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Preparation of new nickel(0) naphthalene complexes, crystal structure of $[\text{Ni}(\text{C}_{10}\text{H}_8)(\text{i-C}_3\text{H}_7)_2\text{PCH}_2\text{CH}_2\text{P}(\text{i-C}_3\text{H}_7)_2]$

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Abstract

The reduction of the nickel(II) chloride complexes $[\text{NiCl}_2(\text{dippm})]$ (**1a**, $\text{dippm} = 1,1\text{-bis}(\text{diisopropylphosphino})\text{methane}$), $[\text{NiCl}_2(\text{dippe})]$ (**1b**, $\text{dippe} = 1,2\text{-bis}(\text{diisopropylphosphino})\text{ethane}$), and $[\text{NiCl}_2(\text{dipp})]$ (**1c**, $\text{dipp} = 1,3\text{-bis}(\text{diisopropylphosphino})\text{propane}$) with one equivalent of potassium naphthalenide in tetrahydrofuran (THF) gives the corresponding nickel(I) chlorides $[\text{NiCl}(\text{dippm})]$ (**2a**), $[\text{NiCl}(\text{dippe})]$ (**2b**) and $[\text{NiCl}(\text{dipp})]$ (**2c**). The bidentate phosphine- Ni^0 intermediates formed by reduction of the Ni^{II} chlorides **1a** and **1b** with an excess of magnesium, also give the mono-chlorides **2a** and **2b** on reaction with equal molar amounts of **1a** and **1b**, respectively. The reduction of **1b** and **1c** with magnesium in the presence of naphthalene produces the nickel(0) complexes $[\text{Ni}(\text{C}_{10}\text{H}_8)(\text{dippe})]$ (**4b**) and $[\text{Ni}(\text{C}_{10}\text{H}_8)(\text{dipp})]$ (**4c**, $\text{C}_{10}\text{H}_8 = \text{naphthalene}$). A crystal structure study of **4b** showed that the naphthalene molecule is η^2 -bonded to the P_2Ni unit.

Introduction

The chemistry of the less common nickel(I) complexes has been reviewed [1]. Only a few examples of phosphine nickel(I) halide complexes have been reported. Their preparations entail the reduction of phosphine-nickel(II) complexes with NaBH_4 [2] or with an excess of sodium sand in toluene [3]. The latter method suffers from the disadvantage that the reduction may proceed to the nickel(0) stage if the progress of the reaction is not monitored carefully. Phosphine-nickel(I) halide complexes may also be prepared from phosphine-nickel(II) halides and the corresponding phosphine-nickel(0) complexes by comproportionation [4,5]. Zerovalent phosphine derivatives of nickel have previously been prepared by reduction of

nickel(II) compounds in the presence of ligands with various reducing agents, including zinc dust, sodium amalgam, NaBH_4 , sodium naphthalenide and aluminium trialkyls [6].

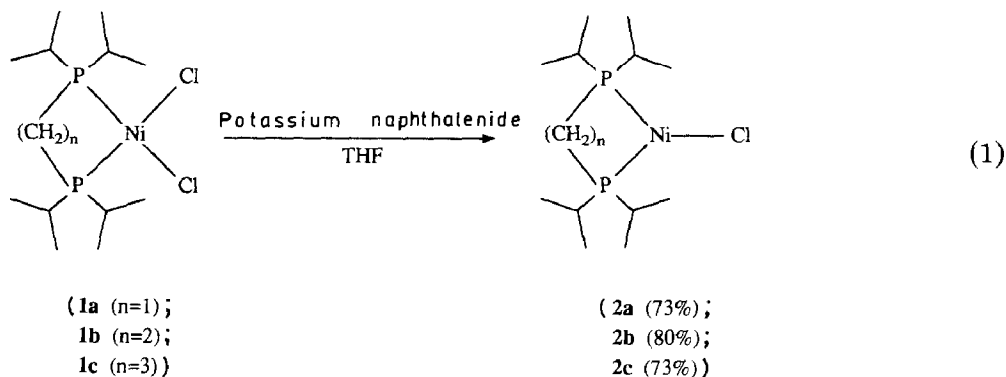
We have established that both potassium naphthalenide and magnesium metal are convenient reagents for reducing several bis(diisopropylphosphino)alkanenickel(II) chloride complexes to give nickel(I) and nickel(0) products. The bis(diisopropylphosphino)alkanenickel(0) species that we obtained by reduction with magnesium were found to coordinate to naphthalene in a η^2 -bonded fashion to give thermally stable complexes. Arene ligands which are η^2 -coordinated to transition metals [5,7,8] are far less frequently encountered than those bonded in a η^6 -coordination.

Results and discussion

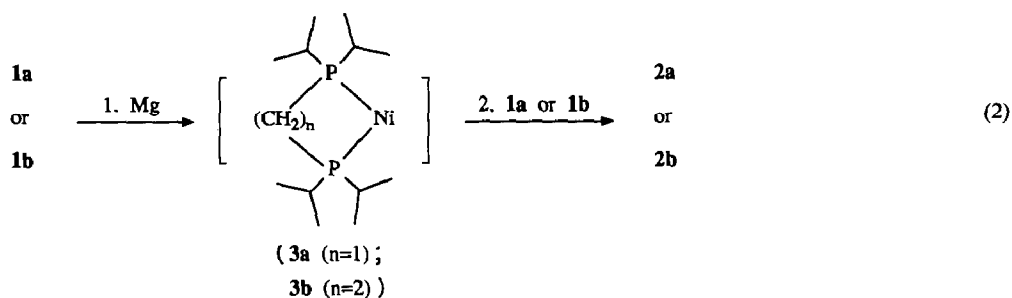
Treatment of the nickel(II) complexes $[\text{NiCl}_2(\text{dippm})]$ (**1a**, $\text{dippm} = 1,1$ -bis(diisopropylphosphino)methane), $[\text{NiCl}_2(\text{dippe})]$ (**1b**, $\text{dippe} = 1,2$ -bis(diisopropylphosphino)ethane) and $[\text{NiCl}_2(\text{dipp})]$ (**1c**, $\text{dipp} = 1,3$ -bis(diisopropylphosphino)propane) with one equivalent of potassium naphthalenide in THF at -78°C produced clear solutions after stirring for 3 to 5 h at room temperature. The corresponding di(phosphino)nickel(I) chlorides, the green **2a**, red **2b** and light yellow **2c**, were isolated in high yields.

The mass spectrum of the nickel mono-chloride **2a** showed a molecular peak at $M^+ 682$, corresponding to a dimer. The mass spectra of the chlorides **2b** and **2c** exhibit molecular ion peaks at $M^+ 355$ and $M^+ 369$ respectively, which correspond to the monomeric species. However, this finding does not exclude the possibility that **2b** and **2c** also exist as easily cleaved dimers.

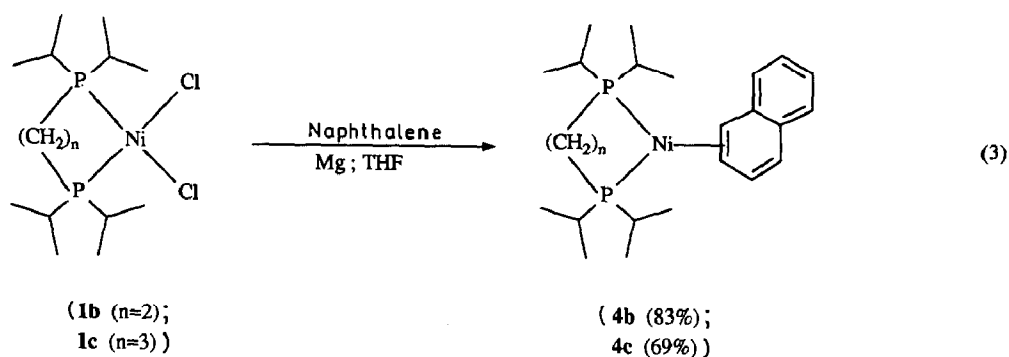
Alternatively, the complexes **2a** and **2b** could also be made in a two-step procedure involving initial reduction of the nickel(II) chlorides **1a** and **1b** with active magnesium [9*] at -30°C in THF. This gave dark red solutions of the nickel(0) intermediates **3a** and **3b** with, as yet unknown identities. Subsequent treatment of these THF solutions with equimolar amounts of the corresponding nickel(II) chlorides **1a** and **1b** gave the products **2a** and **2b** in yields of 82 and 73%, respectively (eq. 2).



* Reference number with asterisk indicates a note in the list of references.



When the reduction of $[\text{NiCl}_2(\text{dippe})]$ (**1b**) and $[\text{NiCl}_2(\text{dipp})]$ (**1c**) with active magnesium in THF is performed in the presence of naphthalene at 0°C the complexes $[\text{Ni}(\text{C}_{10}\text{H}_8)(\text{dippe})]$ (**4b**), and $[\text{Ni}(\text{C}_{10}\text{H}_8)(\text{dipp})]$ (**4c**, $\text{C}_{10}\text{H}_8 =$ naphthalene) are formed in high yields (eq. 3).



The naphthalene complexes **4b** and **4c** were recrystallized from hexane solutions as dark red and red-yellow crystals, respectively. The reduction of $[\text{NiCl}_2(\text{dippm})]$ (**1a**) under similar conditions produced a mixture of unidentified products.

An attempt to prepare an alkylnickel(I) complex by treating **2c** with methyl-lithium was unsuccessful; $[\text{Ni}(\text{CH}_3)_2(\text{dipp})]$ (**5**) was the only product isolated (as dark red crystals) from the mixture. The ^1H NMR spectrum of this complex showed the methyl ligands as two doublets centered at $\delta -0.32$ ppm ($J(\text{P-H})$ 6.2 Hz).

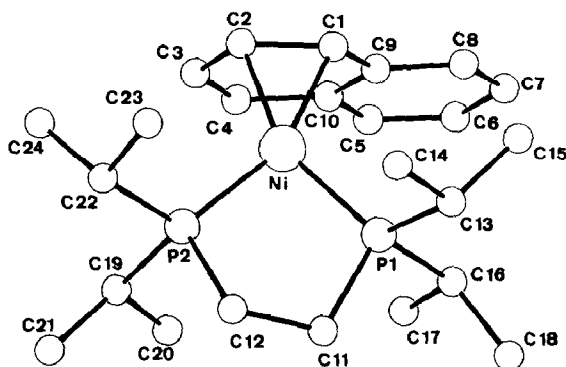


Fig. 1. The ORTEP diagram for **4b**.

Table 1

Crystal structure data for **4b** [23*] ^a

Formula:	C ₂₄ H ₄₀ NiP ₂	Mol. wt. 449.2
<i>a</i>	8.872(1) Å	Crystal system: triclinic
<i>b</i>	9.905(1) Å	Space group: <i>P</i> $\bar{1}$
<i>c</i>	15.572(1) Å	$\lambda(\text{Cu-K}\alpha)$ 1.54178 Å
α	97.67(1)°	<i>T</i> 20 °C
β	103.44(1)°	Scan mode $\omega/2\theta$
γ	107.44(1)°	$\pm h(10), \pm k(11), \pm l(19)$
<i>V</i>	1239.0 Å ³	Reflections measured 5395
<i>Z</i>	2	Reflections observed 4445 (<i>I</i> > 2 σ (<i>I</i>))
<i>D</i> _c	1.20 g cm ⁻³	Parameters refined 244
μ	23.82 cm ⁻¹	Max. shift/esd. 0.01
<i>F</i> (000)	484 e	Residual electron density $\pm 0.40 \text{ e}\text{\AA}^{-3}$
<i>R</i>	0.049	
<i>R</i> _w	0.061 (<i>w</i> = 1/ σ^2 (<i>F</i> _o))	

^a Solution by standard heavy atom method; hydrogen atoms calculated.

Table 2

Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for **4b** (with standard deviations in parentheses)

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} \bar{a}_i^* \bar{a}_j^* \bar{a}_i \cdot \bar{a}_j$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ni	0.4916(1)	0.0328(1)	0.2057(1)	0.043(1)
P(1)	0.4232(1)	0.2231(1)	0.2256(1)	0.046(1)
P(2)	0.2436(1)	-0.1095(1)	0.1874(1)	0.048(1)
C(1)	0.7305(3)	0.0821(3)	0.2123(2)	0.055(2)
C(2)	0.6492(4)	-0.0715(3)	0.1979(2)	0.062(2)
C(3)	0.6668(4)	-0.1360(4)	0.2746(3)	0.076(3)
C(4)	0.7600(4)	-0.0601(4)	0.3580(3)	0.078(3)
C(5)	0.9585(5)	0.1722(5)	0.4591(3)	0.086(3)
C(6)	1.0488(5)	0.3151(6)	0.4728(3)	0.090(3)
C(7)	1.0367(4)	0.3836(4)	0.4018(3)	0.086(3)
C(8)	0.9358(4)	0.3091(4)	0.3175(3)	0.065(2)
C(9)	0.8404(3)	0.1628(3)	0.3013(2)	0.052(2)
C(10)	0.8536(4)	0.0925(4)	0.3743(2)	0.063(2)
C(11)	0.2048(4)	0.1605(3)	0.2277(2)	0.060(2)
C(12)	0.1111(3)	0.0042(3)	0.1755(3)	0.065(2)
C(13)	0.4212(4)	0.3335(3)	0.1381(2)	0.066(3)
C(14)	0.3275(6)	0.2366(5)	0.0456(3)	0.099(4)
C(15)	0.5953(6)	0.4215(5)	0.1405(3)	0.097(4)
C(16)	0.5322(4)	0.3619(3)	0.3323(2)	0.064(2)
C(17)	0.5494(5)	0.2914(5)	0.4123(3)	0.089(3)
C(18)	0.4596(6)	0.4812(4)	0.3471(3)	0.092(4)
C(19)	0.2021(5)	-0.1988(4)	0.2806(3)	0.090(3)
C(20)	0.2893(7)	-0.1130(8)	0.3692(4)	0.150(6)
C(21)	0.0228(6)	-0.2900(5)	0.2668(4)	0.108(4)
C(22)	0.1389(4)	-0.2588(3)	0.0852(2)	0.060(2)
C(23)	0.1627(5)	-0.2037(4)	0.0009(3)	0.084(3)
C(24)	0.2082(5)	-0.3824(4)	0.0942(3)	0.085(3)

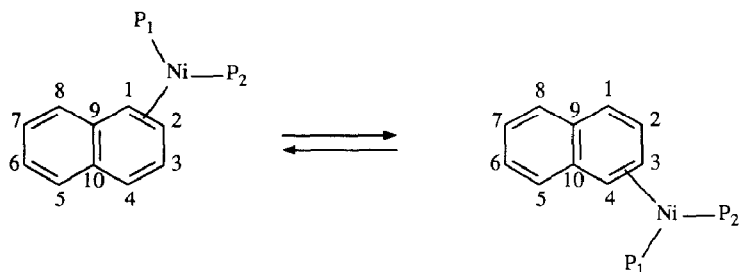
Table 3

Selected bond distances (Å) and angles (°) of **4b**

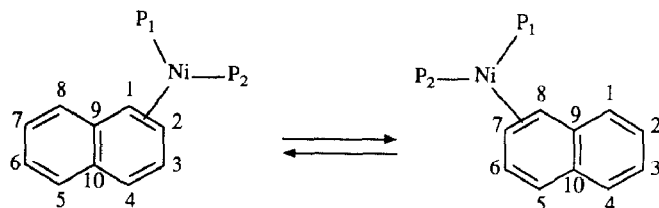
Ni–P(1)	2.153(1)	C(2)–Ni–C(1)	42.2(1)
Ni–P(2)	2.157(1)	C(2)–Ni–P(2)	113.5(1)
Ni–C(1)	2.002(3)	C(2)–Ni–P(1)	154.3(1)
Ni–C(2)	1.987(3)	C(1)–Ni–P(2)	155.7(1)
P(1)–C(11)	1.859(3)	C(1)–Ni–P(1)	112.2(1)
P(2)–C(12)	1.853(3)	P(2)–Ni–P(1)	92.2(1)
C(1)–C(2)	1.436(5)	C(11)–P(1)–Ni	106.8(1)
C(1)–C(9)	1.456(5)	C(12)–P(2)–Ni	106.5(1)
C(2)–C(3)	1.427(6)	C(9)–C(1)–C(2)	119.3(3)
C(3)–C(4)	1.344(6)	C(9)–C(1)–Ni	113.0(2)
C(4)–C(10)	1.445(6)	C(2)–C(1)–Ni	68.3(2)
C(5)–C(6)	1.361(8)	C(3)–C(2)–C(1)	117.9(3)
C(5)–C(10)	1.395(6)	C(3)–C(2)–Ni	106.8(2)
C(6)–C(7)	1.373(7)	C(1)–C(2)–Ni	69.5(2)
C(7)–C(8)	1.368(6)	C(4)–C(3)–C(2)	122.8(4)
C(8)–C(9)	1.396(5)	C(10)–C(4)–C(3)	121.1(4)
C(9)–C(10)	1.411(5)	C(10)–C(5)–C(6)	121.6(4)
C(11)–C(12)	1.526(5)	C(7)–C(6)–C(5)	119.6(4)
		C(8)–C(7)–C(6)	120.5(4)
		C(9)–C(8)–C(7)	121.3(4)
		C(10)–C(9)–C(8)	118.0(3)
		C(10)–C(9)–C(1)	119.8(3)
		C(8)–C(9)–C(1)	122.1(3)
		C(9)–C(10)–C(5)	118.9(4)
		C(9)–C(10)–C(4)	118.7(3)
		C(5)–C(10)–C(4)	122.4(4)
		C(12)–C(11)–P(1)	112.2(2)
		C(11)–C(12)–P(2)	111.9(2)

The crystal structure of the Ni⁰ complex **4b** was determined by an X-ray diffraction study. The ORTEP diagram for **4b** is given in Fig. 1, and the crystal structure data are listed in Table 1.

Atomic coordinates are listed in Table 2 and selected interatomic distances and angles in Table 3. The molecular structure of **4b** involves a η^2 -arene–metal bond and is closely related to that of bis(tricyclohexylphosphine)(1,2- η^2 -anthracene)-nickel(0) (**6**) [10]. In contrast to the anthracene compound **6**, in which the P₂NiC₂ fragment is non-planar owing to steric repulsions between the anthracene atoms and one cyclohexyl group, the coordination of the Ni atom in **4b** is almost trigonal planar (± 0.02 Å). The Ni atom is bonded to P(1) 2.153(1) Å, P(2) 2.157(1) Å, C(1) 2.002(3) Å and C(2) 1.987(3) Å. The P(1)–Ni–P(2) chelate angle of 92.2(1)° in **4b** is much smaller than the corresponding non-cyclic angle of 118.3(1)° in the complex **6**. In both compounds partial deconjugation of the coordinated arenes is observed with localized C(1)=C(2) and C(3)=C(4) double bonds, the former being elongated due to the Ni complexation. The torsion angle C(9)–C(1)–C(2)–C(3) of 6.3°, indicating deviation from planarity in the naphthalene ligand caused by the arene–metal bonding, is significantly smaller in **4b** than the corresponding angle of 12.3° in **6**. Similarly the aromatic ring is bonded at the site with the largest π -density.



Scheme 1. P_1P_2Ni exchange on the same ring of naphthalene.



Scheme 2. P_1P_2Ni exchange between rings on naphthalene.

The solution and solid state ^{13}C and ^{31}P NMR data of **4b** and **4c** have been reported in detail previously [11]. The solid state ^{13}C NMR spectrum of **4b** and **4c** also showed the naphthalene ligands to be η^2 -bonded to nickel. However in solution at $40^\circ C$ only five signals are observed for the naphthalene ligands. Although this suggests that the naphthalene ligands are η^4 -bonded, the observations are best accounted for in terms of rapid exchange between the 1,2 and 3,4 bonds in a η^2 -bonded naphthalene (Scheme 1).

From the NMR spectra [11] the energy barrier for this process in solution can be shown to be not more than 5.4 kcal/mol. Intramolecular exchange processes in η^2 -bonded benzene molecules were recently observed by Taube et al. [8]. At $40^\circ C$ a second process becomes significant, in which the P_2Ni unit is transferred from one ring of the naphthalene to the other (Scheme 2). The energy barrier for the transfer between rings is ca. 15 kcal/mol.

Mononuclear complexes of naphthalene are known to coordinate also in the η^4 - as well as in the η^6 -fashion. The naphthalene ligand can also form homo- and hetero-dinuclear complexes as demonstrated by the preparation of V, Cr, Fe and Co complexes having bridging naphthalene ligands [12].

Experimental

All operations were conducted under argon. Solvents were distilled from potassium-sodium alloy and were stored under argon. 1,1-Bis(diisopropylphosphino)methane, 1,2-bis(diisopropylphosphino)ethane, and 1,3-bis(diisopropylphosphino)propane were prepared by published procedures [13]. The nickel complexes **1a**, **1b** and **1c** were prepared by addition of the corresponding phosphine to degassed ethanol solutions of $NiCl_2 \cdot 6H_2O$. These compounds were isolated by filtration, washed several times with ether, and dried under vacuum. Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim a.d.

Ruhr. The ^1H NMR spectra were recorded on a Bruker AM 200 spectrometer at 200.1 MHz. Melting points were determined in sealed capillaries under argon. Potassium naphthalenide solutions were prepared by stirring potassium metal with a small excess of naphthalene in THF at -40°C for 12 h.

Preparation of [NiCl(dippm)] 2a

To a stirred suspension of 1.5 g (4 mmol) of $[\text{NiCl}_2(\text{dippm})]$ in 50 ml THF at -78°C were added 16 ml of a 0.25 M (4 mmol) THF solution of potassium naphthalenide. The mixture was allowed to reach room temperature and after 5 h stirring a clear solution was obtained. The THF was removed under reduced pressure and the uncomplexed naphthalene was sublimed out under high vacuum (1.33×10^{-2} Pa). The residue was extracted with toluene and the KCl removed by filtration. Evaporation to dryness and recrystallization of the residue from ether at -30°C yielded 1.0 g (73%) green crystals of **2a**. M.p. 177°C (decomposition). Anal. Found: P, 18.02; Cl, 10.29; Ni, 17.14. $\text{C}_{13}\text{H}_{30}\text{ClNiP}_2$ calcd.: P, 18.08; Cl, 10.35; Ni, 17.14%. M.S. 682 (molecular ion of dimer).

Preparation of [NiCl(dippe)] 2b

Red crystals of **2b** were prepared from 5.9 g (15 mmol) $[\text{NiCl}_2(\text{dippe})]$ and potassium naphthalenide (15 mmol) by the procedure described for **2a**. Yield 4.3 g (80%). M.p. 83°C . Anal. Found: P, 17.85; Cl, 10.50; Ni, 16.94. $\text{C}_{14}\text{H}_{32}\text{ClNiP}_2$ calcd.: P, 17.37; Cl, 9.94; Ni, 16.46%. M.S. 355 (molecular ion).

Preparation of [NiCl(dipp)] 2c

Light yellow crystals of **2c** were prepared from 10.15 g (25 mmol) $[\text{NiCl}_2(\text{dipp})]$ and potassium naphthalenide (25 mmol) by the procedure described for **2a**. Yield 6.8 g (73%). M.p. 115°C . Anal. Found: P, 16.68; Cl, 9.40; Ni, 15.94. $\text{C}_{15}\text{H}_{34}\text{ClNiP}_2$ calcd.: P, 16.72; Cl, 9.57; Ni, 15.84%. M.S. 369 (molecular ion).

Preparation of 2a and 2b from 1a and 1b by comproportionation with magnesium in THF

To a suspension of 2.0 g (5.6 mmol) of **1b** in 75 ml of THF at -30°C was added a ten-fold excess (1.4 g) of active magnesium [9*]. The stirred mixture was allowed to warm to 0°C , and after 1 h the dark red solution was decanted into a suspension of 2.0 g **1b** at 0°C in 30 ml THF. The mixture was stirred for an additional 12 h at room temperature. The solvent was removed and the residue worked up as described for **2a** above to yield 1.46 g $[\text{NiCl}(\text{dippe})]$ (**2b**). Complex **2a** was obtained in a 82% yield by this method.

Reaction of [NiCl(dipp)] 2c with MeLi to [Ni(CH₃)₂(dipp)] 5

A solution of 0.74 g (2 mmol) of **2c** in 25 ml of THF at -40°C was treated with 1.45 ml (2 mmol) of a 1.3 M ether solution of MeLi. The dark red mixture was allowed to warm to room temperature, and after 1 h the solvent was removed under vacuum. The crystalline residue was extracted with hexane and the LiCl was removed by filtration. Storage of the filtrate at -30°C produced, after 12 h, red brown crystals, which were isolated by filtration and identified as **5**. Yield 0.28 g (38%). M.p. 95°C . Anal. Found: P, 17.19; Ni, 16.19. $\text{C}_{17}\text{H}_{40}\text{NiP}_2$ calcd.: P, 16.96; Ni, 16.07%. M.S. 349 (molecular ion - 15).

Preparation of [Ni(C₁₀H₈)(dippe)] 4b

To a suspension of 5.2 g (13.3 mmol) of **1b** in 100 ml of THF at 0 °C was added 2.5 g (20 mmol) of naphthalene and 2 g of active magnesium [9*]. After 3 h stirring at room temperature the mixture was evaporated and the uncomplexed naphthalene was sublimed from the product at high vacuum (1.33×10^{-2} Pa). The residue was taken up in hexane and the solution was filtered then kept at -30 °C to yield 4.9 g (83%) dark red crystals of **4b**. M.p. 98 °C. Anal. Found: P, 13.59; Ni, 12.90. C₂₄H₄₀NiP₂ calcd.: P, 13.79; Ni, 13.07%. ¹H NMR (-30 °C, THF-*d*₈, δ in ppm), 0.72–1.08 (24H, 8CH₃, m), 1.47 (4H, 2CH₂, m), 1.77 (2H, 2CH, m), 2.00 (2H, 2CH, m), 5.35 (2H, 2=CH, m), 5.50 (2H, 2=CH, m), 6.77 (2H, 2=CH, m), 7.01 (2H, 2=CH, m). For ³¹P and ¹³C NMR data see ref. 11.

Preparation of [Ni(C₁₀H₈)(dipp)] 4c

Orange red crystals of **4c** were prepared from 4.37 g (10.7 mmol) [NiCl₂(dipp)] and 2.5 g naphthalene with an excess of active magnesium in THF according to the procedure described for **4b**. Yield 3.4 g (69%). M.p. 108 °C. Anal. Found: P, 13.68; Ni, 12.88. C₂₅H₄₂NiP₂ calcd.: P, 13.37; Ni, 12.67%. ¹H NMR (-30 °C, THF-*d*₈, δ in ppm), 0.78–1.09 (24H, 8CH₃, m), 1.33 (6H, 3CH₂, m), 1.68 (2H, 2CH, m), 1.94 (2H, 2CH, m), 5.33 (2H, 2=CH, m), 6.82 (2H, 2=CH, m), 7.09 (2H, 2=CH, m). For ³¹P and ¹³C NMR data see ref. 11.

Crystal structure analysis of 4b

The crystal chosen for data collection had approximate dimensions of 0.25 × 0.43 × 0.36 mm. The unit cell parameters were obtained by a least-squares fit to the θ -values of 72 automatically centered reflections ($17.4 < \theta < 73.2^\circ$). 5397 intensity data ($-10 < h < 10$, $-11 < k < 11$, $0 < l < 19$) were measured within the range $3.0 < \theta < 75.5^\circ$ on an Enraf–Nonius CAD 4 diffractometer with Cu-*K*_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption. $\sigma(F)$ was calculated from $\sigma(F) = ((\sigma(I)^2 + (Ik)^2)^{1/2})/2F$, where $k = 0.02$, 4445 reflections of a total of 5071 unique intensities satisfied the criterion $I > 2\sigma(I)$, and only these were used in the solution and the refinement of the structure. The structure was solved by the heavy atom method. Refinement was performed by full matrix least-squares method, where the function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2(F_o)$. The H atoms were placed at calculated positions ($d(C-H)$ 0.95 Å) and included in the refinement with fixed positions and isotropic thermal parameters (U_H 0.08 Å²). Refinement converged at $R = 0.049$ ($R_w = 0.061$) for 244 variables and 4445 observed reflections. The computer programs used from refs. 14–22. Supplementary material is available [23*].

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