

Influence of Elevated Temperature and Pressure on the Chromium-Catalysed Tetramerisation of Ethylene

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Received: February 20, 2006; Accepted: April 24, 2006



Supporting information for this article is available on the WWW under <http://asc.wiley-vch.de/home/>.

Abstract: A catalyst system comprising a diphenylphosphineamine (PNP) ligand, chromium(III) acetylacetonate and a methylaluminoxane-based activator was studied for the selective tetramerisation of ethylene. The reaction was investigated over a broad temperature and pressure range and the resulting product mixture was interpreted in the light of the recently published, enlarged metallacycle mechanism. Vapour-liquid equilibrium (VLE) data were calculated for the binary ethylene-cyclohexane mixture over the relevant temperature and pressure ranges to deconvolute the influence of ethylene concentration and temperature. Good agreement of the experimental data with the proposed mechanism was found. Enlargement of the metallacycloheptane ring by in-

sertion of ethylene was found to be dependent on the ethylene concentration, albeit to a lesser extent than assumed. The 1-octene selectivity, which reaches a maximum of 72–74 mass %, thus seems to be primarily dependent on the temperature. The formation of the cyclic side products methyl- and methyl-enecyclopentane was in effect independent of the ethylene concentration. This is in good accordance with the proposed mechanism, since it indicates that the formation of the products occurs *via* rearrangement of a metallacycle intermediate.

Keywords: chromium; ethylene tetramerisation; ethylene-cyclohexane VLE; homogeneous catalysis; metallacycle mechanism

Introduction

The oligomerisation of ethylene yielding linear α olefins (LAOs) is a process of vital importance for the chemical industry as the formed products are useful intermediates for the synthesis of polymers (i.e., 1-hexene and 1-octene are the most important co-monomers for LLDPE production), lubricants and plasticiser alcohols. While the major percentage of the world LAO production is still produced *via* processes that yield a Schulz–Flory distribution (i.e., the Shell higher olefin process and Ziegler-type processes),^[1] an interesting alternative to this inflexible, and thus disadvantageous route, has evolved over the last two decades. The selective trimerisation of ethylene gives access to co-monomer grade 1-hexene and is therefore the route of choice to this valuable inter-

mediate.^[2] The first process for the selective production of 1-hexene has been recently commercialised by Chevron Phillips in its 47,000 metric-ton-per-year 1-hexene plant in Mesaieed, Qatar.^[3] While a number of selective ethylene trimerisation catalysts based on chromium^[4] and other transition metals^[5] have been developed, the selective formation of higher olefins such as 1-octene was only discovered very recently.^[6]

The selective tetramerisation of ethylene yielding 1-octene was demonstrated successfully using a chromium source [i.e., Cr(acac)₃], a diphenylphosphineamine ligand of the general structure (Ph₂P)₂N-R and a methylaluminoxane (MAO)-based activator. From a mechanistic point of view, this reaction is of fundamental relevance, since it suggests an extension of the metallacycloheptane intermediate to yield a metallacyclononane intermediate which gives rise to 1-

octene. Recent DFT studies for chromium and other metals support this possibility.^[7]

It has to be noted that *in situ* studies on the reaction mixture using conventional analytical techniques are complicated by the paramagnetic nature of Cr(I–III) compounds and fast reaction rates. A metallacycle mechanism was initially regarded as a highly unlikely route to the formation of long-chain olefins due to the relatively high energy barrier for the insertion of further ethylene molecules in the metallacycloheptane intermediate, compared to the facile reductive elimination to yield 1-hexene. However, extensive deuterium labelling studies in two independent investigations have indicated that long-chain linear α -olefins can indeed be formed by means of a metallacycle mechanism. Overett et al. demonstrated in their studies that the formation of 1-octene from a C_2H_4/C_2D_4 mixture involved no H/D-scrambling, which is in accordance with a metallacycle mechanism and not with a Cossee–Arlman mechanism.^[8] Furthermore, the authors were able to shed light on the formation of the cyclic C_6 side products, methylenecyclopentane and methylcyclopentane, which are formed in a 1:1 ratio by means of a disproportionation pathway. Their findings are in good agreement with observations made by Bercaw et al. on the selective chromium-catalysed trimerisation of ethylene^[9] and Gibson et al. for the oligomerisation of ethylene by chromium catalysis according to a Schulz–Flory type of distribution.^[10] In all these research activities, carried out by established groups in the field of ethylene oligomerisation, a metallacycle mechanism was proven for the selective, Cr-catalysed ethylene oligomerisation.

In the present paper, additional experimental data is provided to verify the proposed mechanism for the tetramerisation of ethylene. For this purpose, a detailed investigation of the temperature and pressure dependency of the tetramerisation reaction has been carried out. The results of this study allow further insight into the detailed mechanism of the Cr-catalysed ethylene tetramerisation.

Results and Discussion

Since the recent discovery of the selective tetramerisation of ethylene to 1-octene, extensive research has been carried out to elucidate the influence of ligand structure on the reaction. Particular emphasis was placed on determining possible switches from tri- to tetramerisation and *vice versa* through a systematic investigation of different substituents at the P-Ar moiety.^[11] Furthermore, kinetic studies on the catalyst system $Cr(acac)_3$, *i*-Pr PNP, MAO in cumene as reaction solvent, have revealed that an increase in pressure from 20 to 45 bar led to an increased formation of 1-octene. This is indicative of a strong ethylene

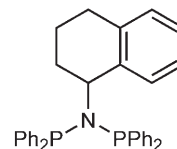


Figure 1. 1,2,3,4-Tetrahydronaphthylamine-bis(diphenylphosphine).

concentration dependence of the product distribution in general and the formation of 1-octene in particular.^[12] This discovery prompted us to carry out an extended study over a very wide pressure range (from 45 to 100 bar) in order to examine whether 1-octene selectivity could be further boosted. Since temperature is known to be an important factor for tri- vs. tetramerisation as well, we decided to include a temperature variation from 40 to 80 °C in our studies. This should allow further insight into the reaction mechanism and the limits of the process parameters with respect to 1-octene formation. It should be noted that our study was not aimed at providing conclusive kinetic data for the design of a commercial reactor. However, throughout the study we ensured that the catalyst efficiencies remained in the same order of magnitude to allow for a realistic comparison of selectivity data. Our ligand of choice was 1,2,3,4-tetrahydronaphthylamine-bis(diphenylphosphine) (= THN PNP, see Figure 1), since this ligand gives a very high yield of the most desired products, namely 1-octene and 1-hexene (i.e., 90% combined yield with THN PNP vs. 80–85% for *i*-Pr PNP). This should facilitate more meaningful mechanistic insight, as side reactions become less significant.

Table 1 displays the results from the above-mentioned pressure (45–100 bar) and temperature (40–80 °C) variation studies. 1-Octene and 1-hexene are clearly the main products under these conditions and their combined yield represents around 90% of the liquid products (column “ S_a ” in Table 1). This combined yield was constant throughout the pressure and temperature range with a variance of only 3–4% over the whole set of experiments. The same applies for the combined C_6 and C_8 fractions, which correspond to approximately 95% of the liquid products. The main side products of the reaction are methylenecyclopentane and methylcyclopentane, which were formed in a 1:1 ratio and are given as “ SC_6 cyclics” in Table 1.

Changes in product distribution of the three main products (1-octene, 1-hexene and cyclic C_6 species) was in good accordance with the metallacycle mechanism proposed by Overett et al.^[8] (Scheme 1) throughout the pressure variation experiments (e.g., entries 4–9, Table 1). According to this mechanism, the aluminoxane-activated chromium catalyst **1** readily coordinates two ethylene molecules through oxida-

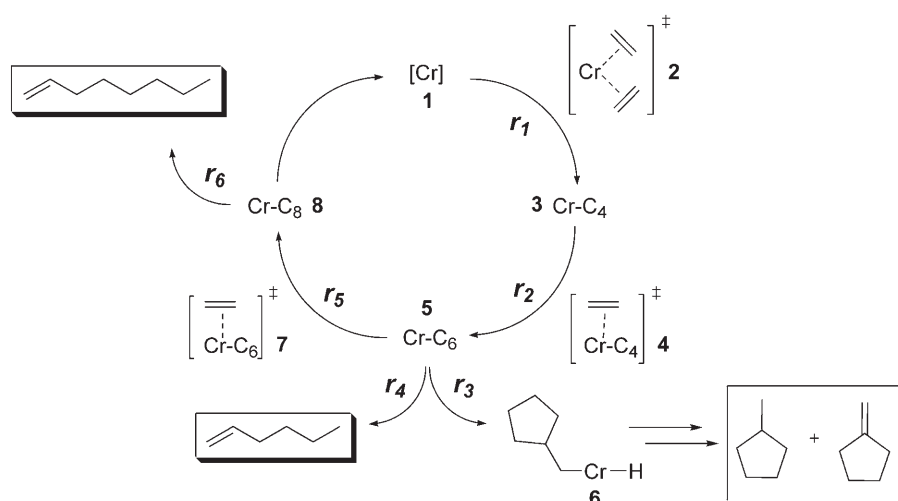
Table 1. Pressure and temperature variation for 1,2,3,4-tetrahydronaphthyl PNP^[a]

No	T [°C]	p [bar]	n _{product} [g]	Efficiency ^[b] [g g ⁻¹ Cr ⁻¹]	Selectivity ^[b] [%]						
					S _{1-C6}	S _{C6 cyclics}	S _{1-C8}	S _α ^[c]	S _{C6+C8}	S _{1-C6 in C6}	S _{1-C8 in C8}
1	40	45	39.9	156,556	16.3	3.8	72.7	88.9	94.4	77.7	99.2
2	40	70	31.5	120,973	14.1	3.6	74.6	88.7	94.0	74.9	99.2
3	40	100	36.4	140,258	13.6	3.6	74.5	88.1	94.2	74.4	98.2
4	60	45	18.3	70,556	32.1	2.8	58.8	90.9	96.6	86.9	98.7
5	60	60	31.9	122,730	28.6	2.8	62.6	91.2	95.7	87.4	99.3
6	60	70	29.8	114,458	27.4	2.7	63.3	90.7	95.2	87.2	99.4
7	60	80	35.6	136,812	26.4	2.7	64.8	91.1	95.6	87.8	98.9
8	60	90	33.6	129,045	26.0	2.8	65.4	91.4	96.7	87.2	97.8
9	60	100	35.3	135,575	25.7	2.8	64.8	90.5	95.8	86.8	97.9
10	80	45	16.4	63,196	49.1	1.8	41.5	89.2	94.5	92.6	98.0
11	80	70	15.3	58,674	41.6	1.9	46.4	88.0	92.7	91.6	98.1
12	80	100	25.7	98,657	40.2	2.1	50.8	91.1	95.9	92.3	97.3

^[a] 5 μmol Cr(acac)₃, L:[Cr] = 1:1, activator: MMAO-3 A (7 wt % solution in heptane from Akzo Nobel), MMAO-3 A:[Cr] = 1:270, solvent: 200 mL of cyclohexane, reaction time: 20 min.

^[b] Calculations based on liquid products alone.

^[c] S_α = total alpha selectivity = S_{1C-6} + S_{1-C8}.



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

tive addition (species **2** in Scheme 1) to form the metallacyclopentane intermediate **3**. A further ethylene unit is inserted into this species *via* intermediate **4** yielding the metallacycloheptane compound **5**. This species can then undergo several possible reaction pathways which will lead to the three main products. From an analysis of the final product mixture, the most prevalent route is the insertion of a fourth ethylene unit into the metallacycle ring (step **r**₅, Scheme 1), thus forming the metallacyclononane intermediate **8** which undergoes rapid elimination to the main reaction product, 1-octene.

The second possible pathway is the reductive elimination of 1-hexene from the metallacycloheptane intermediate **5** (**r**₄ in Scheme 1) and the third potential

pathway is the suggested rearrangement of **5** to a cyclopentylmethyl hydride species **6** (**r**₃ in Scheme 1). The formation of methylenecyclopentane and methylcyclopentane is proposed to occur *via* a subsequent disproportionation step.

This proposed mechanism is in good accordance with the experimental data found in our set of experiments. Upon increasing the ethylene pressure, and thus ethylene concentration, **r**₅ is favoured over **r**₄ which leads to an increased formation of 1-octene at the expense of 1-hexene. Since the insertion of a fifth ethylene unit into intermediate **8** leading to the formation of 1-decene occurs to a relatively small extent, the ethylene concentration dependency of this step cannot be resolved and is therefore neglected in

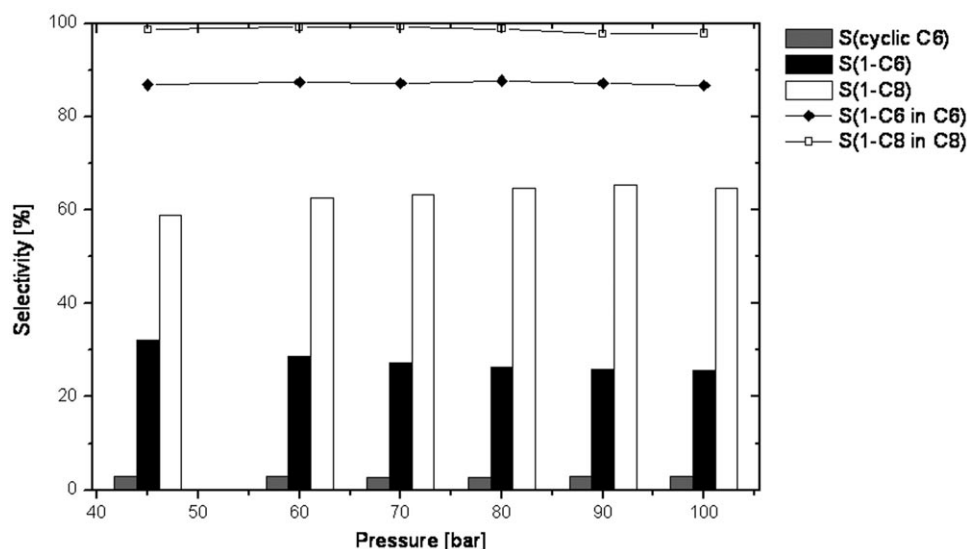


Figure 2. Pressure variation at 60°C; S(1-C6) and S(1-C8) are total selectivities; S(1-C6 in C6) and S(1-C8 in C8) are selectivities relative to the overall amount of C₆ and C₈, respectively.

Scheme 1. The same applies for the likely rearrangement of **8** to give cyclic C₈ products, which is also an alternative pathway to **r**₆. This step plays a minor role and is therefore also ignored. This is consistent with the fact that the effect of ethylene concentration is only detectable in the ratio of the three main products. The effect of ethylene concentration on the minor products was too small to make any sensible conclusions. This is exemplified by Figure 2 which provides an overview of the product distribution with varying ethylene pressure at 60°C.

It is remarkable that the formation of 1-octene only increased by 6% upon increasing the pressure from 45 to 80 bar, while a further increase in pressure to 100 bar did not increase S(1-C8) at all. As we will show below, the ethylene concentration in the liquid phase more than doubles over this pressure range, and we would therefore expect a significant shift in selectivity. However, a maximum yield to 1-octene seems to be reached that cannot be exceeded. Pressure variation experiments at 40°C (entries 1–3, Table 1) and 80°C (entries 10–12, Table 1) are consistent with the same general trend of increasing 1-octene selectivity with increasing ethylene pressure. It is noteworthy that this effect was more pronounced at higher temperatures (i.e., 9% vs. 2% absolute change at 80 vs. 40°C).

The formation of the cyclic C₆ side products seems to be independent of ethylene concentration over this pressure range. For example, the selectivity towards methylenecyclopentane and methylcyclopentane stayed at a precisely constant level of 2.8 ± 0.1% upon varying the pressure from 45 to 100 bar at 60°C. This indicates that the rate-determining step for the

formation of these products is not dependent on the ethylene concentration, which is in good accordance with the proposed mechanism that suggests that methylene- and methylcyclopentane are formed by rearrangement of species **5** or **7**.

The results of the temperature study (see Table 1) reveal considerable changes in the product distribution with temperature variation. In this study the temperature was varied from 40 to 60 to 80°C (at three ethylene pressures of 45, 70 and 100 bar). The common trend here is a significant increase in selectivity towards 1-hexene with increasing temperature, which occurs at the expense of 1-octene and cyclic C₆ products. On the other hand, the total α -selectivity (S_{α}) remained constant at 89–91% throughout the whole temperature range. Concurrently, an increase in temperature leads to a decrease in the formation of cyclic C₆ products and thus an increase in selectivity to 1-hexene within the C₆ fraction (see column “S_{1-C6} in C₆” in Table 1). In terms of the reaction mechanism depicted in Scheme 1 it can be concluded that at higher temperatures, the reductive elimination of 1-hexene (**r**₄) is favoured over β -hydride transfer to chromium (**r**₃), i.e., “S_{cyclic C6}” drops from 4 to 2% upon increasing the temperature from 40 to 80°C while “S_{1-C6 in C6}” in turn increases from 76 to 92%. Furthermore, **r**₄ is favoured over **r**₅ (elimination of 1-hexene from the metallacycloheptane species is favoured over further insertion of ethylene to form the metallacyclononane species), i.e., “S_{1-C6}” increases from 16 to 49% when going from 40 to 80°C, while “S_{1-C8}” concurrently decreases from 72 to 41%. Whereas the first effect should be independent of ethylene pressure as indicated above, the second is clear-

ly influenced by ethylene concentration in the liquid phase, which in turn is a function of both pressure and temperature.

In order to elucidate the temperature and pressure dependence of steps r_4 and r_5 further, and more specifically to be in a position to differentiate ethylene solubility effects from the temperature dependence of the individual rate constants, we decided to determine the ethylene solubility (as molar concentration) in cyclohexane over the temperature and pressure range relevant to these experiments. The VLE data for this binary system were calculated using the perturbed chain SAFT (PC-SAFT) equation of state.^[13] This equation gives reasonable results for the calculation of high-pressure phase equilibria in the sub- and supercritical state. In addition to this it can be used to calculate the phase equilibrium without further parameterisation over a wide pressure and temperature range.^[13] The PC-SAFT equation of state requires three parameters for each pure component and one binary interaction parameter. The pure component parameter for ethylene and cyclohexane has been published previously^[14] and the binary interaction parameter was fitted to published experimental data^[15] to yield a value of 0.031 for k_{ij} . The interaction parameter is not dependent on temperature or composition. Subsequently, the VLE curves were calculated over the desired temperature and pressure range (see the Supporting Information). The molar compositions of the liquid phase relevant to the interpretation of the catalytic data of this study are summarised in Table 2.

As expected, an increase in temperature at constant pressure is accompanied by a decrease in ethylene concentration (i.e., from $X_{\text{ethylene}}=0.52$ to 0.35 for 40 °C and 80 °C at 45 bar, see Table 2). Consequently, reaction conditions with comparable ethylene concentrations have to be considered, e.g., 40 °C and 45 bar ($X_{\text{ethylene}}=0.52$, entry 1 in Table 1) vs. 80 °C and 70 bar ($X_{\text{ethylene}}=0.53$, entry 11 in Table 1) to determine the temperature dependency of r_5 . Comparing the selectivities at these conditions with similar ethyl-

ene solubility clearly reveals that the predominant parameter which determines r_4 and r_5 is in fact the temperature. For example, for $X_{\text{ethylene}}=0.52$ –0.53 the total selectivity towards 1-hexene increases from 16.3 % at 40 °C to 41.6 % at 80 °C, while the selectivity towards 1-octene drops concurrently from 72.7 % at 40 °C to 46.4 % at 80 °C (compare entries 1 and 11, Table 1).

The impact of temperature on selectivity is even more pronounced for reactions at constant pressure (and thus decreasing ethylene concentration). For example, at 45 bar the selectivity towards 1-octene drops from 72.7 % to 40.0 % upon going from 40 to 80 °C (compare entries 1 and 10, Table 1). It can thus be concluded that both r_4 and r_5 are strongly temperature dependent. The pressure influence on the C_6 - vs. C_8 -selectivity is much smaller. This observation is of fundamental interest, since it indicates that the stability of larger metallacycle intermediates (in terms of elimination to 1-alkenes) is predominantly controlled by the reaction temperature. Increasing the concentration of larger metallacycles (i.e., metallacyclononane) by employing higher ethylene concentrations is thus limited to a certain extent. Further optimisation of 1-octene formation and the suppression of side-products by the adjustment of reaction parameters therefore seem unlikely.

Conclusions

In conclusion, we have successfully investigated the pressure and temperature dependency of the recently discovered ethylene tetramerisation reaction over an extended pressure and temperature range. This study was exclusively conducted on the $\text{Cr}(\text{acac})_3/1,2,3,4\text{-tetrahydronaphthylamine-bis(diphenylphosphine)}/\text{MMAO-3A}$ catalyst system.

The experimental findings are consistent with the recently proposed metallacycle mechanism. The insertion of ethylene into the metallacycloheptane species was found to be slightly pressure dependent. However, the reaction temperature seems to be the primary factor that determines whether 1-hexene is eliminated from the metallacycloheptane intermediate or if further ethylene is incorporated to form a larger metallacycle (and ultimately 1-octene). These conclusions were derived by correlating the ethylene concentration at specific reaction conditions with the respective catalytic results at these conditions. The determination of the ethylene concentration in binary ethylene/cyclohexane mixtures was conducted by extending literature VLE curves into the relevant temperature and pressure range with the perturbed chain SAFT (PC-SAFT) equation of state.

The formation of methylenecyclopentane and methylocyclopentane seems to be independent of eth-

Table 2. Molar fraction X_{ethylene} in cyclohexane at different temperatures and pressures.^[a]

T [°C]	Pressure [bar]							
	40	45	50	60	70	80	90	100
40	0.47	0.52	0.58	0.70	0.83	-	-	-
60	0.37	0.42	0.46	0.55	0.63	0.72	0.81	-
80	0.31	0.35	0.39	0.46	0.53	0.59	0.66	0.73

^[a] Calculations based on the PC-SAFT equation of state (for more information see Supporting Information); note that the fields marked “-” represent a monophasic regime. Here, the phase composition could not be detected, as no information on the amount of ethylene in the reactor was available.

ylene pressure which indicates that these side products stem from a rearrangement step that does not involve ethylene.

Experimental Section

General Remarks

All chemicals were handled either in a glove box or under an inert argon atmosphere using standard Schlenk techniques. Solvents were dried using a solvent purification system (degassing with argon and percolation over neutral alumina by a commercial solvent purification system). Chromium acetylacetonate and ligand stock solutions in cyclohexane were prepared and stored in the glove box for precise catalyst quantification. Ethylene 3.5 was obtained from Linde Germany. Catalytic runs were conducted in a 450 mL Parr autoclave equipped with gas entrainment stirrer for optimum gas saturation of the liquid (a publication aiming to show the importance of sufficient gas transfer for gas-liquid reactions is in preparation).

Catalytic Runs

All catalytic runs were carried out according to the following procedure. 5 μmol of $\text{Cr}(\text{acac})_3$ and an equimolar amount of the respective ligand was taken from a prepared stock solution and transferred into a Schlenk tube inside a glove box. This solution was made up with cyclohexane to a total volume of 5 mL. The solution was activated under an inert argon atmosphere with 270 equivalents MMAO-3A (7 wt% solution in heptane) with respect to the chromium. This activated solution was transferred immediately into the autoclave containing 195 mL of cyclohexane at the desired reaction temperature. The reaction was initiated by pressurisation with ethylene which was fed on demand throughout the duration of the experiment. The temperature was monitored via an internal thermocouple and maintained by cooling the autoclave with ice water. After 20 min, the reaction was terminated by closing the ethylene supply, switching off the gas entrainment stirrer and cooling the autoclave to 0°C. Next, the autoclave was depressurised slowly. The liquid product was filtered and submitted for GC-FID analysis (apparatus: Varian 3900, column CP Sil Pona CB 50 m $\times$ 0.21 mm).

Synthesis of 1,2,3,4-Tetrahydronaphthyl PNP

Bis(diphenylphosphino)-1,2,3,4-tetrahydronaphthylamine was synthesized according to procedures reported in the literature.^[16] A solution of 2.54 equivalents of the corresponding amine in 10 mL of toluene was prepared and reacted with 1.0 equivalent diphenylphosphine chloride by dropwise addition at -5°C . The solution was stirred for 30 min. The precipitate (amine hydrochloride) was removed by filtration through a Schlenk frit and washed with toluene (5 mL). Sub-

sequently, the reaction mixture was cooled to -10°C in an ice/salt bath, 1.0 equivalent of triethylamine was added and the solution was stirred for 30 min. The reaction was completed by dropwise addition of 1.0 equivalent of diphenylphosphine chloride and overnight stirring at room temperature. Precipitated amine hydrochloride was removed by filtration through a Schlenk frit and washed with toluene. Purification of the crude product was achieved by filtration over dry silica gel (230–400 mesh) and repeated recrystallisation from toluene/pentane. NMR data were obtained on a Bruker DPX-300 FT spectrometer. ^1H NMR (300 MHz, CDCl_3): δ = 1.32–3.02 (m, 6H), 4.67 (m, 1H, N-CH<), 7.20 (m, 24H, Ar-H); ^{13}C NMR (75 MHz, CDCl_3): δ = 8.6, 21.8, 29.4, 45.8, 125.3, 126.6, 127.9, 128.1, 128.5, 129.0, 132.4, 133.8, 134.1, 138.3, 139.6; ^{31}P NMR (121 MHz, CDCl_3): δ = 51.2 ppm.

Acknowledgements

The authors would like to thank Sasol Technology for financial support and permission to publish these results. In particular we would like to thank Drs. Kevin Blann and Annette Bollmann for great scientific collaboration and helpful advice and Professor Wolfgang Arlt is acknowledged for fruitful discussions in the context of the ethylene solubility calculations. Nicola Taccardi would like to acknowledge the DIAC Polytechnic of Bari (Italy) for giving him the opportunity to work under the supervision of Prof. Wasserscheid.

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