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Convenient synthesis of anionic dinuclear ruthenium(II) complexes $[NR_2H_2][\{RuCl(diphosphine)\}_2(\mu\text{-}Cl)_3]$ [diphosphine = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, 2,2′-bis(di(*p*-tolyl)phosphino)-1,1′-binaphthyl, and 1,2-bis(diphenylphosphino)benzene]: crystal structure of $[NEt_2H_2][\{RuCl(1,2\text{-bis(diphenylphosphino)benzene})\}_2(\mu\text{-}Cl)_3]$

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Dedicated to Professor Martin A. Bennett on the occasion of his retirement from the Australian National University and for his contribution to organometallic and inorganic chemistry.

Abstract

We report a practical one-pot synthesis of dialkylammonium salts of anionic dinuclear ruthenium complexes having chelating diphosphine ligands, BINAPs and DPB, with formula of $[NEt_2H_2][\{RuCl(diphosphine)\}_2(\mu\text{-}Cl)_3]$ [**2a**: diphosphine = 2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl; **6a**: 2,2′-bis(di(*p*-tolyl)phosphino)-1,1′-binaphthyl; **8a**: 1,2-bis(diphenylphosphino)benzene]. Treatment of cationic ruthenium complexes, $[RuCl(\eta^6\text{-}p\text{-cymene})(diphosphine)]Cl$ (**4**) with a slight excess of NEt_2H_2Cl (**5a**) afforded **2a**, **6a**, and **8a** in quantitative yields. Similar reactions with various dialkylammonium salts **5b**–**f** gave the corresponding salts, $[NR_2H_2][\{RuCl(diphosphine)\}_2(\mu\text{-}Cl)_3]$. A one-pot mixture of BINAP or its derivative, $[RuCl_2(\eta^6\text{-arene})]_2$, and NR_2H_2Cl produced salts of the anionic dinuclear complexes which can be applied as catalysts for the asymmetric hydrogenation of ketonic substrates such as acetol and methyl acetoacetate with high activity and high enantioselectivity. The anionic face-sharing bioctahedral structure of these complexes was confirmed by the X-ray analysis of **8a**, which has two hydrogen bonds between two N*H* of the diethylammonium cation and two terminal chloro-ligands. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Anionic dinuclear; Chelating diphosphines

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1. Introduction

Recently various mononuclear ruthenium(II) complexes bearing chiral diphosphines such as BINAP (BINAP = 2,2′ - bis(diphenylphosphino) - 1,1′ - binaphthyl) have extensively been applied as catalyst precursors for the asymmetric hydrogenation of olefins and ketones [1–12]. The first dinuclear Ru(II)–BINAP complex was prepared and formulated as $Ru_2Cl_4(BINAP)_2{\cdot}NEt_3$ (**1**) [13]. Despite the outstanding performance of **1** in asymmetric hydrogenation, the structure of **1** had not been revealed until we and another group reported this complex to be an anionic dinuclear complex, $[NEt_2H_2]$-$[\{RuCl(BINAP)\}_2(\mu\text{-}Cl)_3]$ (**2a**), on the basis of the crystallographic study of $[NEt_2H_2][\{RuCl((R)\text{-}p\text{-MeO-BINAP})\}_2(\mu\text{-}Cl)_3]$ [(*R*)-**3a**] [*p*-MeO-BINAP = 2,2′-bis-(di(*p*-methoxyphenyl)phosphino)-1,1′-binaphthyl] [14] and ESIMS of **2a** [15]. The original synthetic method starting from a mixture of $[RuCl_2(cod)]_n$, NEt_3, and BINAP gave **2a** with severe contamination by the hydride complex, $[RuHCl(BINAP)_2]$, which not only reduced the chemical yield of **2a** but also hampered its

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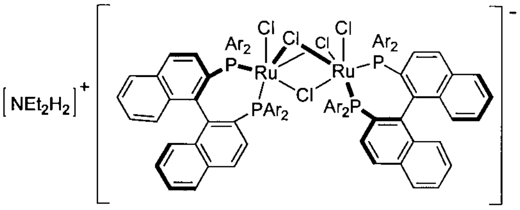
purification [13,14,16]. Thus, a more convenient synthesis of the anionic complex **2a** has been required. Herein we report a convenient one-pot synthesis of **2a** and its derivatives with high purity and high chemical yield by treating $[RuCl_2(\eta^6\text{-arene})]_2$ with BINAP and NR_2H_2Cl. James and co-workers have previously reported that the addition of NEt_2H_2Cl to the five-coordinate complex $[RuCl_2(BINAP)(PPh_3)]$ afforded complex **2a** [17].



(*R*)-**2a** Ar = C_6H_5
(*R*)-**3a** Ar = *p*-MeO-C_6H_4

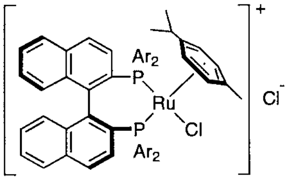
2. Results and discussion

Treatment of a cationic ruthenium complex, [RuCl(η^6-*p*-cymene)((*S*)-BINAP)]Cl [(*S*)-**4a**] [4] with a slight excess of NEt_2H_2Cl (**5a**) in THF for 6 h afforded orange (*S*)-**2a** in quantitative yield after removal of the solvent and washing. The product contained a small amount of **5a**. Similar reactions of (*S*)-**4a** with various dialkylammonium salts **5b**–**f** resulted in the quantitative formation of (*S*)-**2b**–**f**. The $^{31}P\{^1H\}$-NMR spectra of these complexes showed almost the same AB*q* signal (δ 51–57) with the same coupling constant (38 Hz) due to the chirality of the BINAP ligand, indicating that these complexes have the same anionic dinuclear geometry as **2a** and **3a** (Table 1). In the case of much bulkier dialkylammonium salts such as **5c**–**e**, the products were obtained with a slight contamination by the unidentified compound that showed another AB*q* signal at δ 53.9 and 59.3 with a coupling constant of 40 Hz in the $^{31}P\{^1H\}$-NMR spectra of the products. The reactions using ethylammonium chloride $NEtH_3Cl$ or triethylammonium chloride NEt_3HCl also afforded the corresponding complexes, whose $^{31}P\{^1H\}$-NMR spectra displayed typical AB*q* signals [δ 51.1 and 52.9 (40 Hz) for the $NEtH_3Cl$ reaction and δ 50.9 and 52.8 (38 Hz) for NEt_3HCl], while the reaction using NH_4Cl did not. Reactions of [RuCl(η^6-*p*-cymene)((*S*)-*p*-TolBINAP)]Cl [(*S*)-**4b**] [*p*-TolBINAP = 2,2′-bis(di(*p*-tolyl)phosphino)-1,1′-binaphthyl] [4] with **5a**–**c** afforded the corresponding anionic dinuclear complexes, $[NR_2H_2][\{RuCl((S)\text{-}p\text{-TolBINAP})\}_2(\mu\text{-Cl})_3]$ [(*S*)-**6**, **a**: R = Et; **b**: R = Me; **c**: R = ^{i}Pr].

Table 1
$^{31}P\{^1H\}$-NMR spectral data of anionic dinuclear ruthenium complexes bearing BINAP or its derivatives [a]

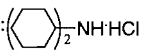
Complex	Chemical shift (δ)		Coupling constant (Hz)
2a	51.8	54.4	38
	52.3	56.5	38 in CD_2Cl_2 [16])
2b	51.5	52.8	38
2c	51.8	55.9	38
2d	51.8	55.9	38
2e	52.1	56.5	38
2f	51.5	52.8	38
3a	49.5	52.0	38
6a	49.5	51.0	38
6b	49.9	49.0	38
6c	49.6	53.3	38

[a] Measured in $CDCl_3$.

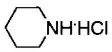


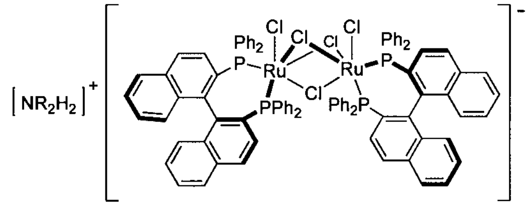
(*S*)-**4**
a: Ar = C_6H_5
b: Ar = *p*-Me-C_6H_4

5a: $Et_2NH \cdot HCl$
5b: $Me_2NH \cdot HCl$
5c: $^iPr_2NH \cdot HCl$
5d: $(PhCH_2)_2NH \cdot HCl$
5e:

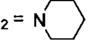


5f:





(*S*)-**2**
a: R = Et
b: R = Me
c: R = ^{i}Pr
d: R = CH_2Ph
e: R = Cy
f: NR_2 =



As the cationic mononuclear ruthenium–BINAP complex **4b** has been prepared by simply mixing $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**7b**) and *p*-TolBINAP [4], the one-pot mixture of (*S*)-*p*-TolBINAP, **7b**, and NEt_2H_2Cl in toluene produced (*S*)-**6a** in quantitative yield with high purity as expected. Similarly, (*R*)-**2b** can be derived from the mixture of (*R*)-BINAP, $[RuCl_2(\eta^6\text{-benzene})]_2$ (**7a**), and NMe_2H_2Cl. These anionic dinuclear ruthenium(II) complexes (*R*)-**2b** and (*S*)-**6a** obtained in a one-pot manner can be used for asymmetric hydrogenation of various organic substrates such as acetol and methyl acetoacetate not only with high enantioselectivity but also with increased catalytic activity, giving (*R*)-1,2-propanediol (93% ee by (*R*)-**2b**) and (*S*)-methyl 3-hydroxybutanoate (99% ee by (*S*)-**6a**).

All attempts to crystallize these anionic dinuclear complexes **2** and **6** resulted in the formation of brittle solids or jelly semisolids, not suitable for X-ray analysis. In the case of 1,2-bis(diphenylphosphino)benzene (DPB), a peraryl chelating diphosphine ligand, we ob-

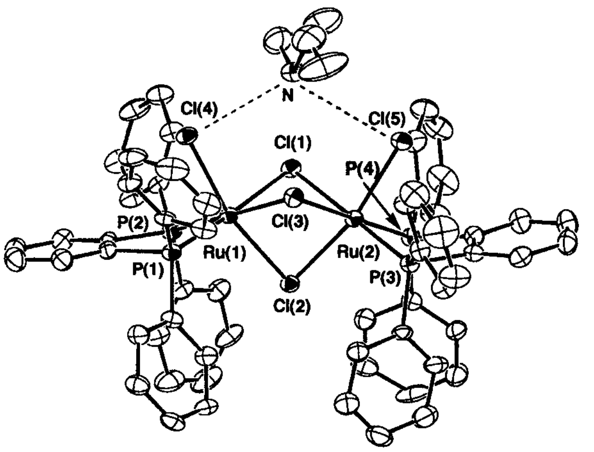
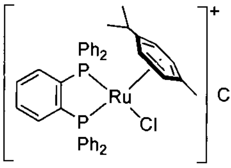


Fig. 1. ORTEP drawing of one of the two crystallographically independent ion pairs of **8a** with the numbering scheme. Hydrogen atoms are omitted for clarity.

tained crystals suitable for an X-ray crystallographic study. Thus, **8a** was prepared by the reaction of [RuCl(η^6-*p*-cymene)(DPB)]Cl (**4c**) [18] with **5a** in THF. The $^{31}P\{^1H\}$-NMR spectrum of **8a** displayed a singlet at δ 79.7, downfield-shifted compared with that (δ 64.2) of **4c**.



4c

Two crystallographically independent ion pairs of **8a** crystallized in a triclinic system and one of them is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 2. This complex has an anionic triply chloride-bridged dinuclear [(RuCl)(μ_2-Cl)$_3$(RuCl)]-core. The distance between the two adjacent ruthenium atoms, Ru(1)–Ru(2) [3.271(1) Å for molecule **I** and 3.279(1) Å for molecule **II**], is comparable to that (3.25–3.35 Å) reported for trichloro bridged Ru$_2$ complexes such as [Ru_2Cl_5(CHIRAPHOS)$_2$] [19], [$Ru_2Cl_5(PR_3)_4$] [20,21], [$Ru_2Cl_4(CS)(PPh_3)_4$] [22], [Ru_2Cl_4(DMSO)(DPPB)$_2$] (DPPB = bis(diphenylphosphino)butane) [23], [$Ru_2Cl_4(\eta^2\text{-}H_2)$(DPPB)$_2$] [17], [$Ru_2Cl_3(PR_3)_6$]$^+$ [20,21,24], and (*R*)-**3a** [14], being well outside the range (2.28–2.95 A) expected for a Ru–Ru single bond [20,21,25–28]. Furthermore, it is of interest that an isoelectronic carbonyl complex, [$\{RuCl(CO)_2\}_2$-(μ-Cl)$_3$]$^-$ also adopts the face-sharing bioctahedral structure [29].

Each ruthenium center adopts a pseudo-octahedral structure, as expected for d^6 Ru(II), defined by the two phosphorus atoms of the DPB ligand and four chlorine atoms. The bridging chloride Cl(2) *trans* to a terminal chlorine atom has a shorter Ru–Cl distance (2.417(2)–2.448(2) Å) than those (2.479(2)–2.515(2) Å) of the bridging chlorides *trans* to phosphorus atoms due to the weaker *trans* effect of the Cl ligand compared with that of the phosphine ligand. Each DPB ligand forms a puckered five-membered-chelate.

The presence of two hydrogen bonds between the two N*H* of the diethylammonium cation and two terminal chloro-ligands, Cl(4) and Cl(5), is revealed by the short distances N–Cl(4) [3.250(9) Å for molecule **I** and 3.290(9) Å for molecule **II**] and N–Cl(5) [3.346(9) Å for molecule **I** and 3.224(10) Å for molecule **II**]. It is noteworthy that the diethylammonium chloride plays

Table 2
Selected bond distances (Å) and angles (°) of **8a**

	Molecule **I**	Molecule **II**
Ru(1)···Ru(2)	3.271(1)	3.279(1)
Ru(1)–Cl(1)	2.515(2)	2.493(2)
Ru(1)–Cl(2)	2.433(2)	2.437(2)
Ru(1)–Cl(3)	2.479(2)	2.479(2)
Ru(1)–Cl(4)	2.411(2)	2.412(2)
Ru(1)–P(1)	2.234(2)	2.239(2)
Ru(1)–P(2)	2.222(2)	2.231(2)
Ru(2)–Cl(1)	2.508(2)	2.501(2)
Ru(2)–Cl(2)	2.417(2)	2.448(2)
Ru(2)–Cl(3)	2.485(2)	2.506(2)
Ru(2)–Cl(5)	2.416(2)	2.417(2)
Ru(2)–P(3)	2.231(2)	2.240(2)
Ru(2)–P(4)	2.242(2)	2.235(2)
Cl(1)–Ru(1)–Cl(2)	79.10(7)	80.51(8)
Cl(1)–Ru(1)–Cl(3)	83.11(7)	84.18(7)
Cl(1)–Ru(1)–Cl(4)	91.05(7)	90.81(9)
Cl(1)–Ru(1)–P(1)	176.18(8)	94.75(8)
Cl(1)–Ru(1)–P(2)	95.63(8)	177.31(9)
Cl(2)–Ru(1)–Cl(3)	80.41(7)	78.96(8)
Cl(2)–Ru(1)–Cl(4)	165.96(8)	164.77(8)
Cl(2)–Ru(1)–P(1)	104.48(8)	103.84(9)
Cl(2)–Ru(1)–P(2)	99.20(8)	100.51(9)
Cl(3)–Ru(1)–Cl(4)	88.57(8)	87.78(9)
Cl(3)–Ru(1)–P(1)	96.08(8)	176.83(9)
Cl(3)–Ru(1)–P(2)	178.72(8)	98.45(8)
Cl(4)–Ru(1)–P(1)	85.20(8)	89.25(9)
Cl(4)–Ru(1)–P(2)	91.64(8)	88.73(9)
P(1)–Ru(1)–P(2)	85.20(9)	82.59(9)
Cl(1)–Ru(2)–Cl(2)	79.56(7)	80.14(8)
Cl(1)–Ru(2)–Cl(3)	83.14(7)	83.48(8)
Cl(1)–Ru(2)–Cl(5)	90.82(8)	88.75(8)
Cl(1)–Ru(2)–P(3)	176.48(8)	98.29(9)
Cl(1)–Ru(2)–P(4)	97.83(8)	176.52(9)
Cl(2)–Ru(2)–Cl(3)	80.60(7)	78.24(8)
Cl(2)–Ru(2)–Cl(5)	166.86(8)	166.10(9)
Cl(2)–Ru(2)–P(3)	100.15(8)	99.85(9)
Cl(2)–Ru(2)–P(4)	100.70(8)	102.70(8)
Cl(3)–Ru(2)–Cl(5)	89.44(8)	92.30(8)
Cl(3)–Ru(2)–P(3)	96.39(8)	177.19(9)
Cl(3)–Ru(2)–P(4)	178.49(9)	95.08(9)
Cl(5)–Ru(2)–P(3)	89.40(8)	89.93(9)
Cl(5)–Ru(2)–P(4)	89.39(8)	88.14(8)
P(3)–Ru(2)–P(4)	82.63(8)	83.3(1)

an important role in the formation of the anionic dinuclear structure through the two NH···Cl hydrogen bonds. We have already reported that the release of the arene ligand bound to the ruthenium of **4** led to the formation of a cationic trinuclear complex $[Ru_3Cl_5(BINAP)_3]^+$, which was found to be inert in catalytic hydrogenation owing to the lack of a coordination site available for substrates and/or hydrogen [30]. The anionic dinuclear complexes, on the other hand, can readily generate a coordination site by eliminating the dialkylammonium chloride, and hence showed high catalyst performance. Dinuclear complexes, in fact, have been previously reported to catalyze hydrogenation [31,32].

In conclusion, we have demonstrated a practical one-pot synthesis of anionic dinuclear ruthenium complexes having chelating diphosphine ligands, BINAPs and DPB. The BINAP complexes showed high catalytic activity in the asymmetric hydrogenation of ketonic substrates. This synthetic procedure requires no difficult manipulations.

3. Experimental

3.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under argon. Mononuclear cationic ruthenium complexes [RuCl(η^6-*p*-cymene)((*S*)-BINAP)]Cl (**4a**) [4], [RuCl(η^6-*p*-cymene)((*S*)-*p*-TolBINAP)]Cl (**4b**) [4], and [RuCl(η^6-*p*-cymene)(DPB)]Cl (**4c**) [18] were prepared according to the literature procedures. ^{1}H (270 MHz and 300 MHz) and ^{31}P(109.25 and 121.49 MHz)-NMR spectra were measured on a JEOL JNM-GSX-270 spectrometer and a Varian MERCURY 300 spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 microanalyzer. All melting points were measured in sealed tubes and were not corrected.

3.2. Preparation of *2a*

A solution of (*S*)-**4a** (29.4 mg, 0.032 mmol) and NEt_2H_2Cl (3.7 mg, 0.032 mmol) in THF (15 ml) was heated for 6 h to give an orange solution, from which complex (*S*)-**2a** was obtained in quantitative yield after removal of the solvent and washing. Similar reactions gave complexes **2b**–**f** and **6a**–**c**, which were characterized by their $^{31}P\{^1H\}$-NMR spectra.

3.3. One-pot synthesis of (R)-*2b*

To a mixture of $[RuCl_2(\eta^6\text{-benzene})]_2$ (**7a**, 0.25 g, 0.5 mmol), (*R*)-BINAP (0.63 g, 1.0 mmol), and NMe_2H_2Cl (83 mg, 1.0 mmol) placed in a 250 ml Schlenk tube was added dry 1,4-dioxane (75 ml). This reddish suspension was heated at 50°C with stirring for 2 h, then refluxed with stirring for 12 h. The resulting clear red–brown solution was cooled to room temperature (r.t.), and the solvent was removed under vacuum to leave brown solids of (*R*)-**2b** in quantitative yield.

3.4. Asymmetric hydrogenation of 2-oxo-1-propanol (acetol) using (R)-*2b* prepared in a one-pot manner

The above catalyst (*R*)-**2b** (83.5 mg, 0.05 mmol) was introduced into a 200 ml stainless steel autoclave. The atmosphere was replaced with nitrogen, then substrate (14.82 g, 200 mmol, $S/C = 4000$) and methanol (30 ml) were added. The nitrogen atmosphere was replaced with hydrogen (1 Mpa) and then the mixture was stirred at 65°C for 16 h. The reaction product, (*R*)-1,2-propanediol (quantitative yield), was analyzed by means of gas chromatography (column: α-DEX 120 (Supelco Inc.)) and 92.8% ee was found.

3.5. One-pot synthesis of (S)-*6a*

To a mixture of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**7b**, 0.31 g, 0.5 mmol), (*S*)-*p*-TolBINAP (0.68 g, 1.0 mmol), and NEt_2H_2Cl (0.11 g, 1.0 mmol) placed in a 250 ml Schlenk tube was added dry toluene (50 ml). The reddish suspension was heated at 50°C with stirring for 2 h, and then refluxed with stirring for 12 h. After the resulting clear red–brown solution was cooled to r.t., all volatiles were removed under vacuum to leave brown solids in quantitative yield.

3.6. Asymmetric hydrogenation of methyl acetoacetate using (S)-*6a* prepared in a one-pot manner

The above catalyst (*S*)-**6a** (18.1 mg, 0.01 mmol) was introduced into a 200 ml stainless steel autoclave. The atmosphere was replaced with nitrogen, then substrate (11.61 g, 100 mmol, $S/C = 10\,000$) and methanol (20 ml) were added. The nitrogen atmosphere was replaced with hydrogen (3 Mpa) and then the mixture was stirred at 50°C for 12 h. The reaction product, (*S*)-methyl 3-hydroxybutanoate (quantitative yield), was analyzed by means of gas chromatography (column: Chiraldex B-TA (ASTEC Inc.)) and 99.2% ee was found.

3.7. Preparation of *8a*

A reaction mixture containing **4c** (180 mg, 0.259 mmol) and NEt_2H_2Cl (56.7 mmol, 0.517 mmol) in THF (60 ml) was heated to reflux for a period of 9 h, giving an orange–yellow solution. All volatiles were removed under reduced pressure. The resulting residue was re-

Table 3
Crystal and refinement data for **8a**

Formula	$C_{65}H_{62}NCl_7P_4Ru_2$
Formula weight	1431.618
Crystal system	Triclinic
Space group	$P\bar{1}$ (#2)
a (Å)	15.700(4)
b (Å)	33.96(1)
c (Å)	13.137(4)
α (°)	98.48(3)
β (°)	104.04(2)
γ (°)	87.74(2)
Z	4
V (Å^3)	6720(3)
D_{calc} (g cm^{-3})	1.415
Radiation	Mo–K$_\alpha$
Reflections measured	$+h$, $+k$, $\pm l$
Crystal size (mm)	0.27 × 0.20 × 0.17
Absorption coefficient (cm^{-1})	8.61
Scan mode	ω
Temperature (°C)	23
2θ max (°)	55.1
Data collected	31 990
Unique data	30 851 ($R_{int} = 0.072$)
No. of observations	30 837
No. of variables	1423
R [$I > 3\sigma(I)$]	0.064
R_w [$I > 3\sigma(I)$]	0.064
R_1 (all data)	0.189
wR_2 (all data)	0.190
Goodness-of-fit on F^2	1.38
Largest difference peak and hole (e Å^{-3})	2.28 and −1.91

crystallized from a mixture of dichloromethane (15 ml) and hexane (15 ml). Orange–yellow crystals of **8a** (87.4 mg, 47% yield) were obtained; m.p. 284–286 (dec.). ^{1}H-NMR (270 MHz, $CDCl_3$, 30°C): δ 1.09 (t, $^2J_{HH} = 7.3$ Hz, 6H, $-CH_2C\mathit{H}_3$), 2.92 (m, 4H, $-C\mathit{H}_2CH_3$), 6.8–7.7 (m, 48H, aromatic protons), 8.16 (broad s, 2H, H_2N). $^{31}P\{^1H\}$-NMR (109 MHz, $CDCl_3$, 30°C): δ 79.7 (s). Elemental analyses showed that **8a** crystallized with free diethylammonium chloride, and thus did not give a satisfactory result.

*3.8. Crystal structure determination of **8a***

Single crystals suitable for X-ray measurements were obtained by recrystallization of **8a** from a mixture of dichloromethane and hexane. A crystal of **8a** was sealed in a glass capillary under an argon atmosphere, and then was mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo–K$_\alpha$ (graphite monochromated, $\lambda = 0.71069$) radiation. Relevant crystal and data statistics are summarized in Table 3. The unit cell parameters and the orientation matrix at 23°C were determined by a least-squares fit to 2θ values of 25 strong higher reflections. Three standard reflections were chosen and monitored every 150 reflections. An empirical absorption correction was applied on the basis of azimuthal scans. The data was corrected for Lorentz and polarization effects.

The structure of complex **8a** was solved by a direct method (SHELXS-86) [33] and refined by the full-matrix least-squares method. Measured non-equivalent reflections were used for the structure determination. In the subsequent refinement, the function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma(\omega F_o^4)]^{1/2}$. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed. All calculations were performed using the TEXSAN crystallographic software package.

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