# **Cationic MethallyInickel Complexes with Chelating** Ligands: A New Dynamic Complex Isomerization Equilibrium<sup>†</sup>

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The synthesis of the cationic complexes [methyl 2-(diphenylphosphino)benzoate- $\kappa^2 P, O$ ]- $(\eta^3$ -methallyl)nickel(II) tetrafluoroborate (1), [methyl 2-(diphenylphosphino)nicotinate- $\kappa^2 P$ , N]- $(\eta^3$ -methallyl)nickel(II) tetrafluoroborate (2), and bis[ $\mu$ -2-(diphenylphosphino)pyridine- $\kappa^2 P$ , N]bis( $\eta^3$ -methallyl)nickel(II) bis(tetrafluoroborate)·CH<sub>2</sub>Cl<sub>2</sub>(**3**) are reported. The crystal structures of 1 and 2 have been disclosed in a preliminary previous paper. The molecular structure of the cation of 2 in the crystal shows that the ligand forms a strained 4-membered ring with a  $\kappa^2 P N$  coordination. In solution a new dynamic complex isomerization was found, indicating an equilibrium between 2 and 4, the latter with a 6-membered ring and a  $\kappa^2 P, O$ coordination of the ligand methyl 2-(diphenylphosphino)nicotinate (5).

### Introduction

Hemilability of organometallic complexes with chelating ligands are of interest in catalytic processes.<sup>2</sup> We are studying the catalytic behavior of neutral and cationic methallylnickel complexes with chelating ligands in the ethene oligomerization.<sup>1</sup> Cationic organometallic nickel complexes with monodentate phosphines have already been thoroughly studied in the alkene oligomerization, but only very scarce results have been published for bidentate or multidentate ligands.<sup>3,4</sup> Since the knowledge about the structure of these cationic complexes in the solid state and in solution is also limited, we wanted first to investigate them in detail.

Two cationic ( $\eta^3$ -methallyl)nickel complexes have been synthesized, namely [methyl 2-(diphenylphosphino)benzoate- $\kappa^2 P, O$ ]( $\eta^3$ -methallyl)nickel(II) tetrafluoroborate (1) and [methyl 2-(diphenylphosphino)nicotinate- $\kappa^2 P_{,N}$ ]- $(\eta^3$ -methallyl)nickel(II) tetrafluoroborate (2), and their crystal structures have been determined, which are schematically presented in Figure 1.

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Figure 1. Schematic molecular structure of the cations of 1 and 2 in the solid state.

The cation moiety of 1 has a  $\kappa^2 P, O$  and 2 a  $\kappa^2 P, N$ coordination of the ligands. It is surprising that methyl 2-(diphenylphosphino)nicotinate (5) forms a strained 4-membered ring with the methallylnickel fragment and not the more common 6-membered ring like observed for methyl 2-(diphenylphosphino)benzoate (6) in complex 1.

In this paper we present the details for the synthesis of 1, 2, and  $bis[\mu-2-(diphenylphosphino)pyridine-\kappa^2 P, N]$  $bis(\eta^3$ -methallyl)nickel(II) bis(tetrafluoroborate) (3) and the crystal structure of 3 and discuss their structures in the solid state and in solution.

### **Results and Discussion**

Synthesis of the Ligands. The bidentate ligand methyl 2-(diphenylphosphino)benzoate (6) was obtained by known procedures.<sup>5</sup> By the adaptation of these methods (Scheme 1), the new 2-(diphenylphosphino)nicotinic acid was obtained with 32% and its pale yellow methyl ester 5 with 74% yield.

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<sup>&</sup>lt;sup>+</sup> Dedicated to Prof. Dr. H.-D. Scharf on the occasion of his 65th birthday.

<sup>&</sup>lt;sup>8</sup> Abstract published in Advance ACS Abstracts, October 1, 1995.
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The ligand 5 offers compared to 6 three possible coordination sites: the phosphorus, the nitrogen, and the ester function can act as Lewis bases. The rigid aromatic ring makes the simultaneous coordination of all three donors in a mononuclear complex difficult.

The bidentate 2-(diphenylphosphino)pyridine (7) was synthesized according to the literature.<sup>6</sup>

Synthesis of the Complexes. Opening the dimeric structure of bis(bromomethallylnickel) in the presence of the phosphorus donor function of the ligands 6, 5, and 7 gives rise to the neutral precursors 8, 9, and 10, which have been isolated and characterized. The bromo ligand can be abstracted by a metathetical exchange with tetrafluoroborate by adding TlBF<sub>4</sub>, and the liberated coordination site is occupied by the second donor function of the ligands, thus providing the red cationic complexes 1-3 (Scheme 2).



The three structures 1-3 depicted for the cationic complexes reflect the structures present in the crystals.

Crystal Structures. The crystal and molecular structures of the mononuclear complexes 1 and 2 have already been published, but their syntheses are reported here.<sup>1</sup> The structure of **3** has also been determined by X-ray diffraction. Figure 2 shows a drawing of the binuclear cation. Selected bonds and angles are listed



Figure 2. ORTEP plot of the cation of complex 3. (The phenyl rings and hydrogen atoms have been omitted for clarity.)

Table 1.	Selected	Bond Le	engths	and l	Distances	( <b>Á</b> )
and A	ngles (des	g) for the	e Čatio	on of (	<b>Complex</b> :	3

			-
Ni(1)-P(1)	2.201(1)	N(1)-C(9)	1.350(6)
Ni(1) - N(1)	1.953(4)	C(9) - P(2)	1.835(5)
Ni(1) = C(1) Ni(1) = C(2)	2.022(6)	C(1) = C(2) C(1) = C(3)	1.408(7) 1.977(9)
Ni(1) - C(2) Ni(1) - C(3)	2.028(6)	$N_i(1)$ , $N_i(2)$	3.932(1)
P(1) - Ni(1) - N(1)	102.2(1)	N(1)-C(9)-P(2)	117.1(4)
C(2) - Ni(1) - C(3)	70.4(2)	Ni(1) - P(1) - C(14)	120.1(1)
Ni(1) - N(1) - C(9)	123.3(3)		

in Table 1. The bond distances for 3, as noticed for complexes 1 and 2, are in the expected range. $^{4,7}$ 

In complex 1 the P O ligand 6 is  $\kappa^2 P, O$  coordinated and forms a 6-membered ring. The ligand 5 offers the possibility to act as a P O or a P N chelating ligand in a mononuclear complex. The formation of a P Ochelated structure analog to 1 is expected to be prefered to a P N coordination which implies a strained 4-membered ring. However the X-ray diffraction of 2 proves the formation of a 4-membered ring. The coordination of the nitrogen instead of the oxygen seems to counterbalance the ring strain. Accordingly, the ligand 7 should also form the strained 4-membered ring, but a dimeric structure was actually found, in which 7 acts as a bridging ligand. Such a bridged structure is known for homo- as well as heterobinuclear transition-metal complexes.<sup>8</sup> The chelating behavior of 7 is also known for Pt complexes.<sup>9</sup> In nickel chemistry only  $\kappa P$  coordination has been proven by X-ray diffraction.<sup>10</sup> The distance between the nickel centers Ni(1) and Ni(2) in 3 is out of the range 2.3-2.8 Å for which a Ni-Ni interaction is considered.<sup>7</sup>

To demonstrate the unusual 4-membered ring coordination for 2, the distances between the coordinated non-carbon atoms of the ligands in the complexes and the angles in the rings are summarized in Table 2.

The angles in the 6-membered ring of 1 reflect a low ring tension. The P-Ni-O(1) angle of 92.6° nearly correspondents with the the ideal value of 90° for the square-planar coordination sphere. The Ni-P-C(8)angle of 108.1° is close to the angle expected for a tetrahedron. The angles around  $sp^2$  carbons C(8) and

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Table 2. Selected Distances (Å), Angles (deg), and a Dihedral Angle (deg) in the Cationic Moieties of 1-3

1		2 3		3		
· · · · · · · · · · · · · · · · · · ·		Dist	ances	a the second		
P, O(1)	2.929(3)	P, N	2.482(5)	P(1), N(1) P(1), N(2)	$3.236(4) \\ 2.736(4)$	
		Ring	Angles			
O(1)-Ni-P	92.6(1)	N-Ni-P	73.9(1)	N(1) - Ni(1) - P(1)	102.2(1)	
Ni-P-C(8)	108.1(1)	Ni-P-C(5)	80.5(2)	Ni(1) - P(1) - C(14)	120.1(1)	
P-C(8)-C(7)	125.5(3)	P-C(5)-N	100.2(4)	P(1)-C(14)-N(2)	115.2(4)	
C(5) - C(7) - C(8)	120.0(4)	C(5)-N-Ni	105.0(3)	C(14) - N(2) - Ni(2)	124.9(3)	
		Torsio	n Angles			
C(7)-C(8)-P-Ni	29.5(4)	P-C(5)-N-Ni	6.4(3)			
		Dihedr	al Angle <sup>a</sup>			
				P(1),N(1),M(12),M(13)		
				P(2),N(2),M(56),M(57)	{48.4(2)	

<sup>a</sup> Least-squares planes with M(12), M(13), M(56), and M(57) midpoints of C(1)-C(2), C(1)-C(3), C(5)-C(6), and C(5)-C(7), respectively.

C(7) have values of approximately 120°, whereas the angles in 2 and 3 exhibit neat differences. Compared to the ideal value of 90°, the P-Ni-N angle is decreased in the 4-membered ring and increased in the binuclear complex. The angles at the phosphorus and the nitrogen show similar behavior. The angle in the ligand between the phosphorus and the nitrogen is in the 4-membered ring of 2 smaller and in 3 bigger than in the noncoordinated ligand 7 with  $111.9^{\circ}.^{11}$ 

The planarity of the hetero rings containing the Ni atom of the two cations 1 and 2 can be shown via the torsion angles in the rings. In the 6-membered ring in 1, the selected torsion angle C(7)-C(8)-P-Ni (29.5°) reflects the lack of planarity. For the 4-membered ring in 2, P-C(5)-N-Ni is equal to 6.4°, which is a sufficient indication for a close to planar structure. The 8-membered hetero ring in the binuclear complex 3 is not planar which is demonstrated via the dihedral angle between the coordination planes P(1),N(1),M(12),M(13)and P(2),N(2),M(56),M(57) of 48.4°.

To demonstrate the influence of the different ring sizes on the coordination spheres, comparisons of the distances between the N-donor and the P-donor bonds to the nickel center in the complexes 2 and 3 are useful. The complexes both have a  $P_{,N}$  coordination mode with the similar ligands 5 and 7. The distances amount to 2.48 and 3.23 Å for the P<sup>N</sup> ligand in 2 and in 3, respectively. In comparison to the free ligand 7 with a P-N distance of 2.65 Å,<sup>11</sup> the distance is shorter in the 4-membered ring in 2 and longer in the binuclear complex 3. In the latter the two donors do not belong to the same ligand. The difference between the N-P distances is approximately 0.8 Å for the complexes 2 and 3.

Structures in Solutions. The X-ray crystal structures for 1-3 present a variety of different coordination modes for the three ligands 6, 5, and 7. The three cationic complexes show the ability of nickel to form a 4-membered ring with  $\kappa^2 P, N$  coordination a 6-membered ring with  $\kappa^2 P, O$  coordination, and a binuclear complex with a bridging ligand in the solid state. The question arises whether these results are observable also in solution. Especially the tridentate  $P \cap N$  ligand 5 offers sites for a possible intramolecular, dynamic behavior. The complexes were studied by IR and NMR spectroscopy.

The IR spectroscopy is especially well adapted for the examination of the coordination of the ester function, since a downfield shift of the CO streching band

Table 3.	v(CO) (cm <sup>-1</sup> ) of the Complexes 1 and 2	
	and the Ligands 6 and 5	

	<b>o</b>						
	mediu	m					
	$\mathrm{CH}_{2}\mathrm{Cl}_{2}$	KBr	$\Delta \nu (\mathrm{CH}_2 \mathrm{Cl}_2)^a$				
	I	igands	· · · · · · · · · · · · · · · · · · ·				
6	1717	0					
5	1723						
	Co	mplexes					
1	1638	-	-79				
2	1737, 1647	$1729^{b}$	+14, -76				

<sup>a</sup> Difference of  $\nu$  (C=O) between the complex and the free ligand. <sup>b</sup> Crystals of **2** were used to prepare the KBr pellet.

indicates its coordination. The results are summarized in Table 3.

The carbonyl function of the free ligands absorbs in the expected region around 1720 cm<sup>-1</sup>. The cationic complex 1 shows a shift of  $\Delta \nu = -79$  cm<sup>-1</sup> which indicates the coordination of the ester moiety of 6. The complex 2 generates two absorption bands in solution: the first one located at 1737 cm<sup>-1</sup> is close to the free ligand 5 and corresponds to a noncoordinated ester function. The same result is observed in the IR spectrum of 2 crystals in KBr pellets, which show only one absorption at 1729 cm<sup>-1</sup>. The second band has a shift of -76 cm<sup>-1</sup>, which can be assigned, as in 1, to the coordinated ester. These results indicate that there are two different species in solution for 2.

 $^{31}P$  NMR is a powerful tool to answer the question about the coordination of the phosphorus and the ring size by examinating the contribution of the ring formation  $\Delta_R\delta$  to the chemical shift  $\delta$  of the phosphorus nucleus. Generally, the formation of 4- and 6-membered rings induces a highfield shift, but the 4-membered ring produces a more negative value for  $\Delta_R\delta$ . Five-membered rings are reflected in a positive  $\Delta_R\delta$ . In rings with a larger size, there is no ring contribution to the chemical shift.<sup>12</sup> There are also examples for nickel complexes.<sup>13</sup> The NMR experiments were carried out at different temperatures. The results are presented in Table 4.

The influence of the temperature on the chemical shift is low. For example a decrease of 52 K changes the chemical shifts for the compounds **5** and **9** by less than 1 ppm. The  $\kappa P$  coordination of the ligands in the neutral precursor complexes **8**-10 is reflected in the  $\Delta\delta$  value of approximately 30 ppm. The complexes 1 and 3 form in solution only one species. The negative  $\Delta_R\delta$  for 1

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Table 4. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm) Data for 1-10

	δ	•		èct		
compd	295 K 243 K		type	295 K	243 K	
		Ligan	ds			
6 5 7	-4.1 4.4 -3.7	4.0				
		Precurs	sors			
8	29.2		$\Delta \delta^a$	33.3		
9	34.5	35.0		30.1	31.0	
10	25.4			29.1		
Complexes						
1	19.7	•	$\Delta_{\mathbf{R}} \delta^b$	-9.5		
2, 4	10 (v br)	5.3(2)		-25	-29.7 (2)	
3	26.0	$20.5 (4)^c$		04	-14.5 (4)	
v	20.0			0.1		

<sup>a</sup> Difference between free ligand and precursor. <sup>b</sup> Difference between precursor and complex, ring contribution. <sup>c</sup> Equilibrium constant K = (integral of 4)/(integral of 2) = 0.41.

indicates the formation of a 6-membered ring in solution, as observed in the crystalline state. The  $\kappa^2 P, O$  coordination is also confirmed by the IR-spectroscopic results. The cationic complex **3** has a ring contribution value close to 0 ppm. Its  $\Delta_R \delta$  is suited to the 8-membered ring of the binuclear complex. Thus, the same structures can be assumed for the crystal and the solution. It should be noticed that the  $\Delta_R \delta$  values include two factors: the formation of the rings and the change of the complex charge from the neutral precursors to the cationic complexes. The latter has only a minor influence so that it can be omitted in the discussion.<sup>4</sup>

The situation for the complex **2** is more complicated, since its spectrum exhibits at room temperature a very broad signal, which indicates a fast exchange in the coordination sphere of the nickel center at the NMR time scale. The signal splits up at 243 K into two sharp peaks with  $\Delta_R \delta = -29.7$  ppm and  $\Delta_R \delta = -14.5$  ppm. The exchange is slowed down, and the two species can be distinguished. The negative  $\Delta_R \delta$  values at low temperature mark the existence of 4- and 6-membered rings. The more negative value must be attributed to a 4-membered ring with a  $\kappa^2 P_{,N}$  coordination of the ligand 5 like in the crystal 2. The less negative  $\Delta_{\rm R}\delta$ value for the second peak implies that the phosphorus atom (4) is a member of a 6-membered ring like in 1 whereas the ligand has  $\kappa^2 P, O$  coordination. These two coordination modes of the ester group in 2 were confirmed by the IR spectra, in which the coordinated and the noncoordinated ester moiety could be identified at room temperature. The equilibrium constant of 2 and **4** is determined by the integration of the <sup>31</sup>P NMR: K= (integral of 4)/(integral of 2) = 0.41. The  $\kappa^2 P_1 N$ structure of 2, which was isolated as crystals, dominates in solution.

The IR and <sup>31</sup>P NMR spectra carried out in solution and the crystal structure of 2 are in agreement with an equilibrium for 2 in solution, as shown in eq 1.



The intramolecular substitution of the nitrogen donor by the oxygen donor and vice versa leads to a dynamic behavior. The equilibrium can also be confirmed by  $^{13}$ C NMR. At low temperature (243 K), different signals can also be identified for the carbons related to 2 and 4.

## **Concluding Remarks**

The structures of three new cationic methallyl complexes in the solid state and in solution are described. Our results show that methallylnickel fragment forms with the PO ligand 6 a cationic complex 1 with a 6-membered ring, in which the ligand is  $\kappa^2 P, O$  coordinated, in solution as well as in the crystal structure. Using the N<sup>P</sup>O ligand 5, two competitive coordination modes, a strained 4-membered ring with a  $\kappa^2 P_{,N}$ coordination (2) and the 6-membered ring (4) as in 1, are observed. A dynamic complex isomerization equilibrium between these two coordination forms exists in solution. In the crystal only 2 coordination occurs. As a chelating ligand in a monomeric complex the P N ligand 7 would have the possibility to form a 4-membered-ring analogue to 2. But in the crystal and in solution the dimeric structure  $\mathbf{3}$ , in which  $\mathbf{7}$  acts as a bridging ligand, is observed.

The results show that the determination of the crystal structure can give only hints to the structure of a complex in solution.

### **Experimental Section**

General Comments. All manipulations were performed under an argon atmosphere using standard Schlenk tube techniques, if not otherwise indicated. Reagents and solvents were purified, dried, and handled under argon with standard laboratory methods. Methyl 2-(diphenylphosphino)benzoate (**6**) was prepared according to the literature procedure.<sup>4</sup> NMR spectra were performed on a Bruker AM250 spectrometer at temperatures listed. The chemical shifts  $\delta$  are given in ppm, and the coupling constants J, in Hz. The numbers appearing in Figure 1, Schemes 1 and 2, and eq 1 for the carbon atoms in the ligands and complexes give convenient help to identify the atoms in the NMR spectra.

2-(Diphenylphosphino)nicotinic Acid. A 4.41 g (192 mmol) amount of sodium was dissolved in approximately 430 cm<sup>3</sup> of liquid ammonia. A 25.22 g (96 mmol) amount of triphenylphosphine was slowly added, and the mixture was stirred for 2.5 h at -40 °C. The resulting orange solution was cooled down to -78 °C, and 15.13 g (96 mmol) of 2-chloronicotinic acid was added. After the addition of 150 cm<sup>3</sup> of THF via a syringe, the reaction mixture was slowly warmed to room temperature overnight. The yellow suspension was dissolved in 400 cm<sup>3</sup> water and worked up under air by extraction with 115 cm<sup>3</sup> of  $Et_2O$ . The aqueous phase was acidified to pH 4 with concentrated HCl and extracted with three 60-cm<sup>3</sup> portions of CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over CaSO<sub>4</sub> and evaporated, and the resulting solid was recrystallized twice from hot MeOH under an argon atmosphere. A 9.53 g (31 mmol, yield 32%) amount of the pale yellow product were isolated. Solvent traces could not be removed by recrystallization from chloroform. Anal. Calcd for C<sub>18</sub>H<sub>14</sub>NO<sub>2</sub> + CH<sub>2</sub>-Cl<sub>2</sub>: C, 63.17; H, 4.46; N, 3.88. Found: C, 65.65; H, 4.64; N 4.04. Melting point: 165 °C. IR (Nujol):  $\nu$ (C=O) 1699 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, [<sup>2</sup>H<sub>6</sub>]acetone):  $\delta = 8.63 \{ d (^{3}J(H,H) = 4.8), \}$  $\begin{array}{l} d ({}^{4}J(H,H)=1.8), 1H, H^{C6} \}, 8.29 \ \{d ({}^{3}J(H,H)=7.9), d ({}^{4}J(H,H) \\ = 1.8), d ({}^{4}J(H,P)=4.3), 1H, H^{C8} \}, 7.40 \ \{d ({}^{3}J(H,H)=7.9), d \\ \end{array}$  $({}^{3}J(H,H) = 4.8), 1H, H^{C7}\}, 7.4-7.2 \{m, 10H, H^{arom}\}. {}^{31}P\{{}^{1}H\}$ NMR (81 MHz, CDCl<sub>3</sub>):  $\delta = 4.5$ . <sup>13</sup>C NMR (63 MHz, [<sup>2</sup>H<sub>6</sub>]acetone):  $\delta = 166.6 \{s, C10\}; 165.0 \{d ({}^{1}J(C,P) = 20), C5\};$ 152.1 {d ( ${}^{1}J(C,H) = 181$ ), C6}; 139–128 {m, C<sup>arom</sup>}; 122.3 {d  $({}^{1}J(C,H) = 167), C7\}.$ 

Methyl 2-(diphenylphosphino)nicotinate (5). At 0 °C under air, a 50-cm<sup>3</sup> of Et<sub>2</sub>O solution of approximately 16.6 mmol of diazomethane<sup>14</sup> was slowly added to a stirred suspension of 4.58 g (14.9 mmol) of 2-(diphenylphosphino)nicotinic acid in 300  $\text{cm}^3$  of Et<sub>2</sub>O. The precipitated product was dissolved by adding MeOH to the reaction mixture at room temperature. After addition of a small amount of acetic acid, the solvents were evaporated till the first crystals were formed. The solid was redissolved by heating to reflux under argon. A 3.52 g (11.0 mmol; yield 74%) amount of the pale yellow product was isolated by cooling to 4 °C. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>NO<sub>2</sub>: C, 71.02; H, 5.02; N, 4.36. Found: C, 70.59; H, 5.20; N, 4.13. Melting point: 94 °C. IR (Nujol): v(C=O) 1717 cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C=O) 1723 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.69 \{ d (^{3}J(H,H) = 4.7), d (^{4}J(H,H) = 1.8), 1H, \}$  $H^{C6}$ }, 8.16 {d ( ${}^{4}J(H,H) = 1.8$ ), d ( ${}^{4}J(H,P) = 4.2$ ), d ( ${}^{3}J(H,H) = 4.2$ ) 7.8), 1H, H<sup>C8</sup>}, 7.8-7.2 {m, 11H, H<sup>arom</sup>}, 3.69 {s, 3H, H<sup>C11</sup>} ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, CDCl<sub>3</sub>):  $\delta = 4.4$  ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, T = 243 K):  $\delta = 4.0$  ppm. <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):  $\delta = 166.5 \{s, C10\}, 164.6 \{d ({}^{1}J(C,P) = 19), m, d ({}^{1}J(C,P) = 19), d ({}^{1}J(C,P) = 19), m, d ({}^{1}J(C,P) = 19), d ({}^{1}J(C,P) = 19), m, d ({}^{1}J(C,P) = 19), d ({}^{1}J(C,P$ C5}, 152.0 {d  $({}^{1}J(C,H) = 178)$ , m, C6}, 137-127 {m, C<sup>arom</sup>}, 121.5 {d ( ${}^{1}J(C,H) = 166$ ), m, C7}, 52.0 {q ( ${}^{1}J(C,H) = 147$ ), C11}.

Bromo[methyl 2-(diphenylphosphino)benzoate-*κ*P]-(η<sup>3</sup>-methallyl)nickel(II) (8). To a solution of 1.12 g (2.89 mmol) of bis[bromo(η<sup>3</sup>-methallyl)nickel] in 5 cm<sup>3</sup> of THF, 1.83 g (5.71 mmol) of **6** in 9 cm<sup>3</sup> of THF was slowly added at approximately -20 °C. The solution was warmed overnight to room temperature. The red precipitate was filtered out, washed with small amounts of THF, and dried under vacuum. A 1.96 g (3.81 mmol; yield 67%) amount of **8** was isolated. IR (Nujol):  $\nu$ (C=O) = 1710 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.15 {m, 1H, H<sup>C12</sup>}, 7.7–6.9 {m, 14H, H<sup>arom</sup>}, 3.90 {s, 3H, H<sup>C6</sup>}, 3.26 {s, 2H, H<sup>C2+3,syn</sup>}, 2.42 {s, 2H, H<sup>C2+3,anti</sup>}, 1.99 {s, 3H, H<sup>C4</sup>} ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, CDCl<sub>3</sub>):  $\delta$  = 29.2. <sup>13</sup>C NMR (50 MHz, [<sup>2</sup>H<sub>8</sub>]THF):  $\delta$  = 167.7 {s, C5}, 136–128 {m, C<sup>arom</sup>}, 121.3 {s, C1}, 52.4 {q (<sup>1</sup>J(C,H) = 147), C6}, 22.6 {q (<sup>1</sup>J(C,H) = 128), C4}.

Bromo[methyl 2-(diphenylphosphino)nicotinate-*κ*P]-(η<sup>3</sup>-methallyl)nickel(II) (9). To a solution of 0.63 g (1.63 mmol) of bis[bromo(η<sup>3</sup>-methallyl)nickel] in 5 cm<sup>3</sup> of THF, 1.05 g (3.27 mmol) of **5** in 5 cm<sup>3</sup> of THF was slowly added at approximately -35 °C. The solution was warmed overnight to room temperature, and the solvent was evaporated under vacuum. A 1.68 g (3.27 mmol; yield 100%) amount of the red crude product was isolated. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C=O) 1713 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (32 MHz, CDCl<sub>3</sub>):  $\delta$  = 34.5. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, *T* = 243 K):  $\delta$  = 35.0.

**Bromo[2-(diphenylphosphino)pyridine-** $\kappa$ **P]methallylnickel(II) (10).** To a solution of 2.21 g (5.70 mmol) of bis-[bromo( $\eta^3$ -methallyl)nickel] in 15 cm<sup>3</sup> of THF, 3.01 g (11.43 mmol) of 5 in 14 cm<sup>3</sup> of THF was slowly added at approximately -25 °C. The solution was warmed overnight to room temperature and the solvent was evaporated under vacuum. A 5.22 g (11.40 mmol; yield 100%) amount of the red crude product was isolated. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 25.4$ .

[Methyl 2-(diphenylphosphino)benzoate- $\kappa^2 P$ ,O]( $\eta^3$ methallyl)nickel(II) Tetrafluoroborate (1). To a solution of 1.16 g (2.26 mmol) of 8 in 30 cm<sup>3</sup> of THF, 0.66 g (2.27 mmol) of TlBF<sub>4</sub> was added at 0 °C and stirred for 2 h. The suspension was reduced to a solid, which was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and filtrated over Celite to remove the thallium bromide formed. By careful addition of 20 cm<sup>3</sup> of Et<sub>2</sub>O on the red solution (approximately 5 cm<sup>3</sup>) red crystals were grown at 4 °C overnight. By cooling down of the sample to -20 °C for 1 h, the crystallization was completed. The solution was removed, and the crystals were washed with Et<sub>2</sub>O. After drying under vacuum, 1.10 g (2.11 mmol, yield = 93%) of 1 was obtained. Anal. Calcd for C<sub>24</sub>H<sub>24</sub>BF<sub>4</sub>NiO<sub>2</sub>P: C, 55.34; H, 4.64. Found: C, 54.49; H, 4.55. IR (Nujol):  $\nu$ (C=O) 1635 cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1638 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, T = 213

Table 5. Crystal Data and Experimental Details for Compound 3

formula mol wt	$C_{43}H_{44}B_2Cl_2F_8N_2Ni_2P_2$ 1012 7
aclon and habit	aranga narallalaninad
	0 40 0 20 0 15
cryst size, mm	$0.40 \times 0.30 \times 0.15$
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Á	13.880(1)
b, Å	18.457(2)
c. Å	17.986(2)
$\dot{\beta}$ , deg	103.86(1)
$V. \overline{A}^{\overline{3}}$	4473.6(9)
Z	4
$D({ m calcd}), { m g} { m cm}^{-1}$	1.504
diffractometer	Enraf-Nonius CAD4
Λ(Μο Κα), Å	0.710 73
$\mu$ , mm <sup>-1</sup>	1.10
transm factor, max–min	1.000 - 0.967
temp, K	295
no. of collcd data	7849, all unique
no. of obsd. data	$3919(I > 3\sigma(I))$
no. of params refined	406
$R, R_{w^{a}}$	0.036, 0.038
	<b>(S</b>

 ${}^{a} R = \sum |F_{o}| - |F_{c}| / \sum |F_{o}|; R_{w} = [\sum w(|F_{o}| - |F_{c}|)^{2} / \sum w |F_{o}|^{2}]^{1/2}.$ 

K):  $\delta = 8.36 \{ \text{s (br), 1H, H}^{C12} \}$ , 7.7–7.1 {m(br), 13H, H<sup>arom</sup>}, 4.33 {s (br), 1H, H<sup>allyl</sup>}, 4.02 {s (br), 3H, H}^{C6} \}, 3.70 {s (br), 1H, H<sup>allyl</sup>}, 2.36 {s (br), 1H, H<sup>allyl</sup>}, 2.23 {s (br), 3H, H}^{C4} \}, 2.08 {s (br), 1H, H<sup>allyl</sup>}. <sup>31</sup>P{<sup>1</sup>H} NMR (36 MHz, CDCl<sub>3</sub>):  $\delta = 19.7$ . <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>, T = 213 K):  $\delta = 171.1 \{ \text{d } (^{3}J(C,P) = 4), C5 \}$ , 135–126 {m, Carom + C1}, 78.1 {tr (<sup>1</sup>J(C,H) = 160), d (<sup>2</sup>J(C,P) = 19), C2 \}, 56.1 {q (<sup>1</sup>J(C,H) = 150), C6 }, 48.5 {tr (<sup>1</sup>J(C,H) = 161), C3 }, 23.5 {q (<sup>1</sup>J(C,H) = 127), C4 }. Molar conductivity:  $\Lambda_m^{0} = 61 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ 

[Methyl 2-(diphenylphosphino)nicotinate  $\kappa^2 P$ , N]( $\eta^3$ methallyl)nickel(II) Tetrafluoroborate (2) and [Methyl 2-(diphenylphosphino)nicotinate- $\kappa^2 P, O$ ]( $\eta^3$ -methallyl)nickel(II) Tetrafluoroborate (4). In a solvent mixture of 45 cm<sup>3</sup> of THF and 30 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>, 1.59 g (3.09 mmol) of 9 was kept in suspension and 0.92 g (3.16 mmol) of TlBF<sub>4</sub> added at 0 °C. The solution was warmed overnight to room temperature and the solvent evaporated under vacuum. The solid was extracted with small amounts of CH<sub>2</sub>Cl<sub>2</sub> and the resulting suspension filtered over Celite. By careful addition of 50 cm<sup>3</sup> of  $Et_2O$  on the red solution (approximately 10 cm<sup>3</sup>), a red solid precipitated. The solution was removed and the solid washed 4 times with 2 cm<sup>3</sup> of  $Et_2O$ . After drying under vacuum, 1.22 g (2.34 mmol, yield = 76%) of 2 was obtained. Anal. Calcd for  $C_{24}H_{24}BF_4NiO_2P$ : C, 52.93; H, 4.44; N, 2.68. Found: C, 52.28; H, 4.42; N, 2.54. IR (Nujol):  $\nu$ (C=O) 1731 cm<sup>-1</sup>. IR (KBr, crystals of 2): 1729 cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1737 + 1647 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, T = 243 K):  $\delta = 8.88$  {s, 1H,  $H^{C6}$ }, 8.62 {d, 1H,  $H^{C7}$ }, 8.0–7.5 {m, 11H,  $H^{arom}$ }, 4.50 {s  $(br), H^{allyl}, 4.10 \{s (br), H^{allyl}\}, 3.68 \{s (br), H^{allyl}\}, 3.19 \{s (br), H^{allyl}\},$ Hallyl}, 2.17 {s (br), H<sup>C4</sup>}.  ${}^{31}P{}^{1}H$ } NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$ = 10 {s (v br)}.  ${}^{31}P{}^{1}H$  NMR (101 MHz, CDCl<sub>3</sub>; T = 243 K):  $\delta = 20.5$  (s, 4, integration 41%); 5.3 {s, 2, integration 100%). In the following <sup>13</sup>C NMR the proposed assignments are marked with an asterisk. <sup>13</sup>C{<sup>1</sup>H} NMR (63 MHz, CDCl<sub>3</sub>):  $\delta$ = 155.8 {s, C6}, 141.1\* {s, C7}, 134-129 {m,  $C^{arom} + C1$ }, 69 {s (v br), C2}, 53.7 {s (br), C11}, 51 {s (v br), C3}, 23.4 {s, C4}. <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>, T = 243 K):  $\delta = 171.4$  {s, C10, 4}, 166.6\* {d ( ${}^{1}J(C,P) = 39$ ), C5}, 161.7\* {s, C10, 2, 156.4 {d ( ${}^{1}J(C,H) = 202$ ), d ( ${}^{3}J(C,P) = 19$ ), C6, 2}, 154.3 {d ( ${}^{1}J(C,H)$ = 187), C6, 4}, 142.9\* {d ( ${}^{1}J(C,H) = 173$ ), C8, 2}, 141.4\* {d  $({}^{1}J(C,H) = 173), C8, 4$ , 134-122 {m, C<sup>arom</sup> + C1}, 78.9 {tr  $({}^{1}J(C,H) = 151), C2, 4\}, 68.4 \{tr ({}^{1}J(C,H) = 163), d ({}^{2}J(C,P) = 163)\}$ 17), C2, 2}, 56.2\* {q ( ${}^{1}J(C,H) = 148$ ), C11, 4}, 53.1\* {q ( ${}^{1}J(C,H)$ = 148), C11, 2}, 51.5\* {tr ( ${}^{1}J(C,H) = 163$ ), C3, 2}, 48.1\* {tr  $({}^{1}J(C,H) = 154), C3, 4\}, 23.7 \{q ({}^{1}J(C,H) = 132), C4\}.$  Molar conductivity:  $\Lambda_m^0 = 50 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ .

{Bis[ $\mu$ -2-(diphenylphosphino)pyridine- $\kappa^2 P$ ,N]bis( $\eta^3$ -methallyl)nickel(II)} Bis(tetrafluoroborate) (3). To a solution of 4.20 g (9.19 mmol) of 10 in THF/CH<sub>2</sub>Cl<sub>2</sub> (120 cm<sup>3</sup>/

<sup>(14)</sup> Technical Information Bulletin; Aldrich: Milwaukee, WI, 1982; No. AL-121.

Table 6. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors  $(10^2 \text{ Å}^2)^a$  for Compound 3

					-				
atom	x/a	y/b	z/c	$U_{ m eq}\!/U_{ m iso}$	atom	x/a	y/b	z/c	$U_{ m eq}\!/U_{ m iso}$
Ni(1)	0.19958(4)	0.61029(4)	0.28395(4)	3.76(4)	C(26)	-0.0459(3)	0.5144(2)	0.2399(2)	4.8(1)*
Ni(2)	0.17591(5)	0.39807(4)	0.28581(4)	3.82(4)	C(27)	-0.1395(3)	0.4847(2)	0.2352(2)	5.7(2)*
C(1)	0.1560(4)	0.7129(3)	0.2979(3)	4.4(3)	C(28)	-0.1849(3)	0.4426(2)	0.1722(2)	$5.8(2)^{*}$
C(2)	0.2367(4)	0.6958(3)	0.3593(3)	5.2(4)	C(29)	-0.1366(3)	0.4302(2)	0.1137(2)	5.4(2)*
C(3)	0.0757(4)	0.6670(3)	0.2876(3)	4.4(3)	C(30)	-0.0430(3)	0.4599(2)	0.1183(2)	5.3(2)*
C(4)	0.1633(4)	0.7703(3)	0.2370(3)	5.6(4)	C(31)	0.2557(2)	0.5186(2)	0.4391(2)	$3.8(1)^*$
C(5)	0.1187(4)	0.3049(3)	0.3176(3)	4.9(4)	C(32)	0.1569(2)	0.5236(2)	0.4435(2)	$5.1(2)^*$
C(6)	0.0758(4)	0.3170(3)	0.2402(3)	5.2(4)	C(33)	0.1319(2)	0.5650(2)	0.5010(2)	$5.3(2)^{*}$
C(7)	0.1098(5)	0.3607(3)	0.3673(4)	5.3(4)	C(34)	0.2058(2)	0.6014(2)	0.5542(2)	$5.5(2)^{*}$
C(8)	0.1886(5)	0.2404(3)	0.3434(4)	5.8(4)	C(35)	0.3046(2)	0.5963(2)	0.5499(2)	5.5(2)*
<b>P</b> (1)	0.12084(9)	0.54618(7)	0.18474(8)	3.55(7)	C(36)	0.3295(2)	0.5549(2)	0.4923(2)	$4.7(1)^{*}$
P(2)	0.2884(1)	0.45984(7)	0.36795(8)	3.59(7)	C(37)	0.3663(3)	0.3883(2)	0.4196(2)	$3.7(1)^*$
N(1)	0.3370(3)	0.5794(2)	0.2954(2)	3.3(2)	C(38)	0.3708(3)	0.3747(2)	0.4966(2)	$5.4(2)^{*}$
C(9)	0.3741(4)	0.5175(3)	0.3310(3)	3.4(3)	C(39)	0.4242(3)	0.3153(2)	0.5330(2)	$5.4(2)^{*}$
C(10)	0.4747(4)	0.5029(3)	0.3408(3)	4.4(3)	C(40)	0.4731(3)	0.2696(2)	0.4924(2)	6.0(2)*
C(11)	0.5354(4)	0.5490(3)	0.3131(3)	4.8(3)	C(41)	0.4686(3)	0.2832(2)	0.4153(2)	$5.8(2)^{*}$
C(12)	0.4961(4)	0.6116(3)	0.2779(3)	5.4(4)	C(42)	0.4152(3)	0.3425(2)	0.3789(2)	4.9(1)*
C(13)	0.3967(4)	0.6245(3)	0.2704(3)	4.2(3)	<b>B</b> (1)	0.4514(2)	0.6652(2)	0.7849(2)	9.5(8)
N(2)	0.2136(3)	0.4148(2)	0.1906(2)	3.3(2)	F(1)	0.4088(3)	0.6675(2)	0.8461(2)	11.4(4)
C(14)	0.1875(4)	0.4742(3)	0.1449(3)	3.5(3)	F(2)	0.5018(3)	0.6013(2)	0.7857(3)	13.2(5)
C(15)	0.2083(4)	0.4793(3)	0.0744(3)	4.6(3)	F(3)	0.5162(3)	0.7220(2)	0.7893(3)	15.1(6)
C(16)	0.2576(4)	0.4212(3)	0.0501(4)	5.4(4)	F(4)	0.3790(3)	0.6702(3)	0.7183(2)	13.2(5)
C(17)	0.2844(4)	0.3627(3)	0.0944(3)	5.3(4)	<b>B</b> (2)	0.1842(2)	0.1482(2)	0.1230(2)	8.6(7)
C(18)	0.2607(4)	0.3618(3)	0.1641(3)	<b>4.2(3)</b>	F(5)	0.2270(3)	0.0820(2)	0.1181(3)	14.7(5)
C(19)	0.0968(2)	0.6128(2)	0.1079(2)	4.5(1)*	<b>F</b> (6)	0.1730(3)	0.1842(2)	0.0549(2)	12.7(4)
C(20)	0.0006(2)	0.6327(2)	0.0699(2)	4.7(1)*	$\mathbf{F}(7)$	0.0932(3)	0.1387(3)	0.1387(3)	15.6(5)
C(21)	-0.0144(2)	0.6893(2)	0.0170(2)	5.6(2)*	$\mathbf{F}(8)$	0.2438(4)	0.1879(3)	0.1804(2)	15.9(6)
C(22)	0.0668(2)	0.7261(2)	0.0021(2)	5.9(2)*	C(43)	0.5135(7)	0.9713(5)	0.6040(6)	12.2(8)
C(23)	0.1630(2)	0.7062(2)	0.0402(2)	5.6(2)*	Cl(1)	0.6254(2)	0.9182(2)	0.6311(2)	12.3(2)
C(24)	0.1779(2)	0.6496(2)	0.0931(2)	$5.4(2)^*$	Cl(2)	0.4185(2)	0.9177(1)	0.5489(2)	11.7(2)
C(25)	0.0024(3)	0.5020(2)	0.1814(2)	$4.1(1)^*$					

 $^{a} U_{eq} = \frac{1}{3}[U_{11} + U_{22} + U_{33}];$  an asterisk denote an isotropic U.

40 cm<sup>3</sup>) 2.90 g (9.96 mmol) of TlBF<sub>4</sub> was added at 0 °C. The solution was warmed overnight to room temperature and the solvent evaporated under vacuum. The solid was extracted with small amounts of CH<sub>2</sub>Cl<sub>2</sub> and the obtained suspension filtered over Celite. By careful addition of 75 cm<sup>3</sup> of Et<sub>2</sub>O on the red solution (approximately 15 cm<sup>3</sup>), red crystals precipitated. The solution was removed and the solid washed with  $Et_2O$ . After drying under vacuum 1.94 g (2.09 mmol; yield = 45%) of 3 was obtained. Anal. Calcd for  $C_{42}H_{42}B_2F_8N_2Ni_2P_2$ +  $CH_2Cl_2$ : C, 51.00; H, 4.38; N, 2.77. Found: C, 52.25; H, 4.37; N, 2.63. <sup>1</sup>H NMR (250 MHz,  $CD_2Cl_2$ ):  $\delta = 9.20$  {d  ${}^{(3}J(H,H) = 4.8), 2H, H^{C13+C18}, 7.9-7.3 \{m, 26H, H^{arom}\}, 3.40$ {s, 2H,  $H^{allyl}$ }, 2.80 {d ( ${}^{3}J(H,P) = 4.7$ ), 2H,  $H^{allyl}$ }, 2.40 {s, 2H,  $H^{allyl}$ , 1.41 {s, 6H,  $H^{C4+C8}$ }, 1.17 {d ( ${}^{2}J(H,P) = 7.0$ ), 2H,  $H^{allyl}$ }. <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, CDCl<sub>3</sub>):  $\delta = 26.0$ . <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 26.1$ . <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>, T = 213K):  $\delta = 158.3 \{ d ({}^{1}J(C,P) = 52), C9 + C14 \}, 154.6 \{ d ({}^{1}J(C,H) \} \}$ = 184), C13 + C18}, 139–125 {m, C<sup>arom</sup> + C1 + C5}, 78.7 {tr  $({}^{1}J(C,H) = 155), C2 + C6\}, 56.3 \{tr ({}^{1}J(C,H) = 158), C3 + C7\},\$ 22.2 {q ( ${}^{1}J(C,H) = 130$ ), C4 + C8}. Molar conductivity (CH<sub>2</sub>-Cl<sub>2</sub>):  $\Lambda_{\rm m}^{0} = 39 \ {\rm S} \cdot {\rm cm}^{2} \cdot {\rm mol}^{-1}$ .

X-ray Structure Determination for 3. Data Collection and Processing. Crystal data are gathered in Table 5. Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer, with graphite-monochromated Mo Ka radiation ( $\Lambda = 0.71073$  Å). The unit-cell parameters were obtained from a least-squares fit of 25 reflections (with  $\theta$ between 11.0 and 16.0°). Data were collected with the  $\omega - 2\theta$ scan technique (scan width  $(0.80 + 0.35 \tan \theta)^{\circ}$ ,  $2\theta$  max = 50°, +h, +k,  $\pm l$ ) and a variable scan rate with a maximum scan time of 60 s per reflection. Three reflections measured every 2 h showed a slight linear decay of standard intensity (-4.1%). Corrections for the Lorentz and the polarization effects and the decay were applied using the MolEN package.<sup>15</sup> Empirical absorption corrections<sup>16</sup> from  $\psi$  scans were applied. The 7849 collected reflections were unique.

Structure Solution and Refinement. The structure was solved by direct methods (SHELXS-8617) and refined by fullmatrix least squares (SHELX-76<sup>18</sup>). A solvent molecule (i.e. dichloromethane) was found. The non-hydrogen atoms were refined anisotropically, except those of phenyl rings which were refined as isotropic rigid groups. The hydrogen atoms were included in calculated positions, riding on the atom to which they are bonded, except the methylenic hydrogens were allowed to vary. H isotropic thermal parameters, first refined, were then kept fixed. The final refinement cycle was based on 3919 observed reflections  $(F_o^2 > 3\sigma(F_o^2))$  and 406 variable parameters and converged to R = 0.036 and  $R_w = 0.038$  with unit weights and goodness of fit 1.336 (largest shift-to-error ratio 0.003). The final Fourier difference map was featureless.

Neutral atom scattering factors, including anomalous dispersion effects, were taken from the standard compilation.<sup>19</sup> All calculations were performed on a MicroVax 3400 computer. Atomic coordinates are listed in Table 6.

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Supporting Information Available: Tables of hydrogen coordinates and U values, anisotropic thermal parameters, complete bond lengths and angles, least-squares planes equations and deviations therefrom, and dihedral and torsion angles and a figure showing the molecule with phenyl rings (7 pages). Ordering information is given on any current masthead page.

#### OM950247I

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