Metal Complexes of Biologically Important Ligands, CLXXV [1]. Pentamethylcyclopentadienyl Halfsandwich Complexes of Rhodium(III) and Iridium(III) with Schiff Bases from 2-(Diphenylphosphino)-benzaldehyde and α-Amino Acid Esters

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Dedicated to Professor Rolf Huisgen on the occasion of his 90th birthday

The reactions of the chlorido-bridged complexes $[Cp^*M(Cl)(\mu\text{-}Cl)]_2$ (M = Rh, Ir) with Schiff bases (P-N-O) from 2-(diphenylphosphino)benzaldehyde and α-amino acid esters afford the complexes $Cp^*M(Cl)_2$(P-N-O) in which the ligands function as monodentate P donors (M = Ir) or as bidentate P-N donors (M = Rh). These complexes can be converted into cationic complexes $[Cp^*M(Cl)(P\text{-}N\text{-}O)]^+$ with bidentate P-N ligands by treatment with NH_4PF_6. The cationic complexes $[Cp^*M(Cl)(P\text{-}N\text{-}O)]^+Cl^-$ have been detected also in solutions of $Cp^*M(Cl)_2$(P-N-O). The P-N-coordinated complex $[Cp^*Rh(Cl)(Ph_2P\text{-}C_6H_4\text{-}C(H)=N\text{-}C(H)(CH_2Ph)CO_2Me)]^+PF_6^-$ was characterized by X-ray diffraction. From $Cp^*M(Cl)_2$(P-N-O) and $AgBF_4$ or $AgPF_6$ (molar ratio 1 : 2) the dicationic complexes $[Cp^*M(P\text{-}N\text{-}O)]^{2+}$ are formed in which the ester group is also coordinated to the metal atom. The Schiff base from 2-(diphenylphosphino)benzaldehyde and allylglycine ester acts as a tridentate ligand, however with coordination of the C=C allyl group instead of the ester function.

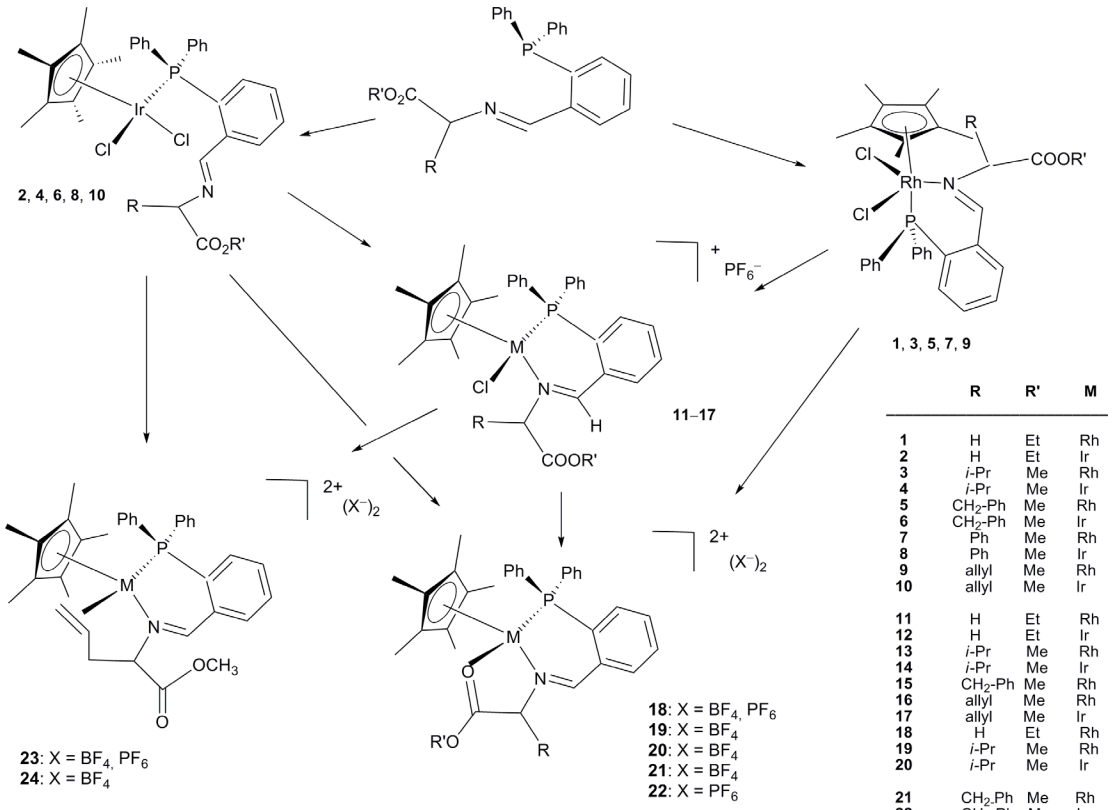
Key words: Pentamethylcyclopentadienyl, Rhodium, Iridium, Schiff Bases, 2-(Diphenylphosphino)benzaldehyde, α-Amino Acid Esters

Introduction

Schiff bases from 2-(diphenylphosphino)benzaldehydes [2 – 4] and amines are valuable ligands [5]. Their complexes derived from optically active amines have been used for asymmetric reactions and catalyses [5]. Recently, we have reported on a series of palladium(II) and platinum(II) complexes with Schiff bases from (2-formylphenyl)diphenylphosphine and α-amino acid esters [1]. Brunner and coworkers [6] have used a P-N ligand obtained from 2-(diphenylphosphino)benzaldehyde and *tert*-butyl-*tert*-leucinate for asymmetric catalysis, and several Schiff bases from 2-(diphenylphosphino)benzaldehyde and dipeptide amides have been employed as ligands for asymmetric conjugate addition of allyl zinc reagents [7].

Results and Discussion

The racemic Schiff bases from 2-(diphenylphosphino)benzaldehyde and α-amino acid esters react as many other N and P donors [8] with the chlorido-bridged complexes $Cp^*(Cl)M(\mu\text{-}Cl)_2M(Cl)Cp^*$ (M = Rh, Ir) [9, 10] under cleavage of the Cl bridges to give the complexes **1** – **10** (Scheme 1). The complexes **3** – **10** form isomers in solution (see below). The neutral compounds **1** – **5**, **9** and **10** are converted into the cationic complexes **11** – **17** by treatment with NH_4PF_6. Abstraction of all chlorido ligands in **1**, **3** – **6**, **10** and **16** – using $AgBF_4$ – affords the dicationic complexes **18** – **24**, whereby in **18** – **22** coordination of the ester group takes place whereas in the *C*-allylglycine-containing complexes **23** and **24** the C=C double bond is coordinated to the metal atom (Scheme 1). The preference of the "soft" C=C bond over the "hard" ester group in coordination is in accordance with Maitlis [9] description of $[Cp^*ML_3]^{2+}$ complexes (L = acetone, MeCN, py, ...) as "soft centers with hard shells". The complexes **23** and **24** can be compared with $[Cp^*Ir(NH_2C(H)(CH_2CH=CH_2)CO_2)]^+$ in which allylglycinate functions as a tridentate ligand [11]. Half-sandwich complexes – similar to **11** – **17** – have been



	R	R'	M
1	H	Et	Rh
2	H	Et	Ir
3	*i*-Pr	Me	Rh
4	*i*-Pr	Me	Ir
5	CH_2-Ph	Me	Rh
6	CH_2-Ph	Me	Ir
7	Ph	Me	Rh
8	Ph	Me	Ir
9	allyl	Me	Rh
10	allyl	Me	Ir
11	H	Et	Rh
12	H	Et	Ir
13	*i*-Pr	Me	Rh
14	*i*-Pr	Me	Ir
15	CH_2-Ph	Me	Rh
16	allyl	Me	Rh
17	allyl	Me	Ir
18	H	Et	Rh
19	*i*-Pr	Me	Rh
20	*i*-Pr	Me	Ir
21	CH_2-Ph	Me	Rh
22	CH_2-Ph	Me	Ir
23	allyl	Me	Rh
24	allyl	Me	Ir

Scheme 1.

obtained with bidentate Schiff bases from salicylaldehyde and α-amino acid esters [12]. The complexes **11** – **24** are Brunner-type compounds [13] with four different ligands and with an "asymmetric" metal atom. Therefore, with α-amino acid esters (except glycine) two diastereomers (as pairs of enantiomers S_MS_C/R_MR_C and S_MR_C/R_MS_C) are formed which could be detected in the NMR spectra particularly by their ^{31}P NMR signals. For **24** one diastereoisomer could be separated by repeated extraction of the product with dichloromethane. In the *C*-allylglycine derivatives **23** and **24** three stereogenic centers (metal atom, α-C, γ-C) are formed by coordination; of the four possible diastereoisomers only two could be detected by NMR spectroscopy, as was also found for the allylglycinate complex $[Cp^*Ir(NH_2C(H)(CH_2\text{-}CH{=}CH_2)CO_2)]^+$ [11].

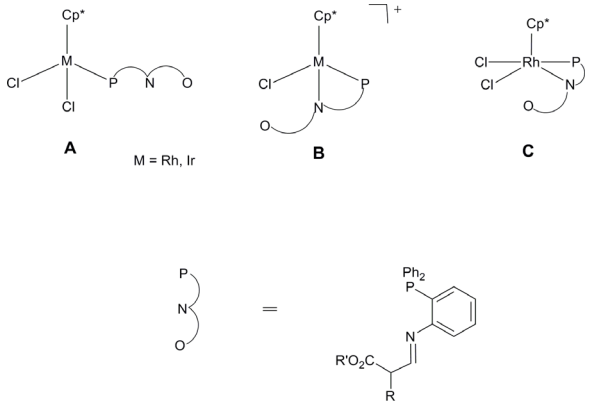
In the IR spectra of **18** – **22** the CO absorption of the coordinated ester group is typically shifted by 64 – 111 cm^{-1} to lower frequencies [14] compared to that in **1** – **17** with free ester groups. The almost unchanged

Table 1. ^{31}P NMR data of the iridium complexes **2**, **4**, **6**, **8**, **10**, **12**, **14**, **17**, **20**, and **24** (δ in ppm rel. to H_3PO_4 as external standard, ^{1}H-decoupled).

	A		B		
	δ	Ratio of isomers (%)	δ	Ratio of isomers (%)	Solvent
2	4.6s	100	–	–	$CDCl_3$
4	4.4s; br	80	12.7s	5	CD_2Cl_2
			13.3s	15	
4	–	–	13.7s	64	CH_3OH
			13.2s	36	
6	4.0s	95	8.8s	2	$CDCl_3$
			10.1s	3	
8	4.1s	94	11.1s	2	$CDCl_3$
			11.4s	4	
10	4.4s; br	93	11.2s	2.5	$CDCl_3$
			10.4s	4.5	
12			10.2s	100	CD_2Cl_2
14			13.6s	29	$CDCl_3$
			12.8s	71	
17			11.2s	29	$CDCl_3$
			10.2s	71	
20			14.5s	43	CD_2Cl_2
			12.2s	57	
24			3.3s	100	CD_2Cl_2

Table 2. ^{31}P NMR data of the rhodium complexes **1**, **3**, **5**, **7**, **9**, **11**, **13**, **16**, **18**, **19**, **21**, and **23** (δ in ppm rel. to H_3PO_4 as external standard, ^{1}H-decoupled, $J = {}^1J(^{103}\text{Rh-}^{31}\text{P})$ in Hz).

			B		**C**		**A**		
	δ	Ratio of isomers (%)	δ	Ratio of isomers (%)	δ	Ratio of isomers (%)	δ	Ratio of isomers (%)	Solvent
1	–		–		32.9d, J = 136.5	100	–		$CDCl_3$
1	–		36.8d, J = 137.8	100					CH_3OH
3	71.7d, J = 174.1	11	39.5d, J = 138.5	8	30.7d, J = 145.9	24	29.5d, J = 145.9	1	$CDCl_3$
			43.0d, J = 143.9	1	31.3d, J = 143.2	54			
3	–		39.5d, J = 139.8	93	–		–		$HOCH_3$
			43.3d, J = 143.9	7					
5	–		33.0d, J = 134.4	100	–		–		$CDCl_3$/[D_6]acetone
7	71.9d, J = 174.1	17	34.3d, J = 136.5	3	30.7d, J = 145.9	27	29.2d, J = 145.9	3	$CDCl_3$
			35.1d, J = 137.8	32	31.2d, J = 147.9	18			
9	71.7d, J = 174.1	19	34.2d, J = 136.4	28	31.2d, br	47	29.6d, J = 145.8	3	$CDCl_3$
11			36.0d, J = 137.8	100					CD_2Cl_2
13			42.8d, J = 143.9	8					CD_2Cl_2
			39.3d, J = 138.5	92					
15			32.1d, J = 135.9	100					CD_2Cl_2
16			34.1d, J = 136.5	92					CD_2Cl_2
			37.9d, J = 138.5	8					
18			34.5d, J = 133.0	100					CD_2Cl_2
19			34.7d, J = 136.7	50					CD_2Cl_2
			32.1d, J = 144.0	50					
21			35.4d, J = 137.3	67					CD_2Cl_2
			33.2d, J = 142.0	33					
23			37.3d, J = 115.6	75					CD_2Cl_2
			35.9d, J = 116.3	25					



Scheme 2.

CO absorption and the shift of the band of the C=C bonds by 135 cm^{-1} to lower frequencies show in accordance with the NMR spetra that in **23** and **24** the allyl group is preferred for coordination. The ν(M-Cl) absorption in **1**–**17** appears at 260–300 cm^{-1}, and **11**–**24** exhibit the absorption of the BF_4^- (1050 cm^{-1}) or the PF_6^- anion (840 cm^{-1}).

Particularly the ^{31}P NMR spectra (Tables 1–2) proved to be very useful for the identification of the type of complexes and their isomers. The iridium complexes **2**, **4**, **6**, **8**, and **10** exhibit an intense ^{31}P NMR signal (Table 1) at δ = 4 (in $CDCl_3$ solution) which we assign to complex type **A** (Scheme 2). By comparison with the ionic PF_6 complexes **12** and **14** the second signal pattern of **4**, **6**, **8**, and **10** at δ = 10–13 can be attributed to the ionic type **B** which for R $\neq$ H appears as a mixture of two diastereoisomers. In accordance with this assignment for **4** only the ionic form **B** was detected in methanol solution (Table 2).

All the ^{31}P signals of the rhodium complexes (Table 2) appear as doublets due to the ^{103}Rh-^{31}P coupling. Our assignment of the ^{31}P NMR signals of the rhodium complexes is shown in Table 2. Three types of complexes **A**–**C** can be recognized (Scheme 2). For **3**, **7**, and **9** four isomers could be observed in solution. The ^{31}P NMR signal of **3**, **7**, and **9** at δ = 30 (Table 2) is comparable with that of $Cp^*Rh(Cl)_2(Ph_2PCl_2CH_2NEt_2)$ [15]. Another example for this type **A**, which cannot form diastereoiso-

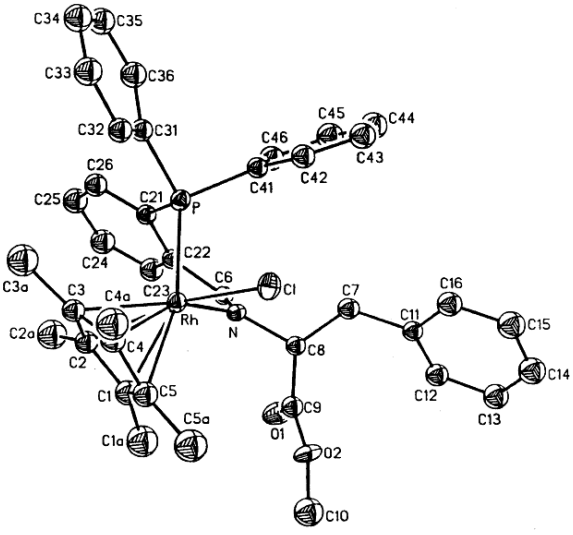


Fig. 1. Molecular structure of **15** in the crystal. Selected bond lengths (pm) and angles (deg): Rh–Cl 239.4(4), Rh–N 213.1(8), Rh–P 231.9(3), N–C6 127(1), N–C6 127(1), C6–C22 148(1), N–C8 149(1), Rh–C1 219(1), Rh–C2 216(1), Rh–C3 220(1), Rh–C4 217(1), Rh–C5 219(1); Cl–Rh–N 93.1(2), Cl–Rh–P 94.0(1), N–Rh–P 79.6(2), Rh–N–C6 126.1(7), C6–N–C8 116.8(8), C7–C8–C9 109.8(9).

mers, is Cp*Rh(Cl)$_2$CNR [16]. The signal at δ = 72 for **3**, **7**, and **9** could not be assigned. The single ^{31}P NMR signal for **24** can be explained by a large difference of the solubility of the two diastereoisomers leaving only one of these in solution. The ionic species (type **B**) of **1**, **3**, **5**, **7**, **9**, **11**, **13**, **15**, **16**, **18**, **19**, **21**, **23** show ^{31}P NMR signals at δ = 35 – 40 (Table 2). An exception is complex **1**, the glycine derivative, which occurs both in $CDCl_3$ and CH_3OH solution as a single isomer for which we assume the neutral 20 electron pentacoordinated structure **C**.

The complexes of type **B** with P-N chelating ligands again appear as two diastereoisomers with the exception of the phenylalanine derivative **15** for which only one doublet signal could be detected suggesting the formation of a single isomer in solution. This finding may be explained by Brunners "β-phenyl effect" [17], *i. e.* the interaction of the cyclopentadienyl ring with the phenyl group. In the ^{1}H NMR spectrum of the glycine derivatives **1**, **2**, **11**, and **12** the signals of the α-CH_2 group are characteristic for coordination of the P-N Schiff bases. Whereas for **1** a CH_2 singlet is observed, AB spin systems are found for the diastereotopic α-CH_2 protons in the P-N chelate ligand in **2**, **11**, and **12**. For the complexes **13**, **14**, **16**, **17**, **19**, **20**, **21**, and **23** two sets of ^{1}H NMR signals were detected, due to the two diastereoisomers. Also in the ^{13}C NMR spectra of **19** and **20** two sets of signals were observed.

The solid-state structure of **15** was determined by X-ray diffraction. Crystals of **15** were obtained by layering a concentrated CH_2Cl_2 solution of **15** with *n*-hexane. The "three-legged piano stool" structure of **15** is shown in Fig. 1 with selected bond lengths and bond angles. Rh–Cl, Rh–C(Cp*) and Rh–N distances comparable to **15** were found, *e. g.* for [Cp*Rh(Cl)(phen)]$^+$ [18] or [Cp*Rh(Cl)(Ph$_2$PCH$_2$CH$_2$NEt$_2$)$_2$]$^+$ [15]. Complex **15** crystallizes as pairs of enantiomers ($R_{Rh}S_{\alpha-C}$)-($S_{Rh}R_{\alpha-C}$).

Experimental Section

The complexes [Cp*M(Cl)(μ-Cl)]$_2$ (M = Rh, Ir) [10] and 2-(diphenylphosphino)benzaldehyde [3] were prepared as described. Unless otherwise noted the NMR spectra were recorded with a Jeol GSX-270 spectrometer.

*Neutral complexes **1** – **10***

*Example complex **2***: [Cp*IrCl$_2$]$_2$ (159 mg, 0.2 mmol) and 2-(diphenylphosphino)benzaldehyde (160 mg, 0.43 mmol) in benzene (10 mL) were heated under reflux for 75 min. The mixture was allowed to cool to r. t. and layered with *n*-hexane (3 mL). After 12 h the precipitate was isolated, washed twice with diethyl ether (10 mL each) and dried *in vacuo* at 60 °C. Complexes **1**, **3** – **10** were prepared by analogous procedures.

1: Orange. Yield 42 %. M. p. 179 – 181 °C. – IR (Nujol, cm^{-1}): ν = 1750s (CO), 1618s (C=N), 280m, 252m (Rh-Cl). – ^{1}H NMR ($CDCl_3$): δ = 9.21 (s, 1H, N=CH), 5.08 (dd, 2H, α-CH), 3.90 (m, 2H, Et), 1.10 (t, 3H, J = 7.1 Hz, Et), 146 (d, 15H, J(H-P) = 3.7 Hz, Cp*). – ^{13}C NMR ($CDCl_3$): δ = 178.0 (d, J(C-P) = 7.3 Hz, C=N), 166.6 (CO), 101.9 (dd, J(C-P) = 3.1 Hz, J(C-Rh) = 9.4 Hz, C_5), 61.5, 13.8 (Et), 9.2 (s, Cp*Me). – $C_{33}H_{37}Cl_2NO_2PRh$ (684.5): calcd. C 57.91, H 5.45, N 2.05; found C 57.15, H 5.63, N 2.05.

2: Orange. Yield 88 %. M. p. 179 – 182 °C. – IR (Nujol, cm^{-1}): ν = 1748s (CO), 1630m (C=N), 288m, 269m (Ir-Cl). – ^{1}H NMR ($CDCl_3$): δ = 9.03 (s, 1H, N=CH), 4.23 (s, 2H, α-CH), 4.13 (q, 2H, Et), 1.24 (t, 3H, J = 7.1 Hz, Et), 1.37 (d, 15H, J(H-P) = 2.0 Hz, Cp*). – ^{13}C NMR (CD_2Cl_2): δ = 165.6 (d, J(C-P) = 7.1 Hz, C=N), 170.4 (CO), 92.9 (d, J(C-P) = 3.7 Hz, C_5), 60.7 (α-C), 60.6, 14.1 (Et), 8.2 (s, Me, Cp*). – $C_{33}H_{37}Cl_2NO_2IrP \cdot {}^1/_2\,C_6H_6$ (812.8): calcd. C 53.20, H 4.96, N 1.72; found C 53.14, H 5.08, N 1.93.

3: Red. Yield 71 %. M. p. 174 – 176 °C. – IR (Nujol, cm^{-1}): ν = 1733s (CO), 1619m (C=N), 278m, 262m (Rh-Cl). – $C_{35}H_{41}Cl_2NO_2PRh$ (712.5): calcd. C 59.00, H 5.80, N 1.97; found C 59.17, H 6.11, N 1.97.

4: Orange. Yield 69 %. M. p. 147 – 149 °C. – IR (Nujol, cm^{-1}): ν = 1737s (CO), 1626m (C=N), 286m, 260m (Ir-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.89 (s, 1H, N=CH), 3.79 (d, 1H, *J*(H-H) = 10.9 Hz, α-C), 2.10 (m, 1H, β-CH), 0.65 (s, br, 6H, γ-CH), 3.62 (s, br, 3H, OMe), 1.33 (d, 15H, *J*(H-P) = 2.1 Hz, Cp*). – ^{13}C NMR (CD_2Cl_2): δ = 164.2 (d, *J*(C-P) = 8.9 Hz, C=N), 93.5 (d, *J*(C-P) = 3.2 Hz, C_5), 78.1 (α-C), 32.2 (β-C), 18.5, 19.7 (γ-C), 51.8 (OMe), 8.5 (s, MeCp*). – $C_{35}H_{41}Cl_2NO_2IrP$ (801.8): calcd. C 52.43, H 5.15, N 1.75; found C 51.98, H 5.18, N 1.90.

5: Orange. Yield 75 %. M. p. 158 – 161 °C. – IR (Nujol, cm^{-1}): ν = 1743s (CO), 1625m (C=N), 279m, 259m (Rh-Cl). – $C_{39}H_{41}Cl_2NO_2PRh$ (760.6): calcd. C 61.59, H 5.43, N 1.84; found C 60.89, H 5.31, N 1.96.

6: Orange. Yield 71 %. M. p. 219 °C. – IR (Nujol, cm^{-1}): ν = 1743s (CO), 1622m (C=N), 290m, 268m (Ir-Cl). – ^{1}H NMR ($CDCl_3$): δ = 9.19 (s, 1H, N=CH), 4.30 (d, br, 1H, α-CH), 3.00 (d, br, 1H, β-CH), 3.57 (s, br, 3H, OMe), 2.1 (s, br, 1H, β-CH), 1.36 (s, br, 15H, Cp*). – ^{13}C NMR (CD_2Cl_2): δ = 164.7 (d, *J*(C-P) = 7.2 Hz, C=N), 171.0 (CO), 93.5 (d, *J*(C-P) = 3.2 Hz, C_5), 73.7 (α-C), 52.0 (OMe), 40.7 (β-C), 8.5 (s, MeCp*). – $C_{39}H_{41}Cl_2NO_2IrP$ (849.8): calcd. C 55.11, H 4.86, N 1.65; found C 54.82, H 4.81, N 1.49.

7: Red. Yield 78 %. M. p. 179 – 181 °C. – IR (Nujol, cm^{-1}): ν = 1751s, 1733sh (CO), 1626m (C=N), 278m, 266m (Rh-Cl). – $C_{38}H_{39}Cl_2NO_2PRh \cdot 1/2\ CH_2Cl_2$ (789.0): calcd. C 58.61, H 5.11, N 1.78; found C 57.96, H 5.41, N 1.75.

8: Orange. Yield 90 %. M. p.188 °C. – IR (Nujol, cm^{-1}): ν = 1749m (CO), 1624m (C=N), 288m, 264m (Ir-Cl). – ^{1}H NMR ($CDCl_3$): δ = 9.11 (s, 1H, N=CH), 5.19 (s, 1H, α-CH), 3.65 (s, br, 3H, OMe), 1.36 (s, br, 15H, Cp*). – $C_{38}H_{39}Cl_2NO_2IrP$ (835.8): calcd. C 54.61, H 4.70, N 1.68; found C 54.19, H 5.14, N 1.63.

9: Orange. Yield 83 %. M. p. 140 – 145 °C. – IR (Nujol, cm^{-1}): ν = 1741s (CO), 1625m (C=N), 1641m (C=C), 290sh, 260sh (Rh-Cl). – $C_{35}H_{39}Cl_2NO_2Rh \cdot C_6H_6$ (788.6): calcd. C 62.45, H 5.75, N 1.78; found C 62.88, H 5.63, N 2.02.

10: Orange. Yield 68 %. M. p. 173 – 178 °C. – IR (Nujol, cm^{-1}): ν = 1742s (CO), 1624m (C=N), 1641w (C=C), 291m, 263m (Ir-P). – ^{1}H NMR (CD_2Cl_2): δ = 9.04 (m, br, 1H, N=CH), 6.82 – 8.38 (17H, arom.), 5.13 (br, 1H, *H*C=CH_2), 4.95 (br, 1H, HC=CH*H trans*), 4.87 (br, 1H, HC=CH*H cis*), 4.16 (br, 1H, α-CH), 3.66 (br, 3H, OMe), 2.41, 2.13 (br, 1H, β-CH), 1.37 (d, 15H, *J*(H-P) = 2.2 Hz, Cp*). – ^{13}C NMR (CD_2Cl_2): δ = 164.3 (d, *J*(C-P) = 7.9 Hz, C=N), 172.5 (CO), 93.0 (d, *J*(C-P) = 3.2 Hz, C_5), 117.6 (δ-C), 71.0 (α-C), 51.8 (OMe), 37.9 (d, *J*(C-P) = 2.6 Hz, β-C), 8.3 (s, MeCp*). – $C_{35}H_{39}Cl_2NO_2IrP \cdot 1/2\ C_6H_6$ (838.9): calcd. C 54.41, H 5.05, N 1.67; found C 53.91, H 5.05, N 1.72.

*Monocationic complexes **11** – **17***

*Example **12***: To the orange solution of complex **2** (40 mg, 0.05 mmol) in methanol (3 mL) a cold, aqueous solution, saturated with NH_4PF_6, was added dropwise until the solution over the precipitate turned colorless. The precipitate was washed four times with water (8 mL each). After drying over P_2O_5 the product was washed with diethyl ether (5 mL) and recrystallized from CH_2Cl_2 / $O(C_2H_5)_2$. Analogous procedures were used for the preparation of complexes **11** and **13** – **17**.

11: Orange. Yield 95 %. M. p. 190 – 191 °C. – IR (Nujol, cm^{-1}): ν = 1742s, 1748s (CO), 1622m (C=N), 835vs (PF_6), 275sh, 286w (Rh-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.39 (ψt, 1H, N=CH), 4.81 (dd, 2H, α-CH), 4.11 (q, 2H, Et), 1.39 (d, 15H, J(H-P) = 3.9 Hz, Cp*), 1.23 (t, 3H, *J*(H-H) = 7.0 Hz, Et). – ^{13}C NMR (CD_2Cl_2): δ = 176.6 (d, *J*(C-P) = 6.8 Hz, C=N), 167.4 (CO), 102.9 (dd, *J*(C-P) = 2.6 Hz, C_5), 66.3 (α-C), 62.9, 14.2 (Et), 9.3 (d, *J*(C-P) = 1.1 Hz, MeCp*). – $C_{33}H_{37}ClF_6NO_2P_2Rh$ (794.0): calcd. C 49.92, H 4.70, N 1.76; found C 49.68, H 4.75, N 1.99.

12: Yellow. Yield 97 %. M. p. 238 – 241 °C. – IR (Nujol, cm^{-1}): ν = 1742s, 1749s (CO), 1617m (C=N), 836vs (PF_6), 280w, 290w (Ir-Cl). – ^{1}H NMR ($CDCl_3$): δ = 8.23 (d, 1H, N=CH), 5.03 (dd, 2H, α-CH), 4.26 (m, 2H, Et), 1.42 (d, 15H, *J*(H-P) = 2.7 Hz, Cp*), 1.31 (t, 3H, *J*(H-H) = 7.0 Hz, Et). – ^{13}C NMR ($CDCl_3$): δ = 174.7 (d, *J*(C-P) = 6.8 Hz, C=N), 167.4 (CO), 97.1 (d, *J*(C-P) = 2.6 Hz, C_5), 71.5 (α-C), 63.2, 14.3 (Et), 9.22 (d, *J*(C-P) = 1.0 Hz, MeCp*). – $C_{33}H_{37}ClF_6NO_2IrP_2$ (883.3): calcd. C 44.87, H 4.22, N 1.59; found C 44.62, H 4.33, N 2.02.

13: Orange. Yield 92 %. M. p. 198 – 200 °C. – IR (Nujol, cm^{-1}): ν = 1743m, 1750m (CO), 1619m (C=N), 834vs (PF_6), 267w, 282w (Rh-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.70 (ψt, 1H, N=CH), 4.37 (d, 1H, *J*(H-H) = 8.1 Hz, α-CH), 3.77 (s, 3H, OCH_3), 1.92 (m, 1H, β-CH), 1.41 (d, 15H, *J*(H-P) = 3.9 Hz, Cp*), 0.77 (d, 3H, *J* = 6.6 (H-H) = Hz, γ-CH_3), 1.03 (d, 3H, *J*(H-H) = 6.8 Hz, γ-CH_3). Minor isomer: 8.55 (m, 1H, N=CH), 4.45 (d, 1H, *J*(H-H) = 8.0 Hz, α-CH), 3.80 (s, 3H, OMe), 1.64 (m, 1H, β-CH), 1.45 (d, 15H, *J*(H-P) = 4.0 Hz, Cp*), 1.14 (d, 3H, γ-CH_3), 0.93 (d, 3H, γ-CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 173.5 (d, *J*(C-P) = 7.3 Hz, C=N), 171.2 (CO), 103.3 (d, *J*(C-P) = 2.6 Hz, C_5), 81.7 (α-C), 54.6 (OMe), 33.9 (β-C), 19.5, 17.7 (γ-C), 9.6 (d, *J*(C-P) = 1.6 Hz, MeCp*). Minor isomer: 103.4 (d, *J*(C-P) = 2.6 Hz, C_5), 84.0 (α-C), 33.0 (β-C), 19.8, 17.9 (γ-C), 10.0 (d, *J* = 1.6 Hz, C_5). – $C_{35}H_{41}ClF_6NO_2P_2Rh$ (822.0): calcd. C 51.14, H 5.03, N 1.70; found C 50.92, H 5.05, N 1.85.

14: Yellow. Yield 96 %. M. p. 205 – 208 °C. – IR (Nujol, cm^{-1}): ν = 1746s (CO), 1613m (C=N), 842vs (PF_6), 290w, 302w (Ir-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.55 (d, 1H, N=CH), 4.75 (d, 1H, *J*(H-H) = 8.7 Hz, α-CH), 3.79 (s, 3H, OMe), 2.45 (m, 1H, β-C), 1.45 (d, 15H, *J*(H-P) = 2.6 Hz, Cp*),

1.11 (d, 3H, J(H-H) = 6.7 Hz, γ-CH_3), 1.00 (d, 3H, J(H-H) = 6.6 Hz, γ-CH_3). Minor isomer: 4.50 (d, J(H-H) = 8.7 Hz, α-CH), 3.82 (s, 3H, OMe), 1.02 (d, 3H, J(H-H) = 6.7 Hz, γ-CH_3), 0.95 (d, 3H, γ-CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 170.8 (d, J(C-P) = 6.6 Hz, C=N), 170.7 (CO), 97.4 (d, J(C-P) = 1.9 Hz, C_5), 86.1 (α-C), 53.3 (OMe), 34.2 (β-C), 18.7, 18.1 (γ-C), 9.1 (MeCp*). Minor isomer: 171.1 (d, J(C-P) = 4.7 Hz, C=N), 169.7 (CO), 98.0 (d, J(C-P) = 1.9 Hz, C5), 87.1 (α-C), 53.3 (OMe), 32.8 (β-C), 18.7, 18.2 (γ-C), 9.3 (MeCp*). – $C_{33}H_{41}ClF_6NO_2IrP_2$ (911.3): calcd. C 46.13, H 4.53, N 1.54; found C 45.44, H 4.58, N 1.38.

15: Orange. Yield 89 %. M. p. 230 – 231 °C. – IR (Nujol, cm^{-1}): ν = 1737s (CO), 1610m (C=N), 840vs (PF_6), 257w (Rh-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.91 (ψt, 1H, N=CH), 5.27 (dd, 1H, α-CH), 3.58 (s, 3H, OMe), 2.22 (dd, 2H, β-CH), 1.33 (d, 15H, J(H-P) = 3.9 Hz, Cp*). – ^{13}C NMR (CD_2Cl_2): δ = 174.9 (d, J(C-P) = 7.4 Hz, C=N), 171.5 (CO), 102.4 (dd, J(C-P) = 2.1 Hz, J(C-Rh) = 6.3 Hz, C_5), 74.2 (α-C), 53.0 (OMe), 40.9 (β-C), 9.2 (MeCp*). – $C_{39}H_{41}ClF_6NO_2P_2Rh$ (870.0): calcd. C 53.84, H 4.75, N 1.61; found C 53.46, H 4.85, N 1.70.

16: Red. Yield 92 %. M. p. 194 – 196 °C. – IR (Nujol, cm^{-1}): ν = 1738s (CO), 1607m (C=N), 1634w (C=C), 830vs (PF_6), 280w (Rh-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.7 (ψt, 1H, N=CH), 7.36 – 7.83 (14H, arom.), 5.12 (ψt , 1H, α-CH), 3.79s (OMe), 2.03 (m, 2H, β-CH), 5.46 (br, 1H, *H*C=CH_2), 5.03 (d, 1H, J(H-H) = 10.0 Hz, HC=CH*H trans*), 4.85 (d, 1H, J(H-H) = 17.0 Hz, HC=CHH *cis*), 1.36 (d, 15H, J(H-P) = 3.8 Hz, MeCp*). – ^{13}C NMR (CD_2Cl_2): δ = 174.6 (d, J(C-P) = 7.4 Hz, C=N), 171.3 (CO), 120.7 (δ-C), 102.5 (dd, J(C-P) = 2.1 Hz, J(C-Rh) = 6.7 Hz, C_5), 73.5 (α-C), 53.5 (OMe), 38.9 (β-C), 9.2 (d, J(C-P) = 1.0 Hz, MeCp*). – $C_{35}H_{39}ClF_6NO_2P_2Rh$ (820.0): calcd. C 51.27, H 4.79, N 1.71; found C 50.90, H 4.84, N 1.83.

17: Yellow. Yield 91 %. M. p. 178 – 182 °C. – IR (Nujol, cm^{-1}): ν = 1749s (CO), 1612m (C=N), 1641w (C=C), 841vs (PF_6), 289w (Ir-Cl). – ^{1}H NMR (CD_2Cl_2): δ = 8.47 (m, 1H, N=CH), 7.35 – 7.71 (14H, arom.), 5.22 – 4.94 (α-CH), 2.60 (m, 2H, β-CH), 3.82 (s, 3H, OMe), 5.67 (m, 1H, *H*C=CH_2), 5.22–4.94 (HC=CH*H cis/trans*), 1.41 (d, 15H, J(H-P) = 2.6 Hz, MeCp*). – ^{13}C NMR (CD_2Cl_2): δ = 171.5 (d, J(C-P) = 6.3 Hz, C=N), 170.1 (CO), 121.5 (δ-C), 96.8 (d, J(C-Rh) = 2.6 Hz, C_5), 78.1 (α-C), 53.5 (OMe), 38.0 (β-C), 8.8 (MeCp*). – $C_{35}H_{39}ClF_6NO_2IrP_2$ (909.3): calcd. C 46.23, H 4.32, N 1.54; found C 45.93, H 4.35, N 1.68.

*Dicationic complexes **18** – **22***

*General procedure for **19** – **22***: In a dry Schlenk tube **3**, **4** or **5** (1 mmol) and $AgBF_4$ (2.2 mmol) were stirred in dichloromethane (10 mL) for 2 h. The solution which contained the product was separated with a pipette, and the solvent was removed *in vacuo*. The residue was dried at 60 °C for 2 h and stirred with diethyl ether (10 mL) for 12 h. The ether was separated from the solid which was washed twice with diethyl ether (10 mL each) and finally dried at 60 °C for 6 h *in vacuo*. Complex **18** was prepared from **11** by use of 1.1 mmol of $AgBF_4$. For the preparation of **22**, 2.2 mmol of $AgPF_6$ was used.

18: Yellow. Yield 87 %. M. p. 192 – 196 °C. – IR (Nujol, cm^{-1}): ν = 1635s (CO), 1612m (C=N), 1050vs (BF_4). – ^{1}H NMR (CD_2Cl_2): δ = 9.00 (s, br, 1H, N=CH), 6.92 – 8.25 (arom.), 3.95 – 4.58 (m , br, α-CH), 4.51 (q, 2H, Et), 1.35 (t, 3H, Et), 1.52 (d, 15H, J(H-P) = 3.5 Hz, Cp*). – $C_{33}H_{37}BF_{10}NO_2P_2Rh \cdot 1/2\ CH_2Cl_2$ (876.9): calcd. C 45.32, H 4.31, N 1.58; found C 45.31, H 4.38, N 1.98.

19: Orange. Yield 92 %. M. p. 155 – 158 °C. – IR (Nujol, cm^{-1}): ν = 1633s (CO), 1616m (C=N), 1046vs (BF_4). – ^{1}H NMR (CD_2Cl_2): δ = 9.05 (s, 1H, N=CH), 6.79–8.33 (arom.), 5.04 (s, br, 1H, α-CH), 4.03 (s, 3H, OMe), 2.84 (m, 1H, β-CH), 1.50 (d, J(H-H) = 2.1 Hz, Cp*), 1.15 (ψq, 3H, γ-CH_3), −0.23 (d, 3H, γ-CH_3). Minor isomer: 8.74 (s, 1H, N=CH), 3.71 (d, 1H, J(H-H) = 10.3 Hz, α-CH), 4.23 (s, 3H, OMe), 2.20 (m, 1H, β-CH), 1.46 (d, 15H, J(H-P) = 2.1 Hz, Cp*), 1.15 (ψq, 6H, γ-CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 170.5 (d, J(C-P) = 6.3 Hz, C=N), 182.0 (CO), 103.6 (m, C_5), 78.5 (α-C), 58.0 (OMe), 26.7 (β-C), 13.2, 18.7 (γ-C). Minor isomer: 176.2 (d, J(C-P) = 7.4 Hz, C=N), 103.6 (m, Cp*), 80.9 (α-C), 57.8 (OMe), 31.1 (β-C), 19.9, 19.3 (γ-C), 9.9 (MeCp*). – $C_{35}H_{41}B_2F_8NO_2PRh \cdot 2\ CH_2Cl_2$ (985.1): calcd. C 45.11, H 4.60, N 1.42; found C 45.46, H 5.13, N 1.54.

20: Orange. Yield 93 %. M. p. 173 – 176 °C. – IR (Nujol, cm^{-1}): ν = 1629s (CO), 1709m (CO, hydrolyzed product), 1610s (C=N), 1057vs (BF_4). – ^{1}H NMR (CD_2Cl_2): δ = 9.05 (d, 1H, J(H-P) = 4.0 Hz, N=CH), 6.90 – 8.33 (arom.), 4.73 (ψt, 1H, α-CH), 4.32 (s, 3H, OMe), 2.92m (1H, β-CH), 1.51 (d, 15H, J(H-P) = 2.5 Hz, Cp*), 1.20 (d, 3H, γ-CH_3), −0.19 (d, 3H, J(H-H) = 6.8 Hz, γ-CH_3). Minor isomer: 8.67 (ψt, 1H, C=NH), 4.13 (s, 3H, OMe), 3.86 (d, 1H, J(H-H) = 10 Hz, α–CH), 2.13 (m, 1H, β-CH), 1.48 (d, 15H, J(H-P) = 2.4 Hz, Cp*), 1.11 (d, 3H, γ-CH_3), 1.29 (d, 3H, J(H-H) = 6.6 Hz, γ-CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 169.9 (d, J(C-P) = 6.8 Hz, C=N), 186.9 (CO), 96.7 (d, J(C-P) = 2.1 Hz, C_5), 79.5 (α-C), 59.5 (OMe), 27.0 (β-C), 19.0, 13.2 (γ-C), 9.6 (MeCp*). Minor isomer: 175.3 (d, J(C-P) = 6.3 Hz, C=N), 187.7 (CO), 96.3 (d, J(C-P) = 2.1 Hz, C_5), 81.1 (α-C), 59.4 (OMe), 30.9 (β-C), 20.2, 18.7 (γ-C), 9.1 (MeCp*). – $C_{35}H_{41}B_2F_8NO_2IrP \cdot 2\ CH_2Cl_2$ (1074.4): calcd. C 41.36, H 4.22, N 1.30; found C 40.95, H 4.49, N 1.38.

21: Orange. Yield 90 %. M. p. 146 – 149 °C. – IR (Nujol, cm^{-1}): ν = 1641s (CO), 1623sh (C=N), 1054vs (BF_4). – ^{1}H NMR (CD_2Cl_2): δ = 9.19 (s, br, N=CH), 6.87 – 8.38 (arom.), 3.80 (s, br, OMe), 2.16 (s, br, β-CH), 1.54 (s, br, MeCp*). Minor isomer: 9.08 (s, br, N=CH), 4.01 (s, br, OMe), 3.15 (s, br, β-CH), 1.54 (s, br, MeCp*). – ^{13}C NMR (CD_2Cl_2): δ = 177.5 (d, J(C-P) = 7.0 Hz, C=N), 183.5 (CO),

104.2 (m, C_5), 58.1 (OMe), 44.5 (β-C), 10.1 (MeCp*). – $C_{39}H_{41}B_2F_8NO_2PRh \cdot 2\ CH_2Cl_2$ (1033.1): calcd. C 47.67, H 4.39, N 1.36; found C 48.13, H 4.69, N 1.54.

22: Orange. Yield 93 %. M. p. 178 – 181 °C. – IR (Nujol, cm^{-1}): ν = 1673s (CO), 1631w (C=N), 1057vs (BF_4). – $C_{39}H_{41}F_{12}NO_2IrP_3 \cdot CH_2Cl_2$ (1153.8): calcd. C 41.46, H 3.76, N 1.21; found C 41.61, H 4.41, N 1.28.

*Dicationic complexes **23** and **24***

24: Complex **10** (67 mg, 0.084 mmol) and $AgBF_4$ (37 mg, 0.19 mmol) were stirred in dichloromethane (5 mL) for 1 h. The solid was centrifuged off, and from the solution (which contained the product) the solvent was removed *in vacuo*. The colorless residue was dried for 2 h at 60 °C, and then stirred with diethyl ether (6 mL) for 12 h. The isolated solid was washed with diethyl ether (8 mL) and dried at 60 °C *in vacuo*. Complex **23** was obtained by an analogous procedure from **16**.

23: Yellow. Yield 95 %. M. p. 143 – 145 °C. – IR (Nujol, cm^{-1}): ν = 1743s (CO), 1625m (C=N), 1505 (C=C), 1059vs (BF_4), 840vs (PF_6). – ^{1}H NMR (CD_2Cl_2): δ = 9.01 (s, br, 1H, N=CH), 6.97 – 8.39 (14H, arom.), 6.05 (m, 1H, β-CH), 4.17 (ψt, 1H, α-CH), 3.76 (s, 3H, OMe), 2.49 (m, 1H, β-CH), 0.33 (m, 1H, *H*C=CH_2), 5.10 (d, 1H, *J*(H-H) = 13.3 Hz, HC=CH*H trans*), 4.58 (m, 1H, HC=C*H*H *cis*), 1.51 (d 15H, *J*(H-P) = 3.7 Hz, Cp*). Minor isomer: 9.25 (s, br, 1H, N=CH), 6.26 (m, 1H, β-CH), 3.95 (s, 3H, OMe), 0.13 (m, 1H, *H*C=CH_2), 1.43 (d, 15H, *J*(H-P) = 3.9 Hz, Cp*). – ^{13}C NMR (CD_2Cl_2): δ = 175.7 (d, *J*(C-P) = 6.3 Hz, C=N), 167.1 (CO), 110.4 (dd, *J*(C-P) = 1.6 Hz, *J*(C-Rh) = 5.2 Hz, C_5), 107.1 (d, *J*(C-P) = 5.6 Hz, γ-C), 83.3 (α-C), 77.3 (dd, *J*(C-P) = 2.1 Hz, *J*(C-Rh) = 6.8 Hz, δ-C), 53.5 (OMe), 9.5 (d, *J*(C-P) = 1.5 Hz, MeCp*). Minor isomer: 179.8 (d, *J*(C-P) = 6.8 Hz, C=N), 167.7 (CO), 110.5 (dd, C_5), 88.0 (α-C), 65.9 (dd, *J*(C-Rh) = 4 Hz, *J*(C-P) = 2 Hz, δ-C), 54.6 (OMe), 34.5 (β-C), 9.7 (d, *J*(C-P) = 1.1 Hz, MeCp*). – $C_{35}H_{39}BF_{10}NO_2P_2Rh$ (871.4): calcd. C 48.25, H 4.51, N 1.61; found C 48.22, H 4.89, N 1.61.

24: Colorless. Yield 90 %. M. p. 131 – 135 °C. – IR (Nujol, cm^{-1}): ν = 1747s (CO), 1622m (C=N), 1500 (C=C), 1058vs (BF_4). – ^{1}H NMR (CD_2Cl_2): δ = 8.48 (s, br, 1H, N=CH), 6.99 – 8.54 (14H, arom.), 4.30 (ψt, 1H, α-CH), 3.77 (s, 3H, OMe), 2.68 (m, 1H, β-CH), 5.40 (m, 1H, β-CH), 0.26 (m, 1H, *H*C=CH_2), 4.87 (d, 1H, *J*(H-H) = 13.7 Hz, HC=CH*H trans*), 4.38 (d, 1H, *J*(H-H) = 7.6 Hz, HC=C*H*H *cis*), 1.54 (d, 15H, *J*(H-P) = 2.5 Hz, MeCp*). – ^{13}C NMR (CD_2Cl_2): δ = 176.5 (d, *J*(C-P) = 6 Hz, C=N), 168.0 (CO), 105.8 (C_5), 88.7 (γ-C), 85.5 (α-C), 54.6 (OMe), 38.9 (β-C), 9.0 (MeCp*). – $C_{35}H_{39}B_2F_8NO_2IrP \cdot CH_2Cl_2$ (987.4): calcd. C 43.79, H 4.19, N 1.42; found C 42.82, H 4.41, N 1.57.

*X-Ray structure determination of **15***

Crystals of **15** were obtained from CH_2Cl_2/*n*-hexane. $C_{39}H_{41}ClF_6NO_2P_2Rh$ (870.0). Crystal size 0.1 × 0.2 × 0.7 mm^3. Syntex R3 diffractometer, MoK_α radiation, λ = 0.71073 Å, T = 20 °C. Monoclinic, $P2_1/c$, a = 904.5(7), b = 1951(2), c = 2206(2) pm, β = 101.71(6)°, V = 3.811(6) nm^3, Z = 4, $\rho_{calcd.}$ = 1.52 g cm^{-3}, μ(MoK_α) = 0.7 mm^{-1}. 2θ range = 2 – 50°, index range $\pm h$, $-k$, $\pm l$, 13220 collected reflections, 6695 unique reflections, 3539 reflections "observed" with $I \geq \sigma(I)$, absorption correction: $T_{rel.}$ (min. / max.) = 0.065 / 0.096. Solution by Direct Methods, refinement by full-matrix least-squares methods. 268 refined parameters, R = 0.0861, Rw = 0.0773, extrema of last Fourier synthesis = +0.80 / −0.90 e · 10^{-6} pm^{-3}.

CCDC 766179 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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