Methoxycarbonylation

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Aluminum Triflate as a Highly Active and Efficient Nonprotic Cocatalyst in the Palladium-Catalyzed Methoxycarbonylation Reaction**

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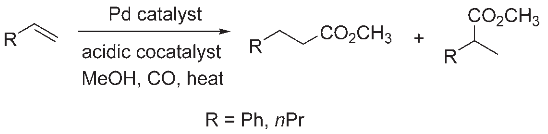
Carboxylic acids and their derivatives, such as esters and anhydrides, are important intermediates and products which have pharmaceutical and agrochemical applications, amongst others.[1] There has been substantial interest in the synthesis of branched esters from vinyl aromatic compounds (for example, in the production of anti-inflammatories, such as ibuprofen[2]) and the production of commodity chemicals from other readily available olefins[3] using the catalytic methoxycarbonylation reaction, which is also known as the hydroesterification reaction. This reaction of alkenes generally requires a catalyst, such as palladium, and a Brønsted acid cocatalyst (usually *p*-toluenesulfonic acid (*p*-TsOH) or $MeSO_3H$[4]) in the presence of carbon monoxide and methanol [Eq. (1)].



(1)

A detailed study on the effect of various acids on the rate of the methoxycarbonylation reaction of ethene indicated *p*-TsOH to be the most active,[5] closely followed by triflic acid (HOTf, OTf = triflate). When propene was the alkene, the acids H_2SO_4, $HClO_4$, and HOTf all showed similar activities. Metal halides of nickel, copper, iron, or cobalt have been used as the promoter, but, although these produce reasonable selectivities, fairly high catalyst loadings (4% Pd) are required,[6] and overall catalyst activity is not as high as in the case of other promoters.[7]

Recently, salicylborates have been shown to be effective promoters in this reaction,[8] and also allow an unusually high degree of the linear product to be generated.[9] Acidic resins with SO_3H groups have also been used.[10] In all cases mentioned, the promoter is present in a substantial excess over the palladium catalyst.

We have reported the excellent Lewis acid catalyst activity of $Al(OTf)_3$ in the alcoholysis[11] and aminolysis[12] of epoxides. With this in mind, and taking note of the bimetallic systems mentioned above, the methoxycarbonylation reaction of styrene and 1-pentene was performed with $Al(OTf)_3$ as a cocatalyst in place of the more usual Brønsted acid promoters. To our knowledge, it is the first case of a strong, stable, recyclable[12] Lewis acid being used as the cocatalyst in the methoxycarbonylation reaction, and we present the observed rate enhancements over the benchmark Brønsted acids and the formation of stable catalyst systems.

Initial experiments in high-pressure Parr reactors (Table 1) were carried out with styrene (St) as the substrate and 2% palladium catalyst (PPh_3/Pd 4:1)[13] in the presence of $Al(OTf)_3$ (Pd/$Al(OTf)_3$ 1:2), and very high conversions were observed. A circa threefold rate enhancement was observed over the *p*-TsOH benchmark reaction after 15 minutes (Table 1, entry 1). As anticipated, the reactions slowed as the substrate was consumed, leading to a convergence of the rates and a less obvious rate enhancement as the reactions proceeded (Table 1, entries 1–3). Interestingly, we were able to reduce the amount of $Al(OTf)_3$ present relative to palladium to substoichiometric ratios (Pd/$Al(OTf)_3$ as low as 1:0.25; Table 1, entries 4–7) while maintaining high activity; no loss of activity was observed at a Pd/$Al(OTf)_3$ ratio of 1:0.75. By comparison, palladium/Brønsted acid ratios of 1:100 are not uncommon for these types of reaction.[8] Under the reaction conditions used, no reaction was observed at all in the absence of the promoter. Importantly, palladium black formation was not observed in any of the runs, indicating

Table 1: Palladium-catalyzed methoxycarbonylation of styrene with $Al(OTf)_3$ as promoter.

Entry	Pd/L/LA/St[a]	% Conv[b]	l/b[c]	*t* [min]
1	1:4:2:50	26 (9)[d]	1.6:1	15
2	1:4:2:50	81 (52)[d]	1.7:1	30
3	1:4:2:50	93 (81)[d]	1.5:1	45
4	1:4:1:50	95	2.4:1	60
5	1:4:0.75:50	94	2.1:1	60
6	1:4:0.5:50	81	2.0:1	60
7	1:4:0.25:50	77	2.2:1	60

[a] Reaction conditions: $Pd(OAc)_2$ (0.045 mmol), MeOH/St 36:1 (v/v, total volume 12.5 mL), 35 atm CO, 80 ± 2 °C internal temperature (118 ± 2 °C oil bath). (L = PPh_3; LA = $Al(OTf)_3$; St = styrene; 1 atm ≡ 101.325 kPa). [b] Conversion into ester products (no detectable by-product formation) determined by ^1H and ^{13}C NMR spectroscopy. [c] l/b is ratio of linear to branched isomers determined by ^1H and ^{13}C NMR spectroscopy. [d] Values in parenthesis relate to analogous reactions using the Brønsted acid *p*-TsOH.

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catalyst stability even with the very low levels of $Al(OTf)_3$. It has been postulated that Brønsted acids convert the palladium catalyst into a cationic species, the conjugate base of which acts as a noncoordinating counterion.[14] It is likely that the $Al(OTf)_3$, being a hard Lewis acid and consequently oxophilic, abstracts the acetate ion from the palladium complex, rendering that complex cationic and providing a large noncoordinating aluminate counterion $[(AcO)Al(OTf)_3]^-$. (We do not know at present whether the triflate ions are inner sphere or outer sphere on the aluminum ion. For lanthanide triflates, the triflate ions were found to be outer sphere.[15] However, it is likely that all of the triflate ions remain in the inner sphere in our system, in light of a crystal structure of a mixed aluminum–rhenium complex, generated from $Al(OTf)_3$, in which the three triflate ions remain inner sphere on the octahedral aluminum ion.)[16] The rates of the reactions slowly decreased (Table 1, entries 4–7) with decreasing amounts of cocatalyst, and we established that a Pd/Al ratio of 1:2 gave optimal catalyst stability and activity, especially at lower catalyst loadings, for a Pd/PPh_3 ratio of 1:4 and with styrene as substrate. To our knowledge, similar rates of reaction (for comparison, see percentage conversion in parentheses, Table 1, for *p*-TsOH) have not previously been observed at such low acid loadings: usually, much more acid relative to palladium is required to achieve comparable activities and catalyst stability.

To test the limits of the system, the catalyst and cocatalyst loadings were systematically reduced, as was the MeOH/styrene ratio (Table 2). The latter move was especially important at low catalyst loadings (0.08% Pd: palladium/styrene 1:1200 and lower) to prevent palladium black formation. We established that the $Pd/Al(OTf)_3$ combination provided a stable active catalyst for this reaction, affording high yields of ester product (> 93% in all cases; the remaining 7% was unreacted starting material). In all instances, no by-products were observed by NMR spectroscopy or GC-FID analysis, and only the anticipated linear and branched ester products were formed. Although there was some sensitivity in the selectivity of the reaction (ratio of linear/branched isomers) to the conditions, this proved to be minor. Catalyst loadings as low as 0.03% (palladium/styrene 1:3000) could be achieved (Table 2, entries 9–10); such reactions required a Pd/L/Al ratio of 1:8:4 to afford active catalysts that did not result in palladium black formation during the 16-hour reaction periods (palladium black was only observed for the reaction noted in Table 2, entry 9). The prolonged reaction times required for essentially quantitative conversion resulted in the formation of small amounts (< 3%) of an insoluble polymeric material in addition to the anticipated high yields of ester. The Lewis acid could be successfully recycled by simple aqueous extraction of the acid followed by removal of water and drying of the residue by heating under vacuum, and using the residue in a new reaction instead of fresh $Al(OTf)_3$. The results from a reaction using recycled $Al(OTf)_3$ (Table 2, entry 5b) was almost indistinguishable from the first cycle of the Lewis acid (Table 2, entry 5a), indicating that the promoter was recovered intact.

Table 2: Palladium-catalyzed methoxycarbonylation of styrene at low catalyst loadings with $Al(OTf)_3$ as promoter.

Entry	Pd/L/LA/St[a]	MeOH/Styrene	%Conv[b]	l/b[c]	*t* [h]
1	1:4:2:100	18	95	1.9:1	1
2	1:4:2:150	12	93	2.1:1	1
3	1:4:2:200	12	93	1.9:1	1
4	1:4:2:200	4.75	95	2.0:1	1
5a	1:4:2:400	4.75	96	2.1:1	1
5b[d]	1:4:2:400	4.75	94	2.1:1	1
6	1:4:2:600	4.75	> 98	2.2:1	2
7	1:4:2:800	4.75	93	2.8:1	2
8	1:4:2:1200	2.4	95	2.8:1	4
9	1:8:2:3000	1.5	97 + Polymer[e]	3.0:1	16
10	1:8:4:3000	1.5	> 98 + Polymer	2.7:1	16

[a] Reaction conditions: $Pd(OAc)_2$ (0.045 mmol), 35 atm CO, 80±2°C internal temperature (118±2°C oil bath), total volume 12.5 mL. ($L = PPh_3$; $LA = Al(OTf)_3$; St = styrene). [b] Conversion into ester products (no detectable by-product formation except as cited for entries 9 and 10) as determined by ^1H and ^{13}C NMR analysis. [c] l/b is ratio of linear to branched isomers determined by ^1H and ^{13}C NMR spectroscopy. [d] Lewis acid recycle reaction: aqueous extraction of $Al(OTf)_3$, removal of water (150°C, 0.1 mm Hg), residue added to fresh palladium catalyst, ligand, solvent, and substrate. [e] palladium black formation observed.

Ligand consumption by alkylation to form the methyltriphenylphosphonium cation is problematic with protic acids,[17] necessitating the use of a large excess of ligand to render the catalyst stable and an excess of the acid as it is consumed in the process. One exception is the salicylborates, which catalyze this process only slowly but which themselves are deactivated by esterification of the salicylic moiety.[8] Even in this instance, the acid is used in large excess. The extent of quaternization of PPh_3 by $Al(OTf)_3$ and some Brønsted acids was investigated in situ by ^{31}P NMR spectroscopy. Table 3 shows that PPh_3 is consumed very slowly under conditions that resemble those of the reaction, and only 7% alkylation is observed after 20 hours in the presence of one equivalent of the Lewis acid. Even with five equivalents of $Al(OTf)_3$, only 27% alkylation was detected (under our reaction conditions the ligand is in excess of the Lewis acid). This result is another demonstrable benefit over the traditional Brønsted acids, which catalyzed this reaction to a significantly greater extent under identical conditions. Importantly, ligand recovery from a typical reaction (Table 2, entry 8) employing $Al(OTf)_3$ demonstrated ligand alkylation of less than 1%.

Following these successful outcomes, we directly compared the $Al(OTf)_3$ cocatalyst, using a standard set of reaction conditions, with the more commonly used high-performance Brønsted acids[5] such as *p*-TsOH and HOTf, and were gratified to note that $Al(OTf)_3$ substantially outperformed the Brønsted acids in all cases in time-limited (2 h) reactions

Table 3: Acid-catalyzed quaternization of PPh_3 in MeOH.[a]

Acid	L/A 1:1 [%]	L/A 1:2 [%]	L/A 1:5 [%]
$Al(OTf)_3$	7	22	27
p-TsOH	28	51	85
TfOH	46	61	91
MsOH	58	75	95

[a] Values in the table are percentage alkylation of PPh_3 to $[MePPh_4]^+$. Reaction conditions: PPh_3 (0.0475 mM), MeOH (1.0 mL), 70°C, 20 h ($L = PPh_3$; A = Lewis or Brønsted acid; $MsOH = CH_3SO_3H$).

(Table 4). At palladium catalyst loadings of 0.08% (palladium/styrene 1:1200) and 0.0625% (palladium/styrene 1:1600), the reactions in which $Al(OTf)_3$ was used as promoter were a factor of 1.6–1.9 faster than the corresponding Brønsted acid-promoted reactions.

Table 4: Palladium-catalyzed methoxycarbonylation of styrene with various acid promoters.

Entry	Pd/L/LA/St[a]	Promoter	% Conv[b]	l/b[c]	TOF[d] ($\times 10^2$)
1	1:4:2:1200	$Al(OTf)_3$	62	2.8:1	3.7
2	1:4:2:1200	*p*-TsOH	39	2.6:1	2.3[e]
3	1:4:2:1200	HOTf	42	2.1:1	2.5
4	1:4:2:1600	$Al(OTf)_3$	31	2.7:1	2.5
5	1:4:2:1600	*p*-TsOH	18	2.5:1	1.4
6	1:4:2:1600	HOTf	22	2.3:1	1.3

[a] Reaction conditions: $Pd(OAc)_2$ (0.045 mmol), 4.75:1 MeOH/St (v/v, total volume 12.5 mL), 35 atm CO, 80 ± 2 °C internal temperature (118 ± 2 °C oil bath), 2 h ($L = PPh_3$; $LA = Al(OTf)_3$; St = styrene). [b] Conversion into ester products (no detectable by-product formation) as determined by ^1H and ^{13}C NMR analysis. [c] l/b is ratio of linear to branched isomers determined by ^1H and ^{13}C NMR spectroscopy. [d] TOF = mol ester produced/mol Pd.h, based on total run, average of three runs. [e] TOF = 2.0×10^2 for 0.4% Pd catalyst, Pd/PPh_3 1:4, Pd/*p*-TsOH 1:10, 35 atm CO.[13]

Encouraged, we compared various Brønsted acids with $Al(OTf)_3$ using 1-pentene as a representative nonaromatic substrate (Table 5). Somewhat modified conditions were applied at lower catalyst loadings than were used with styrene, in line with a previous observation on hydroformylation reactions that 1-alkenes are approximately three times more reactive than styrene,[18] as was also found in this case. In these reactions, it was found that a Pd/L ratio of greater than 1:5 was imperative for catalyst stability (upon which the observed rate of reaction relies); below this level of ligand, significant formation of palladium black was observed. As demonstrated above, this is unlikely to be related to ligand alkylation. Furthermore, a minimum palladium/acid ratio of 1:2 was required, even with $Al(OTf)_3$, for acceptable catalyst activity to be obtained, which is possibly a consequence of the higher ligand concentrations present.

It can be seen from Table 5 that the optimum palladium/acid ratio, as determined from the rates of the reactions, is (sometimes critically) acid-dependent. These optimum ratios range from 1:4 in the case of HCl to 1:30 or more in the case of CH_3SO_3H. With $Al(OTf)_3$, the optimum Pd/Al conversion ratio is 1:8, although some further rate enhancement was observed with ratios up to 1:18. Again, no reaction was observed in the absence of cocatalyst, as was the case with styrene. Of the Brønsted acids tested, anhydrous HBF_4 proved to be superior; however, $Al(OTf)_3$ outperformed that cocatalyst, again from a rate perspective, by a factor of 1.4, with no loss of the selectivity, and by a factor of 1.9 over the more commonly used CH_3SO_3H. The reactions using $Al(OTf)_3$ showed a linear uptake of CO to a conversion of approximately 80%; thereafter the rates of the reactions slowed. This reaction is apparently unaffected by the rapid double-bond isomerization of 1-pentene. This isomerization reached equilibrium within one hour under the conditions employed: the CO uptake curves showed no deviation from linearity at all during the course of the reaction for the cited portion of the curve (pertaining to approximately 80% conversion), which would otherwise be expected to be the case if the reaction was in fact sensitive to this process.

Table 5: Palladium-catalyzed methoxycarbonylation of 1-pentene using various acid promoters.

Entry	Pd/L/HA[a]	Promoter	*T* [°C]	TOF[b] ($\times 10^2$)	% Conv[c]	l/b[d]
1	1:9:2	HCl	115	3.2	–[e]	–[e]
2	1:9:4	HCl	115	6.0	42	2.8:1
3	1:9:6	HCl	115	3.0	–	–
4	1:9:2	CH_3SO_3H	105	3.6	–	–
5	1:9:4	CH_3SO_3H	105	5.7	–	–
6	1:9:14	CH_3SO_3H	105	8.5	62	3.0:1
7	1:9:18	CH_3SO_3H	105	7.7	–	–
8	1:20:30	CH_3SO_3H	105	9.5	70	3.2:1
9	1:9:2	HOTf	100	9.3	–	–
10	1:9:14	HOTf	100	10.4	74	3.1:1
11	1:9:18	HOTf	100	8.8	–	–
12	1:9:2	HBF_4	100	4.5	–	–
13	1:9:6	HBF_4	100	11.2	83	3.4:1
14	1:9:8	HBF_4	100	9.9	–	-
15	1:9:2	$Al(OTf)_3$	100	6.2	–	-
16	1:9:4	$Al(OTf)_3$	100	9.4	68	3.4:1
17	1:9:8	$Al(OTf)_3$	100	14.4	100	3.5:1
18	1:18:18	$Al(OTf)_3$	100	15.8	100	3.5:1

[a] Reaction conditions: 0.1 mmol $Pd(OAc)_2$, Pd/1-pentene 1:4750, MeOH/1-pentene 1:1 (v/v, total volume 100 mL), 50 atm CO, 3 h, ($L = PPh_3$). [b] TOF: mol CO absorbed/mol Pd.h, based on the linear part of the CO uptake curve (to ca. 80% conversion), average of three runs. [c] Conversion into ester products (excluding pentene isomers) as determined by ^1H NMR and GC-FID analysis (no detectable by-product formation). [d] l/b is ratio of linear to branched isomers determined by ^1H and ^{13}C NMR spectroscopy. [e] Analyses performed only for the best reaction in a given set of reactions using a particular Brønsted/Lewis acid.

Further rate enhancements (not presented in Table 5) were obtained by changing the MeOH/1-pentene ratio from 1:1 to 2:1 v/v, which resulted in a rate enhancement of approximately 1.25 and was accompanied by a slight increase in selectivity for the linear product (l/b 4:1).

It is unlikely that triflic acid, generated by methanolysis of $Al(OTf)_3$, is the active species. Recent work on the $Al(OTf)_3$-catalyzed cyclization of alkenols demonstrated activity of this catalyst in the presence of water and 2,6-lutidine as base in CH_3CN solution, conditions under which HOTf was shown to be inactive.[19] Furthermore, our previous work using this Lewis acid in alcohol solvents has also shown that triflic acid is not the active catalyst,[11] and the ligand alkylation study reported herein also contradicts this notion. Nonetheless, $Al(OTf)_3$ does polarize the O–H bond of alcohols,[19] which possibly provides the source of the $\{Pd{-}H\}^+$ species generally accepted to be required to initiate and sustain the catalytic cycle involved with faster catalysts[20] (Pd^{II} has also been shown to react directly with MeOH to form {Pd–H} species[21]), and at the same time this Lewis acid presumably also functions as a noncoordinating aluminate counterion, as mentioned above.

The origin of the heightened activity of the catalyst system most probably lies in its acceleration of the rate-limiting step of the reaction, which has been shown to be the alcoholysis of the acetylpalladium species.[20] In the present case, the $Al(OTf)_3$ may either activate this species towards migratory nucleophilic attack by palladium-bound MeO^-/MeOH (Lewis acid coordination to the carbonyl oxygen) and/or possibly provide a source of MeO^- in the form of the ion $[MeOAl(OTf)_3]^-$ for direct nucleophilic attack. The reaction had a fractional order dependence on the Lewis acid concentration: a rate enhancement of 1.27 was found over the range Pd/LA 1:1 to 1:8 (relative rates for $1:1 = 1$, $1:2 = 1.14$, $1:4 = 1.25$, and $1:8 = 1.27$). The most notable feature of this part of the study was a decrease in the induction period from approximately 30 minutes for the lower $Al(OTf)_3$ ratios to only about 10 minutes for the higher ratios.

The unusual observation of reaction rate linearity (apparent zero-order kinetics in alkene for a significant portion of the reaction) for both styrene and 1-pentene led us to investigate this phenomenon more fully. The observation of rate linearity, together with the fact that, in general, no palladium black formation was observed under the reaction conditions given which led to successful reactions, even at the end of the reaction after depressurization of the reactor, also decidedly points to high catalyst stability and a stable, constant-composition, catalytically active palladium species. We established that the rates of the reactions were indeed apparently independent of the alkene concentration to approximately 80% conversion (for the higher initial concentrations, tapering off to about 70% for the lower initial concentrations) after which the CO uptake curve gradually flattened off until complete conversion was obtained (regression analysis for the linear section of the CO uptake curve provided a fit of better than $R^2 = 0.996$ in all cases, after an induction period of approximately 20–30 minutes) for initial styrene concentrations in the window 0.77–2.88 M. Further studies on CO dependence showed a fractional order dependence. Relative rates were determined for P_{co} (defined as 1 at 25 atm): P_{co} 35 atm = 1.07, P_{co} 45 atm = 1.20, P_{co} 55 atm = 1.25. Additionally, as shown in Table 1 (entries 4–7) and Table 5 (entries 15–18), rate enhancements were also observed with increasing levels of the $Al(OTf)_3$ (as was also observed for the Brønsted acids, Table 5), the results of which point to a fractional order dependence on Lewis acid concentration.

We have presented the unprecedented application of a strong, hydrolytically stable[12] Lewis acid such as $Al(OTf)_3$ in the methoxycarbonylation reaction of styrene and 1-pentene, and that this material may readily take the place of the commonly used Brønsted acids to form the anticipated ester products in high yields. This aluminum-based promoter significantly improves the activity of the catalyst, leading to rates 1.4–1.9 times higher than those observed for even the best benchmark Brønsted acids under comparable conditions. Importantly, $Al(OTf)_3$ is a stable Lewis acid, which we have previously shown to be easily recoverable and reusable without loss of activity,[12] and which we have also demonstrated herein. Stable palladium catalysts are produced in situ and the reaction conditions may be readily manipulated so that no palladium black is formed even at low catalyst loadings. We are currently investigating the application of other Lewis acids to this reaction, and the investigation will also include the industrially important[3] production of methyl methacrylate (MMA) from ethene by the methoxycarbonylation product methyl propanoate, producing MMA upon condensation with formaldehyde or its dimethyl acetal.[22]

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[1] K. Nozaki, I. Ojima in *Catalytic Asymmetric Synthesis*, 2nd ed., Wiley, New York, **2000**, p. 429.
[2] G. Papadogianakis, G. Verspui, L. Maat, L. R. A. Sheldon, *Catal. Lett.* **1997**, *47*, 43.
[3] a) W. Clegg, G. R. Eastham, M. J. Elsegood, R. P. Tooze, W. L. Wang, K. Whiston, *Chem. Commun.* **1999**, 1877; b) W. Clegg, G. R. Eastham, M. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman, S. Zacchini, *Organometallics* **2002**, *21*, 1832.
[4] G. Kiss, *Chem. Rev.* **2001**, *101*, 3435.
[5] E. Drent (Shell), EP 0,106,379, **1988**.
[6] B. S. Wan, S. J. Liao, Y. Xu, D. R. Yu, *J. Mol. Catal. A* **1998**, *136*, 263.
[7] a) T. Fuchikami, K. Ohishi, I. Ojima, *J. Org. Chem.* **1983**, *48*, 3803; b) D. H. Nguyen, Y. Coppel, M. Urrutigoïty, P. J. Kalck, *J. Organomet. Chem.* **2005**, *690*, 2947.
[8] A. Ferreira, R. Crous, L. Bennie, A. M. M. Meij, K. Blann, B. C. B. Bezuidenhout, D. A. Young, M. J. Green, A. Roodt, *Angew. Chem.* **2007**, *119*, 2323; *Angew. Chem. Int. Ed.* **2007**, *46*, 2273.
[9] T. O. Vieira, M. J. Green, H. Alper, *Org. Lett.* **2006**, *8*, 6143.
[10] H. Ooka, T. Inoue, S. Itsuno, M. Tanaka, *Chem. Commun.* **2005**, 1173.
[11] D. B. G. Williams, M. Lawton, *Org. Biomol. Chem.* **2005**, *3*, 3269.
[12] D. B. G. Williams, M. Lawton, *Tetrahedron Lett.* **2006**, *47*, 6557.
[13] A. Seayad, A. A. Kelkar, L. Toniolo, R. V. Chaudhari, *J. Mol. Catal. A* **2000**, *151*, 47.
[14] a) G. P. C. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1992**, *430*, 357; b) B. A. Markies, D. Kruis, M. H. P. Rietveld, K. A. N. Verkerk, J. Boersma, H. Kooijman, M. Lakin, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1995**, *117*, 5263.
[15] a) J. M. Harrowfield, D. L. Kepert, J. M. Patrick, A. H. White, *Aust. J. Chem.* **1983**, *36*, 483; b) A. Chatterjee, E. N. Maslen, K. J. Watson, *Acta Crystallogr. Sect. B* **1988**, *44*, 381.
[16] A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1996**, 2995.
[17] E. Drent, M. Hasselaar (Shell), WO 97/03943, **1997**.
[18] A. Van Rooy, E. N. Orij, P. J. C. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1995**, *14*, 34.
[19] L. Coulombel, M, Rajzmann, J. M. Pons, S. Olivero, E. Duñach, *Chem. Eur. J.* **2006**, *12*, 6356.
[20] P. W. N. M. van Leeuwen, M. A. Zuideveld, B. H. G. Swannenhuis, Z. Freixa, P. C. J. Kamer, K. Goublitz, F. Fraanje, M. Lutz, A. L. Spek, *J. Am. Chem. Soc.* **2003**, *125*, 5523, and references therein.
[21] a) P. W. N. M. van Leewen *Homogeneous Catalysis*, Kluwer, Dordrecht, **2004**, p. 259; b) R. A. M. Roberston, D. J. Cole-Hamilton, *Coord. Chem. Rev.* **2002**, *225*, 67; c) C. Bianchini, A. Meli, W. Oberhauser, S. Parisel, A. V. Gusev, A. M. Kal'sin, N. V. Vologdin, F. M. Dolgushin, *J. Mol. Catal. A* **2004**, *224*, 35.
[22] J. P. Spivey, M. R. Gogate, J. R. Zoeller, R. D. Colberg, *Ind. Eng. Chem. Res.* **1997**, *36*, 4600.