36. Synthesis and NMR Spectroscopic Investigation of a Macrocyclic Diphosphine Ligand and Its Nickel(II) and Palladium(II) Complexes

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The preparation of a macrocyclic diphosphine ligand 5 incorporating a binaphthyl unit and its Ni^{II} and Pd^{II} complexes, 6 and 7, is described. A complete assignment of ¹H,- ¹³C-, and ³¹P-NMR data on the basis of 2D NMR spectroscopy (¹H,¹H-, ¹³C,¹H-, ³¹P,¹H-, ³¹P,¹A-, ²¹P,¹³C-COSY) was possible for 5, and also – in part – for 6 and 7.

Introduction. – With respect to our recent studies dealing with the synthesis and configuration of chiral macrocyclic diphosphines [1], we were interested in an assignment of ¹³C- and ¹H-NMR data of ligands and complexes, a necessary precondition when conformational analysis is intended.

The most promising candidate for our studies was the C_1 -symmetrical, bridged binaphthyl 5 with a conformationally rather stable 14-membered perimeter, owing its rigidity to the presence of three aromatic subunits. This rigidity still will be increased upon complexation with transition metals forming five-membered chelate structures. As the relative configuration of the two Ph groups attached to the P-atoms was estimated to be *cis* (see below), this structure may be understood as a combination of a C_2 -symmetrical binaphthyl unit and a C_s -symmetrical diphosphine moiety. Consequently, the 'overall



Fig. 1. Numbering of macrocycle 5 and complexes 6 and 7

symmetry' has to be C_1 and can be considered as a mutual disturbance of 'local' symmetries. The magnitude of this effect depends on the length and the conformation of the alkyl chain. For convenience, in the following discussion, atoms are numbered arbitrarily as shown in *Fig. 1*.

Results and Discussion. – Diphosphine 5 was accessible from 1,1'-binaphthyl-2,2'-diol (1) in three steps (*Scheme*). Reaction of 1 with *t*-BuOK/ethyl chloroacetate in THF afforded diester 2 in 81% yield. Reduction of 2 with LiAlH₄ yielded 3 (59%) which was converted to the ditosylate 4 under standard conditions (TsCl/Py, 2°, 24 h; 74%). Coupling of 4 with the dilithium salt of 1,2-phenylenebis(phenylphosphine) under high-dilution conditions in THF resulted in the exclusive formation of a single diastereoisomer of macrocycle 5 (71%). Inspection of a *Dreiding* model made a configuration as depicted in *Fig. 1* with opposite configurations, (*R*) and (*S*), at the P-atoms highly probable. This assumption is also in agreement with the ease of complexation. Neutral Ni^{II} and Pd^{II} complexes 6 and 7, respectively, were prepared by mixing equimolar amounts of 5 and NiCl₂ or [PdCl₂(MeCN)₂], respectively, in CH₂Cl₂/EtOH.



From 5 and its Ni¹¹ and Pd¹¹ complexes 6 and 7, respectively, 1D and 2D ¹H-, ¹³C-, and ³¹P-NMR spectra were recorded. The quality of the spectra of 7 and especially 6 suffers from their poor solubility, even in CD_2Cl_2 . Together with the splitting due to ³¹P, ¹³C coupling and the very narrow spectral range of the Ph C-atoms, this fact limited the information content of the ¹³C-NMR spectra, thus preventing a complete assignment of all signals of 6 and 7.

While the eight aliphatic protons appear as well separated m's (*Table 1*), the aromatic range shows only in part clear m structures, the latter arising from the binaphthyl unit

Atom ^b)	Signal position ^c)	¹³ C-NMR			Signal	¹ H-NM	¹ H-NMR		
		5	6	7	position ^c)	5	6	7	
C(1)	8	123.47	121.22	120.47		_	_	_	
C(1')	6	119.52	118.91	118.42		-	_	_	
C(2)	37	155.17	154.90	154.80		-	_	_	
C(2')	36	153.73	154.50	154.11		-	_	_	
H-C(3)	7	120.02	121.57	121.73	16	7.53	6.77	6.70	
H-C(3')	5	112.67	114.51	113.81	12	7.27	7.91	7.75	
H-C(4)	24	130.12	129.43	129.28	21	8.03	ca. 7.61	7.57	
H-C(4')	22	129.67	130.86	130.89	19	7.93	8.17	8.09	
C(4a)	25	130.62	130.42	129.63			_	_	
C(4a')	21	129.30	129.86	130.33		-			
H-C(5)	17	128.41	127.96	127.89	20	7.93	7.77	7.73	
H-C(5')	16	128.28	128.47	128.40	18	7.87	7.95	7.88	
H-C(6)	10	124.48	124.53	124.11	14	7.40	7.33	7.29	
H-C(6')	9	123.84	124.21	124.47	13	7.32	7.35	7.29	
HC(7)	13	126.51	126.44	126.40	12	ca. 7.21	7.18	7.12	
H-C(7')	14	126.80	126.96	126.95	12	ca. 7.21	7.18	7.12	
H-C(8)	12	125.84	125.50	124.97	11	7.13	6.99	6.68	
H-C(8')	11	125.46	125.12	125.37	10	7.05	6.75	6.90	
C(8a)	29	134.34	134.41	134.39		~	_	_	
C(8a')	30	134.70	134.32	134.24		_	-	_	
C(9)	33	140.57	139.35*	138.82*				_	
C(9')	35	149.64	142.07*	140.95*			_		
H-C(10)	28	133.44	133.44*	(133.38)	12	7.28	7.52*	7.62	
H-C(10')	27	131.56	132.66*	(131.30)	9	6.66	7.56*	7.62	
H-C(11)	19	128.65	130.56*	(132.90)	12	7.2-7.3	7.20	7.28	
H - C(11')	23	129.83	132.50*	(133.86)	11	7.13	7.20	7.28	
C(12)	32	135.83	130.94*	130.04*		_	-	_	
C(12')	34	140.93	132.00*	131.60*		_	_	_	
H-C(13)	31	134.93	132.46*	132.35*	17	7.58	7.60*	7.52	
H - C(13')	26	131.10	132.30*	132.19*	12	7.14	7.64*	7.49	
H-C(14)	20	129.22	129.23	129.37*	15	7.44	7.40*	7.33	
H - C(14')	18	128.65	129.23	129.25*	12	7.17	7.42*	7.38	
H-C(15)	23	129.83	131.77*	132.20*	15	7.44	7.46*	ca. 7.40	
H-C(15')	15	127.92	131.48*	131.84*	12	7.15	7.55*	ca. 7.40	
$H_{1}-C(a)$	4	71.73	65.94	65.89	8	4.55	5.83	5.70	
H_{R} -C(a)					6	4.20	4.62	4.53	
$H_{\ell} - C(a')$	3	64.52	67.45	67.12	7	4.37	4.60	4.20	
$H_{n}-C(a')$	-				5	3.84	4.17	3.93	
H_{c} -C(b)	2	29.10	28.63*	29.01	4	2.91	3.12	3.21	
$H_{p}-C(b)$	-				i	2.35	2.79	3.02	
$H_{C} - C(b')$	1	27.83	28.29*	29.32	3	2.54	3.37	3.45	
$H_{D'}-C(b')$					2	2.46	2.62	2.81	

Table 1. Assignment of ¹H- and ¹³C-NMR Chemical Shifts^a)

^a) In CD₂Cl₂; shift values marked by a star * are interchangeable within primed and non-primed atom positions; values in parentheses are not assignable undoubtedly.

^b) See *Fig. 1*: arbitrary atom numbering.

^c) See *Figs. 2* and *3*: italic numbering for signal position in the spectra.

(*Figs. 2* and 3). But Ph protons are concentrated in a narrow shift range to give a total of 22 nonequivalent aromatic protons. A similar situation is found in the ¹³C-NMR spectrum (*Figs. 2* and 3): all 34 aromatic C-resonances appear between 112 and 155 ppm. Additional aid for the assignment are splitting patterns observed due to ³¹P,¹³C coupling and comparison of coupling constants in 5–7. Splittings due to ³¹P were identified by running *J*-modulated ¹³C-NMR spectra at different frequencies (62.9 MHz (*AC-250 F*) or 100 MHz (*AM-400 WB*)) and in a ³¹P,¹H-decoupled mode. The assignment of the 'diphosphine subunit' was supported from comparison with *trans*-1,2-phenylenebis-[methyl(phenyl)phosphine] [2]¹).

The following assignment of all resonances of the binaphthyl unit and the C_2H_4 fragments and in part of the Ph C- and H-signals (*Table 1*) was possible by 2D NMR methods, supplemented by NOE and decoupling experiments. An additional ³¹P,¹H-shift



¹³C-NMR Shift values of 1,2-phenylenebis[methyl(phenyl)phosphine] reported in [2] (numbering corresponding to *Fig. 1*) 147.6 (C(9)); 133.2 (C(10)); 130.8 (C(11)); 142.8 (C(12)); 134.0 (C(13)); 130.1 (C(14)); 128.9 (C(15)).



Fig. 3. ¹³C, ¹H Long-range shift correlation of 5

correlation revealed P–CH₂(b)–CH₂(a)–O connectivities. The problem arising during our work was the difficulty to establish connectivities across P-atoms. Since long-range ¹³C,¹H-COSY experiments gave only an incomplete assignment in this region, ³¹P,¹³C-COSY experiments were performed in addition which proved to be successful in the case of **5**. In the case of **6** and **7**, the situation appeared to be less satisfying as the poor solubilities required extreme spectrometer time and became a main handicap. So the connectivities of the aromatic units with one of the spacer groups could not be established with certainty, and some of the assignments are, therefore, exchangeable (see *Table 1*). A detailed procedure is exemplified below for ligand **5**. Selected coupling constants and ³¹P-shift values are given in *Tables 2* and *3*, respectively.

Table 2. ³¹ P-NMR Data									
	5	6	7		5	6	7		
$\delta(\mathbf{P})$	-22.41	55.08	64.20	Δδ	11.08	1.59	0.89		
$\delta(\mathbf{P}')$	-33.49	56.67	65.09	$J(\mathbf{P},\mathbf{P})$ [Hz]	129	74.2	15.3		

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	5	6	7		5	6	7
$\overline{J(A,B)}$	-11.0	-10.0	-10.0	J(A',B')	a)	-12.0	-11.5
J(A,C)	3.5	2.9	2.5	J(A',C')	9.0	5.5	4.5
J(A,D)	11.7	11.2	11.0	J(A',D')	4.2	6.2	6.5
J(B,C)	11.3	3.0	3.0	J(B',C')	4.5	7.5	7.1
J(B,D)	6.5	4.5	4.2	J(B',D')	9.6	4.5	4.3
J(C,D)	-14.0	-15.0	-15.4	J(C',D')	a)	15.0	-15.0
$J(\mathbf{P},\mathbf{C}(\mathbf{a}))$	36.3, 3.4	2.0	2.0	$J(\mathbf{P},\mathbf{C}(\mathbf{a}'))$	6.4	3.5	3.7
$J(\mathbf{P},\mathbf{C}(\mathbf{b}))$	11.8, 11.8	18.5	10.1	$J(\mathbf{P},\mathbf{C}(\mathbf{b}'))$	18.1, 4.3	17.5	10.7
$J(\mathbf{P}, \mathbf{C}(9))$	27.6, 15.3	50, 38	54.5, 36.8	$J(\mathbf{P},\mathbf{C}(9'))$	35.4, 15.2	50, 38	53.2, 37.5
J(P,C(10))	9.3	6, 1.5	19.0, 3.7	J(P,C(10'))	~<	6, 1.5	19.7, 2.8
J(P,C(11))	0.0	15.6, 1.5	7.9, 1.5	J(P,C(11'))	0.0	15.6, 1.5	7.0, 1.5
J(P,C(12))	14.1, 10.8	ca. 50	55.0	J(P,C(12'))	15.0, 3.5	ca. 50	54.0
J(P,C(13))	15.6	9.5	11.0	J(P,C(13'))	20.8	9.5	11.0
J(P,C(14))	8.0	10.8	4.0	J(P,C(14'))	6.9	10.8	4.0
J(P,C(15))	0.0	2.8	3.0	J(P,C(15'))	0.0	2.8	3.0
^a) Not esti	mated.						

Table 3. Selected Coupling Constants J [Hz]

Aliphatic Range of 5: Eight, partially well resolved m's are observed in the ¹H-NMR between 2.3 and 4.6 ppm, corresponding to 2 *ABCDX* systems of the OCH₂CH₂P segments (*1–8*; see *Table 1*, *Footnote c*, for italic numbering). The 2 five-spin systems are easily identified by ¹H,¹H- and ³¹P,¹H-COSY experiments (see below) and show relationships of signals 1, 4, 6, 8 and 2, 3, 5, 7. ¹³C,¹H-Shift correlation reveals geminal protons 1/4, 2/3, 5/7, and 6/8. Shift differences of methylene C-atoms (3 and 4 relative to 1 and 2) permit an unambiguous assignment of 6/8(H) at 4(C) and 5/7(H) at 3(C) attached to O, but 1/4(H) at 2(C) and 2/3(H) at 1(C) attached to P. The correlation via O to C(2) is found by a long-range ¹³C,¹H-COSY experiment which shows 6/8(H)–O–37(C). ³¹P,¹H Shift correlation shows P (-22.41 ppm) at 2(C) and P' (-33.49 ppm) at 1(C).

Aromatic Range of 5: H-C(3)/H-C(4) and H-C(3')/H-C(4') constitute 2 AB systems (J = 9 Hz) which give cross-peaks 16 (H)/21 (H) and 12 (H)/19 (H). Their assignment to one of the naphthalene halfes is enlightened by the long-range COSY experiment; cross-peaks 21 (H)/37 (C) and 19 (H)/36 (C) are observed. Further assignments of signals due to the binaphthyl system, including quaternary C, are established on the basis of direct and long-range ^{13}C , ¹H-COSY experiments: 21 (H)/24 (C) (H-C(4), C(4)); 16 (H)/7 (C) (H-C(3), C(3)); 19 (H)/22 (C) (H-C(4'), C(4')); 12 (H)/5 (C) (H-C(3'), C(3')). The expected long-range relationships H-C(5), H-C(4), H-C(7)/C(8a), H-C(3), H-C(6), H-C(8)/C(4a), and H-C(3)/C(1) are found, and the four-spin system H-C(5), H-C(6), H-

The assignment of aromatic C-atoms attached to P is difficult. The J-modulated ¹³C-NMR shows 4 quaternary C-atoms as dd's 32, 33, 34, and 35(C), 33 and 35 with a comparably large J(P,C) of ca. 30 Hz. As the connectivities of the Ph rings with the primed and non-primed P-atoms can not be established by a long-range ¹³C, ¹H-COSY experiment with certainty, two ³¹P, ¹³C-shift correlations are conducted for different J(P,C) (Fig. 4), thus revealing the following assignments: *i*) Cross-peaks of P and P' with C(a), C(b) and C(a'), C(b'), respectively, confirm the previous assignment by ³¹P, ¹H-shift correlation. *ii*) Further cross-peaks are found for the C_o 's (31(C)) and C_m 's (20(C)) with P and 26(C) and 18(C) with P', respectively, thus allowing the assignment to C(13), C(14) and C(13'), C(14'), respectively. Moreover, the C_o 's of the bridging phenylene group can be assigned; 28(C) to C(10) and 27(C) to C(10'), their relation to H-C(10) and H-C(10') is found by the C,H-COSY spectrum (12(H) at 7.25 ppm and 9(H)). H-C(11') is located in the *m*11(H) both from the ¹H, ¹H-COSY spectrum (H-C(10')) and by a long-range relationship 11(H)/28(C). From H(11') also C(11') (isochronous with C(15), 23(C)) is identified. Another long-range relationship is found between H-C(13)/H-C(13') and 23(C)/15(C), thus identifying the latter as C(15'), respectively. The last signal of a CH group remaining unidentified is 19(C) which is obviously due to C(11'). The corresponding H-atom cannot be located exactly in the *m*12(H).

Naturally, the assignment of the quaternary C-atoms attached to P is difficult because of their low intensity and ³¹P, ¹³C splitting. The *m* 32(C) shows a long-range relation to 1(H) and 4(H) and is, therefore, assigned to C(12). An analog relation of 34(C) to 2(H) and 3(H) gives C(12'). No cross-peak with H-C(14) is detected. Finally 33(C) is identified as C(9) from a cross-peak with H-C(10') (9(H)).



Fig. 4. ³¹*P*, ¹³*C*-Shift correlation of **5**: a) ${}^{1}J(P,C) = 35 Hz$; b) ${}^{1}J(P,C) = 10 Hz$

Similar procedures permitted the assignments of both ¹H and ¹³C resonances for 6 and 7 with some limitations (Table 1). The most striking difference in the spectra between ligand and complexes is the enforcement of a C_s -symmetrical array of the diphosphine subunit caused by formation of a five-membered chelate structure. This resulted in nearly identical J(P,C) and very similar $\delta(H)$ and $\delta(C)$ values for primed and non-primed atoms. As signals due to the binaphthyl skeleton remained unshifted, we conclude that the biaryl angle is altered only slightly upon complexation. Consequently, a steric strain caused by the complexation and the anisotropic interaction of the MCl₂ fragment will affect the geometry and 'H resonances significantly. A dramatic change of the coupling constants and an increased outspreading of the shift values of the aliphatic protons from 2.46-4.55 to 2.62-5.83 (2.81-5.70) ppm was observed. J(H,H)'s of the CH₂CH₂ fragments were estimated from ${}^{1}H{}^{31}P{}$ spectra. With respect to the supposed deformation of the sp³ geometry by steric strain, no attempts were made to describe their conformation by applying the Karplus equation. Moreover, selected J(P,C) values are given in Table 3 which also seem to be highly sensitive to geometrical changes. Although it appears clearly that there will exist a relationship between the size (and sign) of J(P,C) and the torsional angle H_2C-P [3], no attempt of a quantitative interpretation is made at present, since there are not enough similar structures for an extensive comparative study at the time.

Further investigations on the geometry of macrocyclic diphosphines and their transition-metal complexes using 2D NMR techniques, especially NOESY experiments, are under progress and will be compared to results from X-ray structure determinations and molecular-mechanics calculations.

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Experimental Part

General. Tosyl chloride (TsCl) was recrystallized from petroleum ether. Pyridine was filtered over alumina (act. I) and stored over molecular sieves (4 Å). Tetrahydrofuran (THF) and Et₂O were distilled from LiAlH₄. All other chemicals were of anal. grade and used without further purification. The 1,2-phenylenebis(phenylphosphine) was prepared in three steps starting from 1-bromo-2-chlorobenzene and dichlorophenylphosphine according to [4]. M.p.: *Kofler* melting-point apparatus; uncorrected. NMR Spectra: solns. of **2–4** in CDCl₃; *Bruker-AC-250-F* spectrometer; chemical shifts δ in ppm rel. to internal Me₄Si (¹H,¹³C) or external 85% H₃PO₄ soln. (³¹P), *J* in Hz. MS (*m*/*z* (rel. %)): *Varian MAT-CH7*; high resolution (HR) by using the 'preselected peak-matching method' where the *M*⁺ peak was found to be in agreement with the calulated mol. mass for an isotopically pure compound (error ≤ 2 ppm).

NMR Experiments with 5-7. At 300 K in 5-mm tubes, CD_2Cl_2 (and $CDCl_3$ for 5) solns.; *Bruker-AC-250-F* and a *Bruker-AM-400-WB* spectrometers (for details, see below). Sample concentrations were *ca.* 15 mM for 5, but only *ca.* 2.5 mM for 6 and 7 due to their low solubility. For the ¹H{³¹P} and ¹³C{¹H, ³¹P} experiments, an external synthesizer generating the appropriate P frequencies (*B-SV 3 BX*) and a probehead designed specifically for ¹H, ¹³C, ³¹P triple resonance experiments were employed. Long-time stability was achieved by a deuterium-lock channel and exact temp. control (*AC 250 F: B-VT 2000; AM 400 WB: B-VT 1000*). With the exception of reverse-detected experiments, samples were spun with *ca.* 20 Hz (*AM 400 WB*) or 40 Hz (*AC 250 F*), resp. All 2D spectra except the long-range ³¹P, ¹H-COSY experiment were recorded in the phase-sensitive mode using the TPPI method [5]. Data were processed on the *Aspect 3000* computer of the 250-MHz spectrometer, on a work station (*Bruker Aspect X32*) using the UXNMR software [6], and on PC-level computers running the WIN-NMR software package [7].

Standard 1D ¹H experiment (250.13 MHz): sweep width 4.5 kHz; 32 K data points; no filter function.

J-Modulated 1D ¹³C experiment (SEFT, [8]; 62.9 MHz): sweep width 16 kHz; 64 K data points; relaxation delay 3 s; pulse width ($\pi/2$) 5.6 µs; filter function, exponential weighting; line broadening factor 2 Hz.

Standard 1D ³¹P experiment (161.98 MHz): sweep width 18.5 kHz; 64 K data points; filter function, exponential weighting; line broadening factor 1 Hz.

 1 H{ 31 P} Experiment (400.13 MHz): sweep width 4.5 kHz; 32 K data points; 31 P decoupling power 2 W; filter function, exponential weighting; line broadening factor 0.3 Hz.

 $^{13}C{^{1}H, ^{31}P}$ Experiment (100.62 MHz): sweep width 23.8 kHz; 64 K data points; relaxation delay 5 s; ^{31}P decoupling power 3 W; filter function, exponential weighting; line-broadening factor 1 Hz.

Double-quantum filtered ¹H, ¹H-COSY [5] (250.13 MHz): sweep width 1.8 kHz; 2 K data points in ω_2 , 512 experiments in ω_1 (16 scans); relaxation delay 3 s; pulse width ($\pi/2$) 5.9 µs; zero filling 2 K × 2 K data points (real); filter function, sine bell squared shifted by $\pi/2$ rad in both dimensions.

Reverse ¹³C, ¹H-COSY with BIRD sandwich for main signal suppression and ¹³C decoupling during acquisition (400.13 MHz) [9]: sweep width 2.6 kHz in ω_1 , 0.7 kHz in ω_2 ; 1 K data points in ω_2 , 512 experiments in ω_1 (16 scans); relaxation delay 2 s; BIRD delay 0.8 s; pulse width ($\pi/2$) 14 µs (¹H), 5 µs (¹³C); zero filling, 2 K × 1 K data points (real); filter function, sine bell squared shifted by $\pi/2$ rad in both dimensions. Similar experiments were conducted for the aliphatic and aromatic region.

Long-range reverse ¹³C, ¹H-COSY with low-pass *J*-filter to suppress one-bond correlations (400.13 MHz) [10]: sweep width 13.5 kHz in ω_1 , 2.5 kHz in ω_2 ; 2 K data points in ω_2 , 128 experiments in ω_1 (32 scans); relaxation delay 2.5 s; pulse width ($\pi/2$) 14 µs (¹H), 5 µs (¹³C); delay for evolution of long-range couplings 66 ms (optimized for *J*(C,H) = 7.5 Hz); zero filling 512 data points (real) in ω_1 , no zero filling in ω_2 ; filter function, sine bell squared shifted by $\pi/2$ rad in both dimensions; magnitude representation.

Long-range reverse ³¹P,¹H-COSY (400.13 MHz) [10]: sweep width 3 kHz in both dimensions; 4 K data points in ω_2 , 256 experiments in ω_1 (80 scans); relaxation delay 1.9 s; pulse width ($\pi/2$), 11.2 µs (¹H), 10.5 µs (¹³C); delay for evolution of long-range couplings 62.5 ms (optimized for J(P,H) = 8 Hz [11]); zero filling, 1 K data points (real) in ω_1 , no zero filling in ω_2 ; filter function, sine bell squared shifted by $\pi/2$ rad in both dimensions; magnitude representation.

¹³C,³¹P-COSY Spectra were performed on the *AM*-400-*WB* spectrometer using a 10-mm ¹H, ¹³C, ³¹P tripletuned probehead and a second synthesizer together with an additional amplifier (*B*-SV 3 *BX*) to generate the ³¹P frequencies. From the different possible techniques to run ¹³C, ³¹P-COSY spectra [12], the HMQC experiment [13] was chosen, due to the limitations in the spectrometer hardware only under detection of the C-signals. The necessary phase switching of the ³¹P frequencies was done by RCP pulses together with a pulse inverter. ¹H-Decoupling was performed with composite pulses at a higher power level during the aquisition and a lower power level during the preparation period to generate NOE. Experimental parameters: sweep width 1.9 kHz in ω_1 , 13.5 kHz in ω_2 ; 2 K data points in ω_2 , 32 experiments in ω_1 (640 or 1920 scans); relaxation delay 3 s; ¹J(C,P) 35 or 10 Hz; pulse width ($\pi/2$) 17 µs (¹³C), 40 µs (³¹P); zero filling 256 data points in ω_1 , no zero filling in ω_2 ; filter function, exponential weighting with a line-broadening factor of 2 Hz; magnitude representation. The Ni and Pd complexes 6 and 7 failed to give ¹³C, ³¹P-COSY spectra in an acceptable time, for the reasons of *i*) their low solubility and *ii*) spectrometer hard- and software limitations (no power switching of the ³¹P frequencies and, therefore, no ³¹P decoupling during the acquisition could be performed; no phase-sensitive detection in ω_1 was possible).

Diethyl 2,2'-(1,1'-Binaphthalene-2,2'-diyloxy)bis(acetate) (2). To a soln. of 1,1'-binaphthalene-2,2'-diol (1; 5.72 g, 20 mmol) in dry THF (200 ml), KO'Bu (4.60 g, 41 mmol) was added and the stirred mixture heated to reflux under Ar for a few min to ensure complete conversion to the dipotassium salt. The slurry containing a cream-colored precipitate was cooled to r.t. and ethyl chloroacetate (5.02 g, 41 mmol) was introduced by syringe. The mixture was refluxed for 20–24 h. Precipitated KBr was separated and washed with CH₂Cl₂, the filtrate evaporated, and the residue dissolved in 200 ml of CH₂Cl₂. The soln. was washed with H₂O and brine, dried (Na₂SO₄), and evaporated. The crude oil was further purified by column chromatography (SiO₂, column 40 × 4 cm, AcOEt/ petroleum ether 15:85 to 30:70): **2** (81 %). Crystalline solid. M.p. 100–106°. ¹H-NMR: 1.16 (t, J = 7.1, 6 H); 4.11 (q, J = 7.1, 4 H); 4.55 (s, 4 H); 7.15–7.30 (m, 4 H); 7.30–7.40 (m, 4 H); 7.86 (d, J = 8.1, 2 H); 7.95 (d, J = 9, 2 H). MS (160°): 458 (29), 385 (4), 372 (6), 297 (18), 281 (50), 268 (45), 255 (10), 239 (19), 233 (16). HR-MS: 458.172650 (C₂₈H₂₆O₆, calc. 458.172940).

2,2'-(1,1'-Binaphthalene-2,2'-diyloxy)bis(ethanol) (3). A soln. of 2 (6.87 g, 15 mmol) in abs. Et₂O (50 ml) was added dropwise to an ice-cooled suspension of LiAlH₄ (2.0 g, 53 mmol) in Et₂O (200 ml) with stirring. Stirring was continued for 20 h at r.t., and the reaction was quenched by careful addition of H₂O (20 ml), followed by 6N HCl (50 ml; ice-bath). The org. layer was separated, the aq. phase extracted with Et₂O (2×50 ml), the combined org. extract washed successively with sat. NaHCO₃ soln. and H₂O, dried (Na₂SO₄), and evaporated, and the crude diol

chromatographed (SiO₂, column 30 × 4 cm, AcOEt): **3** (59%). Crystalline solid. M.p. 110–112° ([14]: 112–113°). ¹H-NMR: 2.31 (br. *s*, 2 H); 3.56 (*m*, 4 H); 4.20, 4.00 (*m*, 2 × 2 H); 7.12 (br. *d*, J = 8, 2 H); 7.24 (*ddd*, J = 8, 7, 1.5, 2 H); 7.35 (*ddd*, J = 7, 8, 1.5, 2 H); 7.43 (*d*, J = 9, 2 H); 7.88 (*d*, J = 8, 2 H); 7.97 (*d*, J = 9, 2 H). MS (90°): 374 (100), 344 (4), 330 (32), 314 (1), 299 (4), 286 (75), 268 (28), 239 (30). HR-MS: 374.151175 (C₂₄H₂₂O₄, calc. 374.151810).

2,2'-(1,1'-Binaphthalene-2,2'-diyloxy)bis(ethyl) Bis(toluene-4-sulfonate) (4). TsCl (9.15 g, 4 equiv.) was added to a soln. of **3** (4.49 g, 12 mmol) in dry pyridine (30 ml). The mixture was kept in a tightly stoppered flask in a refrigerator (2°) for 24 h, then poured into 200 ml of ice-water, and extracted with CH₂Cl₂ (3 × 100 ml). The combined extracts were washed with 6N HCl (50 ml) and H₂O (2 × 100 ml), dried (Na₂SO₄), and evaporated at r.t. The crude mixture of mono- and ditosylated product was separated by column chromatography (SiO₂, column 40 × 4 cm, CHCl₃): **4** (74%) as a viscous oil and small amounts of the corresponding monotosylate. **4**: ¹H-NMR: 2.32 (*s*, 6 H); 3.90, 4.27 (*m*, 2 × 2 H); 4.05, 4.15 (*m*, 2 × 2 H); 6.97 (*d*, J = 8.5, 4 H); 7.06 (br. *d*, J = 8.5, 2 H); 7.20 (*d*, J = 8.5, 4 H); 7.21 (*ddd*, J = 8, 7, 1.5, 2 H); 7.35 (*d*, J = 9, 2 H); 7.36 (*m*, 2 H); 7.88 (*d*, J = 8, 2 H); 7.93 (*d*, J = 9, 2 H). MS (250°): 682 (34), 509 (2), 369 (13), 312 (48), 269 (52). HR-MS: 682.169924 (C₃₈H₃₄O₈S₂, calc. 682.169516).

4,7-Diphenylbenzo[e]dinaphtho[2,1-k:1',2'-m]-1,10-dioxa-4,7-diphosphacyclotetradeca-5,11,13-triene (5). All operations were carried out under dry Ar, and all solvents were degassed prior to use. Solns. of 5 (1 mmol) in THF (10 ml) and of the dilithium salt of 1,2-phenylenebis(phenylphosphine) (1.2 mmol; from 353 mg of 1,2-phenylenebis(phenylphosphine) and 1.52 ml of 1.6M BuLi in hexane) in THF (8.5 ml) were prepared in *Schlenk* tubes. These solns. were added synchronously under high-dilution conditions to boiling THF (120 ml) within 1 h (the correct drop rate was easily adjusted as a significant color change to orange occurred upon a slight excess of unreacted dilithium salt). The solvent was distilled off and the residue partitioned between CH₂Cl₂ (200 ml) and H₂O (100 ml). The mixture was filtered over *Celite*, the org. layer dried (Na₂SO₄) and evaporated, and the crude pale yellow foam purified by crystallization or column chromatography (SiO₂, 60 × 2 cm, CH₂Cl₂/petroleum ether 1:1): 5 (71%). MS (270°): 632 (9), 603 (2), 575 (5), 552 (2), 527 (2), 499 (12), 477 (1), 449 (3), 347 (5), 320 (34), 286 (71). HR-MS: 632.203928 (C₄₂H₃₄O₂P₂, calc. 632.203406).

(4,7-Diphenylbenzof e]dinaphtho[2,1-k:1',2'-m]-1,10-dioxa-4,7-diphosphacyclotetradeca-5,11-13-triene)nickel(11) Dichloride (6). To a soln. of 5 (0.1 mmol) in CH₂Cl₂ (1 ml) was added a soln. of NiCl₂·6H₂O (23.8 mg, 0.1 mmol) in EtOH (2 ml). After a few min, the crystallization started, and the mixture was allowed to stand overnight. The crystalline precipitate was dried under vacuum: 6 (82%). Orange plates. Anal. calc. for C₄₂H₃₄Cl₂NiO₂P₂ (762.27): C 66.18, H 4.50, P 8.13; found: C 66.04, H 4.67, P 7.90.

(4,7-Diphenylbenzo[e]dinaphtho[2,1-k:1',2'-m]-1,10-dioxa-4,7-diphosphacyclotetradeca-5,11,13-triene)palladium(II) Dichloride (7). To a soln. of 5 (0.1 mmol) in CH₂Cl₂ (1 ml) was added a soln. of [PdCl₂(MeCN)₂] (38.5 mg, 0.1 mmol) in CH₂Cl₂ (2 ml). EtOH was added slowly and the precipitated product (cream to pale yellow) collected and dried in vacuum: 7 (70%). Anal. calc. for C₄₂H₃₄Cl₂O₂P₂Pd (810.00): C 62.28, H 4.23, P 7.65; found: C 62.46, H 4.24, P 7.70.

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