Hydrocarbon-Bridged Complexes, XL[◇]

Polyene-Bridged Iridium(III), Palladium(II), and Platinum(II) Complexes of Schiff Bases from α,ω-Polyene Dialdehydes and α-Amino Acids or *o*-Aminophenol☆

Armin Fehn, Oliver Briel, and Wolfgang Beck*

Institut für Anorganische Chemie der Ludwig-Maximilians-Universität, Meiserstraße 1, D-80333 München, Germany

Received March 24, 1997

Keywords: Schiff bases / Polyene dialdehydes / α-Amino acids / Pentamethylcyclopentadienyl complexes / P ligands / Iridium / Palladium / Platinum

Schiff bases **1**–**11** were synthesized from α-amino acids or *o*-aminophenol and crocetindialdehyde, 2,7-dimethyloctatrienedial, terephthalaldehyde, or β,β′-*p*-phenylenediacroleine. The reactions of these Schiff bases with chloro-bridged complexes $[(R_3P)(Cl)M(\mu\text{-}Cl)]_2$ (M = Pd, Pt) and $[(C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ gave the dinuclear complexes **12**–**31**.

Introduction

Recently, symmetrical dinuclear complexes with conjugated polyene bridges have found increasing attention because of their potential use as new materials with novel electrical ("molecular wires") and optical properties[2,3]. McCleverty and coworkers[4] found that the electronic metal-to-metal coupling between two $[Mo(Cl)(NO)\{HB(Me_2pz)_3\}]$ fragments along a $4,4'\text{-}NC_5H_4\text{-}(CH{=}CH)_n\text{-}C_5H_4N$ ligand is almost ten times larger than that of a similar complex with the same ligand and with two classical $Ru(NH_3)_5^{2+}$ fragments[4]. Recently, also binuclear bpy complexes with a pentenyl spacer[5] and a series of bis(carbene) complexes linked by a conjugated polyene bridge have been investigated[6]. Also polyene-bridged biferrocenes providing stable redox-active termini found attraction[7]. Other polyene-bridged complexes include those with metal porphyrin and $Fe_2(C_5H_5)_2(\mu\text{-}CO)CCH_3$ fragments[8].

Lehn et al.[9] reported the formation of macrocyclic binuclear complexes by condensation of carotenoid dialdehydes with tripodal amines. In the course of our studies on hydrocarbon-bridged metal complexes[10] we synthesized several polyene-bridged complexes of Schiff bases derived from α,ω-polyenedialdehydes and α-amino acids or *o*-aminophenol. Schiff bases from α-amino acid esters are well known[11] whereas those from α-amino acids are rare[12].

Results and Discussion

We obtained the Schiff base compounds **1**–**11** by condensation of several symmetrical unsaturated dialdehydes with L-valine, L-phenylalanine, L-leucine, and *o*-aminophenol. For the preparation of **1**–**9** the amino acids are dissolved in a NaOMe/MeOH solution under gentle heating. After cooling to room temperature toluene and the dialdehydes are added and the bis(Schiff bases) **1**–**9** (Scheme 1) precipitated as sodium salts after 9–24 h. Compounds **10** and **11** were synthesized by heating the dialdehydes and the *o*-aminophenol in toluene, and separating the produced water in a trap funnel. All new compounds are hygroscopic and sensitive to light and were stored in the dark under nitrogen.

In the IR spectra of **1**–**9** intensive absorptions of the carboxylate, C=N, and C=C groups at 1600 cm^{-1} are characteristic. The C=N bands of **10**, **11** appear at $\tilde{\nu}$ = 1615 cm^{-1}. Principally, three stereoisomers of the diimines could be formed but the appearance of only one singlet in the ^{1}H-NMR spectra of **1**–**11**, the signal for the HC=N at $\delta \approx 8$, proves the formation of only one stereoisomer (*EE* or *ZZ*). All other signals appear with the expected shifts and coupling patterns.

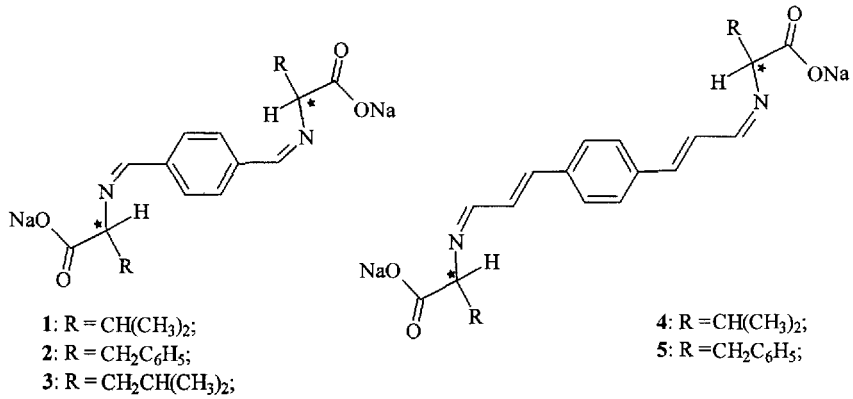
Reactions of **1**–**11** with the chloro-bridged complexes of palladium(II) and platinum(II) $[(R_3P)(Cl)M(\mu\text{-}Cl)]_2$ and with $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ and $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ in methanol gave the complexes **12**–**31** (Scheme 2).

By coordination of the bis(Schiff bases) a characteristic downfield shift of the ^{1}H-NMR signals is observed. For the palladium and platinum complexes the formation of *cis*/*cis*, *cis*/*trans*, and *trans*/*trans* isomers concerning the N–M–L configuration and for the pentamethylcyclopentadienyliridium complexes with stereogenic metal centres formation of diastereoisomers is possible. Indeed, in most cases isomers could be detected in the ^{31}P- and ^{1}H-NMR spectra. For example compound **29** shows in the ^{1}H-NMR spectra for the HC=N resonance two doublets with coupling constants of ca. 13 Hz and ca. 7 Hz which must be due to $^4J_{HP}$. There are four signals in the ^{31}P-NMR spectrum of **29** (4:6:6:10), so all three isomers must have formed. However, we cannot attribute the signals to either the *cis* or the *trans* configu-

[◇] Part XXXIX: Ref.[1].

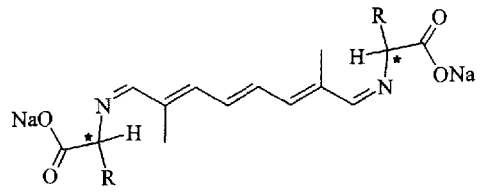
  0009–2940/97/1010–1467 $ 17.50+.50/0

Scheme 1

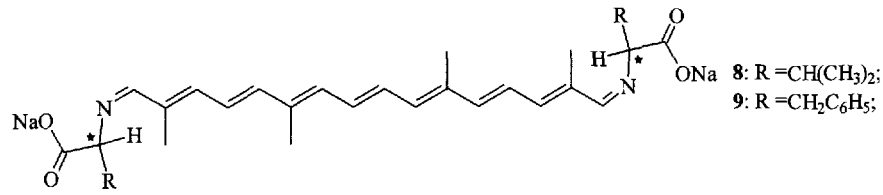


1: R = $CH(CH_3)_2$;
2: R = $CH_2C_6H_5$;
3: R = $CH_2CH(CH_3)_2$;

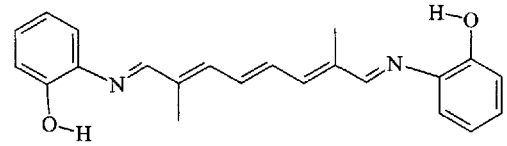
4: R = $CH(CH_3)_2$;
5: R = $CH_2C_6H_5$;



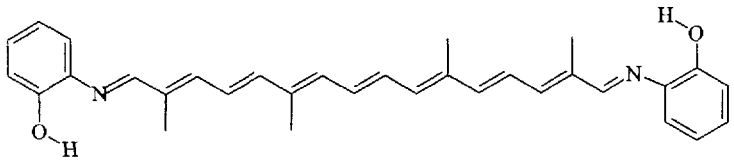
6: R = $CH(CH_3)_2$;
7: R = $CH_2C_6H_5$;



8: R = $CH(CH_3)_2$;
9: R = $CH_2C_6H_5$;



10



11

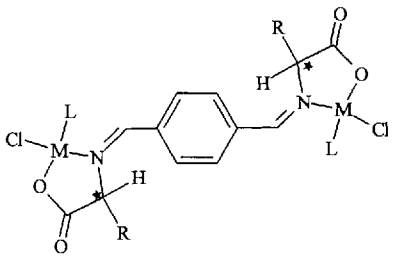
ration. For the platinum complexes in most cases one main product was detected (90% or more) which shows only one ^{31}P-NMR signal; thus, either the *cis/cis* or the *trans/trans* isomer is formed. The ^{13}C-NMR signals of the HC=N carbon atoms in compounds **12**–**27** are downfield shifted by ca. 7–10 ppm compared with those in compounds **28**–**31**. This can be explained by the electron-withdrawing effect of the carboxylate groups of **12**–**27** compared with that of the aromatic rings in **28**–**31** which are rather electron-donating.

In contrast to the complexes with Schiff bases from α-amino acids the metal compounds with Schiff bases from *o*-aminophenol are deeply coloured and show intensive broad Vis absorptions with a maximum at λ = 550 nm (CH_2Cl_2) and λ = 500 nm (MeOH), respectively (CT transition). This large negative solvatochromism may be attributed to solvent-induced dipolemoments[13].

In a forthcoming paper unsymmetrically substituted polyene-bridged complexes and their properties will be reported.

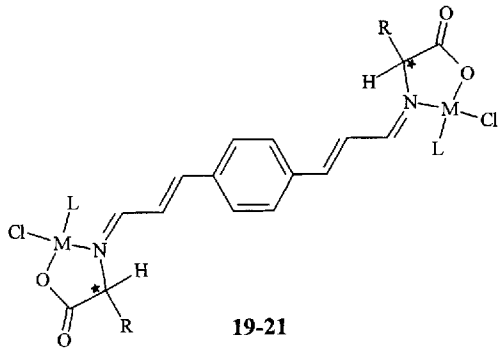
Generous support by *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* is gratefully acknowledged. We thank *BASF AG*, Ludwigshafen, and *F.-Hoffmann-LaRoche AG*, Basel, for generous gifts of the carotenoid dialdehydes and Priv.-Doz. Dr. *K. Sünkel* and Priv.-Doz. Dr. *W. Weigand* for helpful discussions.

Scheme 2



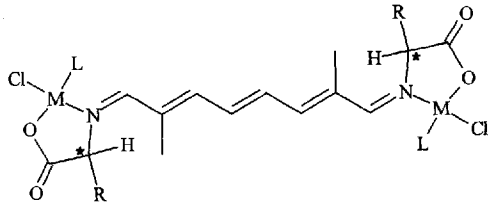
12-18

	ML	Amino Acid
12	Pd $P(Et)_3$	val
13	Pt $P(nBu)_3$	val
14	Pd (η^3-allyl)	val
15	Pd $P(Et)_3$	phe
16	Ir (Cp*)	phe
17	Pd $P(Et)_3$	leu
18	Ir (Cp*)	leu



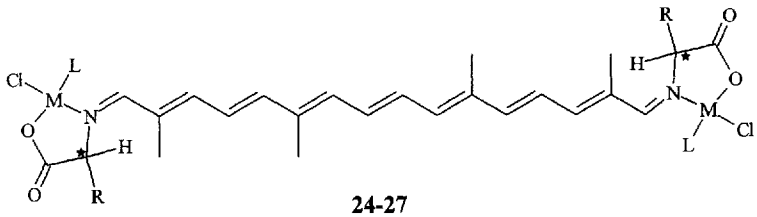
19-21

	ML	Amino Acid
19	Pd $P(Et)_3$	val
20	Ir (Cp*)	val
21	Pd $P(Et)_3$	phe



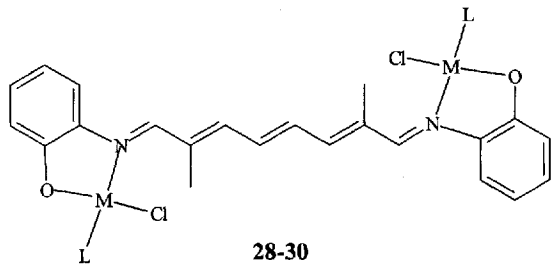
22-23

	ML	Amino Acid
22	Pt $P(nBu)_3$	val
23	Ir (Cp*)	phe



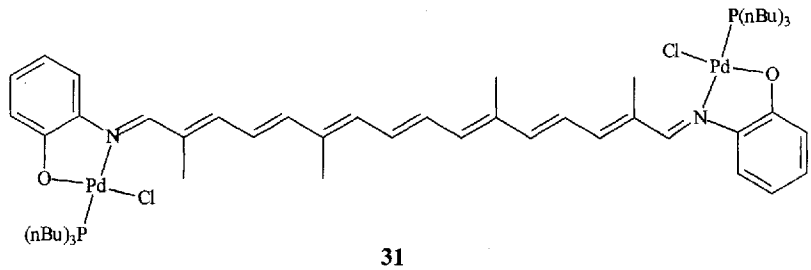
24-27

	ML	Amino Acid
24	Pd $P(nBu)_3$	val
25	Ir (Cp*)	val
26	Pd $P(nBu)_3$	phe
27	Ir (Cp*)	phe



28-30

	ML
28	Pt $P(Et)_3$
29	Pd $P(Et)_3$
30	Pd $P(nBu)_3$



31

Experimental Section

All operations were carried out under nitrogen using Schlenk techniques. Solvents were dried by destillation from sodium/benzophenon or calcium hydride. – NMR spectra: Jeol GSX 270 (^{1}H: 270.17 MHz; ^{13}C: 67.94 MHz; ^{31}P: 109.38 MHz) or Jeol EX 400 (^{1}H: 399.78 MHz; ^{13}C: 100.53 MHz). – IR: Perkin-Elmer 841, Nicolet 520 FT-IR. – UV/Vis: Philips PU 8710.

General Procedure for the Synthesis of the Schiff Base Derivatives **1**–**3**: NaOMe (2 mmol) in methanol is slowly combined with the amino acid (2 mmol) and gently heated until most of the amino acid is dissolved (for **2**: 3 mmol of NaOMe, for **8**, **9**: 4 mmol of NaOMe and 4 mmol of amino acid). After cooling to room temperature, 20 ml of toluene is added; after stirring for a few minutes, the dialdehyde is added. After stirring for 3 h to 24 h in the dark, a precipate is obtained, which is centrifugated off and for purification washed twice with a toluene/methanol mixture (10:1) and dried in vacuo at 50°C.

1: White hygroscopic powder, 631 mg (80%); m.p. 219°C (dec.). – IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1617 vs, br. (CO_2Na, C=C, C=N). – ^{1}H NMR (400 MHz, CD_3OD): δ = 8.30 (s, 2H, HC=N), 7.87 (s, 4H, C_6H_4), 3.49 [d, ^3J = 7.8 Hz, 2H, $CHCH(CH_3)_2$], 2.32 [m, 2H, $CH(CH_3)_2$], 0.99 [d, ^3J = 6.7 Hz, 6H, $CH(CH_3)_2$], 0.89 [d, ^3J = 6.7 Hz, 6H, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 179.86 (CO_2Na), 162.29 (HC=N), 139.60, 129.64, 86.31 (αC), 32.85 [$CH(CH_3)_2$], 20.46/19.47 [$CH(CH_3)_2$]. – UV/Vis (MeOH, nm, lg ε): λ_{max} = 268 (4.25). – $C_{18}H_{22}N_2Na_2O_4 \cdot H_2O$ (394.4): calcd. C 54.82, H 6.13, N 7.10; found C 55.20, H 6.16, N 6.46.

2: White hygroscopic powder; 849 mg (85%) m.p. >250°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1633 sh (C=N), 1600 vs, br. (CO_2Na, C=C). – ^{1}H NMR (400 MHz, CD_3OD): δ = 7.82 (s, 2H, HC=N), 7.67 (s, 4H, C_6H_4), 7.15 (m, 10H, C_6H_5), 3.99 (d, ^3J = 4.0 Hz, 2H, αH), 3.39 [d(d), ^2J = 13.4 Hz, ^3J = 4.0 Hz, 2H, $CHCH_\alpha H_\beta$], 3.10 [d(d), ^2J = 13.4 Hz, ^3J = 9.8 Hz, 2H, $CHCH_\alpha H_\beta$]. – UV/Vis (MeOH, nm, lg ε): λ_{max} = 277 (4.32). – $C_{26}H_{22}N_2Na_2O_4 \cdot 1.5\ H_2O$ (499.5): calcd. C 62.52, H 5.04, N 5.60; found C 62.44, H 5.04, N 5.31.

3: Light yellow hygroscopic powder, m.p. >250°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1635 sh (C=N), 1596 vs, br. (CO_2Na, C=C). – ^{1}H NMR (400 MHz, CD_3OD): δ = 8.35 (s, 2H, HC=N), 7.87 (s, 4H, C_6H_4), 3.98 [d(d), ^3J = 8.3 Hz, ^3J = 5.9 Hz, 2H, αH], 1.83 [m, 4H, $CH_2CH(CH_3)_2$], 1.55 [m, 2H, $CH(CH_3)_2$], 0.95/0.92 [d, ^3J = 6.6 Hz, 12H, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 180.51 (CO_2Na), 162.62 (HC=N), 139.59, 129.73, 76.75 (αC), 44.35 (CH_2), 27.87 [$CH(CH_3)_2$], 23.78/21.91 [$CH(CH_3)_2$]. – UV/Vis (MeOH, nm, lg ε): λ_{max} = 276 (4.23). – $C_{20}H_{26}N_2Na_2O_4 \cdot 1.5\ H_2O$ (431.5): calcd. C 55.67, H 6.72, N 6.49; found C 55.43, H 6.47, N 6.05.

4: Light brown powder. – IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1634 sh (C=N), 1603 vs (CO_2Na, C=C). – ^{1}H NMR (400 MHz, CD_3OD): δ = 8.02 (d, ^3J= 8.0 Hz, 2H, HC=N), 7.59 (s, 4H, C_6H_4), 7.11–7.08 (m, 4H, CH=CH), 3.40 (d, ^3J = 7.4 Hz, 2H, αH), 2.82 [m, 2H, $CH(CH_3)_2$], 0.98/0.89 [each d, ^3J = 6.7 Hz, 6H, ^3J = 6.7 Hz, 6H, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 179.80 (CO_2Na), 165.03 (HC=N), 143.21, 138.28, 129.18, 129.01, 83.50 (αC), 32.98 [$CH(CH_3)_2$], 20.35/19.23 [$CH(CH_3)_2$]. – UV/Vis (MeOH, nm, lg ε): λ_{max} = 354 (3.51) sh, 331 (4.23). – $C_{22}H_{26}N_2Na_2O_4 \cdot 0.75\ H_2O$ (462.0): calcd. C 55.79, H 6.27, N 6.34; found C 59.74, H 6.28, N 6.13.

5: Yellow powder. – IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1601 vs, br. (CO_2Na, C=N, C=C). – ^{1}H NMR (400 MHz, D_2O/[D$_6$]acetone): δ = 7.39–6.80 (m, 12H, C_6H_5 and HC=N), 7.02 (s, 4H, C_6H_4), 6.57 [d(d), ^3J = 16.12 Hz, ^3J = 7.8 Hz, 2H, C_6H_4–CH=CH], 6.27 (d, ^3J = 16.12 Hz, 2H, C_6H_4–CH=CH), 3.74–2.79 (m, 6H, $CHCH_2$). – ^{13}C NMR (100.5 MHz, D_2O/[D$_6$]acetone): δ = 178.34 (CO_2Na), 164.47 (HC=N), 142.17, 138.57, 129.14, 128.97, 128.15, 127.31, 126.20, 125.70, 77.08 (αC), 56.86 (CH_2). – $C_{30}H_{26}N_2Na_2O_4$ (533.5): calcd. C 67.53, H 5.10, N 5.25; found C 67.52, H 5.23, N 5.09.

6: Brown hygroscopic powder, 385 mg (87%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1608–1596 vs, br (CO_2Na, C=N, C=C). – ^{1}H NMR (400 MHz, CD_3OD): δ = 7.87 (s, 2H, HC=N), 6.93 [d(d), ^3J = 7.8 Hz, ^3J = 2.9 Hz, 2H, $(CH_3)C=CHCH$], 6.62 [d, ^3J = 7.3 Hz, 2H, $(CH_3)C=CHCH$], 3.33 (d, ^3J = 7.8 Hz, 2H, αH), 2.31–2.21 [m, 2H, $CH(CH_3)_2$], 2.05 (s, 6H, CH_3), 0.95–0.83 (each d, ^3J = 6.8 Hz, ^3J = 6.4 Hz, each 6H, $CH(CH_3)_2$. – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 180.19 (CO_2Na), 166.77 (HC=N), 139.67, 139.33, 133.00, 86.32 (αC), 32.79 [$CH(CH_3)_2$], 20.46/19.51 [$CH(CH_3)_2$] 12.23 (CH_3). – $C_{20}H_{28}N_2Na_2O_4 \cdot 2\ H_2O$ (442.3): calcd. C 54.31, H 7.29, N 6.34; found C 54.58, H 7.18, N 6.20.

7: Yellow-brown powder, 414 mg (81%). – IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1606 vs, br. (CO_2Na, C=N, C=C). – ^{1}H NMR (400 MHz, CD_3OD): δ = 7.42 (s, 2H, HC=N), 7.22–7.09 (m, 10H, C_6H_5), 6.77 [d(d), ^3J = 7.7 Hz, ^3J = 2.9 Hz, 2H, $(CH_3)C=CHCH$], 6.33 [d, ^3J = 7.7 Hz, 2H, $(CH_3)C=CHCH$], 3.88 [d(d), ^3J = 9.7 Hz, ^3J = 4.1 Hz, 2H, αH], 3.33/3.01 [each d(d), ^2J = 13.3 Hz, ^3J = 4.1 Hz, 2H, ^2J = 13.3 Hz, ^3J = 9.7 Hz, 2H, $CH_2C_6H_5$], 1.98 (s, 6H, CH_3). – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 179.97 (CO_2Na), 167.60 (HC=N), 140.74, 139.95, 139.05, 133.08, 130.76, 129.15, 127.08, 80.35 (αC), 41.86 (CH_2), 12.20 (CH_3). – $C_{28}H_{28}N_2Na_2O_4 \cdot 1/2\ H_2O$ (511.5): calcd. C 65.74, H 5.71, N 5.47; found C 65.45, H 5.83, N 4.78.

8: Orange powder, 898 mg (82%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1609 vs, br. (CO_2Na, C=N, C=C). – ^{1}H NMR (270 MHz, CD_3OD): δ = 7.85 (s, 2H, HC=N), 6.80–6.37 (m, 10H, H_{ol}) 2.24 [m, 2H, $CH(CH_3)_2$], 2.02/2.00 (each s, each 6H, CH_3), 0.94/0.82 [each d, ^3J = 6.6 Hz, 6H, ^3J = 6.6 Hz, 6H, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 180.28 (CO_2Na), 166.97 (HC=N), 142.22, 140.61, 137.84, 137.31, 135.67, 132.21, 125.31, 86.30 (αC), 32.74 [$CH(CH_3)_2$], 20.49/19.55 [$CH(CH_3)_2$], 12.78/12.25 (CH_3). – UV/Vis (MeOH, nm lg ε): λ_{max} = 464 (4.23) sh, 436 (4.27). – $C_{30}H_{40}N_2Na_2O_4 \cdot 1/2\ H_2O$ (547.6): calcd. C 65.79, H 7.55, N 5.12; found C 65.77, H 7.58, N 4.99.

9: Orange powder, 1.03 g (79%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1666 sh (C=N), 1608 vs br. (CO_2Na, C=C). – ^{1}H NMR (270 MHz, CD_3OD): δ = 7.43 (s, 2H, HC=N), 7.29–7.06 (m, 10H, C_6H_5), 6.75–6.30 (m, 10H, H_{ol}), 3.86 (dd, ^3J = 9.5 Hz, ^3J = 4.4 Hz, 2H, αH), 3.0/3.32 (dd, 4H, CH_2), 1.98/1.96 (each s, each 6H, CH_3). – $C_{38}H_{40}N_2Na_2O_4 \cdot H_2O$ (547.6): calcd. C 69.92, H 6.49, N 4.29; found C 68.90, H 6.41, N 4.04.

10: 1.64 g of 2,7-Dimethyl-2,4,6-octatriene-1,8-dial (10 mmol) and 2.18 g of *o*-aminophenol (10 mmol) were refluxed in 100 ml of toluene for 4 h using a trap funnel. After removal of 80 ml of toluene, *n*-pentane was poured in the cold solution; a crude product precipitated, which was collected and dried in vacuo giving a fine orange powder, which was not further purified. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1615 (C=N), 1576 (C=C). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 8.50 (s, 2H, CH=N), 7.32–6.83 (m, 12H, H_{ol}, H_{ar}), 2.20 (s, 6H, CH_3). – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 160.00 (HC=N), 152.42, 140.79, 139.20, 135.52, 132.79, 128.77, 119.96, 115.44, 114.75, (C_{ar}, C_{ol}) 11.66 (CH_3). – $C_{22}H_{22}N_2O_2$ (346.2): calcd. C 76.26, H 6.41, N 8.09; found C 75.27, H 6.52, N 8.10.

11: Following the same procedure as described for compound **10**; purple powder. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1613 (C=N), 1587, 1550 (C=C). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.81 (s, 2H, CH=N), 7.23–6.43 (m, 18H, H_{ol}, H_{ar}), 2.15/2.04 (each s, each 6H, CH_3). – $C_{32}H_{34}N_2O_2$ (478.6): calcd. C 80.31, H 7.15, N 5.85; found C 79.87, H 7.25, N 5.79.

General Procedure for the Synthesis of Complexes **12**–**27** *with the Schiff Bases* **1**–**9**: 0.2 mmol of **1**–**9** was dissolved in 5 ml of methanol and slowly added dropwise into a suspension of 0.2 mmol of the chloro-bridged complexes $[(R_3P)(Cl)M(\mu\text{-}Cl)]_2$ (M = Pd, R = Et, M = Pt, R = Bu), $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$, or $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ in 3 ml of methanol. The clear solution was stirred for 1–5 h, then the solvent was removed in vacuo. The crude product was stirred in dichloromethane for at least 1 h. After removing suspended NaCl by centrifugation, hexane was added to the solution. The precipitated complexes were separated from the solvent and dried in vacuo at room temperature.

Complex of **1** *with* $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**12**): Yellow powder, 158 mg (93%), m.p. 169°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1660 vs (C=O, COO-coord.), 1639 sh (C=N). – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (s, 4H, C_6H_4), 8.28 (d, $^4J_{HP}$ = 13.7 Hz, 2H, HC=N), 3.38 (dd, $^4J_{HP}$ = 2.3 Hz, ^3J = 7.3 Hz, 2H, αH), 3.10 [m, 2H, $CH(CH_3)_2$], 1.94–1.85 [m, 12H, $P(CH_2CH_3)_3$], 1.35–1.17 [m, 30H, $P(CH_2CH_3)_3$, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 178.48 (CO_2), 166.93 (HC=N), 134.93, 130.33 (C_{ar}), 83.20 (αC), 33.73 [$CH(CH_3)_2$], 19.77/19.57 [$CH(CH_3)_2$], 14.48 [d, $^1J_{CP}$= 33.22 Hz, $P(CH_2CH_3)_3$], 7.75 [d, $^2J_{CP}$ = 2.8 Hz, $P(CH_2CH_3)_3$]. – ^{31}P NMR (109 MHz): δ = 36.98 (100%). – $C_{30}H_{52}Cl_2N_2O_4P_2Pd_2$ (850.2): calcd. C 42.37, H 6.16, N 3.29; found C 41.68, H 6.16, N 3.27.

Complex of **1** *with* $[(nBu_3P)(Cl)Pt(\mu\text{-}Cl)]_2$ (**13**): Yellow powder, 150 mg (84%), m.p. 174°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1678 vs (C=O, COO-coord.), 1630 s (C=N), 1600 sh (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 530 m (PtN), 345 m (PtCl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 8.64 (d, $^4J_{HP}$ = 12.8 Hz, 2H, HC=N), 8.37 (s, 4H, C_6H_4), 3.97 (dd, $^4J_{HP}$ = 2.7 Hz, ^3J = 8.3 Hz, 2H, αH), 3.05 [m, 2H, $CH(CH_3)_2$], 1.86–1.44 [m, 36H, $P(CH_2CH_2CH_2CH_3)_3$], 1.29/1.23 [each d, ^3J = 6.7 Hz, ^3J = 6.8 Hz, each 6H, $CH(CH_3)_2$], 0.98 [t, ^3J = 7.1 Hz, 18H, $P(CH_2CH_2CH_2CH_3)_3$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 179.46 (CO_2), 167.24 (HC=N), 135.30/130.18 (C_{ar}), 85.14 (αC), 33.53 [$CH(CH_3)_2$], 25.73 [d, $^2J_{CP}$ = 2.5 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 24.06 [d, $^3J_{CP}$ = 14 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 20.38 [d, $^1J_{CP}$ = 38 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 19.82/19.48 [$CH(CH_3)_2$], 13.88 [$P(CH_2CH_2CH_2CH_3)_3$]. – ^{31}P NMR (109 MHz): δ = –1.81 (5%), –3.36 ($^1J_{PtP}$ = 3612 Hz, 95%). – $C_{42}H_{76}Cl_2N_2O_4P_2Pt_2$ (1196.1): calcd.C 42.17, H 6.40, N 2.34; found C 41.84, H 6.43, N 2.32.

Complex of **1** *with* $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ (**14**): White powder, 94 mg (73%), m.p. 162°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1641 vs, br. (C=O, COO-coord., C=C, C=N). – ^1H NMR (270 MHz, $CDCl_3$): δ = 8.53 (s, 2H, HC=N), 8.01 (s, 4H, C_6H_4), 5.48 (m, 1H, H_{allyl}), 4.02 (s, αH), 3.98 (m, 2H, $CH_{2\text{-allyl}}$), 3.05 [m, 2H, $CH(CH_3)_2$], 2.87 (m, 2H, $CH_{2\text{-allyl}}$), 1.26/1.23 [each d, ^3J = 6.8 H_2, ^3J = 6.8 Hz, each 6H, $CH(CH_3)_2$]. – $C_{24}H_{32}N_2O_4P_2Pd_2 \cdot H_2O$ (643.4): calcd. C 44.80, H 5.33, N 4.36; found C 44.57, H 5.47, N 4.44.

Complex of **2** *with* $[Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**15**): Light-brown powder, 141 mg (73%), m.p. 161 (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1654 vs (C=O, COO-coord), 1635 sh (C=N), 1605 sh (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 527 w (Pd–N), 353 w (Pd–Cl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 7.76 (s, 4H, C_6H_4), 7.24 (s, 2H, HC=N), 7.23 (m, 10H, C_6H_5), 4.06/3.57 (each dd, ^3J = 13.2 Hz, ^3J = 2.7 Hz, ^3J = 11.3 Hz, ^3J = 2.7 Hz, each 2H, CH_2Ph), 3.90 (dd, ^3J = 13.2 Hz, ^3J = 11.3 Hz, 2H, αH), 1.84–1.74 [m, 12H, $P(CH_2CH_3)_3$], 1.24 [d(t), $^2J_{PH}$ = 18.1 Hz, ^3J = 7.0 Hz, 18H, $P(CH_2CH_3)_3$]. – ^{31}P NMR (109 MHz): δ = 37.66 s (95%), 35.15 s (5%). – $C_{38}H_{52}Cl_2N_2O_4P_2Pd_2 \cdot H_2O$ (964.5): calcd. C 47.32, H 5.64, N 2.91; found C 47.18, H 5.44, N 2.84.

Complex of **2** with $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)_2$ (**16**): Yellow powder, 178 mg (75%), m.p. 198 (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1656 vs (C=O, COO-coord., C=N), 1600 sh (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 277 w (Ir-Cl). – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 4H, C_6H_4), 7.61 (s, 2H, HC=N), 7.48–7.24 (m, 10H, C_6H_5), 4.38/3.70 (each dd, ^3J = 13.9 Hz, ^2J = 2.2 Hz, ^3J = 1.8 Hz, ^2J = 2.2 Hz, each 2H, CH_2Ph), 2.90 (dd, ^3J = 13.9 Hz, ^3J = 1.8 Hz, 2H, αH), 1.46 [s, 30H, $C_5(CH_3)_5$]. – $C_{46}H_{52}Cl_2Ir_2N_2O_4 \cdot 2\ H_2O$ (1188.3): calcd. C 46.49, H 4.75, N 2.36; found C 46.29, H 4.77, N 2.47.

Complex of **3** *with* $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**17**): Light-brown powder, 86 mg (48%), m.p. 155°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1655 vs (C=O, COO-coord.), 1635 sh (C=N), 1606 sh (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 356 w (PdCl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 8.36 (s, 4H, C_6H_4), 8.30 (d, $^4J_{HP}$ = 12.0 Hz, 2H, HC=N), 4.30 (m, 2H, αH), 2.62/2.40 (m, 4H, $CHCH_2$), 1.93–1.81 [m, 14H, $P(CH_2CH_3)_3$ and $CH(CH_3)_2$], 1.32 [d(t), $^3J_{HP}$ = 17.9 Hz, ^3J = 7.6 Hz, 18H, $P(CH_2CH_3)_3$], 1.08/1.02 [each d, ^3J = 6.6 Hz, ^3J = 6.6 Hz, each 6H, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 166.11 (HC=N), 130.43/129.02 (C_{ar}), 78.48 (αC), 44.90 (CH_2), 24.46 [$CH(CH_3)_2$], 23.20/21.85 [$CH(CH_3)_2$], 14.49 [d, $^1J_{CP}$ = 32.2 Hz, $P(CH_2CH_3)_3$], 7.85 [d, $^2J_{CP}$ = 2.7 Hz, $P(CH_2CH_3)_3$]. – ^{31}P NMR (109 MHz): δ = 37.71 (94%), 34.98 (6%). – $C_{32}H_{56}Cl_2N_2O_4P_2Pd_2$ (896.5): calcd. C 42.88, H 6.52, N 3.13; found C 42.65, H 6.48, N 3.13.

Complex of **3** *with* $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ (**18**): Yellow powder, 183 mg (83%), 187°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1656 vs, br. (C=O, COO-coord., C=N, C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 279 m (IrCl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 8.70 (s, 2H, HC=N), 8.57 (s, 4H, C_6H_4), 4.30 (m, 2H, αH), 2.51 [m, 2H, $CH(CH_3)_2$], 2.17–1.90 (m, 4H, $CHCH_2$), 1.59 [s, 30H, $C_5(CH_3)_5$], 1.10/1.07 [each d, ^3J = 6.8 Hz, each 6H, $CH(CH_3)_2$]. – $C_{40}H_{56}Cl_2Ir_2N_2O_4 \cdot H_2O$ (1102.2): calcd. C 43.59, H 5.30, N 2.54; found C 43.16, H 5.34, N 2.59.

Complex of **4** *with* $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**19**): Yellow powder, 164 mg (90%), m.p. 174°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1656 vs (C=O, COO-coord.), 1625 vs (C=N), 1590 sh (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 535 w (Pd–N), 371 w (Pd–Cl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 8.29 (dd, ^3J = 15.8 Hz, ^3J = 9.4 Hz, 2H, H_{ol}), 7.89 (dd, $^4J_{HP}$ = 13.6 Hz, ^3J = 9.4 Hz, 2H, HC=N), 7.60 (s, 4H, C_6H_4), 7.11 (d, ^3J = 15.8 Hz, 2H, H_{ol}), 3.76 (m, 2H, αH), 2.60 [m, 2H, $CH(CH_3)_2$], 1.95–1.85 [m, 12H, $P(CH_2CH_3)_3$], 1.28 [d(t), $^3J_{HP}$ = 17.6 Hz, ^3J = 7.6 Hz, 18H, $P(CH_2CH_3)_3$], 1.20/1.16 [each d, ^3J = 7.7 Hz, each 6H, $CH(CH_3)_2$]. – ^{31}P NMR (109 MHz): δ = 34.63 (82%), 34.01 (18%). – $C_{34}H_{56}Cl_2N_2O_4P_2Pd_2 \cdot 0.5\ H_2O$ (896.5): calcd. C 44.85, H 6.31, N 3.08; found C 44.60, H 6.37, N 3.14.

Complex of **4** *with* $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ (**20**): Yellow powder, 149 mg (87%), m.p. 230°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1653 vs (C=O, COO-coord.), 1620 vs (C=N), 1600 sh (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 279 w (Ir–Cl). – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, ^3J = 9.4 Hz, 2H, HC=N), 7.44 (s, 4H, C_6H_4), 7.08 (d, ^3J = 16.0 Hz, 2H, H_{ol}), 6.91 (dd, ^3J = 16.0 Hz, ^3J = 9.4 Hz, 2H, H_{ol}), 3.91 (d, ^3J = 10.1 Hz, 2H, αH), 2.02 [m, 2H, $CH(CH_3)_2$], 1.70 [s, 30H, $C_5(CH_3)_5$], 1.25/0.97 [each d, ^3J = 6.7 Hz, ^3J = 6.7 Hz, each 6H, $CH(CH_3)_2$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 178.87 (CO_2), 168.77 (HC=N), 146.29/128.31 (C_{ol}), 137.07, 129.19 (C_{ar}), 85.55 [$C_5(CH_3)_5$], 82.25 (αC), 31.23 [$CH(CH_3)_2$], 20.21/19.19 [$CH(CH_3)_2$], 9.18 [$C_5(CH_3)_5$]. – $C_{42}H_{56}Cl_2Ir_2N_2O_4 \cdot 2\ H_2O$ (1144.2): calcd. C 44.08, H 5.29, N 2.45; found C 43.93, H 5.33, N 2.53.

Complex of **5** *with* $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**21**): Yellow powder, 110 mg (55%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1656 vs (C=O, COO-co-

ord.), 1622 vs (C=N, C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 358 w (Pd–Cl). – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, $^4J_{HP}$ = 16.1 Hz, ^3J = 10.3 Hz, 2H, HC=N), 7.48 (s, 4H, C_6H_4), 7.49–6.12 (m, 14H, C_6H_5 and H_{ol}), 4.10–3.31 (m, 4H, αH and CH_2), 1.95–1.77 [m, 12H, $P(CH_2CH_3)_3$], 1.23 [d(t), $^3J_{HP}$ = 16.6 Hz, ^3J = 7.33 Hz, 18H, $P(CH_2CH_3)_3$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 180.43 (CO_2), 168.58 (HC=N), 79.43 (αC), 42.22 (CH_2), 14.49 [d, $^1J_{CP}$ = 29.8 Hz, $P(CH_2CH_3)_3$], 7.88 [d, $^2J_{CP}$ = 3.3 Hz, $P(CH_2CH_3)_3$]. – ^{31}P NMR (36 MHz): δ = 34.39 (50%), 33.18 (50%). – $C_{42}H_{56}Cl_2N_2O_4P_2Pd_2$ (998.6): calcd. C 50.51, H 5.65, N 2.81; found C 49.39, H 5.77, N 2.96.

Complex of **6** *with* $[(nBu_3P)(Cl)Pt(\mu\text{-}Cl)]_2$ (**22**): Yellow powder, 136 mg (74%), m.p. 150°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1675 vs, br. (C=O, COO-coord.), 1593 s (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 342 w (Pt–Cl). – ^1H NMR (400 MHz, $CDCl_3$). δ = 8.06 (d, $^4J_{HP}$ = 12.9 Hz, 2H, HC=N), 6.97–6.88 (m, 4H, H_{ol}), 3.80 (dd, ^3J = 9.0 Hz, $^4J_{HP}$ = 2.7 Hz, αH), 3.16 [m, 2H, $CH(CH_3)_2$], 2.57 (s, 6H, CH_3), 1.84–1.75/1.66–1.57/1.53–1.44 [each m, 36H, $P(CH_2CH_2CH_2CH_3)_3$], 1.24/1.13 [each d, ^3J = 6.7 Hz, each 6H, $CH(CH_3)_2$], 0.95 [t, ^3J = 6.7 Hz, 18H, $P(CH_2CH_2CH_2CH_3)_3$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 179.61 (CO_2), 170.11 (HC=N), 144.07/136.06/134.30 (C_{ol}), 85.75 (αC), 33.59 [$CH(CH_3)_2$], 25.72 [d, $^2J_{CP}$ = 2.3 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 24.04 [d, $^3J_{CP}$ = 13.8 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 20.34 [d, $^1J_{CP}$ = 37.9 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 19.83/19.47 [$CH(CH_3)_2$], 15.39 (CH_3), 13.80 [$P(CH_2CH_2CH_2CH_3)_3$]. – ^{31}P NMR (109 MHz): δ = –4.06, $^1J_{PtP}$ = 3603 Hz (98%). – $C_{44}H_{88}Cl_2N_2O_4P_2Pt_2$ (1226.1): calcd. C 43.10, H 6.74, N 2.29; found C 42.65, H 6.50, N 2.52.

Complex of **7** *with* $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ (**23**): Orange powder, 135 mg (74%). – IR (KBr), cm^{-1}): $\tilde{\nu}$ = 1657 vs (C=O, COO-coord., C=N). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 277 m (Ir–Cl). – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–6.10 (m, 16H, HC=N, C_6H_5, H_{ol}), 4.23–2.84 (m, 6H, αH, CH_2), 1.63 [s, 30H, $C_5(CH_3)_5$]. – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 180.31 (CO_2), 172.11 (HC=N), 138.49/136.79/143.28/133.26/130.04/129.46/127.79 (C_{ol}), 86.07 (αC), 85.79 [$C_5(CH_3)_5$], 40.55 (CH_2), 15.31 (CH_3), 9.71 [$C_5(CH_3)_5$]. – $C_{48}H_{58}Cl_2Ir_2N_2O_4 \cdot 2\ H_2O$ (1218.4): calcd. C 47.23, H 5.13, N 2.30; found C 47.22, H 5.14, N 2.51.

Complex of **8** *with* $[(nBu_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**24**): Red powder. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1658 vs (C=O, COO-coord., C=N), 1597 s (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 332 vw (PdCl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 7.65 (d, $^4J_{HP}$ = 13.6 Hz, 2H, HC=N), 6.76–6.40 (m, 10H, H_{ol}), 3.58 (dd, $^4J_{HP}$ = 3.6 Hz, ^3J = 9.4 Hz, 2H, αH), 3.31 [m, 2H, $CH(CH_3)_2$], 2.55/2.00 (each s, each 6H, CH_3), 1.87–1.71/1.68–1.57/1.56–1.33 [each m, each 12H, $P(CH_2CH_2CH_2CH_3)_3$], 1.25/1.14 [each d, ^3J = 6.6 Hz, ^3J = 6.6 Hz, each 6H, $CH(CH_3)_2$], 0.96 [t, ^3J = 7.3 Hz, 18H, $P(CH_2CH_2CH_2CH_3)_3$]. – ^{13}C NMR (69.94 MHz, $CDCl_3$): δ = 179.10 (CO_2), 170.20 (HC=N), 146.31/144.42/137.13/136.33/132.16/131.80/123.99 (C_{ol}), 86.88 (αC), 33.81 [$CH(CH_3)_2$], 25.86 [d, $^2J_{CP}$ = 3.2 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 24.06 [d, $^3J_{CP}$ = 13.6 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 21.29 [d, $^1J_{CP}$ = 30.4 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 19.85/19.57 [$CH(CH_3)_2$], 15.25 (CH_3), 13.69 [$P(CH_2CH_2CH_2CH_3)_3$], 12.73 (CH_3). – ^{31}P NMR (67 MHz): δ = 27.92 (85%), 25.83 (15%). – $C_{54}H_{94}Cl_2N_2O_4P_2Pd_2 \cdot 2\ H_2O$ (1217.0): calcd. C 53.29, H 8.12, N 2.30; found C 52.93, H 8.06, N 2.13.

Complex of **8** *with* $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ (**25**): Red-brown powder. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1654 vs br. (C=O, COO-coord., C=N). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 273 m (Ir–Cl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 8.05 (s, 2H, HC=N), 6.74–6.57 (m, 10H, H_{ol}), 3.57 (d, ^3J = 6.8 Hz, 2H, αH), 2.13 [m, 2H, $CH(CH_3)_2$], 2.17/2.04 (each s, each 6H, CH_3), 1.58 [s, 30H, $C_5(CH_3)_5$], 1.25/0.99 [each d, ^3J = 6.5 Hz, ^3J = 6.7 Hz, $CH(CH_3)_2$]. – ^{13}C NMR (67.94 MHz, $CDCl_3$): δ = 178.61 (CO_2), 171.51 (HC=N), 143.13/142.92/137.08/136.25/131.80/129.67/123.56 (C_{ol}), 85.66 (αC), 85.41 [$C_5(CH_3)_5$], 31.46 [$CH(CH_3)_2$], 20.42/19.64 [$CH(CH_3)_2$], 14.76/12.75 (CH_3), 9.42 [$C_5(CH_3)_5$]. – $C_{50}H_{70}Cl_2Ir_2N_2O_4 \cdot 1.5\ H_2O$ (1245.4): calcd. C 48.22, H 5.91, N 2.19; found C 47.87, H 5.79, N 2.19.

Complex of **9** *with* $[(nBu_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**26**): Dark-red powder, 165 mg (84%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1661 vs (C=O), COO-coord., C=N), 1597 s (C=C). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 349 vw (PdCl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 7.80–7.23 (m, 12H, HC=N, C_6H_5), 6.82–6.20 (m, 10H, H_{ol}), 4.90/3.66 (each m, 2H, 4H, αH and CH_2), 2.43/2.17 (each s, each 6H, CH_3), 2.17–1.91/1.90–1.63/1.60–1.49 [each m, each 12H, $P(CH_2CH_2CH_2CH_3)_3$], 0.98 [t, ^3J = 7.0 Hz, 18H, $P(CH_2CH_2CH_2CH_3)_3$]. – ^{31}P NMR (36 MHz): δ = 28.00 (73%), 24.97 (27%). – $C_{62}H_{94}Cl_2N_2O_4P_2Pd_2 \cdot 2\ H_2O$ (1313.1): calcd. C 56.71, H 7.52, N 2.13; found C 56.35, H 7.35, N 2.13.

Complex of **9** *with* $[(\eta^5\text{-}C_5Me_5)(Cl)Ir(\mu\text{-}Cl)]_2$ (**27**): Red powder. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1647 vs br (C=O, COO-coord., C=N). – IR (PE, cm^{-1}): $\tilde{\nu}$ = 279 m (Ir–Cl). – ^1H NMR (270 MHz, $CDCl_3$): δ = 7.51–6.01 (m, 22H, HC=N, C_6H_5, H_{ol}), 4.18–2.76 (m, 6H, αH, CH_2), 1.89/1.87 (each s, each 6H, CH_3), 1.57 [s, 30H, $C_5(CH_3)_5$]. – $C_{58}H_{70}Cl_2Ir_2N_2O_4 \cdot 2\ H_2O$ (1350.5): calcd. C 51.58, H 5.52, N 2.07; found C 50.74, H 5.50, N 2.13.

General Procedure for the Synthesis of Complexes with the Schiff Bases **10**, **11**, *and the Chloro-Bridged Complexes* $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$, $[(Et_3P)(Cl)Pt(\mu\text{-}Cl)]_2$, *and* $[(nBu_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**28**–**31**): 0.05 mmol of the Schiff base **10**, **11** is stirred in 10 ml of methanol and 0.1 mmol of NaOMe in methanol is added. To the resulting solution 0.05 mmol of $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$, $[(Et_3P)(Cl)Pt(\mu\text{-}Cl)]_2$, or $[(nBu_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ is added in one portion. After stirring the mixture for 2 h at room temperature, the solvent is evaporated in vacuo, and 10 ml of dichloromethane is added. Further stirring for 2 h and centrifugation and separation of the solution from the precipitate yields a deep coloured solution of the product, which is purified by precipitation with *n*-pentane and washing with *n*-pentane.

Complex of **10** *with* $[(Et_3P)(Cl)Pt(\mu\text{-}Cl)]_2$ (**28**): Black powder, 85 mg (80%), soluble in all polar organic solvents, to give a purple-black solution. Two isomers (*cis*/*trans*) were obtained which could not be separated but gave different NMR shifts. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1626, 1619, 1610, 1587, 1564 (C=N, C=C). – ^1H NMR ($CDCl_3$): δ = 8.60/8.28 [each d, $^4J_{HP}$ = 13.10 Hz, $^4J_{HP}$ = 6.17 Hz, 2H, CH=N, (1:9)], 7.00–6.39 (m, 12H, H_{ol}, H_{ar}), 2.52/1.90 [each s, 6H, CH_3, (1:4)], 1.98–1.90 (m, 12H, PCH_2), 1.28–1.20 (m, 18H, PCH_2CH_3). – ^{13}C NMR ($CDCl_3$): δ = 162.39 (C=N), 142.52, 133.59, 130.49, 123.79, 118.09, 114.79, 14.82, 14.14, 13.77, 7.63, 7.61. – ^{31}P NMR (67 MHz): δ = 5.30 $^1J_{PtP}$ = 3614 Hz (90%), 4.30 (10%). – UV/Vis (CH_2Cl_2, nm, lg ε): λ_{max} = 412 (4.56), 555 (4.33). – UV/Vis (MeOH, nm, lg ε): λ_{max} = 409 (4.44), 525 (4.29). – $C_{34}H_{50}Cl_2N_2O_2P_2Pt_2 \cdot H_2O$ (1059.8): calcd. C 38.53, H 4.95, N 2.64; found C 38.35, H 4.52, N 2.57.

Complex of **10** *with* $[(Et_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**29**): IR(KBr): $\tilde{\nu}$ = 1613, 1584, 1567 (C=C, C=N). – ^1H NMR ($CDCl_3$): δ = 8.33/8.06 [each d, $^4J_{HP}$ = 12.85 Hz, $^4J_{HP}$ = 6.64 Hz, 2H, CH=N, (1:1)], 7.21 (d, 1H, H_{ar}), 7.00–6.78 (m, 7H, H_{ar}, H_{ol}), 6.69 (d, ^3J = 8.27 Hz, 2H, H_{ol}), 6.53 t, 6.38 t (each 1H, H_{ar}), 2.52/1.87 [each s, 6H, CH_3, (1:1)], 1.97–1.83 (m, 12H, PCH_2), 1.35–1.22 (m 18H, PCH_2CH_3). – ^{31}P NMR (67 MHz): δ = 35.82/35.70/33.22/33.11 (6:4:10:7). – UV/Vis (CH_2Cl_2, nm, lg ε): λ_{max} = 559 (4.17). – UV/Vis (MeOH, nm, lg ε): λ_{max} = 504 (3.98). – $C_{34}H_{50}Cl_2N_2O_2P_2Pd_2$

· 0.5 H_2O (871.09): calcd. C 46.84, H 5.78, N 3.22; found C 46.88, H 6.13, N 3.28.

Complex of **10** *with* $[(nBu_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**30**): Black powder, 83 mg (82%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1584 s, 1566 s (C=C). – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32/8.05 (each d, $^4J_{HP}$ = 12.70 Hz, $^4J_{HP}$ = 6.83 Hz, 2H, CH=N, 2:3), 7.20 (d, 1H, H_{ar}), 7.00–6.78 (m, 6H, H_{ar}, H_{ol}), 6.69 (m, 3H, H_{ar}, H_{ol}), 6.48/6.37 (each t, each 1H, H_{ar}), 2.54/2.52 (each s, 3H, CH_3, 2:1), 1.87–1.80 (m, 15H, PCH_2, CH_3), 1.72–1.61/1.54–1.44 (m, 24H, $PCH_2CH_2CH_2CH_3$), 0.97–0.86 (m, 18H, $PCH_2CH_2CH_2CH_3$). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 163.1/163.2 (C=N), 142.63, 141.94, 138.62, 135.77, 134.35, 134.08, 133.19, 132.92, 130.25, 130.13, 129.99, 123.53, 118.47, 118.38, 115.87, 114.01, 113.96, 34.19, 26.03 [d, $^2J_{CP}$ = 6.20 Hz, $P(CH_2CH_2CH_2CH_3)_3$], 24.37/24.29 [each d, $^3J_{CP}$ = 12.8 Hz, $^3J_{CP}$ = 13.5 Hz, 2:3, $P(CH_2CH_2CH_2CH_3)_3$], 22.28/22.04 [each d, $^1J_{CP}$ = 29.4 Hz, $^1J_{CP}$ = 30.8 Hz, 2:3, $P(CH_2CH_2CH_2CH_3)_3$], 16.35/16.27/14.78/14.10 (CH_3), 13.74 [$P(CH_2CH_2CH_2CH_3)_3$]. – ^{31}P NMR (36 MHz): δ = 27.39/27.26/25.14/25.04 (4:5:5:4). – UV/Vis (CH_2Cl_2, nm, lg ε): λ_{max} = 406 (4.44), 542 (4.31). – UV/Vis (MeOH, nm, lg ε): λ_{max} = 403 (4.31), 494 (4.16). – $C_{46}H_{74}Cl_2N_2O_2P_2Pd_2$ (1030.3): calcd. C 53.58, H 7.24, N 2.72; found C 53.26, H 7.22, N 2.57.

Complex of **11** *with* $[(nBu_3P)(Cl)Pd(\mu\text{-}Cl)]_2$ (**31**): Black powder, 84 mg (70%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1583 s, 1561 vs (C=C). – ^1H NMR ($CDCl_3$, 270 MHz, $CDCl_3$): δ = 8.30/8.03 [each d, $^4J_{HP}$ = 12.90 Hz, $^4J_{HP}$ = 6.37 Hz, 2H, CH=N, (1:2)], 7.20 (d, 1H, H_{ar}), 6.97–6.57 (m, 13H, H_{ar}, H_{ol}), 6.48–6.33 (m, 4H, H_{ol}), 2.54 (s, 2H, CH_3), 2.01 (s, 4H, CH_3), 1.94–1.45 (m, 36H, $PCH_2CH_2CH_2CH_3$), 1.84 (s, 6H, CH_3), 0.99–0.89 (m, 18H, $PCH_2CH_2CH_2CH_3$). – ^{31}P NMR: δ = 26.72/24.56 (2:3). – UV/Vis (CH_2Cl_2, nm, lg ε): λ_{max} = 545 (5.07). – UV/Vis (MeOH, nm, lg ε): λ_{max} = 493 (4.81). – $C_{56}H_{86}Cl_2N_2O_2P_2Pd_2 \cdot H_2O$ (1180.4): calcd. C 56.93, H 7.51, N 2.37; found C 56.98, H 7.55, N 2.17.

☆ Dedicated to Professor *Dieter Seebach* on the occasion of his 60th birthday.

[1] S. Mihan, T. Weidmann, V. Weinrich, D. Fenske, W. Beck, *J. Organomet. Chem.*, in press.

[2] M. D. Ward, *Chem. Soc. Rev.* **1995**, 121–134.

[3] J.-M. Lehn, *Angew. Chem.* **1988**, *100*, 91–116; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89–112; J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347–1362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304–1319.

[4] S. L. W. McWhinnie, J. A. Thomas, T. A. Hamor, C. J. Jones, J. A. McCleverty, D. Collison, F. E. Mabbs, C. J. Harding, L. J. Yellowless, M. G. Hutchings, *Inorg. Chem.* **1996**, *35*, 760–774; A.-C. Ribou, J.-P. Launay, K. Takahashi, T. Nihira, S. Tarutami, C. W. Spangler, *Inorg. Chem.* **1994**, *33*, 1325–1329; S. L. W. McWhinnie, C. J. Jones, J. A. McCleverty, D. Collison, F. E. Mabbs, *J. Chem. Soc., Chem. Commun.* **1990**, 940–942; J. A. McLeverty, J. A. Navas, Badiola, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1994**, 2415–2421; J. R. Reimers, N. S. Hush, *Inorg. Chem.* **1990**, *29*, 4510–4513; S. Woitellier, J. P. Launay, C. W. Spangler, *Inorg. Chem.* **1989**, *28*, 758–762.

[5] A. C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn, B. Marczinke, *J. Phys. Chem.* **1994**, *98*, 7798–7804.

[6] R. Aumann, B. Jasper, R. Fröhlich, S. Kotila, *J. Organomet. Chem.* **1995**, *502*, 137–141; B. A. Etzenhouser, Q. Chen, M. B. Sponsler, *Organometallics* **1994**, *13*, 4176–4178; A. Rabier, N. Lugan, R. Mathieu, G. L. Geoffroy, *Organometallics* **1994**, *13*, 4676–4678; A. Geisbauer, S. Mihan, W. Beck, *J. Organomet. Chem.* **1995**, *501*, 61–66; T. Albrecht, J. Sauer, H. Nöth, *Tetrahedron Lett.* **1994**, *35*, 561–564; H. H. Fox, J. K. Lee, L. Y. Park, R. R. Schrock, *Organometallics* **1993**, *12*, 759–768; R. Aumann, H. Heinen, *J. Organomet. Chem.* **1987**, 211–221.

[7] A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K.-H. Ongania, K. Wurst, J.-P. Launay, *Organometallics* **1997**, *16*, 392–400; A.-C. Ribou, J.-P. Launay, M. L. Sachtleben, H. Li, C. W. Spangler, *Inorg. Chem.* **1996**, *35*, 3735–3740; L. M. Tolbert, X. Zhao, Y. Ping, L. A. Bottomley, *J. Am. Chem. Soc.* **1995**, *117*, 12891–12892; T.-Y. Dong, T.-J. Ke, S.-M. Peng, S.-K. Yeh, *Inorg. Chem.* **1989**, *28*, 2103–2106; F. Delgado-Pena, D. R. Talham, D. O. Cowan, *J. Organomet. Chem.* **1983**, *253*, C43–C46; G. Ferguson, C. Glidewell, G. Opromolla, C. M. Zakaria, P. Zanello, *J. Organomet. Chem.* **1996**, *517*, 183–190.

[8] A. R. Rezvani, C. E. B. Evans, R. J. Crutchley, *Inorg. Chem.* **1995**, *34*, 4600–4604; A. Osuka, N. Tanabe, S. Kawabata, I. Yamazaki, Y. Nishimura, *J. Org. Chem.* **1995**, *60*, 7177–7185; J. M. Spotts, W. P. Schaefer, S. R. Marder, *Adv. Mater.* **1992**, *4*, 100–102; D. Lentz, D. Preugschat, *Angew. Chem.* **1990**, *102*, 308–310; D. Lentz, D. Preugschat, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 315–316; N. Rajapakse, B. R. James, D. Dolphin, *Can. J. Chem.* **1990**, *68*, 2274; L. M. Tolbert, X. Zhao, Y. Ding, L. A. Bottomley, *Inorg. Chim. Acta* **1996**, *251*, 29–33; K.-Y. Shih, R. R. Schrock, R. Kempe, *J. Am. Chem. Soc.* **1994**, *116*, 8804–8805.

[9] J.-M. Lehn, J.-P. Vigneron, I. Bkouche-Waksman, J. Guilhem, C. Pascard, *Helv. Chim. Acta* **1992**, *75*, 1069–1077.

[10] W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* **1993**, *105*, 969–996; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 923–949.

[11] R. Grigg, H. Q. N. Gunaratne, *Tetrahedron Lett.* **1983**, *24*, 4457–4460; R. Grigg, J. Kemp, *Tetrahedron Lett.* **1980**, *21*, 2461–2464; J. J. Fitt, H. W. Gschwend, *J. Org. Chem.* **1977**, *47*, 2639–2641; M. J. O'Donnell, R. L. Polt, *J. Org. Chem.* **1982**, *47*, 2663–2666; N. Ikota, K. Achiwa, S.-I. Yamada, *Chem. Pharm. Bull.* **1983**, *31*, 887–894; G. Wilkinson, F. A. Cotton, *Prog. Inorg. Chem.* **1959**, *1*, 1–124; L. Stryer, *Biochemie*, 3rd ed., Vieweg, **1985**.

[12] F. C. McIntire, *J. Am. Chem. Soc.* **1947**, *69*, 1377–1381; M. Bergmann, H. Enßlin, L. Zervas, *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 1034–1043; O. Gerngroß, E. Zühlke, *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 1482–1489; H. Scheibler, N. Neef, *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 1500–1511; H. Scheibler, P. Baumgarten, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 1358–1379; D. Freiesleben, K. Polborn, C. Robl, K. Sünkel, W. Beck, *Can. J. Chem.* **1995**, *73*, 1164–1174.

[13] W. Kaim, S. Ernst, S. Kohlmann, *Chem. Unserer Zeit* **1987**, *2*, 50–58.

[97066]