Methyl(2-phosphanylphenolato[*P*,*O*])nickel(II) Complexes – Synthesis, Structure, and Activity as Ethene Oligomerization Catalysts

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Reactions of various substituted 2-phosphanylphenols **1a–f** with half-molar amounts of *cis*-$[MeNi(\mu\text{-}OMe)(PMe_3)]_2$ have been found to yield square-planar methyl(2-phosphanylphenolato)(trimethylphosphane)nickel(II) complexes **2a–f**. $^2J_{PP}$ coupling constants of 305–316 Hz at low temperature indicate a *trans*-configuration for the products, while broad ^{31}P-NMR signals at room temperature can be attributed to rapid dissociation of PMe_3. Reaction with excess **1** gave rigid bis(2-phosphanylphenolato)nickel(II) complexes as exemplified by **3e**, whereas addition of PMe_3 to **2a** led to the pentacoordinate methyl(2-phosphanylphenolato)bis(trimethylphosphane)nickel(II) complex **4a**. Higher yields of **4a** and **4d** were obtained by reactions of **1a** and **1d** with $Me_2Ni(PMe_3)_3$. Single-crystal X-ray diffraction analyses of **3e** and **4a** have revealed the structures as square-planar *trans*-bis- and trigonal-bipyramidal mono(2-phosphanylphenolato)nickel(II) P∩O-chelate complexes, respectively. The methylnickel complexes **2** and **4** have been found to be effective one-component catalysts for the oligomerization of ethene. High conversions (> 96%) were achieved with the P-basic derivatives **2e**, **2f**, and **4d** bearing one or two branched alkyl groups (isopropyl, *tert*-butyl), whereas the diphenylphosphanyl derivatives were less active; **4d** gave shorter oligomers than **2e** or **2f**.

Introduction

P∩O-chelate complexes are of crucial importance in the oligomerization of ethene to give linear α-olefins by the Shell Higher Olefins Process.[1] In order to tune the catalyst properties, various P∩O-nickel complexes of varying ring sizes and bearing different functional groups have been investigated.[2,5] In early studies of the oligomerization of ethene, using in situ generated catalysts obtained from 2-diphenylphosphanylphenol and bis(1,5-cyclooctadiene)nickel or nickel salts in the presence of $NaBH_4$, mainly polymers were obtained.[6] Oligomers of ethene were, however, formed using phenyl(2-diphenylphosphanyl-4-hydroxyphenolato)(triphenylphosphane)nickel(II), obtained by phenyl migration from α-benzoyl phosphorus ylides.[2b,7] A recent study of the influence of various auxiliary phosphane ligands on the activity and selectivity of analogously prepared phenyl(2-diphenylphosphanylphenolato)(phosphane)nickel(II) catalysts established that high activity is seen with PPh_3, $P(4\text{-}X\text{–}C_6H_4)_3$ (X = Cl > Me > F), and PPh_2Me, whereas PCy_3 (Cy = cyclohexyl), which has a strong enhancing effect on the activity of the related phenyl(2-diphenylphosphanyl-1-phenylenolato)(phosphane)nickel(II) catalysts, induces only moderate activity. Generally, a marked tendency to produce higher oligomers, from $C_{10=}$ to $C_{90=}$, and only minor amounts of the desired $C_{4=}$ to $C_{10=}$ oligomers is observed. Exceptions are complexes with PMe_3 and $PPhMe_2$ ligands, which give α-olefins of low molecular weight ($C_{4=}$ to $C_{24=}$), although with lower catalytic activity.[3d] In view of the recently reported access to variously substituted 2-phosphanylphenols[8,9] and their high tendency to form P∩O-chelates,[8,10,11] we turned our attention to the synthesis of catalytically active (2-phosphanylphenolato[*P*,*O*])nickel(II) complexes and the tuning of their activity and selectivity by variation of substituents at the phosphorus and the phenolate group. We report here on methyl(2-phosphanylphenolato)nickel complexes, which differ from cyclopentadienyl(2-phosphanylphenolato)nickel(II) complexes[8b,11] in that they are active oligomerization catalysts.

Results and Discussion

Synthesis

Selected 2-phosphanylphenols **1a**–**f** were synthesized either by dilithiation of 2-bromophenols, reaction with the respective chlorophosphane and acid workup,[9c,10i] or, in analogy to the procedure of Rauchfuß,[8b] by *ortho*-metallation of the corresponding phenolmethoxymethyl

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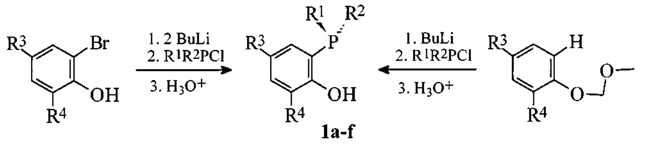
ether with butyllithium, substitution with chlorophosphane, and subsequent acid ether cleavage (Scheme 1).



1	a	b	c	d	e	f
R^1	Ph	Ph	*i*Pr	*t*Bu	*i*Pr	*i*Pr
R^2	Ph	Ph	Ph	Ph	*i*Pr	*i*Pr
R^3	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	F
R^4	*t*Bu	Me	*t*Bu	*t*Bu	*t*Bu	H

Scheme 1. Synthesis of 2-phosphanylphenols

The chosen substitution pattern, i.e. diphenyl, alkylphenyl, and dialkyl groups at phosphorus, 4,6-di-*tert*-butyl-, 4-methyl-6-*tert*-butyl-, and 4-fluoro-substituents at the phenoxy group, provided ligands with widely differing basicities at phosphorus and oxygen, allowing a qualitative appraisal of electronic effects on the oligomerization of ethene by the corresponding nickel P$^{\cap}$O-chelate complexes. Branched alkyl groups were selected since 2-isopropylphenylphosphanyl- and, in particular, 2-*tert*-butylphenylphosphanylcresol have been found to exhibit a lower tendency to form the thermodynamically preferred bis(P$^{\cap}$O-chelates) than 2-methylphenylphosphanyl- or 2-diphenylphosphanyl derivatives[11b] upon reaction with equimolar amounts of nickelocene in toluene. The 6-*tert*-butyl group stabilizes the P$^{\cap}$O-chelate complexes through its steric effect on the periphery, but does not significantly shield the metal center. The steric effect causes a bending of the substituents at oxygen towards the phosphorus, as is evident from the unusual formation of a 2-phosphanylphenolate P$^{\cap}$O-chelate complex with the hard titanium cation,[10h] an extremely increased ${}^{4}J_{\mathrm{PSn}}$ in a 2-phosphanylphenolstannyl ether, and the presence of P···H–O hydrogen bonds in **1c** and **1d**.[9c] In **1e**, the presence of a P···H–O hydrogen bond is evident from a large ${}^{4}J_{\mathrm{PH}}$ coupling constant of 12.4 Hz for the hydroxyl proton, whereas in **1f** this proton gives rise to a broad singlet. An X-ray structure analysis of single crystals of **1e**, performed at –100 °C, reveals a *trans*-eclipsed conformation (Figure 1), which means that the lone electron pair is also directed towards the hydroxyl group in the solid state. The lack of evidence for any such P···H–O hydrogen bond in **1f** underlines the role of the bulky 6-substituent in inducing such interactions.

Reactions of **1a–c** and **1f** with half-molar and of **1d** with equimolar amounts of $[\mathrm{NiMe(PMe_3)(\mu\text{-}MeO)}]_2$ in diethyl ether, THF, or pentane solution proceeded via red intermediates and led to the yellow or red-brown methyl(2-phosphanylphenolato)(trimethylphosphane)nickel(II) complexes **2a–d** and **2f**. However, when the P-basic **1e** was used in slight excess relative to the half-molar amount of $[\mathrm{NiMe(PMe_3)(\mu\text{-}MeO)}]_2$, the air-stable *trans*-bis(P$^{\cap}$O-chelate) complex **3e** was formed in high yield. This can be mainly attributed to the more facile dissociation of PMe$_3$ from **2e**.

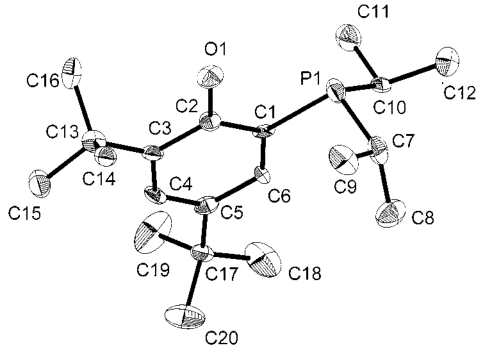
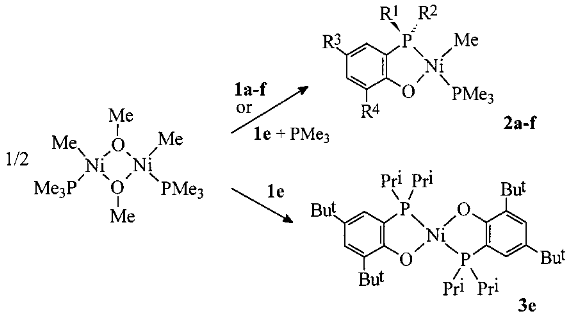


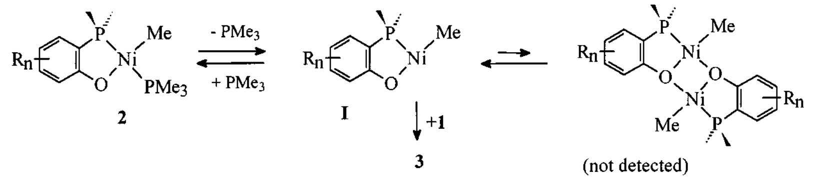
Figure 1. ORTEP plot of the molecular structure of **1e**; selected distances [Å] and angles [°]: P1–C2 1.847(9), P1–C7 1.877(10), P1–C10 1.838(10); P1–C1–C2 118.7(8), P1–C1–C6 122.1(8), O1–C2–C1 119.9(9), O1–C2–C3 116.9(10)

When the reaction was carried out in the presence of one equivalent of PMe$_3$, **2e** was isolated (Scheme 2). The complexes **2** were purified by fractional extraction of the crude products with pentane.

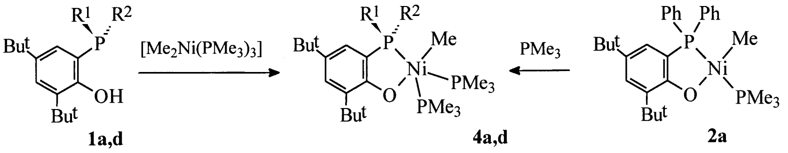


Scheme 2. Synthesis of the nickel complexes **2a–f** and **3e**

Whereas the room-temperature NMR spectra of *cis*- and *trans*-bis(2-phosphanylphenolato[*P*,*O*])nickel(II) chelate complexes **3** feature sharp signals and multiplets showing couplings to both phosphorus atoms for a number of ^{1}H as well as ^{13}C nuclei,[11,12] the room-temperature spectra of **2a–f** reveal couplings of the corresponding ^{1}H and ^{13}C nuclei to only one phosphorus atom, and in the ^{31}P-NMR spectra broad doublets or singlets are observed. At low temperature (–25 to –70 °C), the phosphorus signals of **2a–f** appear as sharp doublets with ${}^{2}J_{\mathrm{PP}}$ couplings in the range 305–316 Hz, indicating a *trans* configuration. These values are similar to the ${}^{2}J_{\mathrm{PP}}$ values of 245–290 Hz recently observed in phenylnickel-*o*-diphenylphosphanylphenolate phosphane complexes.[3d] The ^{1}H and ^{13}C signals of the NiMe groups in **2a–f** are split by couplings with both the phosphorus atoms, whereas the multiplicity of the ^{1}H and ^{13}C signals of the P$^{\cap}$O-ligand (at –25 to –30 °C) arises from coupling with the *o*-phosphorus nucleus only when PH or PC coupling is observed. These observations are indicative of rapid dissociation of the monodentate phosphane at room temperature, whereas exchange reactions of the P$^{\cap}$O-ligands, as indicated, e.g., by the different configurations of a bulky substituted bis(2-phosphanylphenolato)nickel complex in solution and in the solid state,[12] are slow on the NMR time scale. The decreased line-widths of the room-temper-



Scheme 3. Dissociation equilibria of **2**



Scheme 4. Syntheses of the nickel complexes **4a**, **d**

ature phosphorus resonances of the diisopropylphosphanyl complexes **2e** and **2f** and the lower temperature necessary for obtaining sharp doublets (–70 °C) indicate enhanced dissociation in the case of P$^{\cap}$O-ligands with increased donor and diminished acceptor strengths. The dissociation products, the tricoordinate 14-electron nickel intermediates **I**, undergo a rapid back-reaction with PMe_3 (Scheme 3). The presence of excess **1** disrupts this equilibrium by trapping **I**, thereby yielding the more stable bis(P$^{\cap}$O-chelates) **3**. The high reactivity of **I** prevents the observation of equilibrium concentrations. The concentrations of free trimethylphosphane and of dimers of **I** also fall below the limit of detection by NMR, suggesting a rapid association–dissociation equilibrium of PMe_3 with a small equilibrium constant. Dissociation of PMe_3 also seems to be responsible for the rapid aerial oxidation of solutions of **2a** since the solid material is stable in air for several hours.

In order to ascertain whether trimethylphosphane may be scavenged by the 16-electron complexes **2**, generation of the pentacoordinate complex **4a** was attempted by adding excess trimethylphosphane to **2a**. However, this method gave only a low yield (ca. 30%) of the red product. It was found that **4a** and **4d** could be obtained much more readily by reaction of **1a** and **1d**, respectively, with dimethyl tris(trimethylphosphane)nickel(II) in diethyl ether (Scheme 4). Complexes **4a** and **4d** were found to be stable under ambient conditions but lose trimethylphosphane on heating and decompose at around 106–109 °C. As expected for pentacoordinate nickel complexes, **4a** and **4d** are highly fluxional and exhibit two broad phosphorus singlets in their ^{31}P-NMR spectra, even at –30 °C, indicating rapid pseudo-rotation and dissociation of PMe_3. The ^{1}H and ^{13}C nuclei of the P$^{\cap}$O-ligand and the Ni methyl group only show coupling with the rigid chelate-bound phosphorus. As in the case of **2**, the dissociation equilibria account for the fact that solutions of **4** are rapidly oxidized, whereas the isolated complexes can be exposed to air for a short time.

Structural Aspects

In addition to the dynamic effects, the ^{1}H-, ^{13}C-, and ^{31}P-NMR chemical shifts and coupling constants of the rigid phosphanylphenolate ligands confirmed the configurations of **2**–**4**. Further structural information was provided by single-crystal X-ray structure analyses of **3e** and **4a**. In this regard, we will now discuss some trends by comparison of selected data (Table 1). The coordination chemical shifts of the *ortho*-phosphorus atoms (*o*-P) in complexes of types **4**, *cis*-**3**, and *trans*-**3** reveal a greater deshielding in the more highly alkylated P–alkyl$_n$Ph$_{2-n}$ derivative in each case, due to the lower acceptor strength. The same trend is observed for **2a** to **2d**, but the more P-basic diisopropylphosphanyl complexes **2e** and **2f** show smaller than expected values for $\Delta\delta$(*o*-P). Similarly, the coordination chemical shifts of PMe_3 in **2e** and **2f**, which approach those in **4a** and **4d**, are markedly lower than $\Delta\delta(PMe_3)$ in **2a**–**d**. This indicates a higher electron density at nickel(II) and an increased electron-repelling effect due to the lack of back bonding, which is also responsible for the noticeable high-field shifts of the NiMe carbon resonances in **2e** and **2f** as compared with those in **2a**–**d**, the lower $^{1}J_{PC2}$ and slightly lower $^{2}J_{PC1}$ coupling constants, and the aforementioned higher rate of dissociation in **2e** and **2f**. Comparison of the phosphorus coordination shifts of P$^{\cap}$O,P nickel complexes **2** with those of bis(P$^{\cap}$O-chelates) **3** having similar substitution patterns at phosphorus reveals smaller or slightly smaller $\Delta\delta$ values for the *trans* isomers of **3**, but significantly larger deshielding in *cis*-**3**. An even more clear-cut distinction of *cis* and *trans* isomers follows from the different $^{1}J_{PC2}$ ($Jcis > Jtrans$) and $^{2}J_{PC1}$ ($Jcis < Jtrans$) values, which indicate different electronic situations. The latter observation would suggest that substituent effects influence the configuration. Whereas this is true for the rigid bis(P$^{\cap}$O-chelates) **3**,[8a,11,12] monochelate P$^{\cap}$O,P nickel complexes **2** such as acyclic bis(phosphane)bis(phenolate)nickel complexes[13] always preferentially adopt a *trans* configuration. *cis*-Isomers of **2** would be expected to exhibit $^{2}J_{PNiP}$ coupling constants in the range 60–90 Hz.[11b,14,15] Such signals could not be detected, neither for P(R)–aryl nor for dialkylphosphanyl derivatives. Traces of impurities giving rise to sharp phosphorus doublets (J_{PP} = 14–16 Hz) were detected in the spectra of **2a**,**b**,**d**, the nature of which has not yet been established.

A single-crystal X-ray structure analysis of **3e** (Figure 2) confirmed the *trans* configuration and provided the first such data for a *trans*-bis(phosphanylphenolato[*P*,*O*])-nickel(II) complex. Like acyclic *trans*-bis(phosphane)bis-

Table 1. Selected ^{31}P- and ^{13}C-NMR data of **2–4** (nr = not resolved; $N = |J + J'|$)

Compound	$\Delta\delta(o\text{-}^{31}P)$	$\Delta\delta(^{31}PMe_3)$ at 25 °C (at T °C)		$\delta(Ni^{13}CH_3)$ at 25 °C ($^2J_{CP\text{-}2}$ [Hz])	$^1J_{PC1}$ [Hz]	$^2J_{PC2}$ [Hz]
2a	62.6	52.6	57.1 (–50)	–19.9 (25)	49.1	25.1
2b	61.9	55.9	57.7 (–50)	–20.3 (25.1)	48.6	25.8
2c	69.8[a]	55.3		–22.2 (nr)	(nr)	23.4
2d	66.8	55.3	56.8 (–28)	–21.1 (25)	44.5	23.4
2e	63.9	47.9		–24.9 (28.1)	41.2	22.0
2f	60.5	48.7	50.1 (–70)	–26.1 (26.8)	38.3	21.6
4a	56.7	34.8		–18.8 (br)[b]	45.8	28.1
4d	63.3	35.3		–20.7 (22.7)	43.0	24.9
cis-**3a** [12]	71.1	–	–	–	$N = 61.2$	$N = 18.9$
cis-**3c** [12]	77.5	–	–	–	$N = 55.8$	$N = 17.7$
trans-**3d** [12]	54.0	–	–	–	$N = 46.8$	$N = 28.7$
trans-**3e**	62.0	–	–	–	$N = 42.6$	$N = 30.5$

[a] Referred to δ(**1c**) at –15 °C, other peaks to **1** at 25 °C. – [b] At –30 °C, δ = –16.4 (19.6 Hz).

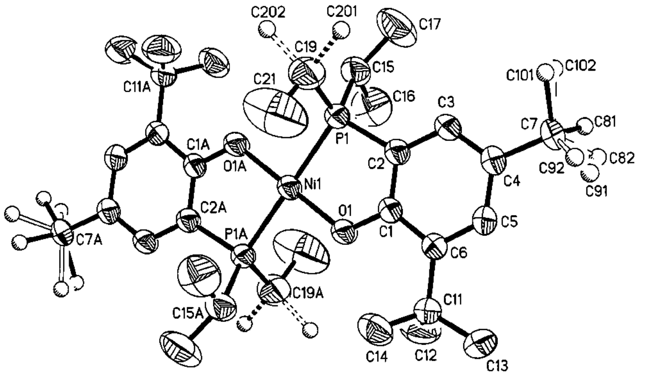


Figure 2. ORTEP plot of the molecular structure of **3e**; selected distances [Å] and angles [°]: Ni1–P1 = Ni1–P1A 2.1997(8), Ni1–O1 = Ni1–O1A 1.857(2), P1–C2 1.794(3), P1–C15 1.841(4), P1–C19 1.819(4), O1–C1 1.338(4), C1–C6 1.424(4); O1–Ni1–O1A 180.0, P1–Ni1–P1A 180.00(4), O1–Ni1–P1A = O1A–Ni1–P1 93.04(7), O1–Ni1–P1 = O1A–Ni1–P1A 86.96(7), C1–O1–Ni1 121.30(19), C2–C1–O1 120.8(3), P1–C2–C1 111.9(2), Ni1–P1–C2 98.80(11), P1–C2–C3 126.7(3), O1–C1–C6 120.4(3)

(phenolato)nickel(II) complexes,[13] **3e** possesses an almost ideal square-planar geometry about the nickel center, with O–Ni–O and P–Ni–P angles of 180°. This is in marked contrast to the distorted structures of *cis*-**3**, where O–Ni–O angles of 85.0 to 87.5° and P–Ni–P angles of 97.9 to 107.1° are found.[11b,12] The latter value relates to **3d**, which occurs in the *cis* form in the solid state, but in the kinetically preferred (*trans* effect) *trans* configuration in solution[12] and may thus represent the degree of steric congestion at the borderline of *cis*- and *trans*-bis(2-phosphanylphenolato)nickel(II) complexes. The Ni–P bond lengths in **3e** are somewhat longer [2.1997(8) Å] while the Ni–O [1.857(2) Å] distances are a little shorter as compared to the values in *cis*-bis(2-phosphanylphenolato)nickel(II) moieties, i.e. 2.1432(13) to 2.172(2) Å (the latter in *cis*-**3d**) and 1.869(10) to 1.889(3) Å, respectively. The angles within the chelate ring are as those in *cis*-**3** and underline the rigidity of the five-membered Ni–P$^\cap$O-chelate ring.

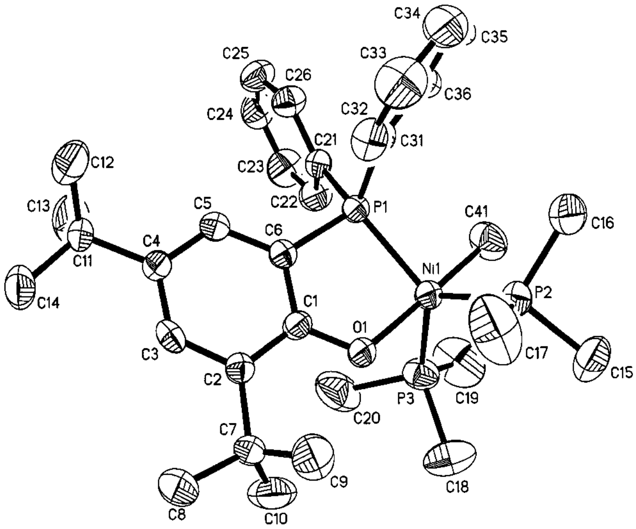


Figure 3. ORTEP plot of the molecular structure of **4a**; selected distances [Å] and angles [°]: Ni1–C41 1.981(5), Ni1–P1 2.191(2), Ni1–P2 2.245(2), Ni1–P3 2.224(2), Ni1–O1 1.984(3), P1–C6 1.797(5), O1–C1 1.332(5), C1–C6 1.411(6); C41–Ni1–O1 177.7(2), C41–Ni1–P1 92.6(2), C41–Ni1–P2 88.9(2), C41–Ni1–P3 91.7(2), P1–Ni1–P2 114.02(6), P1–Ni1–P3 125.16(6), P2–Ni1–P3 120.71(7), O1–Ni1–P1 86.35(10), C1–O1–Ni1 118.9(3), C6–C1–O1 120.1(4), P1–C6–C1 114.3(4), Ni1–P1–C6 99.2(2), P1–C6–C5 124.3(4), O1–C1–C2 122.1(4)

Although single crystals of *trans*-**2a**–**f** suitable for structure determinations could not be obtained, their structures are believed to be similar to those of phenyl(2-diphenylphosphanylenolato)(triphenylphosphane)nickel(II) complexes.[2a,3b] X-ray structure analysis of **4a** reveals an almost ideal trigonal-bipyramidal geometry with the three phosphorus atoms in equatorial positions and the oxygen and the methyl group in axial positions (Figure 3). The Ni–P(1) distance is markedly longer than the Ni–P bond lengths in *cis*-**3**, but is comparable to the corresponding distances in **3e** and phenyl(2-phosphanylenolato)(phosphane)nickel(II) complexes. The axial Ni–O bond is longer than Ni–O bonds in *cis*- and *trans*-**3**, but is comparable to the longer distances found in the (2-phosphanylenolato)(phosphane)nickel or pentacoordinate *o*-benzoyl(trimethylphosphane)nickel complexes.[16] The Ni–C(Me) and Ni–P(2) or Ni–P(3) distances fall in the usual ranges of bond lengths in methylnickel-trimethylphosphane complexes.[17]

Ethene Oligomerization

Toluene solutions of the methylnickel phosphane complexes **2c**,**e**,**f** and **4a**,**d** (ca. 0.1 mmol) were treated with

Table 2. Oligomerization of ethene (at 80 °C, 35 bar in 12 mL of toluene)

Oligomerization no.	I	II	III	IV	V
Catalyst, mg	**2c**, 56.0	**2e**, 58.0	**2f**, 47.9	**4a**, 67.7	**4d**, 70.8
(mmol)	(0.11)	(0.12)	(0.13)	(0.11)	(0.12)
Ethene, g (mmol)	7.7 (274)	7.6 (271)	7.8 (278)	7.5 (267)	7.7 (274)
Time [h]	10	6	6	10	10
Conv. of ethene g (%)	0.8 (10.4)	7.5 (98.7)	7.7 (98.7)	2.2 (29.3)	7.4 (96.1)
TON [mol/mol]	257	2174	2161	713	2218
Products[a]	C_4–C_{24}	C_4–C_{60}	C_4–C_{52}	oligomers[b]	C_4–C_{14}
% 1-olefins	99.0	95.1	93.2	[c]	95.9
K-value[c]	0.84	0.78	0.73	[c]	0.58

[a] Based on MS data. – [b] Oligomer mixture not analyzed. – [c] Calculated for oligomers > C4.

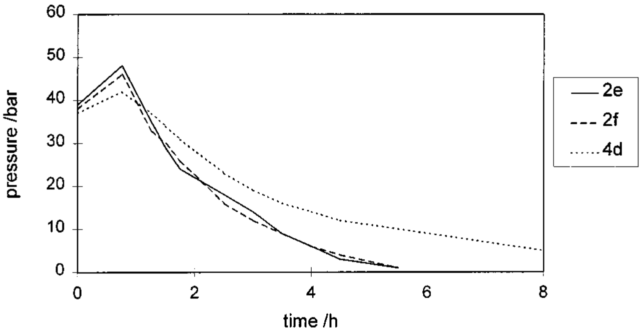
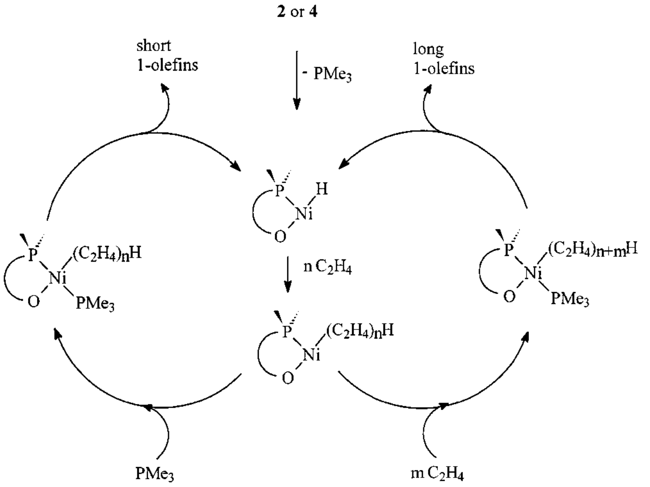


Figure 4. Conversion of ethene at 80 °C in the presence of **2e**, **2f**, and **4d**

ethene (ca. 7.7 g) at 80 °C in a 75 mL autoclave (Table 2). After an initial increase of the starting pressure (35 bar) to 45–50 bar during the induction period (about 30–45 min), the pressure fell at a rate that depended on the one-component catalyst (Figure 4). The bulk of the ethene reacted within ca. 4 h, whereas an almost quantitative conversion required 6 h in the case of **2e** and **2f**, and 10 h in the case of **4d**. The less P-basic diphenylphosphanyl- and alkylphenylphosphanyl representatives of **2** and **4** were much less active. This has a parallel in the low oligomerization activity of phenyl(2-diphenylphosphanylphenolato)(trimethylphosphane)nickel(II) as compared to phenylnickel complexes of this type with other, mainly P-arylated monodentate phosphane ligands.[3d] This is believed to be due to the greater stability of "push-pull" *trans*-diphosphane nickel complexes with a good donor on one side and a good acceptor ligand on the other as compared with the easily dissociating P-basic complexes **2e**, **2f**, and **4d** or phenyl(2-diphenylphosphanylphenolato)(triarylphosphane)nickel(II) species[3d] with similar phosphane ligands on either side.

The products of the catalytic conversion of ethene were oligomers (Scheme 5), mainly linear α-olefins (Table 3). The selectivity decreased somewhat with increasing chain length, from C4 to C12, as detected by GC. The unusually high content of a hexene isomer in II (11.5%) may be attributed to a competing reaction with 1-butene. With **4d**, lower oligomers with a Schultz–Flory distribution[18] and large amounts of 1-butene, 1-hexene, and octenes were observed. The mono-PMe_3 complexes form longer chain oligomers with broad, flat maxima in their molar weight distributions. In experiment I using the catalyst **2c**, the maximum was found in the range C10 to C14 by GC and C12 to C18 by mass spectrometry (based on abundance of [M^+] using direct inlet). The most abundant oligomers (by GC) in experiments II and III using the diisopropylphosphanylphenolate catalysts **2e** and **2f** were 1-hexene and 1-octene, followed by either 1-decene (II/**2e**) or 1-butene (III/**2f**). Besides these, greater amounts of C14+ oligomers ($n > 7$) (33 and 51 mass%) were observed. Interestingly, the mass spectrum of the oligomer mixture of II revealed low abundance maxima due to the molecular ions of oligomers $n = 10$–12 and $n = 23$–25. The higher conversion and the occurrence of longer olefins using the diisopropylphosphanylphenolate catalysts **2e** and **2f** may be explained by the higher degree of dissociation allowing, over time, a proportionally faster uptake of ethene. Since diisopropylphosphanylphenolate catalysts, prepared in situ from **1e** or **1f** and $Ni(COD)_2$ and free of monodentate phosphanes, give higher polyethenes than diphenyl- or alkylphenyl-substituted species,[19] the lower-oligomer maxima seen in the catalysis using **2e** and **2f** might be induced by stronger promotion of β-hydride elimination in the alkyl(2-diisopropylphosphanylphenolato)(phosphane)nickel(II) intermediates than in intermediates formed using **2c**. This is in line with the higher electron density at nickel in **2e** and **2f** as compared with that in **2a**–**d**, which is reflected in a high-field shift of the methyl group ^{13}C resonance by ca. 4 ppm (Table 1). Coordination of an alkylphos-



Scheme 5. Proposed mechanism of oligomerization of ethene catalyzed by **2** or **4**

Table 3. Composition of ethene oligomers obtained with **2c**,**e**,**f** and **4d**

Oligomerization (catalyst)	I (**2c**)	II (**2e**)	III (**2f**)	V (**4d**)
% C4 (% 1-olefin)	3.0	8.0 (100)	11.2 (100)	44.1 (100)
% C6 (% 1-olefin)	8.2 (90)	19.2 (99)	16.1 (87)	38.3 (99)
[% most abund. isoolefin]	[10]	[1]	[11.5]	
% C8 (% 1-olefin)	10.3	19.5 (99)	15.7 (94.4)	12.0 (85)
[% most abund. isoolefin]			[4]	
% C10 (% 1-olefin)	11.2	15.1 (85)	5.1 (91)	2.7 (79)
[% most abund. isoolefin]		[6]	[4.5]	
% C12	11.6	3.9 (79)	0.42	2.1 (69)
[% most abund. isoolefin]		[8]		
% C14	11.6	0.9	0.48	0.7
% C14+	[a]	33.3	51	

[a] C16 10.9%, C18 9.6%, C20 8.8%, C22 7.8%, C24 7%.

phane ligand will accelerate β-hydride transfer in the case of C_{2n}-alkyl chains at nickel. A small proportion of active centers, depending on the equilibrium concentration of PMe_3, may produce somewhat longer chains, promoted by a decreasing association of PMe_3 with increasing chain length.

Conclusions

Tertiary 2-phosphanylphenols **1** bearing phenyl and alkyl groups at phosphorus react with $[MeNi(\mu\text{-}OMe)(PMe_3)]_2$ to give 16-electron methyl(2-phosphanylphenolato)(trimethylphosphane)nickel(II) complexes **2** with *trans*-square-planar structures. Complex **2** reacts with excess **1** to give nickelbis(P$^\cap$O-chelates) **3** or adds PMe_3 to form 18-electron trigonal-bipyramidal methyl(2-phosphanylphenolato)bis(trimethylphosphane)nickel(II) complexes **4**. Higher yields of **4** are obtained from **1** and $Me_2Ni(PMe_3)_3$. Both **2** and **4** are fluxional molecules, particularly their dialkylphosphanyl derivatives. This is attributed to rapid dissociation–association equilibria; **4** may additionally undergo rapid pseudorotation. Both the expected unsaturated 14-electron species **I** (or dimers thereof) and free PMe_3 escape detection by NMR because of their low concentrations (low equilibrium constants). Nevertheless, alkylphenyl- or dialkylphosphanyl derivatives of **2** and **4** have proved to be effective one-component catalysts in the oligomerization of ethene. Since addition of ethene to **2** will be much less favorable than addition to **I**, and since electron-rich 2-dialkylphosphanylphenolates **2**, which bind trimethylphosphane in a *trans* fashion less tightly than 2-diphenylphosphanyl derivatives, form the more efficient catalysts, **I** can be regarded as the active species, which may even be formed by dissociation of **4**. The short chain lengths of the oligomers obtained with **2** as compared to those of the polymers produced with catalysts prepared in situ from **1** and $Ni(COD)_2$[6a,11b,19] and the even lower molecular weights of the oligomers formed with **4** suggest that β-hydride elimination is favored by coordination of PMe_3 at a free coordination site of the catalyst.

Experimental Section

General Procedures and Materials: All procedures were carried out under an atmosphere of purified argon using standard vacuum line or Schlenk techniques. Solvents (THF, diethyl ether, pentane) were dried with sodium (ketyls) and freshly distilled prior to use. $[NiMe(PMe_3)(\mu\text{-}OMe)]_2$,[16,17] *trans*-$Me_2Ni(PMe_3)_3$,[20] and the 2-phosphanylphenols **1a**,[9c] **1b**,[10i] and **1c**[9c] were prepared according to known procedures; $i\text{Pr}_2PCl$ was purchased from Aldrich and used without further purification. – IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. – NMR spectra were recorded on Bruker AM 200, WM 300, or ARX 300 multinuclear Fourier transform spectrometers and are referenced to tetramethylsilane for ^{1}H and ^{13}C and to H_3PO_4 (85%) for ^{31}P. The measuring temperature was 298 K unless otherwise stated. For resonances that are part of an AXX' spin system (X,X' = ^{31}P), vc and τ denote "virtual coupling" and the triplet appearance of the A resonance, respectively. – Melting points were determined in sealed capillaries (Büchi type 510) and are uncorrected. – Elemental analyses were carried out using CHN 240 A (Perkin–Elmer) or CHNS-932 (LECO) analyzers.

Ligand Preparation

4,6-Di-*tert*-butyl-2-(diisopropylphosphanyl)phenol (1e): At –40 °C, a hexane solution of *n*BuLi (21.0 mL, 1.6 N, 33.6 mmol) was slowly added to 2,4-di-*tert*-butylphenyl methoxymethyl ether (8.3 g, 33.2 mmol) in Et_2O (60 mL). After stirring for 4 h at 20 °C, chlorodiisopropylphosphane (5.0 g, 32.8 mmol) was rapidly added at 0 °C, the suspension was stirred for 1 h at room temperature, and then filtered. The filtrate was concentrated to dryness and the residue was treated with degassed 2 N HCl (200 mL) at 60 °C. After heating for 5 h, the volatiles were removed in vacuo and the residue was crystallized from methanol. Yield 7.8 g (73%) of **1e** as white crystals; m.p. 67–68 °C. – IR (Nujol): $\tilde{\nu}_{OH}$ = 3322 cm^{-1} s. – ^{1}H NMR (C_6D_6): δ = 0.86 (dd, $^3J_{PH}$ = 12.2, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*), 1.00 (dd, $^3J_{PH}$ = 16.5, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*), 1.34 (s, 9 H, CMe_3), 1.60 (s, 9 H, CMe_3), 1.94 (m, $^3J_{HH}$ = 7, $^2J_{PH}$ = ca. 3.5 Hz, 2 H, CH), 7.22 (ps. t, $^4J_{HH}$ = 2.4, $^3J_{PH}$ = ca. 2.6 Hz, 1 H, 3-H), 7.55 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, 5-H), 7.76 (d, $^4J_{PH}$ = 12.4 Hz, 1 H, OH). – ^{13}C NMR (75.5 MHz, C_6D_6): δ = 18.6 (d, $^2J_{PC}$ = 7.0 Hz, CH*Me*), 20.0 (d, $^2J_{PC}$ = 17.9 Hz, CH*Me*), 23.1 (d, $^1J_{PC}$ = 6.9 Hz, C*H*Me), 29.8 (C*Me*$_3$), 31.8 (C*Me*$_3$), 34.5 (*C*Me$_3$), 35.4 (d, $^4J_{PC}$ = 2.0 Hz, *C*Me$_3$), 117.8 (d, $^1J_{PC}$ = 5.2 Hz, C-2), 125.6 (C-5), 127.1 (d, $^2J_{PC}$ = 1.1 Hz, C-3), 135.2 (d, $^3J_{PC}$ = 1.7 Hz, C-6), 141.2 (C-4), 158.1 (d, $^2J_{PC}$ = 18.8 Hz, C-1). – ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = –24.3. – MS (EI, 70 eV): *m*/*z*: 323 [M$^+$], 307 [M$^+$ – CH$_3$], 281 [M$^+$ – C$_3$H$_6$], 266 [M$^+$ – *t*Bu], 239 [M$^+$ – 2 C$_3$H$_6$], 57 [*t*Bu]. – $C_{20}H_{35}OP$ (322.47): calcd. C 74.49, H 10.94; found C 74.19, H 10.97.

4-Fluoro-2-(diisopropylphosphanyl)phenol (1f): At –40 °C, *n*BuLi (38.5 mL 1.6 N in hexane, 61.5 mmol) was added to 9.6 g (61.5 mmol) of 4-fluorophenyl methoxymethyl ether in Et$_2$O (100 mL) and the mixture was allowed to warm to room temperature. After 2 h, chlorodiisopropylphosphane (9.4 g, 61.6 mmol) was added. The resulting suspension was stirred for 1 h at 20 °C and then filtered. The filtrate was concentrated to dryness and the residue was treated with degassed aqueous 2 N HCl solution as above. After 5 h at 60 °C, the volatiles were removed in vacuo. The residue was crystallized from methanol to give 4.9 g (35%) of **1f** as white needles; m.p. 61–64 °C. – IR (Nujol): $\tilde{\nu}_{OH}$ = 3302 cm^{-1} s. – ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ = 0.70 (dd, $^{3}J_{PH}$ = 12.5, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH*Me*), 0.89 (dd, $^{3}J_{PH}$ = 16.5, $^{3}J_{HH}$ = 7.0 Hz, 6 H, CH*Me*), 1.68 (m, $^{3}J_{HH}$ = 7, $^{2}J_{PH}$ = ca. 3.5 Hz, 2 H, CH), 6.73 (m, $^{3}J_{HH}$ = 9.0, $^{3}J_{FH}$ = 8.1, $^{4}J_{HH}$ = 3.1 Hz, 1 H, 5-H), 6.82 (m, $^{3}J_{HH}$ = 9.0, $^{4}J_{FH}$ = 5.1, $^{4}J_{PH}$ = 3.9 Hz, 1 H, 6-H), 6.91 (m, $^{3}J_{FH}$ = 8.3, $^{4}J_{HH}$ $^{3}J_{PH}$ 2.8 Hz, 1 H, 3-H), 7.02 (br. s, 1 H, OH). – ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = 19.3 (d, $^{2}J_{PC}$ = 7.6 Hz, CH*Me*), 20.5 (d, $^{2}J_{PC}$ = 18.0 Hz, CH*Me*), 23.8 (d, $^{1}J_{PC}$ = 7.7 Hz, *C*HMe), 117.2 (dd, $^{3}J_{FC}$ = 7.2, $^{3}J_{PC}$ = 1.7 Hz, C-6), 119.0 (dd, $^{2}J_{FC}$ = 21.1, $^{2}J_{PC}$ = 1.7 Hz, C-3), 119.0 (d, $^{2}J_{FC}$ = 23.1 Hz, C-5), 120.8 (dd, $^{1}J_{PC}$ = 4.5, $^{3}J_{FC}$ = 12.4 Hz, C-2), 157.6 (d, $^{1}J_{FC}$ = –239.7 Hz, C-4), 158.7 (dd, $^{2}J_{PC}$ = 18.7, $^{4}J_{FC}$ = 1.7 Hz, C-1). – ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = –21.8. – MS (EI, 70 eV): *m*/*z*: 228 [M$^+$], 186 [M$^+$ – C$_3$H$_6$], 144 [M$^+$ – 2 C$_3$H$_6$], 111 [M$^+$ – P*i*Pr$_2$]. – $C_{12}H_{18}FOP$ (228.25): calcd. C 63.15, H 7.95; found C 63.01, H 7.91.

Preparation of Complexes

{4,6-Di-*tert*-butyl-2-(diphenylphosphanyl)phenolato[*P*,*O*]}methyl(trimethylphosphane)nickel(II) (2a): At –78 °C, **1a** (649 mg, 1.66 mmol) was added to a solution of *cis*-[NiMe(PMe$_3$)(μ-OMe)]$_2$ (300 mg, 0.83 mmol) in Et$_2$O (60 mL). A rapid color change from yellow-brown to red was observed and after 3 h the mixture became orange. The solvent was then removed in vacuo and the residue was extracted with warm pentane, from which 580 mg (65%) of **2a** was obtained as yellow crystals; dec. at 162–163 °C. **2a** was found to be slightly contaminated with **3a**. – IR (Nujol): $\tilde{\nu}$ = 955 cm^{-1} s (ρ_1 PMe$_3$). – ^{1}H NMR (300 MHz, [D$_8$]THF): δ = –0.82 (d, $^{3}J_{PH}$ = 7.4 Hz, 3 H, NiMe), 1.15 (s, 9 H, PMe$_3$), 1.34, 1.38 (2 s, 18 H, 2 CMe$_3$), 6.95 (d, $^{3}J_{PH}$ = 8.0 Hz, 1 H, 3-H), 7.12 (s, 1 H, 5-H), 7.39 (m, 6 H, Ph), 7.65 (m, 4 H, Ph). – ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = –19.9 (d, $^{2}J_{PC}$ = 25 Hz, NiMe), 10.8 (d, $^{1}J_{PC}$ = 22.5 Hz, PMe$_3$), 27.9 (C*Me*$_3$), 30.3 (C*Me*$_3$), 32.6 (*C*Me$_3$), 33.9 (*C*Me$_3$), 115.9 (d, $^{1}J_{PC}$ = 49.1 Hz, C-2), 124.7 (C-5), 125.5 (C-3), 127.3 (d, $^{3}J_{PC}$ = 9.5 Hz, *m*-C), 128.6 (*p*-C), 132.2 (d, $^{2}J_{PC}$ = 11.4 Hz, *o*-C), 132.6 (C-4), 133.5 (d, $^{1}J_{PC}$ = 47.7 Hz, *i*-C), 135.9 (C-6), 173.6 (d, $^{2}J_{PC}$ = 25.1 Hz, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –10.7 (br. s, PMe), 32.9 (br. s, 2-P). – Low-temperature NMR: ^{1}H NMR (200 MHz, [D$_8$]THF, 208 K): δ = –0.83 (m, 3 H, NiMe), 1.15 (s, 9 H, PMe$_3$), 1.35 (s, 9 H, CMe$_3$), 1.39 (s, 9 H, CMe$_3$), 7.00 (d, $^{3}J_{PH}$ = 8.6 Hz, 1 H, 3-H), 7.09 (s, 1 H, 5-H), 7.46 (m, 6 H, Ph), 7.64 (m, 4 H, Ph). – ^{31}P NMR (81 MHz, [D$_8$]THF, 223 K): **2a:** δ = –6.1 (d, $^{2}J_{PP}$ = 316 Hz, PMe), 32.7 (d, $^{2}J_{PP}$ = 316 Hz, 2-P); trace impurities: δ = 1.4 (d, J_{PP} = 15.9 Hz), 32.9 (d, J_{PP} = 15.9 Hz), 42.1 (**3a**). – $C_{30}H_{42}NiOP_2$ (539.30): calcd. C 66.81, H 7.85, P 11.49; found C 66.24, H 7.68, P 11.76.

{6-*tert*-Butyl-4-methyl-2-(diphenylphosphanyl)phenolato[*P*,*O*]}-methyl(trimethylphosphane)nickel(II) (2b): At –78 °C, **1b** (1.73 g, 4.97 mmol) was added to a solution of *cis*-[NiMe(PMe$_3$)(μ-OMe)]$_2$ (900 mg, 2.49 mmol) in Et$_2$O (80 mL), resulting in a color change to orange. After stirring for 3 h, the solvent was evaporated in vacuo and the residue was extracted with warm pentane. On cooling of the combined extracts, yellow crystals of **2b** were deposited. Yield 2.05 g (83%); dec. at 129 °C. – IR (Nujol): $\tilde{\nu}$ = 1166 s (NiMe), 956 cm^{-1} s (ρ_1 PMe$_3$). – ^{1}H NMR (300 MHz, [D$_8$]THF): δ = –0.82 (d, $^{3}J_{PH}$ = 7.4 Hz, 3 H, NiMe), 1.34 (s, 9 H, CMe$_3$), 1.37 (d, $^{2}J_{PH}$ = 8.6 Hz, 9 H, PMe$_3$), 2.07 (s, 3 H, 4-Me), 6.75 (d, $^{3}J_{PH}$ = 7.4 Hz, 1 H, 3-H), 6.85 (d, $^{5}J_{PH}$ = 1.7 Hz, 1 H, 5-H), 7.39 (m, 6 H, Ph), 7.65 (m, 4 H, Ph). – ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = –20.3 (d, $^{2}J_{PC}$ = 25.1 Hz, NiMe), 12.7 (d, $^{1}J_{PC}$ = 22.2 Hz, PMe$_3$), 20.7 (s, 4-Me), 29.7 (C*Me*$_3$), 35.4 (*C*Me$_3$), 118.3 (d, $^{1}J_{PC}$ = 48.6 Hz, C-2), 122.0 (d, $^{3}J_{PC}$ = 7.0 Hz, C-4), 129.1 (d, $^{3}J_{PC}$ = 9.2 Hz, *m*-C), 130.2 (C-5), 130.4 (*p*-C), 131.2 (C-3), 134.1 (d, $^{2}J_{PC}$ = 11.2 Hz, *o*-C), 134.5 (d, $^{1}J_{PC}$ = 47.0 Hz, *i*-C), 138.4 (d, $^{3}J_{PC}$ = 9.1 Hz, C-6), 173.8 (d, $^{2}J_{PC}$ = 25.8 Hz, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –7.4 (br. d, $^{2}J_{PP}$ = 286 Hz, PMe), 32 (br. d, $^{2}J_{PP}$ = 259 Hz, *o*-P); trace impurity: δ = 0.5 (d, J_{PP} = 14.9 Hz, PMe), 32.3 (d, J_{PP} = 14.7 Hz, *o*-P). – Low-temperature NMR: ^{31}P NMR (81 MHz, [D$_8$]THF, 223 K): δ = –5.6 (d, $^{2}J_{PP}$ = 316 Hz, PMe), 32.1 (d, $^{2}J_{PP}$ = 316 Hz, *o*-P); trace impurity: δ = 2.0 (d, J_{PP} = 14.6 Hz, PMe), 32.0 (d, J_{PP} = 14.8 Hz, *o*-P). – $C_{27}H_{36}NiOP_2$ (497.22): calcd. C 65.22, H 7.30, P 12.46; found C 64.83, H 7.78, P 12.31.

{4,6-Di-*tert*-butyl-2-(isopropylphenylphosphanyl)phenolato[*P*,*O*]}-methyl(trimethylphosphane)nickel(II) (2c): At –78 °C, THF (80 mL) was condensed into a mixture of **1c** (0.90 g 2.52 mmol) and *cis*-[NiMe(PMe$_3$)(μ-OMe)]$_2$ (0.46 g, 1.27 mmol). On warming to room temperature the mixture became orange in color. The solvent was then replaced by pentane (60 mL). Crystallization furnished 0.28 g (22%) of yellow microcrystalline **2c**; m.p. 88–90 °C (dec.). An additional portion of orange, powdery **2c** was obtained by removal of the solvent from the mother liquor to give a total yield of 0.94 g (74%) of **2c**. – IR (Nujol): $\tilde{\nu}$ = 1138 m (NiMe), 953 cm^{-1} s (ρ_1 PMe$_3$). – ^{1}H NMR (200 MHz, [D$_8$]THF, 296 K): δ = –0.93 (d, $^{3}J_{PH}$ = 1.8 Hz, 3 H, NiMe), 0.98–1.24 (m, 12 H, CH*Me*$_A$, CMe$_3$), 1.30–1.45 (m, 21 H, CH*Me*$_B$, CMe$_3$, PMe$_3$), 2.67 (m, 1 H, CH), 6.93 (m, 1 H, 3-H), 7.13 (d, $^{2}J_{PH}$ = 2.4 Hz, 1 H, 5-H), 7.39 (m, 3 H, Ph), 7.64 (m, 2 H, Ph). – ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = –22.2 (m, NiMe), 10.8 (d, $^{1}J_{PC}$ = 22.2 Hz, PMe$_3$), 16.0 (br., Me), 17.6 (br., Me), 24.2 (d, $^{1}J_{PC}$ = 37.2 Hz, CH), 27.8 (C*Me*$_3$), 30.3 (C*Me*$_3$), 32.6 (*C*Me$_3$), 33.8 (*C*Me$_3$), 113.6 (m, C-2), 124.9 (C-5), 125.2 (C-3), 127.2 (d, 9.0 Hz, *m*-C), 128.1 (*p*-C), 131.2 (d, $^{2}J_{PC}$ = 9.0 Hz, *o*-C), 131.9 (C-4), ca. 133 (*i*-C), 135.6 (d, $^{4}J_{PC}$ = 9.0 Hz, C-6), 174.3 (d, $^{2}J_{PC}$ = 23.4 Hz, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –8.0 (d, $^{2}J_{PP}$ = 310 Hz, PMe), 40.0 (d, $^{2}J_{PP}$ = 308 Hz, 2-P). – $C_{27}H_{44}NiOP_2$ (505.29): calcd. C 64.18, H 8.78, P 12.26; found C 63.64, H 8.55, P 12.56.

{4,6-Di-*tert*-butyl-2-(*tert*-butylphenylphosphanyl)phenolato[*P*,*O*]}-methyl(trimethylphosphane)nickel(II) (2d): At –78 °C, **1d** (1.13 g, 3.05 mmol) was added to a solution of [NiMe(PMe$_3$)(μ-OMe)]$_2$ (1.10 g, 3.04 mmol) in diethyl ether (80 mL). After stirring for 3 h at room temperature, the solvent was removed in vacuo from the dark-red solution and the residue was extracted with pentane. On cooling of the combined extracts, 1.15 g (73%) of **2d** was deposited as red-brown crystals; m.p. 78–79 °C. – IR (Nujol): $\tilde{\nu}$ = 1138 m (NiMe), 952 cm^{-1} s (ρ_1 PMe$_3$). – ^{1}H NMR (300 MHz, [D$_8$]THF): δ = –0.88 (d, $^{3}J_{PH}$ = 7.5 Hz, 3 H, NiMe), 1.24 (s, 9 H, CMe$_3$), 1.30 (br. s, 9 H, PMe$_3$), 1.39 (s, 9 H, CMe$_3$), 1.44 (d, $^{3}J_{PH}$ = 13.7 Hz, 9 H, PCMe$_3$), 7.01 (dd, $^{3}J_{PH}$ = 7.8, $^{4}J_{HH}$ = 2.5 Hz, 1 H, 3-H), 7.17 (d, $^{4}J_{HH}$ = 2.5 Hz, 1 H, 5-H), 7.43 (m, 3 H, Ph), 7.88 (m, 2 H, Ph). – ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = –21.1 (br. d, $^{2}J_{PC}$ = 25 Hz, NiMe), 12.8 (d, $^{1}J_{PC}$ = 20.4 Hz, PMe$_3$), 28.9 (d, $^{2}J_{PC}$ = 5.3 Hz, PC*Me*$_3$), 29.7 (C*Me*$_3$), 32.2 (C*Me*$_3$), 34.4 (*C*Me$_3$), 35.4 (d,

$^{1}J_{PC}$ = 21.1 Hz, P*C*Me$_3$), 35.7 (*C*Me$_3$), 117.2 (d, $^{1}J_{PC}$ = 44.5 Hz, C-2), 126.8 (C-5), 127.4 (C-3), 128.9 (d, $^{3}J_{PC}$ = 9 Hz, *m*-C), 129.9 (*p*-C), 133.0 (d, $^{1}J_{PC}$ = 33.2 Hz, *i*-C), 134.1 (d, $^{2}J_{PC}$ = 8.3 Hz, *o*-C), 134.6 (d, $^{3}J_{PC}$ = 6.1 Hz, C-4), 137.5 (d, $^{3}J_{PC}$ = 8.3 Hz, C-6), 175.3 (d, $^{2}J_{PC}$ = 23.4 Hz, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –8.0 (br. d, $^{2}J_{PP}$ = 293.7 Hz, PMe), 47.8 (br. d, $^{2}J_{PP}$ = 307.7 Hz, 2-P); trace impurities: δ = –0.9 (d, J_{PP} = 13.9 Hz), 52.6 (d, J_{PP} = 13.6 Hz), 35.2 (**3d**). – Low-temperature NMR: ^{1}H NMR (200 MHz, [D$_8$]THF, 248 K): δ = –0.93 (dd, $^{3}J_{PH}$ = 11.2, $^{3}J_{P'H}$ = 7.6 Hz, 3 H, NiMe), 1.20 (s, 9 H, CMe$_3$), 1.31 (s, 9 H, PMe$_3$), 1.34 (s, 9 H, CMe$_3$), 1.38 (d, $^{3}J_{PH}$ = 13.8 Hz, 9 H, PCMe$_3$), 6.97 (dd, $^{4}J_{HH}$ = 2, $^{3}J_{PH}$ = 7.7 Hz, 1 H, 3-H), 7.11 (d, $^{4}J_{HH}$ = 2 Hz, 1 H, 5-H), 7.42 (m, 3 H, Ph), 7.83 (m, 2 H, Ph). – ^{31}P NMR (81 MHz, [D$_8$]THF, 245 K): δ = –6.5 (d, $^{2}J_{PP}$ = 308.3 Hz, PMe), 47.9 (d, $^{2}J_{PP}$ = 308.5 Hz, *o*-P); trace impurities: δ = 0.5 (d), 52.3 (d), 34.9 (**3d**). – $C_{28}H_{46}NiOP_2$ (519.31): calcd. C 64.76, H 8.93, P 11.93; found C 64.75, H 7.83, P 11.85.

{4,6-Di-*tert*-butyl-2-(diisopropylphosphanyl)phenolato[*O*,*P*]}-methyl(trimethylphosphane)nickel(II) (2e): At –78 °C, **1e** (1.42 g, 4.4 mmol) and PMe$_3$ (0.34 g, 4.4 mmol) were added to a solution of *cis*-[NiMe(PMe$_3$)(μ-OMe)]$_2$ (0.80 g, 2.2 mmol) in diethyl ether (50 mL). After stirring for 3 h at room temperature (color change through red to brown), the solvent was evaporated in vacuo and the residue was treated with a small volume of pentane, yielding 1.78 g (86%) of **2e** as red-brown crystals; m.p. 79–81 °C. – ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ = –0.66 (d, $^{3}J_{PH}$ = 7.4 Hz, 3 H, NiMe), 1.01 (d, 9 H, $^{2}J_{PH}$ = 8.1 Hz, PMe$_3$), 1.21 (dd, $^{3}J_{PH}$ = 13.7, $^{3}J_{HH}$ = 7.0 Hz, CH*Me*$_a$), 1.30 (dd, $^{3}J_{PH}$ = 15.6, $^{3}J_{HH}$ = 7.1 Hz, CH*Me*$_b$), 1.43 (s, 9 H, CMe$_3$), 1.65 (s, 9 H, CMe$_3$), 2.21 (m, 2 H, C*H*Me$_2$), 7.19 (d, $^{4}J_{HH}$ = 2.5 Hz, partly superimposed, 3-H), 7.54 (d, $^{4}J_{HH}$ = 2.5 Hz, 1 H, 5-H). – ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = –24.9 (d, $^{2}J_{PC}$ = 28.1 Hz, 3 H, NiMe), 13.0 (d, $^{1}J_{PC}$ = 21.2 Hz, PMe$_3$), 18.8 (C*Me*$_a$), 19.7 (d, $^{2}J_{PC}$ = 4.8 Hz, C*Me*$_b$), 24.8 (d, $^{1}J_{PC}$ = 22.8 Hz, CH), 30.4 (C*Me*$_3$), 32.9 (C*Me*$_3$), 34.8 (*C*Me$_3$), 36.2 (*C*Me$_3$), 115.8 (d, $^{1}J_{PC}$ = 41.2 Hz, C-2), 125.4 (C-5), 127.4 (C-3), 135.2 (d, $^{3}J_{PC}$ = 5.3 Hz, C-4), 137.9 (d, $^{3}J_{PC}$ = 8.3 Hz, C-6), 176.2 (d, $^{2}J_{PC}$ = 22.0 Hz, C-1). – ^{31}P NMR (121.5 MHz, C$_6$D$_6$, 298 K): δ = –15.4 (br. s, PMe), 39.6 (br. s, 2-P); trace impurity: δ = 31.4 (br. s). – ^{31}P NMR (121.5 MHz, [D$_8$]toluene, 203 K): δ = –13.2 (d, $^{2}J_{PP}$ = 305 Hz, PMe), 39.6 (d, $^{2}J_{PP}$ = 305 Hz, 2-P). – MS (EI, 70 eV): *m*/*z* (%) = 470 (10) [M$^+$]. – $C_{24}H_{46}NiOP_2$ (471.27): calcd. C 61.17, H 9.84; found C 60.34, H 9.65.

{4-Fluoro-2-(diisopropylphosphanyl)phenolato[*O*,*P*]}-methyl(trimethylphosphane)nickel(II) (2f): At –78 °C, **1f** (0.23 g, 1.01 mmol) was added to a solution of *cis*-[NiMe(PMe$_3$)(μ-OMe)]$_2$ (0.21 g, 0.58 mmol) in pentane (30 mL) and the resulting mixture was stirred for 1 h at room temperature (color change through red to yellow). The solvent was then evaporated in vacuo and the residue was extracted with diethyl ether to afford 228 mg (60%) of yellow **2f**. – ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ = –0.73 (d, $^{3}J_{PH}$ = 7.9 Hz, 3 H, NiMe), 0.93 (d, $^{2}J_{PH}$ = 8.4 Hz, 9 H, PMe$_3$), 1.06 (dd, $^{3}J_{PH}$ = 13.8, $^{3}J_{HH}$ = 7.1 Hz, 6 H, CH*Me*$_a$), 1.21 (dd, $^{3}J_{PH}$ = 15.8, $^{3}J_{HH}$ = 7.1 Hz, 6 H, CH*Me*$_b$), 1.96 (m, 2 H, C*H*Me$_2$), 6.75 (dτ, $^{3}J_{HH}$ = 8.9, J_{PH} and J_{FH} = ca. 4.5–4.7 Hz, 1 H, 6-H), 6.87–6.98 (m, 2 H, 3-H, 5-H). – ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = –26.1 (d, $^{2}J_{PC}$ = 26.8 Hz, 3 H, NiMe), 11.3 (d, $^{1}J_{PC}$ = 22.4 Hz, PMe$_3$), 17.9 (Me$_a$), 18.8 (d, $^{2}J_{PC}$ = 5.2 Hz, Me$_b$), 23.9 (d, $^{1}J_{PC}$ = 21.9 Hz, CH), 115.4 (d, $^{1}J_{PC}$ = 38.3 Hz, C-2), 115.8 (d, $^{2}J_{FC}$ = 21.7 Hz, C-5), 118.8 (ps. t, $^{3}J_{PC}$ and $^{3}J_{FC}$ = ca. 8 Hz, C-6), 120.0 (d, $^{2}J_{FC}$ = 23.4 Hz, C-3), 153.3 (dd, $^{1}J_{FC}$ = 230.8, $^{3}J_{PC}$ = 6.4 Hz, C-4), 176.0 (d, $^{2}J_{PC}$ = 21.6 Hz, C-1). – ^{31}P NMR (121.5 MHz, C$_6$D$_6$, 298 K): δ = –14.6 (s, PMe), 38.7 (s, 2-P). – $C_{16}H_{29}FNiOP_2$ (377.04).

***trans*-Bis{4,6-di-*tert*-butyl-2-(diisopropylphosphanyl)phenolato-[*O*,*P*]}nickel(II) (3e):** *cis*-[NiMe(PMe$_3$)(μ-OMe)]$_2$ (0.43 g, 1.19 mmol) was dissolved in THF (60 mL) and the solution was cooled to –50 °C. **1e** (0.98 g, 3.04 mmol) was then added, resulting in a color change from brown through orange to yellow-green. After stirring for 1 h at room temperature, the solvent was removed in vacuo. The residue was extracted with pentane (40 mL) and crystallized from this solvent yielding 0.84 g (79%) of **3e** as green crystals; m.p. 228–230 °C (with color change to brown), dec. at 234 °C. – ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.38 (s, 18 H, CMe$_3$), 1.35 (τd, N = 14.2, $^{3}J_{HH}$ = 7.0 Hz, 12 H, Me$_A$), 1.49 (s, 18 H, CMe$_3$), 1.64 (τd, N = 16.8, $^{3}J_{HH}$ = 7.4 Hz, 12 H, Me$_B$), 2.36 (m, 4 H, CH), 7.18 (τd, N 8, $^{4}J_{HH}$ = 2.3 Hz, 2 H, 3-H), 7.39 (d, $^{4}J_{HH}$ = 2.3 Hz, 2 H, 5-H). – ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = 18.2 (s, C*Me*$_A$), 19.5 (τ, N = 6.0 Hz, C*Me*$_B$), 24.8 (τ, N = 22.0 Hz, CH), 29.8 (C*Me*$_3$), 32.1 (C*Me*$_3$), 34.0 (*C*Me$_3$), 35.3 (*C*Me$_3$), 113.1 (τ, N = 42.6 Hz, C-2), 125.3 (C-5), 126.9 (C-3), 136.2 (τ, N = 6.4 Hz, C-4), 138.5 (τ, N = 7.4 Hz, C-6), 175.2 (τ, N = 30.5 Hz, C-1). – ^{31}P NMR (121.5 MHz, C$_6$D$_6$): δ = 37.7. – MS (70 eV): *m*/*z* (%) = 701 (100) [M$^+$], 336 (24) [M – Lig – *i*Pr$^+$], 321 (31) [Lig – H$^+$], 280 (22) [Lig – *i*Pr$^+$] (Lig = **1e**-H$^+$). – $C_{40}H_{68}NiO_2P_2$ (701.62): calcd. C 68.48, H 9.77; found C 68.48, H 9.86.

{4,6-Di-*tert*-butyl-2-(diphenylphosphanyl)phenolato[*O*,*P*]}-methylbis(trimethylphosphane)nickel(II) (4a): At –78 °C, **1a** (945 mg, 2.42 mmol) was added to a solution of NiMe$_2$(PMe$_3$)$_3$ (800 mg, 2.52 mmol) in Et$_2$O (60 mL). On warming to room temperature and stirring for 3 h, the color of the mixture turned from yellow-brown to dark-red. Crystallization from diethyl ether containing PMe$_3$ furnished 1.06 g (71%) of **4a** as red crystals; m.p. 109 °C. – IR (Nujol): ṽ = 1159 m (NiCH$_3$), 937 cm^{-1} s (ρ$_1$ PMe$_3$). – ^{1}H NMR (300 MHz, [D$_8$]THF): δ = –0.69 (d, $^{3}J_{PH}$ = 8.8 Hz, 3 H, NiMe), 1.12 (s, 9 H, CMe$_3$), 1.15 (d, $^{2}J_{PH}$ = 3.3 Hz, 18 H, PMe$_3$), 1.34 (s, 9 H, CMe$_3$), 7.03 (br. d, $^{3}J_{PH}$ = 8.4 Hz, 1 H, 3-H), 7.09 (d, $^{5}J_{PH}$ = 2.3 Hz, 1 H, 5-H), 7.35 (m, 6 H, Ph), 7.62 (m, 4 H, Ph). – ^{13}C NMR (75.5 MHz, [D$_8$]THF, 293 K): δ = –18.8 (br., NiMe), 12.5 (d, $^{1}J_{PC}$ = 6.5 Hz, PMe$_3$), 28.1 (C*Me*$_3$), 30.3 (C*Me*$_3$), 32.6 (*C*Me$_3$), 34.0 (*C*Me$_3$), 117.1 (d, $^{1}J_{PC}$ = 45.8 Hz, C-2), 125.0 (C-5), 125.3 (C-3), 127.1 (d, $^{3}J_{PC}$ = 9.3 Hz, *m*-C), 128.0 (*p*-C), 132.0 (d, $^{2}J_{PC}$ = 11.7 Hz, *o*-C), 133.3 (d, $^{3}J_{PC}$ = 5.0 Hz, C-4), 134.5 (d, $^{1}J_{PC}$ = 36.5 Hz, *i*-C), 136.1 (d, $^{3}J_{PC}$ = 8.9 Hz, C-6), 173.3 (d, $^{2}J_{PC}$ = 28.1 Hz, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –28.5 (br. s, PMe$_3$), 27.0 (br. s, *o*-P); trace impurity: δ = –15.9 (s), 41.4 (s). – Low-temperature NMR: ^{13}C NMR (75.5 MHz, [D$_8$]THF, 243 K): δ = –16.4 (d, $^{2}J_{PC}$ = 19.6 Hz, NiMe), 15.4 (d, $^{1}J_{PC}$ = 9.8 Hz, PMe$_3$), 30.2 (C*Me*$_3$), 32.2 (C*Me*$_3$), 34.5 (*C*Me$_3$), 35.9 (*C*Me$_3$), 120.4 (d, $^{1}J_{PC}$ = 43.0 Hz, C-2), 126.0 (C-5), 127.8 (C-3), 128.9 (d, $^{3}J_{PC}$ = 8.1 Hz, *m*-C), 129.3 (*p*-C), 133.5 (d, $^{2}J_{PC}$ = 11.9 Hz, *o*-C), 134.0 (br., C-4), 138.0 (d, $^{3}J_{PC}$ = 8.9 Hz, C-6), 138.6 (d, $^{1}J_{PC}$ = 30.0 Hz, *i*-C), 174.8 (d, $^{2}J_{PC}$ = 31.1 Hz, C-1). – $C_{33}H_{51}NiOP_3$ (615.38): calcd. C 64.41, H 8.35, P 15.10; found C 64.67, H 8.06, P 15.18.

{4,6-Di-*tert*-butyl-2-(*tert*-butylphenylphosphanyl)phenolato-[*O*,*P*]}methylbis(trimethylphosphane)nickel(II) (4d): At –78 °C, **1d** (945 mg, 2.55 mmol) was added to a solution of NiMe$_2$(PMe$_3$)$_3$ (800 mg, 2.52 mmol) in Et$_2$O (60 mL) and the mixture was stirred for 3 h at room temperature. The bulk of the solvent was then removed. Crystallization of the residue from diethyl ether containing PMe$_3$ furnished 1.07 g (71%) of **4d** as dark-red crystals; m.p. 106–109 °C. – IR (Nujol): ṽ = 1157 m (NiCH$_3$), 937 cm^{-1} s (ρ$_1$ PMe$_3$). – ^{1}H NMR (300 MHz, [D$_8$]THF): δ = –0.87 (d, $^{3}J_{PH}$ = 8.1 Hz, 3 H, NiMe), 1.22 (s, 9 H, CMe$_3$), 1.25 (br. s, 18 H, PMe$_3$), 1.34 (s, 9 H, CMe$_3$), 1.36 (d, $^{3}J_{PH}$ = 12.8 Hz, 9 H, PCMe$_3$), 7.06 (dd, $^{3}J_{PH}$ = 7.4, $^{4}J_{HH}$ = 2.5 Hz, 1 H, 3-H), 7.12 (d, $^{4}J_{HH}$ = 2.5 Hz, 1 H, 5-H), 7.37 (m, 3 H, Ph), 7.81 (m, 2 H, Ph). – ^{13}C NMR (75.5 MHz, [D$_8$]THF): δ = –20.7 (d, $^2J_{PC}$ = 22.7 Hz, NiMe), 15.1 (br. s, PMe$_3$), 28.5 (d, $^2J_{PC}$ = 5.3 Hz, PC*Me*$_3$), 29.3 (C*Me*$_3$), 31.7 (C*Me*$_3$), 33.9 (*C*Me$_3$), 35.0 (d, $^1J_{PC}$ = 20.4 Hz, P*C*Me$_3$), 35.2 (*C*Me$_3$), 117.3 (d, $^1J_{PC}$ = 43.0 Hz, C2), 125.9 (C-5), 127.2 (C-3), 128.3 (d, $^3J_{PC}$ = 8.3 Hz, *m*-C), 128.9 (*p*-C), 133.2 (d, $^2J_{PC}$ = 8.3 Hz, *o*-C), 133.6 (d, $^3J_{PC}$ = 5.3 Hz, C-4), 133.8 (d, $^1J_{PC}$ = 29.4 Hz, *i*-C), 137.1 (d, $^3J_{PC}$ = 9.1 Hz, C-6), 174.7 (d, $^2J_{PC}$ = 24.9 Hz, C-1). – ^{31}P NMR (81 MHz, [D$_8$]THF): δ = –28.0 (v br. s, PMe$_3$), 44.4 (br. s, *o*-P). – $C_{31}H_{55}NiOP_3$ (595.39): calcd. C 62.54, H 9.31, P 15.61; found C 62.06, H 9.11, P 15.31.

Complex-Catalyzed Oligomerization of Ethene. – General Procedure: A solution of the appropriate nickel complex **2** or **4** (ca. 0.1 mmol) in toluene (12 mL) was transferred at room temperature into an argon-filled stainless steel autoclave (75 mL) equipped with a magnetic stirrer. Ethene was introduced with stirring until the pressure remained constant at 35 bar (7.5–7.8 g by weight difference), then the valve was closed and the autoclave was heated at 80 °C for 6–10 h. After cooling to ca. 20 °C and weight control, the valve was opened and the gases were passed through a cooling trap (–60 °C) to condense gaseous butenes. The remaining material was flash distilled at 25–30 °C/10^{-2} Torr to separate volatile oligomers (condensed at –60 °C) and waxes. The former were analyzed by GC and in some cases by GC/MS. The results are summarized in Table 2 and 3.

Crystal Structure Analysis

1e: A crystal of **1e** was sealed under argon in a glass capillary, mounted on a Siemens R3m/V diffractometer, and examined using graphite-monochromated Mo-K^{α} radiation, λ = 0.71073 Å. Lattice parameters were determined from 25 selected reflections. The structure was solved by a full-matrix least-squares refinement (SHELXL-97). Non-hydrogen atoms were treated anisotropically, hydrogen atoms were fixed in idealized positions. Crystal data are presented in Table 4; selected bond lengths and angles are indicated in Figure 1.

3e: A green crystal of **3e** was sealed under argon in a capillary; data were collected as above on a Bruker P4 diffractometer. Lattice parameters were refined from 28 reflections in the range $15 \leq 2\Theta \leq 40°$. During data collection, 3 standard reflections were checked every 397 intensities and were found to show only random deviations. Lorentz and polarization corrections were applied, as well as an absorption correction based on psi-scans. The structure was solved by direct and conventional Fourier methods, with full-matrix least-squares refinement based on F^2. All atoms other than the H-atoms and disordered C-atoms were refined anisotropically. The *tert*-butyl group C7–C102 and the isopropyl group C19–C21 were each found to be disordered over two sites and were refined with a split model. Site occupancy factors were refined to 0.43(1) and 0.57(1) for the *tert*-butyl group and to 0.29(1) and 0.71(1) for the isopropyl group, respectively. Hydrogen atoms were refined at idealized positions with a riding model. Further crystallographic and refinement data are given in Table 4; selected bond lengths and angles are indicated in Figure 2.

4a: A red crystal of **4a** was sealed under argon in a glass capillary. Data collection was performed as described for **3e**. Lattice parameters were refined from 25 reflections in the range $17 \leq 2\Theta \leq 34°$. Standard reflections showed a decrease of 7%. Lorentz, polarization, and absorption corrections were applied as above. Structure solution and refinement and the positioning of the hydrogen atoms was as described above. Further crystallographic and refinement data are given in Table 4; selected bond lengths and angles are indicated in Figure 3.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-136785 (**1e**)], [CCDC-135904 (**3e**)], [CCDC-135905 (**4a**)] can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@chemcrys.cam.ac.uk].

Table 4. Crystallographic data of compounds **1e**, **3e**, and **4a**

	1e	3e	**4a**
Empirical formula	$C_{20}H_{35}OP$	$C_{40}H_{68}NiO_2P_2$	$C_{33}H_{51}NiOP_3$
Molecular mass	322.47	701.59	615.36
Crystal size [mm^3]	0.49 × 0.56 × 0.39	0.58 × 0.55 × 0.50	0.35 × 0.21 × 0.10
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*P*21/*c*	Pbca	*P*-1
Unit cell dimensions			
a [Å]; α [°]	11.2190(4); 90	10.425(2); 90	9.646(2); 98.90(2)
b [Å]; β [°]	10.0580(6); 90.8(3)	18.611(2); 90	10.236(2); 95.86(2)
c [Å]; γ [°]	18.9040(8); 90	21.529(6); 90	18.837(4); 107.24(2)
V [Å ^{3}]; *Z*	2132.93(17); 4	4177.0(15); 4	1733.2(6); 2
Density (calcd.) [Mg/m^3]	1.004	1.116	1.179
Temperature [K]	193	298(2)	293(2)
Absorption coefficient [mm^{-1}]	0.097	0.570	0.720
F(000)	712	1528	660
θ range for data collection [°]	2.00 to 17.50	2.38 to 27.50	2.22 to 25.00
Limiting indices	–9 *h* 9	–1 *h* 13	–12 *h* 12
	0 *k* 8	–1 *k* 24	–13 *k* 13
	0 *l* 15	–27 *l* 1	0 *l* 24
Reflections collected	3384	5889	6289
Independent reflections	1357	4788 (R_{int} = 0.0176)	6094 (R_{int} = 0.0564)
Absorption correction	–	Psi-scan	Psi-scan
Max./min. transmission		0.779/0.748	0.883/0.805
Data/restraints/parameters	1357/3/111	4788/332/203	3122/11/356
Goodness-of-fit on F^2	1.144	1.023	1.034
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.077$; $wR2 = 0.2364$	$R1 = 0.0599$, $wR2 = 0.1491$	$R1 = 0.0540$, $wR2 = 0.1093$
R indices (all data)	$R1 = 0.1018$; $wR2 = 0.2795$	$R1 = 0.1016$, $wR2 = 0.1732$	$R1 = 0.1423$, $wR2 = 0.1434$
Largest diff. peak and hole	0.39/–0.41 eÅ^{-3}	0.566/–0.355 eÅ^{-3}	0.321/–0.348 eÅ^{-3}

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