2,3-Bis(diarylphosphanyl)-1,4-diazadienes: P,P Coordination of Pd^{II}, Pt^{II} and a Nickelacyclopentanone with Subsequent Formation of Quinoxalines by a Ring-Closure Reaction at the Periphery

Dirk Walther,*[a] Stefan Liesicke,[a] Reinald Fischer,[a] Helmar Görls,[a] Jennie Weston,[b] and Ariadna Batista[b]

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The solid-state structures of several 2,3-bis(phosphanyl)-1,4-diazadiene ligands of the general formula RN=C(PPh_2)–C(PPh_2)=NR (**B**: R = 4-tolyl; **C**: R = 4-*tert*-butylphenyl; **D**: R = mesityl) were determined by single-crystal X-ray diffraction. The ligands **B** and **C** are nonplanar and lie between the (*E*) and the (*Z*) form (N=C–C=N is 99.5° in **B**, 94.0° in **C**, and 128.2° in **D**). In the presence of air, **B** is oxidized to its corresponding phosphane oxide. Reaction of **D** with elemental sulfur yields the corresponding phosphane sulfide. Furthermore, ligand **C** reacts with [$PtCl_2$(cod)] and [$PdCl_2(CH_3CN)_2$] to form mononuclear complexes (**1** and **2**, respectively) in which the two P atoms are bound to the metal center. X-ray structural analysis showed that in both complexes the 1,4-diazadiene functionality at the periphery had undergone a ring-closure reaction with one of the aromatic N-substituents thus resulting in a quinoxaline ring. The bulkier ligand **D** reacts with [$PdCl_2(CH_3CN)_2$] to form the mononuclear complex **3**. In the solid state, the two phosphorus atoms are coordinated to the metal center in a five-membered chelate ring. In contrast to **1** or **2**, a cyclohexadiene system is formed as result of a cycloaddition reaction of one aromatic N-substituent with the 1,4-diazadiene system. The nickel complex [Ni(tmeda)(C_2H_4COO)] reacts with **D** by displacement of tmeda to form a mononuclear complex **4a** with P,P coordination. A subsequent ring-closure reaction (cycloaddition) at the periphery does not occur in **4a**. If the ligand is sterically less demanding (**B** or **C**), a cycloaddition between the 1,4-diazadiene system and one aromatic substituent takes place in the nickel complex to form complexes of the type **5** containing a quinoxaline ring. This reaction could be monitored by ^{31}P NMR spectroscopy for ligand **C**.

Introduction

2,3-Bis(phosphanyl)-1,4-diazadienes contain perhaps the two most important chelating functionalities, a conjugated 1,4-diazadiene and a 1,2-bis(phosphanyl)ethane, within the same ligand. Both of these structural units are known to form stable five-membered metal chelate ring systems which have general importance in organometallic and coordination chemistry. Numerous catalysts for homogeneous reactions are, for example, based on these chelate complexes.[1–16]

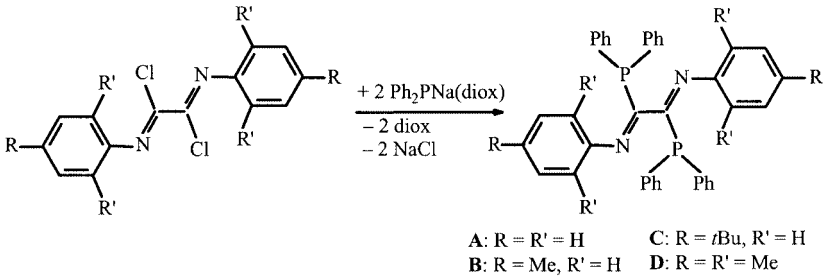
In an initial communication, we reported a synthetic procedure for obtaining hitherto unknown 2,3-bis(diarylphosphanyl)-1,4-diazadienes.[17] These are the first experimentally accessible representatives that unify the two functionalities mentioned above. As one would expect, they react readily with Ni^{II}, Cu^{I}, and Mo^{0} fragments thus giving rise to a rich complex chemistry. Some of these chelating ligands chelate by P,P complexation with nickel(II) bromide and then subsequently undergo a rather unusual ring-closure reaction at the periphery of the ligand to form a quinoxaline.[17] This opens a simple route for the synthesis of bis(diphenylphosphanyl)ethylenes containing a quinoxaline backbone. Continuing with our investigations, we now report an alternative synthesis for obtaining these ligands. We have further investigated their structural and electronic properties as well as their behavior towards oxygen and sulfur. In order to gain a deeper understanding of their coordination behavior, as well as their interesting peripheral ring-closure reaction, we have extended the palette of metal fragments employed to include Pd^{II} and Pt^{II} as well as an organometallic derivative of Ni^{II}.

[a] Institut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität Jena, 07743 Jena, Germany
[b] Institut für Organische Chemie und Makromolekulare Chemie der Friedrich-Schiller-Universität Jena, 07743 Jena, Germany

Results and Discussion

Synthesis of the Bis(diarylphosphanyl)-1,4-diazadienes A–D

In analogy to the previously reported 2,3-bis(diarylphosphanyl)-1,4-diazadienes **B**–**D**,[17] we succeeded in preparing



Scheme 1

the 2,3-bis(diphenylphosphanyl)-1,4-diphenyl-1,4-diazadiene (**A**) in 40% yield from sodium diphenylphosphide and the corresponding imidoyl chloride in THF (Scheme 1).

This new ligand has one singlet $^{31}P\{^1H\}$ resonance (δ = 4.7 ppm) in the same spectral region as the ^{31}P NMR signals of ligands **B**–**D**. The ^1H and ^{13}C NMR spectra of **A** are very simple, typical for a symmetrical structure in solution, and are directly comparable with those reported for the ligands **B**–**D**.[17]

An alternative route to **D** is the reaction of the corresponding imidoyl chloride with diphenyl(trimethylsilyl)phosphane (Scheme 2).

This preparative route leads to pure **D** in a much higher yield (64%) without the time-consuming necessity of purifying the raw material. The reaction mixture for this alternative route contained, in addition to **D**, a small amount of the hitherto unknown 2-(diphenylphosphanyl)-1,4-dimesityl-1,4-diazabutadiene (**G**) which could be isolated as yellow crystals and fully characterized by NMR spectroscopy and X-ray diffraction analysis.

The Structure and Electronic Properties of Ligands A–D

Single crystals of **B**–**D** suitable for an X-ray diffraction analysis could be grown from a solution in either toluene or chloroform. All of these ligands possess the same structural motif in the solid state. As a representative example, Figure 1 illustrates the molecular structure of compound **D**, which co-crystallizes with 1 equiv. of $CHCl_3$. Selected geometrical parameters can be found in the figure caption.

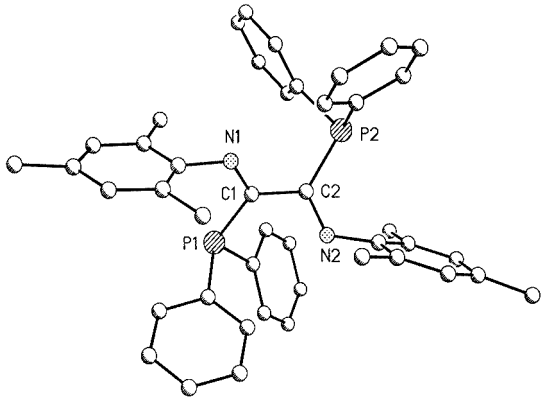
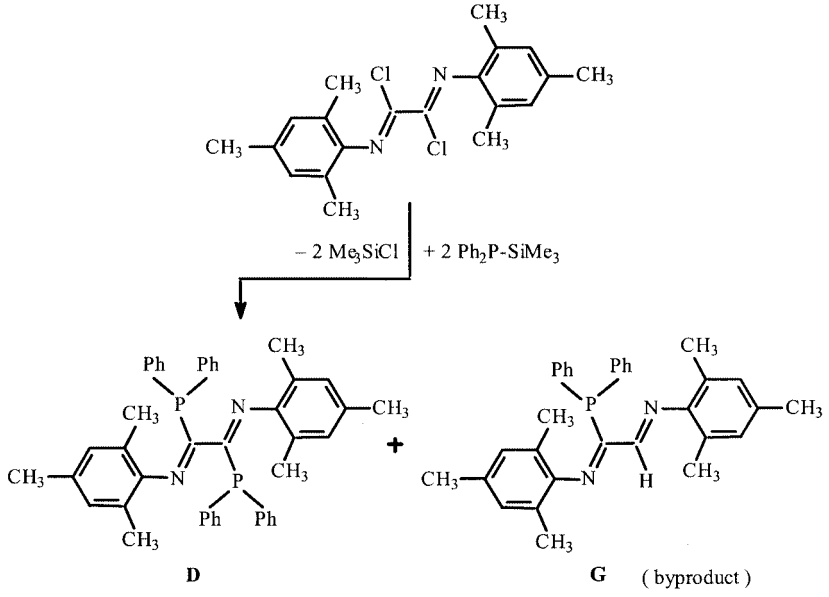


Figure 1. Solid-state structure of compound **D**; selected bond lengths [Å] and bond angles [°]: C1–P1 1.874(2), C1–N1 1.280(2), C1–C2 1.517(2), C2–P2 1.875(2), C2–N2 1.266(2); P1–C1–N1 119.5(1), P2–C2–N2 121.7(1), P1–C1–C2 125.4(1), N1–C1–C2 114.9(1), P2–C2–C1 124.7(1), N2–C2–C1 113.5(1)



Scheme 2

The central C−C bond in **D** is a typical single bond (1.517 Å) and the C−N bond lengths are typical of double bonds (1.280 and 1.266 Å). The bulky PPh_2 group results in large P−C−C bond angles (125.4 and 124.7°); the N−C−C angles (114.9 and 113.5°) are rather small due to the effect of the lone pair on the nitrogen atom. Perhaps the most unusual feature of ligand **D** is that, in spite of the 1,4 diazabutadiene unit, it is not planar and assumes a twisted (*E*) conformation (the N−C−C−N dihedral angle is 128.2°). The twist angle is even larger in **B** (N−C−C−N = 99.5°) and **C** (N−C−C−N = 94.0°), leading to an almost orthogonal conformation. A conformational search for **D** at the B3LYP/lanl2dz level of theory confirmed that this nonplanar geometry is the global minimum (and the only stable conformation on the hypersurface). All calculated geometrical parameters agree quite satisfactorily with the solid-state values. An NBO analysis for **D** showed that a residual delocalization between the two C=N double bonds is present [$\pi_{C=N} \rightarrow \pi^*_{C=N}$ = 10.2 kcal/mol] in spite of the relatively large twist angle.

The by-product 2-(diphenylphosphanyl)-1,4-dimesityl-1,4-diazabutadiene (**G**, Scheme 2), which lacks the bulk of a second PPh_2 group, assumes a planar (*E*) conformation in the solid state (not depicted; the N−C−C−N torsion angle is 158.8°). This prompted us to explore the rotational process about the central C−C bond in the absence of steric hindrance (Figure 2).

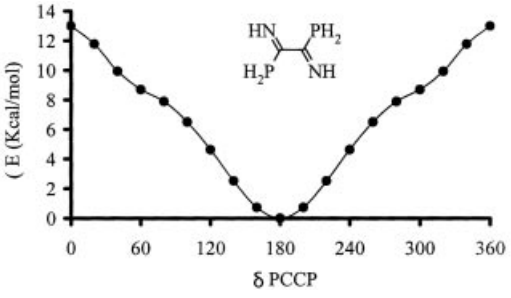


Figure 2. Torsional potential for rotation about the central C−C bond in a simple diphosphanyl-diazabutadiene, calculated at the B3LYP/6-311++G(3df,3pd) level of theory

The (*E*) conformation (P−C−C−P = 180°) is the only stable minimum on the hypersurface of this bifunctional chelating unit. The (*Z*) conformer is the transition structure for rotation about the C−C bond due to strong electronic repulsions between the lone electron pairs on the nitrogen atom in this orientation. It is interesting that two inflection points occur in the rotational barrier at ca. 60 and 300°. In the neighborhood of these points, the repulsion between the lone pairs of the nitrogen atoms is becoming quite weak and a $\pi_{C=N} \rightarrow \pi^*_{C=N}$ delocalization is beginning to appear. This delocalization is responsible for the preferred (E) conformation. If bulky substituents on P are introduced, these inflection points are stabilized and become minima on the hypersurface at the expense of the planar (E) conformation.

There are several possibilities for the coordination of **D** to a metal ion (P,P, N,N and two P,N modes) but, as discussed below, P,P coordination is generally favored. In each case, a lone pair on the heteroatom functions as a donor orbital to the metal ion. The NBO analysis of **D** (Table 1) shows that the lone pair orbital on P lies significantly higher in energy (−7.7 eV) than on N (−8.6 eV). This difference is probably responsible for the observed preference of a P,P coordination mode since the lone electron pair on P can interact more effectively with low-lying unoccupied orbitals on the metal ion.

Table 1. Selected electronic properties of ligand **D**, calculated at the B3LYP/6-31+G(d,p)//B3LYP/lanl2dz level of theory

Atomic charge		Orbital	Occupancy	Energy [eV]
q_C	0.05	n_N	1.82	−8.6
q_N	−0.46	n_P	1.80	−7.7
q_P	+0.76			

Reactivity towards Oxygen and Sulfur

The ligands **B**−**D** all decompose in the presence of water and are oxidized by air to yield the corresponding phosphane oxides. We succeeded in isolating the phosphane oxide **E**, resulting from the reaction of **B** with hydroperoxide or with oxygen, as single crystals. Its solid-state structure and relevant geometrical parameters can be found in Figure 3.

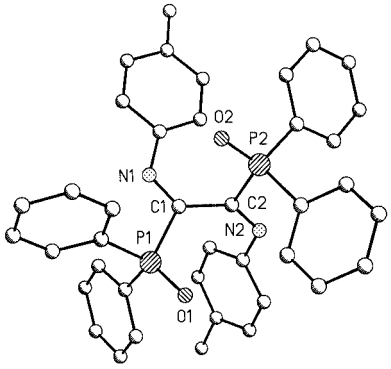


Figure 3. Solid-state structure of compound **E**; selected bond lengths [Å] and bond angles [°]: P1−O1 1.484(2), P1−C1 1.857(3), C1−N1 1.285(3), C1−C2 1.522(4), P2−O2 1.483(2), P2−C2 1.857(3), C2−N2 1.280(3); O1−P1−C1 112.1(1), O2−P2−C2 111.1(1), P1−C1−N1 113.0(2), P2−C2−N2 116.4(2), P1−C1−C2 115.9(2), N1−C1−C2 130.9(3), P2−C2−C1 115.9(2), N2−C2−C1 127.2(3)

Ligand **E** also assumes a nonplanar conformation. Rather than being almost orthogonal, the torsion angle (N−C−C−N = 118.6°) is significantly shifted towards an (*E*) conformation (N−C−C−N in **B** is 99.5°). This may possibly be due to the higher coordination number and thus increased steric bulk of the phosphorus functionalities which force them to be (*E*) to each other.

Adding elemental sulfur to a solution of **D** resulted in the formation of the corresponding disulfide **F**, which could then be characterized by MS and NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum of **F**, a singlet at δ = 34.9 ppm (shifted downfield relative to **D**) was observed. In the ^{13}C NMR spectrum at room temperature, all expected 11 sig-

nals were detected. Surprisingly, the resonance of the P−C=N carbon atoms occurs at δ = 159.3 ppm as a broad signal, thus suggesting the presence of a hindered rotation about the central PNC−CNP single bond.

Pd^{II} and Pt^{II} Complexes of These Ligands

We observed in our initial investigation that a ring-closure reaction at the periphery of a metal-complexed 2,3-bis(diarylphosphanyl)-1,4-diazadiene unit only occurred when P,P coordination is present and only when the metal ion was Ni^{II}.[17] Corresponding Cu^{I} or $Mo(CO)_4$ complexes did not promote this reaction. This fact prompted us to investigate the coordination chemistry of the related d^8 metal ions Pd^{II} and Pt^{II}.

Ligand **C** reacts with $[PtCl_2(cod)]$ to yield the mononuclear complex **1** as the only product. The two phosphorus atoms are nonequivalent as can be seen from two resonances (δ = 25.0 and 20.0 ppm) in the $^{31}P\{^1H\}$ spectrum of **1**. In addition, the ^1H and ^{13}C NMR spectra of **1** in $[D_8]$THF are in agreement with the unsymmetrical structure shown in Scheme 3.

For example, two different signals, each integrating to nine protons, were observed at δ = 1.05 and 1.24 ppm for the two *tert*-butyl groups. The NMR spectroscopic data suggest that **1** is the product of a ring-closure reaction between the 1,4-diazadiene system at the periphery of the complex with one *tert*-butylphenyl substituent of a nitrogen atom yielding a quinoxaline system by subsequent tautomerization (Scheme 3).

Figure 4 shows the solid-state structure of **1**, which confirms the existence of a mononuclear complex in which a ring-closure reaction to form a quinoxaline ring has occurred. The coordination geometry of the platinum center is square-planar with two *cis*-chloro ligands. The two phosphorus donor atoms form a five-membered chelate ring. Typical for this structure is the C1−C2 double bond (1.342 Å). As expected, the C−C bond lengths in the peripheral benzene ring are equivalent to each other within experimental errors and correspond to typical C−C bond lengths in aromatic systems. The C1−N1 and the C3−N1 bond lengths are those of typical single bonds [1.448(6), and 1.449(7) Å]. In contrast, the C2−N2 and C4−N2 bonds [1.380(7), 1.404(6) Å] are slightly shortened, indicating

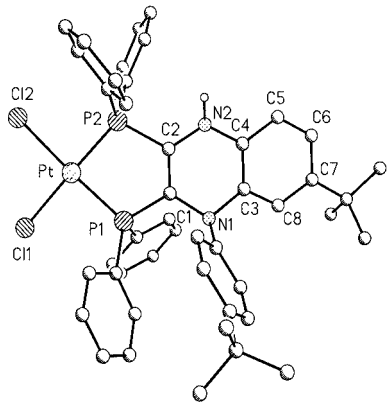
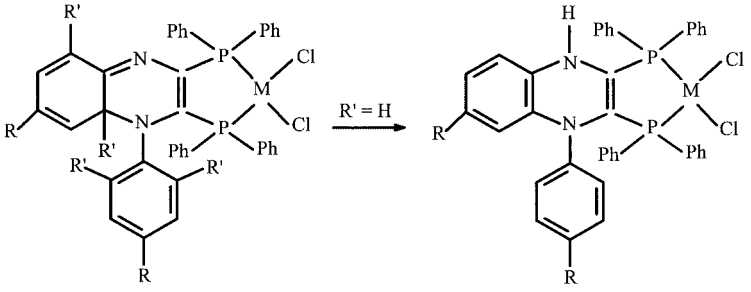


Figure 4. Solid-state structure of complex **1**; selected bond lengths [Å] and bond angles [°]: Pt−Cl1 2.361(1), Pt−Cl2 2.360(1), Pt−P1 2.214(1), Pt−P2 2.206(1), P1−C1 1.795(6), C1−C2 1.342(8), C1−N1 1.448(6), N1−C3 1.449(7), P2−C2 1.830(5), C2−N2 1.380(7), N2−C4 1.404(6), C4−C3 1.387(8), C4−C5 1.390(8), C5−C6 1.390(8), C6−C7 1.392(8), C7−C8 1.391(8), C8−C3 1.399(7); Cl1−Pt−Cl2 91.31(5), Cl1−Pt−P1 91.42(5), Cl1−Pt−P2 178.48(5), Cl2−Pt−P1 177.04(6), Cl2−Pt−P2 89.77(5), P1−Pt−P2 87.48(5)

charge delocalization in the C1−C2−N2−C4 part of the quinoxaline ring. Consequently, N1 is pyramidal and N2 is planar. This difference may be explained by steric reasons: N1 bears an aryl substituent in the neighborhood of the Ph_2P group whereas N2 bears the much smaller hydrogen substituent.

Ligand **C** also reacts with $[PdCl_2(CH_3CN)_2]$ to form the mononuclear complex **2** even if an excess of the palladium compound was employed. Analogous to the Pt compound, the $^{31}P\{^1H\}$ spectrum show that the two phosphorus atoms are unsymmetrical (two doublets at δ = 43.5 and 37.6 ppm). The ^1H and ^{13}C NMR spectra also indicate that a ring-closure reaction has taken place (see Exp. Sect.). Brown crystals of the palladium complex **2** could be isolated from THF. However, their quality was insufficient for the exact determination of bond lengths and bond angles in the solid state. Only the structure motif of the planar complex containing a peripheral quinoxaline ring could be unequivocally confirmed in the solid state.

Ligand **D** contains, in contrast to **C**, methyl groups in both *ortho* positions of the N substituents. This effectively prevents tautomerization to form a benzene ring. Coordi-



3: R = R' = Me, M = Pd

1: R = *t*Bu, R' = H, M = Pt

2: R = *t*Bu, R' = H, M = Pd

Scheme 3

nation of a metal ion to both phosphorus atoms, followed by a peripheral ring closure, must then stop at the cyclohexadiene stage of the reaction.[17]

Ligand **D** does indeed react with $[PdCl_2(CH_3CN)_2]$ in THF to form the mononuclear complex **3**. ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra are in complete agreement with a 1,3-cyclohexadiene ring at the periphery of the metal complex. The solid-state structure of **3** confirmed the presence of the expected 1,3-cyclohexadiene ring with its typically alternating bond lengths (Figure 5). The N1−C3 bond length (1.300 Å) is that of a double bond and therefore much shorter than the corresponding bond length in the N1−C1 single bond of **1** (1.448 Å). Bond lengths and angles in the (P,P)Pd chelate ring are very similar to those in **1**.

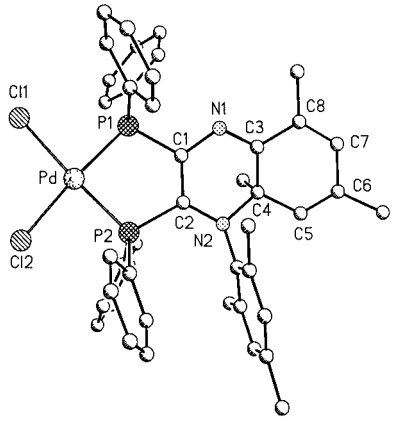


Figure 5. Solid-state structure of complex **3**; selected bond lengths [Å] and bond angles [°]: Pd−Cl1 2.354(1), Pd−Cl2 2.346(1), Pd−P1 2.194(1), Pd−P2 2.227(1), P1−C1 1.789(5), C1−N1 1.394(7), C1−C2 1.350(7), N1−C3 1.300(7), C2−N2 1.386(7), N2−C4 1.530(7), C4−C3 1.520(7), C4−C5 1.460(7), C5−C6 1.331(8), C6−C7 1.447(9), C7−C8 1.331(8), C8−C3 1.459(8); Cl1−Pd−Cl2 95.26(6), Cl1−Pd−P1 89.62(6), Cl1−Pd−P2 176.20(6), Cl2−Pd−P1 174.31(6), Cl2−Pd−P2 88.07(6), P1−Pd−P2 87.14(5), P1−C1−N1 116.8(4), P2−C2−N2 125.0(4), P1−C1−C2 120.9(4), P2−C2−C1 114.8(4), N1−C1−C2 122.0(5), N2−C2−C1 120.1(5)

These results allow us to conclude that bromides and chlorides of d^8 systems (Ni^{II}, Pd^{II}, and Pt^{II}) generally favor P,P coordination with 2,3-bis(phosphanyl)-1,4-diazadienes over P,N or N,N coordination. The formation of a mononuclear complex is then directly followed by an unusual peripheral ring-closure reaction to form a quinoxaline derivative, independent of the size of the metal ion.

Reaction of These Ligands with a Nickelacycle

We then modified the metal fragment employed to find out if the peripheral ring-closure reaction depends on the nature of the additional ligand(s) coordinated to the metal ion. Our metal fragment of choice was the nickelacycle [Ni(tmeda)(C_2H_4COO)], which contains a doubly negatively charged 1-oxo-2-nickelacyclopentan-5-one chelate ring on one side of the square-planar complex. On the other side is the neutral chelating ligand *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda). Displacement of tmeda by either **B**, **C**, or **D** should result in the initial formation of an [Ni{2,3-bis(diarylphosphanyl)-1,4-diazadiene}(C_2H_4COO)] complex. If the ring closure is affected by the additional metal ligands, one would expect a different reactivity of this complex compared to the related $NiBr_2$ complex, which undergoes a fast ring-closure reaction.

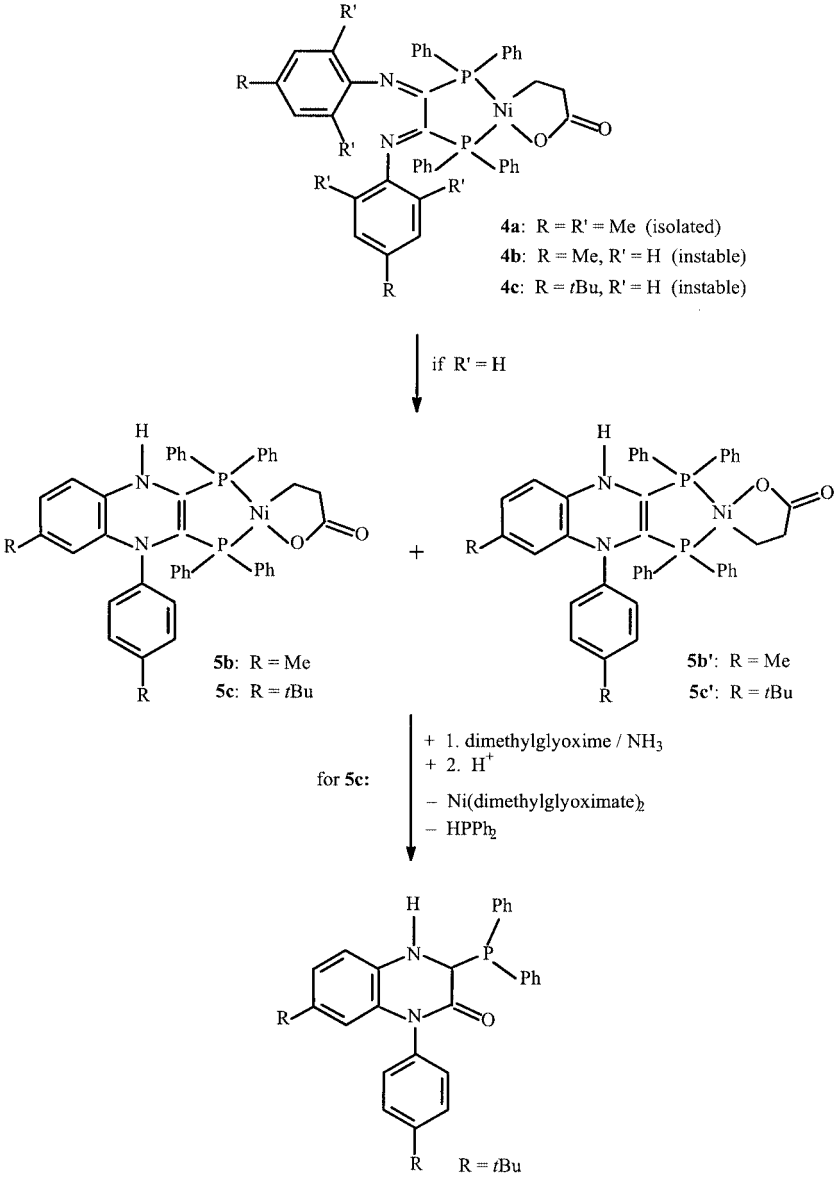
Treatment of the nickelacycle with the bulk ligand **D** in a solution of DMF followed by removal of tmeda by distillation in vacuo resulted in the expected organometallic complex [Ni(**D**)(C_2H_4COO)] (**4a**; Scheme 4) which turned out to be dark red. There are theoretically four possibilities for the coordination of **D** to the nickelacyclic fragment in this compound (P,P, N,N, and two P,N coordination modes). NMR spectroscopic data show that both phosphorus donor atoms coordinate to the nickelacycle in a different chemical environment (double signal sets for the mesityl groups in the ^1H NMR spectrum and two doublets at δ = 19.8 and 44.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **4a**). Isolation of single crystals of **4a** from benzene and subsequent X-ray diffraction analysis (Figure 6) showed that both phosphorus atoms are coordinated to the nickel center (square-planar P,P mode) in the solid state. In addition, an oxygen and a carbon atom of the C_2HC_4COO moiety are bound to the nickel center. The 1,4-diazadiene unit of **D** is not involved in coordination. A ring-closure reaction of the 1,4-diazadiene and one mesityl substituent at the nitrogen atom to yield a quinoxaline ring *did not take place* upon coordination of the diphosphane unit to the nickelacycle.

The diazabutadiene unit in ligand **D** is not planar (N−C−C−N torsional angle is 52.4°) but is definitely closer to a (*Z*) arrangement than to the *twist*-(*E*) conformation of the free ligand **D** (N−C−C−N = 128.2°). Ligand bond lengths do not differ significantly between the free ligand **D** and the coordinated complex **4a**.

The less bulky ligand **B** also reacted with the nickelacycle [Ni(tmeda)(C_2H_4COO)] to yield an orange chelate complex, which could be isolated in good yields (54%) from dichloromethane as an adduct of the composition "[Ni(**B**)(C_2H_4-COO)(CH_2Cl_2)]". Analogous to **4a**, the $^{31}P\{^1H\}$ NMR spectrum of this complex in $CDCl_3$ shows a low-field shift relative to the free ligand and indicates a P,P coordination mode but, in this case, *two* sets of two doublets are observed at δ = 28.3 [d, $^2J(^{31}P^{31}P)$ = 19.0 Hz], 39.0 [d, $^2J(^{31}P^{31}P)$ = 24.2 Hz], 46.1 [d, $^2J(^{31}P^{31}P)$ = 24.2 Hz], and 48.9 [d, $^2J(^{31}P^{31}P)$ = 19.0 Hz] ppm.

This is not compatible with the "open coordination form" observed for **4a** but can be rationalized by an unsymmetrical chelate ring system formed by ring-closure reaction between the 1,4-diazadiene unit and an aromatic N-substituent to form the regioisomers **5b/5b′** (Scheme 4).

The ^1H NMR spectroscopic data support this conclusion. In the ^1H NMR spectrum two sets of signals for the CH_3 protons at δ = 1.84, 1.91, 2.11, and 2.15 ppm were found whereas the CH_2 protons of the metallacyclic ring appear as multiplets. The $^{13}C\{^1H\}$ NMR spectrum is very complicated due to the ^{31}P coupling pattern of the ^{13}C signals of the two very similar regioisomers. Therefore, not all expected signals could be resolved (see Exp. Sect.).



Scheme 4

The formation of a quinoxaline system at the periphery was confirmed by X-ray diffraction analysis. Figure 7 shows the molecule structure of a single crystal of the regioisomer **5b·CH_2Cl_2** grown from dichloromethane. Unfortunately, the quality of the crystals was insufficient for satisfactory refinement of all parameters.

Ligand **B** thus behaves in a fundamentally different way to ligand **D**. This clearly demonstrates the subtle dependence of the ring-closure reaction upon ligand environment and identity in the metal complex. Both the nature of the metal and the coordination geometry of the complex formed in the first step of the complex formation, and the nature of the other ligands surrounding the metal center, influence the subsequent cycloaddition reaction at the periphery.

When the closely related ligand **C** was treated with the nickelacycle [Ni(tmeda)(C_2H_4COO)], an initial intermediate was formed which could be monitored by time-resolved $^{31}P\{^1H\}$ NMR spectroscopy at 5 °C. The "open coordination form", characterized by two doublets at δ = 42.7 and 60.9 ppm, could be assigned to this intermediate [Ni(**C**)(C_2H_4COO)] (**4c**; Scheme 4).

As the reaction progressed, two sets of two doublets appeared at δ = 30.5/51.0 and 37.7/49.0 ppm and grew in intensity over time. The signals assigned to the "open form" intermediate **4c** completely disappeared after 2 h at room temperature, and, except for a very small amount of the free ligand, only the two sets of two doublets were observed, which we concluded was the "quinoxaline form" **5c/5c′** resulting from the peripheral ring-closure reaction. A com-

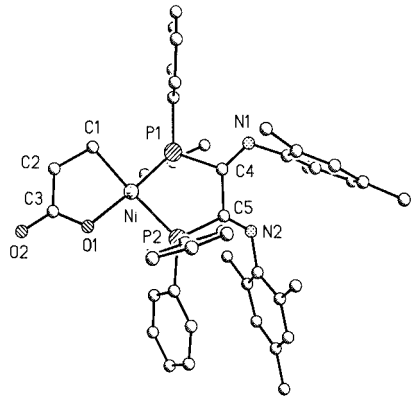


Figure 6. Solid -state structure of complex **4a**; selected bond lengths [Å] and bond angles [°]: Ni−P1 2.096(1), Ni−P2 2.170(1), Ni−O1 1.882(3), Ni−C1 1.952(4), C1−C2 1.526(6), C2−C3 1.512(6), C3−O1 1.306(5), C3−O2 1.227(5), P1−C4 1.853(4), P2−C5 1.864(4), C4−C5 1.530(5), C4−N1 1.271(5), C5−N2 1.267(5); P1−Ni−P2 90.30(4), P1−Ni−O1 170.55(9), P1−Ni−C1 88.6(1), P2−Ni−O1 96.00(9), P2−Ni−C1 171.5(1), O1−Ni−C1 86.2(1), P1−C4−N1 120.9(3), P2−C5−N2 133.4(3), P1−C4−C5 110.1(2), P2−C5−C4 110.4(2), N1−C4−C5 128.9(3), N2−C5−C4 115.0(3)

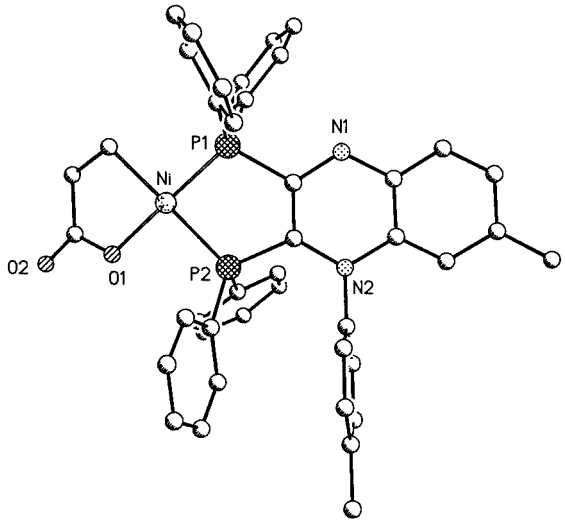


Figure 7. Solid-state structural motif of complex **5b** (the solvent CH_2Cl_2 has been omitted for clarity)

parison of the ^{31}P NMR spectrum of the closely related complex pair **5b/5b′** completely supports this assignment. There is no evidence for any other stable intermediate occurring during the ring-closure reaction.

In order to separate the quinoxaline ligand from the nickelacycle, the reaction mixture was treated with a solution of dimethylglyoxime in ethanol and aqueous ammonia. After separation of bis(dimethylgyoximato)nickel(II), thin white needles of 4-(*p*-*tert*-butylphenyl)-9-*tert*-butyl-3,4-dihydro-3-(diphenylphosphanyl)-1*H*-quinoxalin-2-one were isolated from the mother liquor, and were identified by IR measurements, mass spectra, ^1H, ^{13}C, and ^{31}P NMR spectra. The formation of this product can easily be explained by hydrolysis of the free 1,2-bis(diphenylphosphanyl)quinoxaline according to Scheme 4.

Experimental Section

General: ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra were recorded at ambient temperature with a Bruker AC 200 MHz spectrometer unless otherwise stated. All spectra were referenced to TMS or deuterated solvent as an internal standard. FAB mass spectra were obtained with a Finnigan MAT SSQ 710 system (2,4-dimethoxybenzyl alcohol as matrix), ESI mass spectra were recorded with a Finnigan MAT, MAT 95 XL. IR measurements were carried out with a Perkin−Elmer System 2000 FT-IR. All manipulations were carried out by using Schlenk techniques under argon. Prior to use, tetrahydrofuran, diethyl ether, and toluene were dried with potassium hydroxide and distilled from Na/benzophenone. $[PtCl_2(cod)]$ and $[PdCl_2(CH_3CN)_2]$ (Aldrich) were used as received. Oxalic imidoyl chlorides R−N=C(Cl)−C(Cl)=N−R,[18,19] $NaPPh_2$(dioxane) and $K(PPh_2)(dioxane)_n$,[20] and the nickelacycle [Ni{(tmeda)-C_2H_4COO}][21] were prepared according to the literature.

Computational Methods: All calculations reported in this article were performed using the Gaussian 98[22] program package using the gradient-corrected B3LYP[23−25] density functional. Default convergence criteria were used for all optimizations. The size of ligand **D** limited optimizations and frequency calculations to the lanl2dz basis set developed by Hay and Wadt[26] as implemented in Gaussian 98. Atomic charges, orbital and hyperconjugative interaction energies were obtained at the B3LYP/6-31+G(d,p)//B3LYP/lanl2dz level using the natural bond orbital (NBO) analysis of Reed et al.[27] as implemented in Gaussian 98. The torsional barrier of diphosphanyl-diazabutadiene (Figure 2) was calculated using the very large 6-311++G(3df,3pd) basis set.

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, and (only for **1**) for absorption effects.[28,29] The structures were solved by direct methods (SHELXS[30]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[31]). For the molecules **B**, **C**, **D**, **E**, and **G**, the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[4] Since the quality of the data of compounds **2** and **5c** was too low, we will only publish the conformation of **5b** and the crystallographic data of **2** and **5b**. We have not deposited the data in the Cambridge Crystallographic Data Centre. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for B:[32] $C_{40}H_{34}N_2P_2$, M_r = 604.63 g·mol^{-1}, colourless prism, size 0.21 × 0.18 × 0.10 mm, monoclinic, space group *C*2, *a* = 21.7489(8), *b* = 6.3620(2), *c* = 12.8609(6) Å, β = 115.479(2)°, *V* = 1606.4(1) Å^3, *T* = −90 °C, *Z* = 2, $\rho_{calcd.}$ = 1.250 g·cm^{-3}, μ(Mo-K_α) = 1.67 cm^{-1}, *F*(000) = 636, 4265 reflections in *h*(−30/30),*k*(0/7),*l*(−18/18), measured in the range 3.22° ≤ Θ ≤ 30.54°, completeness to Θ_{max} 95%, 2532 independent reflections, R_{int} = 0.029, 2233 reflections with $F_o > 4\sigma(F_o)$, 267 parameters, 1 restraint, $R1_{obs}$ = 0.038, $wR2_{obs}$ = 0.083, $R1_{all}$ = 0.048, $wR2_{all}$ = 0.087, GOOF = 1.004, Flack parameter 0.1(1), largest difference peak/hole 0.240/−0.199 e·Å^{-3}.

Crystal Data for C:[32] $C_{46}H_{46}N_2P_2$, M_r = 688.79 g·mol^{-1}, colourless prism, size 0.32 × 0.30 × 0.28 mm, orthorhombic, space group *Fdd*2, *a* = 31.3604(9), *b* = 38.780(1), *c* = 6.3478(2) Å, *V* = 7719.9(4) Å^3, *T* = −90 °C, *Z* = 8, $\rho_{calcd.}$ = 1.185 g·cm^{-3}, μ(Mo-K_α) = 1.47 cm^{-1}, *F*(000) = 2928, 9627 reflections in *h*(−43/

44),*k*(−55/55),*l*(−9/0), measured in the range 3.34° ≤ Θ ≤ 30.49°, completeness to Θ_{max} 99.2%, 3155 independent reflections, R_{int} = 0.049, 2727 reflections with $F_o > 4\sigma(F_o)$, 318 parameters, 1 restraint, $R1_{obs}$ = 0.047, $wR2_{obs}$ = 0.090, $R1_{all}$ = 0.061, $wR2_{all}$ = 0.094, GOOF = 1.060, Flack parameter 0.07(9), largest difference peak/hole: 0.220/−0.278 e·Å^{-3}.

Crystal Data for D:[32] $C_{44}H_{42}N_2P_2{\cdot}CHCl_3$, M_r = 780.10 g·mol^{-1}, yellow prism, size 0.10 × 0.10 × 0.06 mm, triclinic, space group $P\bar{1}$, *a* = 10.9955(2), *b* = 11.0908(4), *c* = 18.6186(6) Å, α = 88.207(1), β = 77.765(2), γ = 65.120(2)°, *V* = 2008.7(1) Å^3, *T* = −90 °C, *Z* = 2, $\rho_{calcd.}$ = 1.290 g·cm^{-3}, μ(Mo-K_α) = 3.42 cm^{-1}, *F*(000) = 816, 14121 reflections in *h*(−11/14),*k*(−14/13),*l*(−20/24), measured in the range 2.03° ≤ Θ ≤ 27.48°, completeness to Θ_{max} 98.3%, 9053 independent reflections, R_{int} = 0.055, 6598 reflections with $F_o > 4\sigma(F_o)$, 641 parameters, 0 restraints, $R1_{obs}$ = 0.047, $wR2_{obs}$ = 0.131, $R1_{all}$ = 0.067, $wR2_{all}$ = 0.140, GOOF = 1.059, largest difference peak/hole 0.287/−0.461 e·Å^{-3}.

Crystal Data for E:[32] $C_{40}H_{34}N_2O_2P_2$, M_r = 636.63 g·mol^{-1}, orange prism, size 0.32 × 0.20 × 0.10 mm, monoclinic, space group $P2_1/c$, *a* = 16.4345(5), *b* = 12.3660(5), *c* = 16.3540(4) Å, β = 94.429(3)°, *V* = 3313.68(19) Å^3, *T* = −90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.276 g·cm^{-3}, μ(Mo-K_α) = 1.7 cm^{-1}, *F*(000) = 1336, 24310 reflections in *h*(−18/20),*k*(−15/15),*l*(−20/20), measured in the range 3.16° ≤ Θ ≤ 26.33°, completeness to Θ_{max} 99.7%, 6730 independent reflections, R_{int} = 0.128, 4229 reflections with $F_o > 4\sigma(F_o)$, 551 parameters, 0 restraints, $R1_{obs}$ = 0.061, $wR2_{obs}$ = 0.115, $R1_{all}$ = 0.119, $wR2_{all}$ = 0.134, GOOF = 1.015, largest difference peak/hole 0.215/−0.344 e·Å^{-3}.

Crystal Data for G:[32] $C_{32}H_{33}N_2P$, M_r = 476.57 g·mol^{-1}, orange prism, size 0.20 × 0.18 × 0.12 mm, triclinic, space group $P\bar{1}$, *a* = 11.3416(6), *b* = 11.7240(5), *c* = 12.1736(7) Å, α = 116.217(3), β = 103.457(2), γ = 95.600(3)°, *V* = 1374.6(1) Å^3, *T* = −90 °C, *Z* = 2, $\rho_{calcd.}$ = 1.151 g·cm^{-3}, μ(Mo-K_α) = 1.22 cm^{-1}, *F*(000) = 508, 9420 reflections in *h*(−11/14),*k*(−15/12),*l*(−15/14), measured in the range 2.01° ≤ Θ ≤ 27.49°, completeness to Θ_{max} 97.3%, 6133 independent reflections, R_{int} = 0.030, 4556 reflections with $F_o > 4\sigma(F_o)$, 448 parameters, 0 restraints, $R1_{obs}$ = 0.060, $wR2_{obs}$ = 0.116, $R1_{all}$ = 0.091, $wR2_{all}$ = 0.128, GOOF = 1.049, largest difference peak/hole 0.208/−0.277 e·Å^{-3}.

Crystal Data for 1:[32] $C_{46}H_{46}Cl_2N_2P_2Pt{\cdot}2C_4H_8O$, M_r = 1098.99 g·mol^{-1}, yellow prism, size 0.20 × 0.18 × 0.10 mm, monoclinic, space group $P2_1/n$, *a* = 18.5552(9), *b* = 14.0777(6), *c* = 21.6152(7) Å, β = 104.845(2)°, *V* = 5457.7(4) Å^3, *T* = −90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.337 g·cm^{-3}, μ(Mo-K_α) = 27.66 cm^{-1}, semiempirical,[2] trans(min) 0.507, trans(max) 0.849, *F*(000) = 2232, 21216 reflections in *h*(−24/24),*k*(−18/17),*l*(−26/25), measured in the range 1.84° ≤ Θ ≤ 27.55°, completeness to Θ_{max} 95.7%, 12062 independent reflections, R_{int} = 0.060, 6529 reflections with $F_o > 4\sigma(F_o)$, 563 parameters, 0 restraints, $R1_{obs}$ = 0.044, $wR2_{obs}$ = 0.101, $R1_{all}$ = 0.095, $wR2_{all}$ = 0.109, GOOF = 0.886, largest difference peak/hole 1.120/−0.853 e·Å^{-3}.

Crystal Data for 2: $C_{46}H_{46}Cl_2N_2P_2Pd{\cdot}3C_4H_8O$, M_r = 1082.40 g·mol^{-1}, brown prism, size 0.18 × 0.12 × 0.10 mm, monoclinic, space group $P2_1/n$, *a* = 18.5913(3), *b* = 14.0835(4), *c* = 21.5903(6) Å, β = 104.930(1)°, *V* = 5462.2(2) Å^3, *T* = −90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.316 g·cm^{-3}, μ(Mo-K_α) = 5.41 cm^{-1}, *F*(000) = 2264, 20954 reflections in *h*(−23/24),*k*(−17/18),*l*(−28/28), measured in the range 1.84° ≤ Θ ≤ 27.49°, completeness to Θ_{max} 99.2%, 12444 independent reflections, R_{int} = 0.077.

Crystal Data for 3:[32] $C_{44}H_{42}Cl_2N_2P_2Pd{\cdot}1.5C_4H_8O$, M_r = 946.19 g·mol^{-1}, yellow prism, size 0.18 × 0.12 × 0.10 mm, monoclinic, space group $P2_1/n$, *a* = 14.4502(6), *b* = 24.9850(10), *c* = 14.6521(5) Å, β = 112.360(3)°, *V* = 4892.2(3) Å^3, *T* = −90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.285 g·cm^{-3}, μ(Mo-K_α) = 5.91 cm^{-1}, *F*(000) = 1960, 13135 reflections in *h*(−16/16),*k*(−28/28),*l*(−16/16), measured in the range 1.73° ≤ Θ ≤ 24.09°, completeness to Θ_{max} 96.7%, 7502 independent reflections, R_{int} = 0.037, 4810 reflections with $F_o > 4\sigma(F_o)$, 508 parameters, 8 restraints, $R1_{obs}$ = 0.057, $wR2_{obs}$ = 0.165, $R1_{all}$ = 0.081, $wR2_{all}$ = 0.177, GOOF = 0.953, largest difference peak/hole 1.069/−0.475 e·Å^{-3}.

Crystal Data for 4a:[32] $C_{47}H_{46}N_2NiO_2P_2{\cdot}0.5C_6H_6$, M_r = 830.56 g·mol^{-1}, red prism, size 0.10 × 0.10 × 0.08 mm, monoclinic, space group $P2_1/n$, *a* = 12.6055(3), *b* = 16.4881(4), *c* = 20.9493(6) Å, β = 99.186(2)°, *V* = 4298.3(2) Å^3, *T* = −90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.283 g·cm^{-3}, μ(Mo-K_α) = 5.68 cm^{-1}, *F*(000) = 1748, 45176 reflections in *h*(−15/16),*k*(−21/21),*l*(−22/27), measured in the range 2.39° ≤ Θ ≤ 27.42°, completeness to Θ_{max} 98.6%, 9656 independent reflections, R_{int} = 0.115, 6543 reflections with $F_o > 4\sigma(F_o)$, 499 parameters, 0 restraints, $R1_{obs}$ = 0.069, $wR2_{obs}$ = 0.162, $R1_{all}$ = 0.114, $wR2_{all}$ = 0.191, GOOF = 1.055, largest difference peak/hole 1.412/−0.611 e·Å^{-3}.

Crystal Data for 5b: $C_{43}H_{38}N_2NiO_2P_2{\cdot}2CH_2Cl_2$, M_r = 904.70 g·mol^{-1}, prism, size 0.20 × 0.18 × 0.12 mm, monoclinic, space group $P2_1/c$, *a* = 8.8883(3), *b* = 26.1761(9), *c* = 19.3778(6) Å, β = 95.384(2)°, *V* = 4488.6(3) Å^3, *T* = −90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.391 g·cm^{-3}, μ(Mo-K_α) = 8.4 cm^{-1}, *F*(000) = 1936, 16022 reflections in *h*(−11/11),*k*(−33/31),*l*(−25/25), measured in the range 2.89° ≤ Θ ≤ 27.46°, completeness to Θ_{max} 93.9%, 9655 independent reflections, R_{int} = 0.101.

Preparation of the Ligands

Ph−N=C(PPh$_2$)−C(PPh$_2$)=N−Ph (Ligand A): A solution of $NaPPh_2$ (7.17 mmol 15% excess) in 10 mL of cold THF (−78 °C) was added dropwise to a solution of diphenyloxalylimidoyl chloride (0.9 g, 3.24 mmol) in 50 mL of THF at −78 °C. The reaction mixture was then allowed to warm to room temperature. After removing the solvent in vacuo and recrystallization from toluene 0.75 g (40%) of **A** was isolated as a light yellow powder. ^{1}H NMR ([D$_8$]THF, 25 °C, 200 MHz): δ = 7.04 (m, CH-phenyl) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 25 °C, 81 MHz): δ = 4.59 (s) ppm. MS (CI): 577 (basic peak $[M+1]^+$ ($C_{38}H_{30}N_2P_2 + H^+$), 499 ($[M+1]^+ - C_6H_6$, 3%), 409 ($[M+1]^+ - C_{12}H_{12}N$, 3%), 393 ($[M+1]^+ - C_{12}H_9P$, 16%), 288 ($[M+1]^+ - C_{19}H_{16}NP$, 37%), 185 ($[M+1]^+ - C_{26}H_{21}N_2P$, 15%).

Mes−N=C(PPh$_2$)−C(PPh$_2$)=N−Mes·CHCl$_3$ [D(CHCl$_3$)]

a) From Mes−N=CCl−CCl=N−Mes and KPPh$_2$: A solution of dimesityloxalylimidoyl chloride (2.7 g, 7.5 mmol) and $Pd(OAc)_2$ (85 mg, 0.038 mmol) in 100 mL of toluene was cooled to −40 °C in a three-necked flask equipped with a stirrer and a dropping funnel. Over 1 h, a solution of $KPPh_2$ (15.0 mmol) in 42 mL of dioxane/THF (1:1) was added. The color of the solution turned from yellow to dark red. The dry-ice bath was then removed and the reaction mixture was kept at room temperature overnight. The precipitated KCl was then filtered off. The solvent was removed in vacuo and the residue dissolved in hexane. The mixture was then filtered through Celite and the filtrate concentrated to dryness. The

residue is a slowly crystallizing oil. Recrystallization from chloroform/hexane gave 3.96 g (80%) of **D(CHCl$_3$)** as yellow crystals. M.p. 170 °C. $C_{45}H_{43}N_2P_2Cl_3$ (780.1): calcd. C 69.28, H 5.56, Cl 13.63, N 3.59; found C 69.97, H 5.67, Cl 13.18, N 3.55. ^{1}H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 1.42 (s, 12 H, *o*-CH_3), 2.17 (s, 6 H, *p*-CH_3), 6.45 (s, 4 H, *m*-H, Mes), 7.19−7.21 (m, 12 H, Ph), 7.50−7.54 (m, 8 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50.32 MHz, 298 K): δ = 17.7 [t, $J(^{13}C^{31}P)$ = 2.5 Hz, CH_3), 20.6 (CH_3), 124.4 (C), 128.1 (CH), 128.1 [d, $J(^{13}C^{31}P)$ = 8.3 Hz, CH], 128.8 (CH), 132.8 (C), 133.8 [br., d, $J(^{13}C^{31}P)$ = 10.5 Hz, C], 135.2 [br., d, $J(^{13}C^{31}P)$ = 23.4 Hz, C], 145.3 [br., d, $J(^{13}C^{31}P)$ = 9.3 Hz, C], 175.2 [dd, $J(^{13}C^{31}P)$ = 58.1, $J(^{13}C^{31}P)$ = 4.5 Hz, C] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 9.0 (s) ppm. MS (EI): *m*/*z* = 660 [M^+], 330 [M^+/2]. **G** was separated by column chromatography (Florisil, hexane, toluene) as the most nonpolar compound from the residue of the mother liquor. Yield: 0.18 g (5%) of yellow crystals. The yield can be increased up to 44% by addition of $HPPh_2$ *before* $KPPh_2$. ^{1}H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 1.55 (s, 6 H, *o*-CH_3), 2.02 (s, 6 H, *o*-CH_3), 2.14 (s, 3 H, *p*-CH_3), 2.17 (s, 3 H, *p*-CH_3), 6.65 (s, 2 H, *m*-H), 6.73 (s, 2 H, *m*-H), 7.34−7.64 (m, 11 H, Ph, =CH−) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50.32 MHz, 298 K): δ = 17.5 (CH_3), 17.6 (CH_3), 20.6 (CH_3), 124.4 [d, $J(^{13}C^{31}P)$ = 1.8 Hz, C], 126.7 (C), 128.4 [d, $J(^{13}C^{31}P)$ = 18.8 Hz, CH], 128.4 (*m*-CH, Mes), 128.6 (*m*-CH, Mes), 129.1 (CH), 132.7 (C), 133.8 (C), 134.4 [d, $J(^{13}C^{31}P)$ = 6.6 Hz, C], 135.0 (CH), 135.2 (CH), 135.1 [d, $J(^{13}C^{31}P)$ = 20.1 Hz, C], 157.5 [d, $J(^{13}C^{31}P)$ = 23.4 Hz, C], 175.5 [d, $J(^{13}C^{31}P)$ = 14.2 Hz, C] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 2.4 (s) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 81.01 MHz, 298 K): δ = 5.7 (s) ppm. MS (EI): *m*/*z* = 446 [M^+], 330 [$Ph_2PCNMes^+$], 146 [$MesNCH^+$].

b) From Mes−N=CCl−CCl=N−Mes and Me$_3$Si−PPh$_2$: A mixture of dimesityloxalylimidoyl chloride (2.25 g, 6.23 mmol) and diphenyl(trimethylsilyl)phosphane (3.25 g, 12.58 mmol) was held at 100 °C in a water bath for 12 h. Trimethylsilyl chloride was then distilled off the reaction mixture, which became more and more solid. The residue was then extracted with *n*-hexane. Yield: 2.63 g (64%) of **D** as yellow crystals. M.p. 170 °C.

Phosphane Oxide E by Oxidation of B: A solution of **B** in THF was treated with an equimolar amount of hydrogen peroxide at room temperature and a few milligrams of $CuSO_4$ were added. After 6 h, the solvent was removed and the residue was treated with chloroform. The organic phase was separated and dried with $NaSO_4$. After removing the solvent, a yellow product was isolated. White single crystals of **E** were obtained from THF at −20 °C. Similarly, the oxidation can also be carried out with air in the presence of a copper salt. MS (EI): *m*/*z* = 636 [$M^+ = C_{40}H_{34}N_2O_2P_2$], 402 [$(Ph_2PO)_2$], 318 [$M^+$/2], 201 [$Ph_2PO$]. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 23.56 ppm. ^{1}H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 2.14 (s, 6 H, *p*-CH_3), 6.62. 6.78 (AA′BB′, 8 H, CH-tolyl), 7.24−7.70 (m, phenyl, solvent) ppm.

Phosphane Sulfide F by Oxidation of D with Sulfur: A solution of **D(CHCl$_3$)** (1.01 g, 1.30 mmol) in toluene was treated with sulfur (85 mg, 2.65 mmol) and stirred at room temperature for 24 h. The solution slowly turned dark red. The signal of **D** in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture disappeared and a new signal at δ = 33.8 ppm appeared. The solvent was removed in vacuo. Recrystallization of the crude product from diethyl ether gave 0.60 g of Mes−N=C[P(S)Ph$_2$]−C[P(S)Ph$_2$]=N−Mes (**F**) (63.6%) as dark red thin plates. M.p. 242−243 °C. $C_{44}H_{42}N_2P_2S_2$ (724.8): calcd. C 72.90, H 5.84, N 3.86, S 8.85; found C 72.55, H 6.08, N 3.83, S 8.43. IR (nujol mull): ν(C=N) = 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 1.74 (s, 12 H, *o*-CH_3), 1.97 (s, 6 H, *p*-CH_3), 6.20 (s, 4 H, *m*-H), 1.74 (s, 12 H, *o*-CH_3), 7.17 (m, 8 H, *m*-H), 7.24 (m, 4 H, *p*-H), 7.81 (m, 8 H, *o*-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50.32 MHz, 298 K): δ = 19.0 (*o*-CH_3), 20.3 (*p*-CH_3), 123.5 (*o*-C), 127.8 (m, *o*-CH), 129.1 (*i*-C), 130.5 (*p*-CH), 131.5 (m, *m*-CH), 132.4 (*p*-C), 133.2 (*m*-CH), 142.5 (m, *i*-C), 159.3 [br., t, *J* ≈ 29 Hz, $(N=C-P)_2$] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 34.9 (s) ppm. MS *m*/*z* = 725 [M^+ + H].

Complex 1 [PdCl$_2$(C$_{46}$H$_{46}$N$_2$P$_2$)]: A solution of **C** (0.873 mmol, 0.601 g) in 25 mL of THF was added dropwise to a solution of $[PdCl_2(CH_3CN)_2]$ (0.873 mmol, 0.226 g) in 25 mL of THF whilst stirring. Shortly after warming the solution up to 60 °C, complex **1** precipitated almost quantitatively. After filtration, the compound was dried in vacuo at room temperature. It is only very slightly soluble in organic solvents. $C_{50}H_{54}Cl_2N_2OP_2Pd$ [**1(THF)**] (938.26): calcd. C 64.01, H 5.80, N 2.99; found C 63.25, 62.94, H 6.24, 5.98, N 2.89. ^{1}H NMR ([D$_8$]THF, 25 °C, 200 MHz): δ = 1.06, 1.15 (s, 18 H, CH_3-*t*Bu), 6.79−7.67 (m, 28 H, Ph) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF, 25 °C, 81 MHz): δ = 37.67 (d), 43.54 (d) ppm.

Complex 2 [PtCl$_2$(C$_{46}$H$_{46}$N$_2$P$_2$)]: A solution of **B** (0.32 mmol) in 10 mL of THF was added to [PtCl$_2$(cod)] (0.32 mmol, 0.12 g), dissolved in 10 mL of THF. Shortly after warming the solution up to 60 °C, complex **2** crystallized in more than 95% yield. $C_{50}H_{54}Cl_2N_2OP_2Pt$ [**2(THF)**] (954.82): calcd. C 58.48, H 5.30, N 2.73; found C 58.44, H 5.61, 5.44, N 2.65. ^{1}H NMR ([D$_8$]THF, 27 °C, 200 MHz): δ = 1.11, 1.15 (s, 18 H,CH_3), 6.38−8.01 (m, 25 H, Ph and NH); ^{31}P{^{1}H} NMR ([D$_8$]THF, 27 °C, 81 MHz): δ = −1.49 (d), 4.38 (d), 20.16 (d, *J* = 12 Hz), 25.05 (d, *J* = 13 Hz), 41.82 (d), 45.80 (d) ppm. MS (DEI): 953 [$M^+ = C_{46}H_{46}N_2P_2Cl_2Pt$], 918 [$M^+$ − Cl], 784 [$M^+ - C_{10}H_{13}Cl$], 696 [$M^+ - C_{12}H_{11}PCl_2$].

Complex 3 [PdCl$_2$(C$_{44}$H$_{42}$N$_2$P$_2$)]: A solution of 1.17 mmol of **D** in 20 mL of THF was added dropwise to a solution of [PdCl$_2$(acetonitrile)$_2$] (1.17 mmol, 0.292 g) in 25 mL of THF whilst stirring at room temperature. The complex precipitated after a short time in almost quantitative yield. After filtration, the product was washed with cold THF and dried in vacuo. $C_{48}H_{50}Cl_2N_2OP_2Pd$ [**3(THF)**] (910.21): calcd. C 63.34, H 5.53, N 3.08; found C 63.37, H 6.06, N 3.12. ^{1}H NMR ([D$_8$]THF, 27 °C, 200 MHz): δ = 0.89, 0.99, 1.46, 1.59; 1.89, 2.17 (s, each 3 H, CH_3), 5.13, 5.97 (s, each 1 H, olefin-H), 6.08, 6.70 (s, each 1 H, mesityl-CH), 7.06−8.30 (m, 20 H, Ph), ^{31}P{^{1}H} NMR ([D$_6$]DMSO, 25 °C, 81 MHz): δ = 46.86 (d, *J* = 46 Hz), 53.63 (d, *J* = 46 Hz) ppm. MS (EI): *m*/*z* = 802 [$C_{44}H_{42}N_2P_2ClPd = M^+ - Cl$].

Ligand Exchange Reaction of [Ni(C$_2$H$_4$COO)(tmeda)] with B, C, and D

[Ni{Mes−N=C(PPh$_2$)−C(PPh$_2$)=N−Mes}(C$_2$H$_4$COO)] (4a): [Ni(tmeda)(C_2H_4COO)] (1.05 g, 4.26 mmol) and **D** (2.82 g, 4.26 mmol) in 20 mL of DMF were stirred for 20 min. During this time, the solution (initially light green) turned dark red. The volatile part of the reaction mixture was then removed at 50 °C in vacuo. The residue was washed with diethyl ether, extracted with benzene and crystallized at 5 °C by addition of diethyl ether. Yield 1.22 g (33.5%) red crystals of **4a(C$_6$H$_6$)$_{0.5}$**. ^{1}H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 0.91 (m, 2 H, Ni−CH_2), 1.33 (s, 6 H, CH_3), 1.37 (s, 6 H, *o*-CH_3), 1.74 (s, 3 H, *p*-CH_3), 2.10 (s, 3 H, *p*-CH_3), 2.10 (m, 2 H, COO-CH_2), 5.67 (s, 2 H, CH Mes), 6.56 (s, 2 H, CH Mes), 7.20−7.64 (m, 20 H, Ph) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 19.8 [br. d, $^2J(^{31}P^{31}P)$ = 19.3 Hz], 44.8 [br. d, $^2J(^{31}P^{31}P)$ = 19.3 Hz] ppm.

Preparation of [Ni($C_{40}H_{34}N_2P_2$)(C_2H_4COO)] (5b/5b′): A mixture of [Ni(tmeda)(C_2H_4COO)] (0.76 g, 3.08 mmol) and **B** (1.85 g, 3.08 mmol) in 20 mL of THF was warmed up until both compounds dissolved. A few minutes later, an orange-colored compound precipitated. Recrystallization from dichloromethane gave 1.36 g (54%) of **5b/5b′(CH_2Cl_2)** as orange crystals. This compound loses dichloromethane very easily in vacuo. $C_{43}H_{38}N_2NiO_2P_2$ (735.4): calcd. C 70.22, H 5.21, N 3.81; found C 69.83, H 5.61, N 3.74. IR (nujol): ν(C=O) = 1606 cm^{-1} (s), ν(N−H) = 3140 cm^{-1} (w). ^1H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 0.70 (m, 2 H, CH_2-Ni), 1.84 (s, 3 H, CH_3), 1.91 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.20 (m, 2 H, CH_2−COO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.32 MHz, 298 K): δ = 20.6 (CH_3), 20.8 (CH_3); CH: δ = 128.2 [d, $J(^{13}C^{31}P)$ = 2.4 Hz], 128.2 [d, $J(^{13}C^{31}P)$ = 2.4 Hz], 129.3 [d, $J(^{13}C^{31}P)$ = 4.9 Hz], 129.4 [d, $J(^{13}C^{31}P)$ = 4.9 Hz], 129.5 (s), 129.9 [d, $J(^{13}C^{31}P)$ = 2.4 Hz], 130.4 (s), 132.5 [d, $J(^{13}C^{31}P)$ = 1.8 Hz], 132.7 (s), 132.8 [d, $J(^{13}C^{31}P)$ = 4.7 Hz], 133.1 [d, $J(^{13}C^{31}P)$ = 5.9 Hz]; C: δ = 113.4 (s), 113.6 (s), 117.7 (s), 119.6 (s), 123.7 (s), 124.4 (s), 127.5 (s), 131.4 [t, $^1J(^{13}C^{31}P)$ = 22.0 Hz, $(NPC=)_2$], 133.3 [d, $J(^{13}C^{31}P)$ = 8.2 Hz], 136.3 (s), 136.7 (s), 137.2 (s), 139.8 (s), 142.0 (s) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 28.3 [d, $^2J(^{31}P^{31}P)$ = 19.0 Hz], 39.0 [d, $^2J(^{31}P^{31}P)$ = 24.2 Hz], 46.1 [d, $^2J(^{31}P^{31}P)$ = 24.2 Hz], 48.9 [d, $^2J(^{31}P^{31}P)$ = 19.0 Hz] ppm.

In situ Preparation of 5c/5c′ and Reaction with Dimethylglyoxime and Aqueous Ammonia: A mixture of [Ni(tmeda)(C_2H_4COO)] (175 mg, 0.71 mmol) and **C** (484 mg, 0.70 mmol) in 20 mL of THF was stirred at 5 °C for 30 min. All of the starting materials dissolved and the color of the solution changed from light green to yellow. The complete ring-closure reaction of the intermediate [Ni(**C**)(C_2H_4COO)] to the orange-colored product [Ni($C_{46}H_{46}N_2P_2$)(C_2H_4COO)] was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR (C_6D_6/THF, 81.01 MHz, 298 K): δ = 30.5 [d, $^2J(^{31}P^{31}P)$ = 18.7 Hz], 37.7 [d, $^2J(^{31}P^{31}P)$ = 24.7 Hz], 49.0 [d, $^2J(^{31}P^{31}P)$ = 24.7 Hz], 51.0 [d, $^2J(^{31}P^{31}P)$ = 18.7 Hz] ppm. Intermediate [Ni{*p*-*t*Bu−Ph−N=C(PPh_2)−C(PPh_2)=N−Ph-*p*-*t*Bu}(C_2H_4COO)]: $^{31}P\{^1H\}$ NMR (C_6D_6/THF, 81.01 MHz, 298 K): δ = 42.7 [d, $^2J(^{31}P^{31}P)$ = 23.0 Hz], 60.9 [d, $^2J(^{31}P^{31}P)$ = 23.0 Hz] ppm.

9-*tert*-Butyl-4-(*p*-*tert*-butylphenyl)-3,4-dihydro-3-(diphenylphosphanyl)-1*H*-quinoxalin-2-one: A solution of dimethylgyoxime (165 mg, 1.42 mmol in 20 mL of methanol), followed by 10 drops of concentrated aqueous ammonia, were added dropwise to a solution of [Ni($C_{46}H_{46}N_2P_2$)(C_2H_4COO)] (0.70 mmol in 5 mL THF). Red bis(dimethylglyoximato)nickel(II) precipitated from the reaction mixture and was then filtered off. The filtrate was distilled to dryness in a rotary condenser and the residue recrystallized from alcohol/chloroform. Yield 0.21 g (57%) of 9-*tert*-butyl-4-(*p*-*tert*-butylphenyl)-3,4-dihydro-3-(diphenylphosphanyl)-1*H*-quinoxalin-2-one. M.p. 288−292 °C. $C_{34}H_{37}N_2OP$ (520.6): calcd. C 78.43, H 7.16, N 5.38; found C 77.88, H 6.83, N 5.34. IR (nujol): ν(C=O) = 1663 cm^{-1}. ^1H NMR ($CDCl_3$, 200.13 MHz, 298 K): δ = 1.18 (s, 9 H, *t*Bu), 1.35 (s, 9 H, *t*Bu), 6.70 (s, 1 H), 7.14−7.70 (m, 16 H), 8.00 (br., 1 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.32 MHz, 298 K): δ = 30.8 (*t*Bu), 30.9 (*t*Bu), 34.8 (C, *t*Bu), 35.2 (C, *t*Bu), 112.0 (CH), 121.2 (CH), 127.0 (C), 127.3 [d, $J(^{31}P^{13}C)$ = 42.3 Hz], 127.8 (CH), 128.3 [d, $J(^{31}P^{13}C)$ = 5.5 Hz, CH], 128.9 (CH), 129.7 (CH), 132.0 (CH), 132.2 [d, $J(^{31}P^{13}C)$ = 9.7 Hz], 132.6 (CH), 133.5 (C), 134.5 (C), 134.7 (CH), 152.3 (C), 154.0 (C) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz, 298 K): δ = 0.0 (br) ppm. MS (CI) (m/z): 519 $[M-1]^+$.

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[32] CCDC-202223 (**B**), -202224 (**C**), -202225 (**D**), -202226 (**E**), -202227 (**G**), -202228 (**1**), -202229 (**3**) and -202230 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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