Highly efficient P–N nickel(II) complexes for the dimerisation of ethylene†

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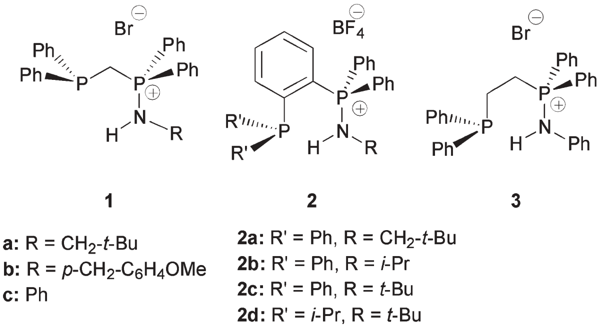
New P–N ligands featuring a phosphino group and an iminophosphorane moiety were successfully employed in the nickel-catalysed dimerisation of ethylene.

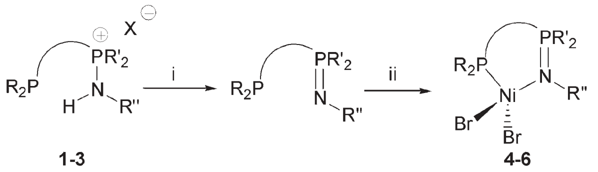
Short chain length α-olefins have found numerous applications for the preparation of commercially relevant compounds.[1] Particularly, they are used as comonomers in the synthesis of low-density polyethylene. Among processes that are able to furnish α-olefins (cracking of paraffins, dehydrogenation, dehydration, chain growth) the oligomerisation of ethylene is probably the most rewarding process since it can produce selectively C_4, C_6 and C_8 α-olefins which are the most valuable compounds in terms of their scope of applications.[2] Not surprisingly, the last decade has seen a rapid development of homogeneous catalysts operating under "Ziegler–Natta" conditions.[3,4] Despite recent advances in the nickel-catalysed dimerisation of ethylene,[5–9] the design of highly selective catalysts is still a challenging area of research. Needless to say, the development of easily available low-cost ligands is also greatly desirable.

Recently we devised two straightforward routes to mixed P–N ligands[10] of general formula (R_2P–spacer–PR_2 = N–R) that incorporate both a phosphino group and an iminophosphorane[11] moiety. A whole family of ligands featuring different backbones and substituents was accessible. As part of a wide program dedicated to the use of these new systems in homogeneous catalysis, their activity in the nickel promoted dimerisation of ethylene was explored. Indeed, unsymmetrical bidentate P∼N type ligands have already proved to be efficient systems for this process.[12,13] Phosphinoiminophosphorane ligands were generated *in situ* by deprotonation of the corresponding phosphinoaminophosphonium salts **1**, **2** and **3** (Scheme 1). The latter being easily synthesized following a two-step procedure from bis(diphenylphosphino)methane (dppm), triphenylphosphine and bis(diphenylphosphino)ethane (dppe), respectively.

Nickel dibromide complexes **4**, **5** and **6** were then readily prepared in good yields by reacting **1**, **2** and **3** with *n*-butyllithium followed by a subsequent trapping reaction of the formed iminophosphorane with $NiBr_2$.DME (DME = dimethoxyethane) in THF at room temperature (Scheme 2).‡



Scheme 1 Phosphinoaminophosphonium salts selected for this study.



Scheme 2 *Reagents and conditions*: (i) *n*-BuLi (1 equiv.), THF, −78 °C to r.t.; (ii) $[NiBr_2(DME)]$ (1 equiv.), THF, r.t.

Complexes **4–6** are all paramagnetic and were characterized by elemental analysis, mass spectrometry and by X-ray crystallography in some cases.§

As a representative example, a view of complex **5b**¶ is given in Fig. 1, and the most relevant metric parameters are listed in the corresponding caption. As expected, the geometry around the d^8 nickel atom is pseudo-tetrahedral (bond angles Br–Ni–P(1) of 107.27(4) and 103.87(2)°).

The catalytic activity of complexes **4–6** (Scheme 3) was then evaluated in the oligomerisation of ethylene. In a first set of experiments, reactions were conducted at 45 °C in the presence of MAO as cocatalyst (300 equiv.), toluene as solvent, and under 30 bar of ethylene.|| Results of these experiments are summarized in Table 1. A first important point concerns the distribution of products: just butenes and hexenes were formed (only traces of octenes were detected by GC in some experiments). No polyethylene is produced during the reaction. This dimerisation process even turns out to be very selective giving butenes (between 89.8 and 96.7%) with up to 85% of 1-butene, and few hexenes (between 3.6 and 10%). Such selectivities compare favorably with the performances of best known systems.[5,13] Yet, the productivity observed (up to 106 × 10^3 $mol_{C_2H_4}$ mol_{Ni}^{-1} h^{-1}) is slightly better than that of other efficient catalysts (TOF around 80 × 10^3 $mol_{C_2H_4}$ mol_{Ni}^{-1} h^{-1}).[5,9]

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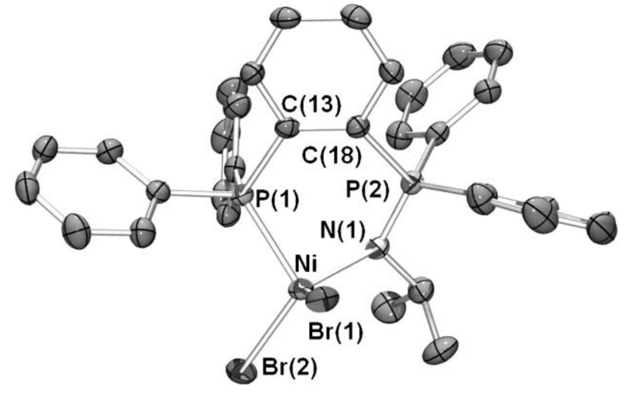
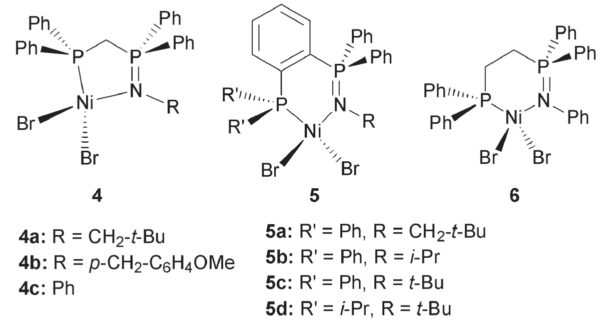


Fig. 1 Molecular structure of complex **5b**. Thermal ellipsoids are drawn to the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Br(1)–Ni(1) 2.3912(4), Br(2)–Ni(1) 2.3667(4), Ni(1)–N(1) 1.969(2), Ni(1)–P(1) 2.2741(7), P(1)–C(13) 1.824(2), P(2)–N(1) 1.600(2), P(2)–C(18) 1.813(3), C(13)–C(18) 1.407(3); N(1)–Ni(1)–P(1) 91.43(6), N(1)–Ni(1)–Br(2) 122.94(6), P(1)–Ni(1)–Br(2) 107.26(2), N(1)–Ni(1)–Br(1) 107.35(6), P(1)–Ni(1)–Br(1) 103.87(2), Br(2)–Ni(1)–Br(1) 118.68(2), C(13)–P(1)–Ni(1) 107.46(8), N(1)–P(2)–C(18) 114.1(1), P(2)–N(1)–Ni(1) 123.7(1), C(18)–C(13)–P(1) 122.2(2), C(13)–C(18)–P(2) 127.2(2).



Scheme 3 Nickel dibromide phosphinoiminophosphorane complexes selected for this study.

It clearly appears that catalysts **5** which feature a rigid six-membered metallacycle are more active than catalysts **4** (see entries 1 and 4). However the increase of activity observed with complexes **5** is accompanied by a decrease of the selectivity in 1-butene (from 83.4 to 67.5% with catalysts **4a** and **5a** which feature the same substitution pattern at phosphorus and nitrogen). Interestingly, catalyst **6** despite its six-membered but flexible metallacyle gives only moderate results in term of both productivity and selectivity (entry 8). Moreover, the nature of the functional group at the nitrogen atom seems to affect the catalytic performances. of complexes **4** only to a minor extent (see entries 1–3), while it plays a decisive role for complexes **5**. For example, the presence of *t*-Bu group dramatically reduces their catalytic activity (compare entries 4, 5 with entry 6). Besides, the phosphorus substituent has only a minor influence on the selectivity of the catalytic reaction (entries 6 and 7). Overall, the most promising results were obtained with complex **5b** (entry 5, TOF = 106×10^3 $\mathrm{mol_{C_2H_4}\ mol_{Ni}^{-1}\ h^{-1}}$).

Table 1 Ethylene oligomerisation with complexes **4–6**[a]

Entry	Catalyst	TOF × 10^{-3} [b]	C_4 (%) [1-C_4 (%)][c]	C_6 (%) [1-C_6 (%)][c]
1	**4a**	45.3	93.9 [83.4]	6.1 [32.7]
2	**4b**	65.8	92.8 [77.0]	7.2 [29.4]
3	**4c**	42.0	94.6 [85.9]	5.4 [45.1]
4	**5a**	96.7	96.3 [67.5]	3.7 [39.8]
5	**5b**	106.5	97.7 [61.4]	2.3 [73.9]
6	**5c**	21.1	95.1 [67.9]	4.9 [45.8]
7	**5d**	23.6	89.8 [55.4]	10.2 [58.6]
8	**6**	44.1	96.7 [57.1]	3.3 [36.3]

[a] *Conditions*: T = 45 °C, 30 bar C_2H_4, 1 h, 2×10^{-2} mmol Ni complex, 300 equiv. MAO, solvent: toluene (30 mL). [b] TOF = mol ethylene consumed per mol of Ni h^{-1}. [c] C_n, amount of olefin with n carbon atoms in the oligomers; α-C_n, amount of terminal alkene in the C_n fraction; as determined by quantitative GLC.

Table 2 Influence of reaction time and temperature on catalysis with **5b**

Entry	T/°C	t	TOF × 10^{-3} [a]	C_4 (%) [1-C_4 (%)][b]	C_6 (%) [1-C_6 (%)][b]
1	45	1 h	106.5	97.7 [61.4]	2.3 [73.9]
2	r.t.	1 h	166.0	97.1 [73.6]	2.9 [59.3]
3	45	20 min	248.8	96.6 [68.0]	3.4 [52.1]
4	r.t.	20 min	324.5	96.7 [72.9]	3.3 [49.7]

[a] TOF = mol ethylene consumed per mol of Ni h^{-1}. [b] C_n, amount of olefin with n carbon atoms in the oligomers; α-C_n, amount of terminal alkene in the C_n fraction; as determined by quantitative GLC.

On the grounds of these very encouraging results, we then focused our attention on the effect of the temperature and the catalyst lifetime. Complex **5b** which provided the best performances was selected for these experiments. Oligomerisations were carried out at room temperature or at 45 °C and the reactions were quenched after 20 min or 1 h. Results of these experiments are reported in Table 2. As can be seen, decrease of the temperature results in a significant increase of the productivity (from 107×10^3 to 166×10^3, entries 1 and 2) and in a slight improvement of the selectivity in favor of 1-butene (from 61.4 to 73.6%). Examination of entries 3 and 4 confirms this observation and indicates that the catalyst lifetime may be short, since after 20 min the TOF increased (325×10^3 *vs.* 166×10^3) by a factor of 2.

In conclusion, these readily synthesized phosphinoiminophosphorane nickel(II) complexes exhibit an excellent catalytic activity in the dimerisation of ethylene and are among the best systems reported so far. Further studies will now focus on the optimization of reaction conditions and on the effects of the substitution pattern of ligands. Theoretical studies are also underway in our laboratories to get some better insights on these new catalytic systems.

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Notes and references

‡ *Synthesis* of nickel complexes **4–6**: BuLi (178.5 μL, 0.285 mmol) was added to a suspension of ligand **1–3** (0.285 mmol) in THF (5 mL) cooled at −78 °C. The cold bath was removed and the solution allowed to warm to room temperature. Then, [$NiBr_2$(DME)] (88 mg, 0.285 mmol) was added and the solution turned immediately from colorless to blue. After stirring for 30 min at room temperature, a blue solid precipitated, which was isolated by filtration. This solid was dissolved in CH_2Cl_2 (5 mL) to remove the insoluble lithium salts. After removal of solvent under vacuum, the obtained blue solid was washed with Et_2O (10 mL).

Crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a solution of **4** or **5** in dichloromethane at room temperature.

4a (157 mg, 80%). HR-EI-MS: 684.9825 (*M*; $C_{30}H_{33}NP_2NiBr_2$; calc. 684.9809). 606.0633 (*M*; $C_{30}H_{33}NP_2NiBr$; calc. 606.0625). Anal. Calc. for $C_{30}H_{33}NP_2NiBr_2$: C, 52.37; H, 4.83; N, 2.04. Found: C, 52.42; H, 4.93; N, 2.18%. **4c** (154 mg, 78%). HR-EI-MS: 690.9351 (*M*; $C_{31}H_{27}NP_2NiBr_2$; calc. 690.9339). 612.0148 (*M*; $C_{31}H_{27}NP_2NiBr$; calc. 612.0156). Anal. Calc. for $C_{31}H_{27}NP_2NiBr_2$: C, 53.65; H, 3.92; N, 2.02. Found: C, 53.72; H, 3.81; N, 2.37%. **5a** (175 mg, 82%) HR-EI-MS: 746.9969 (*M*; $C_{35}H_{35}NP_2NiBr_2$; calc. 746.9965). 668.0761 (*M*; $C_{35}H_{35}NP_2NiBr_2$; calc. 668.0782). Anal. Calc. for $C_{35}H_{35}NP_2NiBr_2$: C, 56.04; H, 4.70; N, 1.87. Found: C, 56.19; H, 4.83; N, 2.06%. **5b** (161 mg, 78%). HR-EI-MS: 718.9645 (*M*; $C_{33}H_{31}NP_2NiBr_2$; calc. 718.9652), 639.0402 (*M*; $C_{33}H_{31}NP_2NiBr$; calc. 639.0390). Anal. Calc. for $C_{33}H_{31}NP_2NiBr_2$: C, 54.89; H, 4.33; N, 1.94. Found: C, 54.64; H, 4.24; N, 1.89%. **5c** (147 mg, 70%). HR-EI-MS: 732.9783 (*M*; $C_{34}H_{33}NP_2NiBr_2$; calc. 732.9809), 654.0595 (*M*; $C_{34}H_{33}NP_2NiBr$; calc. 654.0625). Anal. Calc. for $C_{34}H_{33}NP_2NiBr_2$: C, 55.48; H, 4.52; N, 1.90. Found: C, 55.28; H, 4.34; N, 1.81%. **5d** (143 mg, 75%). HR-EI-MS: 665.0091 (*M*; $C_{28}H_{37}NP_2NiBr_2$; calc. 665.0122), 586.0948 (*M*; $C_{28}H_{37}NP_2NiBr$; calc. 586.0938). Anal. Calc. for $C_{28}H_{37}NP_2NiBr_2$: C, 50.34; H, 5.58; N, 2.10. Found: C, 50.43; H, 5.47; N, 2.20%. **6** (151 mg, 71%). HR-EI-MS: 704.9456 (*M*; $C_{29}H_{32}NP_2NiBr_2$; calc. 704.9496), 626.0304 (*M*; $C_{29}H_{32}NP_2NiBr$; calc. 626.0312). Anal. Calc. for $C_{29}H_{32}NP_2NiBr_2$: C, 54.28; H, 4.13; N, 1.98. Found: C, 54.35; H, 4.22; N, 1.72%.

§ Crystal structures of complexes **4c** and **5a,c,d** will be published elsewhere, for crystal structure of **4b** see ref. 10*a*.

¶ $C_{33}H_{31}Br_2NNiP_2$, $M_r = 722.06$, monoclinic, space group $P2_1/c$, $a = 9.087(1)$, $b = 16.597(1)$, $c = 21.913(1)$ Å, $\beta = 110.180(1)°$, $V = 3102.0(4)$ Å^3, $T = 150.0(1)$ K, $Z = 4$, $F(000) = 1456$, $\mu = 3.328$ cm^{-1}, 10809 reflections measured, 6329 unique data, $R_{int} = 0.0279$. Final $R1 = 0.0315$ ($wR2 = 0.0652$). CCDC 631235. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618401d.

|| *General oligomerisation procedure*: All catalytic reactions were carried out in a magnetically stirred 120 mL stainless steel autoclave, equipped with a pressure gauge and needle valves for injections. The interior of the autoclave was protected from corrosion by a Teflon/protective coating. A typical reaction was performed by introducing in the reactor under nitrogen atmosphere the nickel complex (20 μmol) and 30 mL of toluene. After injection of the MAO solution (300 equiv., 4 mL), the reactor was immediately brought to the desired working temperature and pressure, and continuously fed by ethylene using a reserve bottle. The reaction was stopped by closing the ethylene supply, cooling the system to −70 °C. After the pressure in the reactor has decreased to atmospheric pressure, the reaction was quenched by adding 1 mL of methanol. *n*-Heptane used as internal standard was also introduced and the mixture was analysed by quantitative GC, first calibrated with authentic samples (except in the case of butene for which the calibration was based upon the response factor of *n*-pentane).

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