$NiCl_2$(1,2-Diiminophosphorane) complexes: a new family of readily accessible and tuneable catalysts for oligomerisation of ethylene

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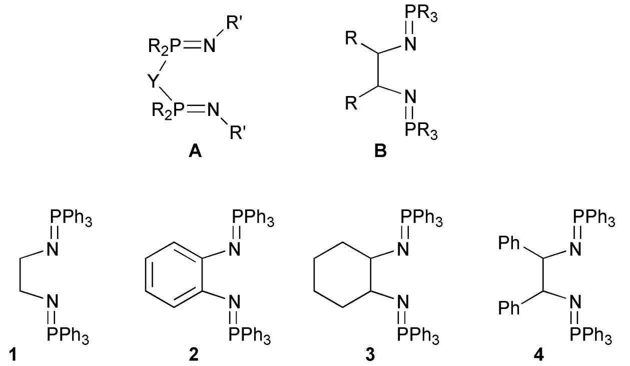
1,2-Diiminophosphoranes **1**–**4** featuring either ethane, benzene, cyclohexane or 1,2-diphenylethane carbon backbones act as tightly bonded 1,4-chelating ligands towards $NiCl_2$, affording the corresponding paramagnetic complexes **5**–**8** in high yield. X-Ray diffraction studies performed on compounds **5** and **6** revealed that the conformation of the five-membered metallacycle depends on the rigidity of the carbon backbone. For both complexes, the coordination sphere of the Ni atom is a distorted tetrahedron with bond lengths and angles around nickel similar to those observed for related Ni(II)(α-diimine) complexes. Complexes **5**–**8** are active for ethylene oligomerisation under mild reaction conditions (0 °C, 1.1 bar) upon activation by alkylaluminum derivatives (Et_2AlCl or MAO). The nature of the carbon backbone of the 1,2-diiminophosphorane ligands has a profound impact on the selectivity of the catalytic systems. The selectivity for trimers and higher oligomers varies from 10% (pre-catalyst **8**) to 81% (pre-catalyst **5**). Effects of varying ethylene pressure, temperature and aluminium co-catalyst/nickel ratios with pre-catalyst **6** are reported. Tailoring the reaction parameters has a modest effect on the oligomer distribution but allows quite high catalytic activities to be achieved with turnover frequencies up to 135×10^3 h^{-1}.

Bidentate ligands containing sp^2-hybridised nitrogen donor atoms have attracted much attention in recent years for the tailoring of transition metal catalysts.[1] An important development in this field was reported by Brookhart *et al.* who showed that α-diimines are efficient ligands for the palladium- and nickel-catalysed oligomerisation and polymerisation of ethylene.[2] The fact that the steric and electronic properties of α-diimine ligands can be easily varied has been a key factor in the optimisation of the catalytic systems.[2]

Derivatives incorporating ylide moieties have been only very recently developed as ligands for homogeneous catalysis,[3] with our own recent research focussing on chelating nitrogen donors featuring iminophosphorane moieties (–N=PR_3).[4] Iminophosphoranes are readily accessible ylides possessing a highly polarised P=N bond. They have found numerous applications as building blocks in organic synthesis and polymer chemistry.[5] Iminophosphoranes coordinate to transition metals *via* their approximately sp^2-hybridised N atom and have been incorporated in hetero-[6] and homobidentate ligands. Two types of homobidentate ligands are known, depending on whether the carbon backbone bridges the two phosphorus atoms (derivatives **A**, Scheme 1) or the two nitrogen atoms (derivatives **B**, Scheme 1). The coordination chemistry of type **A** diiminophosphoranes has been studied in depth and numerous rhodium, palladium and platinum complexes have been described.[7] Nickel(II) complexes bearing ligands **A** (Y = CH_2, CH_2–CH_2) have recently been reported and it should be noted that these complexes are not active for the oligomerisation of ethylene.[3c] The first complexes featuring type **B** 1,2-diiminophosphorane ligands date back to 1975,[8] but the coordination chemistry of these derivatives has only very recently been reinvestigated.[3d,4] We have shown that, in spite of their ylide character, type **B** 1,2-diiminophosphoranes exhibit a relative "hardness" comparable to that of classical sp^2-hybridised nitrogen ligands, and that their coordination behaviour is considerably influenced by the nature of the bridging carbon backbone.[4b] Furthermore, derivatives **B** are expected to exhibit quite different steric and electronic properties than those of the diiminophosphoranes **A**. In particular, they should be more sterically demanding ligands since their bulky phosphino substituents are close to the metal centre.



Scheme 1 Diiminophosphorane ligands.

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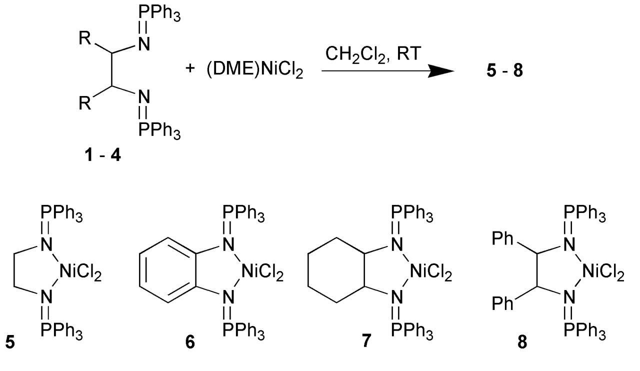
These features prompted us to investigate the use of 1,2-diiminophosphoranes **1**–**4** (Scheme 1) as ligands for the Ni-catalysed oligomerisation of ethylene. Herehein, we report the synthesis, structural characterisation and catalytic performance for ethylene oligomerisation of Ni(II) (1,2-diiminophosphorane) complexes. The influence of the ligand backbone and of reaction conditions (pressure, temperature, nature of aluminium cocatalyst) on their catalytic activity and the resultant product distribution is described.

Results and discussion

Nickel(II)(1,2-diiminophosphorane) complexes

1,2-Diiminophosphoranes **1**–**4** (Scheme 1) were conveniently obtained by condensation of commercially available diamines and Ph_3PBr_2, followed by treatment with a strong base (the Kirsanov reaction).[4,5a–c] *P*-Phenyl substituted iminophosphoranes were selected for this study since they can be easily purified and are not air sensitive. The blue–violet complex **5** (Scheme 2) has already been prepared by reacting the 1,2-diiminophosphorane **1** with $NiCl_2$ in refluxing CH_3CN, followed by treatment at 120 °C under vacuum.[8] As observed for related α-diimines,[2] $NiCl_2$(1,2-dimethoxyethane) reacted at room temperature in CH_2Cl_2 with diiminophosphoranes **1**–**4**, affording the corresponding complexes **5**–**8** (Scheme 2). Derivatives **5**–**8** exhibit low solubility in common organic solvents and, after washing with diethyl ether, are obtained in almost quantitative yield and high purity. They are paramagnetic, preventing any NMR spectroscopic analysis. The new complexes **6**–**8** have been characterised by high-resolution mass spectrometry and gave satisfactory elemental analyses.

The first monomeric Ni-complex featuring an iminophosphorane ligand [$Ph_2P(o\text{-}C_6H_4)\text{–}N{=}PMe_3$] has only been very recently described[6c] and Ni-iminophosphorane complexes are still rare.[3c,6e,8,9] Furthermore, few metal complexes bearing 1,2-diiminophosphorane ligands **B** are known. Solid state structures have been elucidated for only six complexes possessing either derivatives **3** (Co,[3d] Rh,[3d] Pd[4]) or **4** (Pd[4b]) as ligands. Therefore, Ni(II) complexes **5** and **6** were subjected to an X-ray diffraction study in order to evaluate the influence of the carbon backbone rigidity on the coordination behaviour of 1,2-diiminophosphoranes. For both complexes, the Ni atom is located in a distorted tetrahedral coordination environment consisting of two N atoms of the 1,2-diiminophosphorane moieties and two Cl atoms (Fig. 1 and 2, Table 1). The Ni–Cl bond lengths are typical for this class of compounds,[2c,d,10] and are almost identical for the two complexes (Table 1). The geometry around the coordinated nitrogen atoms is essentially planar (sum of the angles >357.8°) and the P–N distances [1.585(5)–1.618(2) Å] are normal values for metal-coordinated iminophosphoranes.[3c,d,4] As expected, the conformation of the two five-membered metallacycles is very different. The five-membered metallacycle of complex **5**, which contains sp^3-hybridised C atoms, adopts a half-chair conformation [Ni(1)–N(1)–C(1)–C(2), 34.5°(8); Ni(1)–N(2)–C(2)–C(1), 35.6°(6)] with the two phosphino groups in a mutually *trans* configuration (Fig. 1). Note that this conformation has also been



Scheme 2 Synthesis of (1,2-diiminophosphorane)$NiCl_2$ complexes.

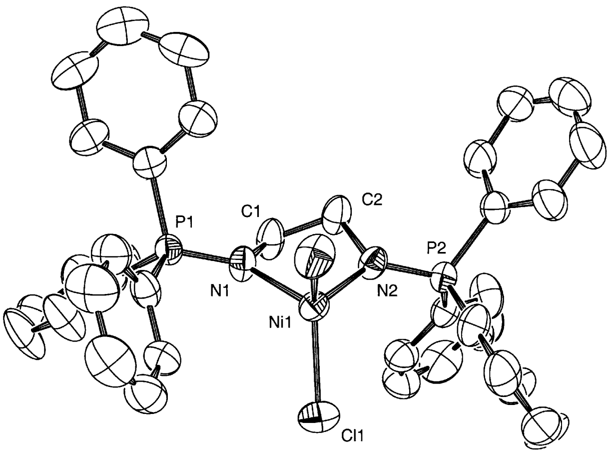


Fig. 1 ORTEP drawing (thermal ellipsoid 50% probability) of complex **5**; the H atoms have been omitted for clarity.

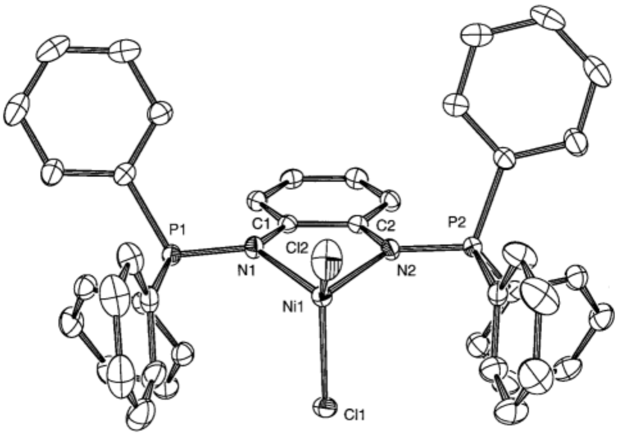


Fig. 2 ORTEP drawing (thermal ellipsoid 50% probability) of complex **6**; the H atoms have been omitted for clarity.

Table 1 Selected bond lengths and angles for complexes **5** and **6**

	5	**6**
Ni(1)–Cl(1)	2.248(2)	2.2811(5)
Ni(1)–Cl(2)	2.258(2)	2.2178(6)
Ni(1)–N(1)	2.017(5)	2.0141(16)
Ni(1)–N(2)	1.987(6)	1.9960(15)
N(1)–C(1)	1.481(8)	1.414(2)
C(1)–C(2)	1.514(10)	1.423(2)
C(2)–N(2)	1.490(9)	1.413(2)
N(1)–P(1)	1.585(5)	1.6185(16)
N(2)–P(2)	1.590(6)	1.6117(16)
Cl(1)–Ni(1)–Cl(2)	123.23(9)	128.09(2)
N(1)–Ni(1)–Cl(1)	107.20(17)	104.15(5)
N(1)–Ni(1)–Cl(2)	112.40(18)	116.55(5)
N(2)–Ni(1)–Cl(1)	113.01(18)	101.27(5)
N(2)–Ni(2)–Cl(2)	108.82(17)	113.51(5)
N(2)–Ni(1)–N(2)	86.0(2)	83.60(6)
Ni(1)–N(1)–C(1)	108.7(4)	110.29(11)
N(1)–C(1)–C(2)	109.4(6)	125.5(17)
C(1)–C(2)–N(2)	109.2(6)	116.23(16)
C(2)–N(2)–Ni(1)	109.3(4)	123.14(13)

observed for a Pd(II) complex possessing the 1,2-diphenylethane bridged ligand **4**.[4b] The metallacycle of complex **6**, featuring sp^2-carbon atoms, formally shows an envelope conformation. The N(1), C(1),C(2) and N(2) atoms lie almost in the same plane [N(1)–C(1)–C(2)–N(2), 1.3(2)°] with the Ni atom being out of this plane [C(1)–C(2)–N(2)–Ni, 10.68(19)°; Ni–N(1)–C(1)–C(2), 12.38(19)°]. However, considering the small values of the C(1)–C(2)–N(2)–Ni and Ni–N(1)–C(1)–C(2) dihedral angles, the metallacycle of **6** (Fig. 2) can be regarded as nearly planar (maximum deviation, 0.06 Å). In spite of these structural differences, complexes **5** and **6** share some important features. Of particular interest, the Ni–N distances [**5**, 1.987(6) and 2.017 (5) Å; **6**, 1.996(2) and 2.014 (2) Å] and the N(1)–Ni(1)–N(2) bite angles [**5**, 86.0(2)°; **6**, 83.60(6)°] are comparable for both compounds. It is very interesting to note that these data are very similar to those recorded for monomeric (α-diimine)-NiX$_2$ complexes. For example, (*N*,*N*′-di-*tert*-butylethylenediamine)NiBr$_2$, which adopts a distorted tetrahedral geometry with planar coordinated N atoms, exhibits Ni–N bond lengths of 1.996(7) and 2.002(8) Å while the N–Ni–N angle reaches 82.5(3)°.[10]

Catalytic studies

The oligomerisation of ethylene is industrialised on a large scale and nickel complexes are the most frequently employed catalysts.[11] High performance Ni catalysts that selectively produce oligomers have been obtained *via* tailoring of the surrounding ligands. A major advance in this field arose from the work of Keim *et al.*[11a–c] on anionic P–O ligands that are used in the prominent Ni-catalysed Shell Higher Olefins Process (SHOP) for the synthesis of linear C$_4$–C$_{20}$ ethylene oligomers. Since 1995, cationic palladium and nickel species bearing aryl-substituted α-diimines have been developed for the homologation of olefins.[2] The nature of the macromolecules obtained depends on reaction conditions and the ligand structure. Bulky nickel complexes catalyse the polymerisation of α-olefins while initiators lacking steric hindrance oligomerise ethylene to α-olefins.[2] It is noteworthy that the polyethylenes produced by these systems differ from those made with early metal d^0 catalysts by their "hyperbranched" structure.

A convenient method for the generation of catalysts involves *in situ* activation of nickel(II) dichloride complexes with an aluminium co-catalyst.[2] The pre-catalysts **5**–**8** were evaluated for ethylene homologation in chlorobenzene at 1.1 bar ethylene pressure and 0 °C for 1 h, using Et$_2$AlCl (DEAC) as the activator (Al/Ni = 70). Under these reaction conditions, complexes **5**–**8** are active for ethylene oligomerisation; relatively high turnover frequencies (TOF's) varying from 8×10^3 to 11×10^3 h^{-1} have been measured (Table 2). The highest catalytic activity is observed with pre-catalyst **6**, bearing a ligand with an aromatic and rigid carbon backbone.

The most attractive feature of these nickel-iminophosphorane catalysts is that the nature of the carbon backbone of the ligands has an important impact on the selectivity of the catalytic systems (Fig. 3). The selectivity in dimers, which are mainly ($E + Z$) internal butenes in all cases, range from 19% (pre-catalyst **5**) to 90% (pre-catalyst **8**). Complexes **5**–**7** afford a similar amount of trimers (*ca.* 30%), consisting in a mixture of hexenes and methyl-2-pentenes, while higher oligomers (>C$_6$) are the major products with the pre-catalyst **5**. The nature of the carbon backbone influences both the electronic and steric properties of 1,2-diiminophosphoranes **1**–**4** and it is difficult to establish structure-property relationships. However, it is noteworthy that the less sterically hindered iminophosphorane-nickel complex **5** gives the highest selectivity (*i.e.*, 54%) for oligomers incorporating more than 3 monomeric units. Under similar reaction conditions, we have checked that Ni(acac)$_2$ gives ethylene dimers and bulky α-diimine-nickel systems yield polymers. These results show that 1,2-diiminophosphoranes are versatile ligands for the Ni-catalysed ethylene oligomerisation; rather high catalytic activities can be achieved and the selectivity towards dimers, trimers and higher oligomers can be tailored by varying the nature of the carbon backbone.

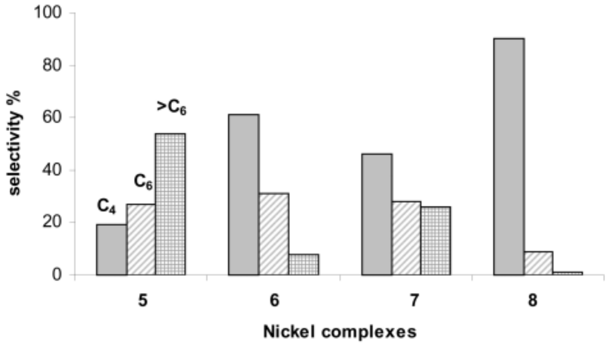


Fig. 3 Effect of the carbon backbone of the 1,2-diiminophosphoranes on the oligomer distribution.

The influence of the reaction conditions, including the addition of phosphine modifiers, on the performance of the catalytic system has been studied in detail for the most active pre-catalyst **6**. At 0 °C under 1.1 atm of ethylene, the TOF's slightly decline for longer reaction times (entries 1 and 2, Table 3). The catalytic activity decreases as the temperature is raised from 0 to 30 °C, regardless of the total pressure (entries 1,4 and 3,6, Table 3); this behaviour has been well-documented and attributed to a probable lowering of ethylene solubility at higher temperatures.[2] The ethylene pressure has a dramatic effect on the catalytic activity. An increase in the pressure results in an increase of the TOF from 11×10^3 (1.1 bar) to 121×10^3 h^{-1} (6.0 bar) at 0 °C. This trend is more pronounced at 30 °C: the same pressure enhancement induces an increase of the TOF's from 3×10^3 to 87×10^3 h^{-1} (entries 4 and 6, Table 3).[12]

As observed for Ni(II)-α-diimine catalysts,[2] the quantity and nature of aluminium co-catalyst dramatically affects the

Table 2 Ethylene oligomerisation with precatalysts **5**–**8**[a]

			C$_4$[c]		C$_6$[c]		>C$_6$[c]
Pre-catalyst	Yield/g	TOF[b]/10^3 h^{-1}	Total (%)	α (%)	Total (%)	Linear (%)	Total (%)
5	7.0	8	19	1	27	23	54
6	10.0	11	61	2	31	33	8
7	7.6	8	46	1	28	23	26
8	4.5	5	90	1	9	59	1

[a] Conditions: 1.1 bar of ethylene (constant pressure), 0 °C, 33 μmol of nickel complex, Et$_2$AlCl/Ni = 70, 50 mL of chlorobenzene, 1 h. [b] TOF = turnover frequency; mol ethylene converted per mol of Ni catalyst per hour. [c] Weight percent determined by GC analysis.

Table 3 Influence of the reaction parameters on the catalytic behaviour of pre-catalyst **6**[a]

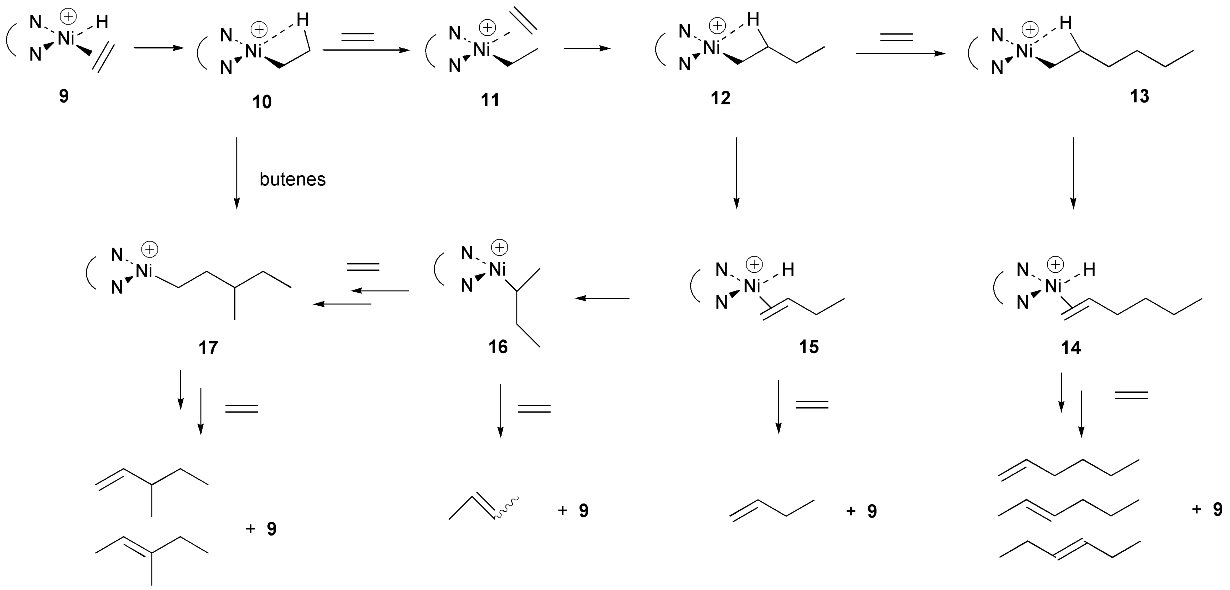
Entry	Aluminum co-catalyst	Al/Ni	Phosphine (P/Ni)	T/°C	P/bar	Time/h	Yield/g	TOF/ 10^3 h^{-1}	C_4[b] Total (%)	C_4[b] α (%)	C_6[b] Total (%)	C_6[b] Linear (%)	$>C_6$[b] Total (%)
1	Et_2AlCl	70	—	0	1.1	1	10.3	11	61	2	31	33	8
2	Et_2AlCl	70	—	0	1.1	2	13.6	7	53	2	38	32	9
3	Et_2AlCl	70	—	0	6.0	1	112	121	52	14	34	53	14
4	Et_2AlCl	70	—	30	1.1	1	3.0	3	70	1	30	43	—
5	Et_2AlCl	20	—	30	6.0	1	8.0	9	76	37	21	64	3
6	Et_2AlCl	70	—	30	6.0	1	80	87	57	23	32	56	11
7	Et_2AlCl	200	—	30	6.0	1	100	108	52	15	36	53	12
8	Et_2AlCl	200	—	50	11	1	125	135	60	17	29	29	11
9	TMA	200	—	50	11	1	0.0	0	—	—	—	—	—
10	MAO	200	—	50	11	1	17.1	18	77	21	18	18	5
11	Et_2AlCl	70	PPh_3 (1)	0	1.1	1	3.4	4	71	2	29	20	—
12	Et_2AlCl	70	PCy_3 (1)	0	1.1	1	9.8	10	58	0	29	12	13
13	Et_2AlCl	70	PCy_3 (2)	0	1.1	1	8.7	10	78	9	19	23	3

[a] Constant ethylene pressure, 33 μmol of nickel complex **6**, 50 mL of chlorobenzene. [b] Weight percent determined by GC analysis.

outcome of the oligomerisation reaction. Augmentation of the Et_2AlCl/Ni ratio from 20 : 1 to 70 : 1 gives an increase in the turnover frequencies from 9×10^3 to 87×10^3 h^{-1} (entries 5 and 6, Table 3). The effect is more modest for further enhancement of the Al/Ni ratio (entries 6 and 7, Table 3). Note that the increase in the production of C_6 and higher olefinic fractions is probably due to co-oligomerisation involving the C_4 products accumulated in the reaction vessel (*vide infra*). Other alkylaluminium compounds gave rise to catalytic systems with lower activities. Trimethylaluminum (TMA) is not an effective co-catalyst. With MAO a TOF of 18×10^3 h^{-1} is observed at 11 bar and 50 °C while, for these optimal reaction conditions, a TOF of 135×10^3 h^{-1} is recorded with Et_2AlCl (entries 8–10, Table 3).[13] It has been observed that the behaviour of Ni-based catalytic systems can be sensitive to the addition of phosphine ligands to the reaction media.[11f] This is not the case with pre-catalyst **6**. A slight decrease of the TOF is observed upon addition of one equivalent of PPh_3 (*cf.* entries 1 and 11, Table 3) whereas addition of one or two equivalent of PCy_3 has almost no effect on the productivity (*cf.* entries 1 with 12 and 13, Table 3).

The reaction conditions have a modest influence on the selectivity of the catalytic system. Variation of ethylene pressure between 1.1 and 6.0 bar does not affect the oligomer distribution (entries 1,3 and 4,6, Table 3) whereas the production of higher oligomers is slightly favoured by lowering the temperature. For example, under a total pressure of 1.1 bar, pre-catalyst **6** produces 30% trimers and higher oligomers at 30 °C whereas this proportion reaches 39% at 0 °C (entries 4 and 1, Table 3). The addition of phosphines also has a marginal effect on the oligomer distribution (entries 1 and 11–13), suggesting that no coordination of the phosphine to the nickel centre occurs, probably due to the steric constraints imposed by the coordinated 1,2-diiminophosphorane. In contrast, the nature and the quantity of the aluminium co-catalyst do influence the selectivity. The production of high oligomers is more efficient with Et_2AlCl than with MAO (entries 8 and 10, Table 3) and is also favoured when the Al : Ni ratio increases from 20 to 70 (entries 5 and 6, Table 3). These latter data preclude a chain termination mechanism by transfer to the alkylaluminum compound.

The C_4 fraction contains 1-butene, 2-*cis*-butene and 2-*trans*-butene and in the C_6 fraction the products were hexenes and methylpentenes. Increasing the pressure and lowering the Al/Ni ratio favour the production of 1-butene; the highest selectivity (37%) is observed under 6 bar for an Al/Ni ratio of 20 : 1 (entry 5, Table 3). The nature of the C_4 products for all other runs is quite similar. The amount of linear products in



Scheme 3 Proposed mechanism for ethylene oligomerisation.

the C_6 fraction increases as the ethylene pressure is raised, this effect is more pronounced at 0 °C (1.1 bar, 33%; 6.0 bar, 53%, entries 1 and 3, Table 3) than at 30 °C (1.1 bar, 43%; 6.0 bar, 56%, entries 4 and 6, Table 3).

All of these products are expected from a classical oligomerisation pathway involving parallel oligomerisation/isomerisation reactions (Scheme 3). The mechanism starts with a hydrido or an alkylnickel species (**9** or **11**, respectively) being formed from the dichloro pre-catalyst and the alkylaluminum co-catalyst. The linear C_6 isomers are produced by sequential coordination and migratory insertion of ethylene into the nickel-alkyl bond *via* intermediate **13**. Alternatively, prior to this reaction sequence, the metal alkyl species **12** could undergo a β-hydride elimination leading to **15**, which can give 1-butene or the intermediate **16** by re-addition. Complex **16** is responsible for the production of internal C_4 olefins and branched alkenes *via* **17**. It should be noted that complex **17** can also be obtained by coordination and insertion of butenes into the Ni-alkyl bond of complex **10**. The formation of internal C_6 alkenes is not presented in Scheme 3 for clarity, but this process implies a sequence of β-hydride elimination-insertion steps starting from complexes **14** and **17**. The mechanism presented in Scheme 3 explains that the amount of linear C_6 products increases when the ethylene pressure is enhanced since a high quantity of ethylene available in the medium favours the formation of (i) **11** over **17** and (ii) of **13** over **15**.

Conclusion

This study shows that azadiylides are promising N-donor bidentate ligands for homogeneous catalysis. (1,2-diiminophosphorane)$NiCl_2$ complexes possess structural features similar to α-diimine complexes. Upon activation by Et_2AlCl, they lead to ethylene oligomerisation catalysts exhibiting rather high catalytic activities under mild reaction conditions. One of the most interesting features of these new catalytic systems is that the selectivity is affected by the nature of the ligand carbon backbone. It is quite surprising that low molecular weight oligomers are obtained in view of the important steric bulk brought by the triphenylphosphino moieties. Tailoring these ligands *via* modification of the P substituents for the development of catalytic systems producing heavier oligomers or polymers is under active investigation.

Experimental

General consideration

All experiments were performed under an atmosphere of dry argon using standard Schlenk tube techniques. Solvents were freshly distilled under argon from sodium–benzophenone (diethyl ether) or from phosphorus pentoxide (dichloromethane). The diiminophosphoranes **1–4** and (DME)$NiCl_2$ were prepared and purified according to literature procedures. Solids were dried under reduced pressure and chlorobenzene was distilled over 3 Å molecular sieves, immediately prior to use. Diethyl aluminum chloride (DEAC) and trimethylaluminum (TMA) were purchased from Aldrich and methylalumoxane (MAO) was purchased from Witco, and were used as received. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass at CRMPO, University of Rennes 1. Elemental analyses were performed by the Centre de Microanalyse du CNRS at Vernaison, France.

Synthesis of nickel complexes

Complex 5. A CH_2Cl_2 solution (10 mL) of diiminophosphorane (1) (1.00 g, 1.72 mmol) was added, at room temperature, to a CH_2Cl_2 solution (10 mL) of (DME)$NiCl_2$ (0.38 g, 1.72 mmol). The reaction mixture immediately turned blue and was stirred for 1 h at room temperature. The volatile materials were removed under vacuum; the residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Complex **5** was obtained as a violet solid (1.19 g, yield 98%). Anal. calcd for $C_{38}H_{34}N_2P_2Cl_2Ni$: C, 64.26; H, 4.83; N, 3.94. Found, C, 64.22; H, 4.41; N, 3.81%.

Complex 6. Following the procedure described for complex **5**, reaction of diiminophosphorane **2** (0.40 g, 0.63 mmol) and (DME)$NiCl_2$ (0.14 g, 0.63 mmol) afforded **6** as a red solid (0.41 g, yield 95%). HR-MS (FAB, mNBA): *m/z* 756.0934 $(M)^+$ calcd for $C_{42}H_{34}N_2P_2Cl_2Ni$: 756.0928. Anal. calcd for $C_{42}H_{34}N_2P_2Cl_2Ni$: C, 66.53; H, 4.52; N, 3.69. Found, C, 66.21; H, 4.08; N, 3.75%.

Complex 7. Following the procedure described for complex **5**, reaction of a mixture of racemic diiminophosphorane **3** (0.40 g, 0.63 mmol) and (DME)$NiCl_2$ (0.14 g, 0.63 mmol) afforded **7** as a blue solid (0.24 g, yield 96%). HR-MS (FAB, mNBA): *m/z* 727.1712 $(M - Cl)^+$, calcd for $C_{42}H_{40}N_2P_2ClNi$: 727.1709. Anal. calcd for $C_{42}H_{40}N_2P_2Cl_2Ni$: C, 66.00; H, 5.28; N, 3.67. Found, C, 65.76; H, 5.30; N, 3.92%.

Complex 8. Following the procedure described for complex **5**, reaction of (1*R*,2*R*)-diiminophosphorane **4** (0.20 g, 0.30 mmol) and (DME)$NiCl_2$ (0.07 g, 0.30 mmol) afforded **8** as a blue solid (0.23 g, yield 95%). HR-MS (FAB, mNBA): *m/z* 825.1870 $(M - Cl)^+$, calcd for $C_{50}H_{42}N_2P_2ClNi$: 825.1825. Anal. calcd for $C_{50}H_{42}N_2P_2Cl_2Ni$: C, 69.63; H, 4.91; N, 3.25. Found, C, 69.38; H, 4.60; N, 3.33%.

Crystallography

Single crystals of compounds **5** and **6** suitable for a single crystal X-ray determinations were obtained by slow evaporation from CH_2Cl_2 solutions at room temperature. The unit cell constant, space group determination, and the data collection were carried out on an automatic CAD4 NONIUS (compound **5**) or a NONIUS Kappa CCD (compound **6**) diffractometer with graphite monochromated Mo-Kα radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections (compound **5**) or with Denzo and Scalepack with 10 frames (psi rotation, 1° per frame, compound **6**). The structures were solved with SIR-97,[14a] which reveals the non-hydrogen atoms of the structure. After anisotropic refinement, all hydrogen atoms may be found with a Fourier difference. Compound **6** crystallises with a CH_2Cl_2 molecule and a cyclopentane set around the symmetry centre. The entire structures were refined with SHELXL97[14b] by full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Ni, P, Cl, C and N atoms, x, y, z in riding mode for the H atoms). Atomic scattering factors were obtained from the *International Tables for X-ray Crystallography*.

Crystal data for compound **5**: $C_{38}H_{34}Cl_2N_2P_2Ni{\cdot}CH_2Cl_2$, $M = 795.22$, monoclinic, $a = 16.921(4)$, $b = 16.112(4)$, $c = 17.597(5)$ Å, $\beta = 115.71(2)°$, $U = 4323.5(19)$ Å^3, $T = 293$ K, space group $P2_1/c$, $Z = 4$, λ(Mo-Kα) = 0.71069 Å, $D_c = 1.091$ Mg m^{-3}, $\mu = 6.70$ cm^{-1}, 9418 independent reflections measured, 4968 observed $[I > 2\sigma(F)]$, 431 variables refined, $R_1 = 0.0943$, $wR_2 = 0.2803$.

Crystal data for compound **6**: $C_{42}H_{34}Cl_2N_2P_2Ni{\cdot}CH_2Cl_2$, C_5H_{10}, $M = 913.19$, monoclinic, $a = 14.9254(2)$, $b = 15.1776(2)$, $c = 18.1566(3)$ Å, $\beta = 92.4895(6)°$, $U = 4109.2(1)$ Å^3, $T = 150$ K, space group $P2_1/n$, $Z = 4$, λ(Mo-Kα) = 0.71073 Å, $D_c = 1.476$ Mg m^{-3}, $\mu = 9.13$ cm^{-1}, 9578 independent reflections measured, 7943 observed $[I > 2\sigma(F)]$, 494 variables refined, $R_1 = 0.0367$, $wR_2 = 0.0920$.

CCDC reference numbers 166395 and 182856. See http://www.rsc.org/suppdata/nj/b1/b109992m/ for crystallographic data in CIF or other electronic format.

Oligomerisation reactions

Ethylene oligomerisation reactions have been performed in a 250 mL double-walled stainless steel autoclave equipped with mechanical stirring, thermocouple and pressure gauge. The reaction temperature was controlled by a thermostatic bath circulation. A typical reaction run was performed by introducing 33 μmol of the nickel(II) complex in 50 mL of chlorobenzene. The system was saturated with ethylene and then 1.2 mL of a 1.8 mol L^{-1} solution of the alkylaluminum co-catalyst was added. The ethylene pressure is raised to the desired value and continuously fed. After 1 h, the reaction was stopped by adding 3 mL of ethanol and the reactor temperature cooled down to $-10\,^{\circ}C$. Ethylene oligomerisation reactions at atmospheric ethylene pressure have been performed similarly using a 120 mL double-walled glass reactor magnetically stirred and continuously fed at 1.1 bar of ethylene. The gas chromatographic analysis of the reaction products has been done on a Varian 3400CX apparatus with a Petrocol HD capillary column (methyl silicone, 100 m long, i.d. 0.25 mm and film thickness of 0.5 μm) working at 36 °C for 15 min and then heating at 5 °C min^{-1} up to 250 °C.

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