Syntheses, Structures, and Reactivity of 1-Phosphanylnaphth-2-ols

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P-tertiary or amino-substituted 1-phosphanylnaphth-2-yl silyl ethers **3** are synthesized by stepwise reaction of lithium 1-lithio-2-naphtholate **1** with chlorophosphanes and $ClSiMe_3$. The free phosphanylnaphthols **4** are prepared by alcoholysis. As established by characteristic coupling constants and X-ray structural analyses (of **3c**, **4c**), **3** exhibit in solution and in the solid state a *cis*-bisecting conformation, whereas **4** prefers the opposite *trans*-bisecting arrangement, allowing easy protonation and formation of chelate complexes. Substitution reactions of phosphanylnaphtholates **2** with Ph_2PCl and formation of chelate complexes LNi-η^5-Cp and L_2Pd are described. Attempts to prepare secondary and primary phosphanylnaphthols failed because of facile cleavage of the P–C(naphthyl) bond in PH-substituted 1-phosphanylnaphth-2-ols.

o-Phosphanylphenols[1–4], which possess both a hard and a soft donor center π-bridged by a C=C unit, represent ambidentate, formally (2π + 4n) ligand systems. They may thus react at either oxygen[2–4], phosphorus, or both nucleophilic sites, and are suitable starting materials for the synthesis of heterocycles[5] or transition metal complexes[1,4,6,7]. Furthermore, PO chelate ligands are of interest in catalysis[8]. Electronic and steric properties can be tuned independently by suitable substituents at phosphorus or on the aromatic ring[8b], which should allow a wide variation of reactivity or catalytic selectivity. We report here on the syntheses, structures, and some reactions of 1-phosphanyl-2-naphthols and their silyl ethers (ligands with a larger planar PO moiety) with some metal complexes.

Synthesis of Phosphanylnaphthyl Silyl Ethers and Phosphanylnaphthols

During our investigations of PO ligands we found a convenient synthetic access to *o*-phosphanylphenols by i) stepwise reactions of lithium 1-lithio-2-naphtholate with chlorophosphanes and chlorotrimethylsilane followed by hydrolysis[2,6] and ii) *o*-metalation of *o*-halophenoxyphosphorus compounds, inducing a rapid intramolecular P–O → P–C rearrangement of the organometallic species initially formed to give *o*-phenolatophosphanes or phosphonic acid esters[3]. However, these syntheses cannot simply be applied unchanged to phosphanylnaphthole derivatives. Lithium 1-lithio-2-naphtholate **1** is a useful reagent, but its substitution reactions are much more sensitive to steric hindrance, and attempts to prepare 1-phosphanylnaphth-2-olates according to the metalation-rearrangement procedure by reaction of 1-bromonaphth-2-oxyphosphanes with sodium failed. The latter is probably due to steric hindrance of the attack at the brominated position 1 by the OPR_2 group and the *peri*-CH as well as to the higher stability of the primarily formed naphthalene radical anions which affect the subsequent reactions.

An ethereal solution of 1-bromonaphth-2-ol reacts with two equivalents of butyllithium in hexane to give a mixed suspension/solution of lithium 1-lithio-2-naphtholate **1**. Addition of equimolar amounts of chlorophosphanes followed by an excess of Me_3SiCl furnished 1-phosphanylnaphth-2-yl trimethylsilyl ethers **3a–e** via the corresponding 1-phosphanylnaphth-2-olates **2a–e** as described by Scheme 1. The free phosphanylphenols were obtained from the purified silyl ethers by refluxing with absolute methanol (**4a** and **4c**) or by heating with glacial acetic acid (**4b**) if the methanolysis is sterically hindered. Direct aqueous work-up of **2a–c** with dilute acids caused problems in the isolation of **4a–c** by formation of oily phosphonium salts with a weaker tendency to crystallize. However, by treatment of the purified trimethylsilyl ethers with hydrochloric acid in THF crystalline phosphonium salts may be isolated, e.g. **4c** · **HCl**.

Problems may arise if the chlorophosphanes contain α-H atoms or large substituents. Attempts to prepare 1-methylphenylphosphanylnaphth-2-yl trimethylsilyl ether were not successful, while the analogous reaction of lithium 2-lithio-*p*-cresolate with MePhPCl afforded 56% of the coupling product[6]. Mixtures with only small amounts of the required product (identified by the ^{1}H-NMR chemical shift of 9-H [δ = 8.91 (ddd, J_{HH} = 8.4, 1 Hz, J_{PH} = 6.7 Hz; Me 1.84 (d, J = 4.4 Hz)]) were obtained. Even with $Me_2CH(Ph)PCl$, containing only one shielded α-CH, the

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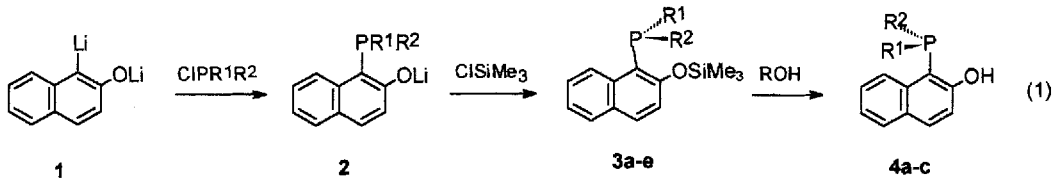
Scheme 1



1 2 3a-e 4a-c

	a	b	c	d	e
R1	Ph	Ph	Ph	Ph	NMe_2
R2	*i*Pr	*t*Bu	Ph	NMe_2	NMe_2

yield of **3a** was low (39%). We assume competing elimination of HCl by the strong and probably bulky cluster base **1** to give unstable $PhP{=}CR_2$. Elimination of $PhP{=}CR_2$ from the substitution products **2** or **3** seems much less likely, although it gives rise to a very strong (96%) peak in the EI(70eV)-induced fragmentation of **3a** (and to the base peak after loss of a further methyl group).

If bulkier chlorophosphanes are allowed to react with **1**, the yields of **3** depend strongly on the solvent and the concentration of the dilithium reagent. Whereas the subsequent substitution reaction of **1** with equimolar quantities of chlorodiphenylphosphane and chlorotrimethylsilane proceeds with high yield of **3c**, the analogous reaction with *t*BuPhPCl and Me_3SiCl furnished only about 20% of **3b**. Formation of diphosphanes and P and O substituted products is indicated by ^{31}P-NMR measurements of the crude reaction mixture. The addition of donor reagents such as THF, TMEDA, or HMPA to **1** improves the selectivity for stepwise C/O disubstitution significantly; yields of **3b** increase to about 30, 50, and 70%, respectively (based on the intensities of ^{31}P-NMR signals in the crude material). In THF the slow rate of substitution led to metal/hydrogen exchange and isolation of ca. 20% naphthyl trimethylsilyl ether. The best results for **3b** were achieved in experiments with 0.02–0.1 mol of **1** using more concentrated suspensions (ca. 3 ml of ether per mmol) obtained from 2.5 M LiBu solution. When the reactants are used on a larger scale the yields decrease again. We assume that this behavior depends on the structure and aggregation of the dilithium species. Unfortunately, we were unable to isolate **1** in a crystalline form for detailed structural investigations. The ^{7}Li-NMR spectrum (1 M LiCl in D_2O, $\delta = 0$) in [D_8]THF at 30°C shows an intensive broad signal at $\delta = 1.75$, a much smaller broad signal at $\delta = 0.36$ and a shoulder at $\delta = 2.75$. This indicates averaged positions of lithium towards carbon and oxygen, as in Schlosser reagents[9] and a strongly dominating cluster type (time-averaged).

Structures of Phosphanylnaphthyl Silyl Ethers 3 and Phosphanylnaphthols 4

The ^{1}H- and ^{13}C-NMR data (Tables 1 and 2) of phosphanylnaphthyl silyl ethers **3a–e** and phosphanylnaphthols **4a–c** furnish information on trends in steric demands and preferred conformations in solution. The coupling constants $^1J_{PC}$ correlate in many cases with the degree of s character in the P–C bond[10,11] and thus with growing steric demands of substituents, widened bond angles and corresponding gradual changes in hybridization. The coupling constants $^1J_{PC1}$ of the naphthyl group increase in the order:

	4c	**/ 4a**	**/ 4b**	**≪ 3c**	**/ 3a**	**/ 3b**	**/ 3e**	**/ 3d**	
$^1J_{PCl}$ (Naph):	8.0	8.6	11.9	17.3	21.7	24.0	25.6	34.9	[Hz]
$^1J_{PCi}$ (Ph):	5.5	5.9	12.2	11.8	14.2	19.2	(4.9)	–	[Hz]
$^1J_{PC1}/^1J_{PCi}$:	1.45	1.46	0.98	1.47	1.53	1.25			

and are consistent with a much higher steric demand of the 2-trimethylsiloxynaphthyl compared to the 2-hydroxynaphthyl group. The average size of the flat phenyl group seems to be smaller than that of isopropyl and much smaller than that of the *tert*-butyl. The differences between Δ^1J_{PC}(**4a–4c**) = 0.6 Hz and Δ^1J_{PC}(**4b–4c**) = 3.9 Hz compared to Δ^1J_{PC}(**3a–3c**) = 4.4 Hz and Δ^1J_{PC}(**3b–3c**) = 6.7 Hz show however no linear correlations.

The $^1J_{PC}$ coupling constants of the *ipso*-carbon atoms of the phenyl groups increase in an order similar to the above one, but they are smaller by about 1/3 compared to those of the naphthyl group; in the case of the sterically strained *tert*-butyl derivatives the values are even higher. This suggests a difference in hybridization and in turn a dependence on the orientation[11,12].

The two- and three-bond couplings are also of stereochemical significance. The values $^2J_{PC}$ and $^3J_{PC}$ exhibit a Karplus-like dependence on the torsion angles C–C–P–lp (lp = lone pair) and C–(C–)C–P–lp with maximum values at $\theta = 0°$ (ca. 30–40 Hz) and 180° (ca. 5 Hz) and (negative) minima at 90–120°[12], thus providing information about the orientation of the substituents in the preferred conformations. For the silyl ethers **3a–d** and free naphthols **4a–c** we find opposite arrangements of the naphthyl substituents. In the case of naphthyl silyl ethers the constants $^3J_{PC9}$ reach maximum values (29–37 Hz), corresponding to small dihedral angles θ(lp–P–C1–C9) and a strong preference for a *cis*-bisecting conformation (Figure 1). The values of $^2J_{PC10}$ are smaller by about one third because of the longer distance to the lone pair. Major steric effects are observed also in the ^{1}H-NMR spectra. The signals of 9-H are shifted downfield to about $\delta = 9$ by the adjacent phosphorus lone pair.

In the phosphanylnaphthols **4a, b, c** $^2J_{PC2}$ = 17.7, 13.7, 12.7 Hz is larger than $^2J_{PC10}$ = 1.0, 4.4, 9.8 Hz; the values correspond to the upper and lower middle range of the

Table 1. ^{31}P- and ^{1}H-NMR data[a] of phosphanylnaphthyl silyl ethers **3a–e** and of phosphanylnaphthols **4a–c**. δ_{TMS} (J_{HH} and J_{PH} in [Hz])

No. ^{31}P	3-H	4-H	6-H	7-H	8-H	9-H	R^1	R^2 [E]
3a	7.06 (d)	7.82 (d)	7.79 (d)	7.37 (m)	7.51 (m)	9.12 (m)	7.1-7.3 /	[b]
-15.8	(8.9)	(8.9)	(8.0)	[c]	(7/8/1.6)	(8.0/7.0/1)	ca. 7.4(m)	[0.18(s)]
3b	7.12 (d)	7.91 (d)	7.86 (d)	7.54 (m)	7.42 (m)	9.14 (m)	7.48/ 7.29/	1.36 (d)
- 2.7	(8.9)	(8.9)	(8.0/br)	(8/6.7/	(7.9/6.8/1.1)	(8.0/7.9/br)	7.21 (m)	(12.7)
				1.4)			(o/m/p)	[0.07(s)]
3c	7.14 (dd)	7.91 (d)	7.83(dd)	7.37 (m)	7.41 (m)	8.72 (m)	7.25-7.33/	$=R^1$
-23.2	(8.9/1.8)	(8.9)	(8/1.3)	(8/7/1-2)	(7/8/1-2)	(7.2/5.4/1.3)	7.4-7.5 (m)	[0.18(s)]
3d	7.06 (dd)	7.83 (d)	7.80(d)	7.36 (m)	7.47(ddd)	8.98 (m)	ca.7.2/7.3	2.79 (d)
+48.1	(8.9/0.7)	(ca.8.9)	(7-8/br)	(7/6.8/1)	(6.8/8.6/1.5)	(8.6/6.6/br)	(m)	($^3J_{PH}$ 9.9)
							[o,m/p]	[0.02(s)]
3e	7.03 (dd)	7.70 (d)	7.74(m)	7.33(m)	7.42(m)	8.75(dm)	$=R^2$	2.64 (d)
+106.9	(8.8/3.4)	(8.8)	(8/1/1)	(8/6.8/1)	(6.8/8.7/1)	(8.7/br)		($^3J_{PH}$ 9.6)
								[0.31(s)]
4a	ca.7.27	7.86 (d)	7.79 (dd)	7.31 (m)	ca. 7.33	7.96 (d)	7.2-7.35 (m)	[b]
-32.4	(m)[c]	(8.7)	(7/2)	[c]	[c]	(8/br)		[8.1(br)]
4b	ca.7.09	7.72 (d)	7.64 (dd)	ca. 7.16	ca. 7.16	7.88 (m)[d]	7.1-7.2/ 7.4-7.5(m)	1.33 (d)
-16.8	(m)[c]	(8.9)	(6-7/2-3)	(m)[c]	(m)[c]	(ca. 9/8/2)		($^3J_{PH}$ 21.2)
4c	7.19 (dd)	7.86 (d)	7.73 (dd)	7.23(m)	7.22(m)	8.06 (m)	7.25-7.3/	$=R^1$
-37.4	(8.9/4.3)	(8.9)	(6.4/2.8)	[c]	[c]	(6.4/3.1/3)	7.4-7.5(m) (o/m,p)	

[a] Coupling constants are approximate values obtained by a first-order analysis of spread signals in 300-MHz spectra. Assignments of signals are supported by CH-COSY experiments with **3b–d** and **4a, b** and correlation with related derivatives. – [b] Isopropyl substituents with diastereotopic methyl groups **3a** δ = 0.95 (dd, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 14.3 Hz, Me_A); 1.44 (dd, $^3J_{HH}$ = 6.9, $^3J_{PH}$ = 19.8 Hz, Me_B); 3.17 (dsept, $^2J_{PH}$ = 8.7, $^3J_{HH}$ = 6.9 Hz, CH); **4a** δ = 0.83 (dd, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 15.5 Hz, Me_A); 1.51 (dd, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 20.1 Hz, Me_B); 3.09 (dsept, $^2J_{PH}$ = 10.4, $^3J_{HH}$ = 6.9 Hz, CH). – [c] Superimposed signals. – [d] Complicated split and low-intensity signal though well-resolved cross peak to C9 in CH-COSY.

coupling constants and depend much more strongly on the third substituent. From the moderate values of the coupling constants we deduce a facilitated (compared to **3**) rotation of the hydroxynaphthyl group about the P–C1 axis and from the relative sizes of $^2J_{PC2}$ and $^2J_{PC10}$ an equilibrium of conformations with preference for a *trans*-bisecting to eclipsed arrangement of the naphthyl group in the order **4a** (R = *i*Pr) > **4b** (R = *t*Bu) > **4c** (R = Ph).

To provide further information about the preferred conformations, the solid-state structures of **3c** and **4c** were determined. The conformation of the naphthyloxysilyl group in **3c** (Figure 2) is very similar to that in solution, indicating a clear preference for a relatively rigid arrangement. A more detailed description of the conformation is given by the dihedral angles ϑ_{ar} involving the aryl planes, the P atoms and the center of gravity X of the C_{ipso} atoms of the three aryl groups[*]. The naphthyloxysilyl group displays a *cis*-bisecting arrangement with θ_{Naph} (X–P–C1–C2) = 2° with the phosphorus lone pair (assumed to point in the opposite direction to P–X) directed parallel to the vector C1–C9 [θ(X–P–C1–C9) = 177°]. The less spatially demanding phenyl groups are arranged propeller-like with dihedral angles of ϑ_{Ph1}(X–P–C11–C16) = −81° and θ_{Ph2}(X–P–C21–C22) = −41°, about 21° and 19° above an eclipsed position.

The diphenylphosphanylnaphthol **4c** is shown in Figure 3. In contrast to **3c**, it displays a *trans*-bisecting conformation of the naphthol substituent with the phosphorus

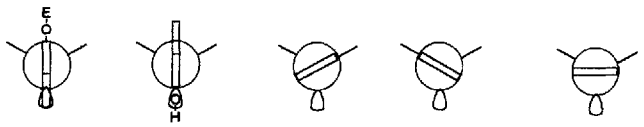
[*] Since the two *ortho* carbon atoms give different values, we define the viewing direction as being from the point X towards the pyramidal PC_3 unit, and we refer to the *o*-C atom lying anticlockwise from the *i*-C.

Table 2. ^{13}C-NMR data of phosphanylnaphthyl silyl ethers **3a–e** and phosphanylnaphthols **4a–c**[a], δ_{TMS} (J_{PC} in Hz)

No.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	R^{1}[b]	R^{2}
3a	*119.5*	*156.8*	119.3	131.9	*129.1*	128.1	123.4	126.4	127.0	*140.0*	*140.9*	[c]
	(21.7)	*(2.4)*	(-)	(1.0)	*(5.6)*	(1.3)	(2.2)	(3.0)	(37.6)	*(24.7)*	*(14.2)*	
											130.8	
											(15.8)	
3b	*118.2*	*155.7*	119.6	132.0	*129.2*	128.1	123.3	126.1	127.7	*140.3*	*140.7*	*33.5*
	(24.1)	*(br)*	(-)	(-)	*(5.6)*	(-)	(1.8)	(2.8)	(36.4)	*(23.9)*	*(19.2)*	*(17.2)*
											130.0	30.5
											(14.9)	(15.1)
3c	*117.6*	*157.7*	119.7	132.7	*129.5*	128.3	123.5	126.5	127.0	*138.5*	*137.1*	$=R^{1}$
	(17.3)	*(4.5)*	(1.4)	(-)	*(4.6)*	(-)	(1.7)	(2.5)	(28.9)	*(19.5)*	*(11.8)*	
											131.9	
											(18.9)	
3d	*118.6*	*155.6*	119.5	132.1	*129.3*	128.3	123.3	126.3	126.2	*139.1*	*142.3*	43.0
	(34.9)	*(2.3)*	(-)	(-)	*(4.4)*		(1.7)	(5.4)	(34.1)	*(23.3)*	*(4.9)*	(15.8)
											128.7	
											(18.6)	
3e	*122.9*	*155.5*	121.8	130.6	*129.8*	128.2	123.2	125.7	125.7	*136.0*	41.6	$=R^{1}$
	(25.6)	*(11.9)*	(-)	(-)	*(-)*	(-)	(-)	(-)	(10.3)	*(8.1)*	(18.0)	
4a	*110.8*	*161.1*	117.4	133.4	*129.4*	128.9	123.0	126.6	125.7	*135.9*	*136.5*	[c]
	(8.6)	*(17.7)*	(1.9)	(-)	*(1.7)*	(-)	(-)	(-)	(7.6)	*(1.0)*	*(5.9)*	
											130.7	
											(14.6)	
4b	*110.5*	*161.0*	117.8	133.3	*129.5*	128.7	122.8	125.9	127.7	*136.4*	*135.9*	*33.0*
	(11.9)	*(13.7)*	(br)	(-)	*(2.3)*	(-)	(-)	(-)	(13.1)	*(4.4)*	*(12.2)*	*(11.4)*
											130.9	29.9
											(14.4)	(14.1)
4c	*109.5*	*160.5*	118.1	134.0	*129.6*	128.8	123.3	126.7	126.5	*136.2*	*133.4*	$=R^{1}$
	(8.0)	*(12.7)*	(2.5)	(-)	*(3.5)*	(-)	(-)	(-)	(17.4)	*(9.8)*	*(5.5)*	
											132.0	
											(17.9)	

[a] Assignments are based on CH-COSY (**3b–d**, **4ab**), CH coupling (**3a**, **d**, **4a**) or DEPT90 measurements (C_q in italics), relative intensities (phenyl carbon atoms) and correlations with related compounds (see Exp.). Signals of $SiMe_3$ appear at 0.09 to 0.55, in **3e** at 0.65). – [b] For R^1 = Ph values for *i*-C and *o*-C atoms are given only. The less indicative signals of *m*- and *p*-carbon atoms are usually observed in the region from δ = 127 to 129 (d, J = 4.7–5.5 Hz) and δ = 127 to 129 (s), resp., in **3b** at somewhat higher field [δ = 127.9 (d, J = 3.6 Hz) and 125.3 (d, J = 1.4 Hz)]. In **4b** they appear again in the normal range [δ = 128.54 (d, J = 4.8 Hz), 127.11 (s)]. – [c] Isopropyl signals: **3a** δ = 23.0 (d, J = 7.8 Hz, CH), 19.9 (d, J = 13.0 Hz, Me_{trans}), 22.3 (d, J = 30.6 Hz, Me_{gauche}); **4a** δ = 23.14 (d; J = 3.7 Hz; CH), 19.50 (d, J = 11.7 Hz, Me_{trans}), 22.32 (d, J = 26.1 Hz, Me_{gauche}) (assignment by DEPT135).

Figure 1. Idealized conformations of arylphosphanes

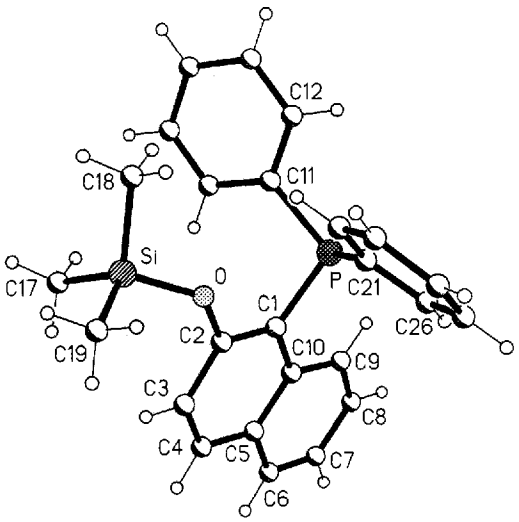


lone pair near the hydroxy group. The P–O distance of 292.5 pm is considerably shorter than the sum of the van der Waals radii (P+O) and indicates a weak intramolecular P···O interaction which may favor the observed orientation and compensate for a slightly increased repulsion of the aryl substituents, as indicated by larger C–P–C bond angles in **4c**[Σ(CPC) = 316.1°] than in **3c**[Σ(CPC) = 312.6°]. The angle P–C1–C10 is markedly widened by this interaction [**4c**: 127.0(5)°, **3c**: 118.01(13)°] and, as a consequence, the angle P–C1–C2 decreases [**4c**: 114.6(5)°, **3c**: 123.16(13)°]. The P–C bond lengths, however, remain nearly unchanged.

The dihedral angle of the naphthol plane in **4c** θ_{Naph}(X–P–C1–C2) = 178° is close to the ideal bisecting angle of 180°, although in solution the flexibility of **4c** is much higher than that of **3c** (see above). The planes of the flexible phenyl groups [θ_{Ph1}(X–P–C11–C16) = –133°, θ_{Ph2}(X–P–C21–C22) = –114°]) lie somewhat above and below an eclipsed arrangement.

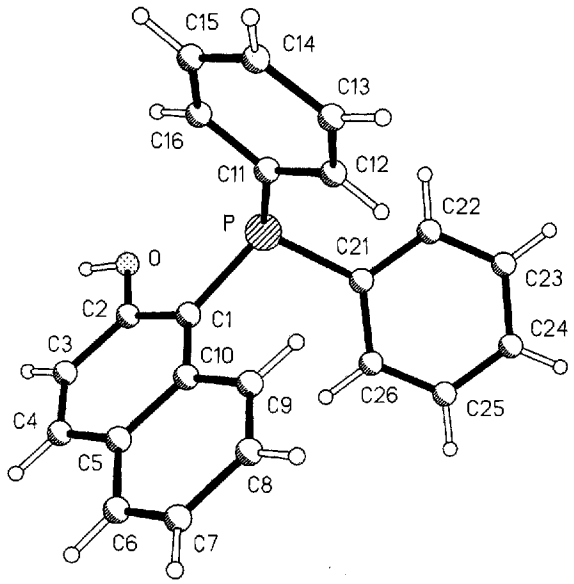
The *trans*-bisecting conformation of the naphthol moiety and the narrow angle P–C1–C2 in **4c** should facilitate the protonation of the phosphanyl group and the formation of chelate complexes (rather than monodentate P- or O-coordination), whereas the *cis*-bisecting conformation of **3c** is not compatible with chelate complexes.

Figure 2. Molecular structure of **3c**



Selected bond lengths [pm] and angles [°]: P–C1 182.8(2), P–C11 182.7(2), P–C21 183.0(2), P···C9 310.7(2), C1–C10 144.1(2), C9–C10 141.8(3), C1–P–C11 104.74(8), C1–P–C21 101.68(8), C11–P–C21 106.19(8), P–C1–C2 123.16(13), P–C1–C10 118.01(13), P–C1···C9 89.91(8).

Figure 3. Molecular structure of **4c**



Selected bond lengths [pm] and angles [°]: P–C1 183.7(6), P–C11 182.7(6), P–C21 180.8(6), P···C9 333.9(6), P···O 292.5(5), C1–C10 142.9(8), C9–C10 141.8(8) and C1–P–C11 104.6(3), C1–P–C21 106.6(3), C11–P–C21 104.9(3), P–C1–C2 114.6(5), P–C1–C10 127.0(5), P–C1···C9 99.1(3), O–C2–C3 115.8(6).

To estimate the steric demand of the ligands **3c** and **4c** the Tolman half-cone angles θ_i[13] for the three aryl groups were calculated by using the solid-state molecular geometry of the ligand, a Ni–P distance of 228 pm along the P–X axis, and Pauling's van der Waals radii, but by neglecting Ni–O interactions. For **4c** the half-cone angles θ_i are 102° (naphthol), 79 and 72° (phenyl), giving an average value of $\theta_{cone} = 2 \cdot (\theta_1 + \theta_2 + \theta_3)/3 = 168.7°$. This is close to the Tolman angles of Cy_3P or $PhP(tBu)_2$ (170°). For **3c** (θ_i = 122.5°, 71.5° and 81.5°) the cone angle $\theta_{cone} = 183.7°$ is similar to that of tBu_3P (182°)[13].

Reactivity of Phosphanylnaphthols

The NMR spectra of pure phosphanylnaphthols provide no evidence for the presence of a tautomeric equilibrium with phosphoniumnaphtholates. Nevertheless, the phosphanylnaphthols are protonated at phosphorus (with remarkable ease) or deprotonated at oxygen by addition of acids and bases, respectively. The addition of small amounts of acids causes broadening of the O*H* and the ^{31}P signals, and the addition of an excess of acid gives phosphonium salts. Even fairly weak acids such as acetic acid form substantial equilibrium amounts of phosphonium salts and induce a broad time-averaged, downfield shifted ^{31}P-NMR signal and an increased $^3J_{PCCH}$ coupling constant (Table 3).

Deprotonation at oxygen also leads to a downfield shift in the ^{31}P-NMR spectrum. 1-Phosphanylnaphtholates **2** are formed with strong bases or with amines and undergo O-substitution by reaction with chlorosilanes (cf. Scheme 1) or with chlorophosphanes. In THF triethylammonium 1-diphenylphosphanylnaphth-2-olate and chlorodiphenylphosphane form 40% of **5c** (Scheme 2) which, like the silyl ethers **3**, prefers the *cis*-bisecting conformation of the O-substituted naphthoxy group. 9-H is strongly deshielded by the adjacent phosphorus lone pair (electron repulsion), and the coupling constant $^4J_{PP}$ is small (3.9 Hz).

The formation of chelate complexes is observed in reactions of **4c** with nickel(II) and palladium(II) compounds. If a solution of nickelocene in benzene is added to a small excess (15%) of **4c** in the same solvent and the product precipitated with ether, a mixture of two high-melting, orange complexes **6a**, **b** is formed in a ratio of 80:20%. **6a** and **6b** are diamagnetic and soluble in benzene, chloroform or dichloromethane and show ^{31}P-NMR signals at $\delta = 36.7$ and 31.2 ($\Delta\delta = 5.5$), corresponding to a deshielding on complexation of $\Delta\delta^{31}P$ (**6a**–**4c**) = 74.1 and $\Delta\delta^{31}P$ (**6b**–**4c**) = 68.6, resp. Magnetic properties and ^{31}P-NMR data are very similar to those of the complexes $LNi(\eta^5\text{-Cp})$ and *cis*-L_2Ni, recently obtained from *o*-[isopropyl(phenyl)phosphanyl]cresole and nickelocene and characterized by X-ray diffraction[14]. The similarity of the content of **6b** to the excess of ligand indicates that the substitution of the Cp ligands proceeds mainly stepwise. Indeed, almost pure **6a** was obtained from the reaction of **4c** with a slight excess (max. 5%) of $NiCp_2$, but attempts at recrystallization led to partial decomposition. The complex **6b** ($\delta^{31}P = 31.2$) is also formed by reaction of **4c** with $NiBr_2 \cdot DME$ in THF on addition of Et_3N. The red precipitate was however not analytically pure; it contained triethylamine and THF. The UV spectrum resembles that of the *trans*-L_2Ni bis(chelate) complex of *o*-[*tert*-butyl(phenyl)phosphanyl]cresol rather than that of the *cis*-L_2Ni of *o*-[isopropyl(phenyl)phosphanyl]cresol while the complexation shift of $\Delta\delta^{31}P = 68.6$ points to the opposite direction[14]. Therefore, the stereochemistry of **6b** needs further investigation.

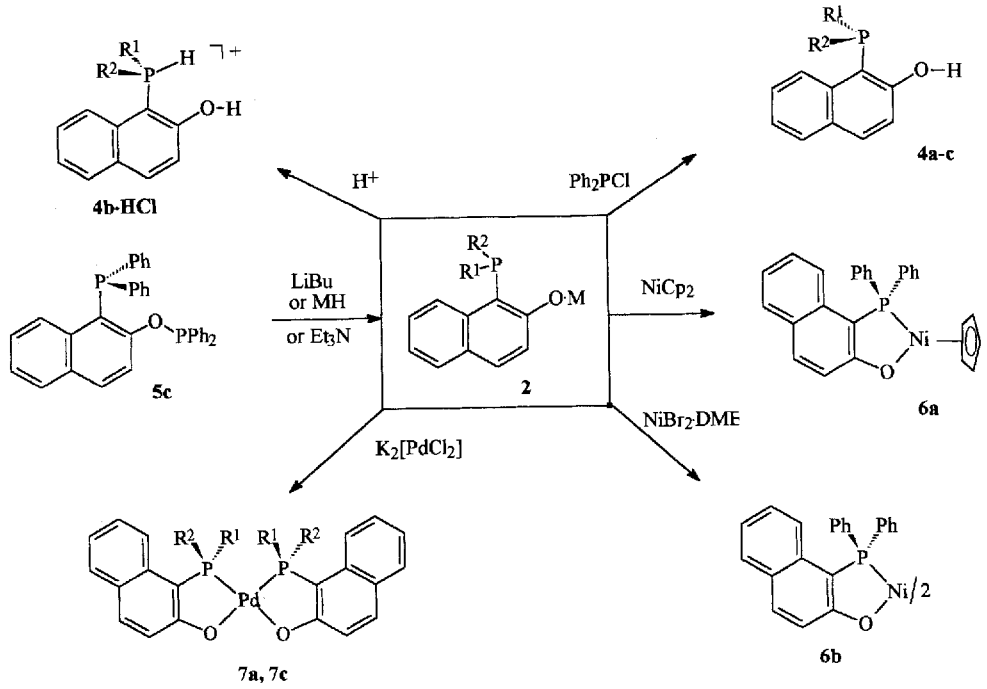
Like ionic nickel complexes, $K_2[PdCl_4]$ also reacts readily with two equivalents of **4**. With **4a** and **4c**, yellow diamag-

Table 3. ^{31}P-NMR and $^{3}J_{PH}$ data of **4b** in the presence of acids and bases[a]

4b /Acid Base	(pure)	HOac (3:1)	HOac (1:9)	HCl (aq.conc.)	HCl (satd.)	NaH (1:1)
^{31}P: δ =	-17.8 (br)	-17.3 (br)	- 5.06 (vbr)	+10.0 (vbr)	+10.94 (sharp)	-7.93
$^{3}J_{PH}$ =[Hz]	14.0	14.05	16.3	18.9	19.5	13.0
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	CD_3OD	$CDCl_3$	[D_8]THF

[a] In $HCl_{conc.}$/[D_6]DMSO δ = 58.34 (broad) is measured, probably corresponding to an oxidized sample.

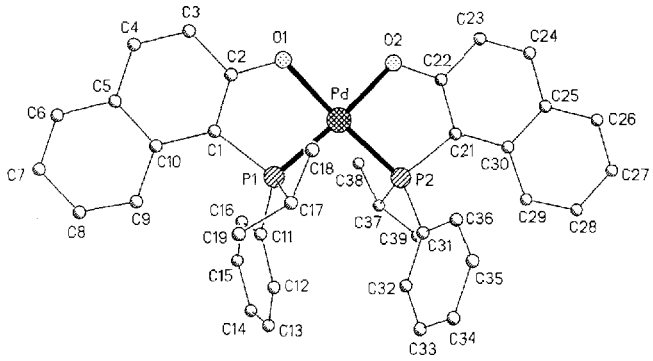
Scheme 2



netic crystals **7a** and **7c** are obtained from CH_2Cl_2 and CH_2Cl_2/EtOH solutions, respectively. They contain solvent of crystallization that cannot be completely removed in vacuo. Recrystallization of **7a** · xCH_2Cl_2 from $CHCl_3$ leads to the defined solvate **7a** · **$CHCl_3$**. The deshielding of phosphorus on complex formation, $\Delta\delta^{31}$P (**7a**–**4a**) = 81.1 and $\Delta\delta^{31}$P (**7c**–**4c**) = 77.9, is here larger than for the Ni complexes. The ^{1}H-NMR spectra reveal strong highfield shifts and negligible coupling to P for 9-H, and increased shielding of 7-H and 8-H. The signals of 3-H are split into doublets of doublets by 4-H and ^{31}P ($^{4}J_{PH}$ = 4.3, 4.6 Hz). The ^{1}H-NMR signals of **7c** are influenced differently on changing the solvent from CH_2Cl_2 to C_6D_6, indicating a solvent-dependent conformational behavior of the phenyl groups and probably also changes in the OPdO angle or H3···H3′ distance. The signals of the hydrogens atoms in the region of the chelating P/O atoms, 3-H (Δδ = +0.44) and 9-H (Δδ = +0.2), are downfield shifted, those of the *m*- and *p*-hydrogen atoms are strongly (0.5 and 0.6), the others slightly highfield shifted. The coupling constants $^{3}J_{PH}$ for PCHMe_2 of **7a** · xCH_2Cl_2 are large, but no coupling with the phosphorus atom of the second ligand was observed. This is in contrast to "triplet" splittings in the ^{1}H-NMR spectra of the square-planar *cis*-L_2Ni complex with *o*-(isopropylphenylphosphanyl)cresol ligands[14]. In the ^{13}C-NMR spectra we observe the X parts of ABX signals (AB = PP′), in most cases as "virtual triplets". The NMR spectra confirm the mono- or bis(chelate) structure of **6a**, **7a** and **7c**. However, reliable conclusions cannot be drawn from the doublet or triplet structure of ^{1}H or ^{13}C signals as to *cis* or *trans* configurations of Pd complexes[15]. Therefore, this question was unabmiguously solved by X-ray structure analysis of **7a** · **$CHCl_3$** (Figure 4).

In **7a** · **$CHCl_3$** the two P-chiral ligands and Pd^{II} combine to form square-planar *cis*-bis(chelate) complexes with *R,R* and *S,S* configuration. Since the structure is centrosymmetric the crystals are however optically inactive. The molecule possesses approximate twofold symmetry. The *cis* configuration is notable, since $P_2X_2Pd^{II}$ complexes are more commonly *trans*-configured; it implies that on introduction of the second chelate ligand the stereochemistry is not controlled by the *trans* effect in the usual way. This uncommon

Figure 4. Molecular structure of **7a** $CHCl_3$



Selected bond lengths [pm] and angles [°]: Pd–P1 222.07(5), Pd–P2 223.09(5), Pd–O1 204.61(14), Pd–O2 205.10(13), P1–C1 179.7(2), P1–C11 181.2(2), P1–C17 184.0(2), C1–C2 139.7(3), C2–C3 143.4(3), C3–C4 135.4(4), C4–C5 141.4(3), C5–C10 142.3(3), C1–C10 144.2(2), C6–C7 135.4(4), C8–C9 137.8(3) and P1–Pd–O1 83.46(4), P2–Pd–O2 84.20(4), P1–Pd–O2 173.07(4), P2–Pd–O1 174.02(4), P1–Pd–P2 101.89, O1–Pd–O2 90.62(5), Pd–P1–C1 100.97(6), Pd–P1–C11 116.69(6), Pd–P1–C17 109.83(6), C1–P1–C11 110.19(9), C1–P1–C17 109.65(9), C11–P1–C17 109.16(10), P1–C1–C10 127.7(2), P1–C1–C2 111.32(13). Solvent of crystallization is not shown.

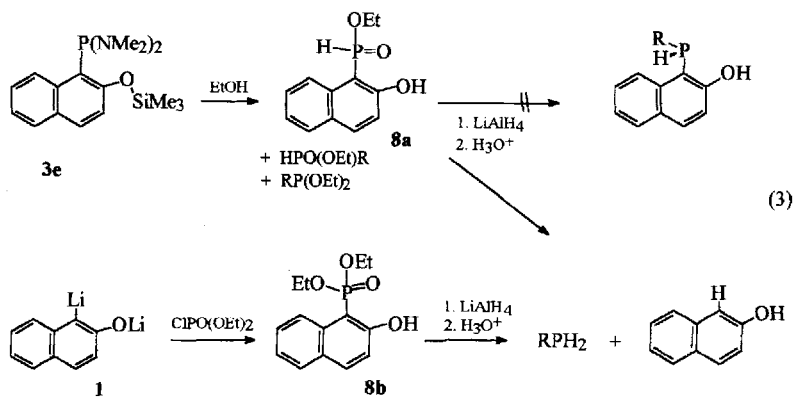
behavior may be attributed to the presence of a second coordination site (oxygen), steric control of the orientation of the P/O ligand in the transition state, and the preferred conformation of phosphanylnaphthols. We anticipate primary attack by the P atom according to a normal associative mechanism, but occupation of the position of the leaving (axial) Cl atom in the trigonal-bipyramidal transition state by oxygen in place of phosphorus. The square-planar configuration is then restored by loss of the remaining chlorine atom. A *cis*-bis(chelate) Pd^{II} complex is also formed with a phosphanyl-enolate bearing tertiary substituents in α-position to phosphorus[16].

The coordination geometry is essentially planar (mean deviation 6 pm), although the rectangular arrangement of the P and O atoms is somewhat distorted. The constraints imposed by the five-membered ring and probable steric requirements of the substituents at phosphorus cause the ring P–Pd–O angles to be lowered to 84.20(4) and 83.46(4)° and the P–Pd–P angle to be widened to 101.89(2)°; the O–Pd–O angle remains at nearly 90°. The naphthyl rings are twisted away from the coordination plane with interplanar angles of 19° to C1–C10 and 15° to C21–C30; an additional distortion is observed for C2, which lies 14 pm out of the mean plane of its ring system. These structural features are similar to those in the complex [{2-trifluoromethyl(diphenylphosphanyl)enolato}Pd(Cl)-(PPh_3)][16] and the five-membered ethylene-bridged chelate complexes [(PP)Pd$(SCN)_2$][17] and [(PN)Pd(SCN)-(NCS)][18]. The phosphorus atom in **7a** · $CHCl_3$ is tetrahedrically surrounded by the three C atoms and Pd. The inclusion in the five-membered ring causes decreased C–P–Pd angles [100.97(6) and 100.58(6),de], which are compensated by larger C(Ph)–P–Pd angles (ca. 116°C). Pd–P and Pd–O distances lie in the normal range.

Secondary and primary 1-phosphanylnaphth-2-oles should, like primary phosphanylphenols[5], be useful synthons for naphthol-anellated heterocycles. We therefore attempted to prepare them from **3d** and **3e** by alcoholysis and subsequent reduction with $LialH_4$. This method works well in a similar preparation of *o*-phosphanylphenol[5,19], although the intermediate ethyl *o*-hydroxyphenylphosphonate (^{31}P δ = 27.9) undergoes ill-defined condensation reactions on heating. Using **3d** and **3e**, however, we observed a complete reductive cleavage (Scheme 3) of the P–C bond, giving β-naphthol, PH_3, and $PhPH_2$. ^{31}P-NMR studies gave evidence of a partial splitting of the P–C(naph) bond of **8a** on alcoholysis at room temperature and more markedly at 60 °C. The remaining *P*-naphthyl compounds **8** are cleaved either by $LiAlH_4$ or, more probably, during the acidic workup. This unusual behavior, reminiscent of the facile acid-mediated cleavage of *o*-arsinophenol[20], is caused at least partly by the steric repulsion between 9-H and the phosphanyl group, inducing a shorter P···O distance (see Figure 3) and facilitated proton transfer, resulting in elimination of RPH_2.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We thank *B. Witt* for NMR, Dr. *A. Müller* for MS measurements and *Steffen Zahn* for the preparation of **5c**.

Scheme 3



Experimental

General experimental techniques were as described earlier[21]. Chloro(dimethylamino)phenylphosphane[22], chloro(*tert*-butyl)phenylphosphane[23], and chloro(methyl)phenylphosphane[24] were prepared according to literature procedures. – NMR spectra were recorded with a multinuclear FT-NMR instrument ACX300 (Bruker) at 300.133 (^{1}H), 121.496 (^{31}P), 75.4686 (^{13}C), and 116.6436 MHz (^{7}Li). $CDCl_3$ was used as solvent unless stated otherwise. References are TMS or indirectly CH_2Cl_2 for ^{1}H and ^{13}C spectra, H_3PO_4 (85%) for ^{31}P, and 1 M LiCl in D_2O for ^{7}Li spectra. Atom numbering corresponds to the figures of the molecular structures. Assignments were supported by CH-COSY and DEPT experiments. The quaternary atoms C10 and C_i(Ph) with similar chemical shifts are distinguished by the only slight differences of the coupling constants J_{PC10}-J_{PC9} of **3a–d** and **4a–c** arising from the same orientation towards the phosphorus lone pair. [In the case of **3c**, **4c** the assignment is unambiguous because of the double intensity of C_i(Ph)]. This assignment is consistent with increasing $J_{PCi(Ph)}$ in the same order as for $^1J_{PC1(Naph)}$.

General Procedure for Synthesis of Phosphanylnaphth-2-ol Trimethylsilyl Ether (**3**): A solution of 1-bromonaphth-2-ol (mmol see text) in dry ether (ca. 5 ml/mmol; for **3b** 2–3 ml/mmol) is cooled to −50°C and two equivalents of a 1.6 M (for **3b** 2.5 M) solution of LiBu in hexane are added with stirring, the first half (strongly exothermic) being added dropwise, the remainder rapidly. Stirring is continued for about 4 h at room temp. The resulting dilithio reagent **1** is partly dissolved, partly suspended. After cooling to −40 to −50°C a solution of one equivalent of the chlorophosphane in an equal volume of ether is added dropwise and the mixture is stirred overnight at ambient temp. Then an excess of Me_3SiCl (1.1–1.2 equivalents) is added at 0–10°C and the mixture is stirred at least for 3–4 h at room temp. (**3b** 1 d). The precipitate, mainly LiCl, is filtered off and washed with ether, the ether evaporated in vacuo and the residue crystallized from ether/petroleum ether (1:3) (**3c**) or distilled to give viscous liquids **3a**, **b**, **d**, **e**.

1-Isopropylphenylphosphanyl-naphth-2-yl Trimethylsilyl Ether (**3a**): Starting from 11.2 g (50 mmol) of 1-bromonaphthol, 63 ml of 1.6 M LiBu in hexane, 9.4 g (50 mmol) of *i*PrPhPCl, and 10 ml (excess) of $ClSiMe_3$, 7.2 g (39%) of viscous liquid, b.p. 165–170°C/0.005 Torr, is obtained. NMR data: Tables 1 and 2. – MS, *m/z* (%) = 366 (9) [M^+], 323 (8) [M^+ − *i*Pr], 302 (11), 260 (9), 216 (96) [M^+ − $PhP{=}CMe_2$], 201 (100) [216 − Me], 185 (25), 147 (41), 73 (40). – $C_{22}H_{27}OPSi$ (366.5): calcd. C 72.10, H 7.43; found C 71.68, H 7.52.

1-(tert-Butylphenylphosphanyl)naphth-2-yl Trimethylsilyl Ether (**3b**): 4.5 g (20 mmol) of 1-bromonaphthol is metalated with 16 ml of 2.5 M LiBu in hexane. 4.0 g of *t*BuPhPCl (20 mmol) is added at −40°C. The mixture is stirred for 1 d at room temp. and treated with 2.5 g (23 mmol) of $ClSiMe_3$ to give 4.7 g (64%) of a viscous liquid, b.p. 170–175°C/0.05 Torr. – $C_{23}H_{29}OPSi$ (380.5): calcd. C 72.59, H 7.68; found C 72.36, H 7.73.

1-(Diphenylphosphanyl)naphth-2-yl Trimethylsilyl Ether (**3c**): Starting from 11.2 g (50 mmol) of bromonaphthol, 63 ml of 1.6 M LiBu in hexane, 11.0 g (50 mmol) of Ph_2PCl and 5.5 g of $ClSiMe_3$, 12.6 g (61%) of colorless crystals, m.p. 92–93°C (petroleum ether), is obtained. – $C_{25}H_{25}OPSi$ (400.5): calcd. C 74.97, H 6.29; found C 74.55, H 6.53.

Phenyl-1-[2-(trimethylsilyloxy)naphthyl]phosphinic Acid Dimethylamide (**3d**): 22.3 g (100 mmol) of 1-bromonaphthol is treated with 126 ml of 1.6 M LiBu in hexane, 18.8 g (100 mmol) of $Me_2NPhPCl$ and 11.5 g of $ClSiMe_3$ to give 22.4 g (61%) of a viscous liquid, b.p. 165–170°C/0.005 Torr, solidifying after distillation, m.p. 75–77°C. – $C_{21}H_{26}NOPSi$ (367.5): calcd. C 68.63, H 7.13; found C 68.18, H 6.95.

1-[2-(Trimethylsilyloxy)naphthyl]phosphonic Acid Bis(dimethylamide) (**3e**): 37.9 g (170 mmol) of 1-bromonaphthol is treated with 214 ml of 1.6 M LiBu in hexane, 26.5 g (170 mmol) of $ClP(NMe_2)_2$ and 19.0 g (175 mmol) of $ClSiMe_3$ to give 22.9 g (41%) of an oil, b.p. 135–143°C/0.005 Torr. – $C_{17}H_{27}N_2OPSi$ (334.5): calcd. C 61.05, H 8.13; found C 60.76, H 7.88.

Phosphanylnaphtholes by Cleavage of Their Trimethylsilyl Ethers

1-(Isopropylphenylphosphanyl)naphth-2-ol (**4a**): A solution of 4.6 g (12.6 mmol) of **3a** in 10 ml of anhydrous MeOH is heated for 1 h. After 1 week the crystals are collected and vacuum-dried to give 2.4 g (65%) of **4a**, m.p. 127–128°C (EtOH). – NMR data: see Tables 1 and 2. – $C_{19}H_{19}OP$ (294.3): calcd. C 77.53, H 6.51; found C 76.93, H 6.75.

1-(tert-Butylphenylphosphanyl)naphth-2-ol (**4b**): Compound **3b** is cleaved very slowly or not at all by MeOH, even in the presence of a catalytic amount of trifluoromethanesulfonic acid. The $SiMe_3$ group is however removed by acetic acid: 2.5 g (6.6 mmol) of **3b** is dissolved in 10 ml of glacial acetic acid. After 1 d the solvent is removed in vacuo (10^{-2} Torr), the residue is dissolved in ether and hexane added until the solution becomes turbid. **4b** precipitates as an oil (2.0 g, 98%) crystallizing slowly over some months, m.p. 90–92°C (after removal of the oily by washing with pentane). – NMR data: see Tables 1 and 2. – $C_{20}H_{21}OP$ (308.4):

1-(Diphenylphosphanyl)naphth-2-ol (**4c**): 5.8 g (14.5 mmol) of **3c** is heated at reflux with 20 ml of anhydrous MeOH. On cooling 4.7 g (99%) of crystalline **4c**, m.p. 112–113°C (EtOH), is obtained. – NMR data: Tables 1 and 2. – $C_{22}H_{17}OP$ (328.4): calcd. P 9.43, C 80.48, H 5.22; found P 9.45, C 79.96, H 5.43.

Reactions of Phosphanylnaphthols

1-(tert-Butylphenylphosphanyl)naphth-2-ol Hydrochloride (**4b** · **HCl**): To a solution of 1.2 g of **3b** in 5 ml of THF 3 drops of conc. HCl are added and crystals form. On recrystallization from EtOH 0.5 g (46%) of colorless needles of m.p. 160–170°C (dec.) is obtained. [On heating and in vacuo (<10^{-2} Torr) HCl is lost]. – ^{1}H NMR (CD_3OD): δ = 1.57 (d, J_{PH} = 18.9 Hz, 9H, CMe_3), 7.29 (dd, *J* = 9.0, 4.8 Hz, 1H, 3-H), 7.49 (ddd, *J* = 8.0, 7.0, 0.7 Hz, 1H, 7-H), 7.63–7.72 (m, 4H, *m*-H + *p*-H + 8-H), 7.96 (dbr, *J* = 8.1 Hz, 1H, 6-H), 8.10 (dd, J_{PH} = 12.8, J_{HH} = 7.9 Hz, 2H, *o*-H), 8.20 (d, *J* = 9.0 Hz, 1H, 4-H), 8.28 (d, *J* = 8.6, 1H, 9-H). – ^{13}C NMR and CH-COSY (CD_3OD): δ = 27.4 (d, *J* = 2.8 Hz, CMe_3), 36.0 (d, *J* = 44.6 Hz, CMe_3), 94.0 (d, *J* = 79.2 Hz, C_q-1), 118.2 (d, *J* = 8.0 Hz, C-3), 118.4 (d, *J* = 79.3 Hz, C_q-*i*), 123.5 (d, *J* = 9.7 Hz, C-9), 125.7 (s, C-7), 130.2 (d, *J* = 8.4 Hz, C_q-5), 130.9 (s, C-8), 131.0 (d, *J* = 8.8 Hz, 2 C-*m*), 131.04 (s, C-6), 135.5 (d, *J* = 5.8 Hz, C_q-10), 135.7 (d, *J* = 2.6 Hz, C-*p*), 135.8 (d, *J* = 10.7 Hz, 2 C-*o*), 140.2 (d, *J* = 1.7 Hz, C-4), 163.7 (d, *J* = 2.1 Hz, C_q-2). – ^{31}P NMR ($CDCl_3$): δ = +11.84. MS (70 eV), *m/z*: 308 (60%) [M^+ without HCl], 258 (100%) [M^+ − C_4H_2], 183 (86%) [PhBuPHOH$^+$]. – $C_{20}H_{22}ClOP$ (344.8): calcd. Cl 10.28; found Cl 9.85.

1-(Diphenylphosphanyl)naphth-2-oxydiphenylphosphane (**5c**): 2.7 g of **4c** is added to 10 ml of triethylamine. Solid triethylammonium salt is formed, which is dissolved in absolute THF. At 0°C a solution of 1.5 ml of Ph_2PCl in 10 ml of ether is added. Since Et_3N · HCl is partly soluble in THF, the solvent is removed in vacuo, ether is added, the precipitate is filtered off and washed with ether. Evaporation of ether leaves an oil, which is dissolved in a small portion of benzene. Addition of a little hexane and stirring of the mixture for 3 weeks gives 1.5 g (40%) of crystalline **5c**. – ^{1}H NMR:

δ = 8.81 (dd, *J* = 8.7 Hz, *J* = 6 Hz, 1H, 9-H), 7.89 (m, *J* = ca. 7/6.9/1.5 Hz, 8-H), 7.42 (m, *J* = 7 Hz, 7-H) (H7/H8 partly superimposed, 2H), 7.05–7.35 (m, 21H, aromatic H). – ^{31}P NMR: δ = +113.01 (d, $^4J_{PP}$ = 3.9 Hz, Ph_2PO), –25.03 (d, $^4J_{PP}$ = 3.9 Hz, C-PPh_2). – $C_{34}H_{26}OP_2$ (512.5): calcd. P 12.09; found P 11.8.

Attempt to Prepare 1-(tert-Butylphenylphosphanyl)naphth-2-oxy-tert-butylphenylphosphane (**5b**): Compound **1** is prepared from 2.2 g (9.9 mmol) of 1-bromonaphthol in ether and 13 ml of 1.6 M LiBu. At –50°C 4.2 g (20.9 mmol) of *t*BuPhPCl is added. After 20 h the precipitate is filtered off and the solvent removed in vacuo. The resulting oil contains much unreacted *t*BuPhPCl, but exhibits ^{31}P-NMR signals at δ = –3.6 and +128.2 which belong to the disubstituted product. It could not be obtained in pure form.

Complexes

Reactions with Nickelocene: 500 mg (2.65 mmol) of nickelocene and 1.0 g (3.045 mmol, 15% excess) of **4c** are dissolved in 50 ml of benzene and the solution is stirred for 2 h. Ca. 40 ml of benzene is removed in vacuo and diethyl ether added. On stirring for 1 d an orange solid precipitates, which is washed with ether and dried in vacuo (10^{-2} Torr) to give 1.1 g of a mixture of **6a** and **6b** in a ratio of 80:20% (based on ^{31}P int.). – ^{31}P NMR: δ = 36.7 (**6a**), 31.24 (**6b**).

6a: 300 mg (0.91 mmol) of **4c** and 190 mg (1.0 mmol) of $NiCp_2$ are dissolved at –10°C in 5 ml of toluene. After 4 h at 20°C 20 ml of ether is added dropwise. 300 mg of orange-yellow (**6a**), slightly contaminated by (**6b**) is collected. **6b** is less soluble than **6a** and is enriched during recrystallization. – ^{1}H NMR: δ = 5.25 (s, 5H, Cp), 6.95 (dd, *J* = 9.1, 5.3 Hz, 1H, 3-H), 6.99–7.45 (m, ca. 10H), 7.56 (dbr, *J* = 9.1 Hz, 4-H), 7.83 (ddd, *J* = 12.3, 8, 1.5 Hz, 4H, *o*-H). – ^{31}P NMR: δ = 36.6 (**6a**). MS (FAB in NBA, 70 eV), *m/z* (%): 453 (14) [M^+_{60Ni} + 1], 451 (99) [M^+_{58Ni} + 1], 327 (10) [M^+ – NiCp], 308 (22) [Ph_2PNiCp^+], 260 (11), 249 (15), 233 (27), 203 (25), 202 (27) [Ph_2PHO^+], 183 (40) [$C_6H_4PC_6H_4^+$], 63 (100). – $C_{27}H_{21}OPNi$ (451.4): calcd. P 6.86; found P 7.15.

6b: A solution of **4c** (726 mg, 2.21 mmol) in 10 ml of THF is added dropwise to a suspension of 294 mg (0.93 mmol) of $NiBr_2$ · 1.1 DME in 20 ml of THF. About 2/3 of the solvent are removed from the brown solution in vacuo after 3 d. Addition of 3 ml of triethylamine causes a red product to precipitate which is washed with THF and dried for 8 h at 10^{-2} Torr to give 471.5 mg (70%) of diamagnetic ($\chi_g \cdot 10^6$ = –0.31 $cm^3\ mol^{-1}$) **6b** containing triethylamine and little THF, m.p. >260°C. – UV (in $CHCl_3$): λ_{max} = 425, 389, 375, 334 nm. Magnetic susceptibility: $\chi_g \cdot 10^6$ = –0.31 $cm^3\ g^{-1}$, $\chi_{mol} \cdot 10^6$ = –18 $cm^3\ mol^{-1}$. – ^{1}H NMR: δ = 1.44 (t, *J* = 7.3 Hz, NEt_3), 3.13 (q, *J* = 7.3 Hz, NEt_3), 6.81 (br. d, *J* = 8.2 Hz, 2H, 6-H), 6.92 (br. t, *J* = 7–8 Hz, 2H, 7-H), 6.97 (br. t, *J* = 7–8 Hz, 2H, 8-H), 7.04 (br. t, J_{HH} ca. 7.5 Hz, 8H, *m*-CH), 7.28 (dd, $^3J_{HH}$ = 9.1 Hz, $^4J_{PH}$ ca. 5 Hz, 3-H), 7.51 (br. dd, J_{PH} = 12.9, J_{HH} = 7 Hz, 8H, *o*-CH), 7.58 (d, *J* = 7.1 Hz, 2H, 9-H), 7.66 (d, *J* = 9.1 Hz, 2H, 4-H). – ^{13}C NMR: δ = 8.7, 46.1 (NEt_3), 105.1 ("t", *J* + *J'* 58.4 Hz, C_q-1), 120.9 (s, C-8), 122.0 (broad s, C-6), 122.5 ("t", *J* + *J'* ca. 15 Hz, C-3), 126.2 ("t", *J* + *J'* = 50.3 Hz, C_q-*i*), 126.4 (s, C-7), 127.9 ("t", *J* + *J'* = 6 Hz, C_q-5), 128.6 ("t", *J* + *J'* = 11.6 Hz, C-*m*), 128.7 (s, C-9), 130.5 (s, C-*p*), 132.6 ("t", *J* + *J'* = 11.1 Hz, C-*o*), 134.2 (s, C_q-10), 135.4 (s, C-4); (C_q-2 low intensity). – ^{31}P NMR: δ = 31.2.

Reactions of **4** *with* $K_2[PdCl_4]$

7a: 0.32 g (1.087 mmol) of **4a** and 0.07 g of KOH are dissolved in 10 ml of EtOH (96%). A solution of 0.18 g (0.55 mmol) of $K_2[PdCl_4]$ in 5 ml of water is added by means of a syringe. After 1 h the yellow precipitate is filtered off and washed with water. Crude **7a** is dissolved in CH_2Cl_2 (100 ml), the solution is dried with Na_2SO_4, filtered and 3/4 of the solvent are evaporated. By slow condensation of pentane into this soltuion, 0.22 g (55%) of **7a** · *x*CH_2Cl_2 with m.p. >260°C (dec.) precipitates. – ^{1}H NMR and H,H-COSY90 ([D_8]THF): δ = 0.89 (dd, $^3J_{PH}$ = 14.3 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, $CHMe_A$), 0.96 (dd, $^3J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, $CHMe_B$), 1.41 (sept, br., *J* ca. 7 Hz, 2H, $CHMe_2$), 5.29 (s, 2H, CH_2Cl_2), 6.59 (d, $^3J_{HH}$ 8.3 Hz, 2H, 6-H), 6.69 ("t"d, $^3J_{HH}$ = 7 Hz, *J* = 1.3 Hz, 2H, 7-H), 6.77 ("t"d, $^3J_{HH}$ = 7–8 Hz, *J* = 1 Hz, 2H, 8-H), 6.90 (dd, $^3J_{HH}$ = 9.1 Hz, $^4J_{PH}$ = 4.3 Hz, 2H, 3-H), 7.43 (br. d, $^3J_{HH}$ = 7.8 Hz, 2H, 9-H), 7.53 (br. d, $^3J_{HH}$ ca. 9.1 Hz, 4-H, partly superimposed), 7.45–7.52 (m, Ph). – ^{13}C NMR and CH-COSY ([D_8]THF; AB*X* spin type): δ = 18.0 ("t", *J* + *J'* = 5.8 Hz, Me_A), 19.4 ("t", *J* + *J'* = 7.9 Hz, Me_B), 25.8 (*J* + *J'* = 32.4 Hz, *CH*), 97.4 (*J* + *J'* = 49.6 Hz, C_q-1), 119.5 (s, C-8), 122.57 ("t", *J* + *J'* = 19.2 Hz, C-3), 122.7 ("t", *J* + *J'* = 4.2 Hz, C-6), 124.9 (s, C-7), 127.5 ("t", *J* + *J'* = 6.4 Hz, C_q-5), 127.8 (s, C-9), 128.8 (*J* + *J'* = 9.8 Hz, C-*m*), 129.8 (*J* + *J'* = 48.8 Hz, C_q-*i*), 130.68 (s, C-*p*), 130.79 ("t", *J* + *J'* = 10.2 Hz, C-*o*), 134.73 (s, C-4), 136.23 (s, C_q-10), 180.35 (*J* + *J'* = 13.3 Hz, C_q-2). – ^{31}P NMR: δ = 48.66. – MS (70 eV, FAB in NBA), *m/z* (%): 693.5 (56) [M^+ without solv.], 399.6 (81) [LPd^+], 357.5 (35) [$LPd^+ - C_3H_6$], 293.4 (100) [L – H^+], 251.4 (77) [L – $C_3H_7^+$], 233 (71), 215.3 (58) [$PhPHPd^+$]. – $C_{38}H_{36}O_2P_2Pd$ · 1/2 CH_2Cl_2 (777.9): calcd. C 62.87, H 5.07; found C 58.92, H 5.17. Recrystallization of **7a** · *x*CH_2Cl_2 from $CHCl_3$ furnished single crystals of **7a** · $CHCl_3$ as shown by the X-ray structure analysis.

7c: 0.61 g (1.9 mmol) of **4c** and 0.12 g of KOH are dissolved in 20 ml of EtOH (96%). A solution of 0.32 g (0.98 mmol) of $K_2[PdCl_4]$ in 5 ml of water is added dropwise. After stirring for 1 h the formed yellow precipitate is filtered off, washed with water and vacuum-dried to yield 0.58 g (78%) of **7c**. Dissolution of **7c** in hot CH_2Cl_2 (70 ml) and cautious addition of EtOH (upper layer, mixing by diffusion) to the solution affords air-stable yellow crystals, m.p. >265°C (dec.). The fresh crystals contain 2 EtOH (^{1}H-NMR analysis) which are partially liberated in vacuo or on recrystallization from another solvent. – ^{1}H NMR (CD_2Cl_2): δ = 6.91–6.97 (3 m, partially superimposed, 6H, 6–8H), 7.05 (td, J_{HH} ca. 8, 2 Hz, 8H, *m*-CH), 7.18 (dd, $^3J_{HH}$ = 9, $^4J_{PH}$ = 4.6 Hz, 2H, H3), 7.31 (br. t, J_{HH} ca. 8 Hz, 4H, *p*-CH), 7.40 (ddd, $^3J_{PH}$ = 12, J_{HH} = 8, 1 Hz, 8H, *o*-CH), 7.61 (dd, *J* = 7.1, 0.9 Hz, 2H, 9-H or 6-H), 7.71 (d, *J* = 9.1 Hz, 2H, 4-H). – ^{1}H NMR (C_6D_6): 6.51 (ddd, J_{HH} = 8.0, 7.6, 2.1 Hz, 8H, *m*-CH), 6.75 (d "q", *J* = 7.4, ca. 1.5 Hz, 4H, *p*-CH), 6.82 (td, *J* = 7.0, 1.3 Hz, 2H, 7-H), 6.88 (td, *J* = 7–8, 1.7, 2H, 8-H), ca. 7.15 (m, 2H, 6-H), 7.26 (ddd, J_{PH} = 12, J_{HH} = 8, 1 Hz, 8H, *o*-CH), 7.40 (d, *J* = 7.7 Hz, 2H, 9-H), 7.50 (d, *J* = 9.1 Hz, 2H, 4-H), 7.62 (dd, J_{HH} = 9.1 Hz, J_{PH} = 4.6 Hz, 2H, 3-H). – ^{13}C NMR (C_6D_6): δ = 102.9 ("d", *J* + *J'* = 57.6 Hz, C_q-1), 120.9 (s, C-8), 122.1 ("t", *J* + *J'* = 5.5 Hz, C-6), 124.2 ("t", *J* + *J'* = 20.2 Hz, C-3), 126.5 (s, C-7), 128.6 ("t", *J* + *J'* = 11.4 Hz, C-*m*), 128.7 ("t", *J* + *J'* = 6.4 Hz, C_q-5), 129.5 (s, C-9), 130.1 (s, C-*p*), 132.9 ("t", *J* + *J'* = 12.6 Hz, C-*o*), 136.0 (s, C_q-10), 136.5 (s, C-4); 179.9 ("t", *J* + *J'* = 14.2 Hz, C_q-2), (C_q-*i* superimposed). – ^{31}P NMR (CD_2Cl_2, kap. 85% H_3PO_4): δ = 40.52. – MS (70 eV, FAB in NBA), *m/z* (%): 761 (20) [M^+], 434 (20) [LPd^+], 307 (42), 154 (100) [Ph_2^+], 136 (83). – $C_{44}H_{32}O_2P_2Pd$ (761.1): calcd. C 69.44, H 4.24; found C 68.22, H 4.56.

Formation of **8** *and Attempts to Prepare Primary 1-Phosphanylnaphth-2-ol. – a)* 22.5 g (67.4 mmol) of **3e** is dissolved in 30 ml of abs. EtOH. An exothermic reaction starts and gaseous Me_2NH evolves. The ^{31}P-NMR spectrum of this solution exhibits signals at δ = 31.4 (74%, J_{PH} = 595, 13, 9 Hz) (**8a**), 17.0 (17%, J_{PH} = 532, 3.7 Hz), and small signals at δ = 17.0, 26.1, 39.7, and 4.7. The solution is heated at 50°C for 4 h and the solvent removed in vacuo

Table 4. Crystallographic data for **3c**, **4c** and **7a** · $CHCl_3$

	3c	**4c**	**7a** $CHCl_3$
Empirical formula	$C_{25}H_{25}OPSi$	$C_{22}H_{17}OP$	$C_{39}H_{37}Cl_3O_2P_2Pd$
Formula weight	400.51	328.33	812.38
Crystal size [mm]	0.65 x 0.50 x 0.30	0.60 x 0.40 x 0.35	0.75 x 0.40 x 0.20
Temperature [K]	143	143	173
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell a [pm] ; α [°]	816.8(2) ; 81.705(14)	1081.7(2) ; 90	1270.73(14); 62.209(8)
b [pm]; β [°]	900.7(2) ; 77.05(2)	887.1(3) ; 99.54(3)	1317.1(2); 82.939(8)
c [pm]; γ [°]	1533.9(3) ; 79.01(2)	1772.5(5) ; 90	1379.33(14); 63.143(8)
V [nm^3] ; Z	1.0734(4) ; 2	1.6773(8) ; 4	1.8107(4); 2
$d_{calcd.}$ [Mg/m^3]	1.239	1.300	1.490
Absorption coefficient [mm^{-1}]	0.197	0.168	0.856
F(000)	424	688	828
θ range for data collection [°]	3.15 to 25.01	3.09 to 25.04	3.00 to 27.49
Limiting indices (h,k,l range)	$-9 \le h \le 9$, $-10 \le k \le 10$ $0 \le l \le 18$	$-12 \le h \le 12$, $0 \le k \le 10$, $0 \le l \le 21$	$-14 \le h \le 15$, $-13 \le k \le 13$ $-17 \le l \le 17$
No. of reflexions collected	3934	3061	12636
independent ($R_{int.}$)	3781 (0.0114)	2962 (0.0715)	7562 (0.0119)
Absorption correction			Psi-scans
Max.& min.transmission			0.992 and 0.798
Data/restraints/parameters	3776/0/256	2935/193/218	7559/80/428
Goodness-of-fit on F^2	1.064	1.097	1.033
Final R indices	R1 = 0.0348,	R1 = 0.0915,	R1 = 0.0246,
[I>2σ(I)]	wR2 = 0.0819	wR2 = 0.1988	wR2 = 0.0614
R indices (all data)	R1 = 0.0422,	R1 = 0.1643,	R1 = 0.0292,
	wR2 = 0.0908	wR2 = 0.2829	wR2 = 0.0636
Largest diff. peak and hole	256 and -230 $e.nm^{-3}$	506 and -373 $e.nm^{-3}$	872 and -496 $e.nm^{-3}$

(10^{-2} Torr) at this temperature. The ^{31}P-NMR spectrum shows partial decomposition of **8a** (δ = 31.4 [45%]) and formation of $P(OEt)_3$ (δ = 139.3 [10%]) and $HPO(OEt)_2$ (δ = 7.9 [25%]). The alcoholysis product is dissolved in twice the volume of dry ether and the solution added dropwise to a suspension of an excess of $LiAlH_4$ [5.0 g = 131.6 mmol, (phosphanylphenolates are stable towards excess $LiAlH_4$)] in 150 ml of ether. After stirring overnight at 0°C a saturated aqueous solution of NH_4Cl is added dropwise until the evolution of gases becomes slower. The $Al(OH)_3$ formed is dissolved by addition of 10% hydrochloric acid, the organic phase is separated, dried twice with sodium sulfate and the solvent is removed in vacuo. In an attempted vacuum distillation some β-naphthol sublimes but no phosphanylnaphthol can be isolated. Crystallization of the remainder gives a further 8 g of β-naphthol.

Alcoholysis of **3d** and subsequent reduction with $LiAlH_4$ reveals a similar P–C cleavage and furnishes β-naphthol and phenylphosphane. – ^{31}P-NMR spectrum 1 h after addition of EtOH: δ = 14.9 (70%), 26.8 (18%), 156.0 (12%); after heating to 60°C and removal of EtOH in vacuo: δ = 26.2 (56%), 156.5 (21%), 156.6 (14%).

b) A suspension of **1** is prepared from 15.5 g (70 mmol) of 1-bromonaphth-2-ol in 200 ml of ether, and 87 ml of 1.6 M BuLi in hexane (140 mmol) and 8.6 g (70 mmol) of $(EtO)_2P(O)Cl$ are added dropwise at −30 to 0°C to yield crude lithium naphth-2-olato-1-phosphonic acid ester (**8b**) [^{31}P (CD_3OD): δ = 29.8, small impurities at δ = −0.5, −0.4, and 1.8]. The solution is added dropwise to a suspension of an excess of $LiAlH_4$ in ether and worked up as above. PH_3 and β-naphthol are formed.

Crystal Structure Analyses: Crystal data are compiled in Table 4. – *Data collection:* Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (**3c**, **4c**: Stoe STADI-4; **7a**: Siemens P4). Data were collected with monochromated Mo-K_α radiation. Cell constants were refined from ±ω angles (Stoe) or setting angles (Siemens) of ca. 50 reflections to $2\Theta_{max}$ 25°. Scan type: ω/Θ (Stoe), ω (Siemens). An absorption correction based on ψ-scans was performed for **7a**. – *Solution and refinement:* Structures were solved by direct methods (**3c**, **4c**) or the heavy-atom method (**7a**) and refined anisotropically on F^2[25]. Hydrogen atoms were included by using a riding model (exception: OH as rigid group).

Complete data of the X-ray structure analyses were deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. This material can be ordered on quoting the depository number CSD-404943 (**3c**), -404944 (**4c**), -404945 (**7a**) and the complete literature references.

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