

Metal Complexes of the Tetradentate Ligands *rac*- and *meso*-N,P,P,N: Synthesis, Separation and Structural Characterization

Gabi Müller,^[a] Martti Klinga,^[b] Markku Leskelä,^[b] and Bernhard Rieger*^[a]

Keywords: N ligands / P ligands / Iron / Palladium / Cobalt

The N,P,P,N ligand 1,2-bis[(2-quinolinemethyl)(phenyl)phosphanyl]ethane (**2**) which contains two stereogenic phosphane units in the ligand backbone [*rac*-**2** (*R/R*, *S/S*) and *meso*-**2** (*R/S*)] and two pendant quinaldine moieties was synthesized. The diastereomeric forms were separated after conversion of the ligands to the corresponding palladium(II) diiodide complexes (*rac*-**3**, *meso*-**3**). The structure of both compounds was determined by X-ray structure analysis and revealed a bidentate coordination through phosphorus leading to the expected square-planar geometry. The free ligands were regenerated by treatment of the palladium(II) diiodides with potassium cyanide and the coordination behavior of *rac*-**2** and *meso*-**2** towards iron(II) and cobalt(II) dichloride (*rac*-**5**,

meso-**5**, M = Fe; *rac*-**6**, *meso*-**6**, M = Co) was investigated by the means of IR and UV/Vis spectroscopy. The results indicate that in the case of Fe^{II} and Co^{II} the quinaldine moieties are not coordinated to the metal center and the ligands therefore act, as in the case of Pd^{II}, as bidentate systems. UV/Vis investigations suggest a tetrahedral coordination environment for the Co^{II} complexes. The Fe^{II} and Co^{II} derivatives were tested for ethene polymerization and the bis(acetonitrile)-palladium compounds (*rac*-**4**, *meso*-**4**) for ethene/CO copolymerization reactions.

(© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

A variety of late-transition-metal polymerization catalysts with different ligand (mono-, bi-, tri- or tetradentate)-metal combinations are known in the literature.^[1–3] Bidentate ligands are often used in nickel-catalyzed olefin homopolymerization and palladium-catalyzed olefin/CO copolymerization reactions. Highly active iron and cobalt complexes with tridentate pyridyl-diimine systems were discovered recently.^[4,5] However less attention has been directed

towards iron and cobalt complexes with tetradentate ligands.

Recently, our group reported the synthesis of a tetradentate quinaldine-amine ligand **1** and on the application of the corresponding palladium complexes for norbornene polymerization.^[6,7] When coordinated to iron(II) or cobalt(II) dichloride, **1** exclusively forms an octahedral, C₂-symmetric complex [(**1**)Fe/CoCl₂], Figure 1].

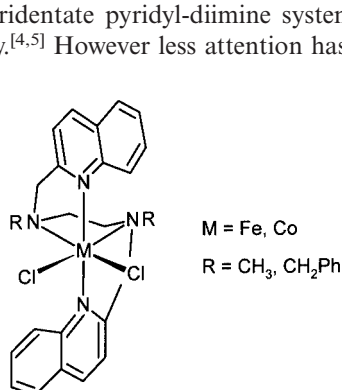


Figure 1. Octahedral C₂-symmetric complexes containing ligand **1**

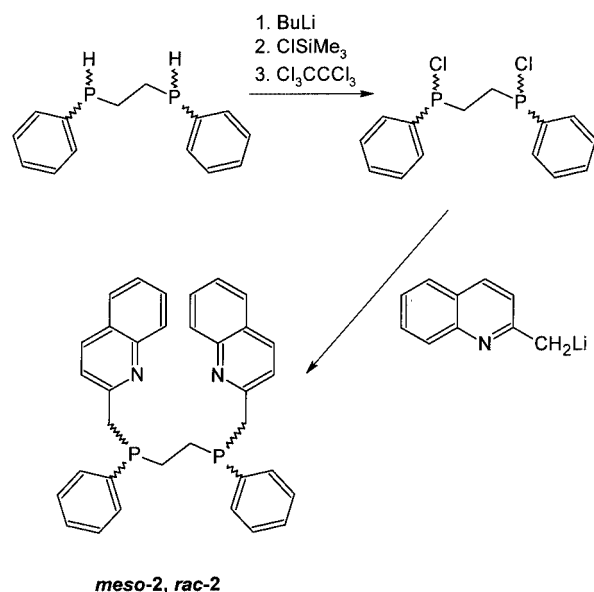


Figure 2. Synthesis of the N,P,P,N ligand **2** (*rac*-**2** and *meso*-**2**)

^[a] Department of Materials and Catalysis, Inorganic Chemistry II, University of Ulm, 89069 Ulm, Germany, Fax: (internat.) +49-(0)731/502-3039 E-mail: bernhard.rieger@chemie.uni-ulm.de

^[b] Laboratory of Inorganic Chemistry, Department of Chemistry, P. O. Box 55, 00014 University of Helsinki, Finland

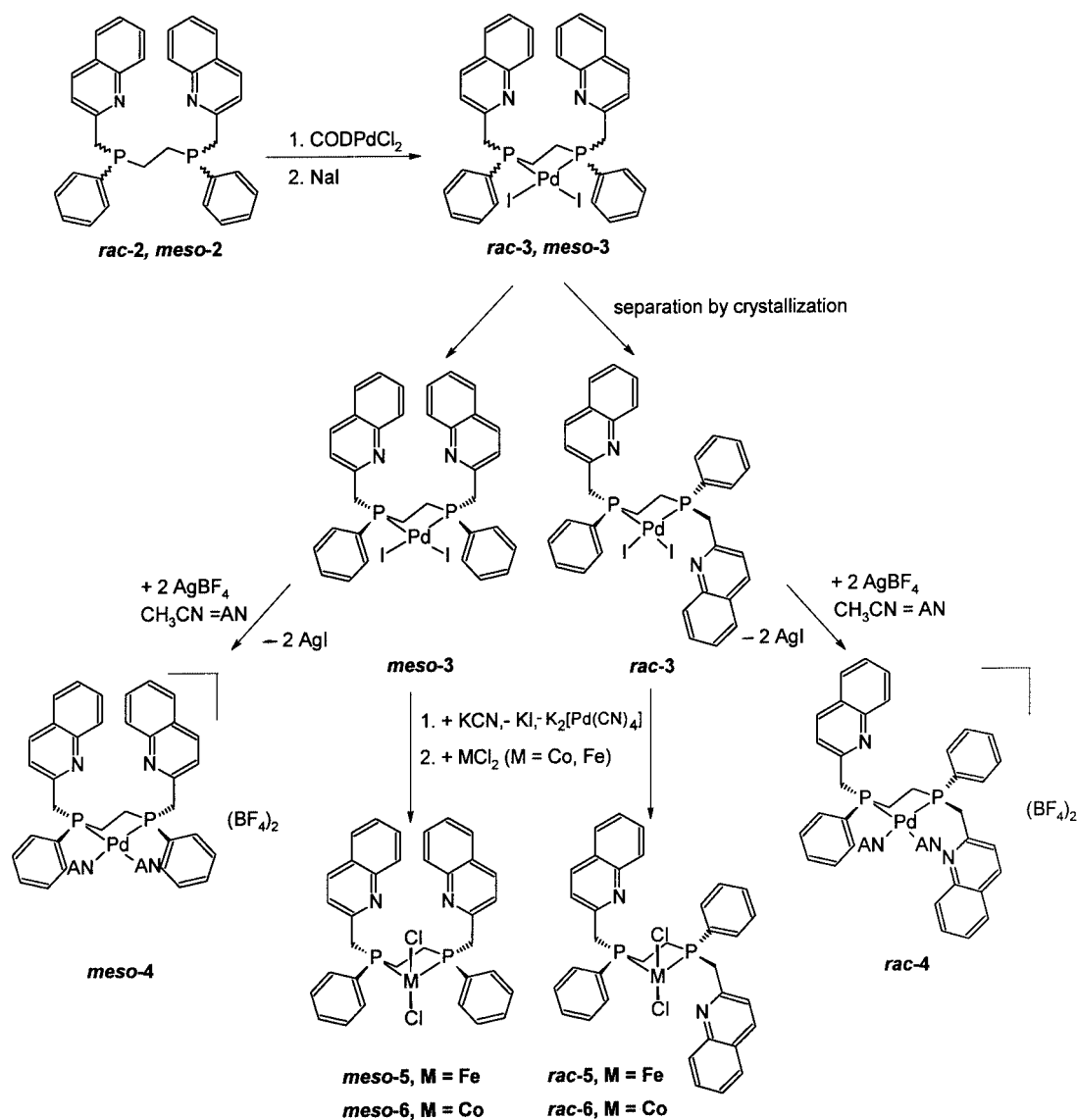
After activation with MAO, (1)CoCl₂ (R = CH₂Ph) forms an active catalyst for the polymerization of ethene.^[8] The molecular weight of the product is relatively high ($M_w \approx 1.5 \times 10^6$ g/mol), however the activity (10 kg PE/[Co]h) of this system is poor due to the low stability of the activated complex.^[8] We report here on the synthesis of a tetradentate, mixed nitrogen/phosphorus-containing ligand **2** which, instead of the donor-amine groups of ligand **1**, carries donor/acceptor phosphane functionalities in the ligand backbone. The overall arrangement with the pendant quinaldine moieties was left unchanged to ensure the formation of the C₂-symmetric, octahedral coordination compound. Pd^{II}, Fe^{II} and Co^{II} complexes bearing the new N,P,P,N ligands were synthesized and tested in ethene and ethene/CO copolymerization reactions.

Results and Discussion

Ligand and Complex Synthesis

The ligand **2** (*rac-2* and *meso-2*) was prepared following the synthetic pathway depicted in Figure 2.^[9]

1,2-Bis(phenylphosphanyl)ethane was converted into 1,2-bis(chlorophenylphosphanyl)ethane by treating the bis(Li phosphide) with ClSiMe₃, followed by the addition of hexachloroethane. Subsequent reaction of Li-quinaldine with 1,2-bis(chlorophenylphosphanyl)ethane afforded the tetradentate N,P,P,N ligand **2** which was isolated as a mixture of two diastereoisomers due to the two stereogenic phosphorus atoms [*rac-2* (*R/R* and *S/S*) and *meso-2* (*S/R*)]. The ratio of *rac-2*/*meso-2* was 1.7:1, indicating a preferred



Scheme 1

formation of the *rac*-form. Attempts to separate the two ligands were unsuccessful.

The mixture of *rac*-**2** and *meso*-**2** was converted into the corresponding, air-stable palladium(II) diiodide complexes (Scheme 1, *rac*-**3**, *meso*-**3**) by treatment with [PdCl₂(COD)] in the presence of sodium iodide.^[10] After purification of the mixture by column chromatography, *rac*-**3** could be separated by repeated crystallization from CH₂Cl₂/EtOAc. A pure sample of *meso*-**3** was isolated by crystallization from hot acetone.

To investigate the catalytic properties of our diastereomeric Pd^{II} complexes for ethene/CO copolymerizations the palladium diiodide compounds were converted into the bis-(acetonitrile) complexes *rac*-**4** and *meso*-**4** by treating the diiodides with silver tetrafluoroborate in acetonitrile.

The diastereomeric ligands *rac*-**2** and *meso*-**2** were isolated in pure form after treatment of the corresponding PdI₂ species with aqueous KCN solution. The iron(II) and cobalt(II) dichloride complexes of *rac*-**2** and *meso*-**2** were synthesized by treatment of the free ligands with the appropriate metal(II) salt (*rac*-**5**, *meso*-**5**, M = Fe; *rac*-**6**, *meso*-**6**, M = Co). Elemental analysis and FAB-MS indicated a 1:1 metal to ligand ratio.

Structural Characterization

Solid State Structures

Single crystals of the palladium(II) diiodide compounds suitable for an X-ray structure determination were obtained by crystallization from CH₂Cl₂/EtOAc (*rac*-**3**) or from acetone/toluene (*meso*-**3**) (Figure 3).

For both complexes a water molecule was located in the unit cell which forms intermolecular hydrogen bonds to neighboring quinaldine moieties. Both compounds crystallize in the monoclinic form. The two iodides (I1 and I2) and the two phosphorus units (P1 and P2) form the expected square-planar coordination sphere around the palladium center. Small deviations might result from crystal packing (Table 1). Bond lengths and angles are within the range expected for this type of complex (Table 2).^[11–13] In *rac*-**3** one of the quinaldine moieties is located above, and the second below, the Pd–P1–P2–I1–I2 coordination plane, while in *meso*-**3** both units lie on the same side of the plane. Considering this geometrical arrangement it is obvious that only the *rac*-form of the ligand is able to coordinate as a tetradentate ligand in a manner identical to the N,N,N,N ligand **1** (see Figure 1), with the quinaldine fragments occupying both axial positions.^[6] Attempts to obtain single crystals of *rac*-**5,6** or *meso*-**5,6** suitable for an X-ray structure analysis were unsuccessful.

IR Analysis

For structure elucidation IR analysis was performed on the free ligands **1**, *rac*-**2** and *meso*-**2** as well as on the corresponding Fe^{II} and Co^{II} complexes. Coordination of an N-heteroaromatic unit to a metal center is indicated by a frequency shift of the heteroaromatic ring vibrations.^[14–16]

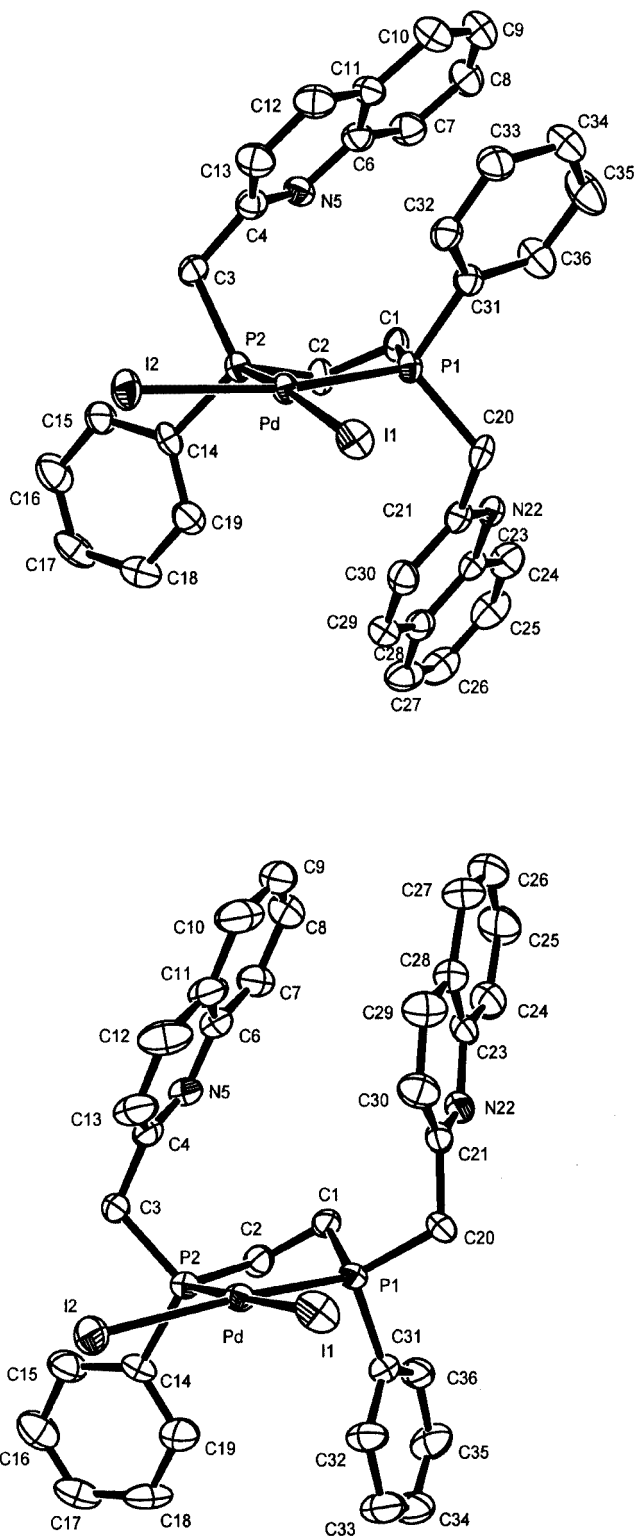


Figure 3. The structure of *rac*-**3** (upper) and *meso*-**3** (lower)

The IR spectra of the octahedral Fe^{II} and Co^{II} complexes of ligand **1** [(**1**)FeCl₂ and (**1**)CoCl₂] were used as references, since in this case the coordination of the quinaldine moieties has been confirmed by an X-ray structure determination.^[6,8]

Table 1. Crystallographic data for *rac*-3 and *meso*-3

	<i>rac</i> -3·H ₂ O	<i>meso</i> -3·0.5(C ₇ H ₈)·H ₂ O
Chemical formula	C ₃₄ H ₃₂ I ₂ N ₂ OP ₂ Pd	C _{37.5} H ₃₆ I ₂ N ₂ OP ₂ Pd
Molecular weight [g/mol]	906.76	952.82
Crystal color and form	yellow plate	yellow prism
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	12.518(5)	35.069(7)
<i>b</i> [Å]	11.243(5)	10.734(2)
<i>c</i> [Å]	23.584(5)	22.419(4)
β [°]	100.63(3)	120.44(3)
Volume [Å ³]	3262(2)	7276(2)
Z	4	8
<i>D</i> _{calcd.} [mg/m ³]	1.846	1.740
Absorption coefficient [mm ^{−1}]	2.590	2.327
<i>F</i> (000)	1760	3720
Crystal size [mm]	0.44 × 0.38 × 0.16	0.48 × 0.45 × 0.43
θ _{max} [°]	25.01	25.03
Number of observed reflections [<i>I</i> > 2σ(<i>I</i>)]	4923	5508
Number of collected reflections	5714	6173
Number of unique reflections	5461	6070
Number of parameters	409	418
Index range	0 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 13 −28 ≤ <i>l</i> ≤ 27	0 ≤ <i>h</i> ≤ 41 0 ≤ <i>k</i> ≤ 12 −26 ≤ <i>l</i> ≤ 22
Goodness-of-fit on <i>F</i> ²	1.039	1.021
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^{[a],[b]}	<i>R</i> 1 = 0.0368 <i>wR</i> 2 = 0.0881	<i>R</i> 1 = 0.0620 <i>wR</i> 2 = 0.1579
<i>R</i> indices (all data) ^{[a],[b]}	<i>R</i> 1 = 0.0427 <i>wR</i> 2 = 0.0912	<i>R</i> 1 = 0.0665 <i>wR</i> 2 = 0.1626
Largest differential peak and hole [e/Å ³]	1.310 and −0.836	2.438 and −2.046

^[a] *R*1 = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|. ^[b] *wR*2 = {Σ[*w*(*F*_o² − *F*_c²)²]/Σ[*wF*_o⁴]}^{1/2}.

Table 2. Selected bond lengths and angles for *rac*-3 and *meso*-3

Bond lengths [Å]	<i>rac</i> -3·H ₂ O	<i>meso</i> -3·0.5(C ₇ H ₈)·H ₂ O
I1–Pd	2.6514(9)	2.6528(8)
I2–Pd	2.6468(8)	2.6499(12)
Pd–P2	2.2429(15)	2.2527(17)
Pd–P1	2.2526(14)	2.2554(17)
P1–C1	1.830(5)	1.828(6)
P1–C20	1.850(5)	1.832(6)
P2–C3	1.832(5)	1.826(6)
P2–C2	1.833(5)	1.834(6)
Bond angles [°]	<i>rac</i> -3·H ₂ O	<i>meso</i> -3·0.5(C ₇ H ₈)·H ₂ O
P2–Pd–P1	87.10(5)	84.78(6)
P2–Pd–I2	87.73(4)	87.23(4)
P1–Pd–I2	170.50(4)	170.55(4)
P2–Pd–I1	171.48(4)	177.22(4)
P1–Pd–I1	90.15(4)	92.44(4)
I2–Pd–I1	96.06(3)	95.55(2)
Pd–P2–C3	115.81(19)	114.0(2)
Pd–P1–C20	117.22(18)	124.1(2)

The high frequency region (1700–1400 cm^{−1}) of the ring deformations of the aromatic and heteroaromatic units is depicted in Figure 4.^[17,18] The IR diagrams **1** (ligand **1** and complexes), **2** (*rac*-**2** and complexes) and **3** (*meso*-**2** and complexes) show the spectra of the free ligand (top), and the iron (middle) and cobalt (bottom) complexes. The ring

vibration of the free ligands at 1614 cm^{−1} and 1595 cm^{−1} (**1**), 1617 cm^{−1} and 1597 cm^{−1} (*rac*-**2**), 1614 cm^{−1} and 1595 cm^{−1} (*meso*-**2**) were attributed to the quinaldine moiety.^[17]

The spectra of the Fe^{II} and Co^{II} complexes of ligand **1** show a high frequency band at 1647 and 1648 cm^{−1}, respectively, which is not present in the spectrum of the free ligand. Also, a distinct shift of the bands in the 1400–1570 cm^{−1} region is detectable upon coordination of the quinaldine moiety. No differences of band positions and intensities in the spectra of the Fe^{II} and Co^{II} complexes were observed.

In the case of the Fe^{II} and Co^{II} complexes of the N,P,P,N ligands *rac*-**2** and *meso*-**2** no band at higher frequencies is detectable, which would indicate a coordination of the quinaldine moiety. The slight variation in the 1400–1570 cm^{−1} region might be due to the coordination of the phosphane units to the metal center. These investigations imply that, in contrast to **1**, which coordinates as a tetradentate ligand, *rac*-**2** and *meso*-**2** form Fe^{II} and Co^{II} complexes where the heteroaromatic unit is not coordinated to the metal center and the ligands therefore act as bidentate systems.

UV/Vis Spectroscopy

To support this hypothesis, UV/Vis measurements were performed on the Co^{II} complexes *rac*-**6** and *meso*-**6** in solution (Figure 5). The spectra of both isomers show a similar structure of band positions and intensities, suggesting the

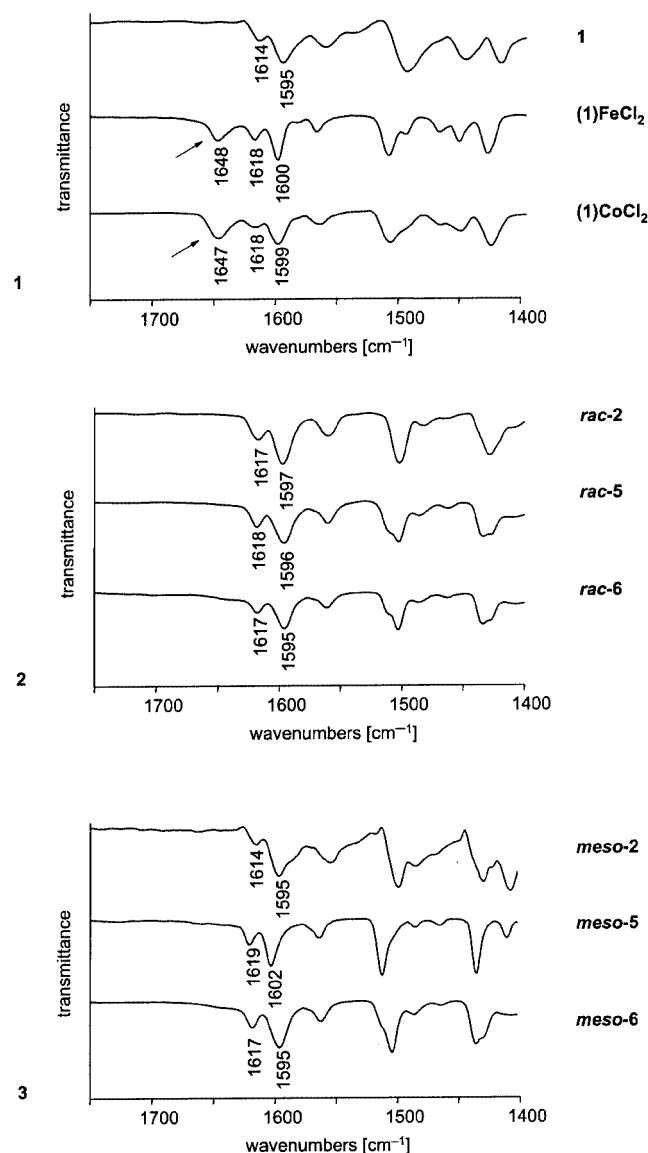


Figure 4. IR spectra of the free ligands (top), the Fe^{II} (middle) and the Co^{II} (bottom) complexes of the ligands **1** (diagram 1), *rac*-**2** (diagram 2) and *meso*-**2** (diagram 3)

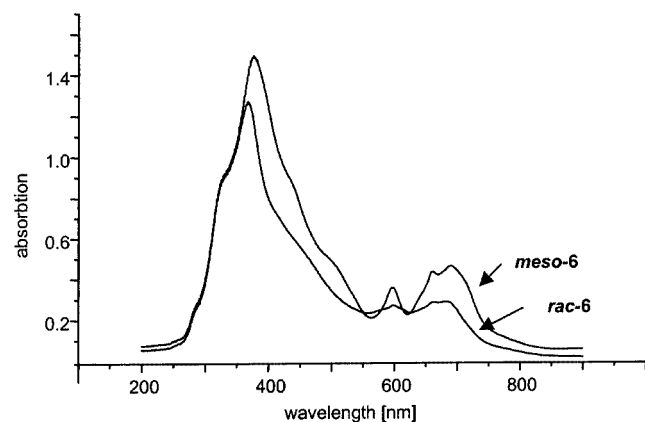


Figure 5. UV/Vis spectra of a solution of *rac*-**6** and *meso*-**6** in CH₂Cl₂

same overall coordination geometry for both complexes (Table 3).

Table 3. Positions of the band maxima and molar extinction coefficient of the UV/Vis spectra of a solution of *rac*-**6** and *meso*-**6** in CH₂Cl₂

	$\lambda_{\max}$ [nm] ($\epsilon_{\max}$ [L·mol ⁻¹ ·cm ⁻¹])			
<i>rac</i> - 6	368 (852)	599 (329)	663 (375)	683 (381)
<i>meso</i> - 6	377 (985)	597 (316)	661 (390)	690 (414)

UV/Vis investigations on other tetrahedral CoCl₂L₂ complexes (L = P donor) have shown that the absorption in the 500–800 nm region can be attributed to the spin-allowed transition $^4A_2 \rightarrow ^4T_1$.^[19–25] The observed absorption spectra for *rac*-**6** and *meso*-**6** resemble the reported spectra for the tetrahedral complex [CoCl₂(PPh₃)₂], indicating a bidentate coordination of *rac*-**2** and *meso*-**2** (through the P units) to give the corresponding tetrahedral CoCl₂ com-

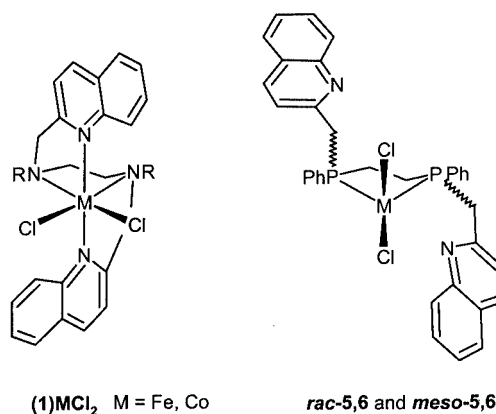


Figure 6. Coordination behavior of **1** and proposed coordination behavior of *rac*-**2** and *meso*-**2** in their Fe^{II} and Co^{II}Cl₂ complexes

plexes (Figure 6).^[20,24] We assume a similar coordination behavior for the Fe^{II} complexes.

Analysis of the bond lengths and angles found for the strained, octahedral complex **(1)FeCl₂** revealed an Fe–N(R)–CH₂ angle of 107°.^[6] This angle, together with the N(R)–Fe bond length determines the distance of the quinaldine moiety from the axial coordination site in the complexes. The strained structure of **(1)FeCl₂** indicates that an angle of 107° together with an N–Fe bond length of 2.25 Å is necessary to allow coordination of the quinaldine moieties.^[6] In the square-planar Pd^{II} complexes *rac*-**3** and *meso*-**3**, where the quinaldine moieties are not coordinated to the metal center, a Pd–P–CH₂ angle of 116° was observed. It is likely that bidentate coordination of the N,P,P,N ligands stabilizes the tetrahedral CoCl₂P₂ complexes (P–Co ≈ 2.2 Å^[26]) sufficiently so that there is no need to diminish this angle considerably, forming a highly constrained ring systems.

The Fe^{II} and Co^{II} complexes were tested for the polymerization of ethene. However, in contrast to the octahedral **(1)CoCl₂**, the tetrahedral complexes *rac*-**5,6** and *meso*-**5,6** of the present study decomposed upon addition of MAO to

give a suspension of the complexes in toluene (black precipitate, most likely Fe^0 or Co^0). Initial experiments showed that the diastereomeric bis(acetonitrile)palladium complexes **rac-4** and **meso-4** are suitable catalyst precursors for the copolymerization of ethene and CO using methanol as cocatalyst. Further investigations on the behavior of the diastereomeric complexes towards the polymerization of 1-olefins and CO are in progress.

Conclusion

Exchanging the backbone nitrogen functionalities in the tetradentate N,N,N,N ligand **1** for phosphorus leads to the formation of two stable diastereoisomers **rac-2** and **meso-2**. At the same time a distinct variation in the coordination behavior of the new N,P,P,N ligands is induced. While the N,N,N,N ligand **1** forms octahedral Fe^{II} and Co^{II} complexes, a tetrahedral environment is suggested for the Fe^{II} and Co^{II} complexes of **rac-2** and **meso-2**. Whereas **(1)CoCl₂** shows some activity for ethene polymerization, the tetrahedral **rac-5,6** and **meso-5,6** complexes undergo fast decomposition upon treatment with MAO. However, the Pd^{II} analogues **rac-4** and **meso-4** show some activity in the ethene/CO copolymerization reaction; this will be investigated further.

Experimental Section

General Remarks: All manipulations except the handling of the palladium diiodide complexes were carried out in dry solvents under an inert atmosphere of argon using standard Schlenk techniques. THF, diethyl ether and toluene were distilled from LiAlH_4 , and CH_2Cl_2 and petroleum ether were distilled from CaH_2 . All solvents were stored over molecular sieves. Commercially available anhydrous acetonitrile and ethanol, BuLi (1.6 M in hexane), hexachloroethane, KCN, anhydrous FeCl_2 and CoCl_2 were used without further purification. Quinaldine and chlorotrimethylsilane were purified by distillation. (*cis,cis*-Cycloocta-1,5-diene)dichloropalladium,^[27] 1,2-bis(phenylphosphanyl)ethane,^[28] ligand **1**, as well as the corresponding iron and cobalt complexes,^[6] were prepared according to literature procedures.

Polymerization experiments were performed in a 100 mL steel autoclave (Roth) with a glass inlet and mechanical stirring. Ethene (BASF, 2.7) and CO (BASF, 2.0) were used without further purification. MAO (10% in toluene) was purchased from Witko.

NMR measurements were conducted on a Bruker DRX 400 spectrometer at 400 MHz (^1H) and 162 MHz (^{31}P). Chemical shifts are reported in ppm. Tetramethylsilane and 85% phosphoric acid were used as references. IR spectra were measured on a Bruker IFS 113v spectrometer, FAB-MS spectra on a Finnigan MAT TSQ 7000 spectrometer using *meta*-nitrobenzyl alcohol (*m*-NBA), 2,3,4-trimethoxyacetophenone (TMAP) or 2-nitrophenyloctyl ether (2-NPOE) as matrices. Elemental analysis were measured on an Vario EL elemental. UV/Vis absorption spectra were conducted on a J & M spectrometer using 2 mm solutions in CH_2Cl_2 .

Synthesis of *rac-2*, *meso-2*: BuLi (55.2 mL, 88 mmol) was added slowly to a solution of 1,2-bis(phenylphosphanyl)ethane (10.9 g,

44 mmol) in THF (300 mL) cooled to -78°C . The reaction mixture was warmed to 0°C and chlorotrimethylsilane (11.4 mL, 90 mmol) was added slowly with a syringe. The solvent was removed under reduced pressure and CH_2Cl_2 (300 mL) was added. The reaction mixture was cooled to 0°C and hexachloroethane (20.9 g, 88 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 72 hours. The solvent was removed under reduced pressure and the solid was suspended in THF (250 mL). In a separate flask BuLi (55.2 mL, 88 mmol) was added slowly to a solution of quinaldine (12 mL, 88 mmol) in 200 mL of THF cooled to -78°C . The dark red solution of the quinaldine anion was allowed to reach room temperature and was then added to the suspension of the chlorophosphane at -78°C until the red color of the quinaldine anion remained. A further 10 mL of quinaldine solution was added to ensure the complete transformation of the chlorophosphane. The reaction mixture was allowed to reach room temperature and was stirred overnight. Water (10 mL) was added and the solvent was removed under reduced pressure. The remaining solid was dissolved in water (300 mL) and CH_2Cl_2 (500 mL). The organic layer was separated and the water layer was extracted with two 200 mL portions of CH_2Cl_2 . The organic layers were dried over sodium sulfate. Evaporation of the solvent left a red oil which contained a 1:1.7 *meso:rac* mixture of the ligand. The crude product was used without further purification. Yield: 80% (18.6 g).

Synthesis of *rac-3*, *meso-3*: $[\text{PdCl}_2(\text{COD})]$ (10.5 g, 36.7 mmol) was added to a solution of the ligand (36.7 mmol) in CH_2Cl_2 (300 mL). NaI (22 g, 1.47 mol) was added after 10 minutes and the reaction mixture was stirred for 12 hours. CH_2Cl_2 (500 mL) was added and the solution was stirred for a further 24 hours. The reaction mixture was filtered and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica using a 10:1 (v:v) mixture of CH_2Cl_2 and ethyl acetate as eluent. The *rac* form was separated by crystallization of the diastereomeric mixture from CH_2Cl_2 and ethyl acetate. A pure sample of the *meso*-isomer was obtained by crystallization of a *meso*-enriched fraction from hot acetone. Overall yields: 37% (12.1 g) **rac-3**, 25% (8.1 g) **meso-3**.

rac-3: ^1H NMR (CDCl_3): δ = 2.13 (m, 1 H), 2.22 (m, 1 H), 2.50 (m, 2 H), 4.14 (dd, J_1 = 15.9, J_2 = 13.1 Hz, 2 H), 4.80 (dd, J_1 = 12.9, J_2 = 10.1 Hz, 2 H), 6.80 (m, 4 H), 7.12 (dd, 2 H), 7.24 (m, 4 H), 7.53–7.61 (m, 4 H), 7.65 (d, J = 8.1 Hz, 2 H), 7.83 (d, J = 8.1 Hz, 2 H), 8.08 (d, J = 8.4 Hz, 2 H), 8.15 (d, J = 8.7 Hz, 2 H) ppm. ^{31}P NMR (CDCl_3): δ = 69.48 ppm. FAB-MS (matrix: 2-NPOE): m/z (%) = 889 (22) $[\text{MH}^+]$, 761 (100) $[\text{M}^+ - \text{I}]$. $\text{C}_{34}\text{H}_{30}\text{I}_2\text{N}_2\text{P}_2\text{Pd}\cdot\text{H}_2\text{O}$ (906.8): calcd. C 45.03, H 3.56, N 3.09; found C 44.65, H 3.45, N 2.95.

meso-3: ^1H NMR (CDCl_3): δ = 1.78–1.96 (m, 2 H), 2.02–2.19 (m, 2 H), 4.27 (dd, J_1 = 14.9, J_2 = 13.6 Hz, 2 H), 4.65 (dd, J_1 = 13.5, J_2 = 10.5 Hz, 2 H), 7.34 (m, 4 H), 7.41–7.50 (m, 4 H), 7.55 (d, J = 8.3 Hz, 2 H), 7.59–7.64 (m, 4 H), 7.74–7.82 (m, 8 H) ppm. ^{31}P NMR (CDCl_3): δ = 67.33 ppm. FAB-MS (matrix: 2-NPOE): m/z (%) = 889 (25) $[\text{MH}^+]$, 761 (100) $[\text{M}^+ - \text{I}]$. $\text{C}_{34}\text{H}_{30}\text{I}_2\text{N}_2\text{P}_2\text{Pd}$ (888.8): calcd. C 45.95, H 3.40, N 3.15; found C 45.54, H 3.71, N 2.96.^[29]

Synthesis of *rac-4*, *meso-4*: Silver tetrafluoroborate (223 mg, 1.13 mmol) was added to a suspension of the palladium diiodide (0.5 g, 0.56 mmol) in acetonitrile (50 mL). The reaction mixture was stirred overnight and the solution was filtered through celite. The solvent was removed under reduced pressure and the remaining solid was extracted twice with 20 mL portions of CH_2Cl_2 . Evaporation of the solvent left a yellow, microcrystalline solid. Yield: 90–95% (0.45–0.47 g).

***rac*-4:** ¹H NMR (CD₃CN): δ = 2.26 (s, CH₃CN), 2.96–3.20 (m, 4 H), 4.34 (m, 2 H), 4.65 (m, 2 H), 7.25 (m, 4 H), 7.47 (m, 2 H), 7.60 (m, 4 H), 7.67–7.71 (m, 4 H), 7.86 (m, 2 H), 8.00 (d, J = 8.1 Hz, 2 H), 8.09 (d, J = 8.6 Hz, 2 H), 8.44 (d, J = 8.5 Hz, 2 H) ppm. ³¹P NMR (CD₃CN): δ = 86.09 ppm. FAB-MS (matrix: TMAP): m/z (%) = 721 (10) [M^+ – 2CH₃CN – BF₄], 653 (92) [M^+ – 2CH₃CN – BF₄ – BF₃], 633 (100) [M^+ – 2CH₃CN – BF₄ – BF₃ – HF]. IR (KI): $\tilde{\nu}$ = 2320 cm^{–1}, 2292 (N≡C–CH₃, m), 1057 (ν BF₄, bs).

***meso*-4:** ¹H NMR (CD₃CN): δ = 2.25 (s, CH₃CN), 2.80–3.18 (m, 4 H), 4.30–4.70 (m, 4 H), 7.25 (m, 2 H), 7.45–7.71 (m, 10 H), 7.84 (m, 4 H), 7.98–8.10 (m, 4 H), 8.43–8.48 (m, 2 H) ppm. ³¹P NMR (CD₃CN): δ = 86.40 ppm. FAB-MS (matrix: *m*-NBA): m/z (%) = 721 (2) [M^+ – 2CH₃CN – BF₄], 653 (52) [M^+ – 2CH₃CN – BF₄ – BF₃], 633 (100) [M^+ – 2CH₃CN – BF₄ – BF₃ – HF]. IR (KI): $\tilde{\nu}$ = 2321 cm^{–1}, 2293 (N≡C–CH₃, m), 1060 (ν BF₄, bs).

Synthesis *rac*-2: *rac*-3 (1 g, 1.125 mmol) and KCN (1.4 g, 22.5 mmol) were added to a mixture of water (20 mL) and toluene (25 mL). The two-phase system was stirred overnight. The water phase was separated and the organic phase was washed four times with 20 mL portions of water. The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure to leave the ligand as a colorless solid. Yield: 84% (0.50 g). ¹H NMR (CDCl₃): δ = 1.77–1.88 (m, 4 H), 3.38 (dd, J_1 = 14.8, J_2 = 13.1 Hz, 4 H), 6.99 (d, J = 8.4 Hz, 2 H), 7.19–7.29 (m, 6 H), 7.34 (m, 4 H), 7.45 (m, 2 H), 7.63 (m, 2 H), 7.70 (d, J = 8.1 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 2 H), 7.94 (d, J = 8.5 Hz, 2 H) ppm. ³¹P NMR (CDCl₃): δ = –14.82 ppm.

Synthesis of *meso*-2: *meso*-3 (500 mg, 0.56 mmol) and KCN (730 mg, 11.25 mmol) were added to a mixture of water (20 mL) and CH₂Cl₂ (15 mL). The two-phase system was stirred for 2 h. The water phase was separated and the organic phase was washed four times with 20 mL portions of water. The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure to leave the ligand as a colorless solid. Yield: 80% (0.24 g). ¹H NMR (CDCl₃): δ = 1.79–1.92 (m, 4 H), 3.39 (s, 4 H), 6.96 (d, J = 8.5 Hz, 2 H), 7.21–7.30 (m, 6 H), 7.37 (m, 4 H), 7.44 (m, 2 H), 7.63 (m, 2 H), 7.70 (d, J = 8.2 Hz, 2 H), 7.86 (d, J = 8.4 Hz, 2 H), 7.92 (d, J = 8.5 Hz, 2 H) ppm. ³¹P NMR (CDCl₃): δ = –14.23 ppm.

Synthesis of *rac*-5, *rac*-6, *meso*-5 and *meso*-6: A solution of the ligand (between 0.4–0.8 mmol) in 15 mL of CH₂Cl₂ was added to a solution of the metal chloride (1 equiv.) in 5 mL of ethanol. The reaction mixture was stirred overnight and the solvent was reduced to 5 mL. The precipitate was isolated and dried under vacuum. Yields: 90–95% (0.25–0.41 mg).

***rac*-5:** FAB-MS (matrix: TMAP): m/z (%) = 619 (100) [M^+ – Cl]. C₃₄H₃₀Cl₂FeN₂P₂·H₂O (673.3): calcd. C 60.65, H 4.79, N 4.16; found C 60.23, H 4.71, N 3.99.

***meso*-5:** FAB-MS (matrix: 2-NPOE): m/z (%) = 619 (100) [M^+ – Cl]. C₃₄H₃₀Cl₂FeN₂P₂ (655.3): calcd. C 62.32, H 4.61, N 4.27; found C 62.48, H 4.85, N 4.23.

***rac*-6:** FAB-MS (matrix: 2-NPOE): m/z (%) = 622 (100) [M^+ – Cl], 587 (61) [M^+ – 2Cl]. C₃₄H₃₀Cl₂CoN₂P₂·H₂O (676.4): calcd. C 60.37, H 4.77, N 4.14; found C 59.92, H 4.60, N 4.08.

***meso*-6:** FAB-MS (matrix: 2-NPOE): m/z (%) = 622 (100) [M^+ – Cl], 587 (35) [M^+ – 2Cl]. C₃₄H₃₀Cl₂CoN₂P₂·H₂O (676.4): calcd. C 60.37, H 4.77, N 4.14; found C 59.86, H 4.85, N 4.05.^[30]

Ethene/CO Copolymerization: A 100 mL stainless steel autoclave equipped with a glass inlet and a stirring bar was purged with argon. The appropriate amount of the complex (50 μmol catalyst),

solvent (50 mL of CH₂Cl₂) and methanol (Cat.:Cocat. = 1:200) were added and the autoclave was pressurized with the ethene (20 bar) and CO (60 bar). After stirring for 1 h at room temp. the gases were vented off and the polymer was isolated by filtration. Yields: 50 mg (*meso*-4), 65 mg (*rac*-4). IR: ECO (*meso*-4): 2912.3 cm^{–1} (ν CH₂), 1693.6 (ν C=O); ECO (*rac*-4): 2912.3 cm^{–1} (ν CH₂), 1693.9 (ν C=O)

X-ray Crystallographic Study: Crystal data of the compounds *rac*-3 and *meso*-3 were collected with a Rigaku AFC7S single-crystal diffractometer at 193(2) K using Mo- K_α radiation (graphite monochromator, λ = 0.71073 Å; omega scans). Intensities were corrected for Lorentz and polarization effects.^[30] A psi-scan absorption correction was performed, 0.592 < T < 1.000 (*rac*-3), 0.920 < T < 1.000 (*meso*-3).^[31] Solution and refinement: SHELX97 (Sheldrick, 1997).^[32,33] The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically with their displacement factors 1.2-times that of the host atom. The hydrogen atoms of the lattice water were picked up from the final electron density map and were not further refined. The solid-state structures are stabilized by hydrogen bonds. The water molecule in both compounds is H-bonded to N5 and N22, the nitrogen acceptor atoms being situated in different complex molecules. In *meso*-3 a toluene molecule is present in the unit cell which lies on a twofold rotation axis and is slightly disordered. All the final electron densities greater than one lie within one angstrom unit from palladium or iodine atoms. CCDC-175209 (*rac*-3) and -175208 (*meso*-3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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].

Acknowledgments

The Fonds der Chemischen Industrie and the DAAD are gratefully acknowledged for their financial support.

- [1] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–448.
- [2] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203.
- [3] *Applied Homogeneous Catalysis with Organometallic Compounds* Vol 1 (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1996**.
- [4] B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050.
- [5] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849–850.
- [6] B. Rieger, A. S. Abu-Surrah, R. Fawzi, M. Steiman, *J. Organomet. Chem.* **1995**, *497*, 73–79.
- [7] A. S. Abu-Surrah, U. Thewalt, B. Rieger, *J. Organomet. Chem.* **1999**, *587*, 58–66.
- [8] A. M. S. Abu-Surrah, PhD Dissertation, Universität Ulm **1997**.
- [9] Attempts to synthesize ligand **2** following the procedures applied for the N,N,N,N ligand **1** by treating the Li phosphide with bromoquinoline were unsuccessful due to metal-halogen exchange reactions.
- [10] The diiodide compounds were prepared instead of the dichloro complexes because of their higher solubility.
- [11] U. Nagel, T. Krink, *Chem. Ber.* **1993**, *126*, 1091–1100.
- [12] CRC, *Handbook of Chemistry and Physics*, 59th edition, CRC Press, inc., Boca Raton, Florida, F-215.

- [13] U. Nagel, B. Rieger, *Chem. Ber.* **1988**, *121*, 1123–1131.
- [14] S. Yurdakul, S. Akyüz, J. E. D. Davies, *J. Mol. Struct.* **1989**, *197*, 355–359.
- [15] M. M. da Mota, J. Rodgers, S. M. Nelson, *J. Chem. Soc.* **1969**, 2036–2044.
- [16] S. Yurdakul, S. Akyüz, J. E. D. Davies, *J. Mol. Struct.* **1988**, *174*, 435–441.
- [17] A. R. Katritzky, R. A. Jones, *J. Chem. Soc.* **1960**, *14*, 2942–2947.
- [18] R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, Inc. **1991**.
- [19] W. E. Hatfield, J. T. Yoke, *Inorg. Chem.* **1962**, *3*, 470–474.
- [20] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, A. Sacco, *J. Am. Chem. Soc.* **1961**, *83*, 4157–4161.
- [21] J. Ellermann, W. H. Gruber, *Zeitschr. Anorg. Allg. Chem.* **1969**, *364*, 55–68.
- [22] K. Heinze, G. Huttner, L. Zsolnai, P. Schober, *Inorg. Chem.* **1997**, *36*, 5457–5469.
- [23] W. V. Dahlhoff, T. R. Dick, S. M. Nelson, *J. Chem. Soc. (A)* **1969**, 2919–2923.
- [24] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, R. H. Holm, *J. Am. Chem. Soc.* **1961**, *83*, 1780–1785.
- [25] W. E. Hatfield, J. T. Yoke, *Inorg. Chem.* **1962**, *3*, 475–481.
- [26] Common P–Co distance, source: Cambridge Crystallographic Data Centre.
- [27] F. H. Allen, O. Kennard, *Chem. Design Automation News* **1993**, *8*, 31.
- [28] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, 3. Band, Ferdinand-Enke-Verlag, Stuttgart **1981**, 1904–1905.
- [29] T.-S. Chou, C.-H. Tsao, S. C. Hung, *J. Org. Chem.* **1985**, *50*, 4329–4332.
- [30] In different cases, we were not able to obtain solvent-free samples of the metal complexes due to instability at higher temperature (especially the iron and cobalt complexes). We assume, therefore, that the deviation of the elemental analysis is due to solvent residues.
- [31] *teXsan, Single Crystal Structure Analysis Software, Version 1.6*, Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA **1993**.
- [32] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351–359.
- [33] G. M. Sheldrick SHELXTL/PC, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA **1990**.
- [34] G. M. Sheldrick, *SHELX97, Program for the Solution and Refinement of Crystal Structures* **1997**.

Received March 14, 2002

[I02129]