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,- ^{13}C-, and ^{31}P-NMR data on the basis of 2D NMR spectroscopy ($^1H,^1H$-, $^{13}C,^1H$-, $^{31}P,^1H$-, $^{31}P,^{13}C$-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 ^{13}C- 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

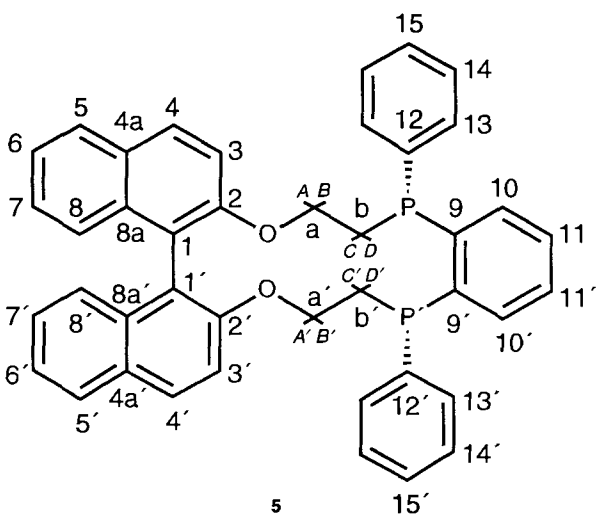

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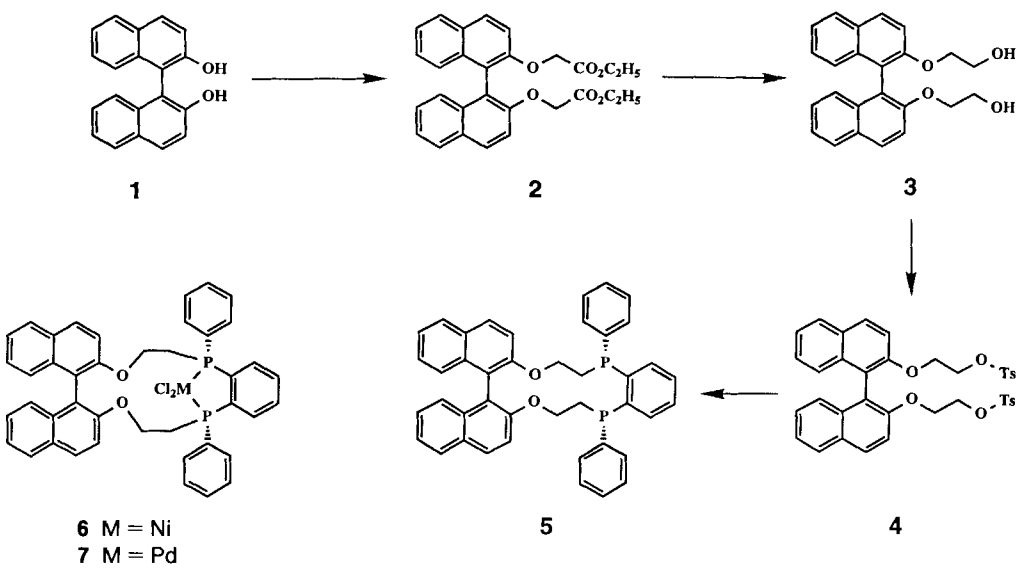
Fig. 1. *Numbering of macrocycle* **5** *and complexes* **6** *and* **7**

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 $LiAlH_4$ 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 $NiCl_2$ or $[PdCl_2(MeCN)_2]$, respectively, in CH_2Cl_2/EtOH.

Scheme



From **5** and its Ni^{II} and Pd^{II} complexes **6** and **7**, respectively, 1D and 2D ^1H-, ^{13}C-, and ^{31}P-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 $^{31}P,^{13}C$ coupling and the very narrow spectral range of the Ph C-atoms, this fact limited the information content of the ^{13}C-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

Table 1. *Assignment of ^{1}H- and ^{13}C-NMR Chemical Shifts*[a])

Atom[b])	Signal position[c])	^{13}C-NMR			Signal position[c])	^{1}H-NMR		
		5	**6**	**7**		**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
H–C(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_A–C(a)	*4*	71.73	65.94	65.89	*8*	4.55	5.83	5.70
H_B–C(a)					*6*	4.20	4.62	4.53
$H_{A'}$–C(a′)	*3*	64.52	67.45	67.12	*7*	4.37	4.60	4.20
$H_{B'}$–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_D–C(b)					*1*	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

[a]) In CD_2Cl_2; 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 ^{13}C-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 ^{31}P,^{13}C coupling and comparison of coupling constants in **5**–**7**. Splittings due to ^{31}P were identified by running *J*-modulated ^{13}C-NMR spectra at different frequencies (62.9 MHz (*AC-250 F*) or 100 MHz (*AM-400 WB*)) and in a ^{31}P,^{1}H-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 ^{31}P,^{1}H-shift

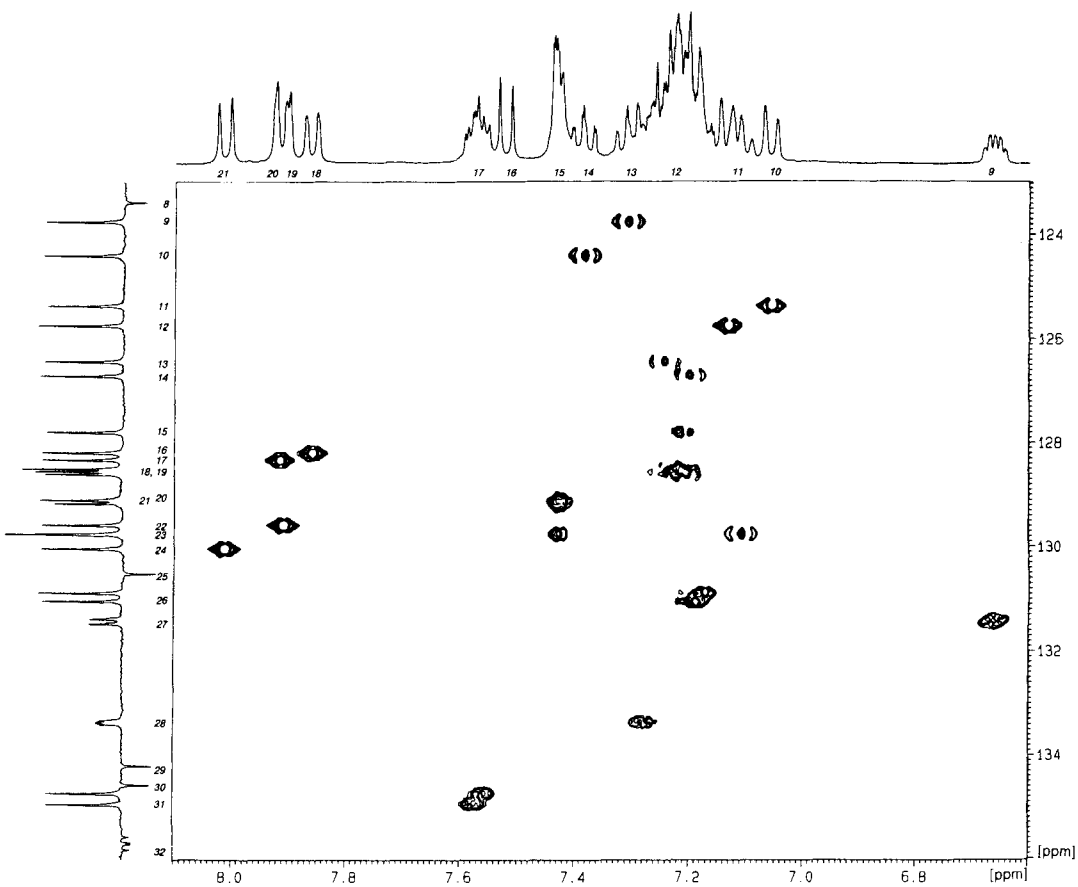


Fig. 2. *^{13}C,^{1}H-Shift correlation of* **5**

[1]) ^{13}C-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)).

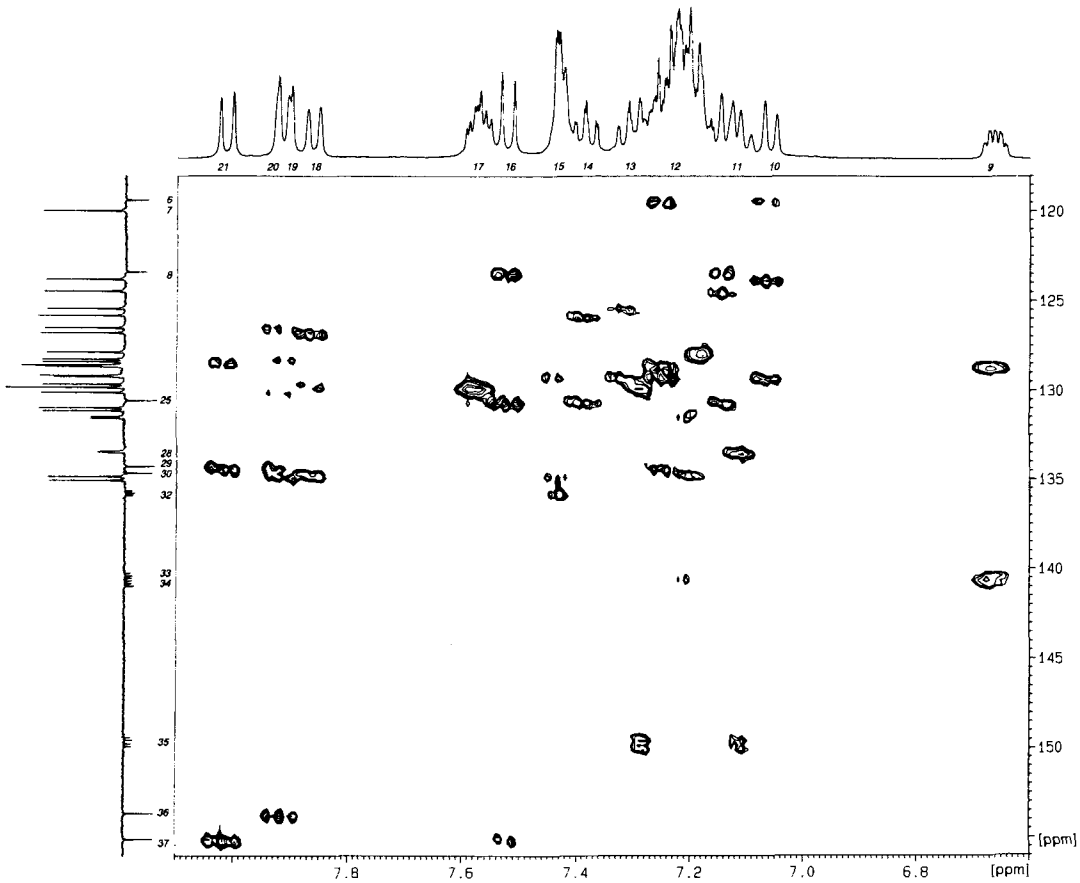


Fig. 3. *$^{13}C,^{1}H$ Long-range shift correlation of* **5**

correlation revealed P–CH_2(b)–CH_2(a)–O connectivities. The problem arising during our work was the difficulty to establish connectivities across P-atoms. Since long-range $^{13}C,^{1}H$-COSY experiments gave only an incomplete assignment in this region, $^{31}P,^{13}C$-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 ^{31}P-shift values are given in *Tables 2* and *3*, respectively.

Table 2. *^{31}P-NMR Data*

	5	**6**	**7**		**5**	**6**	**7**
δ(P)	–22.41	55.08	64.20	$\Delta\delta$	11.08	1.59	0.89
δ(P')	–33.49	56.67	65.09	J(P,P) [Hz]	129	74.2	15.3

Table 3. *Selected Coupling Constants* J [Hz]

	5	**6**	**7**		**5**	**6**	**7**
$J(A,B)$	−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(P,C(a))	36.3, 3.4	2.0	2.0	J(P,C(a'))	6.4	3.5	3.7
J(P,C(b))	11.8, 11.8	18.5	10.1	J(P,C(b'))	18.1, 4.3	17.5	10.7
J(P,C(9))	27.6, 15.3	50, 38	54.5, 36.8	J(P,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 estimated.

Aliphatic Range of **5**: Eight, partially well resolved *m*'s are observed in the ^{1}H-NMR between 2.3 and 4.6 ppm, corresponding to 2 *ABCDX* systems of the OCH_2CH_2P segments (*1–8*; see *Table 1*, *Footnote c*, for italic numbering). The 2 five-spin systems are easily identified by ^{1}H,^{1}H- and ^{31}P,^{1}H-COSY experiments (see below) and show relationships of signals *1*, *4*, *6*, *8* and *2*, *3*, *5*, *7*. ^{13}C,^{1}H-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 ^{13}C,^{1}H-COSY experiment which shows *6*/*8*(H)–O–*37*(C). ^{31}P,^{1}H 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,^{1}H-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*−C(7), *H*−C(8) is identified from the ^{1}H,^{1}H-COSY spectrum (correspondingly for the primed-atom positions).

The assignment of aromatic C-atoms attached to P is difficult. The J-modulated ^{13}C-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 ^{13}C,^{1}H-COSY experiment with certainty, two ^{31}P,^{13}C-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 ^{31}P,^{1}H-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 ^{1}H,^{1}H-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) and 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 ^{31}P,^{13}C 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)).

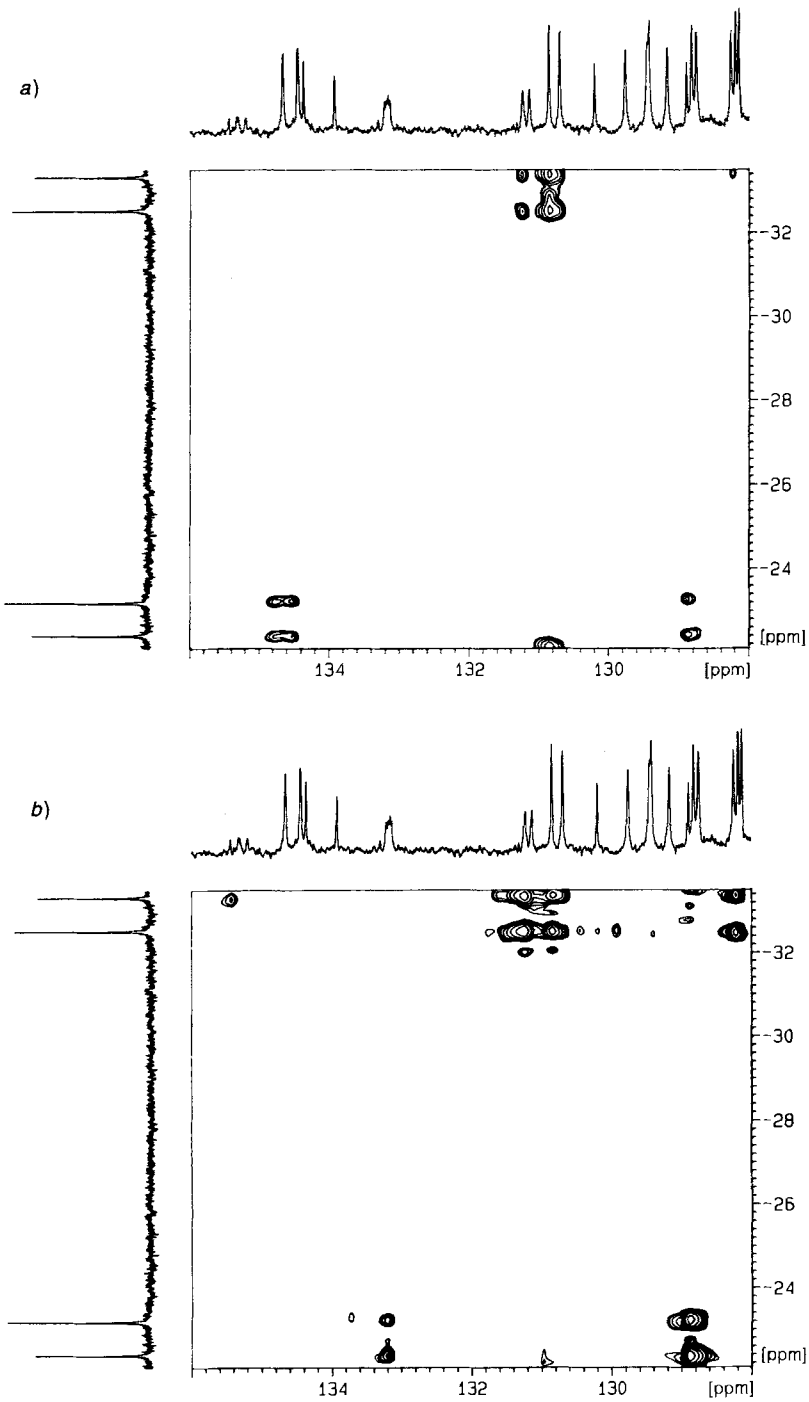


Fig. 4. *$^{31}P,^{13}C$-Shift correlation of* **5**: a) *$^{1}J(P,C) = 35$ Hz*; b) *$^{1}J(P,C) = 10$ Hz*

Similar procedures permitted the assignments of both ^1H and ^{13}C 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 δ(H) and δ(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 MCl_2 fragment will affect the geometry and ^1H 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 CH_2CH_2 fragments were estimated from $^1H\{^{31}P\}$spectra. With respect to the supposed deformation of the sp^3 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 Et_2O were distilled from $LiAlH_4$. 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 $CDCl_3$; *Bruker-AC-250-F* spectrometer; chemical shifts δ in ppm rel. to internal Me_4Si ($^1H,^{13}C$) or external 85% H_3PO_4 soln. (^{31}P), 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 $\leq$ 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 $^1H\{^{31}P\}$ and $^{13}C\{^1H,^{31}P\}$ experiments, an external synthesizer generating the appropriate P frequencies (*B-SV 3 BX*) and a probehead designed specifically for $^1H,^{13}C,^{31}P$ 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 $^{31}P,^1H$-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 ^{13}C 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 ^{31}P experiment (161.98 MHz): sweep width 18.5 kHz; 64 K data points; filter function, exponential weighting; line broadening factor 1 Hz.

$^1H\{^{31}P\}$ 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.

$^{13}C\{^1H,^{31}P\}$ 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 $^{13}C,^1H$-COSY with BIRD sandwich for main signal suppression and ^{13}C 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 (^{13}C); 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 $^{13}C,^1H$-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 (^{13}C); 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 $^{31}P,^1H$-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 (^{13}C); 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.

$^{13}C,^{31}P$-COSY Spectra were performed on the *AM-400-WB* spectrometer using a 10-mm $^1H,^{13}C,^{31}P$ triple-tuned probehead and a second synthesizer together with an additional amplifier (*B-SV 3 BX*) to generate the ^{31}P frequencies. From the different possible techniques to run $^{13}C,^{31}P$-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 ^{31}P 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 (^{13}C), 40 μs (^{31}P); 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 $^{13}C,^{31}P$-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 ^{31}P frequencies and, therefore, no ^{31}P 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^{t}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 CH_2Cl_2, the filtrate evaporated, and the residue dissolved in 200 ml of CH_2Cl_2. The soln. was washed with H_2O and brine, dried (Na_2SO_4), and evaporated. The crude oil was further purified by column chromatography (SiO_2, 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 ($C_{28}H_{26}O_6$, 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. Et_2O (50 ml) was added dropwise to an ice-cooled suspension of $LiAlH_4$ (2.0 g, 53 mmol) in Et_2O (200 ml) with stirring. Stirring was continued for 20 h at r.t., and the reaction was quenched by careful addition of H_2O (20 ml), followed by 6N HCl (50 ml; ice-bath). The org. layer was separated, the aq. phase extracted with Et_2O (2 × 50 ml), the combined org. extract washed successively with sat. $NaHCO_3$ soln. and H_2O, dried (Na_2SO_4), and evaporated, and the crude diol

chromatographed (SiO_2, column 30 × 4 cm, AcOEt): **3** (59%). Crystalline solid. M.p. 110–112° ([14]: 112–113°). ^{1}H-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 ($C_{24}H_{22}O_4$, 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 CH_2Cl_2 (3 × 100 ml). The combined extracts were washed with 6N HCl (50 ml) and H_2O (2 × 100 ml), dried (Na_2SO_4), and evaporated at r.t. The crude mixture of mono- and ditosylated product was separated by column chromatography (SiO_2, column 40 × 4 cm, $CHCl_3$): **4** (74%) as a viscous oil and small amounts of the corresponding monotosylate. **4**: ^{1}H-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 ($C_{38}H_{34}O_8S_2$, 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 CH_2Cl_2 (200 ml) and H_2O (100 ml). The mixture was filtered over *Celite*, the org. layer dried (Na_2SO_4) and evaporated, and the crude pale yellow foam purified by crystallization or column chromatography (SiO_2, 60 × 2 cm, CH_2Cl_2/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 ($C_{42}H_{34}O_2P_2$, calc. 632.203406).

(4,7-Diphenylbenzo[e]dinaphtho[2,1-k:1',2'-m]-1,10-dioxa-4,7-diphosphacyclotetradeca-5,11-13-triene)-nickel(II) Dichloride (**6**). To a soln. of **5** (0.1 mmol) in CH_2Cl_2 (1 ml) was added a soln. of $NiCl_2 \cdot 6H_2O$ (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 $C_{42}H_{34}Cl_2NiO_2P_2$ (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 CH_2Cl_2 (1 ml) was added a soln. of $[PdCl_2(MeCN)_2]$ (38.5 mg, 0.1 mmol) in CH_2Cl_2 (2 ml). EtOH was added slowly and the precipitated product (cream to pale yellow) collected and dried in vacuum: **7** (70%). Anal. calc. for $C_{42}H_{34}Cl_2O_2P_2Pd$ (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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