Paramagnetic Planar Complexes of Ni^{II}: Influence of R and R′ on the Formation, Coordination Geometry and Magnetic Properties of Phosphinic Amidato Bischelates $[R_2P(O)NR']_2Ni$

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After a brief review of previous work the results of the metathesis reaction between $Ni(dme)Br_2$ and $R_2P(O)NR'Li$ [R = *t*Bu, *i*Pr, Ph; R′ = Et, Pr, *i*Pr, (±)-*s*Bu, *t*Bu, *t*Pen, Cy, Ph, (−)-α-methylbenzyl = Mb, 1-adamantyl = Ad] are reported. Complex formation occurred only with lithiated amides of *tert*-butylphosphinic acid, and bischelates $[tBu_2P(O)NR']_2Ni$ were obtained when R′ = *s*Bu, Mb, *t*Pen, Ad (**1d**–**g**). With R′ = Et, Pr bischelation was incomplete. Vis spectroscopy showed the paramagnetic compounds **1d**–**f** to be planar in the solid state but tetrahedral in solution. **1g** is tetrahedral in both phases. The planar structure of **1f** was confirmed by X-ray single-crystal analysis (monoclinic, space group $P2_1/n$). The magnetic moments μ_{eff} of **1d, e, g** are ca. 3.2–3.5 μ_B in both phases and the Curie-Weiss law is obeyed in the range 293–183 K. The same is valid for dissolved **1f**. The μ_{eff} values of solid **1f** are, however, strongly temperature-dependent, varying from 1.38 to 0.55 μ_B (300–90 K). NMR data (^{31}P, ^{1}H, ^{13}C) are reported. Obviously, a favorable combination of electronic and steric factors of substituents R and R′ produces with ligands $[R_2P(O)NR']^-$ the donor quality necessary for bischelation as well as the singular field strength required for the formation of planar paramagnetic species. As the combination of paramagnetism and planarity is bound to the solid state, lattice energy effects may be finally decisive for this unique constellation of tetracoordinated Ni^{II} complexes.

Some time ago we have reported on paramagnetic phosphinic amidato bischelates $[tBu_2P(O)NR']_2Ni$ (**1a**: R′ = *i*Pr[1]; **1b**: R′ = Cy, olive-green and ink-blue isomer; **1c**: R′ = *t*Bu[2]). Crystal structure determination showed **1a** and **1b** (*green*) to be planar and **1b** (*blue*) to be tetrahedral. As the electronic spectrum of **1c** (reflectance spectrum) was very similar to the solid-state spectra of **1a** and **1b** (*green*) it was concluded that **1c** was also planar.

All the compounds **1** mentioned above show a broad absorption between 6500–8000 cm^{-1}, $\tilde{\nu}_{max}$ being shifted from 7300–7500 cm^{-1} in the case of the planar species to 6600 cm^{-1} with the tetrahedral complex **1b** (*blue*). However, their solution spectra proved to be almost superimposable and nearly identical with the powder spectrum of tetrahedral **1b**. So it was assumed that these compounds are predominantly tetrahedral in solution.

While **1a** and **1b** (*green* and *blue*) show μ_{eff} values of 3.3–3.4 μ_B (solid state, room temperature) and Curie-Weiss behavior between 280–90 K (solid state) the magnetic moment of solid **1c** ranges from 1.7 to 0.6 μ_B (280–80 K).

Thus, diamagnetism and lack of ligand-field bands $<10000\ cm^{-1}$[3] turned out to be no longer essential features of planar Ni^{II} complexes.

By extended angular overlap model calculations it was possible to explain the ligand-field spectra of the planar complexes **1a** and **1b** (*green*) and to interpret the triplet ground states of both as well as a singlet ground state with **1c** that is followed by an electronic level of slightly higher energy accessible by thermal energy kT[4].

Now we investigated the influence of R and R′ on the formation, coordination geometry and magnetic properties of chelate complexes of general type **1** more systematically. For this purpose we prepared a series of new phosphinic amides $R_2P(O)NR'H$ with very different substituents R and R′[5] that may be regarded in deprotonated form as potential ligands in complexes of type **1**. Some of the results are now reported.

Bischelate Complexes $[tBu_2P(O)NR']_2Ni$ 1d–g

Preparation

1a–**c** were obtained by a metathesis reaction between $tBu_2P(O)NR'Li$ and $Ni(PPh_3)_2Cl_2$. However, it proved to be somewhat troublesome to separate the PPh_3 set free in this reaction from the complex by fractional crystallization because of similar solubilities. In later experiments we found that this problem can be avoided when $Ni(dme)Br_2$ is used as starting compound. In this case the reaction proceeds smoothly and 1,2-dimethoxyethane (m.p. −58 °C) does not affect the crystallization of the complex. In a typical experiment an equimolar amount of *n*BuLi in hexane is

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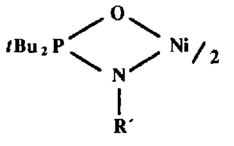
added to a solution of the amide $R_2P(O)NHR'$ in THF, and this solution is added to a stoichiometric amount of $Ni(dme)Br_2$. From the reaction mixture crystals of **1d–g** were isolated in about 40% yield.



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1	**a**	**b**	**c**	**d**	**e**	**f**	**g**
R′	*i*Pr	Cy	*t*Bu	*(±)s*Bu	*(-)*Mb	*t*Pen	Ad

1b: 2 isomers, planar (*green*) and tetrahedral (*blue*)

*s*Bu = *sec*-butyl; Mb = *α*-methylbenzyl; *t*Pen = *tert*-pentyl; Ad = 1-adamantyl

Analogous experiments with $tBu_2P(O)NR'Li$ (R′= Et, Pr) and $Ni(PPH_3)_2Cl_2$ gave no bischelates **1** but complexes of a more complicated composition containing Li and tetrahedral chromophors $NiON_2Cl$.

In these compounds one amidato ligand has a chelating function while a second one is coordinated to the metal only via N[6,7].

No complex **1** was isolated when the following lithiated amides $R_2P(O)NR'Li$ were used in the metathesis reaction: R = *t*Bu R′ = Ph; R = Ph R′ = *i*Pr, Cy, *t*Bu; R = *i*Pr R′ = Pr, Cy, *t*Bu, Ph. The ^{31}P-NMR spectrum of the reaction mixture shows only the resonance of the lithiated amide and at most a very weak resonance in the region between $\delta_P = -850$ and -750 which was found to be typical of complexes **1a–g** and possibly also of complexes of the general type **1**.

General Properties

The complexes **1d–g** are like **1a–c** extremely hydrolyzable and must be prepared and handled with rigorous exclusion of moisture. They rapidly decompose in protic solvents, but are easily soluble in CH_2Cl_2 or THF and less soluble in toluene, benzene or pentane. In benzene they are monomeric. Some properties are listed in Table 1.

Table 1. Some properties of $[tBu_2P(O)NR']_2Ni$ **1d–f**

	R′		m.p.[°C]	δ_P [ppm][a]	μ_{eff} [μ_B][b]	μ_{eff} [μ_B][a]
1d	(±)*s*Bu	green	132	- 809.9	3.36	3.48
1e	(-)Mb	green	72	- 844.9	3.20	3.46
1f	*t*Pen	blue-green	78	- 743.1	1.38	3.47
1g	Ad	blue	253	- 756.7	3.21	3.48

[a] Room temperature in CD_2Cl_2. – [b] 300 K, solid state.

Ligand-Field Vis Spectra

The ligand-field bands of solid and dissolved complexes **1** are listed in Tables 2 and 3. The near infrared ligand-field spectra of **1a** and **1b** (*green*) as well as the Vis spectra of the latter are discussed in ref.[4].

Table 2 shows that the powder spectra of **1d–f** are very similar to that of the green (*planar*) isomer of **1b**, though $\tilde{\nu}_{max}$ of the second band is in the case of **1c** and **1f** shifted to higher wave numbers.

Table 2. Absorption maxima [cm^{-1}] of ligand-field bands of complexes **1** (reflectance spectra, $BaSO_4$ as standard); absorptions at $\tilde{\nu} = 5900-6100$ cm^{-1}, due to ν(CH) overtones and combinatorial vibrations[4], have been omitted

	Absorption maxima [cm-1]			
1b (*green*) [9]	7500	12000	17300	
1d	7650		17270	
1e	7500	12050	17140	
1c [9]	7500	12600	17500	
1f	7500	12990	17690	
1b (*blue*) [9]	6600	12500	16800	18000
1g	6600	12400	16890	18100

So it is safe to assume that **1d–f** are also planar in the solid state, all the more the planar structure of **1f** was confirmed by X-ray single-crystal analysis (see below). The spectrum of **1g**, however, is nearly superimposable with that of the blue (*tetrahedral*) isomer of **1b** and shows the characteristic absorption band with maxima at ca. 16800 cm^{-1} and ca. 18000 cm^{-1} that was also observed with tetrahedral complexes $[R_2P(S)NR']_2Ni$[8].

The solution spectra of compounds **1d–f** (Table 3) are very similar with respect to the position, shape, and intensity of the absorption bands and to that of solid **1b** (*blue ≙ tetrahedral*). From these findings we conclude that the new complexes **1d–f** are planar in the solid state and predominantly tetrahedral in solution as we previously postulated for **1a** and **1b** (*green*). In contrast, **1g** is tetrahedral in both phases.

Table 3. Solution spectra of **1** in toluene (**1g** in CH_2Cl_2); absorption maxima [cm^{-1}], ε [$l\ mol^{-1}\ cm^{-1}$] in parentheses; the spectra of green and blue **1b** are identical

	Absorption maxima [cm-1]			
1b [9]	6400 (54)	12400 (45)	16600(121)	18100(130)
1c [9]	6650 (65)	12400 (32)	16800 (92)	18300 (99)
1d	6300 (51)	12320 (27)	16710 (95)	18310(101)
1e	6600 (53)	12500 (42)	16760 (94)	18230(103)
1f	6700 (37)	12610 (19)	16950 (75)	18350 (87)
1g	6550 (47)	12420 (23)	16810 (90)	18280 (94)

Magnetic Properties

The magnetic moments μ_{eff} of solid **1d**, **1e**, and **1g** amount to 3.2–3.4 μ_B at room temperature (Table 1). Such values are usually observed for tetrahedral Ni^{II} complexes and, as was shown previously, also for the planar paramagnetic compounds **1a** and **1b** (*green*). Moreover, these complexes show a Curie-Weiss behavior from 300–90 K. The magnetic moments of solid **1f**, however, show a strong temperature dependence like those of **1c** and vary from 1.38 to 0.55 μ_B (300–90 K).

A least-squares fit of temperature-dependent molar susceptibilities of **1f** to the van Vleck formula for a diamagnetic ground state and a low-lying excited triplet state at energy ΔE[4] resulted in $\Delta E = 491\ cm^{-1}$ and $\chi_0 = 284 \times 10^{-6}\ cm^3\ mol^{-1}$[10]. These parameters are similar to those of **1c** for which a singlet ground state followed by a triplet state at energy ΔE was postulated, the latter being partially populated at room temperature by a Boltzmann distribution. As ΔE is slightly larger in **1f** the μ_{eff} value of this compound is lower than that of **1c**.

The magnetic moments of **1d–g**, measured in CD_2Cl_2, are alike (Table 1) and the Curie-Weiss law is obeyed between 293–183 K. The values observed match tetrahedral as well as high spin planar species and would be therefore also in agreement with an equilibrium of these two conformers. However, the evidence obtained from the solution spectra of **1d–g** implies that they are, as mentioned above, predominantly tetrahedral in solution.

NMR Spectra

At room temperature the ^{31}P-NMR spectra of **1d–g** (Table 1) show like those of **1a** and **1b** a singlet in the range of $\delta_P \approx -750$ to -850 with half widths of 200–340 Hz.

With respect to δ_P of the corresponding compounds $t\mathrm{Bu_2P(O)NHR'}$[5] and $t\mathrm{Bu_2P(O)NR'Li}$ ($\delta_P = 40-50$) the resonance is shifted upfield by 800–900 ppm. It should be noted that at room temperature the signals of analogous thio compounds $[t\mathrm{Bu_2P(S)NR'}]_2\mathrm{Ni}$ are in the range of $\delta_P = 40-130$[8b]. Variable-temperature measurements (CD_2Cl_2) in the case of **1e–g** show a Curie behavior from 293–193 K[7], indicated by a strictly linear upfield shift of δ_P vs. $1/T$.

For complex **1e** $\delta_P = -1459.5$ (193 K) is observed. This is to our knowledge the largest upfield shift observed in the ^{31}P-NMR spectrum so far.

Because of their paramagnetism complexes **1d–g** show proton resonances covering a range up to 50000 Hz. Heavy line broadening is a further consequence and a fine structure of the signals is often lacking. Signal-structure correlations were found either by 2D-NMR[11] or a careful comparison of signal intensities. In the case of **1e** and **1g** a fine structure of some resonances was observed and used for structure assignments.

Largest isotropic shifts (up to 200 ppm) were found for protons attached to the α-C atom of R′. Within the alkyl chain the ^1H shifts usually decrease with growing distance of the proton from the paramagnetic center, except for **1g**, where the sequence of β- and γ-H is inverted.

The melting point of **1d** is sharp, indicating that it crystallizes purely either as a *racemic* (*R,R*; *S,S*) or *meso* (*R,S*) compound, whereas in solution a doubling of signals was observed due to the presence of *both* diastereomers.

It is possible to group the resonances into two sets corresponding to the two diastereomers (*A*, *B*) regarding the fact that in freshly prepared solutions of **1d** either *A* or *B* exists predominantly (Table 4). On standing, obviously equilibration occurs so that after 24 h finally both sets show equal intensities[7].

The chemical shift difference of the diastereotopic methylene protons is greatly enhanced by the paramagnetism of the complex. Thus, their resonances differ by $\Delta\delta = 9.5$ (*A*) or $\Delta\delta = 10.0$ (*B*) compared with $\Delta\delta = 0.23$ in $t\mathrm{Bu_2P(O)NH}s\mathrm{Bu}$.

Table 4. Proton NMR data of complexes $[t\mathrm{Bu_2P(O)NR'}]_2\mathrm{Ni}$ **1d–g** (CD_2Cl_2, 293 K); δ [ppm], coupling constants [Hz] in parentheses

	R′		PCCH	PNCH	PNCCH	PNCCCH ($^3J_{HH}$)	PNCCCCH ($^2J_{HH}$)
1d[*]	(±) *s*Bu	*A*	- 1.0 - 1.6	200.0	14.6 [a] 19.0 [b] 9.5 [b]	13.6	
		B	- 0.8 - 1.8	200.0	15.2 [a] 18.2 [b] 8.2 [b]	13.2	
1e[*]	(-) Mb		- 0.9	207.6	34.3 [a]	13.4 (6.5) 10.4 (7.0) [c]	15.3
1f	*t*Pen		- 0.4	-	25.3	14.3	
1g	Ad		- 0.4	-	15.2	15.5	4.7 (11.7) 7.1 (11.7)

[*] 298 K. – [a] $PNCCH_3$. – [b] $PNCCCCH_2$. – [c] PNCCCCH. – *A*,*B*: Diastereomers of **1d**.

The signals of the phenyl system of **1e** show some fine structure which together with signal intensities allows their unequivocal assignment. They all appear downfield shifted compared with those of $t\mathrm{Bu_2P(O)NHPh}$, the shift of the *m*-protons being strongest (δ = 15.3) followed by that of the *o*-protons (13.4) and of the *p*-proton (10.4).

In **1f** methyl and methylene resonances β to nitrogen appear as one broad singlet (δ = 25.3) at room temperature which separates on cooling ($\delta_{NCCH_2} = 34.9$, $\delta_{NCCH_3} = 33.6$; 233 K).

In the case of **1g** the chemical shift difference of the diastereotopic methylene protons in δ-position to nitrogen is remarkably enhanced. Δδ is here 2.4 ppm ($^2J_{HH} = 11.7$ Hz, 293 K), whereas with $t\mathrm{Bu_2P(O)NHAd}$ no distinction can be made.

^{13}C-NMR data of paramagnetic complexes are scarce, probably because of the low absolute sensitivity of the ^{13}C isotope and excessive line broadening caused by paramagnetism. Because of their favorable electron spin relaxation times the latter factor is less important with **1d–g** and ^{13}C-NMR spectra are easily obtained. The results are given in Table 5.

All spectra were recorded in concentrated solutions without proton decoupling. The resonances cover the wide range of 1500 ppm. With the exception of the α-C atoms in R′ all resonances are shifted downfield the shift decreasing with growing distance from the paramagnetic center.

It is notable that a decrease in the electron-donating power of R′ is accompanied by a larger high-field shift of the α-^{13}C resonance as well as by a lenghtening of the Ni–O bond[7].

Crystal Structure of 1f[*]

In the solid state, **1f** forms typical van-der-Waals crystals without extraordinary short intermolecular distances. Shortest intermolecular contacts amount to ca. 2.6 Å for H···H and 5.0 Å for Ni···H interactions.

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[*] The crystal-structure determination of **1f** was performed by U. E.

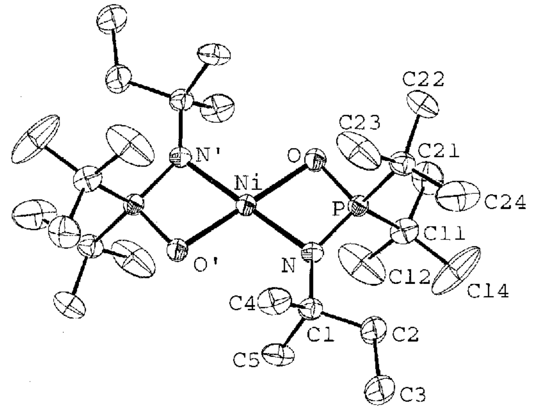
Table 5. ^{13}C-NMR data of **1d** (CD_2Cl_2, 243 K) and **1e–g** (THF, 298 K); δ [ppm]; $^1J_{PC}$[*] and $^1J_{CH}$ [Hz] in parentheses

		PC	PCC	NC	NCC	NCCH3	NCCC
1d	*A*	394.0 371.3	99.7	-214.9	732.2	751.5	32.5 (126)
	B	378.6 386.7					26.0 (126)
1e		280.2 269.7	105.3 (126) 90.3 (126)	-163.8 (114)	833.2	545.3 (124)	133.6 (158) 147.9 [a] (156) 123.1 [b] (154)
1f		251.2 (50) [*]	102.3 (126)	-31.8	484.9 (125)	480.7 (125)	[†]
1g		259.6 (50) [*]	104.5 (123)	-71.0	512.9 (124)		106.8 (130) 47.9 [a] (126)

[a] PNCCCC. – [b] PNCCCCC. – [†] Not observed. – *A,B:* Diastereomers of **1d**.

The molecule (Figure 1) occupies a crystallographic inversion center: As a consequence of the $\bar{1}$ site symmetry, the exactly planar coordination of Ni may be completely characterized by a metal–oxygen distance of 1.924(2) Å, a metal–nitrogen bond of 1.945(3) Å, and a bite angle O–Ni–N of the chelating ligand of 76.8(1)°. The metal and its coordinating atoms on the one hand and the almost perfectly planar four-membered ring Ni/O/N/P (maximum deviation of the least-squares plane: 0.6 pm for the phosphorus atom) on the other hand are coplanar within experimental error.

Figure 1. Molecular structure of **1f** in the crystal (PLATON[20]; ellipsoids are scaled to 30% probability, hydrogen atoms are omitted



Conclusions

So far only certain lithiated amides of *tert-butyl*phosphinic acid were found to react with $Ni(PPh_3)_2Cl_2$ or Ni(dme)Br_2 to form bischelates $[R_2P(O)NR']_2Ni$. Four new compounds of this type [R = *t*Bu; R′ = (±)-*s*Bu, (−)Mb, *t*Pen, Ad] **1d–g** were obtained. They all are paramagnetic and show ligand-field bands at $\tilde{\nu} < 10000$ cm^{-1}.

In the solid state **1d–f** proved to be planar while **1g** is tetrahedral. In solution all compounds **1** are assumed to be predominantly tetrahedral. Thus, diamagnetism and lack of ligand-field absorptions below 10000 cm^{-1} can not any longer be regarded as essential features of planar Ni^{II} complexes.

With the iso(valence) electronic complexes $[R_2P(Y)NR']_2Ni$ (Y = S[8], NR′[12,13]) these criteria proved however to be still valid: $[i\text{Pr}_2P(NMe)_2]_2Ni$ is planar and diamagnetic while $[Ph_2P(NSiMe_3)_2]_2Ni$ is tetrahedral and paramagnetic, the structures of both having been determined by X-ray single-crystal analysis[12,13], only the latter showing a ligand-field band at 6470 cm^{-1}.

It is apparent that only by a favorable combination of electronic and steric factors, ligands $[R_2P(O)NR']^-$ obtain the donor quality necessary for bischelation and the singular ligand-field strength that is required for the formation of paramagnetic planar species. As the combination of paramagnetism and planarity is bound to the solid state, packing effects may be finally decisive for this unique constellation of tetracoordinated Ni^{II} complexes.

Experimental

The complexes **1** were prepared and handled under inert conditions. Melting points (uncorrected) were determined in closed tubes with a melting point apparatus 510 W (Büchi, Switzerland) by using a set of calibrated thermometers. – Vis spectra: Lambda 5 (Perkin-Elmer, Überlingen); DMR 21 (Zeiss, Oberkochen). – Susceptibility measurements: B–E 10 C 8 (Bruker-Physik, Karlsruhe) according to Faraday (solids); in solution by application of the Evans method[14]. Pascal corrections: ref.[15] – ^{31}P-, ^{13}C-, ^{1}H-NMR spectroscopy: Bruker AM 200, 85% H_3PO_4 as external (^{31}P) and TMS as internal reference (^{1}H, ^{13}C). Downfield shifts are positive. – Elemental analyses: CHN: Perkin-Elmer C,H,N-Analyzer 240 C; Ni: Perkin-Elmer AAS 3100. – Cryoscopy: Cryoscopic unit A 0284 (Knauer, Berlin).

X-ray Crystallography of **1f**: $C_{26}H_{58}N_2NiO_2P_2$, formula mass 551.42 g mol^{-1}, monoclinic space group $P2_1/n$ (No. 14), a = 8.206(4), b = 12.531(5), c = 15.504(3) Å, β = 100.23(3)°; V = 1569(1) Å^3; Z = 4/2; $d_{\text{ber.}}$ = 1.167 g cm^{-3}; μ(Cu-K_α) = 20.21 cm^{-1}; F_{000} = 604. ENRAF-Nonius CAD4 diffractometer, Cu-K_α radiation (λ = 1.5418 Å), graphite monochromator. Data collection at room temperature in the ω/2Θ mode (5° ≤ Θ ≤ 74°) on an irregular transparent crystal fragment of ca. 0.3 × 0.3 × 0.2 mm resulted in 3483 reflections. Before averaging symmetry-related parts of the reciprocal lattice an empirical absorption correction[16] was applied. The structure was solved by direct methods[17]. In the final least-squares full-matrix refinement with 2537 independent observations with $I > 1.0\sigma(I)$ a correction for secondary extinction[18] was applied to calculated structure factors. All nonhydrogen atoms were refined with anisotropic displacement parameters whereas H atoms were included in calculated positions [C–H 98 pm, B_{iso}(H) = 1.3 · B_{iso}(C)] by using a riding model: 152 variables, R = 0.059, R_w = 0.077 with $w^{-1} = \sigma^2(F_o)$, max. residual electron density in a final DF map 0.49 e Å^{-3}[19].

Preparation of **1**: 20 mmol of the amide $R_2P(O)NHR'$ [R = *t*Bu; R′ = (±)-*s*Bu, *t*Pen, Ad][5] in THF (50 ml) was treated with *n*-butyllithium (20 mmol, 1.6 M in hexane) and the mixture was briefly refluxed. After cooling the solution was added dropwise to Ni(dme)Br_2 (10 mmol) and the reaction mixture was stirred for 1 h at room temp. After evaporation of the solvents in vacuo the residue was dissolved in 5 ml of toluene or pentane and LiBr was removed by centrifugation. On storage of the solution at −30 °C, **1d**, **f**, **g** crystallized from the clear, intensively colored solution within hours or days, depending on the nature of R′. Yields were about 40% and could be increased by concentration and cooling of the mother liquor.

In the preparation of **1e** (R′ = Mb) Ni(PPh$_3$)$_2$Cl$_2$ was used as a starting reactant. After removal of PPh$_3$ from the centrifuged solution by fractional crystallization (repeated cooling to −30 °C for 12 h; ^{31}P-NMR control) pure **1e** finally crystallized from the solution after several days at −30 °C. Yield 35%.

Bis(P,P-di-tert-butyl-N-(±)-sec-butylphosphinic amidato-N,O)nickel(II) (**1d**): $C_{24}H_{54}N_2NiO_2P_2$ (523.4): calcd. C 55.08, H 10.40, N 5.35, Ni 11.22; found C 54.87, H 10.60, N 5.28, Ni 11.19. − Mol. mass (cryoscopic in benzene): 535 (0.026 molal).

Bis(P,P-di-tert-butyl-N-(−)-α-methylbenzylphosphinic amidato-N,O)nickel(II) (**1e**): $C_{32}H_{54}N_2NiO_2P_2$ (619.5): calcd. C 62.05, H 8.79, N 4.52, Ni 9.48; found C 62.33, H 8.58, N 4.32, Ni 9.42. − Mol. mass (cryoscopic in benzene): 612 (0.101 molal).

Bis(P,P-di-tert-butyl-N-tert-pentylphosphinic amidato-N,O)nickel(II) (**1f**): $C_{26}H_{58}N_2NiO_2P_2$ (551.4): calcd. C 56.63, H 10.60, N 5.08, Ni 10.65; found C 56.46, H 10.45, N 4.91, Ni 10.59. − Mol. mass (cryoscopic in benzene): 537 (0.016 molal).

Bis(P,P-di-tert-butyl-N-1-adamantylphosphinic amidato-N,O)nickel(II) (**1g**): Crystallization from toluene/CH_2Cl_2. − $C_{36}H_{66}N_2NiO_2P_2$ (679.6): calcd. C 63.63, H 9.79, N 4.12, Ni 8.64; found C 63.66, H 9.77, N 3.44, Ni 8.61. − Mol. mass (cryoscopic in benzene): 695 (0.012 molal).

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