Chelating Coordination of Di- and Triallylamines: Syntheses and NMR Studies of Trimethylphosphane Nickel and Cobalt Complexes☆

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16-Electron complexes of zerovalent nickel with diallylamines, $Ni[(C_3H_5)_2NR]L$ [**1**, **2**: L = $P(CH_3)_3$, R = CH_3, C_6H_5; **3**: L = $P(C_6H_5)_3$, R = CH_3] and $[NiP(CH_3)_3]_2CH_2[N(C_3H_5)_2]_2$ (**4**), were synthesized by reduction of $NiCl_2L_2$ with magnesium in tetrahydrofuran. $NiCl(\eta^3\text{-}C_3H_5)[P(CH_3)_3]_2$ (**5**), a low-yield byproduct, was also obtained in high yield from NiL_4 and C_3H_5Cl. With triallylamine as starting material complexes $Ni[(C_3H_5)_3N]L$ [**6**: L = $P(CH_3)_3$; **7**: L = $P(C_6H_5)_3$] were generated exhibiting η^6- and η^4-olefin coordination, respectively. 17-electron cobalt(0) compounds $Co[(C_3H_5)_2NR](PMe_3)_2$ (**8**, **9**: R = CH_3, C_6H_5) were obtained by reaction of $Co(cyclo\text{-}C_5H_8)(PMe_3)_3$ with the corresponding diallylamine, while $CoR(PMe_3)_4$ (R = CH_3, C_6H_5) reacted with *N,N*-diallylaniline to give diagmagnetic $Co[(\eta^3\text{-}C_3H_4)(\eta^2\text{-}C_3H_5)NC_6H_5](PMe_3)_2$, (**10**). The coordination mode of allylic functions was deduced from IR, ESR and especially ^1H- and ^{13}C-NMR spectra including 2D-NMR experiments.

While catalytic transformations of allylamines are of general interest and also of industrial importance[1], there are still only a few investigations of phosphane-supported allylamine complexes[1,2]. Possible coordination modes in nickel and cobalt complexes (metal d^8, d^9, d^{10}) have been found in scattered examples, and very little is known about the structures in solution.

N-substituted diallylamines may act as chelating ligands as in the 17-electron compound $[Co(PMe_3)_2]_2$bis(diallylamino)methane[2]. If a suitable conformation is accessible both olefinic functions can serve as π-bonding ligands in a pseudotetrahedral complex. This coordination mode does not involve the N-donor functions and leaves the paramagnetic valence state of cobalt(0) unchanged. No isomerization is observed that could be envisaged by a shift of C=C bonds or a hydrogen shift generating a π-allyl function by metal catalysis.

In order to investigate a broader range of allylamine complexes we have been looking for a general access to this class of compounds. Starting from low-valent trimethylphosphane nickel and cobalt compounds, we have found efficient syntheses of the title complexes. In this contribution we describe their properties including a detailed study by ^1H- and ^{13}C-NMR techniques and some reactions involving C−H and N−C bond breaking.

Results and Discussion

1. Preparation of Nickel Complexes

In a vigorous reaction $NiCl_2(PR_3)_2$ in THF is reduced by magnesium in the presence of a diallylamine ligand to afford molecular complexes of zerovalent nickel (eqs. 1,2) in good yields.

$$NiCl_2L_2 + (C_3H_5)_2NR + Mg \rightarrow \underset{\mathbf{1-3}}{Ni[(C_3H_5)_2NR]L} + L + MgCl_2 \qquad (1)$$

	L	R	Yield (%)	m.p. [°C]
1	PMe_3	CH_3	63	51−52
2	PMe_3	C_6H_5	77	93−94
3	$P(C_6H_5)_3$	CH_3	43	112−113

$$2\,NiCl_2L_2 + BDAM \xrightarrow[-2\,MgCl_2]{+2\,Mg} \underset{\mathbf{4}}{(NiL_2)_2\,(BDAM)} + 2\,L \qquad (2)$$

L = PMe_3; BDAM = $(C_3H_5)_2N(C_3H_5)_2$

From pentane at −70°C lemon-colored crystals of **1** are obtained that are freely soluble in ether or toluene. Slightly less soluble **2** is also formed by starting from $NiMeCl(PMe_3)_2$ with loss of a methyl group (46% yield)[3]. Light yellow crystals of **4** are as highly soluble as **1**. In the melt under argon **1**−**3** decompose above 170°C, and they ignite spontaneously in air but do not crackle or explode like $Ni(PMe_3)_4$[4].

When compared with trimethylphosphane complexes **1**, **2**, **4**, the nickel center in **3** is more shielded by triphenylphosphane rendering the ocherous crystals of **3** air-stable for some minutes and reducing the solubility in pentane.

In all syntheses (eqs. 1,2) from the residue of $MgCl_2$ small amounts of a byproduct can be extracted with toluene to give red needles. Yields (5−10%) are independent of the temperature or the concentration of ligands or the surface of magnesium turnings.

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By ^{1}H-NMR spectroscopy the byproduct has been shown to be the allylnickel complex **5** of a well-known type that appears to result from some N–C bond breaking reaction. An easy high-yield synthesis of **5** is achieved by an oxidative substitution reaction (eq. 3).

$$\mathrm{Ni(PMe_3)_4 + C_3H_5Cl \rightarrow \underset{\textbf{5}}{Ni(C_3H_5)Cl(PMe_3)_2} + 2\,PMe_3} \qquad (3)$$

When the reactants are combined at −78°C the mixture turns red. From ether air-sensitive red needles of **5** are obtained that are moderately soluble in toluene and freely so in tetrahydrofuran.

Reductions with magnesium (eqs. 1,2) proceed with liberation of one equivalent of PMe_3. The start of the reaction is recognized by a change from red to the violet-blue color of $NiCl_2(PMe_3)_3$[6]. In a similar reduction (eq. 4) the blue color is not observed.

$$\mathrm{3\,NiCl_2L_2 + 2\,N(C_3H_5)_3 \xrightarrow[-\,3\,MgCl_2]{+\,3\,Mg} 2\,\underset{\textbf{6}}{Ni[N(C_3H_5)_3]L} + NiL_4} \qquad (4)$$

L = PMe_3

As soon as generated trimethylphosphane forms stoichiometric amounts of $Ni(PMe_3)_4$.

Separation of the two extremely soluble and air-sensitive compounds has proved difficult. With triphenylphosphane compound **7** is obtained in a 1 : 1 stoichiometry (eq. 5).

$$\mathrm{NiCl_2L_2 + N(C_3H_5)_3 \xrightarrow[-\,MgCl_2]{+\,Mg} \underset{\textbf{7}}{Ni[N(C_3H_5)_3]L} + L} \qquad (5)$$

L = $P(C_6H_5)_3$

The lemon-colored crystals of **7** are air-stable for some minutes and under argon melt at 114–115°C with decomposition starting at 190°C.

2. Preparation of Cobalt Complexes

Diallylmethylamine slowly reacts with Co(*cyclo*-C_5H_8)(PMe_3)$_3$[5] at 20°C replacing the olefin unit and one equivalent of trimethylphosphane (eq. 6).

$$\mathrm{Co(C_5H_8)L_3 + (C_3H_5)_2NR \rightarrow \underset{\textbf{8, 9}}{Co[(C_3H_5)_2NR]L_2} + C_5H_8 + L} \qquad (6)$$

L = PMe_3

	R	Yield (%)	m.p. [°C]
8	CH_3	73	68–69
9	C_6H_5	39	84–85

From pentane dark-blue shining crystals of **8** are isolated which are freely soluble in ether or toluene and are rapidly decomposed by air. Slightly less air-sensitive **9** is obtained from pentane as bright-blue rhomboedric crystals. Although η^4-coordinated diallylamines contain a free N-donor function, they are smoothly replaced by N,N-functions of diazenes (eq. 7, 8).

$$\mathbf{8} + \mathrm{PhN{=}NPh \rightarrow Co(N_2Ph_2)L_2 + (C_3H_5)_2NCH_3} \qquad (7)$$

$$\mathbf{9} + \mathrm{C_{12}H_8N_2 + L \rightarrow Co(C_{12}H_8N_2)L_3 + (C_3H_5)_2NC_6H_5} \qquad (8)$$

$$\mathbf{8} + \mathrm{NO + L \rightarrow Co(NO)L_3 + (C_3H_5)_2NCH_3} \qquad (9)$$

$$\mathbf{9} + \mathrm{CO\,(excess) \rightarrow Co_2(CO)_4L_4 + (C_3H_5)_2NC_6H_5} \qquad (10)$$

L = PMe_3; $C_{12}H_8N_2$ = benzo[c]cinnoline

trans-Azobenzene (eq. 7) and the *cis*-fixed diazene benzo[*c*]cinnoline (eq. 8) form complexes of zerovalent cobalt[7,8]. If the third phosphane ligand is not supplied according to eq. (8) or (9) elemental cobalt is deposited in order to make it available to form paramagnetic diazenecobalt or diamagnetic nitrosylcobalt[9] complexes. Carbonylation of **9** (eq. 10) under 1 bar CO is virtually quantitative giving the expected trimethylphosphane derivative[10] of $Co_2(CO)_8$.

In an attempt to coordinate triallylamine by combining with equimolar amounts of Co(*cyclo*-C_5H_8)(PMe_3)$_3$ a brown oil is obtained containing $CoH(PMe_3)_4$[7] and (μ-PMe_2)$_2$[Co(PMe_3)$_2$]$_2$[11] among other products (IR, MS). This mixture is believed to originate from radical reactions involving the ligands that are not induced by diallylamines.

None of the allylamines can be coordinated by $CoCl(PMe_3)_3$/$NaBF_4$ in tetrahydrofuran, and $Co(PMe_3)_4BF_4$[12] is obtained instead. There occurs no reaction between $CoCH_3(PMe_3)_4$[10] and diallylmethylamine at 20°C. However, *N,N*-diallylaniline smoothly reacts with $CoCH_3(PMe_3)_4$ or $CoC_6H_5(PMe_3)_4$ (eq. 11).

$$\mathrm{CoRL_4 + (C_3H_5)_2NC_6H_5 \rightarrow \underset{\textbf{10}}{Co[(C_3H_4)(C_3H_5)NC_6H_5]L_2} + RH + 2\,L} \qquad (11)$$

L = PMe_3; R = CH_3 (48%), C_6H_5 (64%)

From pentane thin ocherous needles of **10** are obtained that melt at 84–85°C under argon and are rapidly oxidized by air. High solubility in pentane, toluene, or ether and diamagnetism are valuable properties for spectroscopic characterization.

3. Spectroscopic Characterization

Infrared spectra of **1**, **2**, and **4** (nujol solution, 4000–400 cm^{-1}) all contain bands of coordinated trimethylphosphane in their usual positions, while the fingerprint region of **3** is obscured by a number of phenyl absorptions. Medium-intensity bands indicating $\nu_{C=C}$ of allylamines experience a bathochromic shift below 1470 cm^{-1}. This observation suggests that no allyl function has remained uncoordinated in compounds **1**–**4**.

As crystalline compounds **1**–**4** can be sublimed in vacuo with slight decomposition, mass spectra contain the molecular ion as base peak and the expected pattern of fragmentation. Under these conditions **5** shows extensive dissociation of phosphane ligands.

Variable-temperature ^{1}H-NMR measurements on **5** reveal an AX_4 spin system of a fluctuating η^3-allyl ligand and a PCH_3 doublet at room temperature which on cooling becomes a pseudotriplet ($H_9PP'H_9'$ spin system) indicating strong PP coupling under conditions of slow exchange and confirming ligand dissociation at ambient temperatures.

4. Assignment of ^{1}H- and ^{13}C-NMR Spectra of Coordinated Allylamines

The room-temperature ^{13}C-NMR spectra of allylnickel complexes **1**, **2**, and **4** show doublets for $P(CH_3)_3$ and singlets for the C_3H_5 groups with comparable shifts, whereas the ^{1}H-NMR spectra differ slightly in their appearance. In the case of **1** higher-order effects occur, and some line broadening is observed for **2**. Therefore, the ^{1}H-NMR spectrum of **4** is analyzed in more detail.

Assignment is based on the first-order H,H coupling constants and a 2D-C,H COSY spectrum showing a remarkably large difference in chemical shifts of diastereotopic protons 3-H^a and 3-H^b (for numbering see formula in Scheme 1). The high-field shift of the signal of 3-H^a is obviously caused by the nearby nickel atom. Table 1 contains the room-temperature ^{1}H chemical shifts and H,H coupling constants of **4** as well as approximate ^{1}H-NMR data of **1**.

Because of the line broadening mentioned above for **2**, ^{13}C- and ^{1}H-NMR spectra of this compound are recorded at 233 K. Under these conditions the three ^{13}C signals of the allyl ligand exhibit doublet splittings because of coupling with the ^{31}P nucleus amounting to 2–3 Hz for C-1 and C-3 and to 10 Hz for C-2.

Similarly, in the ^{1}H-NMR spectrum of **2** the multiplicity of some signals of the C_3H_5 protons is raised as compared with **4**, again caused by ^{31}P coupling. H,H and P,H couplings can be clearly separated by a 2D-*J*-resolved ^{1}H-NMR spectrum in which the P,H couplings appear in the f_2 dimension and the H,H coupling constants in the f_1 dimension.

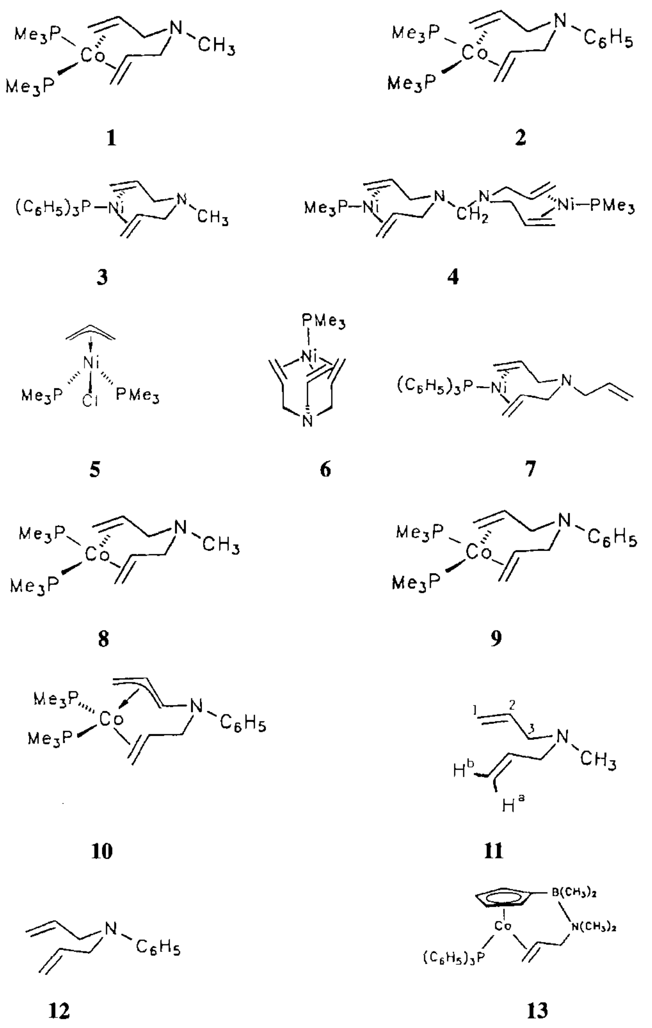
The δ_H, J(P,H), and J(H,H) values thus obtained for **2** at 233 K are given in Table 1 and the δ_C and J(P,C) values in Table 2. When the temperature is raised to 323 K sharper ^{1}H-NMR signals of **2** with reduced multiplicity are observed whereas at still higher temperatures (363 K) the signals of 3-H^a and 3-H^b show extreme line broadening which may be attributed to conformational changes due to nitrogen inversion.

Low-temperature ^{1}H and ^{13}C experiments for **1** and **4** also lead to additional P,H and P,C splittings. The δ_C and J(P,C) values of **1** and **4** are included in Table 2. For reasons of comparison, the ^{1}H- and ^{13}C-NMR parameters of the free ligands $(CH_2{=}CHCH_2)_2NCH_3$ (**11**) and $(CH_2{=}CHCH_2)_2NC_6H_5$ (**12**) are also determined (Tables 1 and 2).

Accordingly, the allyl group is still present in the complexes and no isomerization to enamines has taken place. The ^{1}H- and ^{13}C-NMR signals of the atoms of the coordinated double bond show the typical high-field shifts as compared with those of the free ligands. As far as the ^3J(H,H) couplings through the olefinic double bond are concerned a reduction especially of $^3J^{trans}$(H,H) is observed; for assignments in the complexes the usual relation $^3J^{trans} > {}^3J^{cis}$ is assumed.

The temperature dependence of the NMR spectra of nickel complexes is probably caused by an intermolecular dissociation/association process of the $P(CH_3)_3$ groups. Information regarding the conformation of the allyl ligands may be gained from the large high-field shift of 3-H^a, indicating a tightly spatial proximity to nickel and also from a 2D-NOE experiment (NOESY) of **4** which shows correlation peaks for 1-H^a/3-H^a as well as for 2-H/3-H^b. These observations are in accord with the couplings ^3J(2-H,3-H^a) of 11 and ^3J(2-H,3-H^b) of 3 Hz, indicating an antiperiplaner and a synclinal arrangement, respectively.

Scheme 1. Formulae of compounds **1**–**13**. H- and C-atom numbering throughout as indicated for **1** and **11**; for **10** see also Table 1



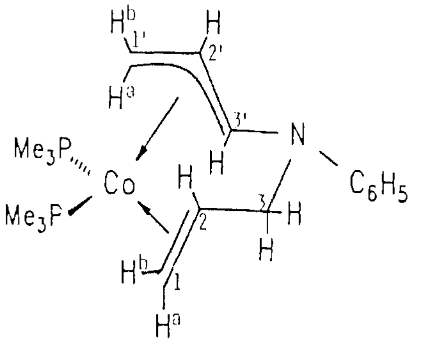
The 300-MHz ^{1}H-NMR spectrum of the cobalt complex **10** shows the expected multiplets of C_6H_5, two doublets of $P(CH_3)_3$ groups and, at least at first glance, seven other single proton resonances (see 1D spectrum in Figure 1). Signals of the two missing protons are overlapped by the $P(CH_3)_3$ peaks at $\delta_H \approx 1.05$ as revealed by the intensities and the results of 2D experiments (see below).

The ^{13}C-NMR spectrum of **10** exhibits again the signals of C_6H_5 and $P(CH_3)_3$ (doublet of doublets) as well as the six signals of the two different C_3 ligands in the region δ_C = 30 to 70. At higher digital resolution they show additional splittings into doublets, doublets of doublets, or triplets which result from couplings with one or both ^{31}P nuclei (Table 2).

In order to detect and assign all ^{1}H-NMR signals a two-dimensional H,H COSYDQF experiment (H,H COSY with double quantum filter) is performed as well as a TOCSY experiment (total correlation) (Figure 1). The two missing signals, both at about δ_H = 1.05 and hidden by one of the $P(CH_3)_3$ doublets, are clearly observed by their cross peaks. Additionally, the two sets of four and five protons, respec-

Table 1. ^{1}H-NMR data for allylamine complexes **1**, **2**, **4**, **10**, and allylamines **11**, **12**

10



	1[a]	**2**[b,c]		**4**[d]	**11**	**12**[e]
	δ_H	δ_H	J(P,H)	δ_H	δ_H	δ_H
1-H^a	2.09	2.10	7.3	2.22	5.11	5.02
1-H^b	2.36	2.39	8.7	2.44	5.03	4.97
2-H	3.53	3.52	4.0	3.68	5.83	5.61
3-H^a	1.10	1.89	0	1.46	2.89	3.61
3-H^b	3.60	4.46	7.6	4.19		
PCH$_3$	0.97[h]	0.84	6.7	0.93[h]	-	-
NCH$_3$	2.26	-	-	-	2.11	-
NCH$_2$N	-	-	-	3.29	-	-
^2J(1-H^a,1-H^b)		1.5			1.9	1.6
^3J(1-H^a,2-H)	11	12.5		12.8	17.2	17.2
^4J(1-H^a,3-H)					1.6	1.6
^3J(1-H^b,2-H)	8	8.5		8.7	10.1	10.2
^4J(1-H^b,3-H)					1.2	1.6
^3J(2-H,3-H^a)	11	11.2		11.0	6.3	4.8
^3J(2-H,3-H^b)	3	3.4		3.0		
^2J(3-H^a,3-H^b	13	13.4		12.3	-	-

10[f,g]

	δ_H	J(P,H)		δ_H	J(P,H)
1-H^a	1.05	12.0; 6.5	1'-H^a	1.03	22
1-H^b	1.32	7.4; 4.0	1'-H^b	1.96	12.1; 2.4
2-H	3.72	1.4	2'-H	4.50	3.1; 3.1
3-H^a	2.33	10.0; 4.0	3'-H	2.63	14.6; 6.4
3-H^b	4.21	9.4			
PCH$_3$	0.58	6.2			
PCH$_3$	1.05	5.7			

	J(H,H)		J(H,H)
^2J(1-H^a,1-H^b)		^2J(1'-H^a,1'-H^b)	
^3J(1-H^a,2-H)	9.5	^3J(1'-H^a,2'-H)	9.5
^4J(1-H^a,3-H)		^4J(1'-H^a,3'-H)	
^3J(1-H^b,2-H)	7.4	^3J(1'-H^b,2'-H)	6.3
^4J(1-H^b,3-H)		^4J(1'-H^b,3'-H)	
^3J(2-H,3-H^a)		^3J(2'-H,3'-H)	6.3
^3J(2-H,3-H^b)	3.7		
^2J(3-H^a,3-H^b)	11.2		

[a] [D$_8$]Toluene, 305 K, estimated values (higher order spectrum). – [b] [D$_8$]Toluene, 233 K. – [c] δ_H values of C$_6$H$_5$: 2-H 6.97; 3-H 7.18; 4-H 6.81. – [d] In C$_6$D$_6$ at 305 K. – [e] δ_H values of C$_6$H$_5$: 2-H 6.65; 3-H 7.18; 4-H 6.73. – [f] δ_H values of C$_6$H$_5$: 2-H 6.99; 3-H 7.21; 4-H 6.74. – [g] For improved comparison of data the numbering for **10** is given as above. – [h] ^2J(P,H) = 6.5 Hz.

Table 2. ^{13}C-NMR data for allylamine complexes **1**, **2**, **4**, **10**, and allylamines **11**, **12**

	1[a]		**2**[b]		**4**[c]		**11**
	δ_C	J(P,C)	δ_C	J(P,C)	δ_C	J(P,C)	δ_C
C-1	45.3	2.6	45.3	2.7	45.3		116.8
C-2	67.9	9.9	66.4	10.1	68.4	9.2	136.8
C-3	61.2	3.1	55.2	2.8	58.0		60.8
PCH$_3$	16.5	23.1	16.3	23.2	16.8	22.7	-
NCH$_3$	44.8	-	-	-			42.0
NCH$_2$N	-	-	-	-			-

12[d]		**10**[e,f]				
δ_C		δ_C	J(P,C)		δ_C	J(P,C)
115.7	C-1	32.4	8.0	C-1'	37.1	8.2; 2.6
134.4	C-2	53.5	12.7	C-2'	64.1	4.0; 2.8
52.8	C-3	50.9	3.5; 3.5	C-3'	69.6	28.0; 2.0
-	PCH$_3$	19.9	18.2; 3.9			
-	PCH$_3$	16.7	16.9; 4.6			

[a] [D$_8$]Toluene, 193 K. – [b] [D$_8$]Toluene, 233 K, δ_C values of C$_6$H$_5$: C^{ipso} 137.5; C-2 117.7; C-3 129.2; C-4 118.9. – [c] C$_6$D$_6$, 263 K; under these conditions P,C coupling was resolved only for C-2. – [d] δ_C values of C$_6$H$_5$: C^{ipso} 149.0; C-2 111.8; C-3 129.5; C-4 116.9. – [e] δ_C values of C$_6$H$_5$: C^{ipso} 150.1; C-2 113.9; C-3 129.4; C-4 116.3. – [f] For improved comparison of data the numbering for **10** is given as in Table 1.

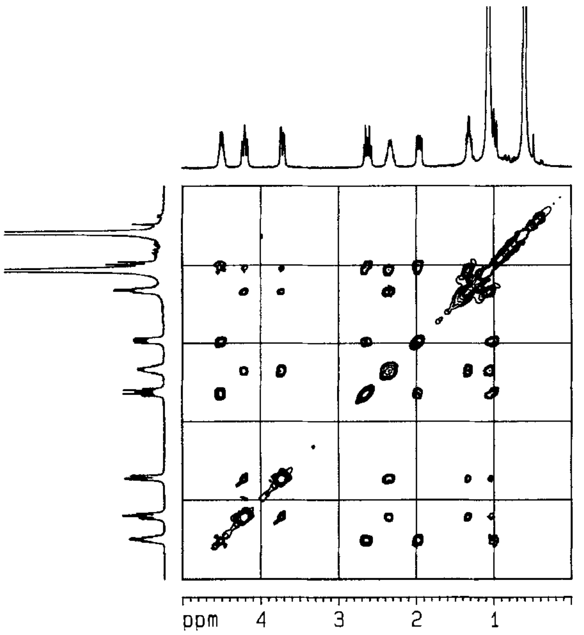


Figure 1. TOCSY spectrum of **10** with 1D ^{1}H-NMR spectra (C$_6$D$_6$, relevant section only)

tively, of the two different C$_3$ ligands are discernible: the C$_3$H$_4$ protons resonate at δ_H = 4.50, 2.63, 1.96, and ≈ 1.03 (partially hidden), whereas the C$_3$H$_5$ ligand protons show δ_H values of 4.21, 3.72, 2.33, 1.32, and ≈ 1.05 (hidden).

3'-H and 3-H^a/H^b protons are identified by a NOE difference experiment with irradiation of the *ortho*-phenyl protons leading to signal enhancements at δ_H = 4.21 (3-H^b) and 2.63 (3'-H). By a one-bond 2D-C,H correlation experiment the assignment is transferred to the ^{13}C-NMR spectrum.

Finally, the analysis of the ^{1}H-NMR multiplets and the determination of the coupling constants are achieved by a 2D-*J*-resolved ^{1}H-NMR spectrum. The H,H couplings appearing in the f$_1$ dimension are assigned by their numbers and homonuclear decoupling experiments, whereas the P,H coupling constants are found in the f$_2$ projection.

Raising the temperature to 363 K does not lead to any changes in the appearance of the ^{1}H- and ^{13}C-NMR spectra, so the P,C and P,H couplings do not vanish under these conditions, and also measurements at 11.7 T (500 MHz ^{1}H, 125.7 MHz ^{13}C) result in no changes[13].

In contrast to the nickel compound with η^2 coordination of both allylic units, the cobalt atom in **10** is η^2- as well as η^3-coordinated.

As far as the $CH_2{=}CH$ fragment of the C_3H_5 ligand is concerned, one observes a further high-field shift of the ^{1}H- and ^{13}C-NMR signals as compared to those of the nickel complex **2**, and the values $^3J^{trans}$, $^3J^{cis}$, and ^2J(3-H^a,3-H^b) are slightly smaller than in **2**. In the case of the C_3H_4 unit the coupling constant ^3J(2′-H,3′-H) of 6.3 Hz could be indicative of a synperiplanar conformation.

But most remarkable are the following observations indicating the presence of a somewhat different configuration in **10** when compared with **2**: in **10** the couplings ^3J(2-H,3-H^a) and ^3J(2-H,3-H^b) differ from those in **2**; only 3-H^a is in close proximity to the *ortho*-phenyl Hs; none of the protons on C-3 are as shielded as in the nickel complexes.

In ref.[14] ^{1}H- and ^{13}C-NMR data have been presented for the cobalt complex **13** but without any assignment. A comparison of chemical shifts does not seem reasonable because of different substituents, and regarding the couplings only a few similarities may be recognized. Crystallographic data of a (diallylamine)cobalt(I) complex[15] have been published without spectral data.

Conclusion

Diallylamines can adopt a suitable conformation for chelating coordination in trigonal-planar nickel(0) and in tetrahedral cobalt(0) complexes containing 16 and 17 metal valence electrons, respectively, while triallylamine can support an 18-electron nickel(0) complex as shown by NMR of **6**. Usually no reactions in the ligands are induced by coordination to the electron-rich and catalytically active metals, and the nitrogen donors are not involved. However, methylcobalt functions can induce deprotonation of an allyl group transforming a diallylamine into an η^2,η^3-chelating π allyl, π olefin ligand. When coordinated to cobalt(I) a novel solution structure of the complex is revealed by NMR as exemplified by **10**.

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Experimental

All air-sensitive material was handled by standard vacuum technique and kept under argon. – Microanalyses: Dornis & Kolbe, Microanalytical Laboratory, Mülheim/Ruhr, FRG. – Melting points/decomposition temperatures: Sealed capillaries, uncorrected. – Chemicals (Merck-Schuchardt) were used as purchased, but liquids were degassed in vacuo by a freeze-thaw procedure. – IR: Nujol mulls between KBr discs, Perkin-Elmer, Type 397. – NMR: One- and two-dimensional ^{1}H- and ^{13}C-NMR spectra (300 and 75 MHz, respectively) were recorded with Bruker AC-300 and ARX-300 instruments by using standard pulse sequences. Prior to Fourier transformation zero-filling and appropriate window functions were applied throughout. The TOCSY spectrum was obtained by using 256 t_1 increments with 32 scans each; the mixing time amounted to 100 ms, and the digital resolution was 5 Hz/point in both dimensions.

$Ni[(C_3H_5)_2NCH_3]PMe_3$ (**1**): 1.62 g (5.75 mmol) of $NiCl_2(PMe_3)_2$ and 1.0 g (41 mmol) of magnesium turnings in 50 ml of THF at −78°C were combined with 630 mg (5.67 mmol) of diallylmethylamine. The mixture was allowed to warm with stirring and turned yellow within 8 h. The volatile components were removed in vacuo, and the residue was extracted with two 40-ml portions of pentane. The combined filtrates were concentrated in vacuo to a volume of 5 ml and kept at −78°C. 890 mg of yellow crystals (63% yield based on nickel) was obtained, m.p. 51–52°C, decomp. >175°C. – MS (FI), *m/z* (%): 245 (100) M, 111 (10) $(C_3H_5)_2NCH_3$, 92 (52) Me_3PO. – $C_{10}H_{22}NNiP$ (246.0): calcd. C 48.83, H 9.01, N 5.69; found C 47.95, H 9.38, N 5.29. – NMR: Tables 1 and 2.

$Ni[(C_3H_5)_2NC_6H_5]PMe_3$ (**2**): In a similar reaction treatment of 2.02 g (7.17 mmol) of $NiCl_2(PMe_3)_2$ and 1.18 g (6.81 mmol) of *N,N*-diallylaniline with 3.24 g (133 mmol) of magnesium powder afforded 1.70 g of lemon-colored crystals (77% based on nickel), m.p. 91–92°C, decomp. >170°C. – MS (FI), *m/z* (%): 307 (100) M, 173 (65) $(C_3H_5)_2NC_6H_5$, 76 (22) PMe_3. – $C_{15}H_{24}NNiP$ (308.0): calcd. C 58.49, H 7.85, N 4.55; found C 58.33, H 7.90, N 4.61. – NMR: Tables 1 and 2.

$Ni[(C_3H_5)_2NCH_3]PPh_3$ (**3**): 1.68 g (2.57 mmol) of $NiCl_2(PPh_3)_2$ and 0.29 g (2.61 mmol) of diallylmethylamine in 50 ml THF were treated with 2 g (82 mmol) of magnesium powder with stirring at −20°C for 8 h. The mixture was allowed to warm, and the volatile components were evaporated. Extraction of the residue with pentane afforded ocherous crystals, yield of **3** 480 mg (43% based on nickel), m.p. 103–104°C, decomp. >186°C. – MS (EI), *m/z* (%): 431 (1) M, 320 (1) $NiPMe_3$, 278 (3) $OPPh_3$, 262 (27) PPh_3, 185 (31) PPh_2, 154 (79) PhPh, 84 (90) $C_5H_{10}N$, 41 (100) C_3H_5. – $C_{25}H_{28}NNiP$ (432.2): calcd. C 69.48, H 6.53, N 3.24; found C 69.21, H 6.60, N 2.96.

$[NiPMe_3]_2[(C_3H_5)_2N]_2CH_2$ (**4**): 3.42 g (12.1 mmol) of $NiCl_2(PMe_3)_2$ and 1.25 g (6.06 mmol) of bis(diallylamino)methane in 70 ml of ether were treated with 2.49 g (102 mmol) of magnesium powder with stirring at 10°C for 18 h. The color changed from red to dark blue and turned yellow after completion of the reaction. After 2 h at 20°C workup as with **1** afforded 2.1 g of yellow crystals (73% based on nickel), m.p. 109–110°C, decomp. >180°C. – MS (FI), *m/z* (%): 474 (100) M, 340 (78) Ni(BDAM)PMe_3. – $C_{19}H_{40}Ni_2N_2P_2$ (475.9): calcd. C 47.95, H 8.47, N 5.89, P 13.02; found C 48.88, H 8.68, N 6.10, P 13.37. – NMR: Tables 1 and 2.

$Ni(C_3H_5)Cl(PMe_3)_2$ (**5**): 1.9 g (5.24 mmol) of $Ni(PMe_3)_4$ in 40 ml of THF at −78°C was combined with 0.40 g (5.23 mmol) of allyl chloride. The mixture turned dark red and was allowed to warm with stirring. The volatile components were evaporated, and the residue was extracted with 150 ml of ether. At −70°C red needles were obtained, yield of **5** 1.1 g (73% based on nickel), decomp. >120°C. – ^{1}H NMR ([D$_8$]toluene, 298 K): δ = 0.98 [d, ^2J(PH) = 8.1 Hz, 18H, PCH_3], 3.0 [d, ^3J(HH) = 9.8 Hz, 4H, CH_2], 4.6 [q, ^3J(HH) = 9.8 Hz, 1H, CH]. – ^{13}C{^{1}H} NMR ([D$_8$]toluene, 298 K): δ = 17.1 [d, ^1J(PC) = 23 Hz, PCH_3], 60.7 (CH_2), 101.4 (CH). – $C_9H_{23}ClNiP_2$ (237.4): calcd. C 37.62, H 8.07, P 21.56; found C 36.38, H 7.93, P 22.19.

$Ni[(C_3H_5)_3N]PMe_3$ (**6**): 1.82 g (6.46 mmol) of $NiCl_2(PMe_3)_2$ and 0.59 g (4.3 mmol) of triallylamine in 60 ml of THF were treated with 2.65 g (109 mmol) of magnesium powder with stirring at −40°C. Within 24 h the mixture was gradually warmed to 20°C.

Evaporation of solvent and extraction of the residue with pentane afforded a yellow wax. This was kept in vacuo at 70°C for 4 h in order to sublime $Ni(PMe_3)_4$. The residue was extracted with 10 ml of pentane to give an ocherous solid containing 2 mol-% of $Ni(PMe_3)_4$ (determined by ^{1}H-NMR analysis), raw yield of **6** 470 mg (ca. 26% based on nickel). – MS (FI), *m/z* (%): 362 (16) $Ni(PMe_3)_4$, 271 (100) M, 137 (47) $(C_3H_5)_3N$, 92 (46) $OPMe_3$, 76 (91) PMe_3. – ^{1}H-NMR ([D$_8$]toluene, 298 K): δ = 0.98 [d, $^2J(PH)$ = 6.5 Hz, 9H, PCH_3], 1.1–4.2 (m, 15H, C_3H_5).

$Ni[(C_3H_5)_3N]PPh_3$ (**7**): 3.49 g (5.33 mmol) of $NiCl_2(PPh_3)_2$ and 0.72 g (5.25 mmol) of triallylamine in 60 ml of THF were treated with 1.5 g (62 mmol) of magnesium powder with stirring at −40°C. Within 18 h the mixture was allowed to warm to 20°C. Evaporation of solvent, extraction of the residue with pentane and crystallization from a volume of 40 ml at −30°C afforded lemon-colored crystals, yield of **7** 1.3 g (53% based on nickel), m.p. 114–115°C, decomp. >190°C. – MS (FI), *m/z* (%): 457 (1(1) M, 278 (42) $OPPh_3$, 262 (100) PPh_3, 154 (58) PhPh, 137 (86) $(C_3H_5)_3N$. – IR (nujol mull, 1700–1600 cm^{-1}): $\tilde{\nu}$ = 1645 w $\nu_{C=C}$. – ^{1}H NMR ([D$_8$]toluene, 298 K): δ = 1.32 [t, $^2J(HH) = {}^3J(HH)$ = 11.0 Hz, 2H, $NCH_2{}^a$], 2.34 [dd, $^3J(HH)$ = 13.0, $^3J(PH)$ = 7.0 Hz, 2H, $C=CH_2{}^a$], 2.53 [t, $^3J(HH)$ = 7.0, $^3J(PH)$ = 7.0 Hz, 2H, $C=CH_2{}^b$], 3.0 [d, $^3J(HH)$ = 6 Hz, 2H, NCH_2 uncoord.] 3.7 (m, 4H, $NCH_2{}^b$ + CH), 5.1 (m, 2H, $C=CH_2$ uncoord.) 6.0 (m, 1H, CH uncoord.), 7.0–7.4 [m, 15H, $P(C_6H_5)_3$]. – $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 298 K): δ = 51.4 (CH_2), 59.6 (NCH_2), 60.8 (NCH_2 uncoord.), 72.3 (CH), 116.1 (CH_2 uncoord.), 133.7 (CH uncoord.). – $C_{27}H_{30}NNiP$ (458.2): calcd. C 70.77, H 6.60, N 3.06; found C 70.79, H 6.67, N 2.87.

$Co[(C_3H_5)_2NCH_3](PMe_3)_2$ (**8**): 3.91 g (11.01 mmol) of Co(*cyclo*-C_5H_8)$(PMe_3)_3$ in 50 ml of pentane at −78°C was allowed to react with 1.23 g (11.06 mmol) of diallylmethylamine. After 3 h at 20°C the volatile components were removed in vacuo, and the residue was extracted with 50 ml of pentane. Crystallization of the crude product with dry-ice cooling afforded 2.6 g of violet-blue crystals, yield of **8** 73% (based on cobalt), m.p. 67–68°C, decomp. >130°C. – MS (FI), *m/z* (%): 322 (39) M, 246 (100) M – PMe_3, 111 (69) $(C_3H_5)NCH_3$, 76 (72) PMe_3. – $C_{13}H_{31}CoNP_2$ (322.3): calcd. C 48.45, H 9.70, N 4.35; found C 47.88, H 9.55, N 4.17.

$Co[(C_3H_5)_2NC_6H_5](PMe_3)_2$ (**9**): According to a procedure used for the preparation of **8** the reaction of 2.67 g (7.52 mmol) of $Co(C_5H_8)(PMe_3)_3$ with 1.30 g (7.50 mmol) of *N,N*-diallylaniline afforded 2.56 g of violet-blue rhombic crystals (yield of **9** 89% based on cobalt), m.p. 84–85°C, decomp. >130°C. – MS (FI), *m/z* (%): 383 (63) M – H, 173 (84) $(C_3H_5)_2NC_6H_5$, 76 (100) PMe_3. – $C_{18}H_{33}CoNP_2$ (384.3): calcd. C 56.25, H 8.65, N 3.64; found C 56.17, H 8.40, N 3.70.

[(1,2,3,6,7-η^5)-4-Phenyl-4-aza-2,6-heptadienyl]bis(trimethylphosphane)cobalt(I) (**10**): 830 mg (1.88 mmol) of $Co(C_6H_5)(PMe_3)_4$ and 350 mg (2.02 mmol) of *N,N*-diallylaniline in 40 ml of THF were allowed to react at 20°C for 18 h. No change of color was observed. The volatile products were removed in vacuo, and the residue was extracted with 20 ml of pentane. Crystallization of the crude product with dry-ice cooling afforded 310 mg of ocherous crystals. Concentration of the mother liquor to 10 ml furnished another crop of 150 mg; total yield of **10** 460 mg (64% based on cobalt), m.p. 84–85°C. – $C_{18}H_{32}CoNP_2$ (383.3): calcd. C 56.40, H 8.41, N 3.65, P 16.16; found C 56.32, H 8.34, N 3.61, P 16.08.

From 670 mg (1.77 mmol) of $CoCH_3(PMe_3)_4$ and 310 mg (1.79 mmol) of *N,N*-diallylaniline in 50 ml of THF under similar conditions 330 mg of **10** (48%) was obtained. – IR (nujol): no bands between 2000 and 1600 cm^{-1}. – MS (FI), *m/z* (%): 383 (100) M, 78 (52) C_6H_6. – NMR: Tables 1 and 2.

Reaction of **8** *with NO:* Into a solution of 290 mg (0.90 mmol) of **8** in 10 ml of ether at −78°C in vacuo 20 ml of nitrogen monoxide was passed. The system was closed and allowed to warm with stirring. After filtration the volatile products were removed, and 150 mg of a red-brown residue was obtained and identified (IR, MS) as $CoNO(PMe_3)_3$ (yield 33%).

Reaction of **8** *with Azobenzene:* A solution of 500 mg (1.55 mmol) of **8** and 280 mg (1.54 mmol) of azobenzene in 40 ml of ether was kept at 20°C for 2 h. After filtration the volatile products were removed to afford 500 mg of $Co(PhNNPh)(PMe_3)_2$[12] (82%).

Reaction of **8** *with Benzo[c]cinnoline:* A solution of 360 mg (1.12 mmol) of **8** and 200 mg (1.11 mmol) of benzo[*c*]cinnoline in 60 ml of ether was kept at 20°C for 2 h. After filtration and concentration of the filtrate to 20 ml crystallization with dry-ice cooling afforded 130 mg of $Co(C_{10}H_8N_2)(PMe_3)_3$[8] (yield 37%).

Carbonylation of **9** *at Ambient Conditions:* A solution of 460 mg (1.20 mmol) of **9** in 30 ml of pentane at −60°C was kept under 1 bar CO and allowed to warm up with stirring. The orange-yellow solution was concentrated to 15 ml and subjected to dry-ice cooling to furnish 260 mg of red crystals which were shown (IR, MS) to be a mixture of $Co_2(CO)_4(PMe_3)_4$ and $Co_2(CO)_5(PMe_3)_3$.

☆ Dedicated to Professor *Wolfgang Luettke* on the occasion of his 75th birthday.

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[17/94]