# Formation of $\eta^1$ -P-(2-Phosphinophenol)Ni(0)(PMe<sub>3</sub>)<sub>3</sub> and Oxidation to *cis/trans*-Bis(2-phosphinophenolato)nickel(II) Complexes

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Dedicated to Prof. Dr. Dr. h. c. Wilhelm Keim on the occasion of his 65th birthday

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Phosphinophenolate, Nickel, Complexes, Structure Elucidation, Solid State Structures

o-Phosphinophenols 1 (P^OH) react with equimolar amounts of Ni(PMe<sub>3</sub>)<sub>4</sub> at low temperatures to give yellow Ni(0) complexes such as [(HO~P)Ni(PMe<sub>3</sub>)<sub>3</sub>] **2a** with only P coordination of the P^OH ligand. Oxidation of solutions of 1 and Ni(PMe<sub>3</sub>)<sub>4</sub> by dioxygen leads to brown bis(o-phosphinophenolato-P^O)nickel chelate complexes **3a-d**. Structure elucidation by NMR is consistent with a *cis*-square planar geometry for **3a-c** and a *trans*-square planar solution structure of the *tert*-butylphenylphosphino derivative **3d**. The geometric isomers were distinguished by different ranges of phosphorus coordination shifts and <sup>31</sup>P-<sup>13</sup>C-2 and <sup>31</sup>P-<sup>13</sup>C-1 coupling constants. In the solid state, **3d** adopts also a *cis*-square planar geometry. The steric stress of the substituents causes *anti*-orientation of the *tert*-butyl groups at phosphorus (*R*, *R* and *S*, *S* diastereoisomers) and a significant distorsion (22°) of the planes of the two five-membered rings. With less bulky substituents the *R*, *S* and *S*, *R* diastereoisomers are preferred as in the *cis*-square planar complex **3c** with *syn*-orientation of the two isopropyl and phenyl groups, respectively.

### Introduction

The recently reported reaction of substituted phenols with Ni(PMe<sub>3</sub>)<sub>4</sub> and molecular oxygen in solution gives access to diphenolatobis(trimethylphosphine)nickel complexes, the first representatives of acvclic molecular diphenolatodiphosphine nickel complexes with a transsquare-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 ohydroxyaryl aldehydes were used, additional coordination occurred leading to octahedral bis(O^Ochelate) complexes with two PMe<sub>3</sub> ligands in transposition [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<sub>3</sub>)<sub>4</sub> 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-phosphinophenol 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

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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<sub>3</sub>)<sub>4</sub> 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<sub>3</sub>)<sub>4</sub> a yellow precipitate (optimum yield in molar ratio 1:3) of the ion-pair compound NiH(PMe<sub>3</sub>)<sub>4</sub> + H<sub>2</sub>(2-ClC<sub>6</sub>H<sub>4</sub>O)<sub>3</sub><sup>-</sup> [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<sub>3</sub> (e. g.  $\rho_{Me}$  at 930 cm<sup>-1</sup>) in the range typical for Ni(0) complexes. The  $\nu_{OH}$  band is very broad and observed in the range 2500 -3300 cm<sup>-1</sup>. The proton NMR reveals a sharp singlet at  $\delta = 0.76$  for three PMe<sub>3</sub> groups and a double quartet for the hydroxyl proton [d, <sup>4</sup>J<sub>PH</sub> = 8 Hz (o-P); qua,  ${}^{6}J_{PH} = 2.4 \text{ Hz} (PMe_3)$ ]. Although the chemical shift of  $\delta = 10.5$  shows an increased acidity relative to free **1a**, a NiHP<sub>4</sub><sup>+</sup> structure ( $\delta = -17$ ) as observed for the more acidic phenols [2] can be excluded. The PMe integral is in accordance with three PMe<sub>3</sub> ligands coordinated to nickel. The <sup>13</sup>C data give evidence for  $\eta^1$ -P coordination of the P^OH ligand by doublets with  ${}^{1}J_{PC-2} = 29$  Hz and  ${}^{1}J_{PC-i} = 24.4$  Hz, respectively, whereas the chemical shift of C-1 is shifted slightly downfield ( $\Delta \delta = 2.3$ ) in contrast to 2-phosphinophenolato Ni(II) complexes ( $\Delta \delta$  = 16 - 19). The  ${}^{13}$ C resonance (AXYZ<sub>2</sub> spin type) of the trimethylphosphine ligands exhibits a pseudoquintet pattern. The <sup>31</sup>P coordination shifts [ $\Delta \delta$  = 42.8 (o-P), 38.6 (PMe<sub>3</sub>)] 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<sub>3</sub>)<sub>4</sub> 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<sub>3</sub>PO. Work-up afforded 52-78 % of fine red or brown crystals identified as bis-(phosphinophenolato-P,O) 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 <sup>13</sup>C (AXX' spin type) and proton  $(A_n XX'A'_n \text{ spin type})$  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.



Compound	$\Delta \delta^{31} P$	$N(^{13}\text{C-1}^{31}\text{P}_2)$	$\Delta \delta^{13}$ C-1	$N(^{13}\text{C}-2^{31}\text{P}_2)$	$\Delta \delta^{13}$ C-2	$N(^{13}\text{C-6}^{31}\text{P}_2)$	$N(^{13}\text{C}-4^{31}\text{P}_2)$
<b>3</b> a	71.1	18.9	17.5	61.2	-1.1	$\approx 14$	$\approx 8$
3b	70.5			60		$\approx 14$	$\approx 8$
<i>rac</i> -3c	77.5	17.7	19.1	55.8	-5.2	12.8	7.2
$[Ni(2-PhiPrP-4-MeC_6H_3O)_2]$ [6]	74.1	16.6	15.5	54	-7.9	13.8	6.9
rac-3d	54.0	28.7	15.5	46.8	-3.7	$\approx 7$	$\approx 5$
trans-[Ni(2-iPr <sub>2</sub> P-4,6-	62.0	30.5	17.1	42.6	-4.7	7.4	6.4
$tBu_2C_6H_2O_2$ [14]							

Table I. Comparison of characteristic NMR data of cis- and trans-bis(2-phosphinophenolato)nickel complexes 3.



### Distinction of cis- and trans-isomers in solution

Whereas unsymmetrical cis- and trans-2phosphinophenolato nickel phosphine complexes can be easily distinguished by the grossly different two-bond <sup>31</sup>P<sup>31</sup>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 <sup>31</sup>P and of <sup>13</sup>C-1 nuclei as well as the <sup>13</sup>C-<sup>31</sup>P 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<sub>2</sub>P-aryIO)<sub>2</sub>] 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-aryIO)<sub>2</sub>] (Alk = Me, *i*Pr) 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-*t*BuPhP-4-MeC<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>] ( $\Delta \delta^{31}P = 43$  [15]) and also of the more P-basic *trans*-[Ni(2-*i*Pr<sub>2</sub>P-4,6-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O)<sub>2</sub>] ( $\Delta \delta^{31}P = 62$  [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  $N(^{13}\text{C}-1^{31}\text{P}_2)$ and  $N(^{13}\text{C}-2^{31}\text{P}_2)$  (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-*i*Pr<sub>2</sub>P-4,6-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O)<sub>2</sub>] (30.5 Hz) [14] and even the monochelate complexes *trans*-[NiMe(2-RR'P-arylO)(PMe<sub>3</sub>)] (22 -26 Hz) [14].

 $N(^{13}\text{C}-2^{31}\text{P}_2)$  shows the opposite trend and is smaller for 3d (46.8 Hz), trans-[Ni(2-iPr<sub>2</sub>P-4,6tBu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O)<sub>2</sub>] (42.6 Hz) and trans-[NiMe(2-RR'ParylO)(PMe<sub>3</sub>)] (41 - 49 Hz) [14] than for the ciscomplexes 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  $N(^{13}C-2^{31}P_2)$  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  ${}^{1}J_{PC-2}$  is underlined by decreasing coupling in the order Ph<sub>2</sub>P > AlkPhP > Alk<sub>2</sub>P and the very low one-bond coupling if back-bonding is not possible, e.g.  ${}^{1}J_{PC-2} =$ 6 Hz of the recently published d°-transition metal 2phosphinophenolato complex [n<sup>5</sup>-CpTiCl<sub>2</sub>(2-Ph<sub>2</sub>P-6-tBuC<sub>6</sub>H<sub>3</sub>O)] [17].

The influence of P-substituents in *cis*-**3a**-**c** on  $\Delta \delta^{31}$ P and  $N(^{13}\text{C}-2^{31}\text{P}_2)$  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



Fig. 1. Molecular structure of (*S*,*R*)-**3c**; selected distances [Å] and angles [°]: Ni1-O1 1.869(10), Ni1-O2 1.890(10), Ni1-P1 2.157(4), Ni1-P2 2.166(5), O1-C6 1.31(2), C6-C1 1.40(2), P1-C1 1.79(2), P1-C18 1.82(2), P1-C15 1.828 (14), C5-C6 1.41(2); O1-Ni1-P2 170.3(3), O2-Ni1-P1 171.2(4), O2-Ni1-O1 85.0(5), P1-Ni1-P2 102.9(2), O1-Ni1-P1 86.4(3), C6-O1-Ni1 122.3(11), O1-C6-C1 120(2), C6-C1-P1 111.6(12), C2-C1-P1 125.5(14), C1-P1-Ni1 99.7(5), C1-P1-C15 109.0(7), C1-P1-C18 107.4(8), C18-P1-C15 106.6(7), O1-C6-C5 122(2), C6-C5-C7 120(2), C4-C5-C7 122(2), C4-C5-C6 118(2), C3-C4-C5 122(2).

whereas  $N(^{13}\text{C}-2^{31}\text{P}_2)$  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-*i*Pr<sub>2</sub>P-4,6-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O)<sub>2</sub>] [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 2phosphino substituents. Two tert-butyl or isopropyl groups at phosphorus favor the formation of transcomplexes as seen for *trans*- $[Ni(2-tBu_2PC_6H_4O)_2]$ [9] and *trans*-[Ni( $2-iPr_2P-4,6-tBu_2C_6H_2O_2$ ] [14]. The  $\alpha$ -branched alkylphenylphosphinophenolato complexes  $[Ni(2-AlkPh-4-MePC_6H_3O)_2]$  (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 sterical hindrance. The P1-Ni-P2 angle is widened to 107.06(8)°, the O1-Ni-O2 and O1-Ni-P1/O2-Ni-P2 angles are diminished to 85.6 and 84.45/85.45(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.

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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), C3-C2-P1 129.3(5), C2-P1-Ni1 99.7(2), C2-P1-C15 105.2(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 122.8(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  $P\bar{1}$ ). 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  $\alpha$ -carbon atoms C15 and C38. The two five-membered rings show different distorsions. 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  $(11.3^{\circ})$  is considerably smaller than for 3d but noticeably larger than in cis-[Ni(2-*i*PrPh-4-MePC<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>] ( $\theta$  = 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  $(1-3^{\circ})$  as compared to [Ni(2-*i*PrPh-4-MePC<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>]. 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.

Tetrakis(trimethylphosphine)nickel(0) [19], N,N-diallylanilin(trimethylphosphine)nickel(0) [20] and the 2phosphinophenols **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 spectrometers. Shift references are tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C, and H<sub>3</sub>PO<sub>4</sub> (85%) for <sup>31</sup>P. For resonances which are part of an AXX' spin system (X,X' = <sup>31</sup>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-(isopropylphenylphosphino)-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-*t*-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 *i*PrPhPCl 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 **1c**, m. p. 64 - 65 °C, was crystallized from methanol, 9.2 g (60%).

Analysis for  $C_{23}H_{33}OP$  (356.48) Calcd C 77.49 H 9.33 P 8.69%, Found C 78.32 H 9.40 P 8.15%.

<sup>1</sup>H NMR (300 MHz, d<sub>8</sub>-THF):  $\delta$  = 0.94 (m, 3H, Me<sub>a</sub>), 1.06 (m, 3H, Me<sub>b</sub>), 1.23 (s, 9H, CMe<sub>3</sub>), 1.40 (s, 9H, CMe<sub>3</sub>), 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). - <sup>13</sup>C NMR (75.5 MHz, d<sub>8</sub>-THF):  $\delta$  = 17.5 (d, <sup>2</sup>*J*<sub>PC</sub> = 15.2 Hz, Me), 18.5 (d, <sup>2</sup>*J*<sub>PC</sub> = 20.5 Hz, Me), 24.2 (d, <sup>1</sup>*J*<sub>PC</sub> = 4.3 Hz, CHMe<sub>2</sub>), 28.2 (CMe<sub>3</sub>), 30.0 (CMe<sub>3</sub>), 33.2 (CMe<sub>3</sub>), 33.9 (CMe<sub>3</sub>), 119.4 (d, <sup>1</sup>*J*<sub>PC</sub> = 3.4 Hz, C-2), 124.3 (C-5), 126.1 (C-3 or C-*p*), 127.2 (d, <sup>3</sup>*J*<sub>PC</sub> = 7.3 Hz, C-*m*), 127.5 (C-*p* or C-3), 132.0 (d, <sup>2</sup>*J*<sub>PC</sub> = 18.2 Hz, C-*o*), 134.0 (C-6), 135.6 (d, <sup>1</sup>*J*<sub>PC</sub> = 7.9 Hz, C-*i*), 140.3 (C-4), 156.0 (d, <sup>2</sup>*J*<sub>PC</sub> = 21.0 Hz, C-1). - <sup>31</sup>P NMR (81 MHz, d<sub>8</sub>-THF):  $\delta$  -23. (NMR data in CDCl<sub>3</sub> [12a]).

### *rac-4,6-Di-tert-butyl-2-(tert-butylphenylphosphino)phenol* (1d)

A solution of 2-bromo-4,6-di-*t*-butylphenol (13.1g, 45.9 mmol) in ether (300 ml) was refluxed with NaH (1.1g, 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 *n*BuLi 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  $C_{24}H_{35}OP(370.51)$ 

Calcd C 77.80 H 9.52 P 8.36%,

Found C 77.89 H 9.35 P 8.39%.

 $^{31}$ P ( $\delta$  -18.8), <sup>1</sup>H and <sup>13</sup>C NMR data in CDCl<sub>3</sub> agree with those given in [12a].

### {4,6-Di-tert-butyl-2-(diphenylphosphino)phenol[P]}tris(trimethylphosphine)nickel(0) (**2a**)

770 mg (2.04 mmol) of **1a** was added at -78 °C to a solution of Ni(PMe<sub>3</sub>)<sub>4</sub> (740 mg, 2.04 mmol) in pentane (50 ml). The resulting yellow solution was stirred for 16 h. Removal of the solvent and of all volatiles afforded 2a as a waxy yellow solid. IR (nujol):  $\bar{\nu} = 956$  st, 933 sst. – <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta = 0.76$  (s, 27H, PMe<sub>3</sub>), 0.79 (s, 9H, CMe<sub>3</sub>), 1.30 (s, 9H, CMe<sub>3</sub>), 6.33 (dd,  ${}^{4}J_{HH} =$ 2.3,  ${}^{3}J_{PH} = 7.1$  Hz, 1H, H-3), 6.76 (m, 7H, Ph, H-5), 7.19 (m, 4H, Ph), 10.5 (d qua,  ${}^{4}J_{PH} = 8.0$ ,  ${}^{6}J_{PH} = 2.4$  Hz, 1H, OH).  $-{}^{13}$ C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 23.6 ("qui", average line distance  $\approx 9.1$  Hz, PMe<sub>3</sub>), 30.5 (CMe<sub>3</sub>), 31.7  $(CMe_3)$ , 32.3  $(CMe_3)$ , 34.5  $(CMe_3)$ , 122.3  $(d \text{ qua}, {}^1J_{PC} =$ 29.0,  ${}^{3}J_{PC} = 6.1$  Hz, C-2), 124.4 (C-5), 128.0 (d,  ${}^{3}J_{PC} =$ 9.2 Hz, C-m), 128.3 (C-p), 128.4 (C-3), 133.0 (d,  ${}^{2}J_{PC} =$ 15.3 Hz, C-o), 134.9 (C-6), 140.2 (d,  ${}^{3}J_{PC}$  = 3.0 Hz, C-4), 141.8 (d qua,  ${}^{1}J_{PC} = 24.4$ ,  ${}^{3}J_{PC} = 8$  Hz, C-*i*), 158.2 (d,  $^{2}J_{PC} = 13.7$  Hz, C-1). –  $^{31}P$  NMR (81 MHz, d<sub>8</sub>-THF):  $\delta = -24.7$  (d,  ${}^{2}J_{PP} = 33.4$  Hz, PMe<sub>3</sub>), 13.1 (qua,  ${}^{2}J_{PP} =$ 33.4 Hz, P-2); impurity at -21.0 (br s).

### *cis-Bis*{4,6-*di-tert-butyl-2-(diphenylphosphino)phenolato*[*O*,*P*]{*nickel*(*II*) (**3a**)

Dry oxygen (50 ml, 2.23 mmol) was introduced into a cold (-78 °C) solution of Ni(PMe<sub>3</sub>)<sub>4</sub> (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  $C_{52}H_{60}NiO_2P_2 \cdot 2$  THF (981.22) Calcd C 73.45 H 7.81 P 6.31%,

Found C 73.98 H 7.65 P 6.95%.

<sup>1</sup>H NMR (300 MHz, d<sub>8</sub>-THF):  $\delta$  = 1.11 (s, 9H, CMe<sub>3</sub>), 1.46 (s, 9H, CMe<sub>3</sub>), 6.61 (m vc, <sup>4</sup>J<sub>HH</sub> ≈ 3, <sup>3</sup>J<sub>PH</sub> ≈ 10 Hz, 1H, H-3), 7.15 (m, 5H, H-5, H-o,m), 7.32 (m, 2H, H-p), 7.45 (m, 4H, Ph). – <sup>13</sup>C NMR (75.5 MHz, d<sub>8</sub>-THF):  $\delta$  = 29.7 (CMe<sub>3</sub>), 32.0 (CMe<sub>3</sub>), 34.6 (CMe<sub>3</sub>), 36.0 (CMe<sub>3</sub>), 118.8 ( $\tau$ , N = 61,2 Hz, C-2), 125.0 (C-5), 128.1 (C-3), 129.3 ( $\tau$ , N = 10.6 Hz, C-m), 130.8 ( $\tau$ , N = 49.1 Hz, C-i), 131.2 (C-p), 134.0 ( $\tau$ , N = 10.6 Hz, C-o), 137.6 ( $\tau$ , N ≈ 8 Hz, C-4), 138.1 ( $\tau$ ,  $N \approx 14$  Hz, C-6), 173.4 ( $\tau$ , N =18.9 Hz, C-1).  $-{}^{31}$ P NMR (81 MHz, d<sub>8</sub>-THF):  $\delta = 41.4$ .

### cis-Bis{6-tert-butyl-4-methyl-2-(diphenylphosphino)phenolato[O,P]{nickel(II) (3b)

Ni(PMe<sub>3</sub>)<sub>4</sub> (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 C46H48NiO2P2 · 1 THF (825.63) Calcd C 72.74 H 6.84 P 7.50%, Found C 71.67 H 6.31 P 7.96%.

<sup>1</sup>H NMR (300 MHz,  $d_8$ -THF):  $\delta = 1.41$  (s, 9H, CMe<sub>3</sub>), 2.01 (s, 3H, 4-Me), 6.39 (vc, 1H, H-3), 6.86 (br s, 1H, H-5), 7.11 (m, 4H, Ph), 7.31 (m, 2H, H-p), 7.44 (m, 4H, Ph).  $-{}^{13}$ C NMR (75.5 MHz, d<sub>8</sub>-THF):  $\delta = 18.8$  (4-Me), 27.9 (CMe<sub>3</sub>), 33.8 (s, CMe<sub>3</sub>), 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-1),  $-{}^{31}$ P NMR (81 MHz, d<sub>8</sub>-THF);  $\delta = 40.7.$ 

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

a) Reaction of crude 1c and Ni(PMe<sub>3</sub>)<sub>4</sub> followed by partial air oxidation gave 3c. Single crystals were grown from a THF solution.<sup>31</sup>P NMR (121.5 MHz, d<sub>6</sub>-acetone):  $\delta = 47.5$ . <sup>1</sup>H- and <sup>13</sup>C NMR data agree with those given below.

b) A solution of 1c (5.81 g, 16.3 mmol) in THF (50 ml) was added at room temperature to a solution of N,N-diallylanilin-(trimethylphosphine)nickel(0) (2.51 g, 8.15 mmol) [20] in THF (30 ml). The resulting red mixture was allowed to stand for 2 d. Then all volatiles were removed in vacuo. The red residue was dissolved in ether / pentane (1:2). From this solution 4.75 g (76%) of red cubic crystals of 3c were obtained which on drying in vacuo loose solvent to form an orange-red powder, m. p. 261 °C (dec.).

Analysis for  $C_{46}H_{64}NiO_2P_2$  (769.62) Calcd C 71.79 H 8.38 P 8.05%, Found C 71.72 H 8.05 P 8.18%.

<sup>1</sup>H NMR (300 MHz,  $d_8$ -THF):  $\delta = 0.92$  (m, 6H, CHMe<sub>a</sub>), 1.23 (s, 18H, CMe<sub>3</sub>), 1.33 (m, 6H, CHMe<sub>b</sub>), 1.45 (s, 18H, CMe<sub>3</sub>), 2.39 (br m, 2H, CHMe<sub>2</sub>), 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).  $-{}^{13}$ C NMR (75.5 MHz, d<sub>8</sub>-THF):  $\delta =$ 15.1 (br, CHMe), 17.7 (br, CHMe), 23.2 ( $\tau$ , N = 27.3 Hz, CHMe<sub>2</sub>), 27.7 (CMe<sub>3</sub>), 30.2 (CMe<sub>3</sub>), 32.6 (CMe<sub>3</sub>), 34.0  $(CMe_3)$ , 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 (*τ*, *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). – <sup>31</sup>P NMR (121.5 MHz,  $d_8$ -THF):  $\delta = 52$ .

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

Dry oxygen (50 ml, 2.23 mmol) was introduced at -78 °C into a solution of 1d (1.76 g, 4.75 mmol) and Ni(PMe<sub>3</sub>)<sub>4</sub> (860 mg, 2.37 mmol) in THF (70 ml) causing a color change to red. After stirring for 16 h at room temperature the volatiles were removed in vacuo. The residue was washed with a small amount of pentane and extracted with ether to afford 1.40 g (74%) of 3d as small brown crystals, m. p. > 220  $^{\circ}$ C.

Analysis for  $C_{48}H_{68}NiO_2P_2$  (797.83) Calcd C 72.26 H 8.59 P 7.76%, Found C 71.65 H 8.54 P 8.10%.

<sup>1</sup>H NMR (300 MHz,  $d_8$ -THF):  $\delta = 1.14$  (s, 9H, CMe<sub>3</sub>), 1.24 (s, 9H, CMe<sub>3</sub>), 1.48 ( $\tau$ , N = 14.9 Hz, 9H, PCMe<sub>3</sub>), 7.07 (d,  ${}^{4}J_{HH}$  = 2.4 Hz, 1H, H-5), 7.28 (m, 1H, H-3), 7.49 (m, 3H, Ph), 8.31 (m, 2H, Ph). - <sup>13</sup>C NMR (75.5 MHz, d<sub>8</sub>-THF): *δ* = 28.1 (PCMe<sub>3</sub>), 29.6 (CMe<sub>3</sub>), 31.5 (CMe<sub>3</sub>), 33.9  $(CMe_3)$ , 34.8 (d,  ${}^{1}J_{PC} = 11.3$  Hz, PCMe<sub>3</sub>), 35.0 (CMe<sub>3</sub>), 115.4 ( $\tau$ , N = 46.8 Hz, C-2), 126.7, 126.8 (C-3 and C-5), 128.6 ( $\tau$ , N = 9.1 Hz, C-m), 130.3 (C-p), 130.8 ( $\tau$ , N =33.2 Hz, C-i), 134.6 ( $\tau$ , N = 11.3 Hz, C-o), 135.9 ( $\tau$ , N  $\approx$  4 Hz, C-4), 138.6 ( $\tau$ ,  $N \approx$  7 Hz, C-6), 173.5 ( $\tau$ , N =28.7 Hz, C-1).  $-{}^{31}$ P NMR (81 MHz, d<sub>8</sub>-THF):  $\delta$  = 35.2.

### 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  $MoK_{\alpha}$  radiation 0.71073 Å. Lattice parameters were refined from 25 centered reflections. Intensities were collected ( $\omega$ -2 $\theta$ 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  $F^2$  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 CH<sub>3</sub> groups by rotation along the common C-C axis. Positions C12-C14, C35, C36, and C81-C83 of the second independent molecule were refined with a split model and half occupation each. Some diffuse electron density in the final  $\Delta F$  map could not be assigned properly but may result from enclosed ether solvent. 3d. Crystal mounting and

	rac-3c	rac-3d		
Empirical formula	$C_{46}H_{64}N_1O_2P_2$	$C_{48}H_{68}N_1O_2P_2$		
Molecular mass	769.62	797.67		
Temperature [K]	293 (2)	293 (2)		
Crystal system	Triclinic	Monoclinic		
Space group	P1	C2/c		
Unit cell dimensions $a$ [Å]	15.790 (4)	28.702 (9)		
<i>b</i> [Å]	18.686 (6)	16.933 (4)		
<i>c</i> [Å]	20.385 (5)	21.747 (5)		
α [°]	109.68 (2)			
β [°]	94.76 (2)	113.63 (2)		
$\gamma$ [°]	114.15 (2)			
$V[Å^3]; Z$	4994 (2); 4	9683 (4); 8		
Density (calculated) [Mg/m <sup>3</sup> ]	1.024	1.094		
Absorption coefficient $[mm^{-1}]$	0.482	0.500		
<i>F</i> (000)	1656	3440		
Crystal size [mm]	$0.40 \times 0.25 \times 0.10$	$0.30 \times 0.21 \times 0.20$		
$\theta$ Range for data collection [°]	2.20 to 22.55	2.23 to 26.07		
Limiting indices	$-17 \le h \le 5, -20 \le k \le 18, 0 \le l \le 21$	$0 \le h \le 35, 0 \le k \le 20, -26 \le l \le 24$		
Reflexions collected	10204	9631		
Independent reflexions	$10030 \ (R_{\rm int} = 0.0557)$	9439 ( $R_{\rm int} = 0.0646$ )		
Absorption correction	Psi-scan	none		
Max. & min.transmission	0.759 and 0.884			
Data / restraints / parameters	10028 / 116 / 898	9437 / 31 / 510		
Goodness-of-fit on $F^2$	1.048	1.018		
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.1033, wR2 = 0.2270	R1 = 0.0700, wR2 = 0.1058		
R indices (all data)	R1 = 0.2439, wR2 = 0.3094	R1 = 0.2522, wR2 = 0.1533		
Extinction coefficient	0.0017(5)	0.00018(3)		
Largest diff. peak and hole	1.041 and $-0.347 \text{ e}\text{\AA}^{-3}$	0.259 and $-0.259 \text{ e}\text{\AA}^{-3}$		

Table II. Crystallographic data of compounds *rac*-3c and *rac*-3d.

data collection as for **3c**. No absorption correction. Structure solution and refinement ( $F^2$ , 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).

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- H.-F. Klein, A. Dal, T. Jung, S. Braun, C. Röhr, U. Flörke, H.-J. Haupt, Eur. J. Inorg. Chem. 1998, 621.
- [2] H.-F. Klein, A. Dal, T. Jung, U. Flörke, H.-J. Haupt, Eur. J. Inorg. Chem. **1998**, 2027.

[3] a) W. Keim, Angew. Chem. 1990, 102, 251; Angew. Chem. Int. Ed. Engl. 29, 235 (1990);
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, 85118 (1985).

- [4] G.A. Nesterov, G. Fink, V.A. Zakharov, W. Frenzl, J. Mol. Catal. 69, 129 (1991).
- [5] a) M. Köhler, Diplomarbeit, Aachen (1996);b) J. Heinicke, M. Köhler, W. Keim, to be published.
- [6] J. Heinicke, M. Koesling, R. Brüll, W. Keim, H. Pritzkow, Eur. J. Inorg. Chem., in press (1999).
- [7] A. Dal, M. He, J. Heinicke, W. Keim, H.-F. Klein, M. Köhler, M. Koesling, Phosph., Sulfur Silicon Rel. El., in press (1999).
- [8] J. Pietsch, P. Braunstein, Y. Chauvin, New J. Chem. 1998, 467.

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- [9] H. D. Empsall, B. L. Shaw, B. L. Turtle, J. Chem. Soc. Dalton Trans. **1976**, 1500.
- [10] T.B. Rauchfuss, Inorg. Chem. 16, 2966 (1977).
- [11] a) J. Heinicke, E. Nietzschmann, A. Tzschach, J. Organomet. Chem. 243, 1 (1983);
  b) J. Heinicke, E. Nietzschmann, A. Tzschach, J. Organomet. Chem. 310, C 17 (1986);
  c) J. Heinicke, R. Kadyrov, J. Organomet. Chem. 520, 131 (1986).
- [12] a) J. Heinicke, R. Kadyrov, M. K. Kindermann, M. Koesling, P. G. Jones, Chem. Ber. **129**, 1547 (1996);

b) J. Heinicke, E. Nietzschmann, A. Tzschach, J. Prakt. Chem. **325**, 511 (1983).

[13] a) O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, J. Organomet. Chem. **522**, 69 (1996);
b) O. Herd, A. Heßler, M. Hingst, P. Machnitzki, M. Tepper, O. Stelzer, Catalysis Today **42**, 413 (1998).

- [14] J. Heinicke, M. He, A. Dal, H.-F. Klein, W. Keim, U. Flörke, H.-J. Haupt, submitted for publication.
- [15] J. Heinicke, E. Klaus, M. Koesling, H. Pritzkow, A. Sebald, Solid State Nucl. Magn. Reson., in press.
- [16] H.-F. Klein, E. Auer, A. Dal, U. Lemke, M. Lemke, T. Jung, C. Röhr, U. Flörke, H.-J. Haupt, Inorg. Chim. Acta 287, 167 (1999).
- [17] C. A. Willoughby, R. R. Duff (Jr.), W. M. Davis, S. L. Buchwald, Organometallics 15, 472 (1996).
- [18] J. Heinicke, R. Kadyrov, M. Koesling, U. Jux, Phosphorus, Sulfur & Silicon 109 - 110, 501 - 504 (1996).
- [19] H.-F. Klein, H. H. Karsch, Angew. Chem. 82, 885 (1970).
- [20] M. Hellwig, Dissertation, TH Darmstadt (1992).
- [21] H.-F. Klein, A. Brand, G. Cordier, Z. Naturforsch. 53b, 307 (1998).