SYNTHESIS OF 17- AND 21- MEMBERED MACROCYCLES INCORPORATING THE CHIRAL 1,1´-BINAPHTHYL BACKBONE AND NITROGEN, OXYGEN, AND PHOSPHORUS DONOR ATOMS

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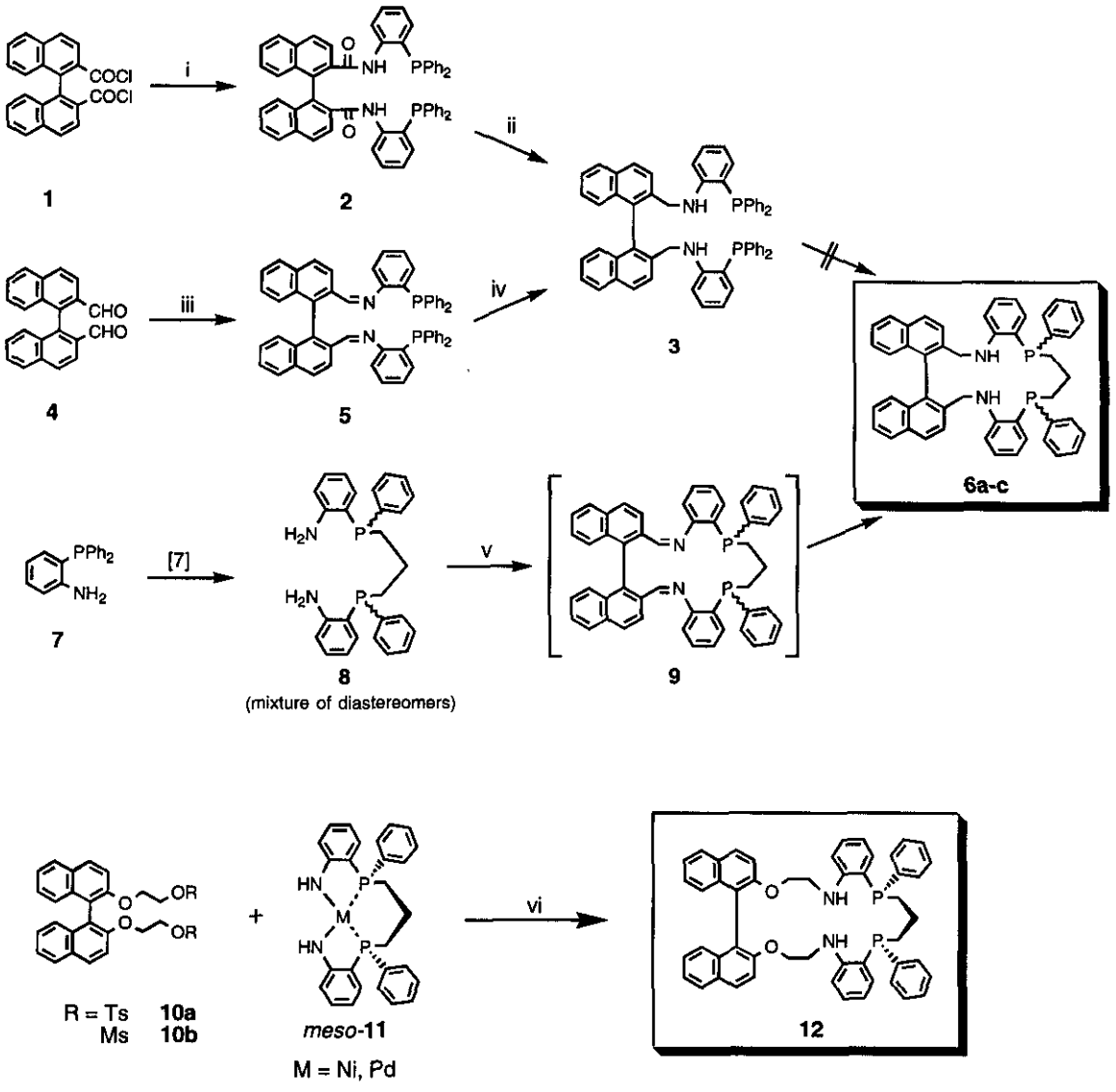
Abstract - A 17-membered diaza-diphospha- and a 21-membered diaza-dioxa-diphospha-macrocycle (**6**) and (**12**), respectively, including the inherent chiral binaphthyl moiety were synthesized. Titanium(IV) mediated cyclization of 1,1´-binaphthyl-2,2´-dicarbaldehyde (**4**) with 1,3-bis[(2-aminophenyl)phenyl-phosphino]propane (**8**) and subsequent reduction afforded **6a-c** as a mixture of three diastereomers in 14% overall yield. Ligand (**12**) was obtained from the nickel amido complex of **8** and 2,2'-bis[2-(4-toluene)sulfonyloxyethoxy]-1,1'-binaphthyl (**10a**) by a template synthesis in the presence of Cs_2CO_3 in 63% yield. X-Ray structure determinations of cationic Ni(II) complexes of **6a** and **12** were performed.

Ligands with phosphorus and/or nitrogen coordination sites have drawn progressive attention since their successful use in asymmetric catalysis.[1] An exceptionally useful ligand is 2,2´-bis(diphenylphosphino)-1,1´-binaphthyl (BINAP), an axially chiral diphosphine, which afforded nearly enantiopure products with

a large number of substrates in various reactions.[2] On the other hand there are numerous examples of asymmetric C-C coupling reactions employing chiral auxiliaries with phosphorus and nitrogen coordination sites.[3,4]



Scheme 1: i: **7** (2 equiv.), Et_3N (4 equiv.), toluene, 0°C; ii: $LiAlH_4$ (8.4 equiv.), $AlCl_3$ (2.1 equiv.), Et_2O/THF, 0°C; iii: **7** (2 equiv.), $TiCl_4$ (4 equiv.), Et_3N (30 equiv.), benzene, 0°C; iv: $LiAlH_4$ (5 equiv.), Et_2O, 0°C; v: a) **4** (1 equiv.), $Ti(i\text{-}PrO)_4$ (4-5 equiv.), benzene; b) $LiAlH_4$ (5 equiv.), Et_2O, 0°C; vi: Cs_2CO_3 (4 equiv.), toluene, reflux.

It seemed therefore reasonable to make further attempts to prepare suitable binaphthyl ligands, which contain phosphorus and nitrogen donor atoms. In continuation of our investigations on binaphthyl-based macrocyclic ligands,[5] we were interested in potentially tetraligating compounds like **6** and **12**, owing their chirality basically from a *N,N'*-spanning binaphthyl bridge. At the starting point of our efforts we tried to introduce an alkyl bridge between the two phosphorus atoms of the non-cyclic diaminodiphosphine (**3**) after selective abstraction of one phenyl ring from each phosphino group.[6] The key intermediate (**3**) was accessible either *via* the diamide (**2**) or diimine (**5**) in 28% and 51%, respectively, as outlined in Scheme 1. Unfortunately all attempts to prepare **6** *via* the dilithium diphosphide failed. Stirring of **3** with lithium metal under various conditions resulted in a color change, but subsequent treatment with water, methyl iodide or 1,3-dichloropropane afforded complex mixtures; no trace of the desired products could be detected. The synthesis of **6** was finally accomplished *via* the cyclic bisimine (**9**). The precursor (**8**) was prepared as a mixture of diastereoisomers (*meso:rac, ca.* 40:60) from (2-aminophenyl)diphenylphosphine after selective cleavage of one phenyl ring with lithium followed by reaction with 1,3-dichloropropane.[7] Repeated treatment of an equimolar mixture of **8** and 1,1'-binaphthyl-2,2'-biscarbaldehyde (**4**) in benzene with excess of titanium(IV) isopropoxide at room temperature afforded **9** after extractive workup as a mixture of three stereoisomers.[8] Since all attempts to purify **9** by adsorption chromatography resulted in decomposition, the crude material was used for the reduction to give **6** in 14% overall yield. The separation of the diastereomers (**6a-c**) was accomplished by column chromatography on deactivated silica gel. The C_1- and one of the C_2-symmetrical isomers were obtained in approximately equal amounts as crystalline products while a further isomer, **6c** (C_2 symmetry), was isolated only in traces and therefore is not fully characterized. Alternatively the reaction can be performed with *meso*- or *rac*-**8** thus facilitating the purification of the isomers. Only from the C_2 symmetrical isomer (**6a**) a Ni(II) complex could be isolated.

The macrocyclic ligand (**12**) was synthesized by a Cs_2CO_3 mediated alkylation of *meso*-**8** with the ditosylate (**10a**).[9] This reaction utilized the kinetic template effect of the neutral Ni(II) complex **11** which was accessible by deprotonation of the dicationic complex with triethylamine.[10] The synthesis of **8** and a

separation of stereoisomers by fractional crystallisation of Ni(II) and Pt(II) complexes have been reported briefly.[7] In our hands the alkylation of lithium (2-aminophenyl)phenylphosphide with 1,3-dichloropropane yielded 63% of **8** (*meso:rac* 45:55). This crude diastereomeric mixture was treated with $Ni(NO_3)_2 \cdot 6H_2O$ to deposit the desired cationic Ni(II) complex of *meso*-**8** which was deprotonated with Et_3N to give *meso*-**11**. On the other hand a separation of the stereoisomers (**8**) can be left undone since it was demonstrated that only the tetracoordinated Ni(II) complex of *meso*-**8**[7] is capable of forming *N,N´*-bridged compounds.[10a] *Rac*-**8** seems to form preferentially tricoordinated metal complexes[7] and is therefore not able to undergo facile cyclization reactions. Therefore alternatively the crude mixture of stereoisomeric Ni complexes of **8** can be precipitated with ether to give a reddish-brown powder which was used without purification in preliminary experiments. Numerous reaction conditions, including variation of the base, transition metal, solvent and reaction temperature have been tested. Alkali metal carbonates could bring up a significant conversion. The best result was obtained when a "Cs-effect" was operating,[9] while yields decreased with K^+ or Na^+; sodium acetate gave no product. The use of 2,2´-bis(2-methane-sulfonyloxyethoxy)-1,1´-binaphthyl (**10b**) instead of **10a** or CsF instead of Cs_2CO_3 did not improve the yield. The reaction in refluxing toluene was superior to that in benzene in a pressure tube (at 115°C); in DMF no reaction took place. The use of Pd instead of Ni showed no effect on reactivity and yield but the free ligand proved to be completely unreactive. Under optimized conditions the cyclization was run on a 100-800 mg scale in refluxing toluene under argon with **10a** (1 equiv.), *meso*- and *rac*-**11** (1 equiv.) and 4 equivalents of Cs_2CO_3. After 20-24 h no unreacted **11** and only a trace of **10a** could be detected. (A small portion of sample was shaken with a few drops of a KCN solution and the organic layer was analyzed by tlc; spots due to **12** and **8** could be colorized by dipping the tlc strip into a concentrated $NiCl_2$ solution in ethanol). After destroying the complexes with KCN the free ligands were isolated by size-exclusion chromatography on cross-linked polystyrene (Biorad S-X3®) in CH_2Cl_2. This method was found to be superior to adsorption chromatography on silica gel, since in the latter case an irreversible adsorption of phosphines was observed.[11] A typical chromatogram is depicted in Figure 1. The purified

cycle showed the expected C_1 symmetry; no trace of the C_2-symmetrical isomer could be detected (nmr). From some unresolved bands eluted shortly after the dead volume only one poorly characterized product with C_2 symmetry (^{13}C nmr) and molecular weight 1563±1 (FAB-ms) could be isolated in 6-10% yield. Further attempts to purify this "dimeric" species remained unsuccessful. Ligand (**12**) was isolated as a white foam and could be stored at -20°C for months without significant decomposition. If the synthesis started from pure *meso*-**8** the macrocycle (**12**) was obtained in 63% yield.

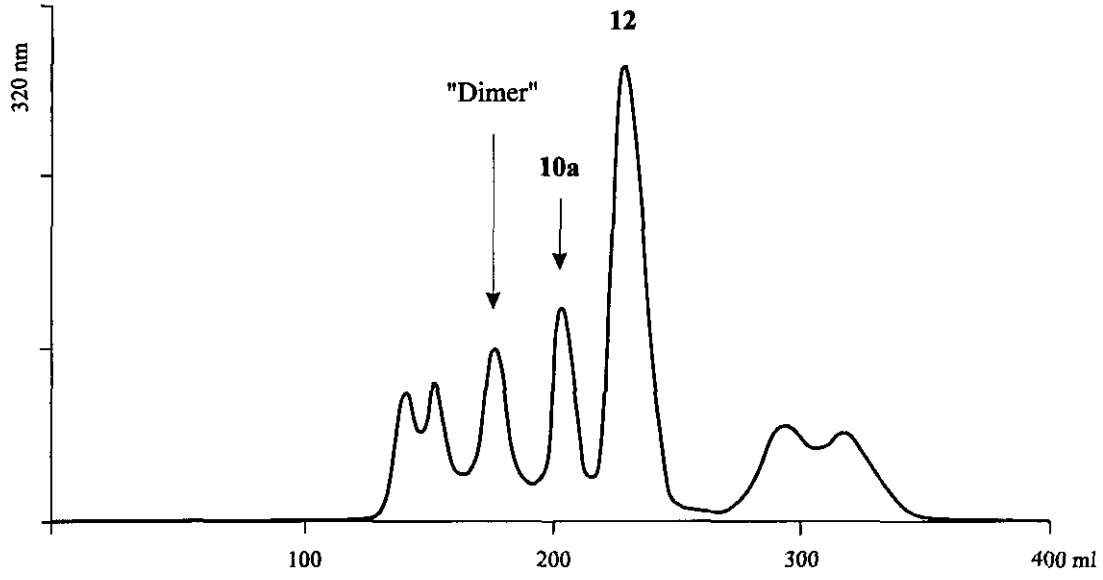


Figure 1: Chromatographic purification of **12** on swollen polystyrene (3% DVB), 37-74 µm, column: 76 x 2.5 cm, CH_2Cl_2, v = 58 ml h^{-1}, sample size: *ca.* 200 mg per run.

A Ni(II) complex of **12** was prepared by mixing concentrated equimolar solutions of **12** (in CH_2Cl_2) and $NiCl_2 \cdot 6H_2O$ (in ethanol). Slow condensation of Et_2O into the dark orange solution resulted in crystallization of the complex (**12**·$NiCl_2$) as orange prisms. The product was soluble in MeOH (or EtOH) / CH_2Cl_2 (9:1), only slightly soluble in CH_2Cl_2 or $CHCl_3$, and insoluble in Et_2O. FAB-ms pointed to a cationic species which is easily deprotonated [873, M^+ (-Cl^-), 837 (-HCl)]. No nmr spectra with acceptable resolution could be obtained.

Crystal structure analyses: X-Ray structure analyses of Ni complexes (**6a**·$NiCl_2$) and (**12**·$NiCl_2$) were finally performed in order to confirm the proposed structures and to determine the conformation and

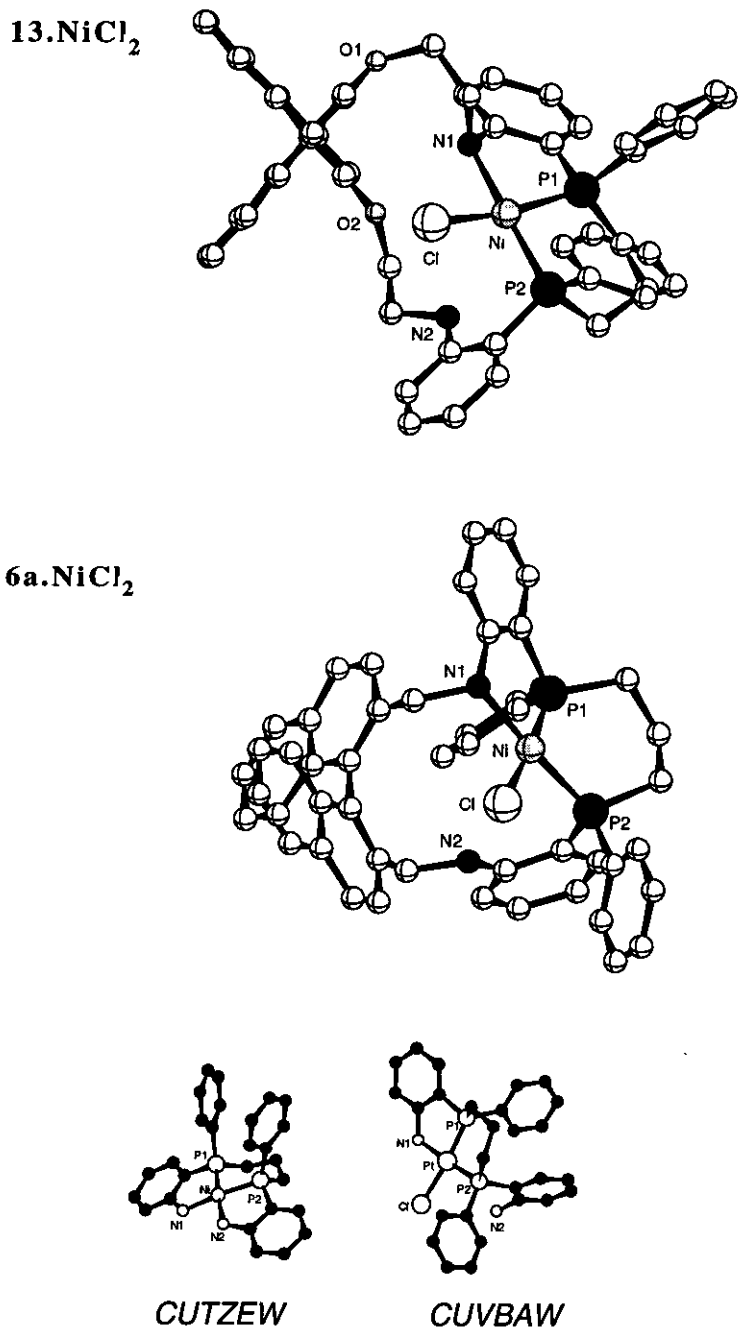


Figure 2: Crystal structures of Ni(II) complexes of **6a** and **13** (top) and similar structures with *REFCODES* from a *CSD* connectivity search (bottom).

geometry of the complexes (Figure 2). The Ni(II) complex (**12**·$NiCl_2$) is tetracoordinated at both phosphorus atoms, one nitrogen atom, and one chlorine atom forming a distorted square-planar array. A connectivity search for similar structures in the *Cambridge Structural Database* yielded two hits; a dicationic Ni complex of *meso*-**8** (*CUTZEW*) and a Pt complex of *rac*-**8** (*CUVBAW*). The Pt complex of *rac*-**8** showed very similar geometric features despite of its different relative configuration at phosphorus atoms [(S,S)/(R,R)-**8** *vs.* (R,S)-**12**]. In both structures the MP_2C_3 array adopts a chair conformation. This supports the assumption of no additional steric strain in the cyclic compound (**12**) merely a pronounced out-of-plane distortion of the chlorine atom in **12**·$NiCl_2$ by 0.507 Å below the Ni-P-P-N plane is obviously caused by the proximity of the uncomplexed nitrogen atom.

For **6a**·$NiCl_2$ a similar crystal structure was found. Unfortunately these crystals included a large quantity of disordered solvent (probably Et_2O) thus resulting in a rather poor quality of the obtained structure (R = 0.112). Despite of this some general geometric features became apparent. Although the relative configuration of phosphorus atoms has changed the geometric similarity of the complexes is evident. The relative configuration was established to be $(R)_{axial}(R,R)_P$ (and $(S)_{axial}(S,S)_P$ for the enantiomer, respectively). The square-planar array of the cationic Ni complex (**6a**·$NiCl_2$) is even less distorted than in the case of **12**·$NiCl_2$ and a potential steric strain caused by the reduction of the ring size is compensated both by an opening of the biaryl angle from 98.7° (**12**·$NiCl_2$) to 106.7°(**6a**·$NiCl_2$) and by an "out-of-ligand-center" torsion of the Ni complex moiety.

It is planned to extend this synthetic concept to homologes of **12** to obtain chiral transition metal complexes with varying distance between chiral unit and metal center. In forthcoming experiments their use in asymmetric catalysis will be investigated.

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

Melting points: Kofler Heiztisch-Mikroskop, uncorrected; nmr: AC 250 F, AM 400 WB (Bruker); unless otherwise noted spectra were recorded in $CDCl_3$ at 400.1 MHz (^1H), 100.6 (^{13}C, *J*-modulated), and 162.0 MHz (^{31}P, proton decoupled), respectively. Chemical shifts δ are given relative to TMS (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). In ^{13}C nmr spectra *J* refers to phosphorus-carbon-coupling constants which were identified by comparison of spectra recorded at 62.9 and 100.6 MHz. In areas of extensive signal overlapping no assignment could be made; these CH-signals of unclear relationship are underlined ignoring multiplet patterns. Ms: Varian MAT-CH7; polarimeter: Perkin-Elmer Polarimeter 241 (1 dm, thermostated); elemental analyses: *Mikroanalytisches Laboratorium der Universität Wien*. THF was distilled from potassium benzophenone ketyl, Et_2O from $LiAlH_4$. Petroleum ether (PE, bp 60-70°C) was used as purchased; ethyl acetate (AcOEt), CH_2Cl_2, chlorodiphenylphosphine, $TiCl_4$ and mesyl chloride were distilled. All the other chemicals were analytical grade. Tlc: aluminium sheets, silica gel 60, F_{254} (Merck). Adsorption chromatography: silica gel 60, 230-400 mesh ASTM (Merck); For the size-exclusion chromatography cross-linked polystyrene was used (3% divinylbenzene; Bio-Beads® S-X3, 200-400 mesh, (Bio Rad), column: 2.5 x 75 cm. Reactions of organolithium compounds were performed under a dry atmosphere of Ar using Schlenk technique. The Ni complex (**11**) was prepared as outlined in ref. 7; the following compounds have been described elsewhere: **1**,[12] **4**,[13] **7**,[14] **10a**.[5b]

2,2'-Bis[N-(2-diphenylphosphinophenyl)aminocarbonyl]-1,1'-binaphthyl (**2**): To a solution from 2.90 g (10.5 mmol) of (2-aminophenyl)diphenylphosphine (**7**) and 2.9 ml (20.8 mmol) of triethylamine in 100 ml of toluene was added 1.99 g (5.2 mmol) of **1** in portions at 0°C. After stirring for 2 h in an ice bath the conversion was complete. Extractive workup (CH_2Cl_2) yielded a yellow foam which was purified by column chromatography (SiO_2, PE/AcOEt 75:25→60:40) to yield 2.54 g (56%) of **2** as a foam; ^1H nmr: δ 6.80 (ddd, 2H, *J* 1.4, 4.4, 7.6 Hz), 6.92 (dt, 2H, *J* 1.1, 7.5 Hz), 7.07-7.40 (m, 32H), 7.82 (d, 2H, *J* 8.2 Hz), 7.85 (d, 2H, *J* 8.5 Hz), 9.16 (d, 2H, *J* 5.2 Hz); ^{13}C nmr: δ 123.23 (CH, d, *J* 2 Hz), 123.52 (CH), 125.10 (CH), 126.51 (CH), 127.04 (CH), 127.11 (CH), 127.89 (CH), 128.27 (C, d, *J* 13 Hz), 128.51 (4CH, d, *J* 7

Hz), 128.77 (3CH), 129.79 (CH), 132.28 (C), 133.57 (2CH, d, *J* 19 Hz), 133.64 (2CH, d, *J* 19 Hz), 133.79 (C), 133.93 (CH), 134.04 (C), 134.61 (C), 135.55 (C, d, *J* 9 Hz), 135.56 (C, d, *J* 9 Hz), 140.99 (C, d, *J* 21 Hz), 168.20 (C); ^{31}P nmr: δ -19.8 (s); ms (300°C): 862 (M^+, 42%); Anal. Calcd for $C_{58}H_{42}N_2O_2P_2$: C 80.92, H 4.92, N 3.25. Found: C 80.67, H 5.14, N 3.04.

2,2'-Bis[N-(2-diphenylphosphinophenyl)iminomethyl]-1,1'-binaphthyl (**5**): A suspension from 1.00 g (3.2 mmol) of 1,1'-binaphthyl-2,2'-dicarbaldehyde (**4**), 1.79 g (6.5mmol) of (2-aminophenyl)diphenylphosphine (**7**), and 13 ml (93mmol) of triethylamine in 30 ml of benzene was degassed and cooled to 0°C. A solution of 0.71 ml (6.5mmol) of $TiCl_4$ in 15 ml of benzene was added dropwise during 0.5 h to give a dark purple precipitate. After stirring for 1 h at 0°C the reaction mixture was worked up under Ar using degassed solvents. Water was added and the precipitate was removed by filtration over celite. The precipitate was repeatedly extracted with CH_2Cl_2 and the organic layer was separated, washed with water and dried with Na_2SO_4. Concentration of the solvent mixture left 2.51g (94%) of crude **5** which was used in the following reduction without further purification. A small portion of sample was filtered over SiO_2 and crystallized from CH_2Cl_2/PE; mp 230-232°C; ^{1}H nmr: δ 6.29 (ddd, 2H, *J* 1.0, 4.4, 7.9 Hz), 6.69 (ddd, 2H, *J* 1.5, 4.4, 7.9 Hz), 6.94 (d, 2H, *J* 8.4 Hz), 6.98 (t, 2H, *J* 7.6 Hz), 7.08-7.29 (m, 24H), 7.49 (ddd, 2H, *J* 1.0, 8.1, 8.4 Hz), 7.64 (s, 2H), 7.90 (d, 2H, *J* 6.9 Hz), 7.91 (d, 2H, *J* 8.4 Hz), 8.23 (d, 2H, *J* 8.9 Hz); ^{13}C nmr: δ 116.92 (CH), 123.50 (CH), 126.07 (CH), 126.88 (CH), 126.98 (CH), 127.52 (CH), 128.14 (CH), 128.18, 128.22, 128.25, 128.29, 128.33, 128.37 (CH), 128.46 (CH), 128.76 (CH), 129.63 (CH), 132.25 (CH), 132.98 (C, d, *J* 11 Hz), 133.03 (C), 133.46 (C), 134.02 (CH, d, *J* 21 Hz), 134.15 (CH, d, *J* 20 Hz), 134.58 (C), 136.75 (C, d, *J* 10 Hz), 136.79 (C, d, *J* 11 Hz), 136.86 (C), 153.60 (C, d, *J* 17 Hz), 157.63 (CH, d, *J* 1 Hz); ^{31}P nmr: δ -13.1 (s); ms (190°C): 828 (M^+, 17%); Anal. Calcd for $C_{58}H_{42}N_2P_2$: C 84.04, H 5.11, N 3.38. Found: C 82.84, H 5.09, N 3.29.

2,2'-Bis[N-(2-diphenylphosphinophenyl)aminomethyl]-1,1'-binaphthyl (**3**): *Method A (Reduction of diamide* (**2**) *with AlH_3 prepared in situ)*: A suspension of 128 mg (3.36 mmol) of $LiAlH_4$ in 20 ml of dry

Et_2O was cooled to -5°C and 112 mg (0.84 mmol) of $AlCl_3$ was added. After stirring for 20 min a solution of 334 mg (0.4 mmol) of **2** in 1 ml of THF was added dropwise via a teflon cannula. After stirring for 15 h at 0°C the reaction was complete (tlc). Water was added carefully and the mixture was extracted with Et_2O. The organic phase was washed with brine and dried with Na_2SO_4. The solvent was removed in vacuum to give a yellow foam which was chromatographed on SiO_2 in PE/CH_2Cl_2 (65:35) to yield 290 mg (50%) of **3** as a white solid.

Method B (Reduction of diimine (**5**) *with $LiAlH_4$):* A suspension of 2.51 g (3.0 mmol) of crude **5** in 70 ml of degassed Et_2O was cooled to 0°C and 575 mg (15 mmol) of $LiAlH_4$ was added. After stirring for 2 h in an ice bath. 1 ml of H_2O and a few drops of NaOH (10%) were added and the resulting precipitate was sucked off and washed thoroughly with CH_2Cl_2. The filtrate was washed with brine and dried with Na_2SO_4. After removal of the solvent the residue was subjected to column chromatography (SiO_2, PE/CH_2Cl_2, 60:40) to give 1.36 g (54%) of **3** as a foam. ^{1}H Nmr: δ 3.91 (d, 2H, *J* 15.3 Hz), 3.99 (d, 2H, *J* 15.3 Hz), 5.04 (br s, 2H), 6.27 (dd, 2H, *J* 5.1, 7.9 Hz), 6.52 (t, 2H, *J* 7.3 Hz), 6.75 (ddd, 2H, *J* 1.5, 7.5, 7.6 Hz), 6.92 (m, 2H), 7.08 (d, 2H, *J* 8.4 Hz), 7.21 (m, 2H), 7.29 (m, 20H), 7.39 (m, 2H), 7.40 (d, 2H, *J* 8.5 Hz), 7.80 (d, 2H, *J* 8.6 Hz), 7.86 (d, 2H, *J* 8.1 Hz); ^{13}C nmr: δ 45.82 (CH_2), 110.55 (CH, d, *J* 2 Hz), 117.28 (CH, d, *J* 2 Hz), 118.89 (C, d, *J* 8 Hz), 124.94 (CH), 125.65 (CH), 125.72 (CH), 126.44 (CH), 128.08 (CH), 128.42 (CH), 128.53 (2CH, d, *J* 7 Hz), 128.71 (CH), 128.75 (CH), 130.47 (CH), 132.48 (C), 132.86 (C), 133.22 (C), 133.64 (CH, d, *J* 19 Hz), 133.72 (2CH, d, *J* 19 Hz), 134.37 (CH, d, *J* 3 Hz), 135.37 (C, d, *J* 8 Hz), 135.42 (C, d, *J* 8 Hz), 135.55 (C), 150.48 (C, d, *J* 18 Hz); ^{31}P nmr: δ -20.9 (s); ms (>300°C): 556 (M^+- NH-C_6H_4-P(C_6H_5)$_2$, 50%); Anal. Calcd for $C_{58}H_{46}N_2P_2$: C 83.62, H 5.57, N 3.36. Found: C 83.41, H 5.59, N 3.31.

4,8-Diphenyldibenzo[b,i]dinaphtho[2,1-m:1',2'-o]-1,11-diaza-4,8-diphosphacycloheptadeca-2,9,13,15-tetraene (**6a-c**): A solution of 200 mg (0.452 mmol) of **8** (1:1 mixture of diastereomers) and 140 mg (0.452 mmol) of dialdehyde (**4**) in 6 ml of dry benzene was treated with 0.6 ml (2 mmol) of Ti(*i*-PrO)$_4$. The solution turned yellow and was stirred under Ar overnight. A small amount of 0.1 N NaOH was

added and the mixture was filtered over celite which was repeatedly washed with CH_2Cl_2. The organic layer was separated and washed with water and brine and dried with Na_2SO_4. Removal of solvent left a yellow foam which was treated for the second time with Ti(*i*-PrO)$_4$ as described above to ensure complete conversion. The crude mixture of the imines was suspended in 15 ml of dry Et_2O cooled to 0°C and 88 mg (2.3 mmol) of $LiAlH_4$ was added. After stirring for 2 h the reaction was quenched by cautious addition of 3 ml of 0.1 N NaOH followed by 10 ml of water. The aqueous layer was extracted several times with 10 ml portions of CH_2Cl_2. The combined organic extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was chromatographed over a short column (SiO_2 deactivated with 22% of water, 2 x 20 cm, CH_2Cl_2/petroleum ether, 25:75). Enriched fractions of the two main products (**6a**, **6b**) were obtained. After the second chromatographic step pure samples of the diastereomers could be isolated which crystallized from CH_2Cl_2/MeOH. The third isomer (**6c**) which was formed in low yield (<1%) is not fully characterized.

6a (C_2-symmetrical): 20 mg (6%), mp 225-228°C; ^{1}H nmr: δ 1.56 (m, 2H), 2.14 (m, 4H), 4.04 (d, 2H, *J* 13.3 Hz), 4.24 (br d, 2H, *J* 13.3 Hz), 5.54 (br s, 2H), 6.41 (m, 2H), 6.57 (t, 2H, *J* 7.4 Hz), 6.93 (m, 2H), 7.06 (m, 2H), 7.18 (d, 2H, *J* 8.4 Hz), 7.28-7.39 (m, 12H), 7.50 (m, 2H), 7.81 (d, 2H, *J* 8.9 Hz), 7.96 (d, 2H, *J* 7.9 Hz), 8.00 (d, 2H, *J* 8.4 Hz); ^{13}C nmr: δ 21.30 (CH_2, t, *J* 16 Hz), 28.09 (CH_2, d, *J* 4 Hz), 46.71 (CH_2), 110.11 (CH), 117.51 (CH), 120.76 (C, m), 125.83 (CH), 125.89 (CH), 126.09 (CH), 126.65 (CH), 128.23 (CH), 128.25 (CH), 128.38 (CH, m), 128.80 (CH), 130.36 (CH), 132.26 (CH, m), 132.73 (CH), 132.98 (C), 133.05 (C), 133.84 (C), 135.36 (C), 137.02 (C, m), 152.21 (C); ^{31}P nmr: δ -41.46 (s); HRms: Calcd for $C_{49}H_{49}N_2P_2$: 720.2823. Found: 720.2829.

6b (C_1-symmetrical): 21 mg (6%), mp 228-232 °C, ^{1}H nmr: δ 1.50-1.63 (m, 2H), 1.64-1.90 (m, 2H), 2.16-2.29 (m, 2H), 3.74 (br d, 1H, *J* 12.3 Hz), 3.86 (br d, 1H, *J* 14.3 Hz), 4.02 (br d, 1H, *J* 14.5 Hz), 4.16 (br d, 1H, *J* 12 Hz), 4.44 (br s, 1H), 5.52 (br s, 1H), 6.37 (dd, 1H, *J* 5.5, 8.5 Hz), 6.41 (br d, 1H, *J* 8 Hz), 6.62 (br t, 1H, *J* 7 Hz), 6.65 (br t, 1H, *J* 7 Hz), 6.76 (d, 1H, *J* 8.5 Hz), 7.05-7.31 (m, 17H), 7.40 (ddd, 1H, *J* 1.5, 7.5, 13.5 Hz), 7.47 (m, 2H), 7.65 (d, 1H, *J* 8.5 Hz), 7.78 (d, 1H, *J* 8.5 Hz), 7.90 (br d, 1H, *J* 9 Hz), 7.92 (br d, 1H, *J* 9 Hz), 7.97 (d, 1H, *J* 8.5 Hz); ^{13}C nmr: δ ~22.8 (CH_2, m), 28.81 (CH_2, dd, *J* 14, 10 Hz), 45.94

(CH_2, s), 46.69 (CH_2, s), 110.00 (CH, br s), 110.30 (CH, d, *J* 3 Hz), 116.39 (CH, d, *J* 14 Hz), 117.59 (CH), 119.35 (C, d, *J* 9 Hz), 125.53 (CH), 125.70 (CH), 125.89 (CH), 125.95 (CH), 125.99 (CH), 126.51 (CH), 126.71 (CH), 126.74 (CH), 127.66 (CH), 127.85 (CH), 128.03 (CH), 128.24 (CH), 128.25 (CH, d, *J* 6 Hz), 128.58 (CH), 128.73 (CH, d, *J* 4 Hz), 128.87 (CH), 130.66 (CH), 130.68 (CH, d, *J* 16 Hz), 131.33 (CH), 131.57 (CH, d, *J* 17 Hz), 132.51 (C), 132.90 (C), 132.95 (C), 132.98 (C), 133.26 (C), 133.31 (CH, d, *J* 3 Hz), 134.46 (C), 134.71 (C), 135.13 (C), 135.36 (C), 137.90 (CH, d, *J* 40 Hz), 138.33 (C, d, *J* 13 Hz), 138.98 (C, d, *J* 9 Hz), 150.94 (C), 152.66 (C, d, *J* 21 Hz); ^{31}P nmr: δ -44.13 (d, *J* 9.6 Hz), -20.56 (br s); HRms: Calcd for $C_{49}H_{42}N_2P_2$: 720.2823. Found: 720.2816.

6c (C_2-symmetrical, selected data): ^{1}H Nmr: δ 1.68 (m, 2H), 2.08 (m, 2H), 2.45 (m, 2H), ~3.92 (br d); ^{31}P nmr: δ -35.32 (br s).

1,3-Bis[(2-aminophenyl)phenylphosphino]propane (**8**):[7] To a degassed solution of 4.00 g (14.4 mmol) of (2-aminophenyl)diphenylphosphine (**7**) in 80 ml of dry THF was added 600 mg (86.5 mmol) of finely cut Li wire with stirring. After a short induction period the solution turned yellow and later changed to brick-red. After stirring for 3.5 h at room temperature remaining pieces of unreacted Li were removed and the reaction mixture was cooled to 0°C. A solution of 1.63 g (1.37 ml, 14.4mmol) of 1,3-dichloropropane in 60 ml of THF was degassed and added dropwise during 1 h. Stirring was continued for 1 h after which time no starting material could be detected (tlc: PE/AcOEt 90:10 or PE/AcOEt 80:20). A small amount of water was added and the bulk of solvent was removed under vacuum. Usual workup with CH_2Cl_2 was followed by column chromatography (70 g SiO_2, PE/AcOEt 80:20→70:30) to yield 1.92 g (60%) of **8** (mixture of diastereomers) as a white solid. ^{1}H nmr: δ 1.68 (m, 2H), 2.21 (m, 4H), 4.07 (br s, 4H), 6.63 (dd, 2H, *J* 5.4, 7.9 Hz), 6.73 (dt, 2H, *J* 3.3, 7.5 Hz), 7.15 (m, 4H), 7.25-7.37 (m, 10H); ^{13}C nmr: δ 22.45 (CH_2, m), 28.11 (CH_2, m), 115.33 (CH), 118.61 (CH), 119.50 (C, d, *J* 11 Hz), 128.22 (CH), 128.42 (CH, d, *J* 7 Hz), 130.22 (CH), 131.98 (CH, d, *J* 18 Hz), 132.67 (CH, d, *J* 3 Hz), 137.92 (C, d, *J* 11 Hz), 150.32 (C, d, *J* 19 Hz); ^{31}P nmr (CD_2Cl_2): δ -35.6 (*meso*), -35.5 (*rac*); ms (220°C): 442 (M^+, 52%).

7,11-Diphenyldibenzo[e,l]dinaphtho[2,1-r:1′,2′-t]-1,17-dioxa-4,14-diaza-7,11-diphosphacycloeicosa-5,12,18,20-tetraene (**12**): A suspension of 499 mg (1 mmol) of **11** (*rac*:*meso*, *ca.* 60:40), 682 mg (1 mmol) of **10a** and 1.30 g (4 mmol) of finely grounded Cs_2CO_3 in 20 ml of dry toluene was degassed and then heated to reflux for 24 h. The deep red mixture was filtered and the residue washed with sufficient amount of CH_2Cl_2. The filtrate was stirred with an aqueous KCN solution (1 g in 50 ml of water) until the color faded. The resulting pale orange solution was washed with water and brine and dried with Na_2SO_4. Evaporation of the solvent left an orange oil which was decolorized by filtration over a short column of deactivated SiO_2 (15% water). The white foam was subjected to a gel chromatography on cross linked polystyrene to afford 260 mg (32%) of **12** as a foam. If the reaction was repeated with pure *meso*-**11** (obtained by fractional crystallisation of Ni complexes of **8**[7]) the yield was raised to 63%. ^{1}H Nmr: δ 1.52 (m, 2H), 2.13 (m, 3H), 2.32 (m, 1H), 2.98 (m, 2H), 3.18 (m, 2H), 3.99 (m, 3H), 4.16 (m, 1H), 5.12 (br s, 2H), 6.14 (dd, 1H, *J* 4.4, 7.4 Hz), 6.40 (dd, 1H, *J* 4.4, 7.9 Hz), 6.52 (m, 2H), 6.86 (m, 1H), 6.93 (m, 1H), 6.98 (m, 1H), 7.10 (m, 1H), 7.12-7.38 (m, 18H), 7.74 (d, 1H, *J* 9 Hz), 7.79 (br d, 1H, *J* 8 Hz), 7.90 (br d, 1H, *J* 8 Hz), 7.96 (d, 1H, *J* 9 Hz); ^{13}C nmr: δ 21.52 (CH_2, t, *J* 15 Hz), 27.07 (CH_2, t, *J* 11 Hz), 27.51 (CH_2, dd, *J* 9, 13 Hz), 43.32 (CH_2), 43.81 (CH_2), 68.26 (CH_2), 70.62 (CH_2, d, *J* 4 Hz), 109.74 (CH, d, *J* 2 Hz), 110.19 (CH, d, *J* 3 Hz), 116.02 (CH), 117.12 (CH, d, *J* 2 Hz), 117.23 (CH, d, *J* 3 Hz), 117.66 (CH), 120.09 (C, d, *J* 12 Hz), 120.51 (C, d, *J* 11 Hz), 120.84 (C), 121.05 (C), 123.80 (CH), 125.33 (CH), 125.36 (CH), 126.15 (CH), 126.35 (CH), 127.66 (CH), 127.91 (CH), 127.94 (CH), 128.02 (CH), 128.31 (CH, d, *J* 5 Hz), 128.36 (CH, d, *J* 5 Hz), 129.39 (CH), 129.56 (C), 129.75 (C), 130.44 (CH), 130.54 (CH), 131.59 (CH, d, *J* 16 Hz), 132.12 (CH, d, *J* 17 Hz), 133.36 (CH, d, *J* 3 Hz), 133.97 (C), 134.08 (C), 134.37 (CH, d, *J* 5 Hz), 137.45 (C, d, *J* 9 Hz), 138.81 (C, d, *J* 10 Hz), 151.60 (C, d, *J* 17 Hz), 151.85 (C, d, *J* 17 Hz), 154.21 (C), 154.72 (C); ^{31}P nmr: δ -37.42 (s), -38.28 (s); ms (260 °C) : 780 (5%); Anal. Calcd for $C_{51}H_{46}N_2O_2P_2$: C 78.44, H 5.94, N 3.59, P 7.93. Found: C 78.12, H 5.97, N 3.46, P 8.18.

12·NiCl₂: A solution of 240 mg (0.31 mmol) of **12** in 2 ml of CH_2Cl_2 was prepared in a 10 ml flask. Addition of 74 mg (0.31 mmol) of $NiCl_2·6H_2O$ in 2 ml of MeOH resulted in an immediate color change to

dark orange. The flask was immersed into a small size exsiccator containing approximately 100 ml of Et_2O. The exsiccator was closed and allowed to stand undisturbed for 1 or 2 days during which time the color of the solution faded and crystal growing occurs. After the volume was doubled by gradual condensation of Et_2O the crystalline product was isolated; yield 160 mg (57%). FAB-ms: 873 (8%), 837 (95%). The isotopic pattern calculated for $C_{51}H_{46}N_2O_2ClNiP_2$ and $C_{51}H_{45}N_2O_2P_2Ni$ fits exactly the experimental data.

6a·NiCl$_2$: A 20 mg ($2.8\cdot10^{-5}$ mol) sample of **6a** was treated with $NiCl_2\cdot6H_2O$ (6.6 mg, $2.8\ 10^{-5}$ mol) as outlined for **12·NiCl$_2$** to give the corresponding Ni(II) complex in quantitative yield as dark red prisms.

2,2´-Bis(2-methanesulfonyloxyethoxy)-1,1´-binaphthyl (**10b**) was prepared from the corresponding diol and mesyl chloride analogously to the tosylate (**10a**).[9] Yield: 58%; mp 150-152°C ($CHCl_3/Et_2O$). ^{1}H Nmr (250 MHz): δ 2.13 (s, 6H), 4.19 (m, 2H), 4.26 (m, 6H), 7.12 (br d, 2H, *J* 8 Hz), 7.25 (ddd, 2H, *J* 7, 6, 1 Hz), 7.37 (ddd, 2H, *J* 7, 6, 1 Hz), 7.43 (d, 2H, *J* 9 Hz), 7.88 (br d, 2H, *J* 8 Hz), 7.99 (d, 2H, *J* 9 Hz); ^{13}C nmr: δ 36.06 (CH_3), 67.14 (CH_2), 68.75 (CH_2), 114.95 (CH), 119.96 (C), 124.28 (CH), 125.23 (CH), 126.84 (CH), 127.93 (CH), 129.54 (C), 129.75 (CH), 133.89 (C), 153.41 (C). Ms (230°C): 530 (32%),

Crystal Structure Determination:[15] Data were collected on a modified STOE diffractometer equipped with a N_2-cold-stream low temperature device (92K) using MoK_α radiation.

Structure solution was carried out by the Patterson method followed by least squares refinement against F^2 with no σ-cutoff being applied. Anisotropic atomic displacement parameters (*adp´s*) were assigned to all non-hydrogen atoms. Positions of hydrogen atoms were calculated according to stereochemical aspects.

Both structures contain disordered solvent.

6a·NiCl$_2$: monoclinic, space group P2(1)/c, a = 12.153 Å, b = 17.593 Å, c = 21.506 Å, β = 91.00°, V =

4597.5 Å^3, Z = 4, d_{calc}: 1.229 g cm^{-3}, maximum 2Θ for data collection: 48°.

Refinement of 546 parameters against 6975 intensity data converged at the following values for reliability indices: $\omega R2 = \Sigma\{\omega(F_o^2 - F_c^2)^2/\Sigma[\omega(F_o^2)^2]\} = 0.255$ for 6979 reflections, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.109$ for 4198 reflections with $F_o > 4\sigma(F_o)$.

12·NiCl$_2$: The crystals are triclinic, space group $P\bar{1}$; a = 12.148(2) Å, b = 12.197(2) Å, c = 16.285(3) Å, α = 76.70(3)°, β = 81.29(3)°, γ = 86.70(3)°, V = 2320.5 Å^3, Z = 2, d_{calc}: 1.303 g cm^{-3}, maximum 2Θ for data collection: 60°.

Refinement of 597 parameters against 8547 intensity data converged at the following values for reliability indices: $\omega R2 = \Sigma\{\omega(F_o^2 - F_c^2)^2/\Sigma[\omega(F_o^2)^2]\} = 0.174$ for 8547 reflections, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.068$ for 4739 reflections with $F_o > 4\sigma(F_o)$.

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