# Metal Complexes of Biologically Important Ligands, CXIII[+]

# Cinchona Alkaloids as Versatile Ambivalent Ligands – Coordination of Transition Metals to the Four Potential Donor Sites of Quinine

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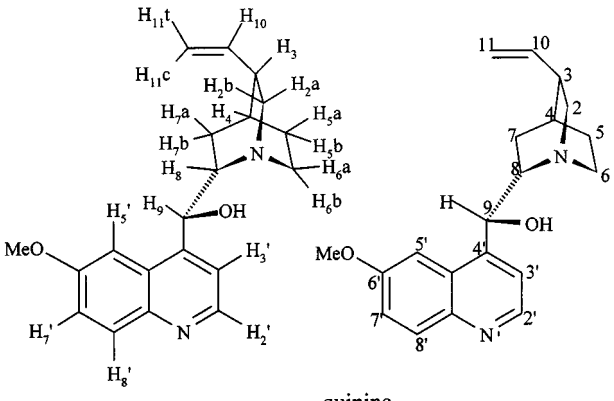
*Dedicated to Professor Helmut Werner on the occasion of his 65th birthday*

**Keywords:** Quinine / Cinchonine / Palladium / Platinum / Silver / Gold

A series of metal complexes in which quinine ($L^1$) and cinchonine ($L^2$) are coordinated via the four possible donor atoms was prepared and characterized. Coordination of the tertiary N atom of quinine is observed in $[L^1MPPh_3]^+NO_3^-$ [M = Au (**1**), Ag (**2**)], $[L^1Pd(COD)(Cl)]^+$ $NO_3^-$ (**3**) and $L^1Pd(Cl)(allyl)$ (**4**). The mono anion of quinine functions as N,O chelate ligand in $(L^1–H^+)M(Cl)(PR_3)$ (M = Pd, Pt, **5**–**10**), $[(L^1–H^+)Pd(en)]^+NO_3^-$ (**11**) and $(L^1–H^+)_2TiCl_2$ (**12**). Protection of the tertiary N atom of quinine by methylation or protonation allows the synthesis of the quinoline complexes $[(L^1CH_3^+)M(Cl)_2(PR_3)]^+$ $BF_4^-$ (M = Pd, Pt, **14**–**18**), $[(L^1CH_3^+)Ir(Cl)_2(Cp^*)]^+$ $BF_4^-$ (**19**), $[(L^1+H^+)M(Cl)_2(PR_3)]^+$ $CF_3SO_3^-$ (M = Pd, Pt, **20**–**22**) and $(L^2+H^+)(ZnCl_3^-)$ (**23**). Quinine and cinchonine act as N,O–N bridge in the complexes $(R_3P)(Cl)M(\mu\text{-}L^1–H^+)M(Cl)_2(PR_3)$ (M = Pd, Pt, **24**, **25**, **27**, **28**), $(Cp^*)(Cl)Ir(\mu\text{-}L^1–H^1)Ir(Cl)_2(Cp^*)$ (**29**), $(EtP_3)(Cl)Pd(\mu\text{-}L^2–H^+)Pd(Cl)_2(PEt_3)$ (**26**), and as N–N bridge in the complexes $[(Ph_3P)Au(\mu\text{-}L^1)Au(PPh_3)]^+NO_3^-$ (**30**) and $(allyl)(Cl)Pd(\mu\text{-}L^1)Pd(Cl)(allyl)$ (**31**). Coordination of quinine via the C=C double bond occurs in $[(L^1+2\ H^+)PtCl_3]^+Cl^-$ (**32**). The structures of **11**, **13**, **19**, **23**, **26** and **32** were determined by X-ray diffraction. In most cases the coordination mode and the conformation of quinine can also be derived from the $^1$H-NMR spectra.

Quinine is a widely used antimalaria drug and its derivatives are applied as optically active auxiliaries in asymmetric synthesis.[3] Most important is the Sharpless asymmetric dihydroxylation of olefins with osmium tetroxide and cinchona alkaloids.[4]

Recently, the interesting mechanism of this reaction was extensively analysed by Sharpless[5] and Corey.[6] The mechanism involves coordination of the tertiary N atom of the quinuclidine residue and the structure of the $OsO_4$ complex with the tertiary *N*-coordinated dihydroquinidine derivative was established by Sharpless et al.[7] To our knowledge only few metal complexes of cinchona alkaloids have been described.[8] In our group several organometallic compounds of cinchona alkaloids were synthesized and the first N,O-chelate complexes of cinchonidine and cinchonine were characterized by X-ray crystallography.[9] In continuation of these studies we now report on the synthesis of quinine complexes using all four potential donor sites of quinine (OH group, tertiary N and pyridine N atoms, olefinic C=C bond). In most cases analysis of the $^1$H-NMR spectra of the various complexes gives information which donor atom is involved in coordination. The $^1$H-NMR spectra of the free ligands have been previously interpreted.[10,11]




quinine

## Results and Discussion

### 1. Coordination at the Quinuclidine N Atom

The most basic donor site of quinine is the quinuclidine N atom and coordination at this donor occurs in the reaction of quinine with in situ prepared $Ph_3PAuNO_3$, $Ph_3PAgNO_3$, $(COD)Pd(Cl)(NO_3)$ and with $(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)_2Pd(\eta^3\text{-}C_3H_5)$ to give the complexes **1**–**4**.

The mode of coordination can be unambiguously derived from the $^1$H-NMR spectra. The signals (which were assigned by 2D-COSY experiments) of the hydrogen atoms situated near the tertiary N atom show a considerable

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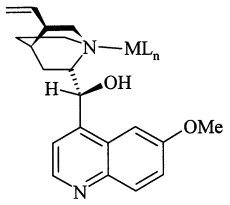
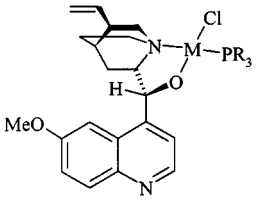



| | $ML_n$ |
|---|---|
| **1** | $AuPPh_3^+NO_3^-$ |
| **2** | $AgPPh_3^+NO_3^-$ |
| **3** | $PdCl(COD)^+NO_3^-$ |
| **4** | PdCl(allyl) |

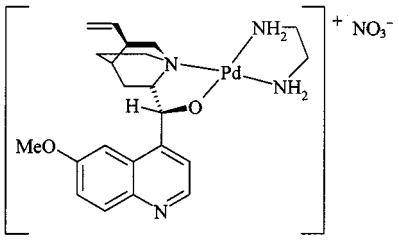
downfield shift in comparison to those of the free quinine. A detailed study of the conformations of cinchona alkaloides has been carried out by Wynberg and Sharpless[11] and four conformers were defined ("closed conformation 1 and 2, open conformation 3 and 4"). The "open conformation 3" in **1**−**4** which was also found for the $OsO_4$ complex[7] and some complexes of Ru, Ir, and Au[9] follows from the downfield shift of the signal of 7b-H as a consequence of the change of the position of 7b-H relative to the aromatic system: In the "open conformation 3" the 7b-H atom lies in the same plane with the quinoline ring and is no longer shielded by the anisotropic cone of the heteroaromatic ring. Hydrogen 7a-H, which is positioned above the quinoline ring, suffers a small upfield shift. In contrast to **5**−**10** (see below) the signals of the aromatic protons are almost not shifted which means that they do not interact with the $d_{z^2}$ orbital of $Pd^{II}$,[12] a further hint for the "open conformation 3".

## 2. N,O-Chelate Complexes

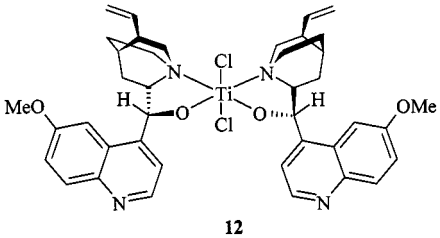
From the chloro-bridged complexes $(R_3P)(Cl)M(\mu\text{-}Cl)_2M(Cl)(PR_3)$ (M = Pd, Pt) and quinine in the presence of NaOMe in methanol the compounds **5**−**10** are obtained.




| | M | R |
|---|---|---|
| **5** | Pt | Et |
| **6** | Pt | Bu |
| **7** | Pd | Et |
| **8** | Pd | Pr |
| **9** | Pd | Bu |
| **10** | Pd | Ph |




**11**




**12**

In order to avoid coordination of the pyridine N atom the reaction was carried out at −78 °C. We assume that the *trans*-P−M−N isomers are formed as main products. Presumably the reaction proceeds stepwise as was found, for example, for the reaction of $[PtCl_3(C_2H_4)]^-$ with α-amino carboxylates.[13] The first step is the opening of the chloro bridge by the quinuclidine N atom and building of the M−N bond. This step is followed by the closure of the chelate ring with displacement of the *cis*-chloride by the oxy group. The P−M−N isomer was also found e.g. for $(Cl)(Ph_3P)Pt[NH_2C(Me)_2CO_2]$.[14] Two further $^{31}$P-NMR signals of low intensity (< 5%) which were only observed for the $Pd^{II}$ complexes may indicate formation of the *cis* isomer and of a complex with quinine coordinated via the pyridine N atom as minor products.

The reaction of $[(en)Pd(OH_2)_2]^{2+}(NO_3^-)_2$ with quinine affords the N,O-chelate complex **11**. The formation of the five-membered chelate ring in **5**−**11** is confirmed by the downfield shift of the $^1$H-NMR signal of 9-H and by the disappearance of the ν(OH) absorption in the IR spectrum.

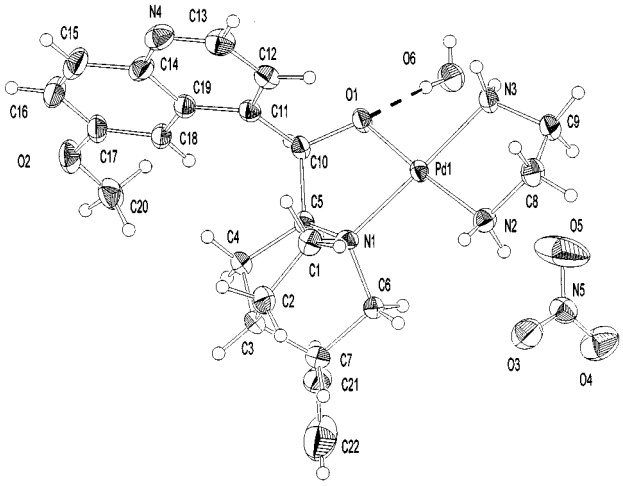



Figure 1. Molecular structure of **11** in the crystal; selected bond lengths [Å] and angles [°]: Pd1−O1 1.982(3), Pd1−N1 2.040(3), Pd1−N3 2.043(3), Pd1−N2 2.041(4), O1−C10 1.406(5), N1−C1 1.485(8), N1−C5 1.505(5) N1−C6 1.518(7), N2−C8 1.474(6), N3−C9 1.481(6), C8−C9 1.505(7), C5−C10 1.543(6), C10−C11 1.525(7); O1−Pd1−N1 85.30(13), O1−Pd1−N3 92.84(13), N1−Pd1−N3 178.0(2), O1−Pd1−N2 175.05(14), N1−Pd1−N2 98.79(15), N3−Pd1−N2 83.11(15), N1−C5−C10 111.2(4), N1−Pd1−O1−C10 6.8(3), N1−Pd1−N2−C8 −163.0(4), N1−C5−C10−O1 40.7(6), N1−C5−C10−C11 −86.9(5)

The conformation of quinine in **5**−**11** can be described as "open conformation 4".[11] The signal of the 3′-H atom in **5**−**11** suffers a downfield shift up to 1.8 ppm which is due to interaction with the $d_{z^2}$ orbital.[12] This is ascertained by the X-ray structure determination of **11**.

Reaction of $TiCl_4$ and quinine in $CH_2Cl_2$ afforded a complex **12** for which − from analytic and $^1$H-NMR data − we assume the shown structure.

## 3. Coordination at the Quinoline N Atom

The quinuclidine N atom of quinine was selectively protected by alkylation with $Me_3O^+$ $BF_4^-$ [15] and from the reaction of the methylquininium tetrafluoroborate **13** with chloro-bridged complexes $(Cl)(R_3P)M(\mu\text{-}Cl)_2M(Cl)(PR_3)$ (M = Pd, Pt) and $(Cl)(Cp^*)Ir(\mu\text{-}Cl)_2Ir(Cl)(Cp^*)$ the compounds **14**−**19** were isolated.

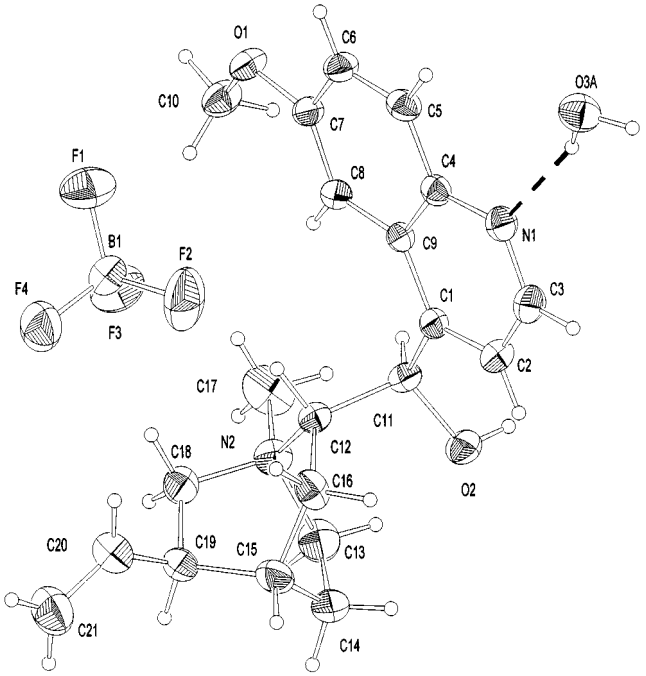



Figure 2. Molecular structure of **13** in the crystal; selected bond lengths [Å] and angles [°]: N2−C17 1.495(4), C1−C11 1.520(4), C11−C12 1.528(4), O2−C11 1.413(3), C1−C11 1.520(4); O2−C11−C1 111.5(2), O2−C11−C12 108.5(2), O2−C11−C12−N2 −68.9(2), C2−C1−C11−C12 106.9(3), C1−C11−C12−N2 168.5(2)

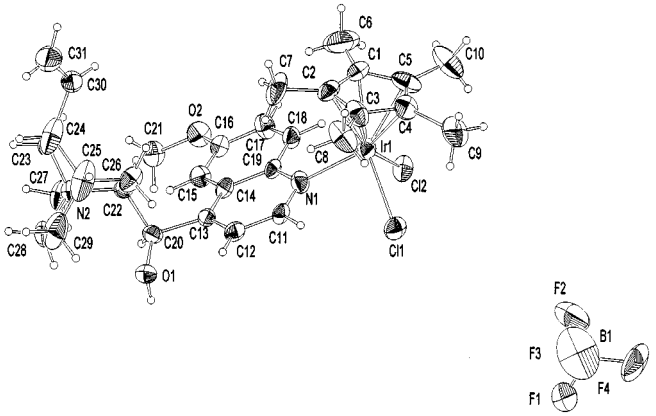
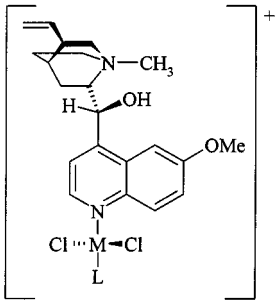
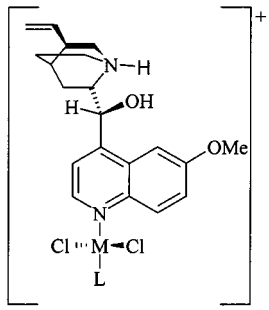



Figure 3. Molecular structure of **19** in the crystal; selected bond lengths [Å] and angles [°]: Ir1−N1 2.139(9), Ir1−Cl2 2.402(3), Ir1−Cl1 2.442(3), Ir1−C1 2.125(12), O1−C20 1.414(13), Ir1−C2 2.144(10), N1−Ir1−Cl1 88.8(3), N1−Ir1 Cl2 91.9(3); O1−C20−C13 112.5(9), N2−C22−C20 114.4(8), C12−C13−C20−O1 −20.2(13), O1−C20−C22−N2 −77.0(11), C13−C20−C22−N2 161.3(9)

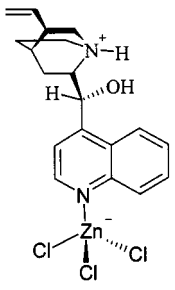
Protection of the quinuclidine N atom is even more easily achieved by protonation of quinine with $F_3CSO_3H$, and the




| | M | L |
|---|---|---|
| **14** | Pt | $PEt_3$ |
| **15** | Pt | $PBu_3$ |
| **16** | Pd | $PEt_3$ |
| **17** | Pd | $PPr_3$ |
| **18** | Pd | $PBu_3$ |
| **19** | Ir | Cp* |




| | M | L |
|---|---|---|
| **20** | Pt | $PEt_3$ |
| **21** | Pd | $PEt_3$ |
| **22** | Pd | $PPr_3$ |




**23**

obtained ammonium salt (which was not isolated) reacted with the chloro-bridged Pd and Pt complexes to give compounds **20**−**22**. Attempts to deprotonate **20**−**22** in order to yield neutral complexes gave mixtures which were not separated.

In the $^1$H-NMR spectra of **14**−**19** and **20**−**22** a downfield shift is observed for the signals of 2′-H and 8′-H, which indicates coordination of the metal center to the quinoline N atom. For **14**, **15** and **20**−**22** a $^4J$(2′-H,P) coupling can be detected. The "open-conformation 3" of coordinated quinine is found for **14**−**22**, like in **1**−**4**. In the IR spectra of **20**−**22** the ν(NH) absorption at 2600−2700 $cm^{-1}$ and the ν(OH) band at ca. 3400 $cm^{-1}$ are characteristic.

A zwitterionic structure is found for the product **23** from cinchonine and $ZnCl_2$ in methanol. Complex **23** may be compared with a molecular L-histidinium trichlorozincate (L-histidine$H^+$) $ZnCl_3$.[16]

## 4. Dinuclear Complexes

The bimetallic complexes **24**−**29** were obtained in two steps using first a stoichiometric ratio of 1/1/0.5 of NaOMe,

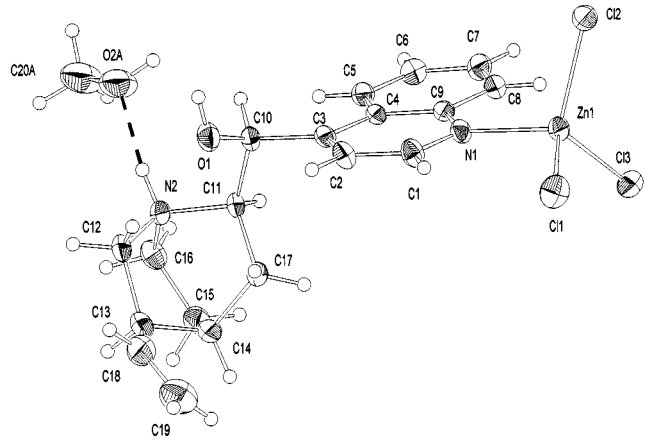
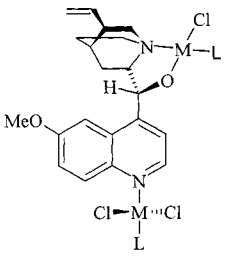
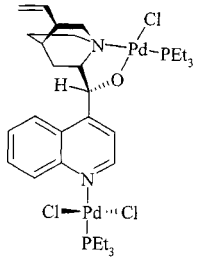



Figure 4. Molecular structure of **23** in the crystal; selected bond lengths [Å] and angles [°]: Zn1−N1 2.088(2), Zn1−Cl2 2.2340(8), Zn1−Cl3 2.2497(10), Zn1−Cl1 2.2732(11), O1−C10 1.418(5), C3−C10 1.524(3), C10−C11 1.540(4), N2−C11 1.520(3); N1−Zn1−Cl2 105.82(6), N1−Zn1−Cl3 109.94(8), Cl2−Zn1−Cl3 112.51(4), N1−Zn1−Cl1 105.57(8), Cl2−Zn1−Cl1 115.81(5), Cl3−Zn1−Cl1 106.90(4), O1−C10−C3 110.8(3), O1−C10−C11 109.4(2), Cl3−Zn1−N1−C1 128.7(2), Cl1−Zn1−N1−C1 13.8(2), Cl2−Zn1−N1−C9 69.4(2), Zn1−N1−C9−C8 0.1(3), O1−C10−C11−N2 52.4(3), C2−C3−C10−O1 21.3(3), C3−C10−C11−N2 174.3(3)

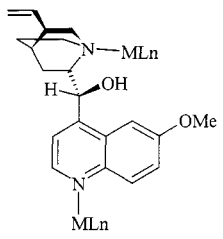
quinine or cinchonine and $[LMCl_2]_2$ to give the N,O-chelates which were not isolated and which by addition of another 0.5 equivalent of $[LMCl_2]_2$ afforded the desired products.




| | M | L |
|---|---|---|
| **24** | Pt | $PEt_3$ |
| **25** | Pd | $PEt_3$ |
| **27** | Pd | $PPr_3$ |
| **28** | Pd | $PBu_3$ |
| **29** | Ir | Cp* |




**26**




| | $ML_n$ |
|---|---|
| **30** | $AuPPh_3^+NO_3^-$ |
| **31** | PdCl(allyl) |

Heterobimetallic complexes could only be obtained as mixtures by this route. The "open conformation 4" of quinine and cinchonine in **24**−**29** is analogous to that in **5**−**10**. The downfield shift of the 2′-H and 8′-H $^1$H-NMR signals caused by the interaction with the $d_{z^2}$ orbital of the metal ion[12] indicates that the chloro ligands in **24**−**29** as in **14**−**19** lie perpendicular to the quinoline plane.

In the dinuclear complexes **30**−**31** quinine functions as a bis(monodendate) bridge. The characteristic $^1$H-NMR signals of **30**−**31** are consistent with an "open conformation 3" of the ligand.

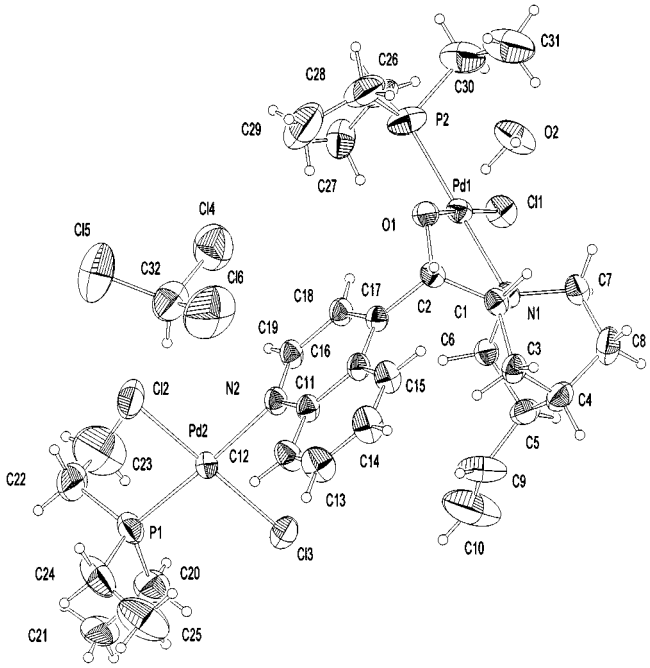



Figure 5. Molecular structure of **26** in the crystal; selected bond lengths [Å] and angles [°]: Pd1−O1 1.989(4), Pd1−N1 2.120(4), Pd1−P2 2.237(2), Pd1−Cl1 2.314(2), Pd2−N2 2.116(4), Pd2−P1 2.2288(15), Pd2−Cl2 2.287(2), Pd2−Cl3 2.291(2), O1−C2 1.402(6), C1−C2 1.534(7), C2−C17 1.524(7), C9−C10 1.109(15); O1−Pd1−N1 84.35(14), O1−Pd1−P2 89.90(12), N1−Pd1−P2 173.86(13), N2−Pd2−P1 176.32(12), N2−Pd2−Cl2 89.69(12), P1−Pd2−Cl2 88.28(7), N2−Pd2−Cl3 89.01(12), N2−Pd2−P1 176.32(12), O1−Pd1−Cl1 177.44(11), N2−Pd2−P1 176.32(12), Cl2−Pd2−Cl3 176.99(9), Cl2−Pd2−N2−C11 98.4(4), Cl3−Pd2−N2−C11 −78.9(4), O1−Pd1−N1−C1 −7.8(3), O1−C2−C17−C18 28.3(6), C1−C2−C17−C18 −98.4(5), N1−C1−C2−C17 81.4(5)

## 5. Coordination at the Olefinic Group

Finally we proved the coordination of a metal ion at the C=C double bond of quinine using the general method[17] for preparing (olefin)platinum complexes.

The reaction of double protonated quinine with $K_2PtCl_4$ in aqueous hydrochloride acid gives the (also thermally) stable complex **32**, which is an analogue of the Zeise salt $K[PtCl_3(C_2H_4)]$. As a consequence of complexation of the C=C double bond an upfield shift is observed for the three $^1$H-NMR signals of the olefinic protons. In the $^1$H-NMR spectrum of **32** two sets of signals in the ratio 1:1 are observed. By coordination of the prochiral C=C double bond the C-10 atom becomes a stereogenic centre, and two diastereoisomers are formed. In contrast to various $Pt^{II}$ complexes with coordinated olefins and optically active amino acids[18] or amines[19] no diastereoselectivity is observed in our case.

Metal complexes of C=C-coordinated quinine may be useful for the derivativization of quinine at the C=C double bond.

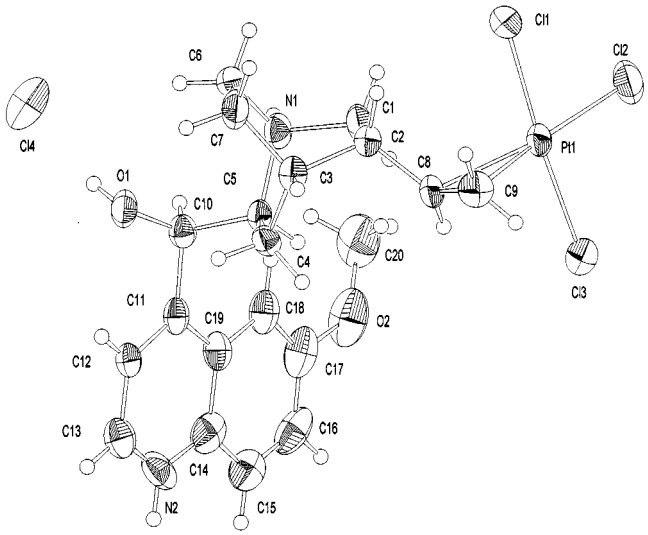
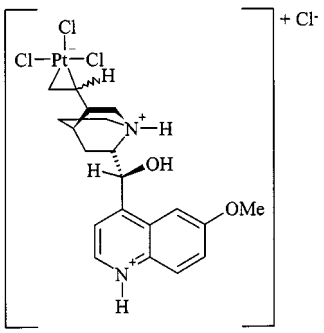



Figure 6. Molecular structure of **32** in the crystal; selected bond lengths [Å] and angles [°]: Pt1−C8 2.164(8), Pt1−Cl3 2.277(3), Pt1−Cl1 2.293(3), Pt1−Cl2 2.321(3), C8−C9 1.396(14), O1−C10 1.399(11), C10−C11 1.524(14), C5−C10 1.537(12); C8−Pt1−Cl1 94.7(3), C8−Pt1−Cl2 154.9(3), Cl3−Pt1−Cl2 90.34(13), Cl1−Pt1−Cl2 88.13(13), O1−C10−C11 110.4(7), O1−C10−C5 111.0(7), N1−C5−C10 111.0(7), Cl3−Pt1−Cl1 175.13(11), O1−C10−C11−C12 −14.6(11), N1−C5−C10−O1 −74.6(9), Cl3−Pt1−C8−C9 93.3(6), Cl1−Pt1−C8−C9 −83.1(6), N1−C5−C10−C11 163.4(7)




**32**

## 6. X-ray Structural Determinations of 11, 13, 19, 23, 26 and 32[28]

Of interest is the conformation of the coordinated cinchona alkaloid in the various complexes which can be derived from the torsion angle C4′−C9−C8−N. The "open conformation 3" is found in the complexes **19**, **23**, **32** and in **13** according to the $^1$H-NMR spectra. The torsion angles of these compounds are in the range of 161−176°. For the "free" cinchonidine a torsion angle of 158° was reported.[20] The formation of the N,O-chelate in **11** and **26** affords a torsion angle C4′−C9−C8−N of 81−85° ("open conformation 4").

In the $Pd^{II}$ complexes **11** and **26** the Pd atoms have a strictly planar environment with distortion of the square. The ligands at the $Zn^{2+}$ ion of **23** form a distorted tetrahedron.

The analysed crystal of **32** contained the diastereoisomer [*S*(C10), *S*(C8), *R*(C9), *S*(C4), *R*(C3)]. The olefinic C=C double bond lies perpendicular to the $PtCl_3$ plane as in $K[PtCl_3(C_2H_4)]$. Also the C=C, Pt−C and Pt−Cl lengths are similar to that of the Zeise salt.[21]

## Experimental Section

Where appropriate, the reactions were carried out in dry solvents under nitrogen. − NMR: Jeol GSX 270 or Jeol EX 400, using the solvent as internal standard. − IR: Nicolet 520 FT-IR. − The starting materials were prepared according to literature procedures: $Ph_3PAuCl$,[22] $[(C_3H_5)PdCl]_2$,[23] $(COD)PdCl_2$,[24] $[R_3PPtCl_2]_2$,[25] $[R_3PPdCl_2]_2$,[24] $(en)PdCl_2$,[26] $[Cp^*IrCl_2]_2$.[27] Quinine and cinchonine were used as supplied (Fluka). $ZnCl_2$ was dried for 2 d at 80°C. PE = polyethylene.

**1:** To a solution of 49.5 mg (0.1 mmol) of $PPh_3AuCl$ in 3 mL of $CH_2Cl_2$ a solution of 17 mg (0.1 mmol) of $AgNO_3$ in 3 mL of methanol was added. After 1 h of vigorous stirring with exclusion of light, AgCl was centrifuged off and 32.4 mg (0.1 mmol) of quinine was added. The light yellow solution was stirred for another 1 h to give a clear colourless solution which was concentrated to about 1 mL and added to 20 mL of pentane. The white precipitate was washed twice with $Et_2O$ and dried in vacuo for a few days. − IR (KBr): $\tilde{\nu}$ = 3379 $cm^{-1}$ m br. (OH), 3074 w ($CH_{arom}$), 2935 m ($CH_{aliph}$). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, 1 H, $^3J_{3'}$ = 4.61 Hz, 2′), 8.10 (d, 1 H, $^3J_{7'}$ = 9.37 Hz, 8′), 7.74 (d, 1 H, $^3J_{2'}$ = 4.35 Hz, 3′), 7.57−7.43 [m. 16 H, $P(C_6H_5)_3$, 5′], 7.35 (dd, 1 H, $^3J_{8'}$ = 9.31 Hz, $^4J_{5'}$ = 2.45 Hz, 7′), 6.02 (s, br., 1 H, 9), 5.77 (ddd, 1 H, $^3J_{11c}$ = 17.47 Hz, $^3J_{11t}$ = 10.15 Hz, $^3J_3$ = 7.32 Hz, 10), 5.02 (d, 1 H, $^3J_{10}$ = 17.43 Hz, 11*c*), 4.98 (d, 1 H, $^3J_{10}$ = 10.03 Hz, 11*t*), 4.0−3.6 (m, 1 H, 6b*), 3.75 (s, 3 H, $OCH_3$), 3.37 (m, 1 H, 2b), 2.93 (m, 1 H, 8), 2.43−1.20 (5m, 8 H, 2a, 6a, 3, 4, 5b, 7b, 5a, 7a). − $^{31}$P NMR (109.3 MHz): δ = 29.8. − $C_{38}H_{39}AuN_3O_5P \times CH_2Cl_2$ (866.9): calcd. C 52.99, H 4.59, N 4.85; found C 52.87, H 5.02, N 4.40.

**2:** To a solution of 34 mg (0.2 mmol) of $AgNO_3$ in 10 mL of methanol a solution of 65 mg (0.2 mmol) of quinine in 5 mL of $CH_2Cl_2$ was added with exclusion of light. After 1 h of vigorous stirring at room temperature, a white precipitate was obtained which was dissolved again by the addition of 52.5 mg (0.2 mmol) of $PPh_3$. The colourless solution was stirred for another 1 h, concentrated to about 0.5 mL and added to 20 mL of $Et_2O$ to give the product as white light-sensitive solid which was washed twice with $Et_2O$ and dried in vacuo for 2 d. − IR (KBr): $\tilde{\nu}$ = 3397 $cm^{-1}$ m br. (OH), 3071 w ($CH_{arom}$), 2939 s ($CH_{aliph}$). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, 1 H, $^3J_{3'}$ = 4.38 Hz, 2′), 7.82 (d, 1 H, $^3J_{7'}$ = 9.36 Hz, 8′), 7.68 (d, 1 H, $^3J_{2'}$ = 4.76 Hz, 3′), 7.52−7.30 [m, 15 H, $P(C_6H_5)_3$], 7.07 (dd, 1 H, $^3J_{8'}$ = 9.19 Hz, $^4J_{5'}$ = 2.04 Hz, 7′), 6.99 (s, 1 H, 5′), 6.06 (s, 1 H, 9), 5.57 (ddd, 1 H, $^3J_{11c}$ = 17.33 Hz, $^3J_{11t}$ = 10.53 Hz, $^3J_3$ = 6.80 Hz, 10), 5.05 (d, 1 H, $^3J_{10}$ = 10.12 Hz, 11*t*), 5.02 (d, 1 H, $^3J_{10}$ = 17.85 Hz, 11*c*), 4.35 (m, 1 H, 6b), 3.77 (s, 3 H, $OCH_3$), 3.56 (dd, 1 H, *J* = 10.66 Hz, *J* = 13.19 Hz, 2b), 3.40 (m, 1 H, 8), 3.23 (m, 2 H, 2a, 6a), 2.70 (m, 1 H, 3), 2.24−2.10 (m, 3 H, 4, 5b, 7b), 1.90- 1.79 (m, 1 H, 5a), 1.42 (m, 1 H, 7a). − $^{31}$P NMR (109.3 MHz): δ = 12.4. − $C_{38}H_{39}AgN_3O_5P \times 0.5\ CH_2Cl_2$ (799.1): calcd. C 57.87, H 5.05, N 5.28; found C 57.93, H 5.15, N 5.63.

**3:** To a solution of 86 mg (0.30 mmol) of $(COD)PdCl_2$ in 10 mL of $CH_2Cl_2$ a solution of 51 mg (0.30 mmol) of $AgNO_3$ in 15 mL of methanol was added. After 1 h of vigorous stirring with exclusion of light, AgCl was centrifuged off and 97 mg (0.30 mmol) of quinine was added. The solution was stirred for another 1 h to give a clear colourless solution which was concentrated to about

Table 1. Crystal data and structure refinement for **11**, **13** and **19**

| | **11** | **13** | **19** |
|---|---|---|---|
| Empirical formula | $C_{22}H_{31}N_4O_2Pd^+ NO_3^- \times H_2O$ | $2\,C_{21}H_{27}N_2O_2^+ \,2\,BF_4^- \times H_2O$ | $C_{31}H_{42}Cl_2IrN_2O_2^+ BF_4^-$ |
| Formula weight | 569.93 | 870.53 | 824.58 |
| $T$ [K] | 293(2) | 293(2) | 293(2) |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1$ (no. 4) | $P2_1$ (no. 4) | $P2_1$ (no. 4) |
| Unit cell dimensions | | | |
| $a$ [Å] | 11.2430(13) | 8.1347(12) | 14.428(4) |
| $b$ [Å] | 8.0008(13) | 15.769(3) | 11.875(3) |
| $c$ [Å] | 27.100(4) | 16.602(2) | 22.727(10) |
| α [°] | 90 | 90 | 90 |
| β [°] | 93.974(11) | 97.883(14) | 92.30(3) |
| γ [°] | 90 | 90 | 90 |
| Volume [Å$^3$] | 2431.9(6) | 2109.6(7) | 3890.8(23) |
| Z | 4 | 2 | 4 |
| Density (calcd.) [g/cm$^3$] | 1.557 | 1.370 | 1.408 |
| μ (Mo-$K_\alpha$) [mm$^{-1}$] | 0.810 | 0.112 | 3.614 |
| F(000) | 1176 | 916 | 1640 |
| Crystal size [mm] | 0.33 × 0.37 × 0.53 | 0.43 × 0.53 × 0.53 | 0.57 × 0.50 × 0.27 |
| 2θ range [°] | 4.88−45.94 | 4.96−47.96 | 4.66−47.94 |
| Index ranges | $\pm h \pm k -l$ | $-h \pm k \pm l$ | $-h \pm k \pm l$ |
| Reflections collected | 6885 | 7496 | 12718 |
| Independent reflections | 6724 [$R$(int) = 0.0159] | 6611 [$R$(int) = 0.0086] | 12178 [$R$(int) = 0.0237] |
| Absorption correction | semiempirical from ψ scan | semiempirical from ψ scan | semiempirical from ψ scan |
| Max./min. transmission | 0.9974/0.9265 | 0.9983/0.9754 | 0.9995/0.6639 |
| Data/parameters | 6724/629 | 6611/576 | 12178/878 |
| Goodness-of-fit on $F^2$ | 0.971 | 1.047 | 1.101 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0261, $wR2$ = 0.0713 | $R1$ = 0.0394, $wR2$ = 0.0975 | $R1$ = 0.0477, $wR2$ = 0.1314 |
| $R$ indices (all data) | $R1$ = 0.0308, $wR2$ = 0.0764 | $R1$ = 0.0487, $wR2$ = 0.1063 | $R1$ = 0.0656, $wR2$ = 0.1465 |
| Largest diff. peak and hole [eÅ$^{-3}$] | 0.575 and −0.422 | 0.312 and −0.192 | 1.222 and −0.460 |

Table 2. Crystal data and structure refinement for **23**, **26** and **32**

| | **23** | **26** | **32** |
|---|---|---|---|
| Empirical formula | $C_{19}H_{23}Cl_2N_2OZn^+ Cl^- \times CH_4O$ | $C_{31}H_{51}Cl_3N_2OP_2Pd_2 \times CHCl_3 \times H_2O$ | $C_{20}H_{26}Cl_3N_2O_2Pt^+ Cl^- \times H_2O \times 1.5\,O$ |
| Molecular mass | 499.16 | 986.21 | 705.33 |
| $T$ [K] | 293(2) | 293(2) | 293(2) |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space group | $P2_1$ (no. 4) | $P1$ (no. 1) | $C2$ (no. 5) |
| Unit cell dimensions | | | |
| $a$ [Å] | 9.2510(11) | 7.772(2) | 24.663(3) |
| $b$ [Å] | 12.957(3) | 12.002(2) | 12.447(4) |
| $c$ [Å] | 9.2976(9) | 12.364(3) | 9.591(2) |
| α [°] | 90 | 97.99(2) | 90 |
| β [°] | 93.147(9) | 94.89(2) | 105.049(13) |
| γ [°] | 90 | 107.33(2) | 90 |
| $V$ [Å$^3$] | 1112.8(3) | 1080.5(4) | 2843.3(11) |
| $Z$ | 2 | 1 | 4 |
| $d$ (calcd.) [g/cm$^3$] | 1.490 | 1.516 | 1.645 |
| μ (Mo-$K_\alpha$) [mm$^{-1}$] | 1.482 | 1.306 | 5.338 |
| $F$(000) | 516 | 500 | 1372 |
| Crystal size [mm] | 0.27 × 0.50 × 0.53 | 0.03 × 0.50 × 0.53 | 0.20 × 0.33 × 0.53 |
| 2θ range [°] | 5.4−48 | 5.34−47.94 | 4.82−47.98 |
| Index ranges | $\pm h \pm k +l$ | $\pm h \pm k \pm l$ | $+h \pm k \pm l$ |
| Reflections collected | 3728 | 6740 | 4540 |
| Independent reflections | 3497 [$R$(int) = 0.0170] | 6738 [$R$(int) = 0.0138] | 4431 [$R$(int) = 0.0123] |
| Absorption correction | semiempirical from ψ scan | semiempirical from ψ scan | semiempirical from ψ scan |
| Max./min. transmission | 0.9991/0.9257 | 0.9991/0.6908 | 0.9994/0.8415 |
| Data/parameters | 3497/255 | 6738/545 | 4431/291 |
| Goodness-of-fit on $F^2$ | 1.031 | 1.200 | 1.081 |
| Final $R$ indices [$I > 2\sigma(I)$] | 0.0243, 0.0654 | 0.0260, 0.0814 | 0.0351, 0.1004 |
| $R$ indices (all data) | 0.0267, 0.0680 | 0.0287, 0.0844 | 0.0388, 0.1050 |
| Largest diff. peak and hole [eÅ$^{-3}$] | 0.217 and −0.186 | 0.422 and −0.374 | 1.175 and −0.457 |

0.5 mL and added to 20 mL of $Et_2O$. The white precipitate was washed twice with $Et_2O$ and dried in vacuo for a few days. − IR (KBr): $\tilde{\nu}$ = 3313 cm$^{-1}$ vs br. (OH), 3073 m ($CH_{arom}$), 2939 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 351 cm$^{-1}$ m (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 10.72 (s, br., 1 H, OH), 8.73 (d, 1 H, $^3J_{3'}$ = 4.63 Hz, 2′), 8.19 (s, br., 1 H, 8′), 7.73 (d, 1 H, $^3J_{2'}$ = 4.72 Hz, 3′), 6.98 (d, 1 H, $^3J_{8'}$ = 8.81 Hz, 7′), 6.64 (d, 1 H, $^4J_{7'}$ = 2.17 Hz, 5′), 6.16 [pd, 4 H, $J$ = 16.74 Hz, NPd($C_8H_8H_{4olef}$)], 5.93 (s, br., 1 H,

9), 5.53 (ddd, 1 H, $^3J_{11c}$ = 17.16 Hz, $^3J_{11t}$ = 10.43 Hz, $^3J_3$ = 6.74 Hz, 10), 5.01 (d, 1 H, $^3J_{10}$ = 10.09 Hz, 11*t*), 4.98 (d, 1 H, $^3J_{10}$ = 17.67 Hz, 11*c*), 4.39−4.33 (m, 1 H, 6b), 3.29 (s, 3 H, $OCH_3$), 3.67−1.30 [9m, 6a, 2a, 2b, 8, 4, 5a, 5b, NPd($C_8H_{8aliph}H_4$), 7a, 7b]. − $C_{28}H_{36}ClN_3O_5Pd \times 0.15\ CH_2Cl_2$ (649.2): calcd. C 52.08, H 5.64, N 6.47; found C 52.06, H 5.89, N 6.59.

**4:** To a solution of 66 mg (0.2 mmol) of quinine in 8 mL of $CH_2Cl_2$, which was cooled to −78°C, 37 mg (0.10 mmol) of $[(allyl)PdCl]_2$ was added. After stirring for 1.5 h, the solvent was removed in vacuo to obtain a white solid which was washed twice with 15 mL of $Et_2O$ and dried in vacuo. − IR (KBr): $\tilde{\nu}$ = 3383 $cm^{-1}$ vs br. (OH), 3070 w ($CH_{arom}$), 2937 vs ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 276 $cm^{-1}$ w (M−Cl). − $^1$H NMR (400 MHz, $CD_2Cl_2$): δ = 8.61 (d, 1 H, $^3J_{3'}$ = 4.16 Hz, 2′), 8.20 (s, br., 1 H, 8′), 7.56 (s, br., 1 H, 3′), 7.43 (s, br., 1 H, 5′), 7.32 (dd, 1 H, $^3J_{8'}$ = 9.22 Hz, $^4J_{5'}$ = 2.65 Hz, 7′), 5.76−5.62 [m, 1 H, NPdC*H*$(CH_2)_2$], 5.62−5.50 (m, 1 H, 10), 5.1 (s, br., 1 H, 9), 4.97 (d, 1 H, $^3J_{10}$ = 17.13 Hz, 11c), 4.88 (d, 1 H, $^3J_{10}$ = 10.43 Hz, 11t), 4.0−3.8 [m, 5 H, 6b*, 8*, 2b*, NPdCH($CH_2$*H*$_{endo}$)$_2$*], 3.93 (s, 3 H, $OCH_3$), 3.2−2.5 [4 m, 5 H, 2a, 6a, OH, NPdCH($CH_2$*H*$_{exo}$)$_2$], 2.26 (m, 1 H, 3), 1.74−1.2 (3 m, 5 H, 4, 7b, 5b, 7a, 5a). − $C_{23}H_{29}ClN_2O_2Pd \times 0.3\ CH_2Cl_2$ (532.8): calcd. C 52.52, H 5.60, N 5.26; found C 52.56, H 6.05, N 5.02.

**General Procedure for the Preparation of 5−10:** A solution of quinine in 10 mL of $CH_2Cl_2$ and the appropriate amount of a solution of NaOMe in methanol was cooled to −78°C. After the addition of $[R_3PMCl_2]_2$, the solution was allowed to warm up to room temperature for 16 h and stirred for another 2 h. The solvent of the light yellow suspension was removed in vacuo and the residue was dissolved again in $CH_2Cl_2$ and stirred for 10 min. The suspension was filtered through Celite to remove NaCl and the resulting clear yellow solution was concentrated to dryness. The yellow solid was washed twice with pentane and once with 10 mL of cold $Et_2O$ and dried in vacuo for 2 d.

**5:** 65 mg (0.2 mmol) of quinine, 0.2 mmol of NaOMe in MeOH and 77 mg (0.1 mmol) of $[(PEt_3)PtCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3076 $cm^{-1}$ m ($CH_{arom}$), 2963 s, 2935 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 333 $cm^{-1}$ m (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.30 (d, 1 H, $^3J_{2'}$ = 4.53 Hz, 3′), 8.89 (d, 1 H, $^3J_{3'}$ = 4.52 Hz, 2′), 8.06 (d, 1 H, $^3J_{7'}$ = 9.16 Hz, 8′), 7.37 (dd, 1 H, $^3J_{8'}$ = 9.16 Hz, $^4J_{5'}$ = 2.69 Hz, 7′), 7.12 (d, 1 H,$^4J_{7'}$ = 2.71 Hz, 5′), 5.97 (ddd, 1 H, $^3J_{11c}$ = 17.21 Hz, $^3J_{11t}$ = 10.31 Hz, $^3J_3$ = 6.87 Hz, 10), 5.76 (dd, 1 H, $^4J_P$ = 9.78 Hz, $^3J_8$ = 6.67 Hz, 9), 5.24 (d, 1 H, $^3J_{10}$ = 10.37 Hz, 11*t*), 5.20 (d, 1 H, $^3J_{10}$ = 17.12 Hz, 11*c*), 4.09 (m, 1 H, 8), 3.92 (s, 3 H, $OCH_3$), 3.79 (d, 1 H, *J* = 12.99 Hz, 2b), 3.52 (m, 1 H, 2a), 3.25 (m, 1 H, 6b), 2.94 (pt, 1 H, $^3J$ = 12.09 Hz, 6a), 2.41 (m, 1 H, 3), 2.26−2.16 (m, 1 H, 7b), 2.10−1.84 [m, 6 H, P($CH_2CH_3$)$_3$], 1.81 (m, 1 H, 4), 1.29 [dt, 9 H, $^3J_P$ = 16.44 Hz, $^3J_{CH2}$ = 7.58 Hz, P($CH_2CH_3$)$_3$], 1.41−1.21 (m, 3 H, 5b*, 7a*, 5a*). − $^{31}$P NMR (109.3 MHz): δ = −4.12 ($^1J_{P\text{-}Pt}$ = 3430 Hz). − $C_{26}H_{38}ClN_2O_2PPt \times 0.5\ CH_2Cl_2$ (714.6): calcd. C 44.54, H 5.50. N 3.92; found C 44.54, H 5.67, N 3.79.

**6:** 39.5 mg (0.122 mmol) of quinine, 0.122 mmol of NaOMe in MeOH and 57 mg (0.061 mmol) of $[(PBu_3)PtCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3072 $cm^{-1}$ m ($CH_{arom}$), 2955 s, 2931 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 330 $cm^{-1}$ m (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.34 (d, 1 H, $^3J_{2'}$ = 4.51 Hz, 3′), 8.88 (d, 1 H, $^3J_{3'}$ = 4.72 Hz, 2′), 8.06 (d, 1 H, $^3J_{7'}$ = 9.41 Hz, 8′), 7.37 (dd, 1 H, $^3J_{8'}$ = 9.09 Hz, $^4J_{5'}$ = 2.54 Hz, 7′), 7.12 (d, 1 H,$^4J_{7'}$ = 2.33 Hz, 5′), 5.99 (ddd, 1 H, $^3J_{11c}$ = 17.13 Hz, $^3J_{11t}$ = 10.46 Hz, $^3J_3$ = 6.78 Hz, 10), 5.75 (dd, 1 H, $^4J_P$ = 9.42 Hz, $^3J_8$ = 6.48 Hz, 9), 5.27 (d, 1 H, $^3J_{10}$ = 10.53 Hz, 11*t*), 5.22 (d, 1 H, $^3J_{10}$ = 17.10 Hz, 11*c*), 4.09 (m, 1 H, 8), 3.95 (s, 3 H, $OCH_3$), 3.1 (d, 1 H, *J* = 12.70 Hz, 2b), 3.55−3.46 (m, 1 H, 2a), 3.23 (m, 1 H, 6b), 2.98−2.90 (m, 1 H, 6a), 2.46−2.39 (m, 1 H, 3), 2.26−2.17 (m, 1 H, 7b), 1.93−1.79 [m, 6 H, P($CH_2C_3H_7$)$_3$], 1.77−1.62 [m, 6 H, P($CH_2CH_2C_2H_5$)$_3$], 1.59−1.54 [m, 6 H, P($C_2H_4CH_2CH_3$)$_3$], 1.29 [t, 9 H, $^3J_{P(C2H4\text{-}CH2\text{-}CH3)3}$ = 6.85 Hz, P($C_3H_6CH_3$)$_3$], 1.93−1.54 (m, 4 H, 4*, 5b*, 7a*, 5a*). − $^{31}$P NMR (109.3 MHz): δ = −11.93 ($^1J_{P\text{-}Pt}$ = 3420 Hz). − $C_{32}H_{50}N_2ClO_2PPt \times CH_2Cl_2$ (841.2): calcd. C 47.12, H 6.23, N 3.33; found C 46.80, H 6.37, N 3.16.

**7:** 65 mg (0.2 mmol) of quinine, 0.2 mmol of NaOMe in MeOH and 59 mg (0.1 mmol) of $[(PEt_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3077 $cm^{-1}$ w ($CH_{arom}$), 2975 s, 2931 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 327 $cm^{-1}$ m (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.12 (d, 1 H, $^3J_{2'}$ = 4.71 Hz, 3′), 8.86 (d, 1 H, $^3J_{3'}$ = 4.77 Hz, 2′), 8.06 (d, 1 H, $^3J_{7'}$ = 9.37 Hz, 8′), 7.36 (dd, 1 H, $^3J_{8'}$ = 9.32 Hz, $^4J_{5'}$ = 2.77 Hz, 7′), 7.06 (d, 1 H,$^4J_{7'}$ = 2.66 Hz, 5′), 5.99 (ddd, 1 H, $^3J_{11c}$ = 17.18 Hz, $^3J_{11t}$ = 10.31 Hz, $^3J_3$ = 6.97 Hz, 10), 5.46 (d, 1 H, $^3J_8$ = 6.59 Hz, 9), 5.19−5.15 (2m, 2 H, 11*c*, 11*t*), 3.94−3.80 (m, 1 H, 8), 3.99 (s, 3 H, $OCH_3$), 3.66 (dd, 1 H, *J* = 13.72 Hz, *J* = 10.22 Hz, 2b), 3.43 (d, 1 H, $^3J$ = 13.59 Hz, 2a), 3.22−3.04 (m, 2 H, 6b, 6a), 2.40 (m, 1 H, 3), 2.12−2.01 (m, 2 H, 7b, 5b), 1.94−1.83 [m, 6 H, P($CH_2CH_3$)$_3$], 1.77 (m, 1 H, 4), 1.35 [dt, 9 H, $^3J_P$ = 16.92 Hz, $^3J_{CH2}$ = 7.60 Hz, P($CH_2CH_3$)$_3$], 1.20−1.0 (m, 2 H, 7a*, 5a). − $^{31}$P NMR (109.3 MHz): δ = 34.89 (0.05 N′PdP), 31.28 (0.05 NPdP$_{cis}$), 30.82 (NPdP$_{trans}$). − $C_{26}H_{38}ClN_2O_2PPd \times 0.25\ CH_2Cl_2$ (603.7): calcd. C 52.23, H 6.43, N 4.64; found C 52.12, H 6.66, N 4.43.

**8:** 76 mg (0.234 mmol) of quinine, 0.234 mmol of NaOMe in MeOH and 79 mg (0.117 mmol) of $[(PPr_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3077 $cm^{-1}$ w ($CH_{arom}$), 2960 s, 2923 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 352 $cm^{-1}$ m, 328 w (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.05 (d, 1 H, $^3J_{2'}$ = 4.49 Hz, 3′), 8.82 (d, 1 H, $^3J_{3'}$ = 4.51 Hz, 2′), 8.01 (d, 1 H, $^3J_{7'}$ = 9.24 Hz, 8′), 7.32 (dd, 1 H, $^3J_{8'}$ = 9.23 Hz, $^4J_{5'}$ = 2.87 Hz, 7′), 7.03 (d, 1 H,$^4J_{7'}$ = 2.60 Hz, 5′), 5.95 (ddd, 1 H, $^3J_{11c}$ = 17.22 Hz, $^3J_{11t}$ = 10.23 Hz, $^3J_3$ = 6.99 Hz, 10), 5.41 (d, 1 H, $^3J_8$ = 6.72 Hz, 9), 5.15−5.10 (2m, 2 H, 11*c*, 11*t*), 3.84 (s, 3 H, $OCH_3$), 3.80 (m, 1 H, 8*), 3.60 (dd, 1 H, $^2J_3$ = 13.62 Hz, $^3J_{2a}$ = 10.34 Hz, 2b), 3.37 (pd, 1 H, $^3J$ = 13.39 Hz, 2a), 3.16−3.01 (m, 2 H, 6b, 6a), 2.34 (m, 1 H, 3), 2.07−1.94 (m, 1 H, 7b), 1.86−1.64 [m, 8 H, P($CH_2CH_3$)$_3$, 5b*, 4*], 1.32 (m, 1 H, 7a), 1.07 [t, 9 H, $^3J_{CH2CH3}$ = 6.83 Hz, P($C_2H_4CH_3$)$_3$, 5a*]. − $^{31}$P NMR (109.3 MHz): δ = 25.73 (0.04 N′PdP), 22.44 (0.05 NPdP$_{cis}$), 22.25 (NPdP). − $C_{29}H_{44}ClN_2O_2PPd$ (624.5): calcd. C 55.77, H 7.10, N 4.49; found C 55.23, H 7.06, N 4.41.

**9:** 47 mg (0.145 mmol) of quinine, 0.145 mmol of NaOMe in MeOH and 55 mg (0.072 mmol) of $[(PBu_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3076 $cm^{-1}$ w ($CH_{arom}$), 2959 s, 2920 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 326 $cm^{-1}$ m, 306 w (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.11 (d, 1 H, $^3J_{2'}$ = 4.53 Hz, 3′), 8.84 (d, 1 H, $^3J_{3'}$ = 4.42 Hz, 2′), 8.03 (d, 1 H, $^3J_{7'}$ = 9.25 Hz, 8′), 7.34 (dd, 1 H, $^3J_{8'}$ = 9.30 Hz, $^4J_{5'}$ = 2.68 Hz, 7′), 7.05 (d, 1 H,$^4J_{7'}$ = 2.67 Hz, 5′), 5.97 (ddd, 1 H, $^3J_{11c}$ = 17.25 Hz, $^3J_{11t}$ = 10.26 Hz, $^3J_3$ = 6.99 Hz, 10), 5.43 (d, 1 H, $^3J_8$ = 6.61 Hz, 9), 5.18−5.11 (2m, 2 H, 11*c*, 11*t*), 3.87 (s, 3 H, $OCH_3$), 3.84 (m, 1 H, 8*), 3.62 (dd, 1 H, $^2J_3$ = 13.69 Hz, $^2J_{2a}$ = 10.26 Hz, 2b), 3.39 (pd, 1 H, $^3J$ = 13.17 Hz, 2a), 3.19−2.99 (m, 2 H, 6b, 6a), 2.44−2.30 (m, 1 H, 3), 2.11−1.96 (m, 1 H, 7b), 1.89−0.9 (m, 5b*, 4*, 5a*, 7a*), 1.89−1.60 [m, 12 H, P($C_2H_4C_2H_5$)$_3$], 1.54−1.41 [m, 6 H, P($C_2H_4CH_2CH_3$)$_3$], 0.98 [t, 9 H, $^3J_{CH2CH3}$ = 6.83 Hz, P($C_3H_6CH_3$)$_3$]. − $^{31}$P NMR (109.3 MHz): δ = 26.75 (0.05 N′PdP), 23.16 (0.05 NPdP$_{cis}$), 22.89 (NPdP). − $C_{32}H_{50}ClN_2O_2PPd \times 0.25\ CH_2Cl_2$ (687.8): calcd. C 56.32, H 7.40, N 4.07; found C 56.58, H 7.48, N 4.05.

**10:** 65 mg (0.2 mmol) of quinine, 0.2 mmol of NaOMe in MeOH and 88 mg (0.1 mmol) of $[(PPh_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3075 $cm^{-1}$ w ($CH_{arom}$), 2969 w, 2940 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 329 $cm^{-1}$ w (M−Cl). − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, 1 H, $^3J_{2'}$ = 4.64 Hz, 3′), 8.37 (d, 1 H, $^3J_{3'}$ = 4.73 Hz, 2′), 8.00 (d, 1 H, $^3J_{7'}$ = 9.03 Hz, 8′) 7.74−7.67 [m, 5 H, $P(C_6H_5)(C_6H_5)_2$ ], 7.50−7.44 [m, 5 H, $P(C_6H_5)(C_6H_5)_2$], 7.42−7.36 [m, 5 H, $P(C_6H_5)(C_6H_5)_2$], 7.33 (dd, 1 H, $^3J_{8'}$ = 9.20 Hz, $^4J_{5'}$ = 2.60 Hz, 7′), 7.01 (d, 1 H,$^4J_{7'}$ = 2.57 Hz, 5′), 5.96 (ddd, 1 H, $^3J_{11c}$ = 17.19 Hz, $^3J_{11t}$ = 10.43 Hz, $^3J_3$ = 6.76 Hz, 10), 5.29 (d, 1 H, $^3J_8$ = 6.56 Hz, 9), 5.18 (d, 1 H, $^3J_{10}$ = 10.65, 11*t*), 5.14 (m,1 H, 11*c*), 4.00 (dt, 1H $^3J$ = 14.6 Hz, $^3J$ = 8.74 Hz, 8), 3.87 (s, 3 H, $OCH_3$), 3.79 (dd, 1 H, *J* = 13.80 Hz, *J* = 10.28 Hz, 2b), 3.53 (d, 1 H, $^3J$ = 13.82 Hz, 2a), 3.40 (d, 1 H, $^3J$ = 11.92 Hz, 6b), 3.17−3.08 (m, 1 H, 6a), 2.45−2.35 (m, 1 H, 3), 2.10−1.99 (m, 1 H, 7b), 1.80−1.72 (m, 1 H, 4), 1.38 (m, 1 H, 5b), 1.24−1.16 (m, 1 H, 7a), 1.13−1.04 (m, 1 H, 5a). − $^{31}P$ NMR (109.3 MHz): δ = 29.05 (0.05 N′PdP), 26.11 (0.05 $NPdP_{cis}$), 25.70 (NPdP). − $C_{38}H_{38}ClN_2O_2PPd \times 0.25\ CH_2Cl_2$ (748.8): calcd. C 61.35, H 5.18, N 3.74; found C 61.03, H 5.63, N 3.63.

**11:** 24 mg (0.1 mmol) of $(en)PdCl_2$ were added to a solution of 34 mg (0.2 mmol) of $AgNO_3$ in 5 mL of water and stirred at 40°C for 4 h in the dark. After AgCl was centrifuged off, the solution was concentrated to 2 mL and added to a solution of 32.5 mg (0.1 mmol) of quinine and 0.1 mmol NaOMe in 3 mL of methanol. After 12 h of vigorous stirring, the solvent was removed in vacuo. The slight yellow residue was crystallized twice from water to give slightly yellow crystals. − IR (KBr): $\tilde{\nu}$ = 3432 $cm^{-1}$ s, 3271 s, 3217 s, 3133 s (NH), 3074 s ($CH_{arom}$), 2980 s, 2945 s, 2915 s ($CH_{aliph}$). − $^1H$ NMR (400 MHz, $D_2O$): δ = 8.98 (d, 1 H, $^3J_{2'}$ = 4.25 Hz, 3′), 8.74 (d, 1 H, $^3J_{3'}$ = 4.76 Hz, 2′), 7.87 (d, 1 H, $^3J_{7'}$ = 9.18 Hz, 8′), 7.34 (dd, 1 H, $^3J_{8'}$ = 9.52 Hz, $^4J_{5'}$ = 2.59 Hz, 7′), 7.06 (d, 1 H,$^4J_{7'}$ = 2.62 Hz, 5′), 5.93 (ddd, 1 H, $^3J_{11c}$ = 16.67 Hz, $^3J_{11t}$ = 10.40 Hz, $^3J_3$ = 6.27 Hz, 10), 5.30 (d, 1 H, $^3J_8$ = 6.85 Hz, 9), 5.09 (d, 1 H, $^3J_{10}$ = 17.68 Hz, 11*c*), 5.08 (d, 1 H, $^3J_{10}$ = 9.29 Hz, 11*t*), 4.75 [$Pd(H_4N_2C_2H_4$*], 3.82−3.70 (m, 1 H, 8), 3.78 (s, 3 H, $OCH_3$), 3.55 (d, 1 H, *J* = 15.72 Hz, 2b), 3.16−3.08 (m, 1 H, 2a), 3.04−2.95 (m, 1 H, 6b), 2.76−2.6 [m, 5 H, 6a, $Pd(H_4N_2C_2H_4)$], 2.39−2.31 (m, 1 H, 3), 2.11−2.01 (m, 1 H, 7b), 1.66−1.59 (m, 1 H, 4), 1.29−1.19 (m, 1 H, 5b), 0.96−0.90 (m, 2 H, 7a, 5a). − $C_{22}H_{31}N_5O_5Pd \times 2\ H_2O$ (587.0): calcd. C 45.01, H 6.01, N 11.93; found C 45.31, H 5.66, N 11.69.

**12:** To a solution of 116 mg (0.358 mmol) of quinine in 10 mL of $CH_2Cl_2$, 178 μL (0.179 mmol) of $TiCl_4$ in $CH_2Cl_2$ was added. At once a light orange precipitate was obtained which was dissolved again by vigorous stirring. After 2 d of stirring, the solution was concentrated to about 0.5 mL and added to 20 mL of $Et_2O$. The white precipitate was washed twice with 15 mL of $Et_2O$ and dried in vacuo for several days. − $^1H$ NMR (400 MHz, $CD_3OD$): δ = 8.77 (d, 1 H, $^3J_{3'}$ = 4.75 Hz, 2′), 8.01 (d, 1 H, $^3J_{7'}$ = 9.19 Hz, 8′), 7.91 (d, 1 H, $^3J_{2'}$ = 5.08 Hz, 3′), 7.57 (d, 1 H, $^4J_{7'}$ = 2.73 Hz, 5′), 7.52 (dd, 1 H, $^3J_{8'}$ = 9.25 Hz, $^4J_{5'}$ = 2.63 Hz, 7′), 6.28 (s, 1 H, 9), 5.77 (ddd, 1 H, $^3J_{11c}$ = 17.33 Hz, $^3J_{11t}$ = 10.31 Hz, $^3J_3$ = 7.02 Hz, 10), 5.12 (dt, 1 H, $^3J_{10}$ = 17.37 Hz, $^2J_{11t}$ = $^4J_3$ = 2.43 Hz, 11*c*), 5.03 (dt, 1 H, $^3J_{10}$ = 10.29 Hz, $^2J_{11c}$ = $^4J_3$ = 2.41 Hz, 11*t*), 4.33−4.24 (m, 1 H, 6b), 4.07 (s, 3 H, $OCH_3$), 3.68−3.58 (m, 2 H, 8, 2b), 3.34−3.26 (m, 2 H, 2a, 6a), 2.88−2.78 (m, 1 H, 3), 2.30−2.16 (m, 2 H, 7b, 5b), 2.12−2.09 (m, 1 H, 5a), 2.03−1.9 (m, 1 H, 5a), 1.60−1.53 (m, 1 H, 7a). − $C_{40}H_{46}Cl_2N_4O_4Ti \times 0.5\ CH_2Cl_2$ (808.1): calcd. C 60.20, H 6.11, N 6.93; found C 60.03, H 6.27, N 6.87.

**13:** 2 g (6.16 mmol) of quinine was dissolved in 50 mL of $CH_2Cl_2$ and cooled to −78°C. After addition of 740 mg (5 mmol) of $(CH_3)_3O^+BF_4^-$, the mixture was stirred for 16 h and was allowed to warm up to room temp. A white precipitate was obtained which was centrifuged off, washed three times with 10 mL of $CH_2Cl_2$ and dried in vacuo at 80°C for 1 d. Crystallization from water gave colourless plates. − IR (KBr): $\tilde{\nu}$ = 3122 $cm^{-1}$ s br. (OH), 3070 w ($CH_{arom}$), 3010 m, 2971 m, 2954 m, 2885 m, 2842 m, ($CH_{aliph}$). − $^1H$ NMR (400 MHz, [$D_6$]acetone): δ = 8.81 (d, 1 H, $^3J_{3'}$ = 4.31 Hz, 2′), 8.03 (d, 1 H, $^3J_{7'}$ = 9.18 Hz, 8′), 7.83 (dd, 1 H, $^3J_{2'}$ = 4.38 Hz, *J* = 0.7 Hz, 3′), 7.46 (dd, 1 H, $^3J_{8'}$ = 9.21 Hz, $^4J_{5'}$ = 2.69 Hz, 7′), 7.30 (d, 1 H, $^4J_{7'}$ = 2.72 Hz, 5′), 6.58 (s, 1 H, 9), 5.84 (s, 1 H, $OH^{not\ sure}$), 5.80 (ddd, 1 H, $^3J_{11c}$ = 17.31 Hz, $^3J_{11t}$ = 10.48 Hz, $^3J_3$ = 6.84 Hz, 10), 5.16 (d, 1 H, $^3J_{10}$ = 18.63 Hz, 11*c*), 5.01 (d, 1 H, $^3J_{10}$ = 11.44 Hz, 11*t*), 4.54−4.45 (m, 1 H, 6b), 4.02 (s, 3 H, $OCH_3$), 3.91 (m, 1 H, 2b), 3.84−3.79 (m, 1 H, 8), 3.71−3.60 (m, 2 H, 2a*, 6a*), 3.69 (s, 3 H, $NCH_3$), 3.07 (m, 1 H, 3), 2.45−2.25 (m, 2 H, 4, 5b), 2.25−2.11 (m, 2 H, 7b, 5a), 1.64−1.54 (m, 1 H, 7a). − $C_{21}H_{27}BF_4N_2O_2 \times CH_2Cl_2$ (511.2): calcd. C 51.69, H 5.72, N 5.48; found C 52.08, H 5.79, N 5.45.

**General Procedure for the Preparation of 14−19:** To a solution of **13** in methanol, the chloro-bridged metal complex was added. After 16 h of vigorous stirring, the clear solution was concentrated to 1 mL and added to 20 mL of cold $Et_2O$. The precipitate was centrifuged off and washed twice with 15 mL of $Et_2O$ and dried in vacuo for 2 d.

**14:** 65 mg of **13** (0.127 mmol) and 49 mg (0.064 mmol) of $[(PEt_3)PtCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3466 $cm^{-1}$ s br. (OH), 3078 w ($CH_{arom}$), 2964 m, 2938 w ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 342 $cm^{-1}$ s (M−Cl). − $^1H$ NMR (270 MHz, $CD_3OD$): δ = 9.40 (d, 1 H, $^3J_{7'}$ = 9.49 Hz, 8′), 8.96 (dd, 1 H, $^3J_{3'}$ = 5.37 Hz, $^4J_P$ = 3.53 Hz, 2′), 7.95 (d, 1 H, $^3J_{2'}$ = 5.35 Hz, 3′), 7.62 (dd, 1 H, $^3J_{8'}$ = 9.48 Hz, $^4J_{5'}$ = 2.57 Hz, 7′), 7.27 (d, 1 H, $^4J_{7'}$ = 2.56 Hz, 5′), 6.33 (s, br., 1 H, 9), 5.73 (ddd, 1 H, $^3J_{11c}$ = 17.32 Hz, $^3J_{11t}$ = 10.36 Hz, $^3J_3$ = 6.96 Hz, 10), 5.13 (dt, 1 H, $^3J_{10}$ = 16.01 Hz, $^2J_{11t}$ = $^4J_3$ = 0.95 Hz, 11*c*), 5.04 (dt, 1 H, $^3J_{10}$ = 10.37 Hz, $^2J_{11c}$ = $^4J_3$ = 1.15 Hz, 11*t*), 4.42−4.28 (m, 1 H, 6b), 4.06 (s, 3 H, $OCH_3$), 3.76−3.50 (m, 3 H, 2a, 2b, 8), 3.43 (s, 4 H, $NCH_3$, 6a* ), 2.94−2.81 (m, 1 H, 3), 2.33−2.20 (m, 2 H, 7b, 4), 2.14−2.08 (m, 1 H, 5b), 2.05−1.91 [m, 6 H, $P(CH_2CH_3)_3$], 1.55−1.41 (m, 1 H, 7a), 1.15 [dt, 9 H, $^3J_p$ = 17.17 Hz, $^3J_{CH2}$ = 7.56 Hz, $P(CH_2CH_3)_3$], 1.38−1.10 (m, 1 H, 5a*). − $^{31}P$ NMR (109.3 MHz): δ = 1.05 ($^1J_{P\text{-}Pt}$ = 3391 Hz). − $C_{27}H_{42}BCl_2F_4N_2O_2PPt \times 0.5\ H_2O$ (819.4): calcd. C 39.58, H 5.29, N 3.42; found C 39.67, H 5.43, N 3.50.

**15:** 61 mg of **13** (0.119 mmol) and 56 mg (0.060 mmol) of $[(PBu_3)PtCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3430 $cm^{-1}$ s br. (OH), 3077 w ($CH_{arom}$), 2957 s, 2931 w ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 342 $cm^{-1}$ s (M−Cl). − $^1H$ NMR (270 MHz, [$D_6$]acetone): δ = 9.45 (d, 1 H, $^3J_{7'}$ = 9.42 Hz, 8′), 9.01 (dd, 1 H, $^3J_{3'}$ = 5.38 Hz, $^4J_P$ = 3.38 Hz, 2′), 8.05 (d, 1 H, $^3J_{2'}$ = 5.12 Hz, 3′), 7.62 (dd, 1 H, $^3J_{8'}$ = 9.52 Hz, $^4J_{5'}$ = 2.60 Hz, 7′), 7.38 (d, 1 H, $^4J_{7'}$ = 2.41 Hz, 5′), 6.64 (s, br., 1 H, 9), 5.81 (ddd, 1 H, $^3J_{11c}$ = 17.34 Hz, $^3J_{11t}$ = 10.30 Hz, $^3J_3$ = 7.03 Hz, 10), 5.15 (dt, 1 H, $^3J_{10}$ = 17.18 Hz, $^2J_{11t}$ = $^4J_3$ = 1.15 Hz, 11*c*), 5.01 (dt, 1 H, $^3J_{10}$ = 10.42 Hz, $^2J_{11c}$ = $^4J_3$ = 1.11 Hz, 11*t*), 4.50−4.41 (m, 1 H, 6b), 4.10−3.60 (m, 2a*, 2b*, 8*, 6b*), 4.06 (s, 3 H, $OCH_3$), 3.70 (s, 3 H, $NCH_3$,), 3.09−2.90 (m, 1 H, 3), 2.83 (s, br., 1 H, OH), 2.47−2.27 (m, 2 H, 7b, 4), 2.2−0.97 (5b*, 7a*, 5a*), 2.07−1.48 [3 m, 18 H, $P(C_3H_6CH_3)_3$], 1.00 [t, 9 H, $^3J_{CH2}$ = 7.28 Hz, $P(C_3H_6CH_3)_3$]. − $^{31}P$ NMR (109.3 MHz): δ = −6.65 ($^1J_{P\text{-}Pt}$ = 3426 Hz). − $C_{33}H_{54}BCl_2F_4N_2O_2PPt$ (894.6): calcd. C 44.31, H 6.08, N 3.13; found C 44.56, H 6.10, N 3.38.

**16:** 86 mg of **13** (0.168 mmol) and 50 mg (0.084 mmol) of $[(PEt_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3450 $cm^{-1}$ s br. (OH), 3077 w ($CH_{arom}$), 2975 m, 2938 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 352 $cm^{-1}$ m (M−Cl). − $^1H$ NMR (400 MHz, $CD_3OD$): δ = 9.13 (s, br., 1 H, 8′), 8.88 (s, br., 1 H, 2′), 7.85 (d, 1 H, $^3J_{2'}$ = 4.88 Hz, 3′), 7.55 (dd, 1 H, $^3J_{8'}$ = 9.06 Hz, $^4J_{5'}$ = 1.53 Hz, 7′), 7.19 (d, 1 H, $^4J_{7'}$ = 2.23 Hz, 5′), 6.27 (s, 1 H, 9), 5.65 (ddd, 1 H, $^3J_{11c}$ = 17.15 Hz, $^3J_{11t}$ = 10.40 Hz, $^3J_3$ = 6.76 Hz, 10), 5.09 (d, 1 H, $^3J_{10}$ = 17.25 Hz, 11*c*), 4.97 (d, 1 H, $^3J_{10}$ = 10.53 Hz, 11*t*), 4.28 (m, 1 H, 6b), 4.00 (s, 3 H, $OCH_3$), 3.67−3.51 (m, 3 H, 2a, 2b, 8), 3.36 (s, 4 H, $NCH_3$, 6a*), 2.81 (m, 1 H, 3), 2.26−2.02 (m, 2 H, 7b, 4), 2.00−1.92 [m, 6 H, $P(CH_2CH_3)_3$], 1.72−1.10 (5b*, 7a*, 5a*), 1.30 [dt, 9 H, $^3J_P$ = 17.87 Hz, $^3J_{CH2}$ = 7.33 Hz, $P(CH_2CH_3)_3$]. − $^{31}P$ NMR (109.3 MHz): δ = 37.48. − $C_{27}H_{42}BCl_2F_4N_2O_2PPd \times H_2O$ (738.8): calcd. C 43.90, H 6.00, N 3.79; found C 44.21, H 5.91, N 3.62.

**17:** 88 mg of **13** (0.172 mmol) and 58 mg (0.086 mmol) of $[(PPr_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3431 $cm^{-1}$ s br. (OH), 3084 w ($CH_{arom}$), 2963 s, 2934 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 349 $cm^{-1}$ m (M−Cl). − $^1H$ NMR (270 MHz, $CD_3OD$): δ = 9.15 (s, br., 1 H, 8′), 8.91 (d, 1 H, $^3J_{3'}$ = 5.24 Hz, 2′), 7.89 (d, 1 H, $^3J_{2'}$ = 5.18 Hz, 3′), 7.59 (dd, 1 H, $^3J_{8'}$ = 9.38 Hz, $^4J_{5'}$ = 2.42 Hz, 7′), 7.23 (d, 1 H, $^4J_{7'}$ = 2.47 Hz, 5′), 6.32 (s, 1 H, 9), 5.70 (ddd, 1 H, $^3J_{11c}$ = 17.21 Hz, $^3J_{11t}$ = 10.33 Hz, $^3J_3$ = 6.89 Hz, 10), 5.13 (d, 1 H, $^3J_{10}$ = 17.23 Hz, 11*c*), 5.02 (d, 1 H, $^3J_{10}$ = 10.44 Hz, 11*t*), 4.40−4.25 (m, 1 H, 6b), 4.05 (s, 3 H, $OCH_3$), 3.77−3.52 (m, 3 H, 2a, 2b, 8), 3.50−3.30 (m, 1 H, 6a*), 3.40 (s, 3 H, $NCH_3$), 2.93−2.79 (m, 1 H, 3), 2.33−2.16 (m, 2 H, 7b, 4), 2.01−1.73 [m, 13 H, $P(C_2H_4CH_3)_3$, 5b*], 1.51−1.37 (m, 1 H, 7a), 1.15 [t, 9 H, $^3J_{CH2}$ = 7.08 Hz, $P(C_2H_4CH_3)_3$], 0.95−0.90 (m, 1 H, 5a). − $^{31}P$ NMR (109.3 MHz): δ = 27.48. − $C_{30}H_{48}BCl_2F_4N_2O_2PPd \times 0.5\ H_2O$ (771.8): calcd. C 46.69, H 6.40, N 3.63; found C 46.61, H 6.37, N 3.64.

**18:** 79 mg of **13** (0.155 mmol) and 58 mg (0.077 mmol) of $[(PBu_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3450 $cm^{-1}$ s br. (OH), 3084 w ($CH_{arom}$), 2956 m, 2932 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 352 $cm^{-1}$ m (M−Cl). − $^1H$ NMR (270 MHz, $CD_3OD$): δ = 9.14 (s, br., 1 H, 8′), 8.91 (d, 1 H, $^3J_{3'}$ = 4.96 Hz, 2′), 7.90 (d, 1 H, $^3J_{2'}$ = 5.22 Hz, 3′), 7.57 (dd, 1 H, $^3J_{8'}$ = 9.38 Hz, $^4J_{5'}$ = 2.57 Hz, 7′), 7.23 (d, 1 H, $^4J_{7'}$ = 2.52 Hz, 5′), 6.32 (s, 1 H, 9), 5.72 (ddd, 1 H, $^3J_{11c}$ = 17.23 Hz, $^3J_{11t}$ = 10.39 Hz, $^3J_3$ = 6.85 Hz, 10), 5.14 (dt, 1 H, $^3J_{10}$ = 16.00 Hz, $^2J_{11t}$ = $^4J_3$ = 0.85 Hz, 11*c*), 5.03 (dt, 1 H, $^3J_{10}$ = 10.36 Hz, $^2J_{11c}$ = $^4J_3$ = 1.15 Hz, 11*t*), 4.39−4.26 (m, 1 H, 6b), 4.05 (s, 3 H, $OCH_3$), 3.78−3.52 (m, 3 H, 2a, 2b, 8), 3.52−3.32 (m, 1 H, 6a*), 3.38 (s, 3 H, $NCH_3$), 2.91−2.80 (m, 1 H, 3), 2.36−2.18 (m, 2 H, 7b, 4), 2.12−0.90 (5b*, 7a*, 5a*), 2.05−1.90 [m, 6 H, $P(CH_2C_3H_7)_3$], 1.86−1.70 [m, 6 H, $P(CH_2CH_2C_2H_5)_3$], 1.66 −1.37 [m, 6 H, $P(C_2H_4CH_2CH_3)_3$], 1.02 [t, 9 H, $^3J_{CH2}$ = 7.35 Hz, $P(C_3H_6CH_3)_3$]. − $^{31}P$ NMR (109.3 MHz): δ = 28.67. − $C_{33}H_{54}BCl_2F_4N_2O_2PPd$ (804.9): calcd. C 49.24, H 6.76, N 3.48; found C 48.99, H 6.75, N 3.43.

**19:** 74.5 mg of **13** (0.146 mmol) and 58 mg (0.073 mmol) of $[Cp^*IrCl_2]_2$ were used. Slow concentration of a solution in acetone gave orange crystals. − IR (KBr): $\tilde{\nu}$ = 3395 $cm^{-1}$ s br. (OH), 3083 w ($CH_{arom}$), 2963 m, 2922 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 281 $cm^{-1}$ s, 254 m (M−Cl). − $^1H$ NMR (400 MHz, [D$_6$]acetone): δ = 9.26 (d, 1 H, $^3J_{3'}$ = 5.65 Hz, 2′), 9.01 (d, 1 H, $^3J_{7'}$ = 9.89 Hz, 8′), 7.55 (d, 1 H, $^3J_{2'}$ = 5.64 Hz, 3′), 7.24 (dd, 1 H, $^3J_{8'}$ = 9.60 Hz, $^4J_{5'}$ = 2.44 Hz, 7′), 6.51 (s, 1 H, 5′), 6.26 (s, 1 H, 9), 5.59 (ddd, 1 H, $^3J_{11c}$ = 17.39 Hz, $^3J_{11t}$ = 10.33 Hz, $^3J_3$ = 7.06 Hz, 10), 5.00 (d, 1 H, $^3J_{10}$ = 17.16 Hz, 11*c*), 4.88 (d, 1 H, $^3J_{10}$ = 10.49 Hz, 11*t*), 4.35−4.21 (m, 1 H, 6b), 4.02 (s, 3 H, $OCH_3$), 3.85 (dd, $^3J$ = 12.96 Hz, $^3J$ = 10.55 Hz, 2b), 3.67 (s, 3 H, $NCH_3$), 3.62−3.45 (m, 2 H, 2a, 8), 3.45−3.33 (m, 1 H, 6a), 2.98−2.78 (m, 1 H, 3), 2.34−2.20 (m, 1 H, 7b), 2.15−1.95 (m, 1 H, 4), 1.68−1.57 (m, 1 H, 5b), 1.38−1.09 (m, 7a*, 5a*), 1.27 [s, 15 H, $C_5(CH_3)_5$]. − $C_{31}H_{42}BCl_2IrF_4N_2O_2 \times H_2O$ (842.6): calcd. C 44.19, H 5.26, N 3.32; found C 44.29, H 5.22, N 3.16.

**General Procedure for the Preparation of 20−22:** To a solution of quinine in 10 mL of $CH_2Cl_2$ and the equivalent amount of $CF_3SO_3H$ the chloro-bridged metal complex was added. After 16 h of stirring, the solvent of the yellow solution was removed in vacuo and the residue was washed twice with 5 mL of cold $Et_2O$. The yellow powder was dried in vacuo for 2 d.

**20:** 53 mg (0.163 mmol) of quinine, 14.3 μL (0.163 mmol) of $CF_3SO_3H$ and 62.7 mg (0.082 mmol) of $[(PEt_3)PtCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3409 $cm^{-1}$ vs br. (OH), 3083 m,sh ($CH_{arom}$), 2971 s, 2938 m ($CH_{aliph}$), 2692 w, 2665 w br. ($N^+$−H). − IR (PE): $\tilde{\nu}$ = 343 $cm^{-1}$ s (M−Cl). − $^1H$ NMR (270 MHz, $CDCl_3$): δ = 9.33 (d, 1 H, $^3J_{7'}$ = 9.52 Hz, 8′), 8.92 (dd, 1 H, $^3J_{3'}$ = 5.30 Hz, $^4J_P$ = 3.43 Hz, 2′), 7.74 (d, 1 H, $^3J_{2'}$ = 5.25 Hz, 3′), 7.44 (dd, 1 H, $^3J_{8'}$ = 9.53 Hz, $^4J_{5'}$ = 2.39 Hz, 7′), 7.05 (d, 1 H, $^4J_{7'}$ = 2.32 Hz, 5′), 6.02 (s, 1 H, 9), 5.55 (ddd, 1 H, $^3J_{11c}$ = 17.12 Hz, $^3J_{11t}$ = 10.40 Hz, $^3J_3$ = 6.72 Hz, 10), 5.06 (d, 1 H, $^3J_{10}$ = 10.40 Hz, 11*t*), 5.03 (d, 1 H, $^3J_{10}$ = 16.93 Hz, 11*c*), 4.61 (s, br., 1 H, OH), 4.01−3.96 (m, 1 H, 6b), 3.74 (s, 3 H, $OCH_3$), 3.52 (dd, 1 H, *J* = 13.15 Hz, *J* = 10.90 Hz, 2b), 3.30 (pt, 1 H, *J* = 8.70 Hz, 8), 3.18−2.98 (m, 2 H, 2a, 6a), 2.75−2.64 (m, 1 H, 3), 2.11−1.74 (5b*, 5a*, 4*, 7b*), 2.01−1.88 [m, 6 H, $P(CH_2CH_3)_3$], 1.38 (m, 1 H, 7a), 1.28 [dt, 10 H, $^3J_P$ = 17.04 Hz, $^3J_{CH2}$ = 7.63 Hz, $P(CH_2CH_3)_3$]. − $^{31}P$ NMR (109.3 MHz): δ = 0.17 ($^1J_{P\text{-}Pt}$ = 3403 Hz). − $C_{27}H_{40}Cl_2F_3N_2O_5PPtS$ (858.6): calcd. C 37.77, H 4.70, N 3.26; found C 37.62, H 4.86, N 3.18.

**21:** 108 mg (0.333 mmol) of quinine, 29.2 μL (0.333 mmol) of $CF_3SO_3H$ and 98 mg (0.166 mmol) of $[(PEt_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3442 $cm^{-1}$ vs br. (OH), 2970 m, 2938 m ($CH_{aliph}$), 2692 w, 2665 w, 2606 w ($N^+$−H). − IR (PE): $\tilde{\nu}$ = 352 $cm^{-1}$ s (M−Cl). − $^1H$ NMR (270 MHz, $CDCl_3$): δ = 9.11 (d, 1 H, $^3J_{7'}$ = 9.22 Hz, 8′), 8.89 (dd, 1 H, $^3J_{3'}$ = 5.21 Hz, $^4J_P$ = 3.41 Hz, 2′), 7.71 (d, 1 H, $^3J_{2'}$ = 5.29 Hz, 3′), 7.43 (dd, 1 H, $^3J_{8'}$ = 9.30 Hz, $^4J_{5'}$ = 2.41 Hz, 7′), 7.02 (d, 1 H, $^4J_{7'}$ = 1.95 Hz, 5′), 5.95 (s, 1 H, 9), 5.23 (ddd, 1 H, $^3J_{11c}$ = 17.01 Hz, $^3J_{11t}$ = 10.40 Hz, $^3J_3$ = 6.64 Hz, 10), 5.04 (d, 1 H, $^3J_{10}$ = 10.24 Hz, 11*t*), 5.01 (d, 1 H, $^3J_{10}$ = 16.64 Hz, 11*c*), 4.65 (s, br., 1 H, OH), 3.99−3.85 (m, 1 H, 6b), 3.79 (s, 3 H, $OCH_3$), 3.50 (dd, 1 H, *J* = 13.04 Hz, *J* = 10.98 Hz, 2b), 3.27 (pt, 1 H, *J* = 8.95 Hz, 8), 3.13−2.98 (m, 2 H, 2a, 6a), 2.68 (m, 1 H, 3), 2.1−1.2 (5b*, 4*, 7b*, 5a*, 7a*), 2.07−1.90 [m, 6 H, $P(CH_2CH_3)_3$], 1.32 [dt, 9 H, $^3J_P$ = 17.83 Hz, $^3J_{CH2}$ = 7.60 Hz, $P(CH_2CH_3)_3$]. − $^{31}P$ NMR (109.3 MHz): δ = 36.15. − $C_{27}H_{40}Cl_2F_3N_2O_5PPdS$ (770.0): calcd. C 42.12, H 5.24, N 3.64; found C 41.62, H 5.66, N 3.49.

**22:** 316 mg (0.974 mmol) of quinine, 85.5 μL (0.974 mmol) of $CF_3SO_3H$ and 328 mg (0.487 mmol) of $[(PPr_3)PdCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3402 $cm^{-1}$ s br. (OH), 2964 s, 2930 m ($CH_{aliph}$), 2692 m, 2665 m br. ($N^+$−H). − IR (PE): $\tilde{\nu}$ = 350 $cm^{-1}$ s (M−Cl). − $^1H$ NMR (270 MHz, $CDCl_3$): δ = 9.18 (s, br., 1 H, NH), 9.11 (d, 1 H, $^3J_{7'}$ = 9.37 Hz, 8′), 8.90 (dd, 1 H, $^3J_{3'}$ = 5.21 Hz, $^4J_P$ = 3.49 Hz, 2′), 7.71 (d, 1 H, $^3J_{2'}$ = 5.31 Hz, 3′), 7.44 (dd, 1 H, $^3J_{8'}$ = 9.43 Hz, $^4J_{5'}$ = 2.53 Hz, 7′), 7.02 (d, 1 H, $^4J_{7'}$ = 2.24 Hz, 5′), 5.98 (d, 1 H, $^3J$ = 3.09 Hz, 9), 5.54 (ddd, 1 H, $^3J_{11c}$ = 17.25 Hz, $^3J_{11t}$ = 10.49 Hz, $^3J_3$ = 6.76 Hz, 10), 5.06 (d, 1 H, $^3J_{10}$ = 10.04 Hz, 11*t*), 5.02 (d, 1 H, $^3J_{10}$ = 16.77, 11*c*), 4.58 (d, 1 H, $^3J$ = 3.54 Hz, $OH^{not\ sure}$), 4.01−3.88 (m, 1 H, 6b), 3.78 (s, 3 H, $OCH_3$), 3.52 (pt, 1 H, *J* = 12.03 Hz, 2b), 3.28 (pt, 1 H, *J* = 8.73 Hz, 8), 3.12−3.01 (m, 2 H, 2a, 6a), 2.68 (s, br., 1 H, 3), 2.07−1.1 (5b*, 4*, 7b*, 5a*,

7a*), 2.07−1.70 [2 m, 12 H, P($C_2H_4CH_3$)$_3$], 1.13 [t, 9 H, $^3J_{CH2}$ = 6.96 Hz, P($C_2H_4CH_3$)$_3$]. − $^{31}$P NMR (109.3 MHz): δ = 26.94. − $C_{30}H_{46}Cl_2F_3N_2O_5PPdS$ (811.1): calcd. C 44.43, H 5.72, N 3.45; found C 43.90, H 5.99, N 3.32.

**23:** To a solution of 261 mg (1.90 mmol) of $ZnCl_2$ in 10 mL of methanol a solution of 621 mg (2.11 mmol) of cinchonine in 10 mL of methanol was added and stirred for 1 h. At once a white precipitate was obtained which was crystallized by slow concentration of a solution in MeOH/$CH_3CN$ to give clear colourless crystals which were powdered and dried in vacuo for 2 d. − IR (KBr): $\tilde{\nu}$ = 3389 cm$^{-1}$ vs br. (OH), 3084 m ($CH_{arom}$), 2944 s ($CH_{aliph}$), 2600 m br. ($N^+$−H). − $^1$H NMR (400 MHz, [$D_6$]acetone): δ = 12.27 (s, br., 1 H, NH), 8.88 (d, 1 H, $^3J_{3'}$ = 4.44 Hz, 2′), 8.49 (d, 1 H, $^3J_{7'}$ = 8.36 Hz, 8′), 7.95 (d, 1 H, $^3J_{6'}$ = 9.87 Hz, 5′), 7.54 (ddd, 1 H, $^3J_{5'}$ = 8.32 Hz, $^3J_{7'}$ = 6.93 Hz, $^4J_{8'}$ = 1.38 Hz, 6′), 7.30 (ddd, 1 H, $^3J_{8'}$ = 8.25 Hz, $^3J_{6'}$ = 6.90 Hz, $^4J_{5'}$ = 1.35 Hz, 7′), 6.78 (d, 1 H, *J* = 3.53 Hz, 9), 6.32 (d, 1 H, *J* = 4.05 Hz), 6.17 (ddd, 1 H, $^3J_{11c}$ = 17.63 Hz, $^3J_{11t}$ = 10.25 Hz, $^3J_3$ = 7.38 Hz, 10), 5.27 (dt, 1 H, $^3J_{10}$ = 17.48 Hz, $^2J_{11t}$ = $^4J_3$ = 1.38 Hz, 11*c*), 5.21 (dt, 1 H, $^3J_{10}$ = 10.27 Hz, $^2J_{11c}$ = $^4J_3$ = 1.16 Hz, 11*t*), 4.29−4.24 (m, 1 H, 2b), 3.60−1.18 (7m, 11 H, 6b, 2a, 8, OH, 3, 6a, 5b, 4, 7b, 7a, 5a).

**General Procedure for the Preparation of 24−29:** A solution of quinine in 10 mL of $CH_2Cl_2$ and the equivalent amount of a solution of NaOMe in methanol was cooled to −78°C. After the addition of 0.5 equivalents of [$R_3PMCl_2$]$_2$ or of [Cp*$IrCl_2$]$_2$, the solution was allowed to warm up to room temp. for 16 h and stirred for another 2 h. To the yellow solution again 0.5 equivalents of [$R_3PMCl_2$]$_2$ or of [Cp*$IrCl_2$]$_2$ were added. After 16 h of stirring, the solvent was removed in vacuo, the residue was dissolved in $CH_2Cl_2$ and the mixture was filtered through Celite to remove NaCl. The solvent was removed again in vacuo and the residue was washed twice with 5 mL of cold $Et_2O$ to give a yellow powder which was dried in vacuo for several days.

**24:** 59 mg (0.182 mmol) of quinine, 0.182 mmol of NaOMe in MeOH and 140 mg (0.182 mmol) of [($PEt_3$)$PtCl_2$]$_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3073 cm$^{-1}$ w ($CH_{arom}$), 2962 s, 2935 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 340 cm$^{-1}$ s, 331 s sh (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.40 (d, 1 H, $^3J_{7'}$ = 9.65 Hz, 8′), 9.27 (d, 1 H, $^3J_{2'}$ = 5.11 Hz, 3′), 8.99 (dd, 1 H, $^3J_{3'}$ = 5.52 Hz, $^4J_P$ = 3.42 Hz, 2′), 7.49 (dd, 1 H, $^3J_{8'}$ = 9.44 Hz, $^4J_{5'}$ = 2.54 Hz, 7′), 7.05 (d, 1 H, $^4J_{7'}$ = 2.48 Hz, 5′), 5.96 (ddd, 1 H, $^3J_{11c}$ = 17.22 Hz, $^3J_{11t}$ = 10.37 Hz, $^3J_3$ = 6.85 Hz, 10), 5.22−5.15 (m, 3 H, 9, 11*c*, 11*t*), 3.94−3.75 (m, 2 H, 8*, 2b*), 3.81 (s, 3 H, $OCH_3$), 3.45−3.41 (m, 1 H, 2a), 3.27−3.21 (m, 1 H, 6b), 3.01−2.92 (m, 1 H, 6a), 2.44 (m, 1 H, 3), 2.20−2.09 (m, 1 H, 7b), 2.09−1.20 (4*, 5b*, 7a*, 5a*) 2.05−1.98 [m, 6 H, N′PtP($CH_2CH_3$)$_3$], 1.92−1.83 [m, 6 H, (N,O)PtP($CH_2CH_3$)$_3$], 1.37−1.23 (m, 18 H, N′PtP($CH_2CH_3$)$_3$, (N,O)PtP($CH_2CH_3$)$_3$]. − $^{31}$P NMR (109.3 MHz): δ = 6.18 (N′PtP, $^1J_{P\text{-}Pt}$ = 3636 Hz), −0.20 [(N,O)PtP, $^1J_{P\text{-}Pt}$ = 3382 Hz]. − $C_{32}H_{53}Cl_3N_2O_2P_2Pt_2$ × 0.5 $CH_2Cl_2$ (1098.7): calcd. C 35.53, H 4.95. N 2.55; found C 35.16, H 5.19, N 2.54.

**25:** 67 mg (0.207 mmol) of quinine, 0.207 mmol of NaOMe in MeOH and 122 mg (0.207 mmol) of [($PEt_3$)$PdCl_2$]$_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3077 cm$^{-1}$ w ($CH_{arom}$), 2964 s, 2931 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 356 cm$^{-1}$ s, 328 m (M−Cl). − $^1$H NMR (270 MHz, $CDCl_3$): δ = 9.20 (d, 1 H, $^3J_{7'}$ = 9.38 Hz, 8′), 9.11 (d, 1 H, $^3J_{2'}$ = 4.92 Hz, 3′), 9.01 (dd, 1 H, $^3J_{3'}$ = 5.24 Hz, $^4J_P$ = 3.50 Hz, 2′), 7.48 (dd, 1 H, $^3J_{8'}$ = 9.46 Hz, $^4J_{5'}$ = 2.54 Hz, 7′), 7.03 (d, 1 H, $^4J_{7'}$ = 2.71 Hz, 5′), 5.96 (ddd, 1 H, $^3J_{11c}$ = 17.12 Hz, $^3J_{11t}$ = 10.25 Hz, $^3J_3$ = 6.77 Hz, 10), 5.44 (d, 1 H, $^3J_8$ = 6.85 Hz, 9), 5.19 −5.12 (2m, 2 H, 11*c*, 11*t*), 3.94−3.78 (m, 1 H, 8*), 3.86 (s, 3 H, $OCH_3$), 3.64 (dd, 1 H, *J* = 13.74 Hz, *J* = 10.32 Hz, 2b), 3.38 (pd, 1 H, *J* = 14.28 Hz, 2a), 3.23−2.93 (m, 2 H, 6b, 6a), 2.39 (m, 1 H, 3), 2.14−1.71 (m, 3 H, 7b*, 5b*, 4*), 2.14−1.95 [m, 6 H, N′PdP($CH_2CH_3$)$_3$], 1.91−1.71 [m, 6 H, (N,O)PdP($CH_2CH_3$)$_3$], 1.48−1.22 (m, 18 H, N′PdP($CH_2CH_3$)$_3$, (N,O)PdP($CH_2CH_3$)$_3$], 1.48−1.02 (m, 2 H, 7a*, 5a*). − $^{31}$P NMR (109.3 MHz): δ = 35.01 (N′PdP), 31.39 [(N,O)PdP]. − $C_{32}H_{53}Cl_3N_2O_2P_2Pd_2$ (878.9): calcd. C 43.73, H 6.08, N 3.13; found C 43.45, H 6.08, N 3.18.

**26:** 188 mg (0.639 mmol) of cinchonine, 0.639 mmol of NaOMe in MeOH and 377 mg (0.639 mmol) of [($PEt_3$)$PdCl_2$]$_2$ were used. Crystals were obtained from a $CHCl_3$/hexane solution. − IR (KBr): $\tilde{\nu}$ = 3084 cm$^{-1}$ w ($CH_{arom}$), 2957 s, 2938 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 359 cm$^{-1}$ s, 324 m (M−Cl). − $^1$H NMR (270 MHz, $CDCl_3$): δ = 9.28 (d, 1 H, $^3J_{3'}$ = 8.31 Hz, 8′), 9.21−9.13 (m, 2 H, 2′, 5′), 7.78 (t, 1 H, $^3J$ = 7.84 Hz, 7′), 7.76 (3′*), 7.49 (t, 1 H, $^3J$ = 7.30 Hz, 6′), 5.52 (d, 1 H, $^3J_8$ = 6.77 Hz, 9), 4.77 (ddd, 1 H, $^3J_{11c}$ = 16.88 Hz, $^3J_{11t}$ = 10.51 Hz, $^3J_3$ = 6.27 Hz, 10), 4.52 (d, 1 H, $^3J_{10}$ = 10.59 Hz, 11*t*), 4.11 (d, 1 H, $^3J_{10}$ = 17.12 Hz, 11*c*), 3.78−3.69 (m, 1 H, 8), 3.44−3.20 (m, 3 H, 6b, 2b, 6a), 2.71−2.61 (m, 1 H, 2a), 2.13−1.07 (3*, 4*, 7a*, 5a*, 5b*), 2.08−1.95 [m, 6 H, N′PdP($CH_2CH_3$)$_3$], 1.88−1.72 [m, 6 H, (N,O)PdP($CH_2CH_3$)$_3$], 1.41−1.22 [m, 18 H, N′PdP($CH_2CH_3$)$_3$, (N,O)PdP($CH_2CH_3$)$_3$]. − $^{31}$P NMR (109.3 MHz): δ = 34.99 (N′PdP), 31.33 [(N,O)PdP]. − $C_{31}H_{51}Cl_3N_2OP_2Pd_2$ × 0.75 $CHCl_3$ (938.4): calcd. C 40.64, H 5.56, N 2.98; found C 40.58, H 5.55, N 2.94.

**27:** 60 mg (0.185 mmol) of quinine, 0.185 mmol of NaOMe in MeOH and 124 mg (0.185 mmol) of [($PPr_3$)$PdCl_2$]$_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3077 cm$^{-1}$ w ($CH_{arom}$), 2957 vs, 2931 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 352 cm$^{-1}$ s, 330 m (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.16 (d, 1 H, $^3J_{7'}$ = 9.53 Hz, 8′), 9.05 (d, 1 H, $^3J_{2'}$ = 5.21 Hz, 3′), 8.97 (dd, 1 H, $^3J_{3'}$ = 5.26 Hz, $^4J_P$ = 3.49 Hz, 2′), 7.45 (dd, 1 H, $^3J_{8'}$ = 9.28 Hz, $^4J_{5'}$ = 2.49 Hz, 7′), 7.00 (d, 1 H, $^4J_{7'}$ = 2.51 Hz, 5′), 5.92 (ddd, 1 H, $^3J_{11c}$ = 17.25 Hz, $^3J_{11t}$ = 10.38 Hz, $^3J_3$ = 6.88 Hz, 10), 5.44 (d, 1 H, $^3J_8$ = 6.78 Hz, 9), 5.14−5.10 (2 m, 2 H, 11*c*, 11*t*), 3.88−3.76 (m, 1 H, 8*), 3.84 (s, 3 H, $OCH_3$), 3.60 (dd, 1 H, *J* = 13.54 Hz, *J* = 10.34 Hz, 2b), 3.33 (pd, 1 H, *J* = 13.93 Hz, 2a), 3.15−3.09 (m, 1 H, 6b), 3.00−2.92 (m, 1 H, 6a), 2.34 (m, 1 H, 3), 2.04−1.60 (m, 3 H, 7b*, 5b*, 4*), 2.04−1.92 [m, 12 H, N′PdP($CH_2C_2H_5$)$_3$, (NO)PdP($CH_2C_2H_5$)$_3$], 1.92−1.60 [m, 12 H, N′PdP($CH_2CH_2CH_3$)$_3$ (N,O)PdP($CH_2CH_2CH_3$)$_3$], 1.36−1.00 (m, 2 H, 7a*, 5a*), 1.2−1.0 [m, 18 H, N′PdP($C_2H_4CH_3$)$_3$, (N,O)PdP($C_2H_4CH_3$)$_3$]. − $^{31}$P NMR (109.3 MHz): δ = 28.67 (0.05 $NPdCl_2P^{not\ sure}$), 25.69 (N′PdP), 22.39 [(N,O)PdP]. − $C_{38}H_{65}Cl_3N_2O_2P_2Pd_2$ (963.1): calcd. C 47.39, H 6.80, N 2.91; found C 47.92, H 7.04, N 2.89.

**28:** 52 mg (0.160 mmol) of quinine, 0.160 mmol of NaOMe in MeOH and 121 mg (0.121 mmol) of [($PBu_3$)$PdCl_2$]$_2$ were used. The residue was washed twice with 10 mL of cold hexane. − IR (KBr): $\tilde{\nu}$ = 3076 cm$^{-1}$ w ($CH_{arom}$), 2960 s, 2930 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 355 cm$^{-1}$ s, 327 m (M−Cl). − $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.15 (d, 1 H, $^3J_{7'}$ = 9.20 Hz, 8′), 9.07 (d, 1 H, $^3J_{2'}$ = 5.19 Hz, 3′), 8.94 (dd, 1 H, $^3J_{3'}$ = 5.09 Hz, $^4J_P$ = 3.68 Hz, 2′), 7.42 (dd, 1 H, $^3J_{8'}$ = 9.35 Hz, $^4J_{5'}$ = 2.63 Hz, 7′), 6.98 (d, 1 H, $^4J_{7'}$ = 2.21 Hz, 5′), 5.91 (ddd, 1 H, $^3J_{11c}$ = 17.15 Hz, $^3J_{11t}$ = 10.24 Hz, $^3J_3$ = 6.91 Hz, 10), 5.38 (d, 1 H, $^3J_8$ = 6.60 Hz, 9), 5.11 (d, 1 H, $^3J_{10}$ = 16.07 Hz, 11*c*), 5.10 (d, 1 H, $^3J_{10}$ = 11.69 Hz, 11*t*), 3.88−3.78 (m, 1 H, 8*), 3.82 (s, 3 H, $OCH_3$), 3.58 (dd, 1 H, *J* = 13.43 Hz, *J* = 10.50 Hz, 2b), 3.33 (pd, 1 H, *J* = 13.59 Hz, 2a), 3.14−3.08 (m, 1 H, 6b), 2.99−2.92 (m, 1 H, 6a), 2.32 (m, 1 H, 3), 2.09−0.90 (7b*, 5b*, 4*, 7a*, 5a*), 2.09−0.90 [4 m, 54 H, N′PdP($C_4H_9$)$_3$, (NO)PdP($C_4H_9$)$_3$]. − $^{31}$P NMR (109.3 MHz): δ = 26.98 (N′PdP), 23.40 [(N,O)PdP]. − $C_{44}H_{77}Cl_3N_2O_2P_2Pd_2$ (1047.4): calcd. C 50.46, H 7.41, N 2.67; found C 50.44, H 7.71, N 2.65.

**29:** 67 mg (0.207 mmol) of quinine, 0.207 mmol of NaOMe in MeOH and 165 mg (0.207 mmol) of $[Cp^*IrCl_2]_2$ were used. − IR (KBr): $\tilde{\nu}$ = 3071 $cm^{-1}$ w ($CH_{arom}$), 2961 m, 2918 s ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 288 $cm^{-1}$ m (M−Cl). − $^1H$ NMR (270 MHz, $CDCl_3$): δ = 9.55 (d, 1 H, $^3J_{3'}$ = 5.20 Hz, 2′), 9.13 (d, 1 H, $^3J_{7'}$ = 8.56 Hz, 8′), 7.96 (d, 1 H, $^3J_{2'}$ = 5.58 Hz, 3′), 7.31 (dd, 1 H, $^3J_{8'}$ = 9.80 Hz, $^4J_{5'}$ = 2.74 Hz, 7′), 6.87 (d, 1 H, $^4J_{7'}$ = 2.85 Hz, 5′), 6.03 (d, 1 H, $^3J$ = 9.74 Hz, 9), 5.28−5.11 (m, 1 H, 10), 4.63 (d, 1 H, $^3J_{10}$ = 18.81 Hz, 11*c*), 4.53−4.35 (m, 1 H, 11*t*), 3.95−3.69 (8*, 2b*), 3.84 (s, 3 H, $OCH_3$), 3.37−3.31 (m, 3 H, 2a, 6a, 6b), 2.11 (m, 1 H, 3), 1.7−1.2 (7b*, 4*, 5b*, 7a*), 1.68 {s, 15 H, N′$IrCl_2[C_5(CH_3)_5]$}, 1.41 {s, 15 H, (N,O)$IrCl[C_5(CH_3)_5]$}, 0.78−0.65 (m, 1 H, 5a). − $C_{40}H_{53}Cl_3Ir_2N_2O_2$ (1084.7): calcd. C 44.29, H 4.93, N 2.58; found C 44.40, H 5.24, N 2.31.

**30:** To a solution of 142 mg (0.287 mmol) of $PPh_3AuCl$ in 5 mL of $CH_2Cl_2$ a solution of 49 mg (0.287 mmol) of $AgNO_3$ in 10 mL of methanol was added. After 1 h of vigorous stirring with exclusion of light, AgCl was centrifuged off and 46.5 mg (0.144 mmol) of quinine was added. The solution was stirred for another 3 h to give a clear colourless solution which was concentrated to about 0.5 mL and added to 20 mL of $Et_2O$. The white precipitate was washed twice with $Et_2O$ and dried in vacuo for 2 d. − IR (KBr): $\tilde{\nu}$ = 3430 $cm^{-1}$ vs br. (OH), 3077 m ($CH_{arom}$), 2938 m ($CH_{aliph}$). − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, 1 H, $^3J_{3'}$ = 5.12 Hz, 2′), 8.33 (d, 1 H, $^3J_{7'}$ = 9.54 Hz, 8′), 8.03 (d, 1 H, $^3J_{2'}$ = 5.01 Hz, 3′), 7.65−7.30 (m, 32 H, 2 $PPh_3$, 5′, 7′), 6.50 (s, br., 1 H, 9), 5.77 (ddd, 1 H, $^3J_{11c}$ = 17.21 Hz, $^3J_{11t}$ = 9.81 Hz, $^3J_3$ = 7.32 Hz, 10), 5.05 (d, 1 H, $^3J_{10}$ = 18.59 Hz, 11*c*), 5.01 (d, 1 H, $^3J_{10}$ = 10.47 Hz, 11*t*), 4.39 (s, br., 1 H, OH), 3.75−3.55 (6b*), 3.63 (s, 3 H, $OCH_3$), 3.5−3.2 (m, 4 H, 2b, 8, 2a, 6a), 2.59 (m, 1 H, 3), 2.24−1.2 (4m, 5 H, 5b, 4, 7b, 5a, 7a). − $^{31}P$ NMR (109.3 MHz): δ = 28.54. − $C_{56}H_{54}AuN_4O_8P_2 \times CH_2Cl_2$(1451.9): calcd. C 47.15, H 3.89. N 3.86; found C 47.32, H 3.95, N 3.91.

**31:** 46 mg (0.126 mmol) of $[(allyl)PdCl]_2$ and 41 mg (0.126 mmol) of quinine were dissolved in 15 mL of $CH_2Cl_2$. After stirring for 3 h, the solvent was removed in vacuo and the grey-green solid was washed twice with pentane and dried in vacuo for 2 d. − IR (KBr): $\tilde{\nu}$ = 3358 $cm^{-1}$ vs br. (OH), 3070 w ($CH_{arom}$), 2934 m ($CH_{aliph}$). − IR (PE): $\tilde{\nu}$ = 276 $cm^{-1}$ s (M−Cl). − $^1H$ NMR (400 MHz, $CD_2Cl_2$): δ = 8.74 (d, 1 H, $^3J_{3'}$ = 5.09 Hz, 2′), 8.45 (d, 1 H, $^3J_{7'}$ = 9.60 Hz, 8′), 7.72 (d, 1 H, $^3J_{2'}$ = 5.24 Hz, 3′), 7.58 (s, br., 1 H, 5′), 7.40 (dd, 1 H, $^3J_{8'}$ = 9.27 Hz, $^4J_{5'}$ = 2.51 Hz, 7′), 6.51 (s, br., 1 H, 9), 5.67−5.47 [m, 3 H, 10, NPdC*H*$(CH_2)_2$, N′PdC*H*$(CH_2)_2$], 5.00 (d, 1 H, $^3J_{10}$ = 17.09 Hz, 11*c*), 4.86 (d, 1 H, $^3J_{10}$ = 10.60 Hz, 11*t*), 4.68 (s, br., 1 H, OH), 4.27 (s, br., 1 H, 6b), 4.01 (s, 3 H, $OCH_3$), 3.91 [m, 6 H, 8*, 2b*, N′PdCH($CH H_{endo}$)$_2$, NPdCH($CH H_{endo}$)$_2$], 3.38−3.30 (m, 1 H, 2a), 3.20−3.10 (m, 1 H, 6a), 3.10−2.90 [m, 4 H, N′PdCH($CH H_{exo}$)$_2$, NPdCH($CH H_{exo}$)$_2$], 2.31 (m, 1 H, 3), 1.75−1.65 (m, 3 H, 4, 7b, 5b), 1.55−1.50 (m, 1 H, 5a), 1.07−1.00 (m, 1 H, 7a). − $C_{26}H_{34}Cl_2N_2O_2Pd_2 \times 0.25\ CH_2Cl_2$ (711.5): calcd. C 44.31, H 4.89, N 3.94; found C 44.29, H 5.10, N 3.66.

**32:** To a solution of 410 mg (1.26 mmol) of quinine in 20 mL of aqueous 0.1 N HCl 524 mg (1.26 mmol) of $K_2PtCl_4$ were added. At once a light red precipitate was obtained which was dissolved again by the addition of 10 mL of 2 N HCl. The red solution was stirred for several hours at 90°C until a yellow precipitate was formed which was washed twice with 10 mL of water, once with 10 mL of ethanol and once with 10 mL of $Et_2O$ and was dried in vacuo. Yellow crystals were obtained from 1 N HCl. − IR (KBr): $\tilde{\nu}$ = 3418 $cm^{-1}$ vs br. (OH), 2827−2448 vs br. ($N^+$−H). − IR (PE): $\tilde{\nu}$ = 332 $cm^{-1}$ s, 304 m (M−Cl). − $^1H$ NMR (400 MHz, [$D_7$]DMF): δ = 12.55 (s, 0.5 H, $NH^+$), 12.35 (s, 0.5 H, $NH^+$), 9.315 (d, 0.5 H, $^3J_{3'}$ = 5.64 Hz, 2′), 9.298 (d, 0.5 H, $^3J_{3'}$ = 5.91 Hz, 2′), 8.45−8.38 (m, 2 H, 3′, 8′), 8.10 (pt, 1 H, $^4J_{7'}$ = 2.64 Hz, 5′), 7.82−7.78(m, 1 H, 7′), 7.20 (s, br., 1 H, N′H), 6.87 (s, 0.5 H, 9), 6.83 (s, 0.5 H, 9), 4.92−4.77 (m, 1 H, 10), 4.26−4.01 (11*t**,11*c**, 8*, 6b*), 4.19 (s, 1.5 H, $OCH_3$), 4.17 (s, 1.5 H, $OCH_3$), 3.72−3.66 (m, 1 H, 2b), 3.42−3.28 (m, 2 H, 2a, 6a), 3.18 (s, br., 0.5 H, 3), 2.8−2.7 (0.5 H, 3), 2.38−1.80 (5m, 5 H, 5b, 4, 5a, 7b, 7a). − $C_{20}H_{26}Cl_4N_2O_2Pt$ (663.3): calcd. C 36.21, H 3.95, N 4.22; found C 35.68, H 4.30, N 4.02.

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