Metal Complexes of Biologically Important Ligands, LXXXVI[1]

Organometallic Complexes of Ruthenium(II), Rhodium(III), Iridium(III), and Gold(I) with Cinchona Alkaloids☆

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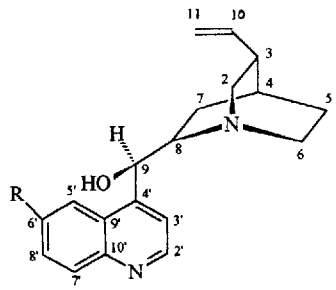
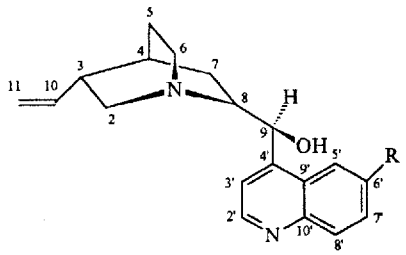
The following chiral organometallic complexes of the cinchona alkaloids quinine (L^1), cinchonidine (L^2), quinidine (L^3), cinchonine (L^4) were prepared: $[(\eta^5\text{-}C_5H_5)(Ph_3P)(OC)Ru(L)]BF_4$ (**1**: $L=L^1$; **2**: $L=L^2$; **3**: $L=L^3$), $ClAuL^1$ (**4**), $[(\eta^5\text{-}C_5Me_5)(Cl_2)Ir(L)]$ (**5**: $L=L^1$; **6**: $L=L^2$; **7**: $L=L^4$), $[(\eta^5\text{-}C_5Me_5)(Cl_2)Rh(L^2)]$ (**8**), $[(\eta^6\text{-}p\text{-cymene})(Cl_2)Ru(L)]$ (**9**: $L=L^1$; **10**: $L=L^2$; **11**: $L=L^4$). In all complexes the tertiary nitrogen atom of the cinchona alkaloids is bound to the metal. Complexes **5**–**11** are formed as mixtures of isomers. Elimination of HCl from **10** and **11** gives the neutral N,O-chelate complexes (η^6-*p*-cymene)(Cl)Ru(L^2 – H^+) (**13**) and (η^6-*p*-cymene)-(Cl)Ru(L^4 – H^+) (**14**) which were structurally characterized by X-ray diffraction.

Cinchona alkaloids are naturally occurring important drugs and are widely used as chiral auxiliaries in organic synthesis[3] and catalysis[4]. Of great interest is the pioneering work by Sharpless on the osmium tetroxide-catalyzed asymmetric dihydroxylation of olefins by use of chinchona alkaloid ligands[4–6]. To our knowledge only a few metal complexes of cinchona alkaloids have been prepared so far[7]. Sharpless et al.[8] reported on the structure of the osmium tetroxide complex of (dimethylcarbamoyl)dihydroquinidine. Metal complexes of these alkaloids which have four potential donor groups have to be assumed as intermediates in asymmetric metal-catalyzed reactions where alkaloids are used as adjuvants.

Complexes with one of the two nitrogen-containing fragments of chinchona alkaloids, quinoline[9] and quinuclidine[10] as ligands were reported. We used the Lewis acids $[(\eta^5\text{-}C_5H_5)(Ph_3P)(OC)Ru]^+$[11], $ClAuSMe_2$[12], and the chlorine-bridged complexes $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$ (M = Rh, Ir) and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$[13] as probes for the complexation of the cinchona alkaloids I and II.



I



II

quinine	Ia R = OCH_3
cinchonidine	Ib R = H
quinidine	IIa R = OCH_3
cinchonine	IIb R = H

Results and Discussion

The in situ [from $(\eta^5\text{-}C_5H_5)(OC)(Ph_3P)RuCl$ and $AgBF_4$] prepared organometallic Lewis acid $(\eta^5\text{-}C_5H_5)(OC)(Ph_3P)Ru^+$ was added to the cinchona alkaloids to give the yellow complexes **1**–**3**.

The gold(I) complex **4** was obtained from Me_2SAuCl and quinine.

As in DsO_4 complexes of dihydroquinidine[8] and quinuclidine[10] the alkaloids are coordinated in **1**–**4** to the quinuclidine nitrogen atom. This follows from the downfield shift of all the ^{1}H-NMR signals of the hydrogen atoms near the nitrogen atom in comparison to those of the free ligands. The chemical shifts of the other hydrogen atoms (except 8-H) are very close to those of the free alkaloids.

For several cinchona alkaloids a conformational analysis was carried out by Wynberg and Sharpless[14]. From

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$^3J_{8\text{-H},9\text{-H}}$ = 6.4 Hz for **1** the dehedral angle 8-H–C-9–C-8–H-9 should be approximately 100°[15]. This value suggests a conformation between "open" (60°) and "closed" (150°) in solution[14a]. From $^3J_{8\text{-H},9\text{-H}}$ = 3.7 Hz for **4** an open conformation similarly to the free quinine[14a] can be assumed.

$[(\eta^5\text{-}C_5H_5)(Ph_3P)(OC)Ru(L)]BF_4$

1 - 3

	L
1	quinine
2	chinchonidine
3	quinidine

ClAu(cinchonine)

4

$(\eta^5\text{-}C_5Me_5)(Cl)_2M(L)$

5 - 8

	M	L
5	Ir	quinine
6	Ir	cinchonidine
7	Ir	quinidine
8	Rh	cinchonidine

$(\eta^6\text{-p-cymene})(Cl)_2Ru(L)$

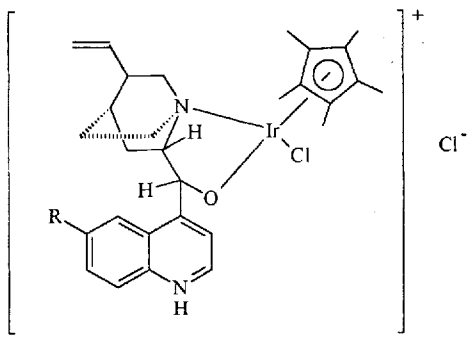
9 -11

	L
9	quinine
10	cinchonidine
11	cinchonine

For the complexes with a chiral metal center **1**–**3** two C_5H_5 ^{1}H-NMR signals and two ^{31}P-NMR signals are observed which we assign to the two diastereoisomers $S_{Ru}R_N$ and $R_{Ru}R_N$. One isomer, presumably $R_{Ru}R_N$, predominates.

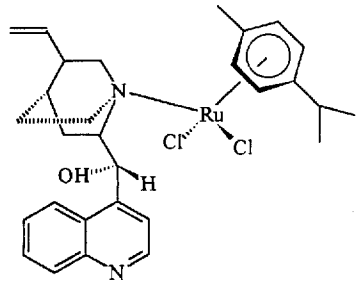
The IR spectra exhibit a remarkable shift of the ν(OH) absorptions of **1**–**4** in comparison with those of the free alkaloids. This indicates the loss of hydrogen bonds in the metal complexes. The reactions of the chloro-bridged complexes $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ and $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$ (M = Rh, Ir) with the alkaloids yield the orange, water-soluble complexes **5**–**11**.

A broad intensive IR absorption at $\tilde{\nu}$ = 2500–2550 cm^{-1} of **5**–**11** is striking. We attribute this band to a N–H$^+$ vibration[16] and therefore we formulate the complexes **5**–**11** (as shown for **5**) with a protonated pyridine ring[17]. The νCH absorptions of **5**–**11** are shifted to higher wavenumbers in comparison with those of the free alkaloids. This was also observed in the IR spectra of piperidine complexes[18].

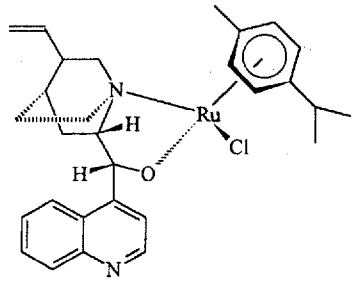


5

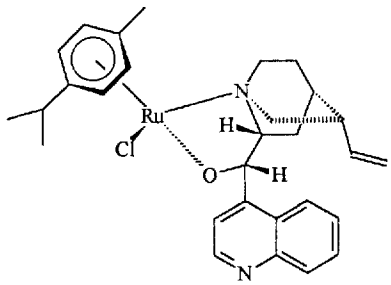
The ^{1}H- and ^{13}C-NMR spectra of **5**–**11** show three sets of signals. Two sets (in a ratio 1 : 1) can be assigned to the two diastereoisomers of **5**–**11** which contain a chiral metal center. The third set with weaker signals can be attributed to neutral complexes, as shown for **12**. Compound **12** could be separated.



12



13



14

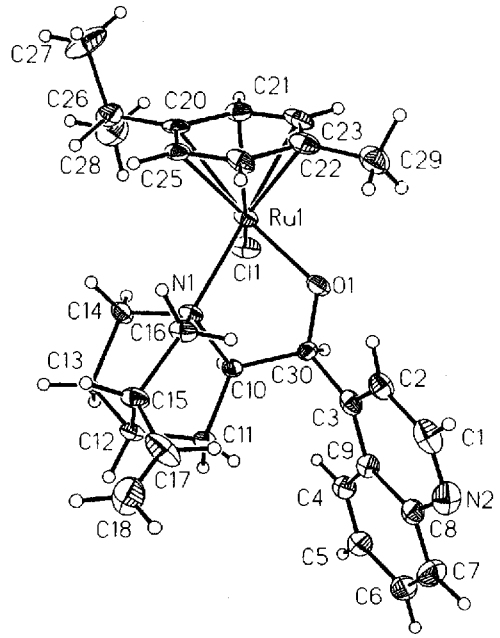
During attempts to recrystallize **10** and **11** from CH_2Cl_2 the neutral chelate complexes **13** and **14** were obtained. Complexes **13** and **14** could be prepared directly from $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ and L^2 in the presence of NaOMe or by deprotonation of **11** with NEt_3. Characteristic of **13** and **14** is the absence of the IR absorption at $\tilde{\nu}$ = 2500 cm^{-1}.

Molecular Structure of 13 and 14

Crystals of **13** and **14** could be obtained from $CHCl_3$/pentane. The X-ray structural determinations confirm the existence of the five-membered N,O-chelate (Figure 1, Table 1)[25]. The unit cell of **13** ($S_{Ru}R_N$) and **14** ($R_{Ru}R_N$) contains only one diastereoisomer. In the crystal of **13**[19] the cymene ligands are strongly distorted and therefore the data are not presented. The unit cell of **14** contains two independent

molecules which differ in the orientation of the *p*-cymene spectator ligand and the vinyl group.

Figure 1. Structure of one molecule of **14** in the crystal[a]



[a] Selected bond lengths [Å], angles [°] and torsion angles [°]: Ru1–O1 1.977(7), Ru1–N1 2.180(8), Ru1–Cl1 2.451(3), O1–C30 1.403(11), C30–C10 1.553(14), N1–C16 1.499(11), N1–C14 1.476(12), N1–C10 1.520(12); O1–Ru1–Cl1 89.5(2), O1–Ru1–N1 76.1(3), N1–Ru1–Cl1 87.2(2), C30–O1–Ru1 118.0(6), C14–N1–Ru1 112.8(6), C10–N1–Ru1 106.8(6); O1–Ru1–N1–C10 −37.8(6), O1–Ru1–N1–C16 −6.4(6), Ru1–O1–C30–C10 −24.8(11), Ru1–O1–C30–C3 −154.2(7), Ru1–N1–C10–C30 35.1(9), Ru1–N1–C10–C11 166.8(7), C16–N1–C10–C30 −84.2(10), O1–C30–C10–N1 −10.0(12).

The bond lengths and angles in **13** and **14** and the free alkaloids differ only slightly[14,20,21]. The torsional angle O–C–C–N of −78° in the free cinchonidine[20] has changed to 8.3 in the complex **13** and from −76.1 in the free cinchonine[21] to −10.0 in **14** as a result of complexation. The Ru–O- and Ru–N-bond lengths in **14** [1.977(7) and 2.180(2) Å] are longer than in a comparable bis(chelate) copper(II) complex of the 1,2-aminoalcoholate of l-ephedrine (1.88 and 2.10 Å)[22]. In the Sharpless complex of OsO_4 with (dimethylcarbamoyl)dihydroquinidine as monodentate N-donor an Os–N bond length of 2.49 Å was determined[8].

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Experimental

The reactions were carried out under dry argon. $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)Cl$[11], $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$[23], $[\eta^5\text{-}C_5Me_5)RhCl_2]_2$[23], $(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$[24] and $ClAuSMe_2$[12] were prepared by reported methods. The chinchona alkaloids were used as supplied (Aldrich). $AgBF_4$ was dried for 2 d in vacuo before use. – NMR: Jeol GSX 270 Q and Jeol EX 400 spectrometers. Selected ^{1}H-NMR signals were assigned as described in ref.[14]. For data denoted by asterisk: Distinct signals were not observed; assignment may be reversed. – IR: Nicolet 5 2DX FT-IR spectrophotometer.

Table 1. Crystal data and data collection of **14**

Empirical formula	$C_{29}H_{35}ClN_2ORu$
Formula weight	1128.22
Crystal size	0.4 x 0.3 x 0.3 mm
Crystal color and habit	red Cube
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 11.087(6) Å
	b = 17.616(11) Å
	c = 26.321(14) Å
Volume	5140.7(51) Å^3
Z	8
Density (calculated)	1.458 Mg/m^3
Absorption coefficient	0.738 mm^{-1}
F(000)	2336
Diffractometer used	Syntex R3
Radiation and wavelength	MoKα with λ=0.71073 Å
Scan type	ω
2θ range for data collection	3.10 to 43.08°
Index ranges	+h, +k, ±l
Reflections collected	6715
Independent reflections	5943 (R_{int} = 0.0407)
Solution	Patterson
Refinement method	Full-matrix Least-Squares on F^2
Hydrogen atoms	riding model, fixed isotropic U
Weighting scheme	$w^{-1}=\sigma^2Fo^2+(0.0426P)^2+0.0000P$
	where $P=(Fo^2+2Fc^2)/3$
Final R indices [F>4σ(F)]	R1 = 0.0517 , wR2 = 0.0946
R indices (all data)	R1 = 0.0871 , wR2 = 0.1096
Goodness-of-Fit on F^2	1.004
Largest difference peak	0.298 eÅ^{-3}
Largest difference hole	-0.289 eÅ^{-3}
Programs used	SHELXTL PLUS 4.11/V
	SHELXL (Sheldrick 1993)

(Carbonyl)(η^5-cyclopentadienyl)(N-quinine)(triphenylphosphane)ruthenium Tetrafluoroborate (**1**): To a solution of $AgBF_4$ (29 mg, 0.15 mmol) in CH_2Cl_2 (5 ml) was added $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)Cl$ (65 mg, 0.13 mmol). The mixture was stirred at room temp. with exclusion of light for 1 h. AgCl was centrifuged off and to the clear, orange solution was added a solution of quinine (52 mg, 0.16 mmol) in CH_2Cl_2. After stirring for 1 h the solvent was removed in vacuo and the yellow solid was washed twice with diethyl ether and dried in vacuo. Yield 92 mg (76%), mp 129°C (dec.). – ^{1}H NMR (CD_3CN, 270 MHz): δ = 5.50/5.42 (6.4 Hz, 9-H), 3.04 (8-H)*, 3.04 (6-H_a)*, 3.45 (6-H_b)*, 3.26 (2-H_a)*, 2.67 (2-H_b)*, 3.92/3.91 (s, 3 H, OCH_3), 5.37/5.16 (s, 5 H, C_5Me_5), 6.98–7.56 [m, 15 H, $(C_6H_5)_3P$]. – ^{31}P NMR (CD_3CN, 109.4 MHz): δ = 49.5/48.9 (88:12). – $C_{44}H_{44}BF_4N_2O_3PRu \cdot 3H_2O$ (921.7): calcd. C 57.34, H 5.47, N 3.04; found C 56.95, H 5.23, N 3.13.

(Carbonyl)(η^5-cyclopentadienyl)(N-cinchonidine)(triphenylphosphane)ruthenium Tetrafluoroborate (**2**): Compound **2** was prepared as described for **1** by using $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)Cl$ (118 mg,

0.24 mmol), $AgBF_4$ (49 mg, 0.25 mmol), and cinchonidine (59 mg, 0.24 mmol). Orange yellow powder, yield 184 mg (87%), mp 134 °C (dec.). – ^1H NMR (CD_3CN, 270 MHz): δ = 3.08 (8-H)*, 2.61 (6-H_a)*, 2.61 (6-H_b)*, 3.50 (2-H_a)*, 3.08 (2-H_b)*, 5.14 (OH), 5.21/5.27 (s, 5 H, C_5Me_5), 7.63–6.97 [m, 15 H, $(C_6H_5)_3P$]. – ^{31}P NMR ($CDCl_3$, 109.4 MHz): δ = 49.4/50.2 (9 : 1). – $C_{43}H_{42}BF_4N_2O_2PRu$ · 1.5 H_2O (864.7): calcd. (59.73, H 5.29, N 3.24; found C 59.75, H 4.97, N 3.15.

(Carbonyl)(η⁵-cyclopentadienyl)(N-quinidine)(triphenylphosphane)ruthenium Tetrafluoroborate (**3**): Compound **3** was prepared as described for **1** by using $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)Cl$ (98 mg, 0.20 mmol), $AgBF_4$ (43 mg, 0.22 mmol), and quinidine (72 mg, 0.22 mmol). Yellow powder, yield 150 mg (85%), mp 135 °C (dec.). – ^1H NMR ([D$_6$]acetone, 270 MHz): δ = 5.67 (5.2 Hz, 9-H)*, 3.20 (8-H)*, 2.28 (6-H_a)*, 2.80 (6-H_b)*, 3.45 (2-H_a)*, 2.98 (2-H_b)*, 3.93/3.97 (s, 3 H, OCH_3), 5.60/5.61 (s, 5 H, C_5Me_5), 7.14–7.66 (m, 15 H, $(C_6H_5)_3P$). – ^{31}P NMR ([D$_6$]acetone, 109.4 MHz): δ = 50.4/51.7 (82 : 18). – $C_{44}H_{44}BF_4N_2O_3PRu$ · H_2O (885.7): calcd. C 59.66, H 5.23, N 3.16; found C 59.55, H 5.28, N 3.19.

(Chloro)(N-quinine)gold(I) (**4**): To a solution of $ClAuSMe_2$ (74 mg, 0.25 mmol) in CH_2Cl_2 (5 ml) a solution of quinine (97 mg, 0.30 mol) in CH_2Cl_2 was added. After stirring for 2 h at room temp. from the clear colorless solution CH_2Cl_2 was removed in vacuo. The solid is washed twice with diethyl ether and dried in vacuo to afford a grey white powder which turned violet upon exposure to light. Yield 111 mg (80%), mp 138 °C (dec.). – ^1H NMR ([D$_6$]acetone): δ = 5.50 (3.7 Hz, 9-H), 4.02 (8-H), 3.53–3.62 (6-H_a)*, 4.38 (6-H_a), 2.68 (2-H_a), 3.53–3.62 (2-H_b)*, 6.78 (OH), 4.00 (s, 3 H, OCH_3). – $C_{20}H_{24}AuClN_2O_2$ (556.8): calcd. C 43.14, H 4.38, N 5.03; found C 42.71, H 4.40, N 4.83.

(Quinine)(η⁵-C_5H_5)$IrCl_2$ (**5**): To a solution of $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (159 mg, 0.20 mmol) in CH_2Cl_2 (5 ml) was added a solution of quinine (265 mg, 0.80 mmol) in CH_2Cl_2. After stirring of the reaction mixture for 1 h at room temp. the solvent was removed in vacuo from the clear orange solution. The light orange solid was washed twice with diethyl ether and dried in vacuo. Yield 202 mg (70%), mp 169 °C (dec.). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.19/6.12 (9-H), 3.94/3.28 (8-H), 1.06/0.52 (7-H), 2.53 (6-H_a)*, 3.28 (6-H_b)*, 4.45/4.30 (2-H_a), 3.14/2.85 (2-H_b), 5.88/5.90 (NH), 3.83/3.66 (s, 3 H, OCH_3), 1.36/1.61 (s, 5 H, C_5Me_5), diastereoisomeric ratio 65 : 35. – $C_{30}H_{39}Cl_2IrN_2O_2$ (722.8): calcd. C 49.86, H 5.44, N 3.88; found C 49.23, H 5.54, N 3.80.

(Cinchonidine)(η⁵-C_5Me_5)$IrCl_2$ · H_2O (**6**): Compound **6** was prepared as described for **5** by using $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (51 mg, 0.06 mmol) and cinchonidine (41 mg, 0.14 mmol). Yield 51 mg (60%), mp 172 °C (dec.). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.22 (9-H)*, 3.93/3.39 (8-H), 1.26/0.39 (7-H), 2.52/1.99 (6-H_a), 3.21 (6-H_b)*, 4.43/4.26 (2-H_a), 2.94 (2-H_b)*, 6.00 (NH)*, 1.38/1.62 (s, 5 H, C_5Me_5), diastereoisomeric ratio 55 : 45. – $C_{29}H_{37}Cl_2IrN_2O_2$ · H_2O (710.8): calcd. C 49.01, H 5.53, N 3.94; found C 49.21, H 6.07, N 4.69.

(Cinchonine)(η⁵-C_5Me_5)$IrCl_2$ · H_2O (**7**): Compound **7** was prepared as described for **5** by using $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (55 mg, 0.07 mmol) and cinchonine (41 mg, 0.14 mmol). Yield 95 mg (68%), mp 128 °C (dec.). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.48 (9-H)*, 4.15/4.01 (8-H), 0.87/0.60 (7-H), 3.32 (6-H_a)*, 3.37 (6-H_b)*, 4.77/4.33 (2-H_a), 3.03 (2-H_b)*, 6.06 (NH)*, 1.42/1.63 (s, 5 H, C_5Me_5), diastereoisomeric ratio 57 : 43. – $C_{29}H_{37}Cl_2IrN_2O_2$ · 4 H_2O (764.8): calcd. C 45.54, H 5.93, N 3.66; found C 45.35, H 2.54, N 3.64.

(Cinchonidine)(η⁵-C_5Me_5)$RhCl_2$ · 0.5 H_2O (**8**): To a solution of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (37.3 mg, 0.06 mmol) in CH_2Cl_2 was added a solution of cinchonidine (70.6 mg, 0.24 mmol) in CH_2Cl_2. The mixture was stirred for 1.5 h at room temp. during which time it turned light red. The solution was then concentrated in vacuo and the red solid was stirred for 15 h with diethyl ether. The ether phase was decanted and the light orange powder was dried in vacuo. Yield 46 (63%), mp 201 °C (dec.). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.13 (9-H)*, 3.34 (8-H)*, 1.22/0.26 (7-H), 2.37/2.30 (6-H_a), 3.20/3.11 (6-H_b), 3.89/4.20 (2-H_a), 2.92 (2-H_b)*, 5.79 (NH)*, 1.55/1.63 (s, 5 H, C_5Me_5), diastereoisomeric ratio 61 : 39. – $C_{29}H_{37}Cl_2N_2ORh$ · 0.5 H_2O (612.4): calcd. C 56.87, H 6.25, N 4.57; found C 56.50, H 6.14, N 4.65.

(η⁶-p-Cymene)(quinine)$RuCl_2$ (**9**): Compound **9** was obtained as described for **5** by using $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (155 mg, 0.25 mmol) and quinine (239 mg, 0.73 mmol). Dark red powder. Yield 240 mg (76%), mp 115 °C (dec.). – ^1H NMR ($CDCl_3$, 270 MHz): δ = 6.28/6.20 (9-H), 3.75/2.95 (8-H), 1.48/0.70 (7-H), 2.58/2.30 (6-H_a), 3.62/2.95 (6-H_b), 4.23/4.19 (2-H_a), 3.62/2.95 (2-H_b), 5.67 (NH)*, 3.75/3.71 (s, 3 H, OCH_3), 1.39 and 1.47/1.39 and 1.41 [d, J = 7 Hz, 6 H, $CH(CH_3)_2$], 1.82/2.36 (s, 3 H, $ArCH_3$), 3.03/3.07 [sept, 1 H, $CH(CH_3)_2$], 5.65–5.04 (m, 4 H, C_6H_4), diastereoisomeric ratio 83 : 17. – $C_{30}H_{38}Cl_2N_2O_2Ru$ (630.6): calcd. C 57.14, H 6.07, N 4.44; found C 57.47, H 6.53, N 4.94.

(Cinchonidine)(η⁶-p-cymene)$RuCl_2$ · H_2O (**10**): Compound **10** was prepared as described for **5** by using $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (74.2 mg, 0.12 mmol) and cinchonidine (71.3 mg, 0.24 mmol). Dark red solid. Yield 105 mg (75%), mp 126 °C (dec.). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.35/5.62 (4.4 Hz, 9-H), 3.75 (8-H)*, 0.67/0.11 (7-H), 3.25–3.01 (6-H_a), 3.72/3.57 (6-H_b), 4.41/4.20 (2-H_a), 3.25–3.01 (2-H_b), 1.20 and 1.25/1.27 and 1.35 [d, J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.24/1.78 (s, 3 H, $ArCH_3$), 2.88/3.06 [sept, 1 H, $CH(CH_3)_2$], 5.64–4.89 (m, 4 H, C_6H_4), diastereoisomeric ratio 55 : 45. – $C_{29}H_{36}Cl_2N_2ORu$ · H_2O (618.6): calcd. C 56.31, H 6.19, N 4.53; found C 56.17, H 6.45, N 4.61.

(Cinchonine)(η⁶-p-cymene)$RuCl_2$ · 1.5 H_2O (**11**): Compound **11** was prepared as described for **5** by using $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (58.7 mg, 0.09 mmol) and cinchonine (56.4 mg, 0.19 mmol). Dark red solid, yield 107 mg (70%), 119 °C. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.50/5.84 (9.6 Hz, 9-H), 3.92/3.82 (8-H), 0.80/0.27 (7-H), 3.46–3.32 (6-H_a), 3.20/2.85 (6-H_b)*, 4.19/3.61 (2-H_a), 3.20/2.85 (2-H_b)*, 1.15 and 1.19/1.29 and 1.37 [d, J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.26/2.28 (s, 3 H, $ArCH_3$), 2.95–3.62 [m, 1 H, $CH(CH_3)_2$], 5.02–5.48 (m, 4 H, C_6H_4), diastereoisomeric ratio 63 : 37. – $C_{29}H_{36}Cl_2N_2ORu$ · 1.5 H_2O (627.6): calcd. C 55.50, H 6.26, N 4.46; found 5.51, H 6.27, N 4.65.

(N-Cinchonidine)(η⁶-p-cymene)$RuCl_2$ (**12**): To a solution of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (79.6 mg, 0.13 mmol) in CH_2Cl_2 (5 ml) was added cinchonidine (79.8 mg, 0.27 mmol). The mixture was stirred for 2 h. After removal of the solvent in vacuo the red solid was stirred with water for 2 h. The orange solid was thoroughly washed with ether. Yield 34 mg (23%), 118 °C (dec.). – ^1H NMR ($CDCl_3$): δ = 5.87 (9-H), 4.02 (8-H), 1.31 (7-H), 3.37 (6-H_a), 3.98 (6-H_b), 3.50 (2-H_a), 3.63 (2-H_b), 5.79 (OH), 1.34 and 1.40 [d, J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.31 (s, 3 H, $ArCH_3$), 3.05 [sept, 1 H, $CH(CH_3)_2$], 4.89, 5.18, 5.30, 5.32 (d, J = 6 Hz, 4 H, C_6H_4). – $C_{29}H_{36}Cl_2N_2ORu$ (600.6): calcd. C 58.00, H 6.04, N 4.66; found C 58.49, H 6.50, N 5.00.

(N,O-Cinchonidine – H^+)(η⁶-p-cymene)RuCl (**13**): To a solution of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ in methanol (5 ml) were added cinchonidine (47.9 mg, 0.16 mmol) and a solution of NaOMe in methanol (0.16 mmol NaOMe). After stirring for 1 h the solvent was evaporated in vacuo from the clear, orange solution. The solid was stirred for 10 min with CH_2Cl_2 · NaCl was centrifuged off. The CH_2Cl_2

solution was evaporated to dryness and the orange solid was washed with pentane and dried in vacuo. Yield 64 mg (68%) mp. 116°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 6.10 (9-H)*, 3.50/4.30 (8-H)*, 1.20/1.30 (7-H), 2.40/2.54 (6-H_a), 3.52/4.31 (6-H_b)*, 3.52/4.31 (2-H_a)*, 3.20/3.28 (2-H_b), 6.10 (NH), 1.40 and 1.41/1.32 and 1.44 [d, J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.27/2.23 (s, 3 H, $ArCH_3$), 2.94 [m,1 H, $CH(CH_3)_2$], 4.81–5.32 (m, 4 H, C_6H_4), diastereoisomeric ratio 57:43. – $C_{29}H_{35}ClN_2ORu \cdot H_2O$ (582.2): calcd. C 59.83, H 6.41, N 4.81; found C 59.44, H 6.51, N 4.86.

(N,O-Cinchonine – H^+)(η^6-p-cymene)RuCl (**14**): To a solution of **11a**, **b** (40 mg, 0.06 mmol) in methanol (5 ml) NEt_3 (6 µl, 0.2 mmol) was added. The red solution was stirred for 30 min at room temp. and evaporated to dryness. The solid was four times extracted with CH_2Cl_2 (3 ml). The solvent was evaporated in vacuo from the combined extracts to give a red powder. Yield 27 mg (80%), mp. 104°C (dec.). – $C_{29}H_{35}ClN_2ORu \cdot 2\ H_2O$ (600.2): calcd. C 58.04, H 6.55, N 4.67; found C 58.30, H 6.40, N 4.88.

☆ Dedicated to Dr. *Janina Altman* on the occasion of her 65th birthday.

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