Synthesis of Cationic and Neutral Methallyl Nickel Complexes and Applications in Ethene Oligomerisation

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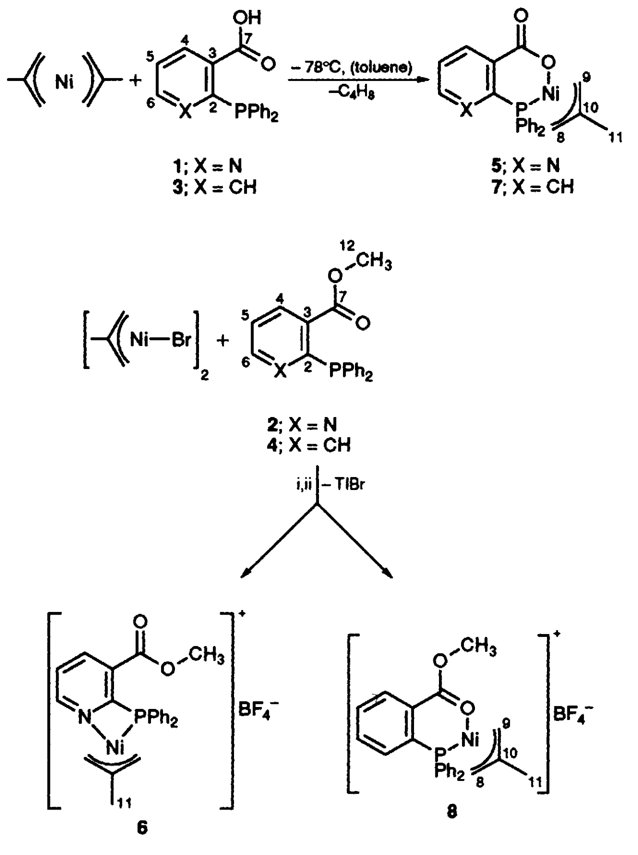
New neutral and cationic methallyl nickel complexes containing a chelating ligand were synthesised, characterised by NMR, IR spectroscopy and X-ray diffraction studies (cationic complexes) and applied to ethene oligomerisation with and without methylalumoxane as co-catalyst.

Neutral organometallic nickel complexes with chelating κ^{2}P,O ligands are of industrial importance as catalysts in the Shell Higher Olefin Process (SHOP)[1] for ethene oligomerisation. Cationic allyl nickel complexes with non-chelating ligands are also known to catalyse the oligomerisation of ethene.[2] However, the synthesis of cationic organo-nickel compounds with chelating ligands is almost unknown and catalytic properties have not been reported.[3] Although methylalumoxane (MAO) is largely studied as a co-catalyst in olefin polymerisation in the presence of zirconium complexes, its use in olefin oligomerisation with nickel compounds has practically no precedent.[4]

Here, we deal with the synthesis of new hybrid ligands, their neutral and cationic methallyl complexes and their use in ethene oligomerisation with and without methylalumoxane (MAO) as co-catalyst.

The ligand 2-(diphenylphosphino)nicotinic acid **1** and its methyl ester **2** were obtained by adapted methods used for 2-(diphenylphosphino)benzoic acid **3** and its methyl ester **4**.[5] By reacting these ligands with bis(η^3-methallyl)nickel and bis[μ-bromo(η^3-methallyl)nickel] (Scheme 1), four new complexes **5**–**8** have been prepared.[‡]

The X-ray crystal structures of **6** (Fig. 1) and **8** (Fig. 2) are surprising.[§] Whereas **8** shows the expected coordination with



Scheme 1 *Reagents and conditions*: i, −20 °C, THF; ii, TlBF$_4$, 0 °C, THF

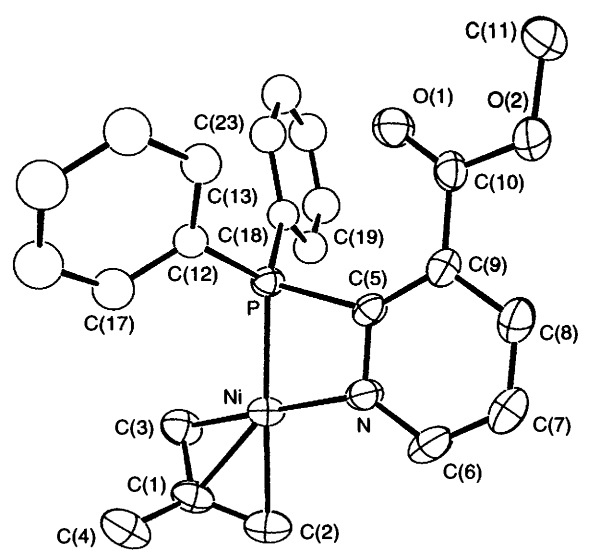


Fig. 1 Molecular structure of cation of **6**. Selected bond lengths (Å) and (°): Ni–P 2.193(2), Ni–N 1.921(5), Ni–C(1) 1.990(7), Ni–C(2) 2.031(7), Ni–C(3) 1.993(7), N–C(5) 1.359(7), P–C(5) 1.850(5), C(1)–C(2) 1.371(9), C(1)–C(3) 1.404(9), P–Ni–N 73.9(1), C(2)–Ni–C(3) 72.3(3), Ni–N–C(5) 105.0(3), Ni–P–C(5) 80.5(2), N–C(5)–P 100.2(4), C(2)–C(1)–C(3) 117.7(7).

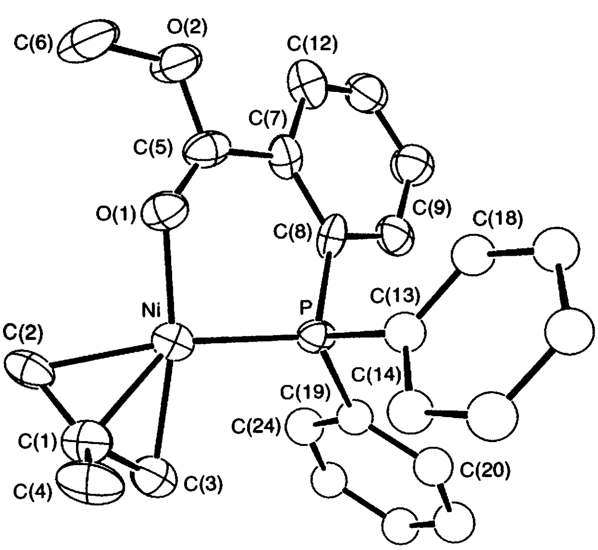


Fig. 2 Molecular structure of cation of **8**. Selected bond lengths (Å) and angles (°): Ni–P 2.141(1), Ni–O(1) 1.905(3), Ni–C(1) 1.983(5), Ni–C(2) 2.055(5), Ni–C(3) 2.008(5), O(1)–C(5) 1.237(6), C(5)–C(7) 1.453(7), C(7)–C(8) 1.412(6), P–C(8) 1.792(4), C(1)–C(2) 1.395(7), C(1)–C(3) 1.402(7), P–Ni–O(1) 92.58(9), C(2)–Ni–C(3) 71.5(2), Ni–O(1)–C(5) 133.1(3), Ni–P–C(8) 108.1(1), O(1)–C(5)–C(7) 129.5(4), C(5)–C(7)–C(8) 120.0(4), P–C(8)–C(7) 125.5(3), C(2)–C(1)–C(3) 116.2(5).

a six-membered chelate ring, complex **6** possesses a four-membered chelate ring with κ^2P,N coordination.

$^{31}P\{^1H\}$NMR and IR spectroscopic data of the ligands and the complexes are summarised in Table 1.

Catalytic experiments were performed with the four complexes **5–8**, laying special emphasis on the chemoselectivity of the cationic ones. To investigate the impact of MAO, the latter was also used as co-catalyst. Table 2 summarises the results of the catalytic runs carried out with and without MAO.

The neutral complexes **5** and **7** yield linear α olefins (linearity > 92%, α-olefins > 85%) comparable to the SHOP derived olefins. The cationic complexes **6/6′** and **8** oligomerise ethene to a mixture of linear and branched olefins under milder conditions. The branched olefins exhibit loss of chemoselectivity, because the primary products issued from ethene are co-oligomerised, thus leading to branching. Addition of MAO to **5–8** yields remarkably active systems, but chemoselectivity is also completely lost. Mixtures of branched and linear olefins are obtained.

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Table 1 $^{31}P\{^1H\}$NMR ($CDCl_3$) and IR data of the ligands and the complexes

Compound	$^{31}P\{^1H\}$, δ	IR, ν(C=O), ν_{as}(COO)/cm^{-1}
1	4.5	1699 (Nujol)
2	4.4	1717 (Nujol)
3	−4.0	1690 (Nujol)
4	−4.1	1712 (Nujol)
5	19.5	1623 (CH_2Cl_2)
6/6′	10 (v br); 5.2, 20.5[a]	1737, 1647 (CH_2Cl_2)
7	18.4	1622 (CH_2Cl_2)
8	19.7	1638 (CH_2Cl_2)

[a] T = 213 K; relative intensity 1/5; impurities at δ ca. 35.

Table 2 Reaction conditions and turnover numbers [TON = (mol reacted ethene)/(mol nickel complex)] for the catalytic ethene oligomerisation in the presence of complexes **5–8** with and without MAO (solvent: 10 ml chlorobenzene)

Complex	Without MAO					With MAO[a]
	n/mmol	p/bar	*T*/°C	*t*/h	TON	TON
5	0.05	40[b]	100	15	4800	7900
6/6′	0.10	3	0	5	130	18500
7	0.05	40[b]	100	15	340	95800
8	0.10	3	0	5	770	26100

[a] Conditions: 0.01 mmol/3 bar/0 °C/2h; (mol nickel complex)/(mol aluminium) = 1/100; MAO solution 5.3% Al in toluene. [b] batch reaction: initial pressure at room temp.; solvent: 10 ml toluene.

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Footnotes

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‡ NMR data for **1**; numbering of H and C atoms according to Scheme 1. **1**: ^1H NMR (250 MHz, [$^2H_6$]acetone): δ 8.63 (dd, ^3J 4.8, ^4J 1.8 Hz, 1H, 6-H), 8.29 (ddd, ^3J 7.9, ^4J 1.8, ^4J 4.3 Hz, 1H, 4-H), 7.40 (dd, ^3J 7.9, ^3J 4.8 Hz, 1H, 5-H) and 7.4–7.2 (m, 10H, H aromatic); ^{13}C NMR (63 MHz, [$^2H_6$]acetone): δ 166.6 (s, C-7), 165.0 (d, ^1J 20 Hz, C-2); 152.1 (d, ^1J 181 Hz, C6), 139–128 (m, C aromatic) and 122.3 (d, ^1J 167 Hz, C5).

§ Crystals of **6** from CH_2Cl_2–pentane solution. *Crystal data* for **6**: [$C_{23}H_{23}NO_2PNi$]BF_4, $M = 521.9$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.940(1)$, $b = 14.052(2)$, $c = 8.806(1)$ Å, $\alpha = 92.45(1)$, $\beta = 103.11(1)$, $\gamma = 79.56(1)°$, $U = 1178.1(3)$ Å,^{3} $Z = 2$, $D_c = 1.471$ g cm^{-3}, $\mu = 9.4$ cm^{-1}. Measurements: Enraf-Nonius CAD4; radiation: Mo-Kα (λ = 0.71073 Å), $T = 293$ K; solution: SHELX programs. 4139 unique reflections, 2518 observed [$I > 3\sigma(I)$], number of variables: 226 (phenyl rings refined as isotropic rigid groups, other non-H atoms anisotropic). $R(F_o) = 0.047$, $R_w = 0.048$.

Crystals of **8** were obtained from CH_2Cl_2–EtO_2 solution. *Crystal data* for **8**: [$C_{24}H_{24}O_2PNi$]BF_4, $M = 520.9$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.371(1)$, $b = 14.537(2)$, $c = 20.109(3)$ Å, $U = 2447.0(9)$ Å^3, $Z = 4$, $D_c = 1.414$ g cm^{-3}, $\mu = 9.1$ cm^{-1}. Measurements: Enraf-Nonius CAD4; radiation: Mo–Kα (λ = 0.71073 Å), $T = 293$ K; solution: SHELX programs. 3124 unique reflections, 2255 observed [$I > 3\sigma(I)$], number of variables: 226 (phenyl rings refined as isotropic rigid groups, other non-H atoms anisotropic). $R(F_o) = 0.025$, $R_w = 0.027$.

Atomic coordinates, bond lengths and angles, and thermal parameters of **6** and **8** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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