Introduction

The recently reported reaction of substituted phenols with Ni(PMe$_3$)$_4$ and molecular oxygen in solution gives access to diphenolato-bis(trimethylphosphine)nickel complexes, the first representatives of acyclic molecular diphenolato-tetraphosphine nickel complexes with a trans-square-planar arrangement of soft phosphorus and hard oxygen donor atoms [1, 2]. Steric protection was found to be essential for the existence of these compounds as monomers. Effective steric shielding was achieved by either a tert-butyl group, a chloro or a bromo substituent in ortho-position. When o-hydroxaryl aldehydes were used, additional coordination occurred leading to octahedral bis(O^-O-chelate) complexes with two PMe$_3$ ligands in trans-position [1]. In this context the reactivity of phenols bearing other donor groups in ortho-position was of interest. o-Phosphinophenols are particularly important as they form nickel complexes which catalyze the polymerization [3 - 7] and oligomerization [7, 8] of ethylene and can be tuned by substituents at phosphorus and at the phenoxy group. Therefore we investigated reactions of 6-tert-butyl-2-phosphinophenols with Ni(PMe$_3$)$_4$ in absence and in presence of dioxygen. In this paper the formation of a new hydroxyfunctional acyclic nickel(0) and of cyclic bis(phosphinophenolato)nickel(II) complexes is described.

Results and Discussion

Synthesis

2-Phosphinophenols are available by various methods, including acid cleavage of 2-phosphino-phenol ethers [9, 10], metallation and rearrangement of 2-halogenophenoxyphosphines [11], substitution of C,O-dilithium reagents with chlorophosphines [12], or Pd(0)-catalyzed arylation of PH-functional...
phosphines by iodophenol [13]. The representatives 1a-d with tert-butyl substituents in o-position to the hydroxyl group were synthesized by reaction of the respective chlorophosphines with C,O-lithium/sodium reagents and acidic work-up.

Reaction of 1a with an equimolar amount of Ni(PMe$_3$)$_4$ dissolved in pentane at low temperature rapidly led to an intensively yellow solution. In contrast to the more acidic o-chlorophenol, which forms with Ni(PMe$_3$)$_4$ a yellow precipitate (optimum yield in molar ratio 1:3) of the ion-pair compound NiH(PMe$_3$)$_4$H$_2$(2-CIC$_6$H$_4$O)$_3$ [2], no crystalline material could be isolated even after prolonged reaction periods at 20 °C and storage at −27 °C. Removal of the solvent and volatile components in vacuo furnished a waxy solid which was identified by IR and multinuclear NMR spectroscopy to be the air-sensitive nickel(0) complex 2a (eq. (1)).

The infrared spectrum of 2a shows the bands for coordinated PMe$_3$ (e.g. $\nu_{Me}$ at 930 cm$^{-1}$) in the range typical for Ni(0) complexes. The $\nu_{OH}$ band is very broad and observed in the range 2500 - 3300 cm$^{-1}$. The proton NMR reveals a sharp singlet at $\delta = 0.76$ for three PMe$_3$ groups and a double quartet for the hydroxyl proton [$d, J_{PH} = 8$ Hz (o-P); $J_{PH} = 2.4$ Hz (PMe$_3$)]. Although the chemical shift of $\delta = 10.5$ shows an increased acidity relative to free 1a, a NiHP$_4^+$ structure ($\delta = -17$) as observed for the more acidic phenols [2] can be excluded. The PMe integral is in accordance with three PMe$_3$ ligands coordinated to nickel. The $^{13}$C data give evidence for $\eta^1$-P coordination of the P^OH ligand by doublets with $^{1}J_{P-C_2} = 29$ Hz and $^{1}J_{P-C_1} = 24.4$ Hz, respectively, whereas the chemical shift of C-1 is shifted slightly downfield ($\Delta\delta = 2.3$) in contrast to 2-phosphinophenolate Ni(II) complexes ($\Delta\delta = 16 - 19$). The $^{13}$C resonance (AXYZ$_2$ spin type) of the trimethylphosphine ligands exhibits a pseudo-quintet pattern. The $^{31}$P coordination shifts [$\Delta\delta = 42.8$ (o-P), 38.6 (PMe$_3$)] are markedly and the $^{2}J_{PP}$-coupling constants (33.4 Hz) are strongly reduced as compared to those of square-planar complexes of Ni(II) with phosphinophenolato ligands [6, 14] and below).

When the reaction of 1a-d with Ni(PMe$_3$)$_4$ in pentane (molar ratio 2:1) was followed by slow addition of dioxygen, 2-phosphinophenolate nickel(II) complexes were formed. The progress of the conversion was perceptible by the color change of the solution to orange-red and later to dark red or brown. The main part of trimethylphosphine was oxidized to Me$_3$PO. Work-up afforded 52- 78% of fine red or brown crystals identified as bis-(phosphinophenolato-P,0) nickel(II) chelates 3a-d (eq. (2)). As shown for 3c these complexes were also formed when the phosphinophenoles were reacted with N,N-diallylanilin(trimethylphosphine)-nickel(0). The structures were elucidated by the characteristic $^{13}$C (AXX' spin type) and proton (A"XX'A" spin type) resonances, partially appearing as triplets or multiplets with “virtual coupling” (X, X' means $^{31}$P). In the cases of 3c and 3d crystal structure analyses were also performed.
Table I. Comparison of characteristic NMR data of cis- and trans-bis(2-phosphinophenolato)nickel complexes 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta\delta^{31}P )</th>
<th>( N(13C-1-31P_2) )</th>
<th>( \Delta\delta^{13}C-1 )</th>
<th>( N(13C-2-31P_2) )</th>
<th>( \Delta\delta^{13}C-2 )</th>
<th>( N(13C-3-63P_2) )</th>
<th>( N(13C-4-31P_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>71.1</td>
<td>18.9</td>
<td>17.5</td>
<td>61.2</td>
<td>-1.1</td>
<td>( \approx 14 )</td>
<td>( \approx 8 )</td>
</tr>
<tr>
<td>3b</td>
<td>70.5</td>
<td>60</td>
<td>14</td>
<td>12.8</td>
<td>7.2</td>
<td>( \approx 8 )</td>
<td></td>
</tr>
<tr>
<td>rac-3c</td>
<td>77.5</td>
<td>17.7</td>
<td>19.1</td>
<td>55.8</td>
<td>-5.2</td>
<td>( \approx 14 )</td>
<td>( \approx 8 )</td>
</tr>
<tr>
<td>[Ni(2-PhPrP-4-MeC_6H_4O_2)] [6]</td>
<td>74.1</td>
<td>16.6</td>
<td>15.5</td>
<td>54</td>
<td>-7.9</td>
<td>13.8</td>
<td>6.9</td>
</tr>
<tr>
<td>rac-3d</td>
<td>54.0</td>
<td>28.7</td>
<td>15.5</td>
<td>46.8</td>
<td>-3.7</td>
<td>( \approx 7 )</td>
<td>( \approx 5 )</td>
</tr>
<tr>
<td>trans- [Ni(2-iPrP-4,6-tBuC_6H_4O_2)] [14]</td>
<td>62.0</td>
<td>30.5</td>
<td>17.1</td>
<td>42.6</td>
<td>-4.7</td>
<td>7.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Distinction of cis- and trans-isomers in solution

Whereas unsymmetrical cis- and trans-2-phosphinophenolato nickel phosphine complexes can be easily distinguished by the grossly different two-bond \( 31P^{31}P \)-coupling constants (cis 70 - 90 Hz [6, 15, 16], trans ca. 300 Hz [8, 14]) the pattern for symmetrical cis- and trans-square planar isomers is usually very similar. Pseudo-triplets were found since the intensity of the outer bands which are different for the isomers is too low. A comparison of the multinuclear NMR data of 3a-d with those of related 2-phosphinophenolato nickel complexes [6, 14, 15] indicates, however, that the coordination shifts \( \Delta\delta = \delta(3) - \delta(1) \) of \( 31P \) and of \( 13C-1 \) nuclei as well as the \( 13C-31P \) couplings \( N = |J + J'| \) of C-1 and C-2 (Table I) possess high diagnostic value for the distinction of cis- and trans-square planar bis(phosphinophenolato)nickel complexes.

The phosphorus coordination shifts of cis-[Ni(Ph,P-arylo)]_2 species were found in the region \( \Delta\delta^{31}P = 62 - 70 \) with the 6-tert-butyl derivatives 3a,b at the upper end, those of alkylphenylphosphino derivatives [Ni(AlkPhP-arylo)]_2 (Alk = Me, iPr) with higher donor and lower acceptor strength at phosphorus at noticeably higher values \( \Delta\delta^{31}P = 73 - 78 \). In contrast, the coordination shifts of trans-[Ni(2-iPrPhP-4-MeC_6H_4O_2)] (\( \Delta\delta^{31}P = 43 \) [15]) and also of the more P-basic trans-[Ni(2-iPrP-4,6-tBuC_6H_4O_2)] (\( \Delta\delta^{31}P = 62 \) [14]) are markedly lower. This allows the conclusion that 3a-c prefer a cis-, the more bulky and P-basic tert-butylphenylphosphino substituted complex 3d, however, a trans-square planar configuration in solution. This is further supported by the values of \( N(13C-1-31P_2) \) and \( N(13C-2-31P_2) \) (Table I). The former is significantly larger for 3d (28.7 Hz) than for the cis-complexes 3a,c (19 and 18 Hz) but it is comparable with those of trans-[Ni(2-iPrP-4,6-tBuC_6H_4O_2)] (30.5 Hz) [14] and even the monochelate complexes trans-[NiMe(2-RRP-arylo)(PMe_3)] (22 - 26 Hz) [14].

\( N(13C-2-31P_2) \) shows the opposite trend and is smaller for 3d (46.8 Hz), trans-[Ni(2-iPrP-4,6-tBuC_6H_4O_2)] (42.6 Hz) and trans-[NiMe(2-RRP-arylo)(PMe_3)] (41 - 49 Hz) [14] than for the cis complexes 4a-c (55.8 - 61.2 Hz). The latter effect is observed on a smaller scale also for the carbon atoms C-6 (\( trans N \approx 7 - 9 Hz, cis N \approx 13 - 14 Hz \) and C-4 (\( trans N \approx 4 - 7 Hz, cis N \approx 7 - 8 Hz \) in the other ortho- and the para-position relative to oxygen and it reflects the different donor-acceptor interplay in trans- and cis-complexes with opposite P/P, O,O- or P,O arrangements. The higher \( \Delta\delta^{31}P \) values of cis- as compared to trans-isomers may be attributed to stronger donor interactions with nickel, due to more ionic character of the trans-Ni-O bonds, whereas the higher \( N(13C-2-31P_2) \) values may be interpreted in terms of a strengthened \( \pi \)-back bonding in the P-Ni bonds, enforced by the electron donation from trans-oxygen atoms. The strong influence of the acceptor strength at phosphorus on \( 1J_{PC-2} \) is underlined by decreasing coupling in the order Ph,P > AlkPhP > Alk,P and the very low one-bond coupling if back-bonding is not possible, e.g. \( 1J_{PC-2} = 6 Hz \) of the recently published \( d^0 \)-transition metal 2-phosphinophenolato complex [\( \eta^5-CpTiCl_2(2-Ph,P-6-tBuC_6H_4O_2) \)] [17].

The influence of P-substituents in cis-3a-c on \( \Delta\delta^{31}P \) and \( N(13C-2-31P_2) \) can be separated from the influence of a different geometry by opposite trends of the two values and smaller effects. In the alkylphenylphosphino complex 3c \( \Delta\delta^{31}P \) is larger
whereas $N^{13}$C-$2^{31}$P$_2$ is smaller than in 3a or 3b. The pattern of the proton multiplets of H-3 and the diastereotopic Me groups ($N$ larger for downfield than for up-field Me groups) of the isopropylphosphino derivatives cis-3c and trans-[Ni(2-iPr$_2$P-4,6-tBu$_2$C$_6$H$_2$O)$_2$]$_2$ [14] was found to be different for cis- (“filled in” multiplets) and trans-geometry (doublet of pseudotriplets).

The preference for the cis- or trans-arrangement of the rigid 2-phosphinophenolato ligands depends on the steric demand and/or on the basicity of the 2-phosphino substituents. Two tert-butyl or isopropyl groups at phosphorus favor the formation of trans-complexes as seen for trans-[Ni(2-tBu$_2$PC$_6$H$_2$O)$_2$] [9] and trans-[Ni(2-iPr$_2$P-4,6-tBu$_2$C$_6$H$_2$O)$_2$] [14]. The α-branched alkylphosphinophenolato complexes [Ni(2-AlkPh-4-MePC$_6$H$_2$O)$_2$] (Alk = tBu, iPr) [6, 15, 18] were found to be borderline cases, where replacement of a tert-butyl by an isopropyl group causes a switch from the trans- to the cis-structure. The NMR spectra of 3c and 3d bearing additional bulky substituents in $o$-position to the oxygen atom confirm a similar behavior in solution. The brown color and the high solubility of solid 3d, however, are at variance with the properties of the other trans-complexes which form less soluble green solids suggesting an alternative cis-geometry in the solid state. This was verified by the crystal structure analysis of 3d (Fig. 1). Interestingly, there are considerable differences as compared with the cis-structure of 3c (Fig. 2) investigated for comparison.

Crystal and solid state molecular structures of 3c and 3d

Crystals of compound 3d are monoclinic, space group C2/c, with eight molecules in the centrosymmetric unit cell. S,S and R,R molecules are built up with two pairs of enantiomeric ligands. The bulky tert-butyl groups are in anti-positions, thus reducing steric hindrance. The P1-Ni-P2 angle is widened to 107.06(8°), the O1-Ni-O2 and O2-Ni-P1 angles are diminished to 85.6 and 84.4(14)°, respectively, and the planes of the two five-membered rings (P1/O1/C1/C2/Ni1 and P2/O2/C25/C26/Ni1) are twisted by an angle of 22.3°. The deviation of nickel from the “best plane” of P1/O1/P2/O2 is 0.036(1) Å.
Fig. 2. Molecular structure of (S,S)-3d; selected distances [Å] and angles [°]: Ni1-O1 1.878(4), Ni1-O2 1.874(4), Ni1-P1 2.172(2), Ni1-P2 2.174(2), O1-C1 1.331(6), C1-C2 1.412(8), P1-C2 1.809(6), P1-C19 1.814(6), P1-C15 1.880(7), C1-C6 1.420(8); O1-Ni1-P2 162.4, O2-Ni1-P1 164.7(2), O2-Ni1-O1 85.6(2), P1-Ni1-P2 107.06(8), O1-Ni1-P1 84.45(14), C1-O1-Ni1 120.4(4), O1-C1-C2 120.5(6), C1-C2-P1 108.8(5), C5-C2-P1 129.3(5), C2-P1-Ni1 99.7(2), C2-P1-C15 152.3(3), C2-P1-C19 106.8(3), C19-P1-C15 108.7(3), O1-C1-C6 121.1(6), C1-C6-C7 120.5(6), C5-C6-C7 122.6(6), C5-C6-C1 116.7(6), C4-C5-C6 125.7(7).

The triclinic crystals of 3c contain four molecules in the centrosymmetric unit cell (space group P1). The two independent molecules per asymmetric unit are very similar. Surprisingly the isopropyl and phenyl groups are arranged each in syn-position (RS and SR configuration) with a nearly staggered arrangement of the isopropyl (torsion angle C15-P1-P2-C38 20.3°) and phenyl groups (torsion angle C18-P1-P2-C41 21.0°) which is facilitated by the lack of a third substituent at the α-carbon atoms C15 and C38. The two five-membered rings show different distortions. Whereas the deviation of Ni from the plane P1/P2/O1/O2 is only 0.009(2) Å, the deviations of P1 and P2 from the best planes of ring1 and ring 2 are 0.018 and 0.14 Å, respectively. The dihedral angle of these planes (11.3°) is considerably smaller than for 3d but noticeably larger than in cis-[Ni(2-iPrPh-4-MePc6H3O)2] (θ = 7.1°) [6] with anti-positioned isopropyl and phenyl groups.

The reason of the different structures is not clear. The 6-tert-butyl groups, exerting a strong influence on the conformation of O-substituted 2-phosphinophenols, have rather low steric importance in cis-bis(chelates). The P-Ni-O and O1-Ni-O2 angles are only slightly diminished (1-3°) as compared to [Ni(2-iPrPh-4-MePc6H3O)2]. The distortions in the phenyl rings by the 4- and 6-tert-butyl groups are much larger. One of the tert-butyl groups of 3d and all tert-butyl groups of 3c show rotational disorder around the C-C axis as shown in Fig. 1.

Experimental Section
General procedures and materials

Handling of air-sensitive materials and all reactions were conducted under an atmosphere of purified argon using standard vacuum or Schlenk techniques. Solvents were dried and kept under argon and freshly distilled before use.

Tetakis(trimethylphosphine)nickel(0) [19], N,N-diallylanilin(trimethylphosphine)nickel(0) [20] and the 2-phosphinophenols 1a [12a] and 1b [21] were prepared according to known procedures. The syntheses of 1c and 1d [12a] were improved as given below. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrometer. NMR spectra on Bruker AM200, Bruker WM 300 or Bruker ARX 300 multinuclear Fourier transform spec-
trometers. Shift references are tetramethylsilane for $^1$H and $^{13}$C, and H$_3$PO$_4$ (85%) for $^{31}$P. For resonances which are part of an AX$'$X spin system (X,$X'$ = $^3$P) vc and $\tau$ denote “virtual coupling” and a triplet pattern of the A-resonance, $N = |J + J'|$. Atom numberings in the assignments correspond to numbers according to the nomenclature of phosphinophenols, $i$, $o$, $m$ and $p$ denote the positions in phenyl substituents. Elemental analyses were performed in the microanalytical laboratory of the TUD using a CHN 240A instrument (Perkin Elmer).

rac-4,6-Di-tert-butyl-2-(isopropylphenylphosphinopheno)-phenol (1c)

54 ml of an 1.6 N solution of n-butyllithium (86.4 mmol) in hexane was added with cooling to a solution of 2-bromo-4,6-di-tert-butylphenol (12.7 g, 43.1 mmol) in ether (90 ml). After stirring for 3 h at room temperature 8.06 g (43.1 mmol) of $t$BuPhPCl was added and the mixture was stirred overnight. Then the reaction was quenched by addition of 2 ml of glacial acetic acid. Volatiles were removed in vacuo and the residue was extracted with ether. Ether was evaporated in vacuo and the product of colorless $in vacuo$ and recrystallized to yield 6.6 g (39%) of 1d.

Analysis for $C_{22}H_{33}$OP (356.48)

Caled C 77.49 H 9.33 P 8.69%
Found C 78.32 H 9.40 P 8.15%

$^1$H NMR (300 MHz, d$_6$-THF): $\delta = 0.94$ (m, 3H, Me$_3$), 1.06 (m, 3H, Me$_3$), 1.23 (s, 9H, CMe$_3$), 1.40 (s, 9H, CMe$_3$), 2.49 (m, 1H, CH), 3.27 (s, 1H, OH), 7.19 (m, 1H, H-3), 7.28 - 7.32 (3H, Ph), 7.50 - 7.56 (m, 3H, H-5, Ph). $^{13}$C NMR (75.5 MHz, d$_6$-THF): $\delta = 17.5$ (d, $^2$J$_{PC} = 15.2$ Hz, Me), 18.5 (d, $^2$J$_{PC} = 20.5$ Hz, Me), 24.2 (d, $^2$J$_{PC} = 4.3$ Hz, CHMe$_2$), 28.2 (CMe$_3$), 30.0 (CMe$_3$), 33.2 (CMe$_3$), 33.9 (CMe$_3$), 119.4 (d, $^1$J$_{PC} = 3.4$ Hz, C-2), 124.3 (C-5), 126.1 (C-3 or C-p), 127.2 (d, $^2$J$_{PC} = 7.3$ Hz, C-m), 127.5 (C-p or C-3), 130.2 (d, $^2$J$_{JP} = 18.2$ Hz, C-o), 134.0 (C-6), 135.6 (d, $^1$J$_{PC} = 7.9$ Hz, C-i), 140.3 (C-4), 156.0 (d, $^2$J$_{PC} = 21.0$ Hz, C-C), - $^{31}$P NMR (81 MHz, d$_6$-THF): $\delta = -23$. (NMR data in CDCl$_3$ [12a]).

rac-4,6-Di-tert-butyl-2-(tert-butylphenylphosphinopheno)-phenol (1d)

A solution of 2-bromo-4,6-di-tert-butylphenol (13.1 g, 45.9 mmol) in ether (300 ml) was refluxed with NaH (1.1 g, 45.8 mmol) for 8 h and stirred for 1d at 20 °C, followed by addition of 29 ml of a 1.6 N solution of nBuLi in ether. After 3 h, 9.2 g (45.9 mmol) of $t$BuPhPCl was slowly added at −40 °C. The mixture was stirred for 19 h, and 3 ml (52 mmol) of glacial acetic acid was added. After filtration the volatiles were removed $in vacuo$ (10$^{-2}$ Torr), and the residue was extracted with hot methanol and recrystallized to yield 6.6 g (39%) of 1d.

Analysis for $C_{24}H_{35}$OP (370.51)

Caled C 77.80 H 9.52 P 8.36%
Found C 77.89 H 9.35 P 8.39%

$^{31}$P ($\delta$ = -18.8). $^1$H and $^{13}$C NMR data in CDCl$_3$ agree with those given in [12a].

\[ 4,6-$\text{Di}$-tert-butyl-$2$-(diphenylphosphinopheno)$phenol[P]$-tris(trimethylphosphine)nickel(II) (2a) \]

770 mg (2.04 mmol) of 1a was added at −78 °C to a solution of Ni(PMe$_3$)$_2$ (740 mg, 2.04 mmol) in pentane (50 ml). The resulting yellow solution was stirred for 16 h. Removal of the solvent and all of volatiles afforded 2a as a waxy yellow solid. IR (nujol): $\tilde{\nu} = 956$ st, 933 sst. $^1$H NMR (300 MHz, CD$_2$D$_6$): $\delta = 0.76$ (s, 27H, PMe$_3$), 0.79 (s, 9H, CMe$_3$), 1.30 (s, 9H, CMe$_3$), 6.33 (d, $^2$J$_{HH} = 2.3, ~^2$J$_{HP} = 7.1$ Hz, 1H, H-3), 6.76 (m, 7H, 7H, Ph, H-5), 7.19 (m, 4H, Ph), 10.5 (d qua, $^1$J$_{HP} = 8.0, ~^2$J$_{HP} = 2.4$ Hz, 1H, OH). $^{13}$C NMR (75.5 MHz, CD$_2$D$_6$): $\delta = 23.6$ ("qui"), average line distance $\approx 9.1$ Hz, PMe$_3$), 30.5 (CMe$_3$), 31.7 (CMe$_3$), 32.3 (CMe$_3$), 34.5 (CMe$_3$), 122.3 (d qua, $^1$J$_{PC} = 29.0, ~^3$J$_{PC} = 6.1$ Hz, C-2), 124.4 (C-5), 128.0 (d, $^2$J$_{PC} = 9.2$ Hz, C-m), 128.3 (C-p), 128.4 (C-C), 133.0 (d, $^2$J$_{PC} = 13.7$ Hz, C-1). - $^{31}$P NMR (81 MHz, d$_6$-THF): $\delta = -24.7$ (d, $^2$J$_{PP} = 33.4$ Hz, PMe$_3$), 13.1 (qua, $^3$J$_{PP} = 33.4$ Hz, C-P-2); impurity at −21.0 (br s).

cis-Bis{4,6-$\text{Di}$-tert-butyl-2-(diphenylphosphinopheno)$phenolato[P]$}nickel(II) (3a)

Dry oxygen (50 ml, 2.23 mmol) was introduced into a cold (−78 °C) solution of Ni(PMe$_3$)$_2$ (430 mg, 1.18 mmol) and 1a (831 mg, 2.13 mmol) in THF (70 ml). Within 16 h the colorless solution turned via red-orange to dark red. The solvent was removed $in vacuo$, the residue was washed with ether and then extracted with THF to afford, on cooling, 520 mg (50 %) of red crystals of 3a, m. p. > 220 °C.

Analysis for $C_{26}H_{30}$NiO$_2$P$_2$ - 2 TFH (982.12)

Caled C 73.45 H 7.81 P 6.31%
Found C 73.98 H 7.65 P 6.95%

$^1$H NMR (300 MHz, d$_6$-THF): $\delta = 1.11$ (s, 9H, CMe$_3$), 1.46 (s, 9H, CMe$_3$), 6.61 (m vc, $^2$J$_{HH} \approx 3, ~^2$J$_{HP} \approx 10$ Hz, 1H, H-3), 7.15 (m, 5H, 5, H-o,m), 7.32 (m, 2H, H-p), 7.45 (m, 4H, Ph). $^{13}$C NMR (75.5 MHz, d$_6$-THF): $\delta = 29.7$ (CMe$_3$), 32.0 (CMe$_3$), 34.6 (CMe$_3$), 36.0 (CMe$_3$), 118.8 (t, $N = 61.2$ Hz, C-2), 125.0 (C-5), 128.1 (C-3), 129.3 (t, $N = 10.6$ Hz, C-m), 130.8 (t, $N = 49.1$ Hz, C-i), 131.2 (C-p), 134.0 (t, $N = 10.6$ Hz, C-o), 137.6 (t, $N \approx$}
cis-Bis(6-tert-butyl-4-methyl-2-(diphenylphosphino)phenolato[O,P])nickel(II) (3b)

Ni(PMe₃)₄ (1.0 g, 2.76 mmol) and 1b [21] (1.92 g, 5.51 mmol) were dissolved in THF (70 ml), and dry oxygen (50 ml, 2.23 mmol) was introduced at -78 °C. The resulting orange solution was stirred for 16 h at room temperature, the solvent was removed in vacuo and 1.08 g (47 %) of red 3b, m.p. > 220 °C, was obtained by extraction of the residue with ether and crystallization.

Analysis for C₄₈H₆₄NiO₃P₂ • THF (825.63)
Calcd C 72.74 H 6.84 P 7.50%. Found C 72.67 H 6.31 P 7.96%.

\(^1\)H NMR (300 MHz, d₈-THF): \(\delta = 1.41\) (s, 9H, CMe₃), 2.01 (s, 3H, 4-Me), 6.39 (vc, 1H, H-5), 7.11 (m, 4H, Ph), 7.31 (m, 2H, H-5), 7.14–7.19 (m, 2H, Ph), -13C NMR (75.5 MHz, d₈-THF): \(\delta = 18.8\) (Me), 27.9 (CMe₃), 33.8 (s, CMe₃), 117.8 (\(\tau, N = 60\) Hz, C-2), 122.1 (\(\tau, N \approx 8\) Hz, C-4), 126.8 (C-5), 127.4 (\(\tau, N = 9.2\) Hz, C-m), 128.7 (\(\tau, N = 42.3\) Hz, C-i), 129.3 (C-p), 130.0 (C-3), 132.0 (\(\tau, N = 10.5\) Hz, C-o), 136.9 (\(\tau, N \approx 14\) Hz, C-6), 171 (\(\tau, C-i\)). -31P NMR (81 MHz, d₈-THF): \(\delta = 40.7\).

rac-cis-Bis{4,6-di-tert-butyl-2-(tert-butylphenylphosphino)phenolato[O,P]}nickel(II) (3d)

a) Reaction of crude 1c and Ni(PMe₃)₄ followed by partial air oxidation gave 3c. Single crystals were grown from a THF solution. -31P NMR (121.5 MHz, d₈-acetone): \(\delta = 47.5\). -1H and -13C NMR data agree with those given below.

b) A solution of 1c (5.81 g, 16.3 mmol) in THF (70 ml) was added at room temperature to a solution of N,N-diallylanilin-(trimethylphosphine)nickel(0) (2.51 g, 15.0 mmol) in pentane (1:2). From this solution 4.75 g (76%) of red 3c was obtained which on drying in vacuo loose solvent to form an orange-red powder, m. p. 261 °C (dec.). Analysis for C₄₆H₄₈NiO₂P₂ • 1THF (825.63)
Calcd C 72.74 H 6.84 P 7.50%. Found C 72.67 H 6.31 P 7.96%.

-1H NMR (300 MHz, d₈-THF): \(\delta = 0.92\) (m, 6H, CHMe₂), 1.23 (s, 18H, CMe₃), 1.33 (m, 6H, CHMe₂), 1.45 (s, 18H, CMe₃), 2.39 (br m, 2H, CHMe₂), 6.46 (m, 2H, H-3), 7.13 (m, 2H, H-5), 7.18–7.19 (m, 2H, Ph), 7.46–7.61 (m, 8H, Ph). -13C NMR (75.5 MHz, d₈-THF): \(\delta = 15.1\) (br, CHMe), 17.7 (br, CHMe₂), 23.2 (\(\tau, N = 27.3\) Hz, CHMe₂), 27.7 (CMe₃), 30.2 (CMe₃), 32.6 (CMe₃), 34.0 (CMe₃), 111.6 (\(\tau, N = 54.9\) Hz, C-2), 124.7, 126.2 (C-3 and C-5), 127.8 (\(\tau, N = 9.2\) Hz, C-m), 129.1 (\(\tau, N = 45.8\) Hz, C-i), 129.7 (C-p), 131.3 (\(\tau, N = 9.2\) Hz, C-o), 134.4 (\(\tau, N \approx 7\) Hz, C-4), 136.1 (\(\tau, N = 12.2\) Hz, C-6), 173.3 (\(\tau, N = 18.3\) Hz, C-1). -31P NMR (121.5 MHz, d₈-THF): \(\delta = 52\).

Crystal structure analysis

3c. A crystal was sealed under argon into a glass capillary and mounted on a Siemens R3m diffractometer which used graphite monochromated MoKα radiation 0.71073 A. Lattice parameters were refined from 25 centered reflections. Intensities were collected (ω-2θ scans) and LP and absorption (psi-scans) corrections applied. The structure was solved by direct and conventional Fourier methods. Full-matrix least-squares refinement are based on F² and 898 parameters. All non-hydrogen atoms, except the butyl carbon atoms which were treated with a split model, were refined anisotropically. Hydrogen atoms were refined with a riding model in idealized positions. All butyl groups show disorder of the CH₃ groups. Based on the radic map could not be assigned properly but may result from enclosed ether solvent. 3d. Crystal mounting and
Table II. Crystallographic data of compounds rac-3c and rac-3d.

<table>
<thead>
<tr>
<th></th>
<th>rac-3c</th>
<th>rac-3d</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄₀H₆₀NiO₂P₂</td>
<td>C₄₈H₆₈NiO₂P₂</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>769.62</td>
<td>797.67</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>293 (2)</td>
<td>293 (2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>PI</td>
<td>C2/c</td>
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<tr>
<td>a [Å]</td>
<td>15.790 (4)</td>
<td>28.702 (9)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>18.686 (6)</td>
<td>16.933 (4)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>20.385 (5)</td>
<td>21.747 (5)</td>
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<tr>
<td>α [°]</td>
<td>109.68 (2)</td>
<td>113.63 (2)</td>
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<tr>
<td>β [°]</td>
<td>94.76 (2)</td>
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</tr>
<tr>
<td>γ [°]</td>
<td>114.15 (2)</td>
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<tr>
<td>V [Å³] : Z</td>
<td>4994 (2); 4</td>
<td>9683 (4); 8</td>
</tr>
<tr>
<td>Density (calculated) [Mg/m³]</td>
<td>1.024</td>
<td>1.094</td>
</tr>
<tr>
<td>Absorption coefficient [mm⁻¹]</td>
<td>0.482</td>
<td>0.500</td>
</tr>
<tr>
<td>F(000)</td>
<td>1656</td>
<td>3440</td>
</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.40 x 0.25 x 0.10</td>
<td>0.30 x 0.21 x 0.20</td>
</tr>
<tr>
<td>θ Range for data collection [°]</td>
<td>2.20 to 22.55</td>
<td>2.23 to 26.07</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-17 ≤ h ≤ 5, -20 ≤ k ≤ 18, 0 ≤ l ≤ 21</td>
<td>0 ≤ h ≤ 35, 0 ≤ k ≤ 20, -26 ≤ l ≤ 24</td>
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<tr>
<td>Reflections collected</td>
<td>10204</td>
<td>9631</td>
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<tr>
<td>Independent reflections</td>
<td>10030 (Rint = 0.0557)</td>
<td>9439 (Rint = 0.0646)</td>
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<tr>
<td>Absorption correction</td>
<td>Psi-scan</td>
<td>none</td>
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<tr>
<td>Max. &amp; min. transmission</td>
<td>0.759 and 0.884</td>
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</tr>
<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.048</td>
<td>1.018</td>
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<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.1033, wR2 = 0.2270</td>
<td>R1 = 0.0700, wR2 = 0.1058</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.2439, wR2 = 0.3094</td>
<td>R1 = 0.2522, wR2 = 0.1533</td>
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<tr>
<td>Extinction coefficient</td>
<td>0.0017(5)</td>
<td>0.00018(3)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>1.041 and -0.347 eÅ⁻³</td>
<td>0.259 and -0.259 eÅ⁻³</td>
</tr>
</tbody>
</table>

Data collection as for 3c. No absorption correction. Structure solution and refinement (F², 510 parameters) as for 3c. Butyl group at C35 refined with a split model and site occupation factors of 0.76(2) for C361-C381 and 0.24(2) for C362-C382. Pertinent crystal data for both structures are given in Table II.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-120938 (3c), CCDC-120939 (3d)] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) + 44 (1223)336-033, E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

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    b) D. M. Singleton (Shell Oil Comp.), US 4,472,522; C. A. 102, 46405 (1985);
    c) D. M. Singleton (Shell Oil Comp.), US 4,472,525; C. A., 102, 85518 (1985).
[5] a) M. Köhler, Diplomarbeit, Aachen (1996);
    b) J. Heinicke, M. Köhler, W. Keim, to be published.
    b) J. Heinicke, E. Nietzschmann, A. Tzschach, J. Organomet. Chem. 310, C 17 (1986);