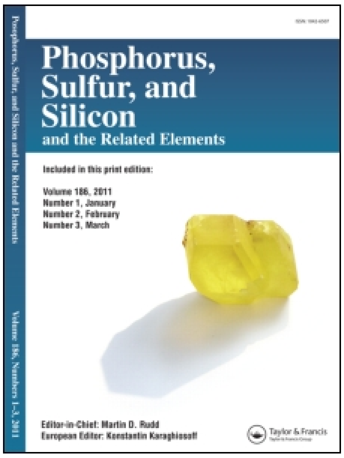


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Phosphanyl Ureas as Ligands for Ethylene Oligomerization: A Cascade Reaction

Olaf Kühl[a]; Peter Lobitz[a]; Normen Peulecke[a]
[a] Institut für Biochemie, Ernst Moritz Arndt Universität Greifswald, Greifswald, Germany

To cite this Article Kühl, Olaf , Lobitz, Peter and Peulecke, Normen(2008) 'Phosphanyl Ureas as Ligands for Ethylene Oligomerization: A Cascade Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 11, 2777 — 2783

To link to this Article: DOI: 10.1080/10426500802004352

URL: http://dx.doi.org/10.1080/10426500802004352

Phosphorus, Sulfur, and Silicon, 183:2777–2783, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802004352

Phosphanyl Ureas as Ligands for Ethylene Oligomerization: A Cascade Reaction

Olaf Kühl, Peter Lobitz, and Normen Peulecke
Institut für Biochemie, Ernst Moritz Arndt Universität Greifswald,
Greifswald, Germany

*The phosphanyl urea ligands MeNHC(O)NMePR$_2$ (**1**: R = Ph and **2**: R = 2,4-tBu$_2$C$_6$H$_3$O) form effective ethylene oligomerization catalysts with [Ni(cod)$_2$] (cod = 1,5 cyclooctadiene). Whereas the primary product with **1** is butene, **2** initiates a cascade reaction leading to hexenes and octenes. In the first reaction cycle ethylene is dimerized to butene, which serves as feedstock for the second dimerization cycle to the final products hexenes and octenes.*

Keywords Cascade reaction; ethylene oligomerization; homogenous catalysis; nickel; phosphino urea; phosphino amine; transition metal

INTRODUCTION

There is great interest to develop catalytical systems for the copolymerization of ethylene with other olefins.[1] A particularly challenging task is to generate the comonomer from ethylene during the reaction. This can be achieved by a few tandem processes recently published by Bazan et al.,[2] in which two catalysts operate simultaneously. A common drawback of commercial ethylene polymerization systems is the need for a cocatalyst to activate the precatalyst species prior to the catalytic chain reaction. These activators are metal containing species that are employed in huge excess (up to 1000 fold) and thus create a major waste and product purification problem. This and reproducibility problems are the reasons for a great industrial interest to find ethylene oligomerization and polymerization processes that dispense with the need for cocatalysts.[3]

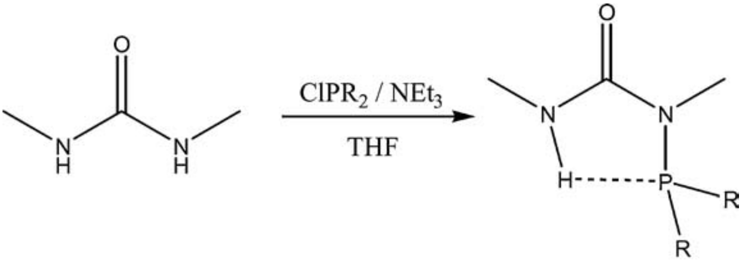
Received 6 February 2008; accepted 16 February 2008.

We thank Prof J. Heinicke, for his ongoing support and the use of his laboratory facilities.

Address correspondence to PD Dr. Olaf Kühl, Institut für Biochemie, Ernst Moritz Arndt Universität Greifswald, Felix-Hausdorff-Strasse 4, D-17489 Greifswald, Germany. E-mail: dockuhl@gmail.com

RESULTS AND DISCUSSION

The ligands **1** and **2** were prepared from *N*,*N*′-dimethyl urea and the appropriate chlorophosphine or chlorophosphite in THF with triethyl amine as auxiliary base (Scheme 1).[4] Toluene or dichloromethane as solvents lead in the case of chlorodiphenylphosphine to the disubstituted product.



1: R = Ph

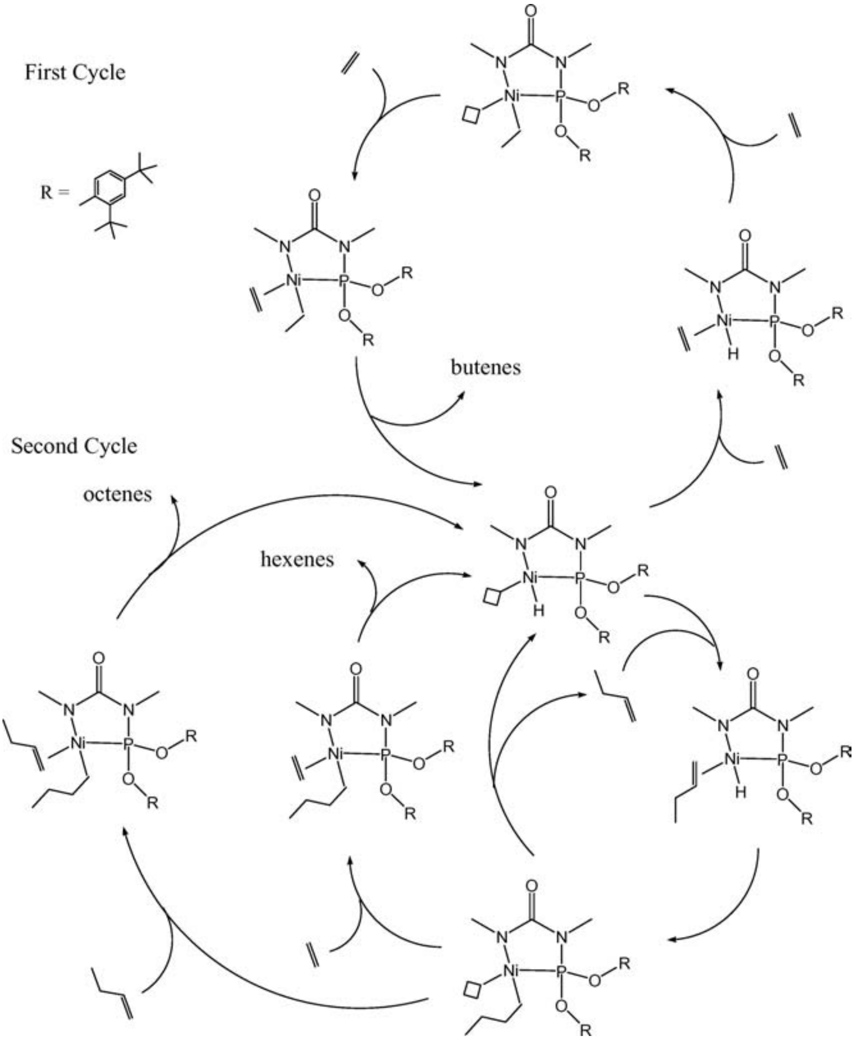
2: R = 2,4-tBu$_2$C$_6$H$_3$

SCHEME 1 Synthesis of the ligands.

Reaction of the ligands **1** and **2** with [Ni(cod)$_2$] in toluene affords dark orange solutions. When these solutions are transferred into a steel autoclave with magnetic stirring and 50 bar ethylene pressure and are then placed into a 100°C hot oil bath, ethylene is oligomerized to C$_4$-C$_8$ olefins after a short initiation period. Attempts to carry out the reaction at lower temperatures failed.

The structure of the active catalyst is unknown, but it can be assumed that ligand **1** or **2** binds to nickel with the phosphorus terminus displacing one of the COD ligands. Oxidative addition of the N-H group to nickel then renders the catalytically active Ni-H bond. Keim et al. have established a mechanism for the formation of the active catalyst from [Ni(COD)$_2$] that might very well be operative in the present case.[5]

The two ligands **1** and **2** were carefully selected for their relative electronic properties and steric requirements. **2** has the sterically more demanding and the more electron withdrawing phosphorus group compared to **1**. With the Brookhart catalysts,[6] the steric bulk of the ligand provides steric shielding of the metal's axial positions usually resulting in ethylene polymerization rather than oligomerization for sterically less demanding ligands. **2** is obviously incapable of effectively shielding both axial positions at nickel since the steric bulk is entirely at the phosphorus atom leaving the nitrogen end wide open for chain transfer



SCHEME 2 Proposed mechanism of the cascade reaction using ligand **2**.

reactions. However, it was hoped to see a difference in chain length of the resulting oligomer distribution by going from **1** to **2**. Similarily, a decrease in electron density on the metal due to a more electron withdrawing ligand is expected to result in faster ethylene consumption and thus greater TOF values.[7,8]

Running the ethylene oligomerization reactions under equal conditions—100 μmol catalyst, 50 bar initial ethylene pressure, 100°C

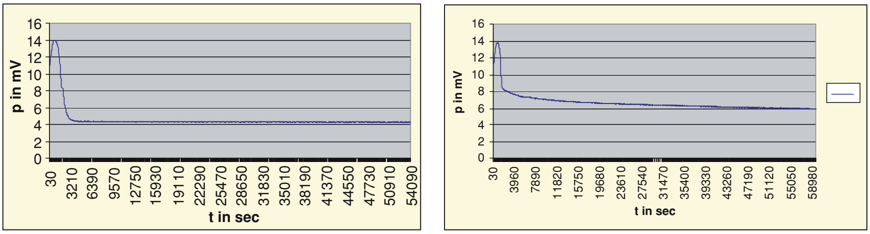


FIGURE 1 Pressure time plot for ethylene oligomerization with ligand **1** (left) and **2** (right).

oil bath temperature, and toluene as solvent—is accompanied indeed by different product distributions and a marked difference in the reaction rates. Whereas **3** yields predominantly 1-butene and *n*-hexenes with a small amount of octenes and an average TOF of 6,000 mol ethylene h^{-1} (mol $Ni)^{-1}$, **4** results in branched hexenes with a much smaller butene fraction and larger share of branched octenes with a significantly increased average TOF of 15,000 mol ethylene h^{-1} (mol $Ni)^{-1}$ during the first cycle [9]. The second cycle displays significantly smaller TOF.

Surprisingly, the main difference between the two ligands was not the chain length or the difference in reaction rates, but the preference of branched oligomers for **4** as opposed to linear ones for **3**. The pressure time plots for the two batch oligomerizations (see Figure 1) also display a marked difference. Whereas the plot for **3** shows normal exponential decay, the plot for **4** displays a transition point where the rate of decay becomes noticeably smaller. As the pressure time plots usually show decay down to a base value (4 mV) corresponding to the butene formed during the reaction, any pressure above this base value originates from the ethylene present in the reaction mixture. A transition point in the pressure time plot thus indicates a sudden decrease in the ethylene uptake rate and thus the occurrence of a second reaction that does not rely on ethylene as a major feedstock.

Uptake of oligomers formed during the reaction cannot be shown from the product distribution simply because branching can have two possible causes.[7] As the oligomer chain grows, a series of β-hydrogen eliminations and subsequent reinsertion normally referred to as "chain walking"[10] leads to isomerization and inner olefins that after adding another ethylene unit result in a branched product. The same product may be obtained by inserting an olefinic oligomer into a metal ethyl bond. The former process is clearly ethylene oligomerization, whereas the latter can best be referred to as ethylene/oligomer cooligomerization.

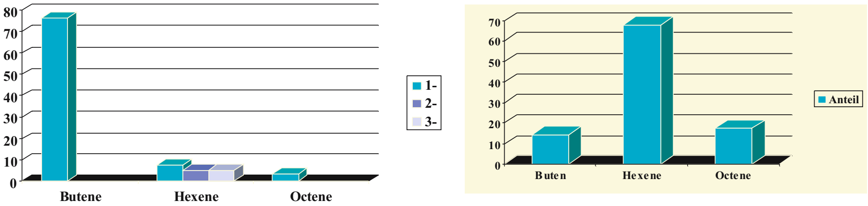


FIGURE 2 Product distribution for ethylene oligomerization with ligand **1** (left) and **2** (right).

Analysis of the pressure time plot can be helpful in distinguishing between the two mechanisms. In chain walking isomerization has to be fast compared to chain propagation and thus the reaction depends on the ethylene uptake. The result is a single rate pressure time plot without any transition points. If during the reaction the uptake and insertion of any oligomer formed becomes significant, then the reaction continues via oligomer uptake at the expense of ethylene consumption. This results in more shallow pressure decay and thus a transition point in the pressure time plot as seen for **4**.

From the product distribution (see Figure 2) for the two ligands it can be seen that the chain length for the products from **4** is essentially one ethylene group longer than for **3**. To infer from this, that the steric requirements of **2** result in an increased preference for chain propagation compared to **1**, could be ill advised. It might only reflect the difference in feedstock used by the two dimerization catalysts. Catalyst **3** dimerizes ethylene to butenes with a significant amount of trimerization occurring, whereas **4** seemingly generates octenes by dimerization of butene rather than chain propagation using ethylene as feedstock.

The process observed with **4** can be explained as a cascade reaction (see Scheme 2). In the first step the catalyst dimerizes ethylene to butene that is used as feedstock in the second dimerization reaction. The butyl complex initially formed can then either use ethylene to form hexenes in a heterodimerization reaction or a second molecule of butene in a homodimerization reaction to form octenes. Such reactions are rare in ethylene oligomerization reactions and usually occur only as a minor side reaction at prolonged reaction times.[7,11] Here incorporation of higher olefins is the main reaction after only 20 min.

The second process in the cascade is slower than the first as seen from the pressure time plot in combination with the product distribution. However, as butene binds more strongly to nickel than ethylene[12] the butyl complex is formed and cycle 1 is suppressed, once a critical concentration of butene is reached or the solution is sufficiently depleted of ethylene due to low solubility of ethylene in toluene.

Even in the second cycle uptake of ethylene by the intermediate butyl complex is more rapid than that of butene as can be seen from the product distribution (far more hexene than octene is formed).

EXPERIMENTAL

All operations with phosphines and catalyst solutions were carried out under carefully dried, oxygen-free argon, using Schlenk techniques. Toluene was ketyl-dried and distilled before use. $Ni(COD)_2$,[13] phosphanylurea[4] and phosphitylurea[4] were synthesized as reported; all other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. GC analyses were carried out using a gas chromatograph Hewlett Packard 5890, column HP-5(30 m) (cross linked 5% PhMe silicone), 40–150°C, 10 min isotherm, 4°C/min. The turnover frequency (TOF) was determined as average TOF over the effective reaction time. The effective reaction time was monitored with online pressure registration (HEJU pressure sensor 1–100 bar from Juchheim connected to digital multimeter and PC) with the end point detected when a stable pressure was reached (pressure caused by low boiling point products, i.e., butene).

Ethylene Oligomerization—General Procedure

Compound **1** (27.8 mg, 100 μmol) or compound **2** (29.0 mg, 100 μmol) and $[Ni(COD)_2]$ (27.5 mg, 100 μmol) were dissolved in toluene (each in 8 mL) at 0°C, combined, and stirred for 5 min at 0°C and for 10 min at 20°C to give orange or yellow solutions. The solutions were transferred by a syringe (Teflon canula) to a stainless-steel autoclave (75 mL), equipped with a Teflon coated magnetic stirrer, gas inlet and sample inlet valves, mechanic or electronic pressure gauge, and a safety diaphragm. Ethylene was added (p_{start} ca. 50 bar), and the autoclave was placed into a preheated bath (100°C) and heated overnight (ca. 15 h). After cooling unreacted ethylene was allowed to escape, volatiles were condensed in a cooling trap (−78°C); mass loss was usually <2%.

REFERENCES

[1] F. Speiser, P. Braunstein, L. Saussine, and R. Welter, *Organometallics*, **23,** 2613 (2004).

[2] (a) Z. J. A. Komon, G. M. Diamond, M. K. Leclerc, V. Murphy, M. Okazaki, and G. C. Bazan, *J. Am. Chem. Soc.*, **124,** 15280 (2002); (b) Z. J. A. Komon, X. Bu, and G. C.

Bazan, *J. Am. Chem. Soc.*, **122,** 1830 (2000); (c) R. W. Barnhart, G. C. Bazan, and T. Mourey, *J. Am. Chem. Soc.*, **120,** 1082 **(**1998).

[3] (a) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben, and M. W. Day, *Organometallics*, **17,** 3149 (1998); (b) S. Y. Desjardins, K. J. Cavell, J. L. Hoare, B. W. Skelton, A. N. Sobolev, A. W. White, and W. J. Keim, *J. Organomet. Chem.*, **544,** 163 (1997); (c) J. L. Hoare, K. J. Cavell, R. Hecker, B. W. Skelton, and A. W. White, *J. Chem. Soc., Dalton Trans.*, 2197 (1996).

[4] (a) O. Kühl, P. Lönnecke, *Inorg. Chem.*, **41,** 4315 (2002); (b) O. Kühl, *Dalton Trans.*, 949 (2003); (c) O. Kühl, W. Langel, *Inorg. Chem. Commun.*, **6,** 74 (2003); (d) S. Blaurock, O. Kühl, and E. Hey-Hawkins, *Organometallics*, **16,** 807 (1997); (e) O. Kühl, S. Blaurock, *Inorg. Chem.*, **43,** 6543 (2004); (f) O. Kühl, S. Blaurock, and T. Carls, *Inorg. Chem.*, **45,** 1723 (2006); (g) O. Kühl, *Coord. Chem. Rev.*, **250,** 2867 (2006).

[5] M. Peuckert and W. Keim, *Organometallics*, **2,** 594 (1983).

[6] (a) G. J. P. Britovsek, V. C. Gibson, and D. F. Waas, *Angew. Chem. Int. Ed.*, **38,** 428 (1999); (b) A. L. McKinnon and M. C. Baird, *J. Organomet. Chem.*, **683,** 114 (2003); (c) C. Bianchini, L. Gonsalvi, W. Oberhauser, D. Sémeril, P. Brüggeler, and R. Gutmann, *Dalton Trans.*, 3869 (2003).

[7] S. A. Svejda and M. Brookhart, *Organometallics*, **18,** 65 (1999).

[8] (a) W.-H. Sun, W. Zhang, T. Gao, X. Tang, L. Chen, Y. Li, and X. Jin, *J. Organomet. Chem.*, **689,** 917 (2004); (b) J. M. Malinoski and M. Brookhart, *Organometallics*, **22,** 5324 (2003).

[9] The average TOF was measured over the entire period of ethylene uptake. As the amount of available ethylene decreased in the course of the reaction, the maximum TOF of the reaction is significantly higher.

[10] M. D. Leatherman, S. A. Svejda, L. K. Johnson, and M. Brookhart, *J. Am. Chem. Soc.*, **125,** 3068 (2003).

[11] (a) B. L. Small and M. Brookhart, *J. Am. Chem. Soc.*, **120,** 7143 (1998); (b) F. Speiser, P. Braunstein, and L. Saussine, *Organometallics*, **23,** 2625 (2004).

[12] J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim, and G. Fink, *Chem. Eur. J.*, **9,** 6093 (2003), and references cited therein.

[13] R. A. Shum, *Inorg. Synth.* **15,** 5 (1974).