# Nickel phenyl complexes with chelating $\kappa^2$-*P*,*O* ligands as catalysts for the oligomerization of ethylene into linear $\alpha$-olefins†

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Starting from $[\mathrm{Ni(COD)_2}]$ and the phosphorus ylide $\mathrm{Ph_3P}(o\text{-}\mathrm{C_6H_4O})$, the complexes $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}(PR_3)}]$ $[\mathrm{PR_3 = PMe_3}$ (**2a**), $\mathrm{PMe_2Ph}$ (**2b**), $\mathrm{PMePh_2}$ (**2c**), $\mathrm{PCy_3}$ (**2d**), $\mathrm{PPh_3}$ (**2e**), $\mathrm{PTol_3}$ (**2f**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4OMe})_3$ (**2g**), $\mathrm{P(OMe)_3}$ (**2h**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4Cl})_3$ (**2i**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4F})_3$ (**2j**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4CF_3})_3$ (**2k**)$]$ were synthesized in the presence of the corresponding phosphine. The bis-chelate complex *cis*-$[\mathrm{Ni\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}_2}]$ (**3**) was formed as a minor by-product during these reactions, but was the only isolable compound when the reactions were conducted at temperatures above 60 °C. Oxidative addition of a P—Ph bond to the $\mathrm{Ni^0}$ centre was also used to synthesize $[\mathrm{NiPh\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PMe_3)}]$ (**1a**) from the $\alpha$-ketophosphorus ylide $\mathrm{Ph_3P{=}CHC({=}O)Ph}$ and $\mathrm{PMe_3}$. Reaction of $[\mathrm{Ph_3P}(o\text{-}\mathrm{C_6H_4NH_2})]\mathrm{Br}$ with $[\mathrm{Ni(COD)_2}]$ and $\mathrm{PTol_3}$ yielded the expected compound $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4NH)\}(PTol_3)}]$ (**6**) *via* deprotonation of the $\mathrm{NH_2}$ function by an excess of $\mathrm{PTol_3}$. Experiments to study the potential of these nickel complexes as catalysts for ethylene oligomerization into linear $\alpha$-olefins (>95%) showed widely varying activities [500–180 000 mol $\mathrm{C_2H_4}$ (mol catalyst h)$^{-1}$] and mass distributions of the $\alpha$-olefins. In contrast to the nickel phosphino enolate complexes of the type $[\mathrm{NiPh\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PR_3)}]$ $[\mathrm{PR_3 = PMe_3}$ (**1a**), $\mathrm{PCy_3}$ (**1b**), $\mathrm{PPh_3}$ (**1c**)$]$, the corresponding nickel phosphino phenolates $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}(PR_3)}]$ (**2**) generally showed a marked tendency to oligomerize ethylene into $\alpha$-olefins of higher molecular weight: $\mathrm{C_{4=}}$ to $\mathrm{C_{30=}}$ for **1** *versus* $\mathrm{C_{4=}}$ to $\mathrm{C_{90=}}$ for **2**. The complex $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4NH)\}(PTol_3)}]$ (**6**), on the other hand, showed no activity for ethylene oligomerization.

**Complexes phénylnickel à ligands chélatants $\kappa^2$-*P*,*O* pour l'oligomérisation catalytique de l'éthylene en $\alpha$-oléfines linéaires**. Les complexes $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}(PR_3)}]$ $[\mathrm{PR_3 = PMe_3}$ (**2a**), $\mathrm{PMe_2Ph}$ (**2b**), $\mathrm{PMePh_2}$ (**2c**), $\mathrm{PCy_3}$ (**2d**), $\mathrm{PPh_3}$ (**2e**), $\mathrm{PTol_3}$ (**2f**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4OMe})_3$ (**2g**), $\mathrm{P(OMe)_3}$ (**2h**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4Cl})_3$ (**2i**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4F})_3$ (**2j**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4CF_3})_3$ (**2k**)$]$ ont été obtenus par réaction de $[\mathrm{Ni(COD)_2}]$ avec les ylures de phosphore $\mathrm{Ph_3P}(o\text{-}\mathrm{C_6H_4O})$, en présence des phosphines correspondantes. Le complexe bis-chélate *cis*-$[\mathrm{Ni\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}_2}]$ (**3**) est un produit secondaire de ces réactions, mais il devient le seul composé isolable lorsque les réactions sont effectuées à des températures supérieures à 60 °C. L'addition oxydante d'une liaison P—Ph au centre $\mathrm{Ni^0}$ a également permis de préparer $[\mathrm{NiPh\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PMe_3)}]$ (**1a**) au départ de l'ylure de phosphore $\alpha$-cétonique $\mathrm{Ph_3P{=}CHC({=}O)Ph}$ et de $\mathrm{PMe_3}$. La réaction entre $[\mathrm{Ph_3P}(o\text{-}\mathrm{C_6H_4NH_2})]\mathrm{Br}$, $[\mathrm{Ni(COD)_2}]$ et $\mathrm{PTol_3}$ conduit au produit attendu $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4NH)\}(PTol_3)}]$ (**6**) suite à la déprotonation de la fonction $\mathrm{NH_2}$ par l'excès de $\mathrm{PTol_3}$. Les tests menés pour évaluer le potentiel de ces complexes du nickel pour l'oligomérisation catalytique de l'ethylène en $\alpha$-oléfines linéaires (>95%) montrent des activités [500–180000 mol $\mathrm{C_2H_4}$ (mol catalyseur h$^{-1}$)] et des distributions en masse des $\alpha$-oléfines variables. Au contraire des complexes phosphino énolates du nickel du type $[\mathrm{NiPh\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PR_3)}]$ $[\mathrm{PR_3 = PMe_3}$ (**1a**), $\mathrm{PCy_3}$ (**1b**), $\mathrm{PPh_3}$ (**1c**)$]$, les complexes phosphino phénolates correspondants $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}(PR_3)}]$ (**2**) montrent en général une forte tendance à oligomériser l'éthylène en $\alpha$-oléfines de poids moléculaires plus élevés: de $\mathrm{C_{4=}}$ à $\mathrm{C_{30=}}$ pour **1** contre $\mathrm{C_{4=}}$ à $\mathrm{C_{90=}}$ pour **2**. Le complexe $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4NH)\}(PTol_3)}]$ (**6**), par contre, n'a montré aucune activité catalytique en oligomérisation de l'éthylène.

The oligomerization of ethylene into linear $\alpha$-olefins by the Shell Higher Olefins Process (SHOP) is of academic as well as industrial interest and has been investigated for a number of years.[2] Research has been particularly focused on tuning the activity and selectivity ($\alpha$-olefin distribution) of catalysts derived from precursor complexes such as $[\mathrm{NiPh\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PPh_3)}]$ (**1c**), which are strongly dependent on the nature of the donor atoms, the electronic and steric effects of the substituents, the ring size of the chelate and the nature of the two-electron donor ligand. For this reason, the environment of the nickel centre was modified in numerous ways, using *P*,*N*-,[1] *P*,*O*-,[3] *As*,*O*-,[4] *O*,*O*-,[5] *S*,*S*-,[6] or *N*,*N*-[7] chelating ligands, but no systematic variation of the phosphine ligands $\mathrm{PR_3}$ appears to have been reported until now. Presumably this is related to earlier statements that the $\mathrm{PR_3}$ ligand does not influence the activity and selectivity of the catalyst, but is only necessary to stabilize the nickel complex.[2] Nevertheless, such an influence has been recognized.[3i,3k,3l,8] In this work we set out to establish a qualitative relationship between the donor properties of some phosphine ligands and their influence on both the activity and the selectivity of the new oligomerization catalysts $[\mathrm{NiPh\{Ph_2P}(o\text{-}\mathrm{C_6H_4O)\}(PR_3)}]$ $[\mathrm{PR_3 = PMe_3}$ (**2a**), $\mathrm{PMe_2Ph}$ (**2b**), $\mathrm{PMePh_2}$ (**2c**), $\mathrm{PCy_3}$ (**2d**), $\mathrm{PPh_3}$ (**2e**), $\mathrm{PTol_3}$ (**2f**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4OMe})_3$ (**2g**), $\mathrm{P(OMe)_3}$ (**2h**), $\mathrm{P}(p\text{-}\mathrm{C_6H_4Cl})_3$ (**2i**), P($p$-

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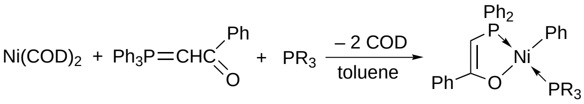
† Complexes with Functional Phosphines. Previous papers, see ref. 1.

$C_6H_4F)_3$ (**2j**), $P(p\text{-}C_6H_4CF_3)_3$ (**2k**)]. Furthermore, the influence of the chelating phosphino phenolate ligand on the catalytic properties of the nickel complexes was evidenced by comparison of **2a**, **2d** and **2e** with the related phosphino enolate complexes $[\mathrm{NiPh\{Ph_2PCH{=}C({=}O)Ph\}(PR_3)}]$ [$PR_3 = PMe_3$ (**1a**), $PCy_3$ (**1b**), $PPh_3$ (**1c**)].

## Results and Discussion

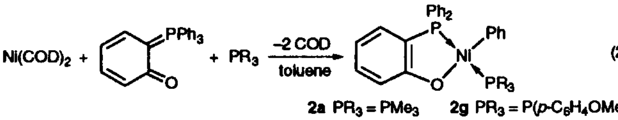
### Synthesis of the complexes

Complexes **1** and **2** were synthesized under conventional conditions by oxidative addition of the phosphorus ylides $Ph_3P{=}CHC({=}O)Ph$ [eq. (1)] and $Ph_3P(o\text{-}C_6H_4O)$ [eq. (2)] respectively, to $[Ni(COD)_2]$ in the presence of the corresponding phosphine (see *Experimental*). This reaction has been originally developed by Keim and coworkers to prepare square-planar complexes containing both a Ni—C σ bond and a bidentate, three-electron donor *P,O*-chelating ligand.[9] The products were generally isolated as yellow powders or, in some cases, as yellow-orange crystals, except for compounds **2i–2k**, which were generated *in situ* and directly used for the catalytic experiments. All complexes are soluble in solvents such as benzene or toluene, but they are sparingly or not soluble in nonpolar hydrocarbons such as pentane.



(1)

**1a** $PR_3 = PMe_3$
**1b** $PR_3 = PCy_3$
**1c** $PR_3 = PPh_3$



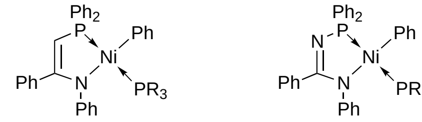
(2)

**2a** $PR_3 = PMe_3$ **2g** $PR_3 = P(p\text{-}C_6H_4OMe)_3$
**2b** $PR_3 = PMe_2Ph$ **2h** $PR_3 = P(OMe)_3$
**2c** $PR_3 = PMePh_2$ **2i** $PR_3 = P(p\text{-}C_6H_4Cl)_3$
**2d** $PR_3 = PCy_3$ **2j** $PR_3 = P(p\text{-}C_6H_4F)_3$
**2e** $PR_3 = PPh_3$ **2k** $PR_3 = P(p\text{-}C_6H_4CF_3)_3$
**2f** $PR_3 = PTol_3$

The yields ranged from 30–80%, but owing to similar solubility properties co-precipitation of starting materials or by-products such as the orange *cis*-$[\mathrm{Ni\{Ph_2P(\mathit{o}\text{-}C_6H_4O)\}_2}]$ (**3**) was observed in many cases. In the case of $PR_3 = PPh_3$, we verified that complex **3** was the only isolable product when the reactions were conducted at temperatures above 60 °C, obviously owing to an instability of the Ni—Ph complexes under these conditions. In order to facilitate comparison of spectroscopic data and physical properties, this bis-chelate complex was independently prepared from $NiCl_2 \cdot 6H_2O$ and two equivalents of $Ph_2P(o\text{-}C_6H_4OH)$ in the presence of $NEt_3$.[10]

The isolated compounds were generally characterized by $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analyses and sometimes by mass spectroscopy. The spectroscopic data are in agreement with previously reported characteristics for compounds of the type $[\mathrm{NiPh(PO)(PR_3)}]$.[1b,3b,9b] Their $^{31}P\{^1H\}$ NMR spectra exhibited typical AB patterns with coupling constants in the range 245–290 Hz while the $PMe_3$ derivatives **1a** and **2a** showed coupling constants of about 300 Hz. Surprisingly, the complexes **2b–2d** and **2h** only gave rise to broad signals at ambient temperature. However, upon cooling of a toluene solution of **2d** to −40 °C, two characteristic doublets appeared in the spectrum, indicating a dynamic equilibrium between the complex and a coordinatively unsaturated species and free phosphine in solution. The $^{31}P\{^1H\}$ chemical shifts for both the chelating and the monodentate phosphines were found in the expected range. The mass spectra showed the characteristic fragment ions generated by successive loss of the phenyl group coordinated to the nickel centre and the monodentate phosphine ligand, leaving behind a fragment with the nickel atom coordinated by the chelating phosphino phenolate.

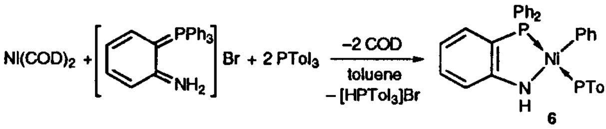
Whereas formation of the complexes $[\mathrm{NiPh\{Ph_2PCH{=}C({=}NPh)Ph\}PR_3}]$ [$PR_3 = PMe_3$ (**4a**), $PMe_2Ph$ (**4b**), $PMePh_2$ (**4c**), $Ph_3P{=}CHC({=}NPh)Ph\text{-}N$ (**4d**)],[1b] and $[\mathrm{NiPh\{Ph_2PN{=}C({=}NPh)Ph\}PR_3}]$ [$PR_3 = PMe_3$ (**5a**), $PMe_2Ph$ (**5b**), $PMePh_2$ (**5c**), $Ph_3P{=}NC({=}NPh)Ph\text{-}N$ (**5d**)][1a] from $[Ni(COD)_2]$, the ylide $Ph_3P{=}CHC({=}NPh)Ph$ or $Ph_3P{=}NC({=}NPh)Ph$, respectively, and tertiary phosphine has been found to be strongly dependent on the steric demand of the phosphine ligand, the new *P,N*-chelate compound $[\mathrm{NiPh\{Ph_2P(\mathit{o}\text{-}C_6H_4NH)\}(PTol_3)}]$ (**6**) was easily obtained [eq. (3)]. This reflects the much lower bulkiness of the NH group in the latter chelate compared with that of the N—Ph group in the former complexes.



**4a** $PR_3 = PMe_3$
**4b** $PR_3 = PMe_2Ph$
**4c** $PR_3 = PMePh_2$
**4d** $PR_3 =$ $Ph_3P{=}CHC({=}NPh)Ph\text{-}N$

**5a** $PR_3 = PMe_3$
**5b** $PR_3 = PMe_2Ph$
**5c** $PR_3 = PMePh_2$
**5d** $PR_3 = Ph_3P{=}NC({=}NPh)Ph\text{-}N$

Again, the oxidative addition of a P—Ph bond to a $Ni^0$ centre was used for the synthesis of **6**, but an important modification had to be introduced owing to the inaccessibility of the phosphorus ylide $Ph_3P(o\text{-}C_6H_4NH)$.[11] One equivalent of $[Ni(COD)_2]$ was reacted with one equivalent of the phosphonium salt $[Ph_3P(o\text{-}C_6H_4NH_2)]Br$ in the presence of two equivalents of $PTol_3$ in order to enable deprotonation of the coordinated $NH_2$ group, as recently observed in related reactions.[12]



(3)

**6**

The product was characterized by its $^{31}P$ NMR spectrum, which showed the usual AB pattern that is typical for square-planar complexes of this type. The catalytic experiments were carried out without further purification of the product.

### Catalytic experiments

Toluene solutions of complexes **1** and **2** were reacted with ethylene (100 μmol catalyst, 60–95 °C, 6 MPa ethylene, 90–300 min)[3b] to form linear α-olefins as oligomerization products. Turnover numbers (TON), averaged over the reaction time, and molecular weight distributions with the Schultz-Flory α value determined from the GC traces when applicable, are given in Table 1. Depending on the nature of the chelate ligand as well as on the auxiliary ligand $PR_3$, different behaviour of the organometallic compounds was observed. Complexes **1**, which all contain the phosphino enolate chelating ligand, all gave linear α-olefins in the range of $C_{4=}$ to $C_{30=}$ (>95% linear α-olefins) with the maximum of the product distribution lying between $C_{8=}$ and $C_{10=}$. Their catalytic activity showed large differences as could be expected from literature data. **1a** was scarcely active in catalytic olefin oligomerization, which is in agreement with earlier observations that $PEt_3$ is a catalyst poison for oligomerization catalysts such as **1c**.[3k,13] Insertion of ethylene into the Ni—Ph bond was verified by performing the reaction with 200 μmol of the nickel complex **1a** and identifying the styrene found in the

**Table 1** Reaction conditions and results for ethylene oligomerization reactions with complexes **1**–**3**, **6** and **7**

| | | | | | | | | | | Molecular weight distribution | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Complex | $n_{complex}$/ µmol | $V_{toluene}$/ ml | $T_{start\text{-}end}$/ °C | $T_{max}$/ °C | Pressure/ MPa | $t_{reaction}$/ min | $TON_{average}$ [a]/ mol (mol h)$^{-1}$ | $C_2H_4$ converted/ g | Linear α-olefins | non S.F.[b] max | Schultz-Flory $\alpha_{SF}$[c] |
| **1a** | 213 | 40 | 75–85 | 85 | 6.0–6.1 | 60 | — | — | $C_{4=}$–$C_{24=}$[d,e] | | 0.5 |
| **1b** | 13 | 40 | 65–90 | >200 | 6.1–6.5 | 12 | 180 000 | 13 | $C_{4=}$–$C_{30=}$ | $C_{40=}$ | |
| **1c** | 26 | 40 | 60–77 | 145 | 6.0–6.1 | 15 | 82 000 | 15 | $C_{4=}$–$C_{30=}$[e] | broad ($C_{10=}$–$C_{20=}$)[e] | |
| **2a** | 147 | 40 | 86–88 | 88 | 6.0–6.1 | 135 | 500 | 5 | $C_{4=}$–$C_{24=}$ | n.d | |
| **2b** | 172 | 40 | 82–88 | 89 | 6.0–6.5 | 85 | 1600 | 11 | $C_{4=}$–$C_{24=}$[e] | | 0.42 |
| **2c** | 78 | 40 | 87–97 | 103 | 6.2–6.3 | 70 | 17 000 | 44 | $C_{4=}$–$C_{90=}$ | n.d. | |
| **2d** | 95 | 40 | 86–90 | 100 | 6.1–6.5 | 110 | 7500 | 37 | $C_{4=}$–$C_{90=}$ | | 0.45 |
| **2e** | 26 | 40 | 71–89 | 93 | 6.0–6.2 | 165 | 18 000 | 36 | $C_{4=}$–$C_{80=}$ | broad ($C_{4=}$–$C_{80=}$) | |
| **2f** | 29 | 40 | 77–86 | 90 | 6.0–6.1 | 160 | 13 000 | 29 | $C_{4=}$–$C_{80=}$ | broad ($C_{4=}$–$C_{80=}$) | |
| **2g** | 111 | 40 | 77–90 | 91 | 6.1–6.4 | 90 | 7300 | 34 | $C_{4=}$–$C_{100=}$ | $C_{26=}$ | |
| **2h** | 98 | 40 | 84–86 | 98 | 6.0–6.1 | 60 | 6900 | 19 | $C_{4=}$–$C_{100=}$ | $C_{40=}$ | |
| **2i** | 60[f] | 40 | 77–87 | 99 | 6.0–6.3 | 65 | 22 000 | 41 | $C_{4=}$–$C_{100=}$ | $C_{30=}$ | |
| **2j** | 120[f] | 40 | 75–89 | 94 | 5.9–6.0 | 40 | 12 500 | 28 | $C_{4=}$–$C_{80=}$ | | 0.87 |
| **2k** | 70[f] | 20 | 85–87 | 88 | 5.9–6.3 | 205 | 900 | 6 | $C_{4=}$–$C_{90=}$ | $C_{22=}$–$C_{48=}$ | |
| **3** + 2 $AlEt_3$ | 30 | 20 | 55–70 | 70 | 4.3–5.6 | 200 | — | — | — | — | — |
| **7** + 2 $AlEt_3$ | 147 | 20 | 68–73 | 150 | 5.0–7.5 | 20 | 7300 | 10 | n.a.[g] | n.d. | |
| **3** + 2 $AlEt_3$ + $PPh_3$ | 60 | 20 | 80–82 | 82 | 5.9–6.4 | 180 | 1000 | 4 | $C_{4=}$–$C_{26=}$[h] | — | — |
| **7** + 2 $AlEt_3$ + $PPh_3$ | 93 | 20 | 70–76 | 76 | 6.2–6.4 | 250 | — | traces | $C_{4=}$–$C_{10=}$[d] | — | — |
| **3** + 2 $AlEt_3$ + $PMe_3$ | 59 | 20 | 78–85 | 85 | 6.0–6.3 | 180 | — | traces | $C_{4=}$–$C_{6=}$[d] | | |
| **7** + 2 $AlEt_3$ + $PMe_3$ | 98 | 20 | 77–81 | 81 | 5.5–6.0 | 120 | — | traces | $C_{4=}$–$C_{10=}$[d] | | 0.45 |
| **6** | 150[f] | 40 | 78–83 | 83 | 5.3–5.5 | 65 | — | traces | $C_{4=}$–$C_{10=}$[d] | | |

[a] Turnover number averaged over $t_{reaction}$; TON = mol $C_2H_4$ converted (mol catalyst h)$^{-1}$. [b] Non-Schultz-Flory distribution, perhaps due to difficulties with the analysis of the solid, liquid and gas phase. [c] $\alpha = X_n/X_{n-2}$. [d] Trace amounts of olefins. [e] Trace amounts of styrene. [f] Complex generated *in situ*; estimated amount. [g] Products were not analysed by GC. [h] Contained some PE or $C_{30}$–$C_{90}$ olefins; solid not analysed by GC.

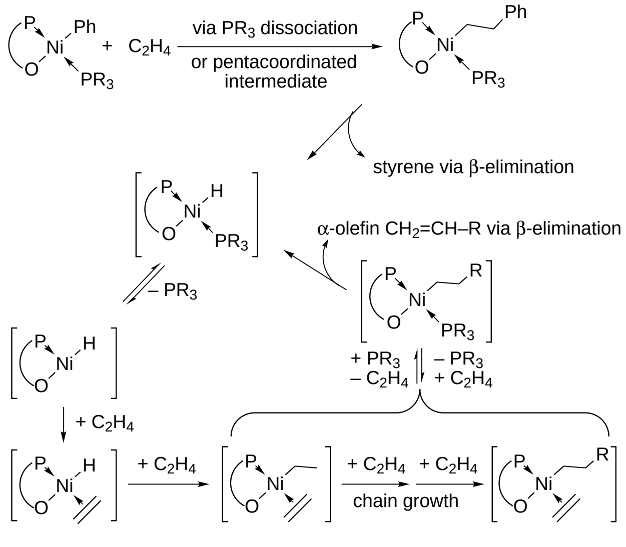
liquid phase together with traces of low molecular weight α-olefins, thus indicating an extremely low catalytic activity. The well-known complex **1c** was reported to exhibit activities ranging from about 6000[2a,9a] to 100 000[2c] mol $C_2H_4$ (mol catalyst h)$^{-1}$ consistent with our own findings (Table 1), while **1b** showed a much higher activity of about 180 000 mol $C_2H_4$ (mol catalyst h)$^{-1}$ (Table 1). Whereas for **1c** the exothermic reaction could still be controlled by cooling and decreasing the amount of catalyst, this was no longer possible for **1b**. With the latter compound the temperature rose to more than 200 °C within less than 30 s after the reaction started, thus leading to almost immediate decomposition of the active species.

In contrast to **1**, the phosphino phenolate complexes **2** generally showed a marked tendency to oligomerize ethylene into α-olefins of higher molecular weight, from $C_{10=}$ to $C_{90=}$ and to produce only minor amounts of the $C_{4=}$ to $C_{10=}$ oligomers. Only **2a** and **2b** gave α-olefins of low molecular weight in the range $C_{4=}$ to $C_{24=}$. The maximum of the product distribution was usually found between $C_{20=}$ and $C_{40=}$ (**2d**–**2i**), but some exceptions were observed: a significant shift to lower molecular weights was found for **2a** and **2b** (both $C_{4=}$ to $C_{6=}$) and **2c** ($C_{8=}$ to $C_{12=}$). A less distinct but unexpected shift was observed for **2j** ($C_{10=}$ to $C_{20=}$). The maximum of the product distribution was shifted to $C_{40=}$–$C_{50=}$ for **2k**. Whereas compounds **2c**–**2j** were highly active catalysts for the oligomerization reaction with turnover rates of 7000–20 000 mol $C_2H_4$ (mol catalyst h)$^{-1}$, complexes **2a**, **2b** and **2k** showed much lower but still noticeable activities of 500–1500 mol $C_2H_4$ (mol catalyst h)$^{-1}$. The exothermic oligomerization reactions were easily controlled by cooling and adjustment of the catalyst concentration. All catalysts proved to be highly selective and produced less than 2% nonlinear or internal olefins.

Reaction of the bis-chelate *cis*-$[\mathrm{Ni}\{\mathrm{Ph_2P}(o\text{-}\mathrm{C_6H_4O})\}_2]$ (**3**) with two equivalents of $AlEt_3$ in toluene only led to an inactive system that did not oligomerize or polymerize ethylene (100 µmol catalyst, 60–95 °C, 6 MPa ethylene, 90–300 min).[3b] This contrasts with the behaviour of the active catalytic species generated *in situ* from *cis*-$[\mathrm{Ni}\{\mathrm{Ph_2PCH{=}C({=}O)Ph}\}]$ (**7**) and two equivalents of $AlEt_3$, which polymerized ethylene in a rapid exothermic reaction (*cf.* ref. 3*j*, 3*k*) at temperatures around 65 °C and 0.6 MPa. It is noteworthy that in the presence of one equivalent of $PPh_3$, both **3** and **7** led to oligomerization catalysts upon reaction with two equivalents of $AlEt_3$, although of very low activity. However, the related complexes **1c** and **2e** showed a much higher activity for ethylene oligomerization than the $AlEt_3$-activated bis-chelate complexes since only traces of linear α-olefins from $C_{4=}$ to $C_{26=}$ were formed by the latter catalysts under similar reaction conditions.

To explain the different properties of complexes **1** and **2** as catalyst precursors in ethylene oligomerization, two important factors that influence the chain length of the olefinic products have to be considered. First, the chelate part of the nickel complexes plays an important role in the modification of the mass distribution of the oligomers, but an influence of the auxiliary ligand $PR_3$ has also to be considered. A slight decrease of the electron-donor ability of the *P,O* chelate was recently found to favor β-elimination and thus formation of lower molecular weight α-olefins.[3b] Thus the clear tendency of complexes **2c**–**2k** to form oligomers of higher molecular weight than those observed with **1b** and **1c** should be related to a higher electron-donor capacity of the phosphino phenolate ligand in **2** compared with the phosphino enolate ligand in **1**. On the other hand, coordination of a strong phosphine ligand *trans* to the phosphorus donor of the phosphino enolate chelate limits the molecular weight of the products, suggesting that a catalyst without any donor ligand would give the highest molecular weights.[3j] The corresponding three-coordinate, 14-electron species is of course unstable and a complex with this stoichiometry was found to be a dimer of the two four-coordinate species, with the enolate oxygen bridging the two nickel centres.[3j] The results of **2a** and **2b** are consistent with this view since their better donor phosphine ligand leads to lower molecular weight oligomers. However, according to ref. 3*k* and 13 and the behaviour of **1a**, complex **2a** was not expected to be an active catalyst and **2b** should show a much smaller activity, if any. These observations undoubtedly reflect the often denied influence of the $PR_3$ ligand on the catalytic activity and the mass distribution of the $\alpha$-olefins.[2,3d] This influence could be explained in terms of an equilibrium in solution between coordinated and free $PR_3$ that is essential for deciding whether $\beta$-elimination or chain growth occurs. Such an equilibrium was first mentioned by Keim[13] and is confirmed by the $^{31}$P NMR data we obtained for some complexes: **2b** and **2c** each showed two broad signals at room temperature in contrast to the usual, well-resolved AB-type pattern for this type of compound. Especially the temperature-dependent spectrum of **2d**, which shows a broad singlet at room temperature and two sharp doublets typical for an AB-system at −40 °C, leads us to consider the occurrence of an equilibrium between coordinated and free $PR_3$ in solution under the conditions of the oligomerization reaction. Of course, this does not preclude the possibility of pentacoordination when the olefin approaches the metal centre. A chain-growth mechanism involving retention of both the *P*,*O* chelate and the $PR_3$ ligand would imply changes of coordination numbers between four and five and does not appear consistent with the lability observed for $PR_3$ in active catalyst complexes.

As shown in Scheme 1, dissociation of the phosphine ligand $PR_3$ generates a free coordination site on the nickel centre and enables coordination of an ethylene molecule, which in a second step undergoes insertion into a Ni—Ph, Ni—H or Ni—alkyl bond and thus leads to chain growth. Chain growth terminates when the phosphine recoordinates to the nickel centre since ethylene can no longer easily enter the coordination sphere of the metal. From this 16-electron nickel complex, the $\beta$-elimination step can procede *via* an 18-electron pentacoordinated intermediate and is able to compete with the otherwise much faster chain-growth reaction and consequently leads to formation of the $\alpha$-olefin products. In the absence of a ligand like $PR_3$ that helps terminate chain growth, catalytic systems would lead to the formation of polyethylene, as indeed observed for the $AlEt_3$-activated bis-chelate complex *cis*-[$\overline{\mathrm{Ni\{Ph_2PCH{=}C({=}O}}\mathrm{)Ph\}_2}$] (**7**).[3k] In the presence of $PPh_3$, the latter exclusively produced linear $\alpha$-olefins, which convincingly supports the described model. Thus, besides the important electronic and steric influence of the chelating ligand,[2–7] the mass distribution also depends on the nature of the auxiliary ligand $PR_3$ and can be tuned by the introduction of different phosphines. As seen above, this influence clearly depends on the ability of the phosphine to coordinate more or less strongly to the metal atom: $\alpha$-olefins of higher molecular weight were produced by the complexes **2d**–**2k** that contain the weakly bound phosphines $PPh_3$, $PTol_3$, *etc*., whereas complexes **2a** and **2b** with the more strongly coordinating ligands $PMe_3$ and $PMe_2Ph$ gave oligomers of lower molecular weight. Compound **2c** with the $PMePh_2$ ligand appeared to behave in an intermediate manner as it gave oligomers in the range of $C_{4=}$ to $C_{80=}$, but with the maximum of the mass distribution still lying at lower molecular masses than for **2d**–**2k**. The notable results with **2j**, which indicated a distinct shift to lower molecular weight $\alpha$-olefins compared to its homologues, lack definitive explanation but appear contradictory since in this case an electron-withdrawing effect of the ligand appears to promote chain transfer of the $\alpha$-olefins. This has already been recognized earlier for other compounds that are active in ethylene oligomerization.[14] That a similar effect is not observed with **2k** is not clearly understood but note that this catalyst was prepared *in situ*.



**Scheme 1**

Concerning the obvious difference between the activities of the $PMe_3$ complexes **1a** and **2a**, the reason should be sought in the different electronic effect of the two chelate ligands. The more electron-donating phosphino phenolate generates an electron-rich metal centre, which disfavours $PMe_3$-coordination and thus leads to low, but noticeable activity [500 mol $C_2H_4$ (mol catalyst h)$^{-1}$]. In **1a** on the other hand, the more electron-deficient nickel centre generated by coordination of the less electron-donating phosphino enolate leads to a stronger Ni—$PMe_3$ bond and consequently this complex showed practically no catalytic activity for the oligomerization of ethylene. For compounds **2a**–**2k** only two rough trends could be observed: first, the more strongly coordinating phosphines in **2a** and **2b** gave rise to low activities, whereas the weaker donor phosphines generated more active systems owing to their lower tendency to coordinate to the nickel centre. Second, sterically hindered phosphines like $PCy_3$ in **2d** also gave rise to highly active species because of easy dissociation of the metal–phosphorus bond (*cf.* the $^{31}P\{^1H\}$ NMR data of **2d**). The relatively low catalytic activity of **2k** was attributed to inhibition by impurities that were present in the material obtained from complex synthesis.

In agreement with recent observations made with the *P*,*N*-chelate compounds of the type **4** and **5**,[1] [$\overline{\mathrm{NiPh\{Ph_2P(}o\mathrm{\text{-}C_6H_4N}}\mathrm{H)\}(PTol_3)}$] (**6**) is not an active catalyst for the conversion of ethylene to higher $\alpha$-olefins under the chosen conditions.[3b] Only traces of $C_{4=}$ to $C_{10=}$ linear $\alpha$-olefins were found at the end of the reaction. This could be due to the instability of the active species under these conditions, as was already proposed for complexes **4** and **5**.

## Experimental

### Reagents and physical measurements

All operations were performed in Schlenk-type flasks under high purity argon, using vacuum line techniques. The solvents were purified and dried under argon by conventional methods. The $^1$H NMR spectra were recorded at 200 MHz on a Bruker AC 200 F, the $^{31}P\{^1H\}$ NMR spectra at 81 MHz on a Bruker CXP 200 and at 122 MHz on a Bruker AC300 instrument. The spectra were recorded at room temperature, except when indicated explicitly. $^1$H and $^{31}$P shifts are given relative to internal TMS and external $H_3PO_4$, respectively. A positive sign denotes a shift downfield from that of the reference. Coupling constants are given in Hz. The electron impact mass spectra (EI, 70 eV) were recorded on a Fisons ZAB-HF spectrometer. Reactions with ethylene were performed in a 130 ml double-walled stainless steel autoclave, fitted with a manometer, a septum inlet and a magnetic stirrer. The products were analyzed by gas phase chromatography with a Hewlett Packard 5890 Series II instrument on a PONA column (methylsilicone, diameter: 0.22 mm, length: 50 m, temperature program from 35–270 °C) for the $C_{4=}$–$C_{30=}$ fraction and on a capillary Supelco Polywax SPB1 column (diameter: 0.53 mm, length: 30 m, "on column injection", 3 min at 5 °C then temperature program 10 °C min$^{-1}$ up to 380 °C) for the $C_{4=}$–$C_{100=}$ fraction. The highest mass detected corresponded to $C_{100=}$. The phosphines P(C$_6$H$_4$X)$_3$ (X = Cl, F, CF$_3$, OMe) were purchased from Strem and used without further purification. The other phosphines were purchased from Aldrich and purified either by recrystallization or by degassing. High purity ethylene was purchased from Air Liquide and used as received.

## Synthesis

[Ni(COD)$_2$],[15] [NiPh{Ph$_2$PCH⋯C(⋯O)Ph}(PR$_3$)] [PR$_3$ = PCy$_3$ (**1b**),[1b] PPh$_3$ (**1c**)[9a]], *cis*-[Ni{Ph$_2$P(*o*-C$_6$H$_4$O)}$_2$] (**3**),[10] *cis*-[Ni{Ph$_2$PCH⋯C(⋯O)Ph}$_2$] (**7**),[16] Ph$_3$P=CHC(=O)Ph,[17] Ph$_3$P(*o*-C$_6$H$_4$O)[11] and [Ph$_3$P(*o*-C$_6$H$_4$NH$_2$)]Br[11] were synthesized according to the published methods.

**[NiPh{Ph$_2$PCH⋯C(⋯O)Ph}(PMe$_3$)] (1a).** A cold solution of 0.39 g (1.4 mmol) [Ni(COD)$_2$] in 30 ml toluene was added slowly to a suspension of 145 µl (1.4 mmol) PMe$_3$ and 0.53 g (1.4 mmol) Ph$_3$P=CHC(=O)Ph in 20 ml toluene at 0 °C. The mixture acquired immediately an intense yellow tint and a clear solution was formed within 1 h. After stirring at room temperature for 16 h, the resulting orange solution was heated to 50 °C for 2 h and subsequently the solvent was removed *in vacuo*. The residue was taken up in 5 ml toluene, the solution was filtered and 100 ml pentane was added. The orange crystals that were formed at −18 °C overnight were isolated, washed with 2 × 5 ml pentane and dried *in vacuo*. Yield: 0.50 g (71%). Anal. calcd for C$_{29}$H$_{30}$OP$_2$Ni (515.20): C, 67.61; H, 5.87; O, 3.11; P, 12.02. Found: C, 67.53; H, 5.90; O, 3.20; P, 12.1. $^1$H NMR (C$_6$D$_6$): 8.3–6.8 (20H, aromatic H), 5.27 (s, 1H, PCH), 0.82 (d, $^2J_{\text{PH}}$ = 8.8, 9H, PMe$_3$); $^{31}$P{$^1$H} NMR (C$_6$D$_6$): AB spin system $\delta_A$ 15.8 (d, Ph$_2$P), $\delta_B$ − 16.7 (d, PMe$_3$), $^2J_{AB}$ = 298.1.

**[NiPh{Ph$_2$P(*o*-C$_6$H$_4$O)}(PMe$_3$)] (2a).** As described for **1a**, 0.46 g (1.7 mmol) [Ni(COD)$_2$] in 30 ml toluene was reacted with a suspension of 176 µl (1.7 mmol) PMe$_3$ and 0.60 g (1.7 mmol) Ph$_3$P(*o*-C$_6$H$_4$O) in 20 ml toluene. The residue obtained after evaporation of the solvent was taken up in 10 ml toluene, the solution was filtered and 100 ml pentane were added. The bright yellow precipitate was isolated by filtration, washed with 2 × 5 ml pentane and dried *in vacuo*. A second crop of the product was obtained from the filtrate at −18 °C. Both fractions still contain some of the bis-chelate complex *cis*-[Ni{Ph$_2$P(*o*-C$_6$H$_4$O)}$_2$] (**3**) due to similar solubility properties. Yield: 0.38 g (47%). Anal. calcd for C$_{27}$H$_{28}$OP$_2$Ni (489.16): C, 66.3; H, 5.77; O, 3.27; P, 12.7. Found: C, 65.1; H, 5.65; O, 3.09; P, 11.9. $^1$H NMR (C$_6$D$_6$): 7.6–6.4 (19H, aromatic H), 0.77 (d, $^2J_{\text{PH}}$ = 9.3, 9H, PMe$_3$); $^{31}$P{$^1$H} NMR (C$_6$D$_6$): AB spin system $\delta_A$ 20.8 (d, Ph$_2$P), $\delta_B$ − 16.6 (d, PMe$_3$), $^2J_{AB}$ = 302.4; MS (EI): *m/z* 488 (M$^+$), 411 (M$^+$ − Ph), 412 (M$^+$ − PMe$_3$), 335 (M$^+$ − Ph − PMe$_3$).

**[NiPh{Ph$_2$P(*o*-C$_6$H$_4$O)}(PMe$_2$Ph)] (2b).** As described for **1a**, 0.43 g (1.6 mmol) [Ni(COD)$_2$] in 30 ml toluene was reacted with a suspension of 227 µl (1.6 mmol) PMe$_2$Ph and 0.56 g (1.6 mmol) Ph$_3$P(*o*-C$_6$H$_4$O) in 20 ml toluene. Usual work-up, as described for **2a**, yielded **2b** as a bright yellow powder with some **3** as an impurity. Yield: 0.30 g (31%). Anal. calcd for C$_{32}$H$_{30}$OP$_2$Ni (551.23): C, 69.73; H, 5.49; O, 2.90; P, 11.2. Found: C, 68.34; H, 5.50; O, 4.10; P, 10.2. $^1$H NMR (C$_6$D$_6$): 7.7–6.4 (24H, aromatic H), 1.06 (br, 6H, P*Me*$_2$Ph); $^{31}$P{$^1$H} NMR (C$_6$D$_6$): AB spin system $\delta_A$ 21.5 (br, Ph$_2$P), $\delta_B$ − 7.4 (br, PMe$_2$Ph), $^2J_{AB}$ not resolved; MS (EI): *m/z* 550 (M$^+$), 473 (M$^+$ − Ph), 412 (M$^+$ − PMe$_2$Ph), 335 (M$^+$ − Ph − PMe$_2$Ph).

**[NiPh{Ph$_2$P(*o*-C$_6$H$_4$O)}(PMePh$_2$)] (2c).** A cold solution of 0.58 g (2.1 mmol) [Ni(COD)$_2$] in 40 ml toluene was added slowly to a suspension of 390 µl (2.1 mmol) PMePh$_2$ and 0.74 g (2.1 mmol) Ph$_3$P(*o*-C$_6$H$_4$O) in 20 ml toluene at 0 °C. The mixture became immediately orange and formed a clear orange solution within 2 h. After stirring at room temperature for another 14 h, the solution was heated to 50 °C for 2 h and subsequently the solvent was removed *in vacuo*. Usual work-up, as described for **2a**, yielded **2c** as a bright yellow powder, still containing some **3** and other unidentified impurities due to similar solubility properties. Yield: 0.58 g (43%). $^1$H NMR (C$_6$D$_6$): 8.0–6.1 (29H, aromatic H), 1.14 (br, 3H, P*Me*Ph$_2$); $^{31}$P{$^1$H} NMR (C$_6$D$_6$): AB spin system $\delta_A$ 22.1 (d, Ph$_2$P), $\delta_B$ 3.0 (d, PMePh$_2$), $^2J_{AB}$ = 245; MS (EI): *m/z* 612 (M$^+$).

**[NiPh{Ph$_2$P(*o*-C$_6$H$_4$O)}(PCy$_3$)] (2d).** A cold solution of 0.53 g (1.9 mmol) [Ni(COD)$_2$] in 30 ml toluene was added slowly to a suspension of 0.53 g (1.9 mmol) PCy$_3$ and 0.67 g (1.9 mmol) Ph$_3$P(*o*-C$_6$H$_4$O) in 20 ml toluene at 0 °C. The mixture acquired immediately an intense yellow tint and formed a clear orange solution within 1 h. After stirring at room temperature for another 15 h, the solution was heated to 50 °C for 2 h and subsequently the solvent was removed *in vacuo*. The residue was taken up in 30 ml toluene, the solution filtered and 60 ml pentane was added. At − 18 °C orange crystals were formed within a few days. These were isolated, washed with 2 × 5 ml pentane and dried *in vacuo*. Yield: 0.88 g (68%). Anal. calcd for C$_{42}$H$_{52}$OP$_2$Ni (693.52): C, 72.74; H, 7.56; O, 2.31; P, 8.93. Found: C, 72.75; H, 7.74; O, 2.18; P, 9.38. $^1$H NMR (C$_6$D$_6$): 7.6–6.4 (19H, aromatic H), 2.1–0.9 (33H, PCy$_3$); $^{31}$P{$^1$H} NMR (C$_6$H$_6$, 20 °C): 19.1 (s); $^{31}$P{$^1$H} NMR (toluene-d$_8$, −40 °C): AB spin system $\delta_A$ 23.4 (d, Ph$_2$P), $\delta_B$ 20.5 (d, PCy$_3$), $^2J_{AB}$ = 269.5.

**[NiPh{Ph$_2$P(*o*-C$_6$H$_4$O)}(PPh$_3$)] (2e).** A cold solution of 0.58 g (2.1 mmol) [Ni(COD)$_2$] in 40 ml toluene was added slowly to a suspension of 0.55 g (2.1 mmol) PPh$_3$ and 0.74 g (2.1 mmol) Ph$_3$P(*o*-C$_6$H$_4$O) in 20 ml toluene at 0 °C. The mixture became dark red immediately and formed a clear red solution within 1 h. After stirring at room temperature for another 15 h, the resulting yellow-orange solution was heated to 50 °C for 2 h and subsequently the solvent was removed *in vacuo*. Usual work-up, as described for **2a**, yielded **2e** as a bright yellow powder, still containing some of the starting PPh$_3$ and **3** due to similar solubility properties. Yield: 0.45 g (33%). Anal. calcd for C$_{42}$H$_{34}$OP$_2$Ni (675.37): C, 74.69; H, 5.07; O, 2.37; P, 9.17. Found: C, 73.88; H, 5.08; O, 3.09; P, 9.06. $^1$H NMR (C$_6$D$_6$): 7.9–5.8 (aromatic H); $^{31}$P{$^1$H} NMR (C$_6$D$_6$): AB spin system $\delta_A$ 23.7 (d, Ph$_2$P), $\delta_B$ 18.7 (d, PPh$_3$), $^2J_{AB}$ = 286.8; MS (EI): *m/z* 674 (M$^+$), 597 (M$^+$ − Ph), 412 (M$^+$ − PPh$_3$), 335 (M$^+$ − Ph − PPh$_3$).

**[NiPh{Ph$_2$P(*o*-C$_6$H$_4$O)}(PTol$_3$)] (2f).** As described for **2e**, 0.53 g (1.9 mmol) [Ni(COD)$_2$] in 30 ml toluene was reacted with a suspension of 0.58 g (1.9 mmol) PTol$_3$ and 0.67 g (1.9 mmol) Ph$_3$P(*o*-C$_6$H$_4$O) in 20 ml toluene. Usual work-up, as described for **2a**, yielded **2f** as a bright yellow powder. Yield: 1.15 g (84%). Anal. calcd for C$_{45}$H$_{40}$OP$_2$Ni (717.45): C, 75.3; H, 5.6. Found: C, 74.9; H, 5.4. $^1$H NMR (C$_6$D$_6$): 7.9–6.2 (31H, aromatic H), (s, 9H, PC$_6$H$_4$*Me*); $^{31}$P{$^1$H} NMR (C$_6$D$_6$): AB spin system $\delta_A$ 25.0 (d, $Ph_2P$), $\delta_B$ 18.5 (d, $PTol_3$), $^2J_{AB} = 287.6$; MS (EI): *m*/*z* 716 ($M^+$), 639 ($M^+ - Ph$), 412 ($M^+ - PTol_3$), 335 ($M^+ - Ph - PTol_3$).

**$[\overline{\mathrm{NiPh\{Ph_2P(}o\text{-}\mathrm{C_6H_4O}}\mathrm{)\}\{P(}p\text{-}\mathrm{C_6H_4OMe)_3\}}]$ (2g).** As described for **2e**, 0.38 g (1.4 mmol) $[Ni(COD)_2]$ in 30 ml toluene was reacted with a suspension of 0.45 g (1.4 mmol) $P(p\text{-}C_6H_4OMe)_3$ and 0.49 g (1.4 mmol) $Ph_3P(o\text{-}C_6H_4O)$ in 20 ml toluene. Usual work-up, as described for **2a**, yielded **2g** as a yellow-ocre powder. Due to similar solubility properties, the product still contained a small amount of **3** and some of the starting phosphine $P(p\text{-}C_6H_4OMe)_3$. Yield: 0.64 g (57%). $^{31}P\{^1H\}$ NMR ($C_6D_6$): AB spin system $\delta_A$ 22.3 (d, $Ph_2P$), $\delta_B$ 14.7 [d, $P(p\text{-}C_6H_4OMe)_3$], $^2J_{AB} = 289.7$.

**$[\overline{\mathrm{NiPh\{Ph_2P(}o\text{-}\mathrm{C_6H_4O}}\mathrm{)\}\{P(OMe)_3\}}]$ (2h).** A cold solution of 0.47 g (1.7 mmol) $[Ni(COD)_2]$ in 30 ml toluene was added slowly to a suspension of 200 μl (1.7 mmol) $P(OMe)_3$ and 0.60 g (1.7 mmol) $Ph_3P(o\text{-}C_6H_4O)$ in 20 ml toluene at 0 °C. The mixture acquired an intense yellow tint within 1 h, but no clear solution was formed. After stirring at room temperature for another 15 h, the resulting orange cloudy solution was heated to 50 °C for 2 h. The now clear solution was evaporated, whereupon a yellow solid precipitated soon. The residue was taken up in 10 ml toluene and the suspension was filtered. The product was washed with 2 × 5 ml pentane and dried *in vacuo*, while 50 ml pentane were added to the solution. Thus, a second crop of **2h** was obtained, which was also washed with 2 × 5 ml pentane and dried *in vacuo*. Due to similar solubility properties, the product still contained a small amount of **3** and residual $P(OMe)_3$. Yield: 0.51 g (53%). $^{31}P\{^1H\}$ NMR ($C_6D_6$): AB spin system $\delta_A$ 24.0 (br, $Ph_2P$), $\delta_B$ 18.1 [br, $P(OMe)_3$], $^2J_{AB}$ not resolved.

**$[\overline{\mathrm{NiPh\{Ph_2P(}o\text{-}\mathrm{C_6H_4O}}\mathrm{)\}(PR_3)}]$ $[PR_3 = P(p\text{-}C_6H_4Cl)_3$ (2i), $P(p\text{-}C_6H_4F)_3$ (2j), $P(p\text{-}C_6H_4CF_3)_3$ (2k)].** As described for **2e**, about 1.5 mmol $[Ni(COD)_2]$ in 30 ml toluene was reacted with suspensions of one equivalent of the corresponding phosphine $PR_3$ and one equivalent of $Ph_3P(o\text{-}C_6H_4O)$ in 20 ml toluene. The dark red solids thus obtained were used for the catalytic experiments without further purification and characterization.

**$[\overline{\mathrm{NiPh\{Ph_2P(}o\text{-}\mathrm{C_6H_4NH}}\mathrm{)\}(PTol_3)}]$ (6).** As described for **2e**, 0.45 g (1.6 mmol) $[Ni(COD)_2]$ in 30 ml toluene was reacted with a suspension of 0.97 g (3.2 mmol) $PTol_3$ and 0.70 g (1.6 mmol) $[Ph_3P(o\text{-}C_6H_4NH_2)]Br$ in 20 ml toluene. At the end of the reaction, the solid $[HPTol_3]Br$ was removed by filtration and the clear red solution was evaporated. The dark red solid thus obtained was used for the catalytic experiments without further purification. $^{31}P\{^1H\}$ NMR ($C_6D_6$): AB spin system $\delta_A$ 28.5 (d, $Ph_2P$), $\delta_B$ 21.9 (d, $PTol_3$), $^2J_{AB} = 276.4$.

### Reactions

**Reactions of 1, 2 and 6 with ethylene.** The nickel complexes (20–200 μmol) were dissolved in 40 ml toluene, transferred *via* canula to the autoclave and stirred under 0.5 MPa ethylene for 16 h. Then temperature and pressure were increased to the standard conditions 80–90 °C and 6 MPa. After 1–3 h, the autoclave was cooled to ambient temperature, the pressure released slowly and the products analyzed by gas phase chromatography.

**Reactions of $AlEt_3$-activated 3 and 7 with ethylene.** Typically, a solution of 30–150 μmol of the nickel bis-chelate complexes in 20 ml toluene was cooled to 0 °C and two equivalents of $AlEt_3$ were added. These mixtures were stirred for 20 min while warming to room temperature, then the resulting yellow/brown clear solutions were transferred *via* canula to the autoclave and the same procedure as described above was followed.

**Reactions of $AlEt_3$-activated 3 and 7 with ethylene in the presence of $PPh_3$ or $PEt_3$.** Solutions of 60–90 μmol of the nickel bis-chelate complexes and one equivalent of $PPh_3$ or $PEt_3$ in 20 ml toluene were reacted with two equivalents of $AlEt_3$ as described above and the usual procedure for the catalysis experiments was followed.

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