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N-substituted diphosphinoamines: Toward rational ligand design for the efficient tetramerization of ethylene

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Abstract

Bis(diphenylphosphino)amine (PNP) ligands with different alkyl and cycloalkyl substituents attached to the *N* atom of the ligand backbone were synthesised and tested together with chromium as ethylene tetramerization catalysts. On activation with a methylaluminoxane-based activator, the catalysts displayed good activity and selectivity toward 1-octene and 1-hexene, with the best ligand systems containing cyclopentyl or cyclohexyl moieties. In addition, it was established that substitution at the 2 position of the cyclohexyl skeleton and, more importantly, an increase in steric bulk at that point, led to a drastic reduction of side product formation (i.e., methyl- and methylenecyclopentane). Interestingly, additional methyl substitution in the 6 position of the cyclohexyl ring changed the selectivity of the catalyst from predominantly tetramerization to a 1:1 mixture of 1-hexene and 1-octene. Structurally similar ligands, such as cyclohexylmethyl and cyclohexylethyl PNP, were also tested and were also found to yield efficient tetramerization catalysts. It was concluded that structural fine tuning of the *N*-alkyl moiety of the PNP ligand is essential for obtaining efficient tetramerization catalysts, with the best systems achieving combined selectivities as high as 88% (1-octene and 1-hexene) with exceptionally high activities exceeding 2,000,000 g/(g-Cr h).

Keywords: Linear α-olefins; Tetramerization; Ethylene; 1-Hexene; 1-Octene; Chromium; Homogeneous catalysis; Bis(diphenylphosphino)amine ligands

1. Introduction

Linear alpha olefins (LAOs) are of vital importance for the chemical industry, particularly as intermediates for the synthesis of polymers; for example, 1-hexene and 1-octene are the most important co-monomers for the production of LLDPE [1]. Although the majority of LAOs are obtained through processes that yield a Schulz–Flory distribution (e.g., the Shell higher-olefin process and Ziegler-type processes), an interesting alternative has evolved over the last 2 decades. The selective trimerization of ethylene allows access to co-monomer grade 1-hexene and thus is an economically attractive route to this valuable intermediate [2]. Although a number of selective ethylene trimerization catalysts based on chromium [3–10] and other transition metals [11–15] have been reported, the selective formation of higher olefins such as 1-octene was discovered only recently [16–18].

The selective tetramerization of ethylene to 1-octene was demonstrated successfully using a chromium source [i.e., $Cr^{III}(acac_3)$], a bis(diphenylphosphino)amine ligand of the general structure $(Ph_2P)_2N–R$ and a methylaluminoxane (MAO)-based activator [16–18]. Extensive deuterium labeling studies have indicated that the olefins produced are indeed formed by means of an extended metallacycle mechanism that is depicted in Scheme 1. According to this mechanism, the activated chromium catalyst **1** coordinates two ethylene molecules (intermediate **2**) to form the chromacyclopentane **3**. A further ethylene unit is inserted into this species via intermediate **4**

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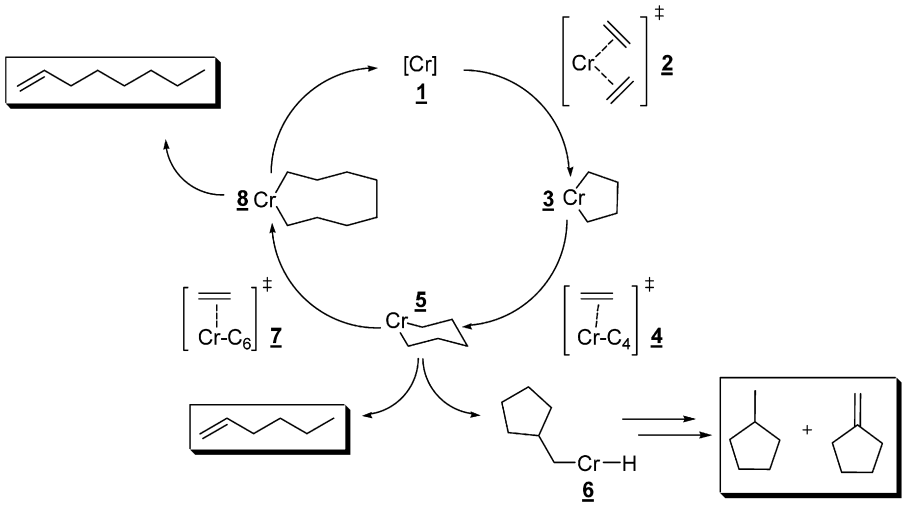

Scheme 1. Metallacycle mechanism for the selective tetramerization of ethylene as postulated by Overett et al. (the most prominent products are boxed).

yielding the chromacycloheptane **5**. This species can then undergo several possible reaction pathways which will lead to the 3 main products. The most prevalent route is the insertion of a fourth ethylene unit into the metallacycle ring, thus forming the chromacyclononane **8** which undergoes rapid elimination to 1-octene. The second possible pathway is the reductive elimination of 1-hexene from the chromacycloheptane **5** and the third potential pathway is the suggested rearrangement of **5** to a cyclopentyl hydride species **6**. The formation of methyl- and methylenecyclopentane is proposed to occur via a subsequent disproportionation step [19]. It was also shown that by varying the steric bulk of the ligand via substitution at the *P*–Ar moiety, the selectivity could be switched from tetra- to trimerization [20]. Furthermore, kinetic studies on the catalyst system $Cr^{III}(acac)_3$, ^{i}Pr PNP, MAO have revealed that an increase in pressure from 20 to 45 bar led to an increased formation of 1-octene [21]. However, studies at even higher pressures (up to 100 bar) have shown that using the $(Ph_2P)_2N$–R ligand system, the maximum yield of 1-octene cannot be boosted beyond the 75% limit by increasing the ethylene concentration [22]. More detailed kinetic studies based on the catalyst system generated from $Cr^{III}(acac)_3$; 1,2,3,4-tetrahydronaphthyl PNP and MMAO-3A have suggested that the formation of 1-octene follows a second-order dependence in ethylene concentration, whereas 1-hexene formation is first order [23].

2. Experimental

2.1. General comments

All synthetic work was carried out under argon using standard Schlenk technique. Solvents were purchased from Aldrich and dried over Na/benzophenone or CaH_2. Ethylene 3.5 was supplied by Linde and used as received. NMR spectra were recorded on a *Bruker* DPX-300 FT spectrometer. GC-MS spectra were recorded on a *Varian* Saturn 2100T. GC/FID analyses were carried out on either a *Varian* 3900 chromatograph using a CP Sil PONA CB 50 m × 0.21 mm column or a Hewlett-Packard 5890 chromatograph using a J&W Scientific 50 m × 0.2 mm PONA column.

2.2. Hydrogenation of aniline derivatives: general procedure

To a solution of 200 ml of substituted aniline, 10 g of Ru/C (supplied by Degussa AG, Germany) were added. The slurry was stirred briefly to ensure fine dispersion before it was transferred to a 600-ml Parr autoclave equipped with gas-intake stirrer to ensure sufficient gas entrainment and internal cooling coil to prevent thermal runaways. The reaction vessel was pressurized and depressurized with 5 barg argon three times to ensure inert conditions. After heating to reaction temperature, hydrogen was fed into the reactor on demand for 24 h. Complete conversion was confirmed via GC-MS. The reaction was terminated by cooling to ambient temperature and depressurization. The catalyst was filtered off and the product was obtained as colourless liquid by vacuum distillation.

2.3. Ligand synthesis: general procedure

The alkylcyclohexyl PNP ligands were synthesised by reacting the amine and diphenylphosphine chloride Ph_2PCl, as described in the literature [24–26]. The ^{31}P NMR shifts (ppm) of all of the ligands are given in the supporting information.

2.4. Tetramerization runs: general procedure

Before each run, the respective autoclave was heated under vacuum at elevated temperature (120 °C) overnight and set under inert gas atmosphere. The reaction vessel was then charged with solvent and heated to the desired reaction temperature. Stock solutions of the catalyst components (with chromium-to-ligand-to-MMAO ratios as indicated in Tables 1, 2, and 3) were transferred into a Schlenk vessel. The catalyst mixture was stirred for 1 min and transferred to the autoclave, and the reaction was started by pressurization with ethylene to the desired pressure. Isothermal process conditions were ensured throughout the duration of the run, with the ethylene fed on demand.

Table 1
Ethylene tetramerization with *N*-cycloalkyl PNP ligands[a]

No	Ligand	Time (min)	Productivity (g/(g-Cr h))	S_{C_6} (wt%)	$S_{cy\text{-}C_6 \text{ in } C_6}$ (%)	$S_{1\text{-}C_6 \text{ in } C_6}$ (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8 \text{ in } C_8}$ (%)	$S_{C_{10}-C_{14}}$ (%)	$S_{C_{16+}}$ (%)	S_α (wt%)	Solids (wt%)
1	**1**	35	464,396	19.5	51.9	44.3	62.5	96.5	8.9	4.8	68.9	1.8
2	**2**	41	390,650	19.2	48.9	47.8	61.2	97.0	10.4	5.6	68.6	1.3
3	**3**	28	544,629	18.6	34.2	63.9	63.7	98.1	9.3	6.4	74.4	2.0
4	**4**	25	725,280	18.7	25.2	73.9	67.2	99.0	8.2	4.3	80.4	0.9
5	**5**	22	737,536	19.8	24.9	74.3	68.1	99.0	7.5	2.6	82.1	1.2
6	**6**	25	757,720	22.6	15.0	84.6	66.4	99.4	8.0	1.6	84.9	0.9

[a] All reactions were carried out in 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 45 barg, 5 μmol $Cr(acac)_3$, 7.5 μmol ligand, 270 eq. MMAO-3A.

Table 2
Ethylene tetramerization with substituted *N*-cyclohexyl PNP ligands[a]

No	Ligand	Time (min)	Productivity (g/(g-Cr h))	Efficiency (g/(g-Cr))	S_{C_6} (wt%)	$S_{cy\text{-}C_6 \text{ in } C_6}$ (%)	$S_{1\text{-}C_6 \text{ in } C_6}$ (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8 \text{ in } C_8}$ (%)	S_α (wt%)	Solids (wt%)
7	**4**	16.5	2,146,787	591,082	19.4	24.0	75.0	68.3	99.0	82.2	0.8
8	**7**	15	2,279,200	569,800	26.6	14.3	85.4	63.7	99.5	86.0	0.7
9	**8**	13.5	2,191,555	493,100	26.5	11.4	88.3	64.5	99.6	87.6	0.3
10	**9**	18	1,878,413	563,524	29.6	6.9	92.9	59.8	99.6	87.1	1.3
11	**10**	13.0	2,134,983	461,183	43.0	4.4	95.4	48.7	99.7	89.5	0.3
12	**11**	30	666,800	333,400	31.3	11.4	88.3	60.8	99.4	88.0	1.2

[a] Reaction conditions: 60 °C, 45 barg, 2.5 μmol $Cr(acac)_3$, 2.5 μmol ligand, 270 eq. MMAO-3A (540 for entries 7 and 10), 100 ml cyclohexane.

Table 3
Ethylene tetramerization with various *N*-substituted PNP ligands[a]

No	Ligand	Time (min)	Productivity (g/(g-Cr h))	S_{C_6} (wt%)	$S_{cy\text{-}C_6 \text{ in } C_6}$ (%)	$S_{1\text{-}C_6 \text{ in } C_6}$ (%)	S_{C_8} (wt%)	$S_{1\text{-}C_8 \text{ in } C_8}$ (%)	S_α (wt%)	Solids (wt%)
13	**12**	33	479,818	19.8	51.3	45.8	63.9	97.3	71.6	1.6
14	**13**	92	167,386	25.4	13.2	86.5	63.3	99.4	84.9	1.9
15	**14**	26	614,662	27.1	10.7	89.1	62.8	99.5	86.7	0.8
16	**15**	20	845,001	22.8	28.7	70.5	65.3	98.8	80.5	3.0

[a] All reactions carried out in 300 ml Parr reactor using 100 ml methylcyclohexane at 60 °C, 45 barg, 5 μmol $Cr(acac)_3$, 7.5 μmol ligand, 270 eq. MMAO-3A.

After the indicated reaction time, the autoclave was cooled to 0 °C in an ice bath and slowly depressurized. A sample of the liquid reaction mixture was filtered and taken for GC analysis. Solid byproducts were collected by filtration, dried in an oven overnight, and weighed.

3. Results and discussion

3.1. Optimization of cycloalkyl PNP ring size

The aim of this study was to optimize the ligand structure to achieve higher combined selectivity toward the two most desired products (1-octene and 1-hexene) at the expense of side product formation. The main side products produced by these catalyst systems are cyclic products (namely methyl- and methylenecyclopentane), higher 1-alkenes generated by enlarged metallacycle growth, and C_{10}–C_{14} branched olefins from the secondary incorporation of the main products, as well as small amounts of polyethylene (PE), into the catalytic cycle. Although the latter reaction depends mainly on product concentration and catalyst time on stream [21], the formation of cyclic side products potentially can be limited by appropriate ligand modification.

In an effort to maximize overall selectivity to desired products, we decided to study the influence of substituents attached to the *N* atom of the PNP moiety. This seemed particularly promising; initial experiments revealed that exchanging a methyl-substituent for an isopropyl or cyclohexyl group led to a significant increase in 1-hexene selectivity within the C_6 fraction, whereas the selectivity toward 1-octene remained fairly unchanged [16].

These encouraging results prompted us to synthesise a broader range of *N*-cycloalkyl PNP ligands with varying ring sizes to gain information on the substitution pattern that would be necessary for improved selectivity. The ligands were synthesised according to standard methodology [24–26] and tested in a pressure autoclave. The results of the ethylene tetramerization experiments with ligands **1**–**6** (see Fig. 1) are given in Table 1.

As is evident from Table 1, ligands with small ring size substituents on the nitrogen (i.e., cyclopropyl and cyclobutyl) proved to form comparatively unselective catalyst systems, because the combined yield of 1-octene and 1-hexene was rather low. This is due to the increased formation of all of the above-mentioned side products. However, a systematic increase in the ring size from cyclobutyl to cyclododecyl led to an incremental improvement in desired selectivity. A striking feature of Table 1, is that a 16% improvement in the total alpha selectivity could be achieved by increasing the ring size from 3 to 12 carbon atoms. Although this can be attributed to lower levels of all the side products, it is mainly due to an increased 1-hexene selectivity within the C_6 cut (from 44 to 85%). A decrease in

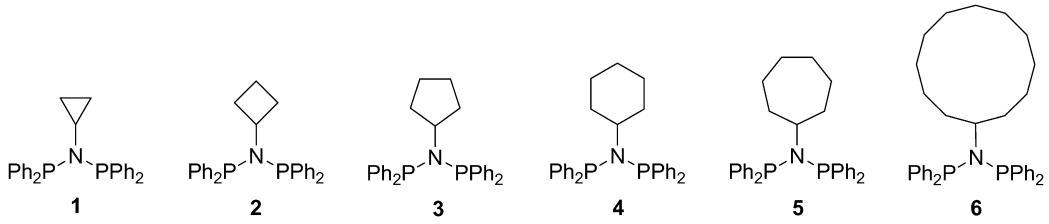

Fig. 1. *N*-cycloalkyl PNP ligands.

the C_{16+} fraction also contributes to the improved total alpha selectivity, although to a lesser extent. It is also evident from Table 1 that an increase in ring size from 4 to 7 carbon atoms, led to a 6.9% increase in 1-octene selectivity, whereas a further increase to 12 carbons caused a slight decrease. Interestingly, the catalyst activity also increases with increasing ring size of the cycloalkyl moiety, probably due to an increase in catalyst solubility.

3.2. Alkyl-substituted cyclohexyl PNP ligands

Based on the above results, a cyclohexyl moiety seemed to be a suitable skeleton to probe the effect of substituents on the cycloalkyl group that are in close vicinity to the *N* atom. This would allow tailoring of the steric environment of the ligand with the aim of further enhancing catalyst selectivities. Initially, it was decided to explore the effect of alkyl substituents on the 2 position of the cyclohexyl moiety. Because the variety of commercially available 2-substituted cyclohexylamines is limited (only 2-methylcyclohexylamine is a commercial compound), different synthetic approaches to prepare these compounds were evaluated. It was found that the most straightforward route was the hydrogenation of the corresponding aniline derivatives, using Ru on carbon as the catalyst. This approach has several major advantages over other pathways, including ease of reaction, high yields, and facile scale-up.

After preliminary optimization of the hydrogenation conditions for the specific substrate 2,6-dimethylaniline, the reaction conditions selected were 135 barg hydrogen pressure and a temperature of 120 °C. Using this protocol, all targeted saturated amines could be obtained in good yields by vacuum distillation. Side reactions like dealkylation, hydroxylation, and condensation—leading to aniline, alcohols and secondary/tertiary amines, respectively—were negligible under these conditions. The further synthesis of the equivalent PNP ligands was carried out according to the literature [24–26] and was reasonably straightforward for all substrates except 2,6-diethylcyclohexyl PNP, which could not be synthesised via this route, probably due to its steric encumbrance. These ligands were again evaluated for efficacy as selective oligomerisation catalysts, and the data is reported in Table 2 and Fig. 2.

As was observed with increasing ring size of the ligands reported in Table 1, the general trend was that substitution with increasingly bulkier alkyl groups at the 2-position of the cyclohexyl moiety (ligands **4**–**9**) led to an increase in total alpha selectivity. The more sterically encumbered ligands favoured the formation of 1-hexene over 1-octene (selectivity toward 1-octene drops from 63.7% to 59.8% when going from 2-methyl

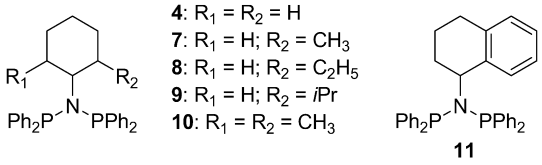

Fig. 2. 2- and 2,6-alkylcyclohexyl PNP ligands.

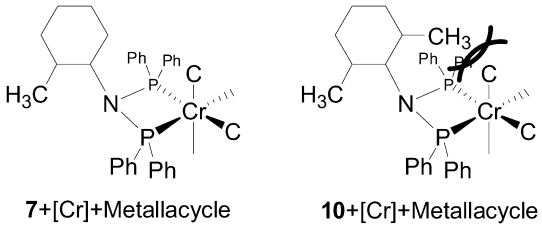

Fig. 3. Proposed steric interactions between ligands **7** and **10** and metallacycle.

to 2-isopropylcyclohexyl PNP). The activities achieved with these ligands were around 2,000,000 g/(g-Cr h) and are to our knowledge among the highest activities reported thus far for a selective ethylene tri- or tetramerization catalyst.

In an effort to maximize 1-hexene selectivity we decided to study the influence of further bulk at the cyclohexyl moiety by introducing two methyl groups (i.e., in the 2 and 6 positions). Consistent with the aforementioned trend (increased bulk leads to increased 1-hexene formation), an even higher 1-hexene selectivitiy of 95.4% in the C_6 fraction could be achieved with this ligand (entry 11, Table 2). Most surprisingly, however, this went hand in hand with a significant swing from predominantly tetramerization to a 1:1 1-hexene/1-octene ratio. This unexpected behaviour could be explained if one considers the steric environment around the catalyst centre. Fig. 3 depicts the proposed steric interactions between ligands **7** and **10** and the growing chromacycle. When using 2-substituted cyclohexyl PNP ligands the sterically demanding substituent in all probabilities does not point toward the metal centre due to geometric constraints. Thus, increasing the bulk from 2-methyl to 2-isopropyl only allows rather subtle selectivity tuning due to rather long-range interactions. Introducing a second methyl group, however, leads to more pronounced interactions with the catalyst centre, because it is obviously impossible for both substituents to rotate in a way that would leave the centre unaffected. If we further assume that chromacyclononane is sterically more demanding than chromacycloheptane, then the swing from tetramerization to 1:1 1-hexene/1-octene could be explained by the preferential elimination of 1-hexene by the steric interactions between ligand and metal centre. A similar trend (increased steric bulk leads to more 1-hexene) has been

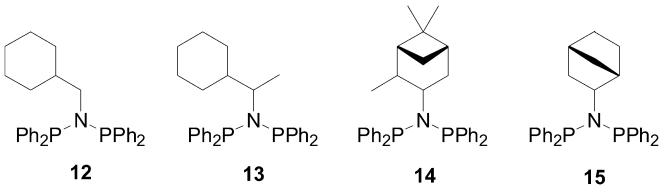

Fig. 4. Various *N*-substituted PNP ligands.

reported in the literature for modifications at the *P* atom of the ligand. Increasing the number of *ortho*-alkyl-aryl groups in $Ar_2PN(CH_3)PAr_2$ from 1 to 4 led from predominantly tetramerization to trimerization [20].

We also tested 1,2,3,4-tetrahydronaphthyl PNP **11** (entry 12, Table 2) with chromium as a tetramerization catalyst, due to its structural similarity to the ligands reported herein. Again, the improved 1-hexene selectivity and thus higher overall yield was observed with this ligand (88.3% in the C_6 cut). Due to the sterically demanding aromatic moiety attached to the cyclohexyl skeleton, the ratio of 1-octene to 1-hexene was 2:1 and thus comparable with that of 2-isopropylcyclohexyl PNP **9**. However, the activity was significantly lower than for the previous ligands; rates around 650,000 g/(g-Cr h) could be achieved.

3.3. Other *N*-substituted PNP ligands

After the encouraging results achieved with the substituted *N*-cyclohexyl PNP ligands, it was decided to broaden the research and explore ligands with structurally related cycloalkyl patterns (see Fig. 4). Although ligands **12** and **13** are very close variations of the cyclohexyl-alkyl motif, ligands **14** and **15** constrain the flexibility of the cyclohexyl ring by methylene bridges and introduce more bulk in the 4 position of the cyclohexyl moiety in the case of **15**. The results of the tetramerization experiments are given in Table 3.

Comparing the data obtained for ligand **12** with that of the cyclohexyl-PNP derivative **4** (entry 4, Table 1), it is clear that introduction of a methylene spacer between the *N* atom and cyclic moiety, and thus subsequent relief of steric strain, led to a ca. 9% drop in total alpha selectivity, due mainly to increased cyclic C_6 formation. Substitution of an H atom for a methyl group on the methylene spacer and consequent reintroduction of steric strain (ligand **13**), resulted in a ca. 13% gain in overall alpha selectivity. The selectivity obtained with this ligand compares favourably with the structurally similar ligand **7**. The slightly increased bulk of ligand **14** produced marginal selectivity gains relative to ligand **7**. As might be expected, removal of the 2-methyl substituent (ligand **15**) gave comparable selectivities to the cyclohexyl-PNP (ligand **4**).

4. Conclusions

In conclusion, we were able to show that excellent fine-tuning of the selectivity is possible for the Cr-catalyzed tetramerization of ethylene by using a number of *N*-substituted bis(diphenylphosphino)amine PNP ligands. An increase in ring size from 3 to 12 carbon atoms of the cycloalkyl moiety leads to drastic improvements in both catalyst performance and combined alpha selectivity. Further optimization of combined alpha-selectivity could be effected by substitution of alkyl groups at the 2-position of the cyclohexyl moiety. Increasing the steric encumbrance of these substituents from methyl to ethyl to isopropyl suppressed the formation of the side products methyl- and methylenecyclopentane. Activities in excess of 2,000,0000 g/(g-Cr h) could be achieved for selected ligands. Increasing the steric encumbrance even further by having methyl substituents on both the 2- and 6-positions led to a significant swing away from 1-octene formation toward a 1:1 1-hexene/1-octene mixture.

Supporting information

The online vision on this article contains additional supplementary information.

Please visit doi: 10.1016/j.jcat.2006.10.020.

References

[1] An excellent general overview is provided by: D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, Wiley–VCH, New York, 2002, p. 240.
[2] For a more recent review on selective trimerization see: J.T. Dixon, M.J. Green, F.M. Hess, D.H. Morgan, J. Organomet. Chem. 689 (2004) 3641–3668.
[3] R.M. Manyik, W.E. Walker, T.P. Wilson, J. Catal. 47 (1977) 197–209.
[4] J.R. Briggs, Chem. Commun. 11 (1989) 674–675.
[5] A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, Chem. Commun. (2002) 858–859.
[6] D.H. Morgan, S.L. Schwikkard, J.T. Dixon, J.J. Nair, R. Hunter, Adv. Synth. Catal. 345 (2003) 939–942.
[7] D.S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J.T. Dixon, A. Bollmann, H. Maumela, F. Hess, U. Englert, J. Am. Chem. Soc. 125 (2003) 5272–5273.
[8] D.S. McGuinness, P. Wasserscheid, W. Keim, J.T. Dixon, J.J.C. Grove, C. Hu, U. Englert, Chem. Commun. (2003) 334–335.
[9] K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, M.J. Overett, Chem. Commun. (2005) 620–621.
[10] D.S. McGuinness, P. Wasserscheid, D.H. Morgan, J.T. Dixon, Organometallics 24 (2005) 552–556.
[11] C. Andes, S.B. Harkins, S. Murtuza, K. Oyler, A. Sen, J. Am. Chem. Soc. 123 (2001) 7423–7424.
[12] P.J.W. Deckers, B. Hessen, J.H. Teuben, Organometallics 21 (2002) 5122–5135.
[13] J. Huang, T. Wu, Y. Qian, Chem. Commun. (2003) 2816–2817.
[14] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, Organometallics 23 (2003) 2545–2547.
[15] B. Hessen, J. Mol. Catal. A 213 (2004) 129–135.
[16] A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Nevelling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid, S. Kuhlmann, J. Am. Chem. Soc. 126 (2004) 14712–14713.
[17] WO 2004056478.
[18] WO 2004056479.
[19] M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, J. Am. Chem. Soc. 127 (2005) 10723–10730.
[20] K. Blann, A. Bollmann, J.T. Dixon, F. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, M.J. Overett, Chem. Commun. (2005) 620–621.
[21] R. Walsh, D.H. Morgan, A. Bollmann, J.T. Dixon, Appl. Catal. A Gen. 306 (2006) 184–191.

[22] S. Kuhlmann, J.T. Dixon, M. Haumann, D.H. Morgan, J. Ofili, O. Spuhl, N. Taccardi, P. Wasserscheid, Adv. Synth. Catal. 348 (2006) 1200–1206.
[23] S. Kuhlmann, K. Blann, M. Ehrig, J.T. Dixon, M. Haumann, D.H. Morgan, K. Obert, N. Taccardi, P. Wasserscheid, J. Am. Chem. Soc. (2006), submitted for publication.
[24] S.J. Dossett, A. Gillon, A.G. Orpen, J.S. Fleming, P.G. Pringle, D.F. Wass, M.D. Jones, Chem. Commun. (2001) 699.
[25] M.S. Balakrishna, T.K. Prakasha, S.S. Krishnamurthy, J. Organomet. Chem. 390 (2) (1990) 203.
[26] N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen, P. Pringle, Organometallics 20 (2001) 4769.