ 4.80 (s, 2H; CH_2O), 6.75 (m, J(H,H) = 8.1 Hz, 2H; aromatic), 6.96 (m, 2H; aromatic) 7.23 (d, J(H,H) = 8.4 Hz, 2H; aromatic), 7.67 (d, J(H,H) = 8.6 Hz, 2H; aromatic); elemental analysis calcd (%) for $C_{16}H_{10}N_2O_2$: C 73.27, H 3.84; found C 72.71, H 3.82.

4-Methylbenzyl 4-methylbenzoate:[32] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 1.96$ (s, 3H; CH_3), 2.07 (s, 3H; CH_3), 5.22 (s, 2H; CH_2O), 6.72 (m, J(H,H) = 8.6 Hz, 2H; aromatic), 6.84–6.95 (m, 4H; aromatic), 7.17 (m, 2H; aromatic), 7.54 (d, J(H,H) = 8.8 Hz, 2H; aromatic), 8.11 (d, J(H,H) = 6.5 Hz, 2H; aromatic); elemental analysis calcd (%) for $C_{16}H_{16}O_2$: C 79.97, H 6.71; found C 79.28, H 6.76.

4-Methylthiobenzyl 4-methylthiobenzoate:[32] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 1.88$ (s, 3H; SCH_3), 1.94 (s, 3H; SCH_3), 5.12 (s, 2H; CH_2O), 7.59 (m, 4H; aromatic), 8.00 (m, 4H; aromatic); elemental analysis calcd (%) for $C_{16}H_{16}S_2O_2$: C 63.13, H 5.30; found C 62.78, H 5.61.

4-Methoxybenzyl 4-methoxybenzoate:[33] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 3.14$ (s, 3H; OCH_3), 3.26 (s, 3H; OCH_3), 5.20 (s, 2H; CH_2O), 6.72 (m, J(H,H) = 8.7 Hz, 2H; aromatic), 7.21 (d, J(H,H) = 8.7 Hz, 2H; aromatic), 7.54 (d, J(H,H) = 8.8 Hz, 2H; aromatic), 8.10 (d, J(H,H) = 8.9 Hz, 2H; aromatic); elemental analysis calcd (%) for $C_{16}H_{16}O_4$: C 70.57, H 5.92; found C 70.01, H 5.70.

4-Dimethylamino 4-dimethylaminobenzoate:[47] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 2.42$ (s, 6H; $(CH_3)_2N$), 2.53 (s, 6H; $(CH_3)_2N$), 4.64 (s, 2H; CH_2O), 6.72 (d, J(H,H) = 8.7 Hz, 2H; aromatic), 7.67–7.71 (m, 1H; aromatic), 8.13–8.18 (m, 2H; aromatic); elemental analysis calcd (%) for $C_{18}H_{22}N_2O_2$: C 72.46, H 7.43, N 9.39; found C 72.70, H 7.85, N 9.30.

Phthalide:[48] ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 5.21$ (s, 2H; CH_2O), 6.51 (d, J(H,H) = 0.8 Hz, 1H; aromatic), 6.83–6.98 (m, 8H; aromatic), 7.68 (d, J(H,H) = 7.4 Hz, 1H; aromatic); elemental analysis calcd (%) for $C_8H_6O_2$: C 71.64, H 4.51; found C 69.35, H 4.59.

Cyclohexylmethyl cyclohexanecarboxylate:[33] ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 0.87$–1.01 (m, 2H), 1.06–1.30 (m, 6H), 1.35–1.54 (m, 2H), 1.55–1.74 (m, 9H), 1,86–1.91 (m, 2H), 2.22–2.33, (m, 1H), 3.85 (d, J(H,H) = 6.4 Hz, 2H; CH_2O), 5.62–6.67 (m, 4H); elemental analysis calcd (%) for $C_{14}H_{24}O_2$: C 74.95, H 10.78; found C 74.37, H 10.50.

3-Cyclohexenylmethyl 3-cyclohexenecarboxylate: ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 1.23$–1.39 (m, 1H), 1.60–2.21 (m, 10H), 2.22–2.26 (m, 2H), 2.50–2.62 (m, 1H), 3.98 (d, J(H,H) = 6.4 Hz, 2H; CH_2O), 5.62–6.67 (m, 4H); elemental analysis calcd (%) for $C_{14}H_{20}O_2$: C 76.33, H 9.15; found C 76.28, H 9.29.

Neopentyl neopentanoate:[33] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 0.80$ (s, 6H; $(CH_3)_3C$), 1.16 (s, 9H; $(CH_3)_3C$), 3.74 (s, 2H; CH_2O); elemental analysis calcd (%) for $C_{14}H_{20}O_2$: C 69.72, H 11.70; found C 68.95, H 11.50.

Isobutyl isobutanoate:[33] ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 0.75$ (d, J(H,H) = 6.7 Hz, 6H; $(CH_3)_2CH$), 1.07 (d, J(H,H) = 7.0 Hz, 6H; $(CH_3)_2CH$), 1.73 (sept, J(H,H) = 6.8 Hz, 1H; $(CH_3)_2CH$), 2.38 (sept, J(H,H) = 6.9 Hz, 1H; $(CH_3)_2CH$), 3.80 (d, J(H,H) = 6.5 Hz, 2H; CH_2O); elemental analysis calcd (%) for $C_8H_{16}O_2$: C 66.63, H 11.18; found C 66.53, H 10.97.

2-Ethyl-1,3-hexanediol monobutyrate:[44] B.p. 81 °C (0.1 mm); ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 0.94$ (m, 8H) 1.26 1–71 (m, 8H), 2.31 (dt, 4H), 3.60 (br, 2H) 4.40–4.30 (m, 2H).

2-Furylmethyl 2-furancarboxylate:[49] ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 5.29$, (s, 2H; CH_2O), 6.38 (dd, J(H,H) = 1.8, 3.3 Hz, 1H), 6.49 (dd, J(H,H) = 1.9, 3.4 Hz, 2H), 7.20 (dd, J(H,H) = 0.7, 3.5 Hz, 1H), 7.44 (dd, J(H,H) = 0.7, 1.8 Hz, 1H), 7.57 (dd, J(H,H) = 0.7, 1.6 Hz, 1H); elemental analysis calcd (%) for $C_{10}H_8O_4$: C 62.50, H 4.20; found C 62.35, H 4.34.

4-Methyl-2-furylmethyl 4-methyl-2-furancarboxylate: ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 1.80$ (s, 3H; CH_3), 1.91 (s, 3H; CH_3), 5.11, (s, 2H; CH_2O), 5.59 (m, 1H), 5.65 (m, 1H), 6.17 (m, 1H), 6.95 (m, 1H); no pure product was obtained.

3-Pyridinecarboxylic acid 3-pyridinylmethyl ester: ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 4.90$ (s, 2H; CH_2O), 6.73 (m, 2H; aromatic), 7.65 (m, 1H), 7.94 (m, 2H; aromatic), 8.52 (m, 2H; aromatic), 9.12 (s, 1H; aromatic); elemental analysis calcd (%) for $C_{12}H_{10}N_2O_2$: C 67.28, H 4.71, N 13.08; found C 67.53, H 4.75, N 12.89.

General procedure for the hydroamination reaction (NMR scale): Compound **1** was weighed under argon into an NMR tube. C_6D_6 (≈ 0.7 mL) was condensed into the tube, and the mixture was frozen to -196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant (product) and the catalyst was exactly calculated by comparison of the integration of alkyne signals with the $N(SiMe_3)_2$ signals. The latter were used as an internal standard for the TOFs measurements. The turnover frequency was calculated according to Ref. [5d]

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Heisenberg fellowship for P.W.R.), the Karl-Winnacker-Stiftung, and the Fonds der Chemischen Industrie. Additionally, generous support from Prof. Dr. D. Fenske is gratefully acknowledged.

[1] Communication in part: M. R. Bürgstein, P. W. Roesky, *Abstract of Papers*, 219th National Meeting of the American Chemical Society, San Francisco, CA, **2000**, INORG 233.

[2] Review: a) F. T. Edelmann, in *Comprehensive Organometallic Chemisty II*, *Vol. 4*, (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 11–210; b) F. T. Edelmann, *Top. Curr. Chem.* **1996**, *179*, 247–276.

[3] a) W. J. Evans, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403; b) G. Jeske, H. Lauke, H. Mauermann, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118; c) V. P. Conticello, L. Brard, M. A. Giardello, Y. Tsuji, M. Sabat, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 2761–2762; d) P. W. Roesky, U. Denninger, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 4486–4492.

[4] a) P. L. Watson, *J. Am. Chem. Soc.* **1982**, *104*, 337–339; b) P. L. Watson, G. W. Parshall, *Acc. Chem. Res.* **1995**, *18*, 51–56; c) E. E. Bunel, B. J. Burger, J. E. Bercaw, *J. Am. Chem. Soc.* **1988**, *110*, 976–981; d) E. B. Coughlin, J. E. Bercaw, *J. Am. Chem. Soc.* **1992**, *114*, 7607–7608; e) P. J. Shapiro, E. E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867–876; f) M. A. Giardello, Y. Yamamoto, L. Brard, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 3276–3277.

[5] a) M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109; b) M. R. Gagné, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 275–294; c) Y Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 707–708; d) Y. Li, T. J. Marks, *J. Am. Chem. Soc*. **1996**, *118*, 9295–9306; e) P. W. Roesky, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 4705–4711; f) Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1757–1771; g) V. M. Arredondo, F. E. McDonald, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 4871–4872.

[6] a) S. P. Nolan, M. Porchia, T. J. Marks, *Organometallics* **1991**, *10*, 1450–1457; b) T. Sakakura, H.-J. Lautenschläger, M. Tanaka, *J. Chem. Soc. Chem. Commun.* **1991**, 40–41; c) G. A. Molander, P. J. Nichols, *J. Am. Chem. Soc.* **1995**, *117*, 4414–4416; d) G. A. Molander, W. A. Retsch, *Organometallics* **1995**, *14*, 4570–4575.

[7] a) G. Erker, R. Aul, *Chem. Ber.* **1991**, *124*, 1301–1310; b) K. N. Harrison, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 9220–9221; c) E. A. Bijpost, R. Duchateau, J. H. Teuben, *J. Mol. Catal.* **1995**, *95*, 121–128.

[8] M. R. Douglass, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 1824–1825.

[9] a) G. A. Molander, in *Comprehensive Organic Synthesis*, *Vol. 1* (Ed.: B. M. Trost, I. Fleming), Pergamon, Oxford **1991**, pp. 251–282; b) T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, London, **1994**.

[10] S. Kobayashi, I. Hachiya, *J. Org. Chem.* **1994**, *59*, 3590–3596.

[11] S. Kobayashi, I. Hachiya, M. Araki, H. Ishitani, *Tetrahedron Lett.* **1992**, *34*, 6815–6518.

[12] S. Kobayashi, I. Hachiya, Y. Yamanoi, *Bull. Chem. Soc. Jpn*. **1994**, *67*, 2342–2344.

[13] S. Kobayashi, I. Hachiya, M. Araki, H. Ishitani, *Tetrahedron Lett.* **1993**, *34*, 3755–3758; b) S. Kobayashi, H. Ishitani, *J. Am. Chem. Soc.* **1994**, *116*, 4083–4084.

[14] A. Kawada, S. Mitamura, S. Kobayashi, *Synlett* **1994**, 545–546.

[15] A. Kawada, S. Mitamura, S. Kobayashi, *J. Chem. Soc. Chem. Commun.* **1993**, 1157–1158.

[16] Review: a) S. Kobayashi, *Synlett* **1994**, 689–701; b) S. Kobayashi, in *Transition Metals for Organic Synthesis*, *Vol. 2* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, pp. 285–312; c) S. Kobayashi, *Top. Organomet. Chem.* **1999**, 63–118.

[17] a) J. L. Namy, J. Souppe, J. Collin, H. B. Kagan, *J. Org. Chem.* **1984**, *49*, 2045–2049; b) T. Okano, M. Matsuoka, H. Konishi, J. Kiji, *Chem. Lett.* **1987**, 181–184.

[18] H. Ohno, A. Mori, S. Inoue, *Chem. Lett.* **1993**, 375–378.

[19] M. P. S. Ishar, A. Wali, R. P. Ganghi, *J. Chem. Soc. Perkin. Trans. 1* **1990**, 2185–2194.

[20] S. J. Danishefsky, B. J. Uang, G. Quallich, *J. Am. Chem. Soc.* **1984**, *106*, 2453–2455.

[21] D. C. Bradley, J. S. Ghorta, F. A. Hart, *J. Chem. Soc. Dalton. Trans.* **1973**, 1021–1023.

[22] H. Berberich, P. W. Roesky, *Angew. Chem.* **1998**, *110*, 1618–1620; *Angew. Chem. Int. Ed.* **1998**, *37*, 1569–1571.

[23] a) K. C. Hultsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845–4846; b) S. Agarwal, C. Mast, S. Anfang, M. Karl, K. Dehnicke, A. Greiner, *Polym. Prepr.* **1998**, *39*, 414–415; c) S. Agarwal, M. Karl, K. Dehnicke, G. Seybert, W. Massa, A. Greiner, *J. Appl. Polym. Sci.* **1999**, *73*, 1669–1675; d) E. Martin, P. Dubois, R. Jerome, *Macromolecules* **2000**, *33*, 1530–1535.

[24] C. Boisson, F. Barbotin, R. Spitz, *Macromol. Chem. Phys.* **1999**, *200*, 1163–1166.

[25] Review: R. Anwander, *Top. Curr. Chem.* **1996**, *179*, 33–112.

[26] a) L. Claisen, *Chem. Ber.* **1887**, *20*, 646–650; b) W. Tishchenko, *Chem. Zentralbl.* **1906**, *77*, 1309.

[27] *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., Wiley-VCH, Weinheim, **1999**.

[28] a) E. G. E. Hawkins, D. J. G. Long, F. W. Major, *J. Chem. Soc.* **1955**, 1462–1468 and quoted patents; b) F. R. Frostick, B. Phillips, (Union Carbide &Carbon Corp.), US 2716123, **1953** [*Chem. Abstr.* **1953**, *50*, 7852f].

[29] W. C. Child, H. Adkins, *J. Am. Chem. Soc.* **1923**, *47*, 789–807.

[30] a) F. J. Villani, F. F. Nord, *J. Am. Chem. Soc.* **1947**, *69*, 2605–2607; b) L. Lin, A. R. Day, *J. Am. Chem. Soc.* **1952**, 74, 5133–5135.

[31] P. R. Stapp, *J. Org. Chem.* **1973**, *38*, 1433–1434.

[32] S. Onozawa, T. Sakakura, M. Tanaka, M. Shiro, *Tetrahedron* **1996**, *52*, 4291–4302.

[33] K.-I. Morita, Y. Nishiyama, Y. Ishii, *Organometallics* **1993**, *12*, 3748–3752.

[34] T. Ito, H. Horino, Y. Koshiro, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504–512.

[35] M. Yamashita, T. Ohishi, *Appl. Organomet. Chem.* **1993**, *7*, 357–361.

[36] For the definition of TOF see: J. Takehara, S. Hashiguchi, A. Fujii, S. Inoue, T. Ikariya, R. Noyori, *Chem. Commun.* **1996**, 233–234.

[37] D. A. Evans, A. H. Hoveyda, *J. Am. Chem. Soc.* **1990**, *112*, 6447–6449.

[38] M. Nishiura, M. Kameoka, T. Imamoto, *Kidorui* **2000**, *36*, 294–295.

[39] Y. Ogata, A. Kawasaki, *Tetrahedron* **1969**, *25*, 929–935.

[40] T. Ooi, T. Miura, K. Takaya, K. Maruoka, *Tetrahedron Lett*. **1999**, *40*, 7695–7698.

[41] M. Yamashita, Y. Watanabe, T.-A. Mitsudo, Y. Takegami, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3597–3600.

[42] F. Le Bideau, T. Coradin, D. Gourier, J. Hénique, E. Samuel, *Tetrahedron Lett.* **2000**, *41*, 5215–5218.

[43] G. Fouquet, F. Merger, R. Platz, *Liebigs Ann. Chem.* **1979**, 1591–1601.

[44] G. M. Villacorta, J. San Fillipo, Jr., *J. Org. Chem.* **1983**, *48*, 1151–1154.

[45] For examples of tandem aldol-Tishchenko reactions, see: a) L. Lu, H.-Y. Chang, J.-M. Fang, *J. Org. Chem.* **1999**, *64*, 843–853; b) P. M. Bodnar, J. T. Shaw, K. A. Woerpel, *J. Org. Chem.* **1997**, *62*, 5674–5675;

c) R. Mahrwald, G. Costisella, *Synthesis* **1996**, 1087 – 1089; d) F. R. Burkhardt, R. G. Bergman, C. H. Heathcock, *Organometallics* **1990**, *9*, 30 – 44.

[46] V. M. Arredondo, F. E. McDonald, T. J. Marks, *Organometallics* **1999**, *18*, 1949 – 1960.

[47] M. A. Pasha, B. Ravindranath, *Ind. J. Chem. Sect. B* **1985**, *24*, 1068 – 1069.

[48] M. Mori, K. Chiba, N. Inotsume, Y. Ban, *Heterocycles* **1979**, *12*, 921 – 924.

[49] V. G. Vladimir, A. Howard, *J. Org. Chem*. **1991**, *56*, 5159 – 5161.

Received: February 7, 2001 [F3059]