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Journal of Organometallic Chemistry 523 (1996) 179–185

Journal of Organometallic Chemistry

Optically active transition metal complexes 110 [1] New rhodium(I) complexes with 2-pyridinecarboxamido ligands

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Received 12 February 1996

Abstract

The reaction of $[Rh(cod)Cl]_2$ with the 2-pyridinecarboxamides **1a–e** in the presence of base affords the new complexes **2a–e** in which the amides act as bidentate ligands coordinating via pyridine-N and the deprotonated amide-N. The structure of **2a** was established by X-ray structure analysis: $C_{14}H_{17}N_2ORh$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.034(4)$ Å, $b = 10.146(6)$ Å, $c = 13.165(4)$ Å, $\alpha = 108.09(3)°$, $\beta = 91.93(3)°$, $\gamma = 89.90(4)°$, $Z = 2 \times 2$, $R = 0.039$, $R_w = 0.036$.

Keywords: Rhodium; Amide; Optically active transition metal complexes; 2-Pyridinecarboxamide ligands; X-ray structure analysis; (*S*)-1-Phenylethyl substitution

1. Introduction

Chiral nitrogen ligands continue to play an important role in enantioselective catalysis [2–4]. In particular, the oxazoline ligands, introduced into enantioselective catalysis with transition metal complexes in 1986 [5], proved to be a successful class of compounds. The oxazoline system contains a special form of a carboxamide, namely its iminoester. Surprisingly, up to now carboxamides themselves have not played a major role as ligands in enantioselective catalysis, either in their neutral form or as anions after deprotonation at the amide nitrogen. The present paper deals with 2-pyridinecarboxamides. Although a number of complexes with these ligands has been reported [6–9], there are only few publications that focus on their catalytic application [10,11]. This study describes the preparation and characterization of some (η^4-1,5-cyclooctadiene)(2-pyridinecarboxamido)rhodium(I) complexes [12], including an X-ray analysis of the crystal structure of the parent compound.

2. Synthesis and spectra of complexes 2a–e

The ligands **1a–e** were synthesized by means of common methods for the preparation of carboxamides: **1a** and **1e** by reaction of 2-pyridinecarboxylic acid chloride with ammonia and (*S*)-1-phenylethylamine respectively, **1b** by the reaction of 2-pyridinecarboxylic acid with methylamine and **1c** and **1d** by the mixed anhydride method.

$[Rh(cod)Cl]_2$ reacts with 2-pyridinecarboxamide **1a** and its *N*-substituted derivatives **1b–e** in alkaline CH_2Cl_2–EtOH (NaOH for **1a–d** and KOH for **1e**) to give the neutral, square-planar rhodium(I) complexes **2a–e** (Scheme 1). After removal of an amide proton, the 2-pyridinecarboxamides act as anionic, bidentate *N*,*N*′-ligands. The remaining two coordination sites are occupied by 1,5-cyclooctadiene.

The IR spectra of the free ligands exhibit the characteristic bands of amides and the pyridyl moiety [13]. For the primary amide **1a**, the amide I band appears at about 1670 cm^{-1} and amide II at 1600 (sh). The secondary amides **1b–e** show amide I at almost the same frequency; amide II is found at about 1530 cm^{-1}.

In contrast to complex **2a**, the IR spectra of **2b–e** do not show ν(N–H) bands at 3290–3400 cm^{-1}, indicating the deprotonation of the amide ligands. Owing to the

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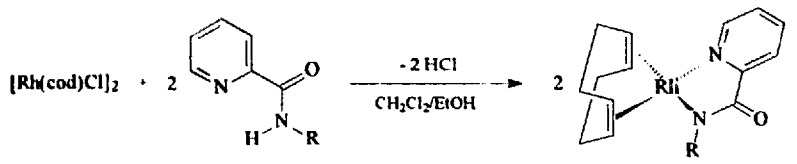
[1] For Part 109 see Ref. [1]. Dedicated to Professor Rainer Dieter Fischer on the occasion of his 60th birthday.

PII S0022-328X(96)06279-1



1a
b
c
d
e

2a R = H
b R = CH_3
c R = $CH(CH_3)_2$
d R = C_6H_5
e R = $CH(CH_3)(C_6H_5)$

Scheme 1.

presence of the 1,5-cyclooctadiene ligand there are a number of peaks of low intensity in the range of 2800–3000 cm^{-1} in all the complexes. The amide I band is shifted to lower frequencies as expected for amide-N coordination. The amide II and III bands are replaced by a medium absorption at about 1340–1380 cm^{-1}, typical for deprotonated amide complexes coordinating via amide-N [9].

The ^1H NMR spectrum of **1a** exhibits two signals for the amide protons at δ 6.63 and 7.92 ppm. In the spectra of the other ligands **1b–e** only one peak is found due to mono substitution of the nitrogen atom. The four pyridine protons result in four multiplets in the range δ 7.3 to 8.6 ppm. They appear in the sequence H^6 (ddd), H^3 (dt), H^4 (td), H^5 (ddd), when going from lower to higher field. The coupling constants are in the normal range ($J_{34} \approx 7.8$ Hz; $J_{35} \approx 1.1$ Hz; $J_{36} \approx 1.1$ Hz; $J_{45} \approx 7.6$ Hz; $J_{46} \approx 1.7$ Hz; $J_{56} \approx 4.6$ Hz).

In the complexes **2a–e** the ^1H NMR signals of the pyridine protons show only small chemical shift differences compared with the free ligands, except H^6 which appears about 1 ppm shifted to higher field. Generally, upon complexation these signals occur at lower field [14], e.g., in rhodium(III) complexes [9,15]. The high field shift in **2a–e** indicates a high electron density in these low valent complexes.

In the spectrum of **2a** there is one signal for the remaining amide proton. In the other spectra no amide proton resonances are found, again evidence for deprotonation.

The 1,5-cyclooctadiene ligand shows two signals for the olefinic protons at about δ 4.3 and 4.0 ppm and two for the methylene protons at about δ 2.5 and 1.9 ppm. Owing to the (*S*)-1-phenylethyl group in complex **2e**, the olefinic signal at lower field is split into two broad signals, because the olefinic protons are diastereotopic. The fact that 1,5-cyclooctadiene appears as four signals in the ^1H NMR spectra proves that it does not rearrange at room temperature. For complex **2b** there is almost no difference between the spectra recorded at room temperature and 170°C. In the literature there are examples for both rearranging [16] and for non-rearranging 1,5-cyclooctadiene complexes [17].

Table 1
Summary of crystal data, data collection and structure refinement [a] for complex **2a**

Crystal parameters	
Elemental formula	$C_{14}H_{17}N_2ORh$
M	332.24
Crystal system	triclinic
Space group (no.)	$P\bar{1}$
a (Å)	10.034(4)
b (Å)	10.146(6)
c (Å)	13.165(4)
α (deg)	108.09(3)
β (deg)	91.93(3)
γ (deg)	89.90(4)
V (Å^3)	1273.2
Z	2×2
D_c (g cm^{-3})	1.73
F(000)	672
μ (mm^{-1})	1.31
Crystal color, shape	dark red, irregular
Crystal size (mm^3)	0.15×0.35×0.40
Data collection	
hkl ranges	0–13, −13–13, −17–17
2θ range (deg)	3.0–54.1
Total no. of unique reflections	5606
No. of observed reflections ($I > 2.5\sigma_I$)	4350
Min., max. transmission factors	0.73, 1.00
Data refinement	
No. of reflections, 2θ range (deg) for empirical absorption correction	7, 9.0–42.0
No. of LS-parameters	326
Largest shift/e.s.d. in final circle	0.03
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.63, 0.47
R [b]	0.039
R_w [c]	0.036

[a] Syntex-Nicolet R3 diffractometer; Mo Kα radiation (λ = 0.71073 Å); 293 K; graphite crystal monochromator, structure solution by Patterson–Fourier methods with SHELXTL PLUS Release 4.11/V programs (SHELXTL PLUS, A program for crystal structure determination, Release 4.11/V, Siemens Analytical X-Ray Instruments, Madison, WI, 1990) on a Micro VAX II computer; position of the H atoms calculated by the option HFIX. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o|w^{1/2}$, $w = 1/\sigma^2(F_o)$.

3. X-ray structure analysis of 2a

A single crystal X-ray structure analysis was carried out for the parent complex **2a**. (Further details of this structure determination have been deposited with the number CSD-404812 at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany.)

Relevant crystallographic data are given in Table 1, atomic coordinates are reported in Table 2 and selected bond distances and angles are listed in Table 3. A view of the structure with the atomic numbering is shown in Fig. 1.

There are four molecules in two almost identical forms in the unit cell (the values for the second molecule are given in parentheses). The 2-pyridinecarboxamide anion is a strictly planar, bidentate ligand. A least squares plane consisting of all non-hydrogen atoms of the ligand (N1, N2, O1, C9–C14) was calculated; no atom deviated more then 0.019 Å (O1) (0.020 Å (C34))

Table 2
Atomic coordinates of **2a**

Atom	x	y	z
Rh1	0.1911	0.4493	0.1282
N1	0.3501	0.5165	0.0692
N2	0.1981	0.6600	0.2203
O1	0.4706	0.7108	0.0713
C1	−0.0119	0.4097	0.1509
C2	0.0638	0.3636	0.2203
C3	0.0940	0.2125	0.2038
C4	0.2180	0.1644	0.1444
C5	0.2508	0.2417	0.0674
C6	0.1627	0.2697	−0.0068
C7	0.0197	0.2211	−0.0254
C8	−0.0743	0.3224	0.0465
C9	0.3802	0.6492	0.1027
C10	0.2919	0.7326	0.1894
C11	0.3070	0.8733	0.2351
C12	0.2228	0.9420	0.3146
C13	0.1287	0.8694	0.3482
C14	0.1189	0.7283	0.3000
Rh2	0.7068	0.5285	0.3812
N3	0.8394	0.4256	0.4469
N4	0.6914	0.3274	0.2722
O2	0.9169	0.2076	0.4365
C21	0.6232	0.6330	0.2784
C22	0.5226	0.6043	0.3382
C23	0.4614	0.7094	0.4313
C24	0.5321	0.7203	0.5370
C25	0.6766	0.6842	0.5283
C26	0.7684	0.7346	0.4716
C27	0.7359	0.8378	0.4141
C28	0.6903	0.7724	0.3002
C29	0.8499	0.2901	0.4047
C30	0.7631	0.2349	0.3048
C31	0.7566	0.0949	0.2488
C32	0.6760	0.0498	0.1584
C33	0.6062	0.1453	0.1244
C34	0.6163	0.2834	0.1823

Table 3
Bond lengths and angles of **2a** [a]

Rh1–N1	2.007(4)	Rh2–N3	2.021(5)
Rh1–N2	2.105(4)	Rh2–N4	2.101(4)
Rh1–C1	2.126(5)	Rh2–C21	2.115(6)
Rh1–C2	2.150(6)	Rh2–C22	2.127(5)
Rh1–C5	2.102(5)	Rh2–C25	2.116(5)
Rh1–C6	2.125(4)	Rh2–C26	2.141(5)
C1–C2	1.359(8)	C21–C22	1.387(8)
C2–C3	1.512(8)	C22–C23	1.501(7)
C3–C4	1.492(8)	C23–C24	1.512(8)
C4–C5	1.506(9)	C24–C25	1.495(7)
C5–C6	1.389(7)	C25–C26	1.397(8)
C6–C7	1.505(7)	C26–C27	1.499(9)
C7–C8	1.504(7)	C27–C28	1.495(7)
N1–C9	1.312(6)	N3–C29	1.318(7)
C9–O1	1.254(6)	C29–O2	1.234(7)
C9–C10	1.506(6)	C29–C30	1.507(6)
C10–C11	1.373(7)	C30–C31	1.383(7)
C11–C12	1.379(7)	C31–C32	1.370(7)
C12–C13	1.364(9)	C32–C33	1.370(8)
C13–C14	1.376(7)	C33–C34	1.373(7)
N2–C14	1.348(6)	N4–C34	1.335(6)
N2–C10	1.345(6)	N4–C30	1.345(7)
N1–Rh1–N2	78.7(1)	N3–Rh2–N4	78.7(2)
N1–Rh1–C1	159.2(2)	N3–Rh2–C21	160.4(2)
N1–Rh1–C2	163.7(2)	N3–Rh2–C22	160.7(2)
N1–Rh1–C5	91.9(2)	N3–Rh2–C25	93.3(2)
N1–Rh1–C6	94.0(2)	N3–Rh2–C26	97.7(2)
N2–Rh1–C1	97.9(2)	N4–Rh2–C21	96.7(2)
N2–Rh1–C2	101.6(2)	N4–Rh2–C22	97.4(2)
N2–Rh1–C5	158.9(2)	N4–Rh2–C25	155.0(2)
N2–Rh1–C6	159.5(2)	N4–Rh2–C26	165.4(2)
C1–Rh1–C2	37.1(2)	C21–Rh2–C22	38.2(2)
C1–Rh1–C5	97.4(2)	C21–Rh2–C25	98.0(2)
C1–Rh1–C6	82.2(2)	C21–Rh2–C26	81.9(2)
C2–Rh1–C5	82.1(2)	C22–Rh2–C25	82.3(2)
C2–Rh1–C6	90.8(2)	C22–Rh2–C26	90.5(2)
C5–Rh1–C6	38.4(2)	C25–Rh2–C26	38.3(2)
C8–C1–C2	126.4(5)	C28–C21–C22	124.9(4)
C1–C2–C3	123.9(4)	C21–C22–C23	124.6(5)
C2–C3–C4	113.6(5)	C22–C23–C24	113.0(5)
C3–C4–C5	113.9(5)	C23–C24–C25	114.2(4)
C4–C5–C6	126.0(5)	C24–C25–C26	125.3(5)
C5–C6–C7	123.6(5)	C25–C26–C27	124.3(5)
C6–C7–C8	113.2(4)	C26–C27–C28	113.4(4)
C7–C8–C1	114.0(4)	C27–C28–C21	114.2(5)
Rh1–N1–C9	119.0(3)	Rh2–N3–C29	119.3(3)
N1–C9–O1	128.0(4)	N3–C29–O2	129.4(4)
N1–C9–C10	113.3(4)	N3–C29–C30	111.9(5)
C9–C10–N2	115.7(4)	C29–C30–N4	117.2(4)
Rh1–N2–C10	113.0(3)	Rh2–N4–C30	112.4(3)
N2–C10–C11	122.0(4)	N4–C30–C31	121.1(4)
C10–C11–C12	118.8(5)	C30–C31–C32	119.4(5)
C11–C12–C13	119.9(5)	C31–C32–C33	119.0(5)
C12–C13–C14	118.7(5)	C32–C33–C34	119.6(5)
C13–C14–N2	122.2(5)	C33–C34–N4	121.7(5)

[a] Estimated standard deviations are shown in parentheses.

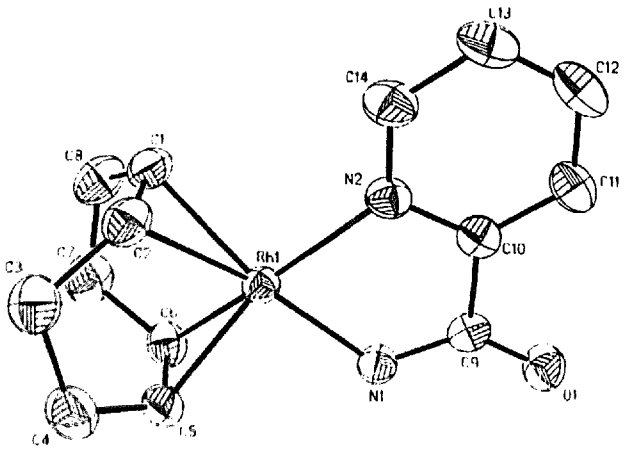


Fig. 1. ORTEP diagram of **2a** showing the labeling scheme used. Ellipsoids are drawn at the 40% probability level; hydrogen atoms have been omitted for clarity

from that plane. The bond lengths are almost the same as in the free ligand [18], the largest difference is 0.025 Å (0.036 Å) for C11–C12 (C31–C32). In other transition metal complexes containing deprotonated 2-pyridinecarboxamide as a ligand, there are significant differences in the bond lengths between free and coordinated amide [19,20].

The rhodium–amide–N bond is markedly shorter than the rhodium–pyridine–N bond (2.007 Å (2.021 Å) and 2.105 Å (2.101 Å) respectively). This is also observed in other complexes containing 2-pyridinecarboxamides in their deprotonated form [15]. The distances between rhodium and the double bond centers are 1.997 and 2.022 Å (2.005 and 2.010 Å), at the short end of the range found in heavy-metal complexes with 1,5-cyclooctadiene [21].

The coordination geometry about the rhodium atom is planar. A least squares plane, consisting of Rh1, N1, N2, M1 and M2, where M1 and M2 are the midpoints of C1–C2 and C5–C6 respectively, was calculated and the atoms showed deviations of 0.010–0.020 Å (0.029–0.049 Å) from that plane. The N1–Rh1–N2 angle of 78.7(1)° (78.7(2)°) departs markedly from square-planar geometry. A similar angle (78.9°) was found in (η^4-1,5-cyclooctadiene)(2-pyrrolcarbald-(*S*)-1-phenylethyliminato)rhodium(I) [22]. The M1–Rh1–M2 angle of 88.0° agrees well with the corresponding angles in other Rh(cod) complexes [23–25].

The 1,5-cyclooctadiene ligand adopts its customary 'tub' conformation. The double bonds, C1–C2 and C5–C6, have lengths of 1.359(8) Å (1.387(8) Å) and 1.389(7) Å (1.397(8) Å) respectively, compared with the distance of 1.34 Å of an uncoordinated olefin [26]. A least squares plane was calculated for the four olefinic carbons, showing deviations of 0.052–0.053 Å (0.057–0.058 Å) for these atoms. The angle between this plane and the coordination plane is 89.18° (92.20°). Carbon–carbon single bond distances range from 1.492(8) to 1.512(8) Å (1.495(7) to 1.512(8) Å), typical for 1,5-cyclooctadiene bonded to a heavy metal [26].

4. Experimental part

All reactions were carried out under an atmosphere of nitrogen. All solvents were dried and distilled before use, according to standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 and a Bruker ARX 400 spectrometer with TMS as internal reference. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 PC FT-IR and a Beckman Acculab 3 spectrometer. Mass spectra were determined on a Finnigan MAT 95 (FD) and on a Finnigan MAT 112 S (EI) mass spectrometer. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. C,H,N analyses were performed by the microanalytical laboratory of the University of Regensburg.

4.1. Synthesis of the ligands

4.1.1. 2-Pyridinecarboxamide **1a**

2-Pyridinecarboxylic acid (5 g, 40 mmol) was suspended in 50 ml (690 mmol) of freshly distilled thionyl chloride and the resulting mixture was stirred for 40 h at ambient temperature. During this time the green suspension turned to a red solution. The solution was poured into 150 ml of pentane and stirred for 30 min. Then the solvent was poured off and the residue was dried. The pink powder (2.8 g) was suspended in concentrated aqueous ammonia and the mixture was stirred for about 1 h. The solution was extracted three times with chloroform, then the solvent was evaporated. The residue was recrystallized from ethanol to give **1a** as white crystals. Yield: 1.3 g (27%), m.p. 105–106°C (Ref. [27]: 106.3–106.8°C). IR (KBr, cm^{-1}): 3419m, 3174br (N–H), 1664s (C=O, amide I), 1604sh (amide II). ^{1}H NMR ($CDCl_3$): δ 8.57–8.60 (m, 1H, py-H^6), 8.20–8.24 (m, 1H, py-H^3), 7.92 (broad, 1H, NH), 7.83–7.89 (m, 1H, py-H^4), 7.42–7.48 (m, 1H, py-H^5), 6.63 (broad, 1H, NH). Anal. Found: C, 58.96; H, 4.95; N, 22.79. $C_6H_6N_2O$ (122.14). Calc.: C, 59.00; H, 4.96; N, 22.94%. MS (EI): 122 *m/e* ($M^{+\cdot}$).

4.1.2. N-Methylpyridine-2-carboxamide **1b**

A mixture of 2.7 ml (20 mmol) of ethyl 2-pyridinecarboxylate and 2.6 ml (30 mmol) of 40% aqueous methylamine was refluxed for 18 h. The excess of methylamine was evaporated at reduced pressure. The resulting red liquid was distilled at 0.05 Torr/b.p. 41–43°C yielding 1.8 g (68%) of a colorless liquid. IR

(film, cm^{-1}): 3392br (N–H), 1675/1660s (amide I), 1530s (amide II), 1280 (amide III). ^1H NMR ($CDCl_3$): δ 8.52–8.55 (m, 1H, py-H^6), 8.18–8.22 (m, 1H, py-H^3), 8.08 (br, 1H, NH), 7.80–7.87 (m, 1H, py-H^4), 7.39–7.44 (m, 1H, py-H^5), 3.04 (d, $J(CH_3–NH) = 5.1$ Hz, 3H, CH_3). Anal. Found: C, 61.20; H, 5.99; N, 20.60. $C_7H_8N_2O$ (136.17). Calc.: C, 61.74; H, 5.93; N, 20.58%. MS (EI): 136 *m/e* ($M^{+\cdot}$).

4.1.3. N-(2-Propyl)-2-pyridinecarboxamide 1c

2-Pyridinecarboxylic acid (3.1 g, 25 mmol) was dissolved in THF (100 ml) and cooled to −15°C. Triethylamine was added (3.5 ml, 25 mmol), followed by ethyl chloroformate (2.4 ml, 25 mmol). The suspension was stirred for 30 min, then 2-aminopropane (2.2 ml, 25 mmol) was added and stirring was continued for 1 h. The hydrochloride was filtered off and washed with THF. The filtrate was combined with the washing liquids and evaporated. The residue was dissolved in boiling petroleum ether 50–70 and crystallized at −30°C to give the product **1c** as a white crystalline mass. Yield: 2.1 g (52%), m.p. 35°C. IR (KBr, cm^{-1}): 3382w (N–H), 1669s (amide I), 1524s (amide II). ^1H NMR ($CDCl_3$): δ 8.53–8.56 (m, 1H, py-H^6), 8.18–8.22 (m, 1H, py-H^3), 7.81–7.87 (m, 2H, py-H^4, NH), 7.38–7.44 (m, 1H, py-H^5), 4.22–4.35 (m; 1H, CH), 1.29 (d, $J(CH–CH_3) = 6.6$ Hz, 6H, CH_3). Anal. Found: C, 65.47; H, 7.38; N, 16.84. $C_9H_{12}N_2O$ (164.23). Calc.: C, 65.82; H, 7.38; N, 17.06%. MS (EI): 164 *m/e* ($M^{+\cdot}$).

4.1.4. N-Phenyl-2-pyridinecarboxamide 1d

1d was prepared similarly to **1c**. The amine component was freshly distilled aniline (2.3 ml, 25 mmol). After evaporating the solvent the residue was dissolved in methanol and water was added until crystallization was complete. Recrystallization from petroleum ether 50–70 afforded the anilide **1d** as white needles. Yield: 4.0 g (80%), m.p. 75°C (Ref. [28]: 76°C). IR (KBr, cm^{-1}): 3336m (N–H), 1671s (amide I), 1530s (amide II), 1236w (amide III). ^1H NMR ($CDCl_3$): δ 10.03 (br, 1H, NH), 8.59–8.62 (m, 1H, py-H^6), 8.28–8.32 (m, 1H, py-H^3), 7.85–7.92 (m, 1H, py-H^4), 7.76–7.81 (m, 2H, *o*-phenyl-H), 7.34–7.49 (m, 3H, py-H^5, *m*-phenyl-H), 7.11–7.18 (m, 1H, *p*-phenyl-H). ^{13}C NMR ($CDCl_3$): δ 162.00 (carbonyl-C), 149.98 (py-C^2), 147.98 (py-C^6), 137.84, 137.62 (phenyl-C^1, py-C^4), 129.07 (phenyl-C^3), 126.37 (py-C^5); 124.30 (py-C^3), 122.41 (phenyl-C^4), 119.75 (phenyl-C^2). Anal. Found: C, 72.66; H, 4.96; N, 14.15. $C_{12}H_{10}N_2O$ (198.23). Calc.: C, 72.70; H, 5.10; N, 14.14%. MS (EI): 198 *m/e* ($M^{+\cdot}$).

4.1.5. N-[(S)-1-Phenylethyl]-2-pyridinecarboxamide 1e

1e was prepared by a method described previously [29]. Yield: 3.90 g (57%), m.p. 53–54°C (Ref. [29]: 55°C). IR (KBr, cm^{-1}): 3374m, 3360m (N–H), 1660s, 1652s (amide I), 1513s (amide II). ^1H NMR ($CDCl_3$): δ 8.51–8.54 (m, 1H, py-H^6), 8.34 (br, 1H, NH), 8.17–8.21 (m, 1H, py-H^3), 7.78–7.84 (m, 1H, py-H^4), 7.22–7.43 (m, 6H, py-H^5, phenyl-H), 5.33 (m, 1H, CH), 1.62 (d, $J(CH_3–CH) = 7.7$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 163.40 (carbonyl-C), 150.11 (py-C^2), 148.03 (py-C^6), 143.39 (phenyl-C^1), 137.28 (py-C^4), 128.67 (phenyl-C^3), 127.30, 126.07 (py-C^3, -C^5), 126.23 (phenyl-C^2), 122.29 (phenyl-C^4), 48.86 ($CH(CH_3)(C_6H_5)$), 22.08 (CH_3). Anal. Found: C, 74.16; H, 6.29; N, 12.38. $C_{14}H_{14}N_2O$ (226.30). Calc.: C, 74.30; H, 6.25; N, 12.38%. MS (EI): 226 *m/e* ($M^{+\cdot}$).

4.2. Synthesis of the complexes

4.2.1. General procedure for complexes 2a–e

Into a CH_2Cl_2 solution (10 ml) containing the ligand (123.3 mg, 1.01 mmol) and $[Rh(cod)Cl]_2$ (249.0 mg, 0.50 mmol) was added an equimolar amount of NaOH (40.4 mg, 1.01 mmol) in 5 ml of ethanol (for complexes **2a–d**) or the double amount of KOH (113.3 mg, 2.02 mmol) in 5 ml of ethanol (for complex **2e**). The mixture was stirred for 10 min at room temperature, then the solvent was evaporated. The resulting yellow solid was dissolved in 2–3 ml of CH_2Cl_2 and filtered through celite. The solvent was removed and the yellow solid was dissolved in toluene (complexes **2a–d**) or THF (complex **2e**). Pentane was added to form the upper layer. Refrigeration afforded the compounds as orange microcrystalline powders. Crystals suitable for X-ray diffraction studies of **2a** were obtained by the slow evaporation of a CH_2Cl_2 solution in the open air.

4.2.2. η^4-1,5-Cyclooctadiene(2-pyridinecarboxamidato)rhodium(I) 2a

Yield: 206 mg (62%), m.p. 200°C (decomp.). IR (KBr, cm^{-1}): 3265w (N–H), 1592s (C=O), 1373m (C–N). ^1H NMR ($CDCl_3$): δ 8.02–8.04 (m, 1H, py-H^3), 7.89–7.94 (m, 1H, py-H^4), 7.65–7.67 (m, 1H, py-H^6), 7.39–7.42 (m, 1H, py-H^5), 5.13 (br, 1H, NH), 4.35 (s, 2H, =CH (cod)), 4.01 (s, 2H, =CH (cod)), 2.47–2.52 (m, 4H, CH_2 (cod)), 1.96–1.99 (m, 4H, CH_2 (cod)). ^{13}C NMR ($CDCl_3$): δ 174.07 (C=O), 156.30 (py-C^2), 145.79 (py-C^6), 139.42 (py-C^4), 126.25 (py-C^5), 124.98 (py-C^3), 81.43 (d, $J(^{13}C–^{103}Rh) = 12.7$ Hz, =CH (cod)), 78.63 (d, $J(^{13}C–^{103}Rh) = 11.9$ Hz, =CH (cod)), 30.99 (CH_2 (cod)), 30.51 (CH_2 (cod)). Anal. Found: C, 50.87; H, 5.19; N, 8.62. $C_{14}H_{17}N_2ORh$ (332.24). Calc.: C, 50.61; H, 5.17; N, 8.43%. MS (FD, MeOH): 332 *m/e* ($M^{+\cdot}$).

4.2.3. η^4-1,5-Cyclooctadiene(N-methyl-2-pyridinecarboxamidato)rhodium(I) 2b

Yield: 197 mg (57%), m.p. 195°C (decomp.). IR (KBr, cm^{-1}): 1591s (C=O), 1367m (C–N). ^1H NMR

($CDCl_3$): δ 8.02–8.05 (m, 1H, py-H^3), 7.85–7.91 (m, 1H, py-H^4), 7.57–7.59 (m, 1H, py-H^6), 7.31–7.38 (m, 1H, py-H^5), 4.39–4.40 (m, 2H, =CH (cod)), 3.97–3.98 (m, 2H, =CH (cod)), 2.70 (s, 3H, CH_3), 2.46–2.56 (m, 4H, CH_2 (cod)), 1.92–2.06 (m, 4H, CH_2 (cod)). Anal. Found: C, 51.70; H, 5.64; N, 8.14. $C_{15}H_{19}N_2ORh$ (346.27). Calc.: C, 52.03; H, 5.54; N, 8.09%. MS (FD, MeOH): 346 *m/e* ($M^{+\cdot}$).

4.2.4. *η⁴-1,5-Cyclooctadiene[N-(2-propyl)-2-pyridinecarboxamidato]rhodium(I)* **2c**

Yield: 251 mg (67%), m.p. 230°C (decomp.). IR (KBr, cm^{-1}): 1587s (C=O), 1341m (C–N). ^1H NMR ($CDCl_3$): δ 7.97–8.01 (m, 1H, py-H^3), 7.82–7.89 (m, 1H, py-H^4), 7.53–7.55 (m, 1H, py-H^6), 7.29–7.34 (m, 1H, py-H^5), 4.21–4.22 (m, 2H, =CH (cod)), 3.94–3.95 (m, 2H, =CH (cod)), 2.45–2.74 (m, 5H, C*H*(CH_3)$_2$, CH_2 (cod)), 1.92–2.04 (m, 4H, CH_2 (cod)), 1.45 (d, J(CH_3–CH) = 7.5 Hz, 6H, CH_3). Anal. Found: C, 54.45; H, 6.24; N, 7.60. $C_{17}H_{23}N_2ORh$ (374.33). Calc.: C, 54.54; H, 6.21; N, 7.49%. MS (FD, MeOH): 374 *m/e* ($M^{+\cdot}$).

4.2.5. *η⁴-1,5-Cyclooctadiene(N-phenyl-2-pyridinecarboxamidato)rhodium(I)* **2d**

Yield: 237 mg (58%), m.p. 235°C (decomp.). IR (KBr, cm^{-1}): 1594s (C=O), 1368m (C–N). ^1H NMR ($CDCl_3$): δ 8.09–8.13 (m, 1H, py-H^3), 7.87–7.94 (m, 1H, py-H^4), 7.63–7.65 (m, 1H, py-H^6), 7.36–7.42 (m, 1H, py-H^5), 7.01–7.34 (m, 5H, phenyl-H), 3.98–4.00 (m, 2H, =CH (cod)), 3.84–3.87 (m, 2H, =CH (cod)), 2.35–2.60 (m, 4H, CH_2 (cod)), 1.79–1.98 (m, 4H, CH_2 (cod)). ^{13}C NMR ($CDCl_3$): δ 171.24 (d, J(^{13}C–^{103}Rh) = 0.9 Hz, C=O), 156.92 (py-C^2), 147.09 (d, J(^{13}C–^{103}Rh) = 1.1 Hz, phenyl-C1), 145.00 (py-C^6), 139.46 (py-C^4), 128.39, 126.70 (phenyl-C^2, -C^3), 126.15, 125.56, 124.30 (py-C^3, -C^5, phenyl-C^4), 85.49 (d, J(^{13}C–^{103}Rh) = 12.7 Hz, =CH (cod)), 77.81 (d, J(^{13}C–^{103}Rh) = 12.2 Hz, =CH (cod)), 30.72 (CH_2 (cod)), 30.37 (CH_2 (cod)). Anal. Found: C, 58.32; H, 5.31; N, 6.68. $C_{20}H_{21}N_2ORh$ (408.36). Calc.: C, 58.82; H, 5.19; N, 6.86%. MS (FD, MeOH): 408 *m/e* ($M^{+\cdot}$).

4.2.6. *η⁴-1,5-Cyclooctadiene[N-[(S)-1-phenylethyl]-2-pyridinecarboxamidato]rhodium(I)* **2e**

Yield: 249 mg (57%), m.p. 230°C (decomp.). IR (KBr, cm^{-1}): 1591s (C=O), 1382m (C–N). ^1H NMR ($CDCl_3$): δ 7.92–7.95 (m, 1H, py-H^3), 7.78–7.84 (m, 1H, py-H^4), 7.50–7.57 (m, 3H, py-H^6, 2 phenyl-H), 7.25–7.33 (m, 3H, py-H^5, 2 phenyl-H), 7.11–7.16 (m, 1H, *p*-phenyl-H), 4.30 (br, 1H, =CH (cod)); 4.18 (br, 1H, =CH (cod)), 3.96–4.02 (m, 3H, =CH(2×), C*H*(CH_3)(C_6H_5)), 2.51–2.58 (m, 4H, CH_2 (cod)), 1.95–1.98 (m, 4H, CH_2 (cod)), 1.79 (d, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.74 (C=O), 157.50 (py-C^2), 145.80 (phenyl-C^1), 144.23 (py-C^6), 139.27 (py-C^4), 127.72, 126.48 (phenyl-C^2, -C^3), 125.67, 125.45, 125.07 (py-C^3, -C^5, phenyl-C^4), 84.90, (d, J(^{13}C–^{103}Rh) = 12.8 Hz, =CH (cod)); 84.35, (d, J(^{13}C–^{103}Rh) = 12.8 Hz, =CH (cod)), 77.84 (d, J(^{13}C–^{103}Rh) = 12.0 Hz, =CH (cod)), 53.71 (*C*H(CH_3)(C_6H_5)), 31.14 (CH_2 (cod)), 30.23 (CH_2 (cod)), 18.68 (CH_3). Anal. Found: C, 60.55; H, 5.60; N, 6.39. $C_{22}H_{25}N_2ORh$ (436.04). Calc.: C, 60.55; H, 5.79; N, 6.42%. MS (FD, MeOH): 436 *m/e* ($M^{+\cdot}$).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF AG (Ludwigshafen) for support of this work. This study is part of a project which is funded by the Bundesministerium BMBF.

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