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Metal Complexes with 2,3-Bis(diphenylphosphino)-1,4-diazadiene Ligands: Synthesis, Structures, and an Intramolecular Metal-Mediated [4 + 2] Cycloaddition Employing a Benzene Ring as a Dienophile

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2,3-Bis(diphenylphosphino)-1,4-diazadienes RN═C(PPh$_2$)–C(PPh$_2$)═NR (**1a**, R = 4-tolyl; **1b**, R = 4-*tert*-butylphenyl; **1c**, R = mesityl) were used as novel ligands for transition metals. The metal complexes [(**1c**)Mo(CO)$_4$] (**2a**), {(**1c**)[Mo(CO)$_4$]$_2$} (**2b**), [(**1a**)Cu(Cl)(PPh$_3$)] (**3**), and {(**1b**)[(NiBr$_2$(THF))]$_2$} (**4**) were characterized by elemental analysis, MS, and ^{31}P{^{1}H}, ^{1}H, and ^{13}C NMR spectra (except the paramagnetic complex **4**). Additionally, the molecular structure of the complexes in the solid state was determined by single-crystal X-ray diffraction. In **2a** and **2b** the chelating ligand coordinates via the N,P donor set, whereas in **3** the chelating ligand coordinates via the two P atoms. **4** contains a square-planar (P,P)NiBr$_2$ moiety on the one side of the bridging ligand **1b**. On the opposite side the 1,2-diimine unit bonds to another Ni center having octahedral geometry. The bulkier ligand **1c** reacts to form the mononuclear compound **5**. X-ray diffraction analysis of single crystals shows that **5** contains a quinoxaline derivative with a cyclohexa-1,3-diene ring in the peripheral position. Furthermore, it contains a bis(diphenylphosphino)-ethylene unit coordinating the NiBr$_2$. This arrangement is the result of an intramolecular [4 + 2] cycloaddition between the 1,2-diimine unit (as diheterodiene) and the benzene ring of the 4-tolyl–N substituent (as dieneophile). The same type of ring-closing reaction followed by a tautomerization reaction to form the mononuclear compound **6** occurred by dissolution of the binuclear complex **4** in methanol. This reaction can be used as a simple method for the synthesis of novel 1,2-bis(diarylphosphanyl)ethylenes containing a quinoxaline backbone.

Introduction

1,4-Diazadiene- and 1,2-bis(phosphino)ethane-type ligands are among the most prominent ligands used in the synthesis of many stable five-membered metal complexes and organometallics as well as for tuning of catalytic properties of many metal catalysts.

These ligands continue to attract considerable attention. For example, 1,2-diimine nickel or palladium complexes bearing bulky N-substituents constitute a new family of catalysts capable of polymerizing ethylene and copolymerizing ethylene with polar olefins.[1−4] Bidentate chelating phosphines have been proven to be powerful ligands in a range of homogeneous catalytic reactions[5−8] and have been found to stabilize new metallacumulenes.[9,10] Furthermore,

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Table 1. Crystal Data

	2a	**2b**	**3**	**4**	**5**	**6**
empirical formula	$C_{48}H_{42}N_2O_4P_2Mo$	$C_{52}H_{42}N_2O_8P_2Mo_2$	$C_{66}H_{65}N_2O_2ClP_3Cu$	$C_{64}H_{82}N_2O_{4.50}Br_4P_2Ni_2$	$C_{44}H_{42}N_2ClNbBr_2P_2Ni$	$C_{54}H_{62}N_2O_2Br_2P_2Ni$
fw ($g \cdot mol^{-1}$)	868.72	1076.70	1110.10	1450.32	879.27	1051.53
temp (K)	183(2)	183(2)	183(2)	183(2)	120(2)	183(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.45085	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)	Cc (No. 9)	$P2_1/n$ (No. 14)
a (Å)	9.8386(2)	22.178(1)	22.3892(4)	21.0209(3)	20.3600(3)	18.571(2)
b (Å)	21.4220(5)	11.6526(6)	19.2933(4)	17.5667(3)	11.0980(1)	14.239(1)
c (Å)	20.0408(3)	20.267(1)	26.6209(5)	18.3020(3)	17.9282(2)	21.549(3)
β (deg)	95.692(1)	113.403(4)	100.098(1)	108.304(1)	104.96(2)	
V (Å^3)	4203.0(1)	4806.8(4)	11499.2(4)	6653.6(2)	3846.01(8)	5505(1)
Z	4	4	8	4	4	4
ρ_{calcd} ($g \cdot cm^{-3}$)	1.373	1.488	1.282	1.448	1.519	1.269
μ (mm^{-1})	0.435	0.644	0.556	3.062	1.442	1.900
R [$I > 2\sigma(I)$]^a	R1 = 0.0385 wR2 = 0.0904	R1 = 0.0456 wR2 = 0.1151	R1 = 0.0440 wR2 = 0.1057	R1 = 0.0506 wR2 = 0.1251	R1 = 0.0184 wR2 = 0.0498	R1 = 0.0596 wR2 = 0.1567
R (all data)^a	R1 = 0.0594 wR2 = 0.1000	R1 = 0.0602 wR2 = 0.1261	R1 = 0.0852 wR2 = 0.1123	R1 = 0.0855 wR2 = 0.1481	R1 = 0.0186 wR2 = 0.0500	R1 = 0.01675 wR2 = 0.1944

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $wR2 = [[\Sigma w(|F_o^2 - F_c^2|)^2]/[\Sigma w(F_o^2)]]^{1/2}$, $w = 1/[(\sigma F_o)^2 + (aP)^2]$. The value of aP was obtained from structure refinement.

they act as supporting ligands in complexes with unique properties or structures (recent examples: refs 11−16).

In the context of the important role of these ligands it is surprising that 2,3-bis(diphenylphosphino)-1,4-diazadienes, which combine the above chelating units within the same molecule, are hitherto unknown. 2,3-Bis(diphenylphosphino)-1,4-diazadienes should be able to coordinate either as P,N-, P,P-, or N,N-chelating ligands thus giving rise to a very rich metal chemistry including the formation of mono-, bi-, and oligonuclear complexes. In addition, they should function as novel controlling ligands for metal-catalyzed reactions. Furthermore, these are very flexible ligands which could possibly undergo isomerization reactions upon coordination of one metal ion.

We report here on the synthesis of three bis(diphenylphosphino)-1,4-diazadienes and show that, depending on the nature of the metal, mono- or binuclear complexes can be formed in which the ligand coordinates in different ways. Of particular interest are ring-closure reactions of the ligands at the periphery under the influence of Ni(II) which lead to the formation of 2,3-bis(diphenylphosphino)-substituted quinoxalines in a highly selective reaction.

Experimental Section

General Procedures. All manipulations were carried out by using Schlenk techniques under an atmosphere of argon. Prior to use, tetrahydrofuran, diethyl ether, and toluene were dried over potassium hydroxide and distilled over Na/ benzophenone. All other reagents (Aldrich) were used as received. ^1H and ^{13}C spectra were recorded on a Bruker AC 200 F spectrometer. Mass spectra were recorded on a Finnigan MAT SSQ 710. Values for m/z are for the most intense peak of the isotope envelope. The measured isotopic pattern for the nickel- and molybdenum-containing species are in good agreement with the calculated isotopic pattern using the program ICIS (version 8.2.1, Finnigan). Elemental analyses were performed with Leco CHNS-932. (Norbornadiene)$Mo(CO)_4$ was obtained from $Mo(CO)_6$ and norbornadiene in toluene prepared according to ref 17[17]; oxalic imidoyl chlorides $R{-}N{=}C(Cl){-}C(Cl){=}N{-}R$,[18] $NaPPh_2$(dioxane) and $K(PPh_2)(dioxane)_n$,[19] and $Cu(PPh_3)_3Cl$[20] were prepared according to the literature.

X-ray data for compound **6** were collected on a Nonius CAD4 diffractometer and for compounds **2a** to **4** on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. For compound **5** measurements were carried out at beamline ID11 at the European Synchrotron Radiation Facility (ESRF), because **5** formed very small crystals. Data were collected using a Bruker "SMART" CCD-camera system at fixed 2θ, while the sample was rotated over 0.1° intervals during 2 s exposures. Data were corrected for Lorentz and polarization effects, but for absorption only for compounds **4** and **6**.[21−23] The structures were solved by direct methods (SHELXS[24]) and refined by full-matrix least squares techniques against F_o^2 (SHELXTL97−2[25]). The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[25] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic information is provided in Table 1.

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(4-Tolyl-N=C(PPh$_2$)C(PPh$_2$)=N-4-tolyl) (1a). Bis(4-tolyl)oxalic imidoyl chloride (1.07 g, 3.5 mmol) dissolved in THF (40 mL) and NaPPh$_2$(dioxane) (8.27 mmol, 15% excess) dissolved in THF (10 mL) were stirred at -78 °C. After 4 h the reaction mixture was allowed to warm to room temperature. Then the THF was removed under vacuum, yielding a brown solid, which was extracted with toluene at 60 °C. The pure ligand **1a** crystallized at -20 °C.

Yield: 0.962 g (45%), yellow crystals. Anal. Calcd for $C_{40}H_{34}N_2P_2$ (604.67 MW): C, 79.45; H, 5.67; N, 4.63. Found: C, 79.16; H, 5.71; N, 4.56. MS (DEI) $m/z = 604$ (M^+, 3%), 527 ($M^+ - C_6H_5$, 2%), 419 ($M^+ - C_{12}H_{10}$, 3%), 370 ($M^+ - C_{16}H_{14}N_2$, 13%), 302 ($M^+ - C_{20}H_{17}NP$ basic peak), 85 ($M^+ - C_{28}H_{24}N_2$, 97%). $^{31}P\{^1H\}$ NMR (CDCl$_3$, rt, 81 MHz, δ, ppm): 3.82 (s). ^1H NMR (THF-d_8, rt, 200 MHz, δ, ppm): 2.10 (s, 6H, CH$_3$,), 6.19, 6.69 (2d, AA′BB′, $^3J_{H,H} = 8{,}0$ Hz, 8H, CH-tolyl), 7.28 (m, 26H, phenyl). ^{13}C NMR (THF-d_8, rt, 200 MHz, δ, ppm): 20.7 (CH$_3$), 120.0−136.8 (C_{aromat}), 148.5 (C_{bridge}).

(4-*tert*-Butyl-C$_6$H$_4$-N=C(PPh$_2$)C(PPh$_2$)=N-C$_6$H$_4$-4-*tert*-butyl) (1b). To bis(4-*tert*-butylphenyl)-oxalic imidoyl chloride (0.72 g, 1.85 mmol) dissolved in toluene (150 mL) and cooled to -78 °C was dropwise added a solution of NaPPh$_2$(dioxane) (1.25 g, 3.7 mmol) in THF (10 mL). The dark brown reaction mixture was allowed to warm to room temperature. After 24 h of stirring, the THF and most of the toluene were removed under vacuum. The concentrated solution was warmed to 60 °C and filtered. **1b** crystallized at 4 °C. Yield: 0.708 g (56%), yellow crystals. Anal. Calcd for $C_{46}H_{46}N_2P_2$ (688.83 MW): C, 80.2; H, 6.73; N, 4.07. Found: C, 79.84; H, 6.67; N, 4.20. MS (CI): 689 ($(M + 1)^+$, basic peak), 611 ($(M + 1)^+ - C_6H_6$, 2%), 503 ($(M + 1)^+ - C_{12}H_{12}$, 2%,), 370 ($(M + 1)^+ - C_{22}H_{24}$, 2%,), 344 ($(M + 1)^+ - C_{23}H_{23}NP$, 45%), 185 (19%, $(M + 1)^+ - C_{34}H_{37}N_2P$). $^{31}P\{^1H\}$ NMR (THF-d_8, rt, 81 MHz; δ, ppm): 5.04 (s). ^1H NMR (THF-d_8, 25 °C, 200 MHz; δ, ppm): 1.19 (s, 18H, CH$_3$-^{t}Bu), 6.9 (m, 30H, phenyl). ^{13}C NMR (THF-d_8, 25 °C, 50 MHz; PENDANT; δ, ppm): 31.6 (CH$_3$-^{t}Bu), 34.6 (C-^{t}Bu), 119.8−148.3 (phenyl and C_{bridge}).

(Mes-N=C(PPh$_2$)C(PPh$_2$)=N-Mes)(CHCl$_3$) [(1c)(CHCl$_3$)]. Bis(mesityl)oxalic acid imidoyl chloride (2.7 g, 7.5 mmol) and Pd(acetate)$_2$ (85 mg, 0.038 mmol) as cross coupling catalyst were dissolved in toluene (100 mL). At -40 °C a solution of KPPh$_2$ (15.0 mmol) in dioxane/THF (42 mL, 1:1) was added dropwise within 1 h with stirring of the mixture. The yellow solution turned to dark red. After 1 h the reaction mixture was allowed to warm to room temperature. The color of the solution turned in this time to blue-green. After filtration of KCl the solvent was removed under vacuum and the residue was dissolved in *n*-hexane. Upon filtration the solvent was removed under vacuum, yielding a dark red oil, which slowly crystallized. The product was recrystallized from hexane/chloroform. Yield: 3.96 g (80%), yellow crystals, mp 170 °C. Anal. Calcd for [(**1c**)(CHCl$_3$)]: $C_{45}H_{43}Cl_3N_2P_2$ (780.1 MW): C, 69.28; H, 5.56; N, 3.59; Cl, 13.63. Found: C, 69.97; H, 5.67; N, 3.55; Cl, 13.18. MS (EI) m/z: 660 (M^+), 330 ($M^+/2$). $^{31}P\{^1H\}$ NMR (CDCl$_3$, rt, 200 MHz; δ, ppm): 9.0 (s). ^1H NMR (CDCl$_3$, rt, 200 MHz; δ, ppm): 1.42 (s, 12H, *o*-CH$_3$), 2.17 (s, 6H, *p*-CH$_3$), 6.45 (s, 4H, *m*-H), 7.19−7.21 (m, 12H, phenyl), 7.50−7.54 (m, 8H, phenyl). ^{13}C NMR (CDCl$_3$, rt, 200 MHz; δ, ppm): 17.7 (d, $J(^{13}C^{31}P) = 2.5$ Hz, *o*-CH$_3$), 20.6 (*p*-CH$_3$), 124.4 (C, mesityl), 128.1 (CH, mesityl), 128.1 (d, $J(^{13}C^{31}P) = 8.3$ Hz, CH, phenyl), 128.8 (CH, Ph), 132.8 (C, mesityl), 133.8 (br, d, $J(^{13}C^{31}P) = 10.5$ Hz, C, phenyl), 135.2 (br, d, $J(^{13}C^{31}P) = 23.4$ Hz, C, phenyl), 145.3 (br, d, $J(^{13}C^{31}P) = 9.3$ Hz, C, mesityl), 175.2 (dd, $J(^{13}C^{31}P) = 58.1$ Hz, $J(^{13}C^{31}P) = 4.5$ Hz, N=CP).

[(Mes-N=C(PPh$_2$)C(PPh$_2$)=N-Mes)Mo(CO)$_4$] (2a). (C$_7$H$_8$)Mo(CO)$_4$ (240 mg, 0.8 mmol) and [(**1c**)(CHCl$_3$)] (530 mg, 0.8 mmol) were dissolved in THF (5 mL). The color of the solution changed immediately from yellow to dark red. After 1 h of stirring at room temperature the volatile part of the solution was removed under vacuum. The solid residue was recrystallized from a mixture of benzene and THF. Yield: 530 mg (76%), dark red crystals. Anal. Calcd for $C_{48}H_{42}MoN_2O_4P_2$ (868.54 MW): C, 65.40; H, 5.01; N, 3.32. Found: C, 65.33; H, 5.07; N, 2.60. MS (CI) (m/z): 870 (M, basis peak), 842 (M − CO, 3%), 814 (M − 2CO, 1%), 790 (M − 3CO, 1%), 660 ligand, 8%). $^{31}P\{^1H\}$NMR (C$_6$D$_6$, rt, 200 MHz): 7.2 (PPh$_2$, noncoordinated), 69.3 (PPh$_2$, coordinated). ^1H NMR (CDCl$_3$, rt, 200 MHz) δ (in ppm): 1.49 (6H, br, CH$_3$), 1.66 (s, 6H, s, CH$_3$), 1.95 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 6.19 (s, 2H, *m*-CH, mesityl), 6.73 (s, 2H, *m*-CH, mesityl), 7.21−7.39 (m, 16H, phenyl), 7.64 (t, 4H, $J = 8.0$ Hz, CH, phenyl). ^{13}C NMR: (CDCl$_3$, rt, 200 MHz) δ (ppm): 18.1 (CH$_3$), 18.2 (CH$_3$), 20.2 (CH$_3$), 20.8 (CH$_3$), 123.1 (C), 128.0 (d, $J(^{31}P-^{13}C) = 10.1$ Hz, CH, phenyl), 128.2 (CH, mesityl), 128.5 (d, $J(^{31}P-^{13}C) = 9.0$ Hz, CH, Ph), 129.3 (CH, mesityl), 130.1 (d, $J(^{31}P-^{13}C) = 19.4$ Hz, CH, phenyl), 133.4 (C), 133.6 (d, $J(^{31}P-^{13}C) = 13.9$ Hz, CH, phenyl), 135.5 (C), 136.6 (d, $J(^{31}P-^{13}C) = 25.4$ Hz, CH, phenyl), 142.7 (d, $J(^{31}P-^{13}C) = 5.5$ Hz, C), 150.8 (d, $J(^{31}P-^{13}C) = 10.9$ Hz, C), 168.7 (d, $J(^{31}P-^{13}C) = 25.6$ Hz, C), 185.7 (d, $^1J(^{31}P-^{13}C) = 56.1$ Hz, N=C−P), 186.0 (d, $^1J(^{31}P-^{13}C) = 55.8$ Hz, N=C−P), 209.8 (d, $^2J_{cis}(^{31}P-^{13}C) = 8.3$ Hz, Mo(CO)$_2$), 213.2 (d, $^2J_{trans}(^{31}P-^{13}C) = 32.8$ Hz, Mo(CO)), 222.3 (d, $^2J_{cis}(^{31}P-^{13}C) = 6.8$ Hz, Mo(CO)). IR (Nujol, cm^{-1}): 1854, 2014, 1910, 1891 (ν(CO)).

(Mes-N=C(PPh$_2$)C(PPh$_2$)=N-Mes)[Mo(CO)$_4$]$_2$ (2b). (C$_7$H$_8$)Mo(CO)$_4$ (510 mg, 1.70 mmol) and [(**1c**)(CHCl$_3$)] (660 mg, 0.85 mmol) were dissolved in THF (5 mL). The color of the solution turned immediately from yellow to dark red and then gradually to dark blue. After 1 h of stirring at room temperature, the volatile part of the solution was removed under vacuum. The solid residue was recrystallized from a mixture of benzene and ether to form black crystals. Yield: 800 mg (87%). Anal. Calcd for $C_{52}H_{42}Mo_2N_2O_8P_2$ (1076.68 MW): C, 58.27; H, 4.19; N, 2.54. Found: C, 58.00; H, 3.93; N, 2.60. ^1H NMR (C$_6$D$_6$, rt, 200 MHz; δ ppm): 1.66 (s, 6H, *p*-CH$_3$), 2.17 (s, 12H, *o*-CH$_3$), 5.86 (s, 4H, *m*-CH), 6.65−7.56 (m, 20H, phenyl). ^{13}C NMR (CDCl$_3$, rt, 200 MHz; δ, ppm): 17.7 (*p*-CH$_3$), 20.3 (*o*-CH$_3$), 20.6 (*o*-CH$_3$), 125.7 (CH), 128.9 (d, $J = 11.0$ Hz, CH), 129.9 (*m*-CH, mesityl), 131.5 (C), 131.6 (d, $J = 58.3$ Hz, C), 135.5 (d, $J = 15.8$ Hz, CH), 136.5 (C), 150.3 (d, $J = 4.2$ Hz, C), 180.8 (dd, $J = 25.7$ Hz, $J = 22.5$ Hz, N=C−P), 210.6 (d, $^2J_{cis} = 8.1$ Hz, Mo(CO)$_2$), 213.1 (d, $^2J_{trans} = 32.8$ Hz, Mo(CO)), 222.7 (d, $^2J_{cis} = 6.7$ Hz, Mo(CO)). $^{31}P\{^1H\}$ NMR (C$_6$D$_6$, rt, 200 MHz; δ, ppm): 82.5. IR (Nujol, cm^{-1}): 1830, 1859, 1892, 1938, 2010, 2014, 2025 (ν(CO)).

[(1a)Cu(Cl)(PPh$_3$)] (3). To **1a** (368 mg, 0.6 mmol) dissolved in THF (60 mL) was added a solution of CuCl(PPh$_3$)$_3$ (539 mg, 0.6 mmol) in THF (40 mL) by a cannula. The color of the solution turned from yellow to dark red. After 1 h of stirring, the solution was concentrated under vacuum and diethyl ether (30 mL) was added dropwise. Upon keeping overnight the red microcrystalline solid was filtered off, washed twice with ether (20 mL), and dried under vacuum. Single crystals of **3** could be obtained form the mother liquor at -20 °C. Yield: 413 mg (70%). Anal. Calcd for $C_{58}H_{49}CuP_3N_2Cl$ (965.96 MW): C, 72.12; H, 5.11; N, 2.90; Cl, 3.67. Found: C, 72.14; H, 5.26; N, 2.70; Cl, 3.67. MS (EI): $m/z = 604$ (ligand$^+$, 2%), 262 (PPh$_3^+$, 100%). ^1H NMR (CD$_2$Cl$_2$, rt, 200 MHz; δ, ppm): 2.16 (s, 6H, CH$_3$), 5.69 (m, 4H, aromatic CH of 4-tolyl), 6.57 (m, 4H, aromatic CH of 4-tolyl), 7.17−7.95 (m, 35H, PPh$_2$ + PPh$_3$). ^{13}C NMR (CD$_2$Cl$_2$, rt, 200 MHz; δ, ppm): 20.7 (CH$_3$), 119.04, 119.9, 129.0, 129.1, 131.6, 134.5, 134.9, 135.8, 136,7, 137.5 (phenyl), 148.4 (quart C of the central C−C unit).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt, 200 MHz; δ, ppm): one very broad singlet between −5 and 5 ppm.

{(1b)[(NiBr$_2$(THF)]$_2$} (4). To a stirred solution of **1b** (328 mg, 0.476 mmol) in THF (10 mL) at −78 °C was added $NiBr_2(THF)_{1.46}$ (308 mg, 0.952 mmol) in THF (10 mL). The reaction mixture was allowed to warm to −40 °C. After 24 h the product containing four molecules of THF per Ni was separated by filtration and dried under vacuum. Yield: 490 mg (73%). Single crystals of {(**1b**)-[($NiBr_2$(THF)]$_2$} suitable for X-ray analysis were obtained from the mother liquor at −40 °C. Anal. Calcd for $C_{62}H_{78}Br_4N_2Ni_2O_2P_2$ ({(**1b**)[($NiBr_2$(THF)]$_2$}(THF)$_2$) (1414.23 MW): C, 52.65; H, 5.56; N, 1.98. Found: C, 52.71; H, 5.85; N, 2.01. MS (FAB): m/z = 827 (M^+ − 4THF − $NiBr_2$ − Br), 688 (M^+ − 4THF − 2$NiBr_2$). Due to the paramagnetism no NMR spectra were monitored.

Complex 5. 1c (708 mg, 1.07 mmol) and $NiBr_2(THF)_{1.46}$ (357 mg, 1.1 mmol) in THF (10 mL) were stirred at room temperature. After 1 h the reaction mixture was heated to 60 °C for about 10 min and filtered. **5** containing one molecule of THF per Ni was obtained from the solution at room temperature. Single crystals of the THF free complex were grown from the mother liquor. Yield: 915 mg (90%), red crystals. Anal. Calcd for $C_{48}H_{50}Br_2N_2NiOP_2$ (**5**(THF)) (951.33 MW): C, 60.60; H 5.30; N 2.95. Found: C, 60.40; H, 5.11; N, 2.90. MS (CI): m/z = 880 ($(M + 1)^+$ − THF; 34%). MS (DEI): 801 (M^+ + 2H − Br − THF, 0.4%), 585 (M^+ − THF − $C_6H_5Br_2Ni$), 476 (M^+ − THF − $C_{12}H_{10}PBr_2Ni$), 185 (M^+ − $C_{32}H_{32}N_2PBr_2Ni$, basis peak). $^{31}P\{^1H\}$ NMR (C_6D_6, rt, 81 MHz; δ, ppm): 45.8 (d, J = 78 Hz), 61.1 (d, J = 78 Hz). ^1H NMR (THF-d_8, rt, 400 MHz; δ, ppm): 0.82, 1.0, 1.42, 1.48, 1.89, 2.17 (s, 3H each, CH_3), 5.04 (s, olefinic-H, 1H), 6.08 (s, olefinic-H, 1H), 6.22 (s, 1H mesityl-CH), 6.68 (s, 1H mesityl-CH), 7.06−8.30 (m, 20H, phenyl). ^{13}C NMR (THF-d_8, rt, 100 MHz; δ, ppm): 16.8, 16.9, 18.6, 20.7, 20.9, 21.2 (CH_3), 126.1−135.1 (C_{arom} and C_{bridge}).

Complex 6. 1b (580 mg, 0.84 mmol) in THF (10 mL) was reacted with $NiBr_2$(dme) (260 mg, 0.84 mmol) at room temperature. Alternatively, $NiBr_2(THF)_2$ can be used. After 4 h the product was separated by filtration and washed with THF. Yield of the crude product: 610 mg (80%). The pure complex containing one THF was obtained by extraction of the product with methanol at reflux temperature. Single crystals of the THF free complex suitable for X-ray diffraction were isolated upon keeping the methanol solution at −40 °C.

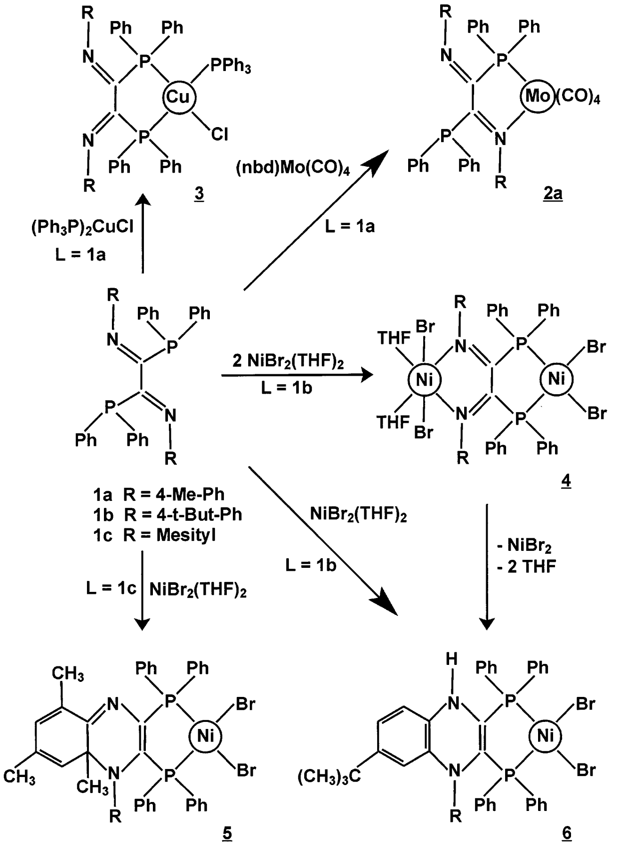
Alternatively, complex **4** was suspended in warm methanol. After 1 h the suspension was filtered. Upon keeping the methanol solution at −20 °C **6** crystallized.

Anal. Calcd for $C_{50}H_{54}Br_2N_2NiOP_2$ (979.44 MW) (**6**(THF)): C, 61.32; H, 5.56; N, 2.86. Found: C, 61.42; H, 5.95; N, 2.75. MS (CI) m/z = 988 (M + 1^+ + Br − THF, 23%), 908 (M + 1 − THF, 65%). $^{31}P\{^1H\}$ NMR (THF-d_8, rt, 81 MHz; δ, ppm): 50.2 (d, J = 83 Hz), 41.6 (d, J = 83 Hz). ^1H NMR (THF-d_8, 60 °C, 200 MHz; δ, ppm): 1.05 (s, 9H, ^{t}Bu), 1.24 (s, 9H, ^{t}Bu), 6.15−8.31 (m, 29H, phenyl), 6.76 (s, 1H, NH). ^{13}C NMR(THF-d_8, rt, 50 MHz; δ, ppm): 31.0 (CH_3), 31.3 (CH_3), 34.4 (^{t}Bu), 34.7 (^{t}Bu), 113.7−146.9 (C_{arom} and C_{tert}).

1c from 5. Complex **5**(THF) (0.30 g, 0.316 mmol) dissolved in THF (10 mL) was dropwise added to a stirred THF/n-hexane solution (5 mL) of diacetylglyoxime (0.033 g, 0.632 mmol) and BuLi (0.632 mmol in n-hexane). Upon 24 h the solvent was removed under vacuum. The organic material was dissolved in diethyl ether and filtered. Removal of the diethyl ether under vacuum resulted in a yellow-orange solid. A comparison of the analytical data with an authentic sample of **1c** showed them to be identical.

Similarly, complex **6** was reacted with diacetylglyoxime and BuLi to give the free quinoxaline derivative; light orange solid. MS (DEI): m/z = 688 (M^+, 33%), 631 (M^+ − C_4H_9, 2%), 518 (3%), 425 (3%), 369 (3%), 185 (M^+ − $C_{34}H_{36}N_2P$), 57 (C_4H_9, basis peak). $^{31}P\{^1H\}$ NMR (THF-d_8, 27 °C, 81 MHz; δ, ppm): −13.0 (d, J = 172 Hz), − 2,6 (d, J = 172 Hz). ^1H NMR (THF-d_8, 27 °C, 200 MHz; δ, ppm): 1.13, (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu), 6.22−7.52 (m, 28H, phenyl). ^{13}C NMR (THF-d_8, rt, 50 MHz; δ, ppm): 31.6 (CH_3), 31.8 (CH_3), 34.3 (^{t}Bu), 34.8 (^{t}Bu), 114.0−148.0 (C_{arom} and C_{tert}).

Scheme 1. Formation of Complexes **2**−**6** from the Ligands **1a**−**1c**



Results and Discussion

The ligands **1a**−**1c** (Scheme 1) can be easily synthesized by reacting 1 equiv of a substituted oxalic imidoyl chloride with 2 equiv of $MPPh_2$ (M: Na, K) in THF or toluene at −40 °C (eq 1). **1a**−**1c** form thermally stable yellow,

$$2MPPh_2 + RN{=}C(Cl)C(Cl){=}NR \rightarrow RN{=}C(PPh_2)C(PPh_2){=}NR + 2MCl \quad (1)$$

$$(M:\ Na,\ K)$$

moisture- and air-sensitive crystals which could be characterized by elemental analyses, MS, and $^{31}P\{^1H\}$, ^1H, and ^{13}C NMR spectroscopy. These compounds are soluble in many organic solvents including THF, $CHCl_3$, and toluene; however their solubility in n-alkanes is low. Only one resonance is observed in $^{31}P\{^1H\}$ NMR spectra for these compounds. In addition, the ^1H NMR/^{13}C NMR spectra show the expected patterns.

These ligands undergo complexation reactions with transition metals that result in metal complexes with differing

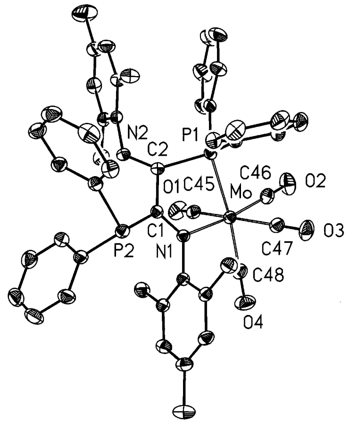


Figure 1. ORTEP diagram of complex **2a** with thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): Mo−P1 2.4994(6), Mo−N1 2.284(2), C1−C2 1.514(3), C1−N1 1.295(3), C1−P2 1.868(2), C2−N2 1.271(3), C2−P1 1.876(2), P1−Mo−N1 74.76(5), P1−C2−C1 110.3(2), P1−C2−N2 133.4(2), N2−C2−C1 115.0(2), C2−C1−N1 114.9(2), C2−C1−P2 125.4(2), C1−N1−Mo 125.6(2), Mo−P1−C2 96.92(7).

nuclearities and coordination patterns of the ligands (Scheme 1). This demonstrates that a rich coordination chemistry of 2,3-bis(diphenylphosphino)-1,4-diazadiene-type ligands is possible. Subsequent reactions at the periphery of mononuclear Ni complexes (**4** and **6**, respectively, Scheme 1) are even possible for these ligands.

Complexes **2**−**6** are formed in good yields and have been characterized by standard spectroscopic and analytical methods, as well as by single-crystal X-ray crystallography in the solid state.

The mononuclear complex [(**1c**)Mo(CO)$_4$] (**2a**) was obtained by mixing (norbornadiene)Mo(CO)$_4$ and an equimolar amount of **1c** in THF at room temperature. In complex **2a** the ligand is coordinated via one N,P donor set as seen in the ^{31}P{^{1}H} NMR spectrum in C$_6$D$_6$ (two singlets were observed). The resonance at 7.2 ppm is attributable to the noncoordinated phosphorus atom (9.0 ppm in the free ligand), and the low-field shifted signal at 69.3 ppm is assigned to the coordinated P atom. As expected, the IR spectrum shows four carbonyl frequencies between 1834 and 2014 cm^{-1}.

An X-ray crystallographic study of single crystals obtained from THF confirms this structure for the solid state (Figure 1).

Reaction of complex **2a** with 1 equiv of (norbornadiene)-Mo(CO)$_4$ resulted in the formation of a binuclear compound {(**1c**)[Mo(CO)$_4$]$_2$} (**2b**). The ^{31}P{^{1}H} NMR spectrum of **2b** in C$_6$D$_6$ shows only one signal at 82.5 ppm which is indicative for coordination of both PPh$_2$ groups. This suggests that **1c** acts as a bridging ligand in **2b** and coordinates with one imine nitrogen and one phosphorus atom to each Mo atom. The ^{1}H and ^{13}C NMR spectra are in agreement with this structure in solution.

Figure 2a shows the ORTEP diagram of **2b** with an atomic labeling scheme and contains selected bond distances and angles in the figure caption. There are no significant differences in the relevant bond lengths and angles when comparing **2a** to **2b**. For example, the central C1−C2 (C1−C1A) bond distances are 1.514(3) in **2a** and 1.497(7) Å) in **2b**. The C−N bond lengths of the 1,2-diimine units (**2a**, C1−N1(coordinated) = 1.295(3), C2−N2(noncoordinated) = 1.271(3) Å; **2b**, C1−N1A(coordinated) = 1.302(4) Å) are typical for C=N double bonds and are only slightly lengthened upon coordination of the Mo atom. Upon binding to the metal there is significant decrease (110.3(2)°) in the C1−C2−P1 angle in **2a** with P1 being bonded to Mo. The noncoorinated C2−C1−P2 angle is much larger (125.4(2)°).

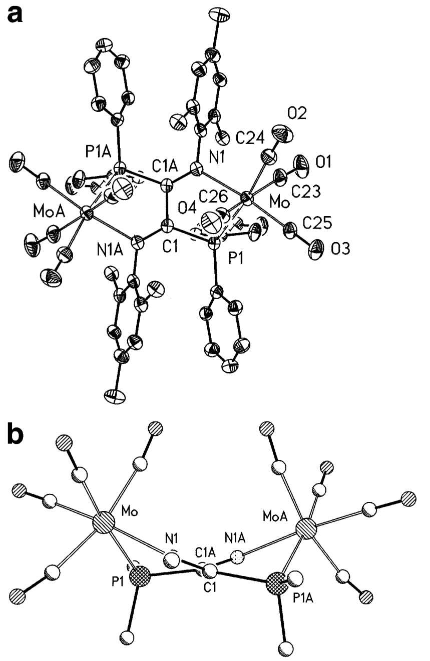


Figure 2. (a) ORTEP diagram of complex **2b** with thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): Mo−N1 2.289(3), Mo−P1 2.512(1), P1−C1 1.883(3), C1−C1A 1.497(7), C1−N1A 1.302(4), N1−Mo−P1 74.43(8), Mo−N1−C1A 122.8(2), N1−C1A−P1A 130.9(3), N1−C1A−C1 117.3(4), C1A−C1−P1 110.9(3), C1−P1−Mo 95.9(1). Symmetry transformations used to generated equivalent atoms: A $-X + 1$, Y, $-Z + {}^3/_2$. (b) Ball-and-stick reprensentation of the view along the C1−C1A line for complex **2b**.

This effect is also seen with the coordinated C−C−P angles being quite small (110.9(3)°).

The most interesting feature in **2b** is that both Mo(CO)$_4$ fragments are arranged cis to each other with respect to the central C1−C1A bond of the chelating ligand (Figure 2b).

In contrast to the Mo(CO)$_4$ moiety, Cu(PPh$_3$)$_3$Cl reacted to form mononuclear Cu complexes even if the smaller ligand **1a** was used. [(**1a**)Cu(Cl)(PPh$_3$)] (**3**) was prepared from Cu-(PPh$_3$)$_3$Cl and **1a** (molar ratio: 2:1) in THF and could be isolated as air-sensitive red crystals in good yields (70%). All attempts to react **3** with a second metal have failed so far.

The solid-state structure of **3** (Figure 3) was established by X-ray diffraction of single crystals obtained from THF at −20 °C. In contrast to the Mo complexes, the chelating ligand coordinates in a different manner where the two P atoms are bonded to the Cu center. As expected, the Cu atom is in a tetrahedral environment created by the P,P donor set of the chelating ligand, one Ph$_3$P ligand, and one chloride. All bond lengths lie within the expected range and need not be discussed.

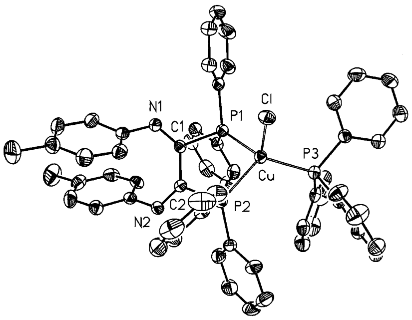


Figure 3. ORTEP diagram of complex **3** with thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): Cu−Cl 2.3060(7), Cu−P1 2.2787(7), Cu−P2 2.2761(7), Cu−P3 2.611(7), P1−C1 1.871(2), P2−C2 1.865(2), C1−C2 1.536(3), C1−N1 1.268(3), C2−N2 1.271(3), Cl−Cu−P1 105.07(3), Cl−Cu−P2 110.22(3), Cl−Cu−P3 109.00(3), P1−Cu−P2 92.21(2), P1−Cu−P3 121.23(3), P2−Cu−P3 117.63(2), P1−C1−N1 119.5(2), P1−C1−C2 112.5(2), P2−C2−N2 119.7(2), P2−C2−C1 113.6(2), N1−C1−C2 127.8(2), N2−C2−C1 126.7(2).

The ^{1}H NMR and the ^{13}C NMR spectra of **3** in $CDCl_3$ are in accordance with the symmetrical struture shown in Figure 3. Only one resonance for the methyl protons of the 4-tolyl group was observed at 2.16 ppm in $CDCl_3$ at room temperature. The aromatic protons of the 4-tolyl group can be distinguished from the other signals of the PPh_2 group, and the PPh_3 ligand. The ^{13}C NMR spectrum also confirms the symmetrical structure. Besides the signals for the aromatic carbons, only a single low-field shifted resonance at 148.4 ppm appears for the quaternary carbons of the central C−C bond in the chelating ligand. In addition, only one resonance for the methyl groups was observed at 20.7 ppm. In contrast to this, the ^{31}P NMR, spectrum, recorded between −60 °C and room temperature, shows only a very broad signal (between −5 and +5 ppm) which may be explained by both the overlap of the three resonances of coordinated phosphines in **3** and ligand exchange to give the three-coordinated Cu complex in equilibrium with **3**.

Whereas **1a** only forms a mononuclear Cu(I) complex, $NiBr_2(THF)_{1.46}$ reacted with the closely related ligand **1b** in a molar ratio 2:1 in THF to form the binuclear complex **4**. NMR spectra could not be recorded due to the paramagnetic nature of the complex.

A single-crystal X-ray diffraction study reveals that the two Ni atoms possess different coordination geometries. An ORTEP diagram of **4** is given in Figure 4. The most relevant bond distances and angles are listed in the figure caption.

The 2,3-bis(diphenylphosphino)-1,4-diazadiene **1b** acts as bridging ligand and is bidentately bound on one side to the square-planar nickel center via the two phosphorus atoms. Two bromide ligands occupy the other two positions. On the other side the chelate ligand binds to the octahedral nickel via the 1,2-diimine unit. In addition, two bromides occupy trans positions of the octahedron, and two THF molecules coordinate cis to each other.

As expected, the two Ni1−Br distances of the octahedral complex fragment (on average 2.535(6)) are significantly longer than those of the square-planar Ni2 at the opposite side (on average 2.323(7) Å). The bond distances of the C═N bonds are equal within experimental error and lie in the usual range (1.2837(5) and 1.278(5) Å). In contrast to **1a**, the bulkier ligand **1c** containing mesityl groups on the nitrogen atoms of the 1,2-diimine unit reacts with $NiBr_2(THF)_{1.46}$ under essentially the same conditions used for the formation of the binuclear complex **4** to form the mononuclear Ni complex **5**. X-ray quality red crystals of **5** could be obtained from THF at −20 °C. Figure 5 displays the molecular structure of the complex and contains selected bond lengths and angles in the figure caption.

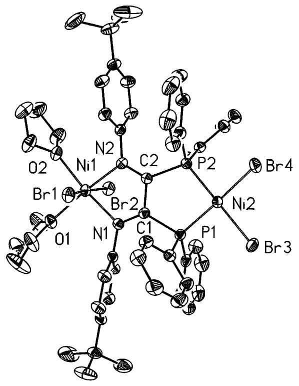


Figure 4. ORTEP diagram of complex **4** with thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): Ni1−Br1 2.5377(6), Ni1−Br2 2.5394(6), Ni1−O1 2.105(3), Ni1−O2 2.118(3), Ni1−N1 2.076(3), Ni1−N2 2.074(3), Ni2−P1 2.132(1), Ni2−P2 2.129(1), Ni2−Br3 2.3251(7), Ni2−Br4 2.3276(7), C1−C2 1.495(5), C1−N1 1.287(5), C2−N2 1.278(5), C1−P1 1.854(4), C2−P2 1.856(4), N1−C1−C2 116.0(3), N1−C1−P1 129.4(3), N2−C2−C1 116.3(3), N2−C2−P2 129.5(3), P2−C2−C1 114.2(3).

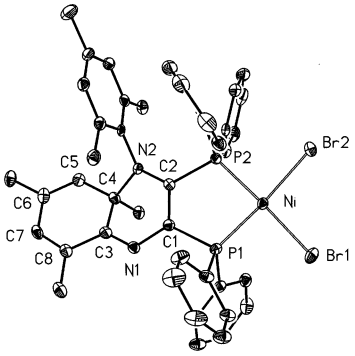


Figure 5. ORTEP diagram of compound **5** with thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): Ni−Br1 2.3118(4), Ni−Br2 2.3398(3), Ni−P1 2.1314(6), Ni−P2 2.1449(7), P1−C1 1.788(2), P2−C2 1.820(2), C1−C2 1.379(4), C1−N1 1.379(3), N1−C3 1.295(4), C3−C4 1.516(4), C3−C8 1.458(4), C7−C8 1.339(4), C6−C7 1.464(4), C5−C6 1.334(4), C4−C5 1.493(4), N2−C4 1.510(3), Br1−Ni−Br2 95.45(1), Br1−Ni−P1 88.69(2), Br1−Ni−P2 176.65(2), Br2−Ni−P1 173.68(2), Br2−Ni−P2 87.63(2), P1−Ni−P2 88.35(2), N1−C1−C2 122.3(2), N1−C1−P1 119.7(2), P1−C1−C2 117.8(2), N2−C2−C1 118.3(2), N2−C2−P2 127.2(2), P2−C2−C1 114.3(8).

The formation of **5** required a significant reorientation of the ligand in the precursor (Figure 5). Only the two phosphorus atoms act as ligands toward the "*cis*-$NiBr_2$" fragment to form a square-planar complex. Surprisingly, the five-membered chelate ring contains a bis(diphenylphosphino)ethylene unit instead of the bis(diphenylphosphino)ethane unit of the precursor with a newly formed central C═C double bond (C1−C2 = 1.379(4) Å). This double bond is part of the quinoxaline ring.

The most interesting feature of this structure, however, is the cyclohexa-1,3-diene ring formed in the peripheral position of the complex as the result of an intramolecular [4 + 2] cycloaddition reaction of the 1,2-diimine with a benzene ring of a mesityl substituent. In this reaction the benzene ring acts as (dihetero)dienophile. The length of the C3−N1 bond (1.295(4) Å) is indicative of a C═N double bond. In contrast, the C4−N2 bond of the heterocyclic ring system of 1.510(3) Å is that of a single bond. Furthermore, the bond distances C5−C6 and C7−C8 (1.334(4) and 1.339(4) Å, respectively) are typical for C═C bonds in a cyclohexa-1,3-diene ring. As expected, the C4−C5 distance is that of a single bond (1.493(4)), whereas the C6−C7 and C3−C8 bond lengths as part of a conjugated system are slightly shortened (1.464(4) and 1.458(4) Å, respectively) compared with a typical C−C single bond.

NMR spectroscopic measurements in CDCl$_3$ indicate that the solid-state structure is also present in solution. As expected for **5**, two doublets in the ^{31}P{^{1}H} NMR spectrum are observed at 61.1(J = 81 Hz) and 45.8 (J = 81 Hz) ppm indicating the coordination of both nonequivalent phosphorus atoms. In comparison with the ^{31}P signal of the free ligand both resonances are strongly low-field shifted. Moreover, in the ^{1}H NMR spectrum (in CDCl$_3$ at room temperature) the expected six singlets of the nonequivalent methyl groups between 0.82 and 2.17 ppm were observed. The olefinic protons at C5 and at C7 of the cyclohexa-1,3-diene system gave rise to two singlets at 5.04 and 6.08 ppm, each integrating to 1. In addition, in the ^{13}C NMR spectrum shows six signals between 16.8 and 21.2 ppm, which are attributable to the six nonequivalent methyl carbons.

To the best of our knowledge the ring-closure reaction yielding **5** is the first metal-mediated [4 + 2] cycloaddition with a benzene ring as a (dihetero)dienophile in which a cyclohexa-1,3-diene ring is formed. Generally, such thermally induced [4 + 2] cycloaddition reactions yielding a cyclohexa-1,3-diene originating from benzene are extremely rare. Only in one case has such a reaction been described using a specially designed organic ring system which reacts in an unselective reaction at high temperatures.[26] In other cases, a fast rearrangement of the cyclohexa-1,3-diene intermediate to form an aromatic ring was observed.[27−29] Furthermore, there are also a few examples for such reactions in organic chemistry which are photochemically activated resulting in cyclohexa-1,3-diene intermediates which rearrange to form benzene derivatives in most cases.[30−36] It is noteworthy that the binuclear Ni complex **4**, suspended in methanol, eliminates NiBr$_2$(THF)$_2$ from the 1,4-diazadiene unit to form the mononuclear complex **6** (Scheme 1) in which a similar [4 + 2] cycloaddition reaction has occurred as in **5**. In this case, however, a subsequent tautomerization results in the rearrangement of the benzene system of the peripheral ring. In addition, complex **6** is also formed by reaction of NiBr$_2$(THF)$_{1.46}$ with **1c** (1:1) in THF at ambient temperature.

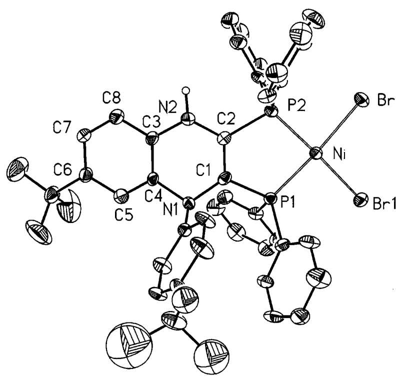


Figure 6. ORTEP diagram of compound **6** with thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): Ni−Br1 2.331(1), Ni−Br2 2.336(1), Ni−P1 2.143(2), Ni−P2 2.141(2), P1−C1 1.807(7), P2−C2 1.817(7), C1−C2 1.338(9), C1−N1 1.440(9), N2−C3 1.402(9), C3−C4 1.386(10), C3−C8 1.383(10), C7−C8 1.384(10), C6−C7 1.388(10), C5−C6 1.409(10), C4−C5 1.368(10), N1−C4 1.469(8), N2−C2 1.377(9), Br1−Ni−Br2 95.02(4), Br1−Ni−P1 89.51(6), Br1−Ni−P2 176.75(7), Br2−Ni−P1 175.07(7), Br2−Ni−P2 87.42(6), P1−Ni−P2 87.99(7), N1−C1−C2 122.0(6), N1−C1−P1 120.7(5), P1−C1−C2 116.9(5), N2−C2−C1 120.3(6), N2−C2−P2 122.8(5), P2−C2−C1 116.7(5).

Figure 6 shows the molecular structure determined from single crystals of **6**.

In contrast to complex **5**, where the N1−C3 bond distance of 1.295(4) Å is that of a double bond, the related bond length N(1)−C(4) (1.469(8) Å) in complex **6** is a typical single bond. As expected, also the other C−N distances (N(1)−C(1) = 1.440(9) Å, N(2)−C(2) = 1.377(9) Å, and N(2)−C(3) = 1.402(9) Å) are single bonds. The C−C bond lengths in the peripheral ring typical for a benzene ring are equivalent to each other within experimental error. This is in direct contrast to the C−C bond lengths in complex **5**. In addition, the central C1−C2 (1.338(9) Å) distance in the five-membered metal chelate ring is that of a double bond.

^{31}P{^{1}H}, ^{1}H, and ^{13}C NMR studies were conducted in THF-d_8 and showed all expected shifts and splitting patterns associated with the molecule structure of **6**. For example, two doublets at 41.6 and 50.2 ppm were observed in the ^{31}P{^{1}H} NMR spectrum at room temperature indicating coordination of both P atoms. In addition, the expected two signals for the protons of the different *tert*-butyl groups were observed at 1.05 and 1.24 ppm with each integrating to nine protons.

The highly varying coordination behavior of the ligands depending on the identity of the transition metal may be rationalized as following: In the first step one phosphorus atom reacts with the metal center to form a monocoordinated species followed by the formation of the chelate ring by using the nitrogen donor atom of the imine group. This chelate ring is kinetically inert in the case of molybdenum. In

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contrast to this, Ni(II) chelate rings are kinetically more labile and undergo isomerization to form the thermodynamically more stable (P,P)Ni coordination. In the next step $NiBr_2$ may react in a fast reaction with the 1,2-diimine unit on the opposite side of the complex, provided there is enough space for coordination. This is the case for ligand **1b**, which bears the relatively small 4-*tert*-butylphenyl group on the nitrogen atoms of the 1,2-diimine unit. In the resulting binuclear complex **4** the 1,2-diimine unit is "protected" by the metal center. Consequently, a ring-closure reaction to form a quinoxaline system does not occur. If complex **4** eliminates $NiBr_2$ in methanol, the "deprotected" 1,2-diimine system undergoes a fast intramolecular ring-closure ([4 + 2] cycloaddition) reaction with the *N*-4-*tert*-butylphenyl substituent, which results in the formation of the quinoxaline derivative. However, the cyclohexa-1,3 diene ring intermediately formed is unstable because the $-HC(C,C)-CH{=}N-$ unit of C3−C4−N2 underdoes a fast tautomerization to form the $=C-C(C,C)-NH-$ system in complex **6** containing C3 and C4 as part of the benzene ring (Scheme 1 and Figure 6).

In contrast, ligand **1c** bears bulky mesityl groups on the nitrogens which prevent the coordination of a second nickel center on the 1,2-diimine unit. Consequently, the [4 + 2] cycloaddition reaction occurs to yield the quinoxaline derivative containing the cyclohexa-1,3-diene ring. This ring is stable since the system $(CH_3)C(C,C)-C{=}N-$ is not able to undergo subsequent tautomerization to a benzene ring (Figure 5).

It is noteworthy that the [4 + 2] cycloaddition product in **5** is only stable in the metal complex. Decomplexation of **5** with diacetyldioxime/LiBu in THF results in the reorganization of the free ligand **1c** which was isolated from the reaction mixture. It was characterized by comparison of its spectroscopic data with those of an authentic sample of **1c** which were identical.

In contrast, decomplexation of **6** under essentially the same conditions yielded the free quinoxaline derivative offering a simple way of synthesizing new types of chelating bis(diarylphosphino)ethylenes containing a quinoxaline backbone. As expected, two ^{31}P signals were observed in its $^{31}P\{^1H\}$ NMR spectrum which are high-field shifted compared with the related signals in **6** (doublets at −12.96, $J = 172$ Hz, and −2.61, $J = 172$ Hz). However, in comparison with the ^1H and ^{13}C NMR spectra of the coordinated state in **6**, the NMR spectra of the free quinoxaline are very similar. As also expected, its NMR spectra are very different from those of the isomeric ligand **1b** (see Experimental Section).

Conclusions

This work demonstrates that the newly synthesized 2,3-bis(diphenylphosphino)-1,4-diazadienes give rise to a very rich coordination chemistry with transition metals. The ligands can coordinate in three different bidentate modes, (P,N)M, (P,P)M, and (N,N)M, and are able to yield mono- and dinuclear compounds.

The ring-closure reaction ([4 + 2] cycloaddition) resulting in quinoxaline derivatives upon coordination of one $NiBr_2$ at the two P donor atoms is very sensitive toward the nature of the metal center. Whereas tetrahedral Cu(I) in **3** does not promote this [4 + 2] cycloaddition, Ni(II) in a square-planar environment does. Generally, this reaction opens a simple route for preparing bis(diphenylphosphino)ethylenes containing a quinoxaline backbone, provided the ortho position of the nitrogen substituents contain hydrogen.

The course of the metal-mediated ring-closure reaction, the influence of the nature of the metals on this reaction, and the ability of the new ligands in tuning catalytic properties of coordinated metals are the subjects of ongoing studies.

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Supporting Information Available: Tables giving complete details of the X-ray diffraction studies of the complexes **2**−**6**. Crystallographic details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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