Metal Complexes of Biologically Important Ligands, CLXXIV [1]. Palladium(II) and Platinum(II) Complexes with Schiff Bases from 2-(Diphenylphosphino)benzaldehyde and α-Amino Acid Esters

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Z. Naturforsch. **2010**, *65b,* 503 – 510; received December 7, 2009

Dedicated to Professor Reinhard Schmutzler on the occasion of his 75th birthday

A series of palladium(II) and platinum(II) complexes Cl_2M(P-N-O) (M = Pd, Pt) with bidentate Schiff bases (P-N-O) from 2-(diphenylphosphino)benzaldehyde and α-amino acid esters has been synthesized, using $PdCl_2$ or $K[PtCl_3(C_2H_4)]$, respectively. Abstraction of chloride from Cl_2M(P-N-O) (using $AgBF_4$) has afforded the cationic complexes $[(P\text{-}N\text{-}O)M(Cl)]^+BF_4^-$ in which the Schiff bases function as tridentate ligands with coordination of the ester group. The structures of $Cl_2Pd(Ph_2PC_6H_4C(H){=}N\text{-}CH_2CO_2Et)$ and of $[(Cl)Pd(Ph_2PC_6H_4C(H){=}N\text{-}C(H)(CH_2CH{=}CH_2)CO_2Me)]^+BF_4^-$ have been determined by X-ray diffraction. Complexes $(L)MCl_2$ and $[(L)MCl]^+BF_4$ (M = Pd, Pt) have also been prepared with the reduced Schiff base $Ph_2PC_6H_4CH_2NHC(H)(CH_2Ph)CO_2Me$.

Key words: 2-(Diphenylphosphino)benzaldehyde, 2-Formylphenyldiphenylphosphine, Palladium, Platinum, α-Amino Acid Esters, Schiff Bases

Introduction

2-(Diphenylphosphino)benzaldehyde [2 – 4] (2-formylphenyldiphenylphosphine) is a very versatile and frequently employed reagent in coordination chemistry and in metal-catalyzed synthesis [5]. It has been introduced as P-donor in metal complexes [6], for the formation of acyl complexes [7a] or for the formation of dendrons [7b] or Salpen-like ligands [7c]. Mostly it has been used for reactions with amines or functionalized amines to synthesize iminophosphine ligands (Schiff bases) [8] and optically active iminophosphines from optically active amines for asymmetric reactions [9]. Reactions of 2-(diphenylphosphino)benzaldehyde with polyamines afford multidentate iminophosphines [10]. Brunner and coworkers reported optically active P,N-ligands from 2-formylphenyldiphenyl-phosphine and optically active amines from which chelate complexes were obtained, and these were used for metal-catalyzed asymmetric hydrogenation and hydrosilylation [4, 11] and allylation [12, 13].

In the course of our studies on metal complexes of Schiff bases from α-amino acids [14] we report in the following on palladium(II) and platinum(II) complexes of imines from 2-(diphenylphosphino)benzaldehyde and α-amino acid esters. During optimization reactions for optically active P,N-ligands, Brunner *et al.* [12] have synthesized a P,N Schiff base from 2-(diphenylphosphino)benzaldehyde and *tert*-butyl-*tert*-leucinate, and several Schiff bases from 2-(diphenylphosphino)benzaldehyde and dipeptides have been developed as ligands for asymmetric conjugate additions of allylzinc reagents [15].

Results and Discussion

The Schiff bases **1 – 5** (Scheme 1) have been obtained by condensation of 2-(diphenylphosphino)benzaldehyde with α-amino acid esters. Polarometric measurements showed that racemization took place [16] when L-amino acids were used. The reactions of **1 – 5** with $PdCl_2$ or $K[PtCl_3(C_2H_4)]$ (Zeise's salt) afforded the yellow complexes **6 – 15** (Scheme 1). The complexes **6**, **9 – 11** and **14** were converted into the cationic compounds **16 – 20** by treatment with $AgBF_4$.

The IR spectra of **6 – 15** exhibit two $\nu(M\text{-Cl})$ absorptions at $\sim 350\ cm^{-1}$, as expected for the *cis*-MCl_2

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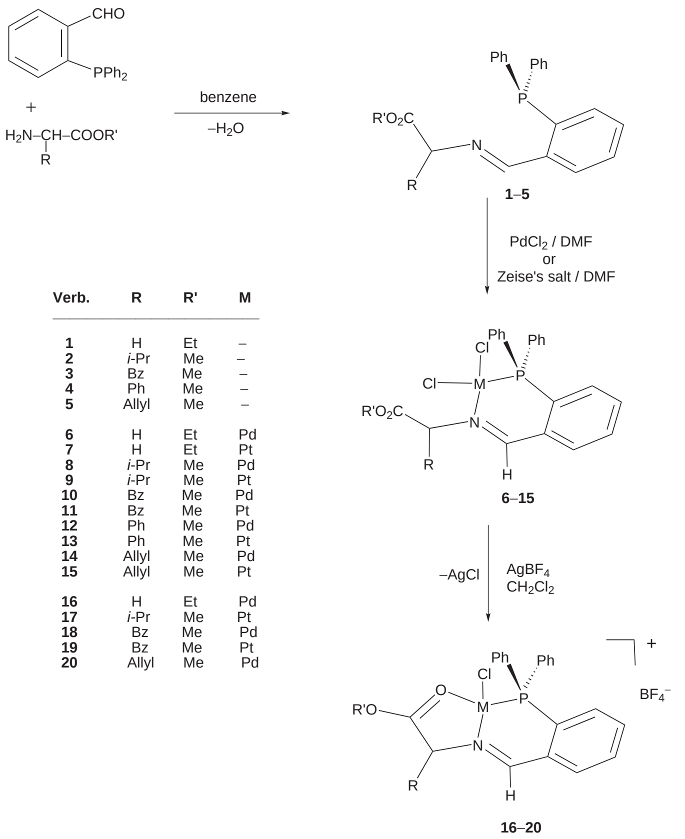


Verb.	R	R'	M
1	H	Et	–
2	*i*-Pr	Me	–
3	Bz	Me	–
4	Ph	Me	–
5	Allyl	Me	–
6	H	Et	Pd
7	H	Et	Pt
8	*i*-Pr	Me	Pd
9	*i*-Pr	Me	Pt
10	Bz	Me	Pd
11	Bz	Me	Pt
12	Ph	Me	Pd
13	Ph	Me	Pt
14	Allyl	Me	Pd
15	Allyl	Me	Pt
16	H	Et	Pd
17	*i*-Pr	Me	Pt
18	Bz	Me	Pd
19	Bz	Me	Pt
20	Allyl	Me	Pd

Scheme 1.

group. The ν(C=N) band of the complexes **6**–**15** is shifted by N-M coordination to lower frequencies in comparison to the free Schiff bases **1**–**5**. The large shift of the ester carbonyl absorption in **16**–**20** to lower frequencies (compared to that in **1**–**15**, $\Delta = 60-100\ \mathrm{cm}^{-1}$) is clear evidence for coordination of the ester function [1] which causes also a characteristic low-field shift of the methyl and ethyl ester signals in the ^{1}H NMR spectra and a low-field shift of the carbon signal of the coordinated carbonyl group in the ^{13}C NMR spectra. The ^{31}P NMR spectra of **1**–**20** spectra exhibit, as expected, only one signal. The planar structures of **6** (Fig. 1) and **20** (Fig. 2) could be confirmed by X-ray structure determination (Table 1). The two Pd–Cl bond lengths in **6** are distinctly different. The Pd–Cl bond in *trans* position to the stronger P-donor is longer than that of the Pd–Cl bond *trans* to the weaker N-donor. The structure of **20** shows the coordination of the ester group [1] (Pd–O2 = 214.3(8) pm) and the noncoordinated allyl group. The P–Pd–N angle in **20** with a six-membered chelate ring is by 5° larger than that in **6** with a five-membered ring (92.7(2) and 88.1(2)°,

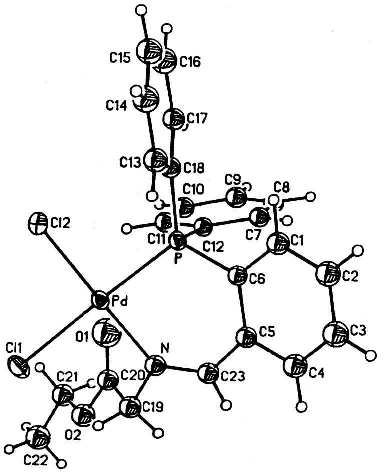
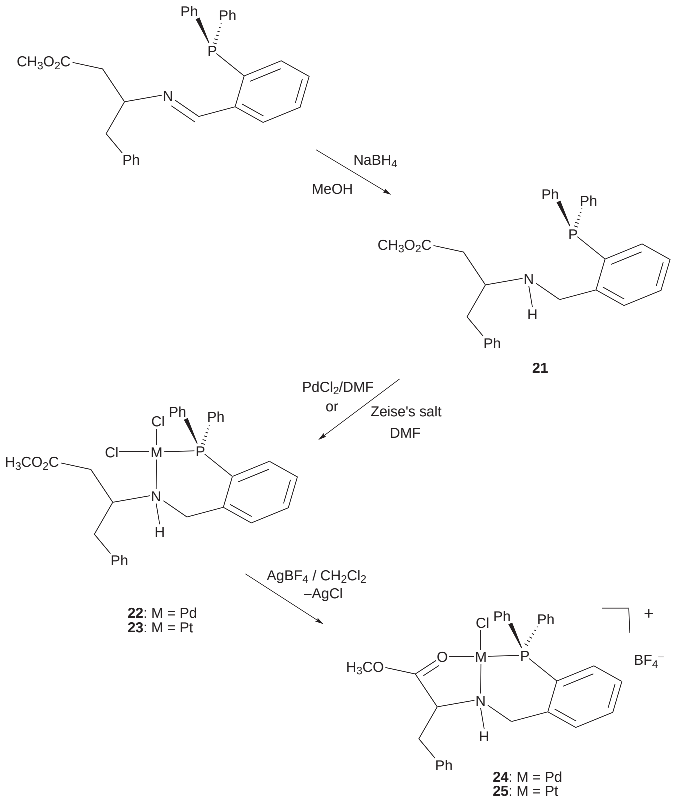


Fig. 1. Molecular structure of **6** in the crystal. Selcted bond lengths (pm) and angles (deg): Pd–Cl1 238.9(2), Pd–Cl2 228.6(2), Pd–N 205.4(5), Pd–P 222.5(2), N–C23 128(1), C5–C23 148(1), C20–O1 120(1); Cl2–Pd–Cl1 89.2(1), Cl1–Pd–N 92.4(2), P–Pd–N 88.1(2), P–Pd–Cl2 91.0(1), P–Pd–Cl1 172.5(1), Cl2–Pd–N 174.9(2), C6–C5–C23 124.0(6), C5–C23–N 126.8(6), Pd–N–C23 129.1(5), Pd–N–C19 116.0(4).



Scheme 2.

resp.). The racemization of the Schiff base made it possible that complex **6** subsequently crystallized in the centrosymmetric space group $P2_1/n$.

The Schiff base **3** was converted into the amine **21** by treatment with tetrahydridoborate, and **21** was again used as a ligand to give the neutral (**22**, **23**) and cationic (**24**, **25**) palladium(II) and platinum(II) complexes (Scheme 2). The nitrogen atom in **22**–**25** is a second chiral center; therefore two diastereomers (S_NS_C/R_NR_C and S_NR_C/R_NS_C) are formed which can be detected by their NMR signals.

The IR spectra of **24** and **25** exhibit the characteristic CO absorption of the coordinated ester group which is typically [1] shifted by $\sim$ 100 cm^{-1} to lower wavenumbers from that of **22** and **23** with a free ester group. The $\nu(M\text{-Cl})$ bands of **24** and **25** are found at 350 cm^{-1}. In the ^{13}C NMR spectra of **22** and **23** two sets of signals for the two diastereoisomers are observed. The coordination of the ester group in **24** and **25** causes again a large low field shift of the carbonyl signal. Two diastereoisomers can be observed also in the ^{31}P NMR spectra of **22**, **23** and **25** which show two ^{31}P signals, whereas **24** offers four signals which, presumably, can be attributed to conformational isomers of the two diastereoisomers [17].

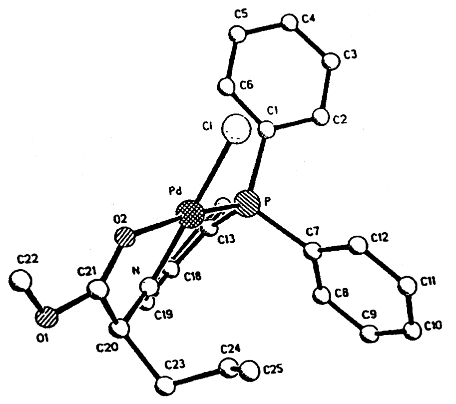


Fig. 2. Molecular structure of **20** in the crystal. Selcted bond lengths (pm) and angles (deg): Pd–Cl 226.5(2), Pd–P 217.5(3), Pd–O2 214.3(8), Pd–N 200.0(7), O2–C21 122.7(12), N–C19 129.4(14), N–C20 147.3(15), P–C7 182.0(10), C18–C19 148.8(17); P–Pd–Cl 91.9(1), P–Pd–N 92.7(2), Cl–Pd–N 178.1(3), P–Pd–O2 173.5(2), Cl–Pd–O2 94.2(2), N–Pd–O2 81.1(3), Pd–P–C1 116.2(2), Pd–N–C20 110.6(6), Pd–O2–C21 110.0(7).

Table 1. Crystallographic data of **6** and **20**.

	6	**20**
Formula	$C_{23}H_{22}Cl_2NO_2PPd$	$C_{25}H_{24}BClF_4NO_2PPd$
Formula weight	552.8	630.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, pm	1017.6(5)	1047.7(2)
b, pm	2081.3(9)	2246.4(4)
c , pm	1220.5(7)	1221.9(2)
β, deg	102.76(4)	110.93(1)
Volume, nm^3	2.520(5)	2.6860(8)
Z	4	4
$\rho_{\text{calcd.}}$, g cm^{-3}	1.46	1.56
μ, mm^{-1}	1.0	0.9
Diffractometer	Syntex R3	Siemens R3 m/V
Temperature, K	303	295
Index ranges	$\pm h, +k, \pm l$	$+h, +k, \pm l$
Range 2θ, deg	4 – 50	5 – 50
Reflections collected	9426	5261
Unique reflections	4335	4739
Refls $[I \geq 2\sigma(I)]$	3996	3286
Refined parameters	150	331
R/R_w	0.077 / 0.091	0.081 / 0.046
$\Delta\rho_{\text{fin}}$ (max / min), e $\times 10^{-6}$ pm^{-3}	1.71 / −0.81	1.01 / −0.91

Experimental Section

2-(Diphenylphosphino)benzaldehyde [3] and K[$PtCl_3$-(C_2H_4)] (Zeise's salt) [18] were obtained as described. Unless otherwise noted, the NMR spectra were recorded on a Jeol GSX-270 spectrometer.

*Schiff base **3***

2-(Diphenylphosphino)benzaldehyde (4.0 g, 13.8 mmol) and freshly destilled L-phenylalanine methyl ester (2.33 g, 13.8 mmol) were heated in benzene (120 mL) under reflux by use of a water separator for 15 h. The solvent was removed *in vacuo*, the oily residue was dissolved in diethyl ether (20 mL), and the product was precipitated with *n*-pentane. The colorless Schiff base was recrystallized from diethyl ether/*n*-pentane at −35 °C and dried over P_4O_{10} at r. t. The Schiff bases **1**, **2**, **4** and **5** were prepared by analogous procedures.

1: Yield 71 %. M. p. 85 – 87 °C. – IR (KBr, cm^{-1}): ν = 1745s (CO), 1636m (C=N). – ^{1}H NMR ([D$_6$]acetone): δ = 9.01 (d, 1H, J(H-P) = 5.3 Hz, N=CH), 6.86 – 8.18 (14H, arom.), 4.26 (d, 2H, J(H-P) = 1.2 Hz, α-CH), 4.10 (q, 2H, Et), 1.19 (t, 3H, Et). – ^{13}C NMR ([D$_6$]acetone): δ = 163.0 (d, J = 22 Hz, C=N), 127.6 – 139.1 (arom.), 61.6 (α-C), 60.4, 13.8 (OEt). – ^{31}P NMR ([D$_6$]acetone): δ = −14.2(s). – $C_{23}H_{22}NO_2P$ (375.4): calcd. C 73.58, H 5.91, N 3.73; found C 73.43, H 6.06, N 3.61.

2: Oil. Yield 76 %. – IR (Nujol, cm^{-1}): ν = 1740s (CO), 1631m (C=N). – ^{1}H NMR ([D$_6$]acetone): δ = 8.93 (d, 1H, J(H-P) = 5.3 Hz, N=CH), 6.92 – 7.47 (14H, arom.), 3.59 (d, 1H, J = 7.6 Hz, α-CH), 2.11m (1H, β-CH), 0.71 (d, 3H, J = 6.7 Hz, γ-CH), 0.79 (d, 3H, J = 6.2 Hz, γ-CH), 3.57 (s, 3H, OMe). – ^{13}C NMR ([D$_6$]acetone): δ = 161.5 (d, J = 22 Hz, C=N), 171.4 (CO), 128.0 – 139.6 (arom.), 79.7 (α-C), 31.4 (β-C), 18.0, 19.0 (γ-C), 51.2 (OMe). – ^{31}P NMR ([D$_6$]acetone): δ = −12.8 (s). – $C_{25}H_{26}NO_2P$ (403.4): calcd. C 74.42, H 6.50, N 3.47; found C 73.55, H 6.88, N 3.92.

3: Yield 83 %. M. p. 91 – 93 °C. – IR (Nujol, cm^{-1}): ν = 1737s (CO), 1632m (C=N). – ^{1}H NMR ($CDCl_3$): δ = 8.69 (d, 1H, J(H-P) = 5.4 Hz, N=CH), 6.84 – 8.70 (19H, arom.), 4.10 (dd, α-CH), 3.23 (dd, 1H, J = 5.9, 13.7 Hz, β-CH), 2.89 (dd, 1H, J = 8.3, 13.6 Hz, β-CH), 3.57 (s, 3H, OMe). – ^{13}C NMR ($CDCl_3$): δ = 162.4 (d, J = 22.0 Hz, C=N), 171.8 (CO), 126.5 – 139.1 (arom.), 74.6 (α-CH), 39.7 (β-CH), 52.0 (OMe). – ^{31}P NMR ($CDCl_3$): δ = −14.2 (s). – $C_{29}H_{26}NO_2P$ (451.5): calcd. C 77.12, H 5.81, N 3.10; found C 76.86, H 5.83, N 3.36.

4: Yield 65 %. M. p. 55 – 58 °C. – IR (Nujol, cm^{-1}): ν = 1740s (CO), 1630s (C=N). – ^{1}H NMR ($CDCl_3$): δ = 9.05 (d, 1H, J(H-P) = 5.3 Hz, N=CH), 6.88 – 8.20 (19H, arom.), 5.09 (s, 1H, α-CH), 3.61 (s, 3H, OMe). – ^{13}C NMR ($CDCl_3$): δ = 163.0 (d, J = 22.7, C=N), 171.9 (CO), 128.4 – 140.0 (arom.), 77.0 (α-C), 52.9 (OMe). – ^{31}P NMR ($CDCl_2$): δ = −13.7 (s). – $C_{28}H_{24}NO_2P \cdot MeOH$ (469.5): calcd. C 74.19, H 6.01, N 2.98; found C 73.72, H 5.97, N 3.03.

5: Yield 71 %. M. p. 48 – 50 °C. – IR (Nujol, cm^{-1}): ν = 1728s (CO), 1631m (C=N), 1638 sh (C=C). – ^{1}H NMR (CD_2Cl_2): δ = 8.88 (s, 1H, J(H-P) = 5.4 Hz, N=CH), 6.88 – 8.02 (14H, arom.), 5.48 (m, 1H, *H*C=CH$_2$), 4.88 (d, 1H, J = 10.3 Hz, HC=CH*H trans*), 4.95 (dd, 1H, J = 17.1 Hz, ^2J = 2.0 Hz, HC=CHH *cis*), 3.90 (ψt, 1H, α-CH), 2.38 (m, 1H, β-CH), 2.54 (m, 1H, β-CH), 3.60 (s, 3H, OMe). – ^{13}C NMR (CD_2Cl_2): δ = 162.4 (d, J = 23.1 Hz, C=N), 172.1 (CO), 128.2 – 139.7 (arom.), 73.1 (α-C), 38.0 (β-C), 118.0 (δ-CH$_2$), 52.3 (OMe). – ^{31}P NMR (CD_2Cl_2): δ = −14.1(s). – $C_{25}H_{24}NO_2P$ (401.4): calcd. C 74.80, H 6.03, N 3.49; found C 74.20, H 6.06, N 3.40.

*N-(2-Diphenylphosphino)benzyl-phenylalaninmethylester (**21**)*

To a solution of Schiff base **3** (2.11 g, 4.67 mmol) in methanol (25 mL) sodium tetrahydroborate (276 mg, 7.30 mmol) was added slowly at 0 °C. The mixture was heated under reflux for 1 h and methanol was removed *in vacuo*. The yellow-brown oily residue was dissolved in diethyl ether, and the solution was filtered. After addition of water (10 mL) the organic phase was separated. The aqueous phase was extracted with diethyl ether. The united ether phases were dried over Na_2SO_4 and filtered over silica gel [10 cm, Merck Kieselgel 60 (70 – 210 mesh)]. The ether was removed *in vacuo*, and the oily residue was treated with *n*-

pentane. At −30 °C a colorless powder was obtained, which was dried at r. t. *in vacuo*.

21: Colorless. Yield 63 %. M. p. 105 – 108 °C. – IR (KBr, cm^{-1}): ν = 3345m (NH), 1737 (CO), 1582m, 1495m (C=C, δNH). – ^{13}C NMR (CDCl$_3$): δ = 174.7 (CO), 126.6. – 144.1 (arom.), 62.0 (α-C), 51.5 (OMe), 50.3 (d, J = 21, NCH$_2$), 39.4 (β-C). – ^{31}P NMR (CDCl$_3$): δ = −15.5. – $C_{29}H_{28}NO_2P$ (453.5): calcd. C 76.80, H 6.22, N 3.09; found C 75.89, H 6.38, N 3.02.

*Palladium complex **6***

A suspension of PdCl$_2$ (177 mg, 1 mmol) in DMF (10 mL) was heated under reflux for 3 h. The deep-red solution was cooled to r. t., and the Schiff base **1** (376 mg, 1 mmol) was added. After stirring for 1 h the orange-yellow solution was separated with a pipette and its volume reduced to 4 mL. The solution was layered with diethyl ether (15 mL). At −30 °C yellow, DMF-containing needles were obtained which were washed three times with diethyl ether (10 mL each). The other palladium complexes **8**, **10**, **12**, **14** and **22** were prepared by analogous procedures.

*Platinum complex **23***

To Zeise salt (K[PtCl$_3$C$_2$H$_4$], 369 mg, 1 mmol) dissolved in DMF (12 mL) compound **21** (404 mg, 1 mol) was added. After stirring for 12 h the light-yellow solution was separated with a pipette and its volume reduced to 4 mL while warming to r. t. and layered with *n*-pentane (15 mL). At −30 °C colorless crystals were obtained which were washed three times with diethyl ether (10 mL each). The other platinum complexes **7**, **9**, **11**, **13** and **15** were prepared by analogous procedures.

6: Yellow. Yield 86 %. M. p. 224 – 228 °C. – IR (Nujol, cm^{-1}): ν = 1736 (CO), 1626m (C=N), 252m, 340m (Pd-Cl). – ^{1}H NMR ([D$_7$]DMF): δ = 8.77 (s, 1H, N=CH), 7.25 – 8.11 (14 H, arom.), 5.39 (s, 2H, α-CH), 4.08 (q, 2H, Et), 1.16 (t, 3H, J = 7.0 Hz, Et). – ^{13}C NMR ([D$_7$]DMF): δ = 171.1 (d, J = 8.4 Hz, C=N), 168.8 (s, CO), 122.1 – 138.3 (arom.), 66.1 (α-C), 61.8, 14.3 (Et). – ^{31}P NMR ([D$_7$]DMF): δ = 29.5 (s). – $C_{23}H_{22}Cl_2NO_2PPd \cdot 1/2$ DMF (589.3): calcd. C 49.94, H 4.36, N 3.57; found C 49.40, H 4.24, N 3.63.

7: Orange. Yield 80 %. M. p. 206 – 209 °C. – IR (Nujol, cm^{-1}): ν = 1733s (CO), 1626m (C=N), 304m, 350sh (Pt-N). – ^{1}H NMR ([D$_7$]DMF): δ = 9.06 (s, 1H, N=CH), 7.30 – 8.15 (14H, arom.), 5.58 (s, 2H, α-CH), 4.07 (q, 2H, Et), 1.15 (t, 3H, Et). – ^{13}C NMR ([D$_7$]DMF): δ = 170.0 (d, J = 7.3 Hz, C=N), 168.8 (CO), 121.2 – 138.0 (arom.), 66.7 (α-C), 61.9, 14.2 (Et). – ^{31}P NMR ([D$_7$]DMF): δ = 3.7 (s, J(Pt-P) = 3738.8 Hz). – $C_{23}H_{22}Cl_2NO_2PPt$ (641.4): calcd. C 43.07, H 3.46, N 2.18; found C 42.90, H 3.69, N 2.24.

8: Yellow. Yield 57 %. M. p. 231 – 232 °C. – IR (Nujol, cm^{-1}): ν = 1740s (CO), 1623m (C=N), 282m, 346m (Pd-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.44 (s, 1H, N=CH), 7.03 – 7.87 (14H, arom.), 5.94 (d, 1H, J = 9.1 Hz, α-CH), 2.17 (m, 1H, β-CH), 0.82 (d, 6H, J = 6.5 Hz, γ-CH), 3.57 (s, 3H, OMe). – ^{13}C NMR (CD$_2$Cl$_2$): δ = 167.9 (d, J = 8.1 Hz, C=N), 171.6 (CO), 120.1 – 138.1 (arom.), 78.2 (α-C), 33.7 (β-C), 18.9, 19.3 (γ-C), 53.1 (OMe). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 32.0 (s). – $C_{25}H_{26}Cl_2NO_2PPd$ (580.8): calcd. C 51.7, H 4.51, N 2.41; found C 51.72, H 4.56, N 2.70.

9: Light yellow. Yield 67 %. M. p. ¿ 270 °C. – IR (Nujol, cm^{-1}): ν = 1745s (CO), 1615m (C=N), 280m, 348m (Pt-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.56 (s, 1H, J(Pt-H) = 107 Hz, N=CH), 6.96 – 7.91 (14H, arom.), 6.01 (d, 1H, J = 9.7 Hz, α-CH), 2.12 (m, 1H, β-CH), 0.81 (d, 3H, J = 6.4 Hz, γ-CH), 0.88 (d, 3H, J = 5.9 Hz, γ-CH), 3.58 (s, 3H, OMe). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 6.0 (s, J(Pt-P) = 3728.0 Hz). – $C_{25}H_{26}Cl_2NO_2PPt$ (669.5): calcd. C 44.85, H 3.91, N 2.09; found C 44.47, H 3.95, N 2.39.

10: Yellow. Yield 71 %. M. p. 198 – 202 °C. – IR (Nujol, cm^{-1}): ν = 1741s (CO), 1631m (C=N), 280m, 348m (Pd-Cl). – ^{1}H NMR (CDCl$_3$): δ = 7.89 (s, 1H, N=CH), 6.98 – 7.73 (19H, arom.), 6.33 (dd, 1H, J = 4.2 Hz, J = 8.8 Hz, α-CH), 3.70 (dd, 1H, J = 4.4 Hz, ^2J = 13.2 Hz, β-CH), 3.22 (dd, 1H, J = 9.0, ^2J = 13.2 Hz, β-CH), 3.36 (s, 3H, OMe). – ^{13}C NMR (CDCl$_3$): δ = 167.8 (d, J = 8.4 Hz, C=N), 170.6 (CO), 121.4 – 137.1 (arom.), 73.0 (α-C), 40.6 (β-C), 52.3 (OMe). – ^{31}P NMR (CDCl$_3$): δ = 32.2 (s). – $C_{29}H_{26}Cl_2NO_2PPd$ (628.8): calcd. C 55.39, H 4.17, N 2.23; found C 54.89, H 4.31, N 2.27.

11: Yellow. Yield 69 %. M. p. 185 – 188 °C. – IR (Nujol, cm^{-1}): ν = 1741s (CO), 1616m (C=N), 290m, 346m (Pt-Cl). – ^{1}H NMR (CDCl$_3$): δ = 8.05 (s, 1H, J(Pt-H) = 102 Hz, N=CH), 7.02 – 7.68 (19H, arom.), 6.55 (dd, 1H, J = 4.2 Hz, J = 8.6 Hz, α-CH), 3.67 (dd, 1H, J = 4.2 Hz, ^2J = 13.2 Hz, β-CH), 3.22 (dd, 1H, J = 8.6 Hz, ^2J = 13.2 Hz, β-CH), 3.41 (s, 3H, OMe). – ^{13}C NMR (CDCl$_3$): δ = 166.2 (d, J = 7.3 Hz, C=N), 170.8 (CO), 122.1 – 137.1 (arom.), 74.2 (d, ^5J = 4.2 Hz, α-C), 53.2 (OMe). – ^{31}P NMR (CDCl$_3$): δ = 6.4 (s, J(Pt-P) = 3752.2. – $C_{29}H_{26}Cl_2NO_2PPt$ (717.5): calcd. C 48.54, H 3.65, N 1.95; found C 48.23, H 3.74, N 2.00.

12: Yellow. Yield 65 %. M. p. 201 °C. – IR (Nujol, cm^{-1}): ν = 1740s (CO), 1620m (C=N), 278m, 342m (Pd-Cl). – ^{13}C NMR (CDCl$_3$): δ = 168.7 (d, J = 7.9 Hz, C=N), 170 (CO), 121.4 – 137.1 (arom.), 77.3 (α-C), 53.2 (OMe). – ^{31}P NMR (CDCl$_3$): δ = 32.4 (s). – $C_{28}H_{24}Cl_2NO_2PPd$ (614.8): calcd. C 54.70, H 3.93, N 2.28; found C 54.49, H 3.96, N 2.47.

13: Light-yellow. Yield 79 %. M. p. 214 °C. – IR (Nujol, cm^{-1}): ν = 1742s (CO), 1620m (C=N), 290m, 350m (Pt-Cl). – ^{13}C NMR (CDCl$_3$): δ = 169.5 (CO), 167.4 (d, J = 7.4 Hz, C=N), 121.9 – 136.0 (arom.), 76.7 (α-C), 53.2 (OMe). – ^{31}P NMR (CDCl$_3$): δ = 6.0 (s, J(Pt-P) = 3739.8 Hz). – $C_{28}H_{24}Cl_2NO_2PPt$ (703.5): calcd. C 47.81, H 3.44, N 1.99; found C 47.79, H 3.54, N 2.22.

14: Yellow. Yield 63 %. M. p. 210 °C. – IR (Nujol, cm^{-1}): ν = 1723s (CO), 1629m (C=N), 1640w (C=C), 286m, 352 m (Pd-Cl). – ^{1}H NMR (CDCl$_3$/[D$_7$]DMF): δ = 8.44 (s, 1H, C=NH), 7.00 – 7.97 (14H, arom.), 6.16 (ψt, 1H, α-CH), 2.65 (m, 1H, β-CH), 2.83 (m, 1H, β-CH), 5.55 (m, 1H, *H*C=CH$_2$), 4.88 (s, 1H, HC=CH*H* *trans*), 4.83 (d, 1H, *J* = 5.3 Hz, HC=CH*H* *cis*), 3.55 (s, 3H, OMe). – ^{13}C NMR (CDCl$_3$/[D$_7$]DMF): δ = 170.1 (d, *J* = 8.7 Hz, C=N), 170.7 (CO), 120.1 – 138.1 (arom.), 72.7 (α-C), 38.4 (β-C), 119.1 (δ-C), 53.0 (OMe). – ^{31}P NMR (CDCl$_3$/[D$_7$]DMF): δ = 32.1 (s). – $C_{25}H_{24}Cl_2NO_2PPd$ (578.8): calcd. C 51.88, H 4.18, N 2.42; found C 51.50, H 4.30, N 2.81.

15: Yellow. Yield 81 %. M. p. 212 °C. – IR (Nujol, cm^{-1}): ν = 1724s (CO), 1618m (C=N), 1641w (C=C), 286m, 353m (Pt-Cl). – ^{13}C NMR (DMF/[D$_7$]DMF): δ = 168.9 (d, *J* = 7.3 Hz, C=N), 170.9 (CO), 121.2 – 138.0 (arom.), 73.8 (α-C), 38.5 (β-C), 119.3 (δ-C), 53.1 (OMe). – ^{31}P NMR (DMF/[D$_7$]DMF): δ = 6.4 (s, *J*(Pt-P) = 3724.0 Hz). – $C_{25}H_{24}Cl_2NO_2PPt \cdot 1/4$ DMF (685.7): calcd. C 45.10, H 3.79, N 2.55; found C 44.08, H 3.70, N 2.50.

22: Yellow. Yield 75 %. M. p. 218 – 220 °C. – IR (Nujol, cm^{-1}): ν = 3192m (NH), 1733s (CO), 1491m, 1567w, 1581w, 1599 (C=C, NH), 295m, 338m (Pd-Cl). – ^{13}C NMR (DMF/CD$_2$Cl$_2$): δ = 170.4 [170.6] (CO), 123.3 – 139.3 (arom.), 64.5 [66.4] (α-C), 52.6 [53.7] (O*C*H$_3$), 52.3 (N*C*H$_2$), 40.1 [38.6] (β-C). – ^{31}P NMR (DMF/CD$_2$Cl$_2$): δ = 17.7, 18.4. – $C_{29}H_{28}Cl_2NO_2PdPd$ (630.8): calcd. C 55.22, H 4.47, N 2.22; found C 54.70, H 4.65, N 2.41.

23: Light-yellow. Yield 66 %. M. p. 191 – 196 °C. – IR (KBr, cm^{-1}): ν = 3180m (NH), 1739s (CO), 1480m, 1567w, 1583w, 1598w (C=C, NH), 300m, 342m (Pt-Cl). – ^{13}C NMR (DMF/CD$_2$Cl$_2$): δ = 169.0, 169.9 (CO), 122.6 – 139.1 (arom.), 66.5, 67.9 (α-C), 52.9 (O*C*H$_3$), 52.3 (N*C*H$_2$), 41.0, 37.7 (β-C). – ^{31}P NMR (DMF/CD$_2$Cl$_2$): δ = −4.3 (*J*(Pt-P) = 3927 Hz), −6.5 (*J*(Pt-P) = 3887 Hz). – $C_{29}H_{28}Cl_2NO_2PPt \cdot 1/2$ DMF (756.1): calcd. C 48.45, H 4.20, N 2.78; found C 48.56, H 4.16, N 2.88.

*Cationic complexes **16 – 20**, **24** and **25***

In a dry Schlenk tube to 1 mmol of **6**, **9**, **10**, **11**, **14**, **15**, **22** or **23** and 1.1 mmol of AgBF$_4$ dichloromethane (10 mL) was added, and the mixture was stirred for 2 h. Then, the solution was filtered, and the solvent was removed from the filtrate *in vacuo*. The residue was dried *in vacuo* at 60 °C and then stirred with diethyl ether (15 mL) for 14 h. The diethyl ether was decanted, and the solid product was washed twice with diethyl ether (10 mL each) and dried *in vacuo* at 60 °C for 6 h.

16: Yellow. Yield 91 %. M. p. 180 – 182 °C. – IR (Nujol, cm^{-1}): ν = 1646 (CO), 1613m (C=N), 1062vs (BF$_4$), 353w (Pd-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.81 (d, 1H, *J*(H-P) = 2.4 Hz, N=CH), 7.30 – 8.20 (14H, arom.), 5.30 (s, 2H, α-CH), 4.54 (q, 2H, Et), 1.40 (t, 3H, *J* = 7.2, Et). – ^{13}C NMR (CD$_2$Cl$_2$): δ = 168.0 (d, *J* = 5.8 Hz, C=N), 181.4 (d, *J* = 1.5 Hz, CO), 117.3 – 140.4 (arom.), 66.4 (α-C), 67.6, 14.0 (Et). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 39.7 (s). – $C_{23}H_{22}BClF_4NO_2PPd$ (604.1): calcd. C 45.73, H 3.67, N 2.32; found C 45.12, H 3.93, N 2.55.

17: Yellow. Yield 90 %. M. p. 175 – 180 °C. – IR (Nujol, cm^{-1}): ν = 1642s (CO), 1618s (C=N), 1058vs (BF$_4$), 354m (Pt-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.99 (s, 1H, *J*(H-Pt) = 110 Hz, N=CH), 7.26 – 8.32 (14H, arom.), 5.42 (d, 1H, *J* = 5.7 Hz, α-CH), 2.38m (m, 1H, β-CH), 1.00 (d, 3H, γ-CH), 0.91 (d, 3H, *J* = 6.8 Hz, γ-CH), 4.23 (s, 3H, OMe). – ^{13}C NMR (CD$_2$Cl$_2$): δ = 165.3 (d, *J* = 4.2 Hz, C=N), 187.1 (CO), 117.1 – 140.4 (arom.), 83.4 (α-C), 36.4 (β-C), 18.3, 18.7 (γ-C), 53.3 (d, *J* = 2.1 Hz, OMe). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 2.3 (*J*(Pt-P) = 4199.8 Hz). – $C_{23}H_{30}BClF_4NO_2PPt \cdot CH_2Cl_2$ (809.7): calcd. C 38.56, H 3.98, N 1.73; found C 50.72, H 4.15, N 2.08.

18: Light-yellow. Yield 96 %. M. p. 218 °C. – IR (Nujol, cm^{-1}): ν = 1662s, 1642m (CO), 1617sh (C=N), 1062vs (BF$_4$), 356m (Pd-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.16 (d, 1H, *J*(H-P) : 3.0 Hz, N=CH), 6.62 – 8.02 (19H, arom.), 5.67 (dd, 1H, α-CH), 3.53 (dd, 1H, ^{2}J = 14 Hz, *J* = 5.0 Hz), 3.24 (dd, 1H, ^{2}J = 14.0 Hz, *J* = 8.8 Hz, β-CH), 4.14 (s, 3H, OMe). – ^{13}C NMR (CD$_2$Cl$_2$): δ = 166.9 (d, *J* = 6.0 Hz, C=N), 183.9 (CO), 118.0 – 140.7 (arom.), 79.0 (α-C), 42.0 (β-C), 58.6 (OMe). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 39.5 (s). – $C_{29}H_{26}BClF_4NO_2PPd$ (680.2): calcd. C 51.21, H 3.85, N 2.06; found C 50.72, H 4.15, N 2.08.

19: Light-yellow. Yield 92 %. M. p. 234 – 236 °C. – IR (Nujol, cm^{-1}): ν = 1648s (CO), 1627m (C=N), 1058vs (BF$_4$), 361m (Pt-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.28 (s, 1H, *J*(H-Pt) = 111 Hz), 6.62 – 7.93 (19H, arom.), 5.81 (dd, 1H, *J* = 4.4 Hz, *J* = 8.8 Hz, *J*(H-Pt) = 30 Hz, α-CH), 3.53 (dd, 1H, ^{2}J = 14.0 Hz, *J* = 4.7 Hz, β-CH), 3.27 (dd, 1H, ^{2}J = 14.0 Hz, *J* = 9.0 Hz, β-CH), 4.25 (s, 3H, OMe). – ^{13}C NMR (CD$_2$Cl$_2$): δ = 164.5 (d, *J* = 4.2 Hz, C=N), 187.2 (d, *J* = 1.6 Hz, CO), 116.4 – 140.2 (arom.), 79.4 (α-C), 42.2 (β-C), 58.5 (Me). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 1.6 (*J*(Pt-P) = 4218.7 Hz). – $C_{29}H_{26}BClF_4NO_2PPt \cdot 1/2CH_2Cl_2$ (811.4): calcd. C 43.67, H 3.35, N 1.73; found C 43.05, H 3.64, N 1.72.

20: Yellow. Yield 93 %. M. p. 193 – 196 °C. – IR (Nujol, cm^{-1}): ν = 1663s (CO), 1611w (C=N), 1640sh (C=C), 1058vs (BF$_4$), 348w (Pd-Cl). – ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.66 (d, 1H, *J*(H-P) = 3.4 Hz, N=CH), 7.19 – 8.23 (14H, arom.), 5.75 (m, 1H, *H*C=CH$_2$), 5.00 (d, 1H, *J* = 10.2 Hz, HC-C*H*H *trans*), 4.46 (d, 1H, *J* = 16.6 Hz, HC=CH*H* *cis*), 5.42 (ψt, 1H, α-CH), 2.71 (m, 1H, β-CH), 2.82 (m, 1H, β-CH), 4.01 (s, 3 H, OMe). – ^{13}C NMR (CD$_2$Cl$_2$): δ = 167.4 (d, *J* = 5.1 Hz, C=N), 181.4 (CO), 117.6 – 140.3 (arom.), 78.1 (α-C), 39.5 (β-C), 56.6 (Me), 122.2 (δ-C). – ^{31}P NMR (CD$_2$Cl$_2$): δ = 40.3 (s). – $C_{25}H_{24}BClF_4NO_2PPd$ (630.1):

calcd. C 47.66, H 3.84, N 2.22; found C 47.14, H 3.95, N 2.32.

24: Yellow. Yield 91 %. M. p. 202 – 208 °C. – IR (Nujol, cm^{-1}): ν = 3180 m, br (NH), 1641s, 1737w (CO), 1499w, 1571w, 1589w (C=C, NH), 1060vs (BF_4), 345 (Pd-Cl). – ^{13}C NMR (CD_2Cl_2): δ = 185.1 (CO), 128.4 – 135.0 (arom.), 70.9 (α-C), 56.7 (OMe), 53.9 (NCH_2), 38.0 (β-C). – ^{31}P NMR (CD_2Cl_2): δ = 32.2, 28.1, 25.0, 24.8 (1 : 3 : 4 : 1). – $C_{29}H_{28}BClF_4NO_2PPd \cdot 1/2CH_2Cl_2$ (724.7): calcd. C 48.90, H 4.03, N 1.93; found C 48.49, H 4.25, N 2.25.

25: Colorless. Yield 85 %. M. p. 210 – 214 °C. – IR (Nujol, cm^{-1}): ν = 3175m, br (NH), 1741w, 1630s (CO), 1496w, 1569w, 1576sh, 1580sh (C=C, NH), 1080vs (BF_4), 348w (Pt-Cl). – ^{13}C NMR (CD_2Cl_2): δ = 187.5 (CO), 121.6 – 137.5 (arom.), 69.6 (α-C), 36.4 (β-C), 53.5 (N-CH_2), 36.4 (β-C). – ^{31}P NMR (CD_2Cl_2): $\delta = -5.5$ (*J*(Pt-P) = 4287 Hz), -3.2 (*J*(Pt-P) = 4337 Hz) (3 : 1). – $C_{29}H_{28}BClF_4NO_2PPt \cdot 1/2\ CH_2Cl_2$ (813.3): calcd. C 43.56, H 3.59, N 1.72; found C 42.71, H 3.87, N 2.10.

*Crystal structure determination of **6** and **20***

X-Ray intensities were collected at r. t. with four-circle diffractometers using graphite-monochromatized MoK_α radiation. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied for **6**. The phase problem was solved by Direct Methods (**20**) and Patterson techniques (**6**). The SHELXTL-PLUS suite of programs were used for structure solution and refinement [19]. The crystallographic data are compiled in Table 1.

CCDC 766317 (**6**) and 759892 (**20**) contain 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.

Acknowledgement

We thank Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Wacker-Chemie AG München, and Ludwig-Maximilians-Universität München for support.

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