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Metal complexes of biologically important ligands
Part LXIV**. Pentamethylcyclopentadienyl–rhodium(III) complexes with α-amino acid derivatives as bridging ligands and with several chiral metal centers: synthesis and structure of [Cp*Rh(μ-L-phenylalaninato)]$_3$(BF$_4$)$_3$ and [Cp*Rh(μ-NHCOCH$_2$NCO$_2$CH$_2$Ph)]$_2$

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Abstract

Elimination of chloride from Cp*Rh(L-PheO)Cl with AgBF$_4$ leads to the trinuclear complex [Cp*Rh(μ-L-PheO)]$_3^{3+}$(BF$_4^-$)$_3$ (**2**), in which the amino acidate acts both as an (N, O)-chelating and as a carboxylate bridging ligand according to the X-ray structural determination. Trimerization of [Cp*Rh(PheO)]$^+$ occurs with chiral self recognition, i.e. in solution and in the crystal only diastereomers with the same configuration at the three chiral rhodium atoms ($R_{Rh}R_{Rh}R_{Rh}$ and $S_{Rh}S_{Rh}S_{Rh}$) are formed. Reaction of [Cp*RhCl$_2$]$_2$ with carbobenzoxy glycine amide in the presence of base gives the dimeric complex [Cp*Rh(μ-NHCOCH$_2$NCO$_2$CH$_2$Ph)]$_2$ (**3**). X-ray diffraction showed that the two rhodium atoms with $R_{Rh}S_{Rh}$ configuration are bridged by the deprotonated glycine amide N atom. Complexes **2** and **3** may be of interest as chiral catalysts; they catalyze the ester exchange of *N,N*-dimethylglycine ethylester in CD$_3$OD.

Introduction

Recently we described organometallic complexes with α-amino acid ligands of the general formula Cp*M(Cl)(OOCCHRNH$_2$) (M = Rh, Ir) [1a] which have also been obtained by Carmona *et al.* [1b]. The rapid epimerization at the chiral metal center in solution has been demonstrated by ^{1}H NMR spectroscopy.

Here we describe polynuclear complexes with L-phenylalaninate and with doubly deprotonated *N*-carbobenzoxy glycine amide as bridging ligands. The compounds contain several chiral metal centers, in which optical configuration is mutually dependent.

Experimental

Reactions were carried out under nitrogen. Methanol (puriss.) was obtained from Fluka and stored under nitrogen. [Cp*RhCl$_2$]$_2$ was prepared as described in the literature [2]. Workup and crystallization were performed in technical-grade solvents. Spectra were recorded on the following instruments: Nicolet ZDX 5 (IR), Jeol GSX 270 (NMR).

Tris[(η^5-pentamethylcyclopentadienyl)(μ-L-phenylalaninato)rhodium(III)]tris(tetrafluoroborate) (2)

To a solution of **1** [1] (88 mg, 0.20 mmol) in methanol (10 ml) was added AgBF$_4$ (0.20 mmol, 0.20 ml of a 1.00 M MeOH solution). After ½ h the AgCl precipitate was centrifuged and the clear yellow solution layered with excess diethyl ether. After 4 days dark yellow needles were isolated and vacuum-dried. Yield 90 mg (92%).

Anal. Calc. for C$_{57}$H$_{75}$B$_3$F$_{12}$N$_3$O$_6$Rh$_3$ (1467.3): C, 46.66; H, 5.15; N, 2.86. Found: C, 46.20; H, 5.29; N, 2.95%.

Bis[(μ-N-carbobenzoxy glycine amide)(η^5-pentamethylcyclopentadienyl)rhodium(III)] (3)

To a solution of [Cp*RhCl$_2$]$_2$ [2] (93 mg, 0.15 mmol) and *N*-carbobenzoxy glycine amide (62 mg, 0.30 mmol) in methanol (10 ml) was added NaOMe (0.60 mmol, 0.60 ml of a 1 M MeOH solution, freshly titrated) dropwise with stirring. The colour of the reaction mixture changed to dark red. After 5 h stirring the solvent was evaporated *in vacuo*, the residue dissolved in 10 ml of dichloromethane and the NaCl precipitate removed by

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**For Part LXIII see ref. 10.

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centrifugation. The dark red solution was layered with excess hexane. After some days orange crystals were isolated and recrystallized from dichloromethane/hexane. The product was finely ground and dried for 6 h *in vacuo*. Single crystals suitable for X-ray analysis could be obtained from a saturated MeOH solution of **3** with excess ether. Yield 95 mg (71%).

Anal. Calc. for $C_{40}H_{50}N_4O_6Rh_2$ (888.6): C, 54.06; H, 5.67; N, 6.30. Found: C, 53.56; H, 5.73; N, 6.14%.

Catalysis of the ester exchange reaction of Me_2NCH_2COOEt in CD_3OD by 1, 2 and 3

To a 0.28 M solution of Me_2NCH_2COOEt in CD_3OD at room temperature 1/25 equiv. of catalyst was added. The reaction was followed by integration of the ^1H NMR signal of the $COOCH_2$ CH_3 protons or the CH_2 protons of the ethanol produced. In the case of **3** the consumption of Me_2NCH_2COOEt followed first order kinetics with $t_{1/2} = 51$ min. Initially, **2** catalyzed the ester exchange reaction with similar activity to **3**, but seemed to be inactivated during the reaction. With **1** as catalyst the reaction was very slow, $t_{1/2} > 3.9 \times 10^4$ min.

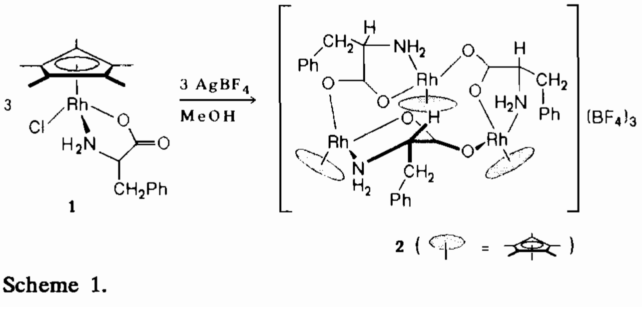
Results and discussion

The L-phenylalaninato complex **1** reacts with $AgBF_4$ in methanol with precipitation of AgCl to generate the $[Cp^*RhPheO]^+$ fragment which trimerizes to form the complex $[Cp^*Rh(\mu\text{-L-PheO})]_3(BF_4)_3$ (**2**) (Scheme 1).

The amino acidate acts both as an (N,O)-chelating and as a carboxylate bridging ligand. This coordination mode is only rarely found for α-amino acids, one such example being the tetrameric complex [(COD)-Ru(Cl)(PheO)]$_4$ [3].

In the solid state IR spectrum of **2** (Nujol mull) an intensive ν(CO) absorption of the bridging carboxylate groups is found at 1580 cm^{-1} which is at about 50 cm^{-1} lower wavenumbers than the ν(CO) absorption of **1**. ν(NH) absorptions appear at 3321(m) and 3270(m) cm^{-1}.

The Cp* ligand is an excellent probe to study the behavior of **2** in solution by ^1H NMR. In CD_3OD (270 MHz, solvent as internal reference) two Cp* signals appear; their relative intensities are strongly temperature dependent (1.81 ppm/1.66 ppm; −60 °C: 36/64, 45 °C: 4/96). We assign these signals to the diastereoisomers $S_cS_cS_cR_{Rh}R_{Rh}R_{Rh}$ [4] **2a** (1.81 ppm) and $S_cS_cS_cS_{Rh}S_{Rh}S_{Rh}$ **2b** (1.66 ppm) which are in thermodynamic equilibrium (Scheme 2).



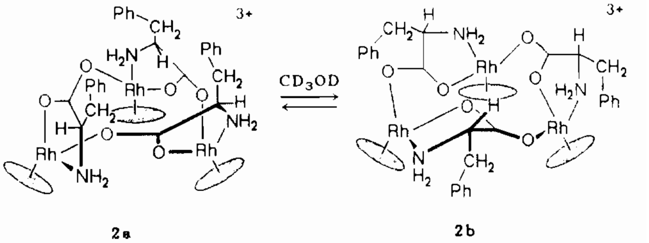
Scheme 1.

The upfield shift of one of the diastereotopic methylene protons in **2a** (2.62 ppm, d of d) compared to the CH_2 resonances in **1** (3.05 and 3.31 ppm) and **2b** (2.95–3.3 ppm, m, together with H^α) indicates that the trimeric structure exists also in solution. The proximity of the benzyl groups in **2a** results in a shielding of one of the CH_2 protons by the phenyl groups.

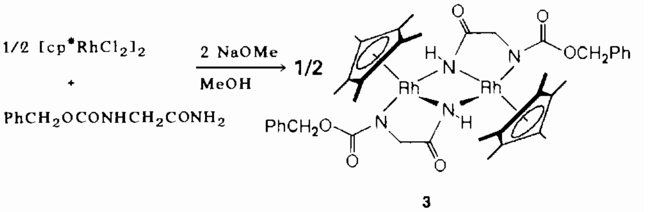
In the ^1H NMR spectrum of **2** no evidence was found for a diastereoisomer with differently configured Rh atoms ($R_{Rh}R_{Rh}S_{Rh}$ or $R_{Rh}S_{Rh}S_{Rh}$). For such a compound three different Cp* signals of equal intensity would be expected as a result of the lowered symmetry. The trimerization of the $[Cp^*Rh(\text{L-PheO})]^+$ unit to **2** is an example of chiral self-recognition between metal complex fragments*.

N-Carbobenzoxy glycine amide is coordinated to the Cp*Rh unit in the presence of a strong base by the deprotonated amide and urethane nitrogen atoms. In the solid state the dimeric compound **3** with bridging amide nitrogen atoms is formed (Scheme 3).

Bridging of two metal ions by a deprotonated amide N atom is unusual and was recently found to occur also in the binuclear complex $(Ph_3P)(OC)Ru(\mu\text{-}NHCOC_6H_4)(\mu\text{-}NHCOPh)(\mu\text{-}H)Ru(CO)(PPh_3)_2$ [6a].



Scheme 2.



Scheme 3.

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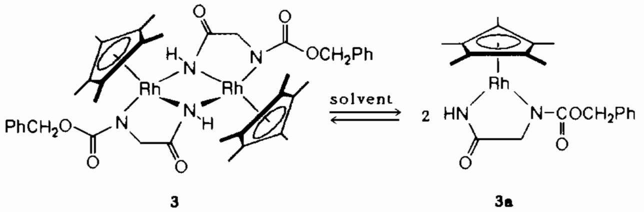
*Other examples of chiral self recognition of metal complexes include the Michael addition of $CpFe(CO)(PPh_3)(COCH_2\text{-})$ to $CpFe(COCH{=}CH_2)(CO)(PPh_3)$ which gives (*RR*)- and (*SS*)-$CH_2[CH_2C(O)Fe(Cp)(CO)(PPh_3)]_2$ [5a] and the dimerization of $[(Cl)PtC(H)(CH_2CH_2CH{=}CH_2)(CH_2NHR)]$ fragments with identical optical configuration at the chiral C-atom [5b, c].



Scheme 4.

A dimethylplatinum(IV) complex containing deprotonated glycinate as an amido-bridging ligand has been reported [6b].

ν(CO)-amide and ν(CO)-urethane absorptions of **3** in the IR region are observed at 1652s, 1645sh cm^{-1} (Nujol mull). ν(NH) appears as a single, sharp band at 3290m cm^{-1}.

The ^1H NMR spectrum of **3** ($CDCl_3$, 270 MHz, int. TMS) is more complicated than that of **2**. The main species in solution is the binuclear compound with differently configured Rh atoms ($R_{Rh}S_{Rh}$), which is also found in the solid state. The Cp* signal is shifted to high field due to the shielding of Cp* protons by the phenyl groups (Cp*: 1.26 (s); N-CH_2: 4.58 (d, $^2J=19.5$), 3.74 (d, $^2J=19.5$); O-CH_2: 5.19 (d, $^2J=12.0$), 5.04 (d, $^2J=12.0$); N-H=3.55 (s); aryl-*o*-H: 7.57 (d, $^3J=6.8$), aryl-*m*-H: 7.37 (t, $^3J=6.8$); aryl-*p*-H: 7.29 (d, $^3J=6.8$); δ in ppm, J in Hz).

Another set of signals with chemically equivalent methylene protons may be assigned to the monomeric subunit **3a**, to which **3** partially dissociates in solution (Cp*: 1.77 (s), N-CH_2: 3.50 (s); O-CH_2: 5.21 (s); NH: 6.24 (s, br); aryl-H: 7.3–7.5 (m); δ in ppm).

In 1,2-dichloroethane the dissociation of **3** to **3a** is slow enough to be followed by ^1H NMR spectroscopy (Cp* signal). We assume that **3a** is a 16-electron complex with a very rapidly racemizing metal center (Scheme 4).

Recently the 16-electron complex Cp*Ru(acac) which is comparable to **3a**, has been isolated and characterized by an X-ray structure analysis [7]. In addition to the Cp* ^1H NMR signals of **3** and **3a** some smaller signals between 1 and 2 ppm appeared, whose assignments are uncertain.

Compounds of type **2** and **3** may be of interest as chiral catalysts. Cleavage of the ligand bridges provides a coordination site suitable for substrate binding. We

TABLE 1. Crystallographic data for $C_{40}H_{50}N_4O_6Rh_2$ and $(C_{19}H_{25}NO_2Rh)_3(BF_4)_3$

Formula	$C_{40}H_{50}N_4O_6Rh_2$	$(C_{19}H_{25}NO_2Rh)_3(BF_4)_3$
Formula weight	888.7	1467.4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
a(pm)	933.8(2)	1312.4(4)
b(pm)	1549.1(4)	1224.8(4)
c (pm)	1299.4(2)	2093.9(5)
β (°)	93.80(1)	104.73(2)
V (10^6 pm^3)	1875.5	3255.1
Z	2	2
D_{calc} (g/cm^3)	1.57	1.50
Crystal size (mm)	$0.5\times0.05\times0.05$	$0.13\times0.2\times0.4$
Instrument	Siemens R3m/V	Enraf-Nonius CAD4
μ (Mo Kα) (cm^{-1})	9.2	8.2
Temperature (K)	295	294
2θ range (°)	5–50	4–46
Scan mode	ω-scan	ω-scan
Reflections collected	3733	8808
Unique reflections	3298	8382
Reflections considered observed	$2597\,\|F\|>3\sigma\|F\|$	$8021\,\|F\|>4\sigma\|F\|$
Corrections applied	LP and numerical absorption correction	LP and empirical absorption correction
Min./max. transmission	0.936/0.973	0.884/0.999
Residuals		
R	0.0482	0.0403
R_w	0.0349	0.0358
R_g	0.0277	0.0368
GOF	1.73	3.82
Parameters refined	243	758
Weighting scheme	$w=1/\sigma^2$	$w=1/\sigma^2$
Max. features in final difference Fourier map ($e\times10^{-6}$ pm^{-3})	0.51/−0.50	1.20/−0.79
Absolute configuration		$\eta=1.14(6)$

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $(C_{19}H_{25}NO_2Rh)_3(BF_4)_3$

	x	y	z	$U_{(eq)}$[a]
Rh(1)	2206(1)	8049	9254(1)	47(1)
O(1)	1646(4)	9271(4)	8536(2)	49(1)
O(2)	468(4)	9589(4)	7593(3)	52(1)
N(1)	600(5)	7574(5)	8856(3)	53(2)
C(1)	3798(6)	8044(9)	9869(3)	59(2)
C(2)	3203(8)	7213(8)	46(4)	71(2)
C(3)	2345(7)	7659(9)	256(4)	74(2)
C(4)	2384(7)	8762(9)	191(4)	69(2)
C(5)	3296(7)	8989(8)	9949(4)	68(2)
C(6)	4800(6)	7911(9)	9670(4)	85(2)
C(7)	3456(7)	5997(9)	29(5)	105(2)
C(8)	1539(7)	6991(9)	511(5)	118(2)
C(9)	1664(8)	9650(8)	340(5)	108(2)
C(10)	3625(8)	126(9)	9836(5)	115(2)
C(11)	159(5)	8070(7)	8205(3)	47(2)
C(12)	810(6)	9062(6)	8117(4)	45(2)
C(13)	−1012(5)	8360(8)	8108(4)	67(2)
C(14)	−1650(6)	8291(8)	6870(4)	74(2)
C(15)	−2197(7)	8733(9)	6275(5)	84(2)
C(16)	−2701(7)	9726(8)	6291(5)	84(2)
C(17)	−2672(7)	181(8)	6872(6)	87(2)
C(18)	−2123(6)	9769(7)	7463(5)	68(2)
C(19)	−1618(6)	8818(8)	7461(4)	61(2)
Rh(2)	4106(1)	7908(1)	7169(1)	49(1)
O(1A)	3462(3)	7886(5)	7998(2)	49(1)
O(2A)	2317(4)	7022(4)	8439(3)	53(1)
N(1A)	3408(4)	6333(5)	7115(3)	49(2)
C(1A)	4994(7)	9189(8)	6846(5)	71(2)
C(2A)	5107(6)	8168(8)	6522(4)	57(2)
C(3A)	5612(6)	7448(7)	7020(4)	55(2)
C(4A)	5734(5)	7957(10)	7649(4)	70(2)
C(5A)	5358(6)	9041(8)	7529(5)	68(2)
C(6A)	4518(8)	160(8)	6482(5)	99(2)
C(7A)	4847(6)	7987(9)	5824(3)	75(2)
C(8A)	5949(7)	6360(8)	6939(5)	91(2)
C(9A)	6256(6)	7438(8)	8318(4)	91(2)
C(10A)	5319(8)	9850(9)	8051(5)	107(2)
C(11A)	2521(6)	6351(6)	7427(4)	47(2)
C(12A)	2821(6)	7158(6)	8003(3)	42(2)
C(13A)	2149(6)	5242(6)	7581(4)	57(2)
C(14A)	191(6)	5412(6)	7133(5)	63(2)
C(15A)	−775(7)	5366(7)	7185(5)	77(2)
C(16A)	−943(8)	5144(8)	7817(6)	91(2)
C(17A)	−112(8)	4930(8)	8347(5)	89(2)
C(18A)	885(7)	4970(7)	8268(4)	65(2)
C(19A)	1039(6)	5194(6)	7655(4)	54(2)
Rh(3)	1080(1)	929(1)	7179(1)	46(1)
O(1B)	2261(4)	9842(4)	7047(3)	52(1)
O(2B)	2554(4)	8290(4)	6576(2)	50(1)
N(1B)	269(5)	44(5)	6317(3)	49(2)
C(1B)	1935(7)	2412(6)	7189(5)	60(2)
C(2B)	876(8)	2518(6)	6820(4)	70(2)
C(3B)	190(7)	2326(7)	7225(5)	66(2)
C(4B)	824(9)	2123(7)	7844(5)	75(2)
C(5B)	1902(8)	2135(6)	7829(4)	64(2)
C(6B)	2872(7)	2545(7)	6936(5)	104(2)
C(7B)	541(8)	2894(9)	6106(4)	116(2)
C(8B)	−962(7)	2451(8)	7022(6)	131(2)
C(9B)	490(9)	1832(9)	8446(5)	142(2)
C(10B)	2833(8)	1952(8)	8397(5)	112(2)
C(11B)	856(6)	9030(7)	6238(4)	50(2)
C(12B)	1987(5)	9062(7)	6647(3)	42(2)
C(13B)	748(6)	8710(7)	5520(4)	68(2)
C(14B)	991(11)	451(11)	4973(7)	154(2)
C(15B)	1545(11)	1084(14)	4660(7)	190(2)
C(16B)	2492(10)	781(12)	4578(7)	161(2)
C(17B)	2731(9)	9733(11)	4661(6)	134(2)
C(18B)	2215(8)	9019(11)	4967(6)	122(2)
C(19B)	1350(8)	9426(8)	5167(4)	76(2)
B(1)	1612(4)	3509(5)	185(2)	141(2)
F(1)	2318(6)	3054(7)	9915(4)	258(2)
F(2)	2101(5)	4097(5)	705(3)	148(2)
F(3)	1047(6)	2734(6)	374(3)	208(2)
F(4)	983(7)	4152(7)	9747(4)	313(2)
B(1A)	2045(3)	5467(4)	5389(2)	107(2)
F(1A)	1489(4)	5989(5)	4859(2)	148(2)
F(2A)	3029(3)	5830(6)	5541(3)	175(2)
F(3A)	1624(4)	5642(5)	5893(2)	156(2)
F(4A)	2037(5)	4405(4)	5262(3)	154(2)
B(1B)	4650(4)	9144(5)	1780(3)	175(2)
F(1B)	5069(8)	9803(9)	1413(5)	394(2)
F(2B)	5168(6)	9254(7)	2408(3)	214(2)
F(3B)	4718(6)	8120(6)	1591(5)	278(2)
F(4B)	3646(4)	9404(7)	1708(4)	213(2)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

found that the ester exchange reaction* of *N,N*-dimethylglycine ethylester with the solvent CD_3OD is effectively catalyzed by **2** and **3**, whereas the monomeric complex **1** showed only very low catalytic activity.

Crystal structures (Table 1–3)

Yellow single crystals of **2** suitable for X-ray analysis could be grown from methanol/ether. The trimeric structure is shown in Fig. 1(a) and (b). The crystal investigated was that of diastereoisomer **2b** ($S_cS_cS_cS_{Rh}S_{Rh}S_{Rh}$). The molecule has no three-fold symmetry axis. Selected bond lengths and angles are given in Table 4. The Rh–O and C–O lengths in the chelate ring and in the carboxylate bridges do not differ markedly and lie in the ranges 211–215 and 123–127 pm, respectively. As in [(COD)Ru(PheO)Cl]$_4$ [3] the carboxylate bridges in **2** may be regarded as more or less symmetrical.

An X-ray structural analysis demonstrated compound **3** to exist as a dimer (Fig. 2(a) and (b)). The orange single crystal examined was obtained from methanol/

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*The acceleration of the ester exchange reaction of α-amino acid esters in alcohols in the presence of transition metal ions or complexes is well known, see for examples ref. 8.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $C_{40}H_{50}N_4O_6Rh_2$

	x	y	z	U_{eq}[a]
Rh	−755(1)	−947(1)	86(1)	30(1)
N(1)	−1715(5)	−462(3)	−1295(3)	34(2)
N(2)	−1176(5)	362(3)	429(4)	32(2)
O(1)	−541(4)	−1301(3)	−2342(3)	48(1)
O(2)	−2240(4)	−378(3)	−3035(3)	56(2)
O(3)	−3321(4)	1113(3)	280(3)	51(2)
C(1)	−727(7)	−2339(3)	16(5)	44(2)
C(2)	82(6)	−2087(4)	957(5)	45(2)
C(3)	−833(6)	−1597(3)	1570(4)	35(2)
C(4)	−2243(6)	−1567(3)	1024(4)	35(2)
C(5)	−2163(6)	−2042(3)	98(4)	40(2)
C(6)	−186(8)	−2923(4)	−793(5)	80(3)
C(7)	1588(6)	−2353(4)	1278(5)	73(3)
C(8)	−497(7)	−1216(4)	2627(4)	63(3)
C(9)	−3541(6)	−1165(4)	1429(4)	52(2)
C(10)	−3411(7)	−2211(4)	−667(4)	63(3)
C(11)	−2463(6)	620(3)	−70(4)	35(2)
C(12)	−2793(6)	181(4)	−1103(4)	43(2)
C(13)	−1580(6)	−669(3)	−2272(4)	38(2)
C(14)	−115(6)	−1487(4)	−3370(4)	52(2)
C(15)	1355(6)	−1142(3)	−3507(4)	41(2)
C(16)	2488(7)	−1314(4)	−2782(4)	47(2)
C(17)	3822(6)	−966(5)	−2896(5)	57(2)
C(18)	4061(8)	−456(5)	−3727(6)	69(3)
C(19)	2977(9)	−299(4)	−4458(5)	69(3)
C(20)	1634(7)	−638(4)	−4352(5)	54(3)

[a] U_{eq} are defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Selected distances (pm) and angles (°) of $(C_{19}H_{25}NO_2Rh)_3(BF_4)_3$

Rh1–N1	214.0(6)	O1–Rh1–N1	77.7(2)
Rh1–O1	211.6(5)	O2a–Rh1–N1	78.0(2)
Rh1–O2a	215.3(5)	O2a–Rh1–O1	86.1(2)
O1–C12	124.4(8)	O1a–Rh2–N1a	77.0(2)
O2–C12	125.3(9)	O2b–Rh2–N1a	80.5(2)
Rh2–N1a	212.6(6)	O2b–Rh2–O1a	87.7(2)
Rh2–O1a	211.5(5)	O1b–Rh3–N1b	78.2(2)
Rh2–O2b	215.0(4)	O2–Rh3–N1b	78.1(2)
O1a–C12a	122.8(9)	O2–Rh3–O1b	86.1(2)
O2a–C12a	126.7(10)		
Rh3–N1b	214.2(6)		
Rh3–O1b	211.3(5)		
Rh3–O2	210.9(5)		
O1b–C12b	126.2(9)		
O2b–C12b	123.5(9)		

TABLE 5. Selected distances (pm) and angles (°) of $C_{40}H_{50}N_4O_6Rh_2$

Rh–N1	209.2(4)	N2–Rh–N1a	76.2(2)
Rh–N2	212.0(5)	N2–Rh–N2a	80.5(2)
Rh–N2a	216.4(5)	N1–Rh–N2a	84.4(2)
N2–C11	138.6(7)	Rh–N2–Rha	99.5(2)
C11–O3	121.6(7)	Rh–N2–C11	110.1(4)
N1–C13	132.4(7)	Rha–N2–C11	116.7(4)
		Rh–N1–C12	111.3(2)
		Rh–N1–C13	132.4(4)
		C12–N1–C13	116.2(4)

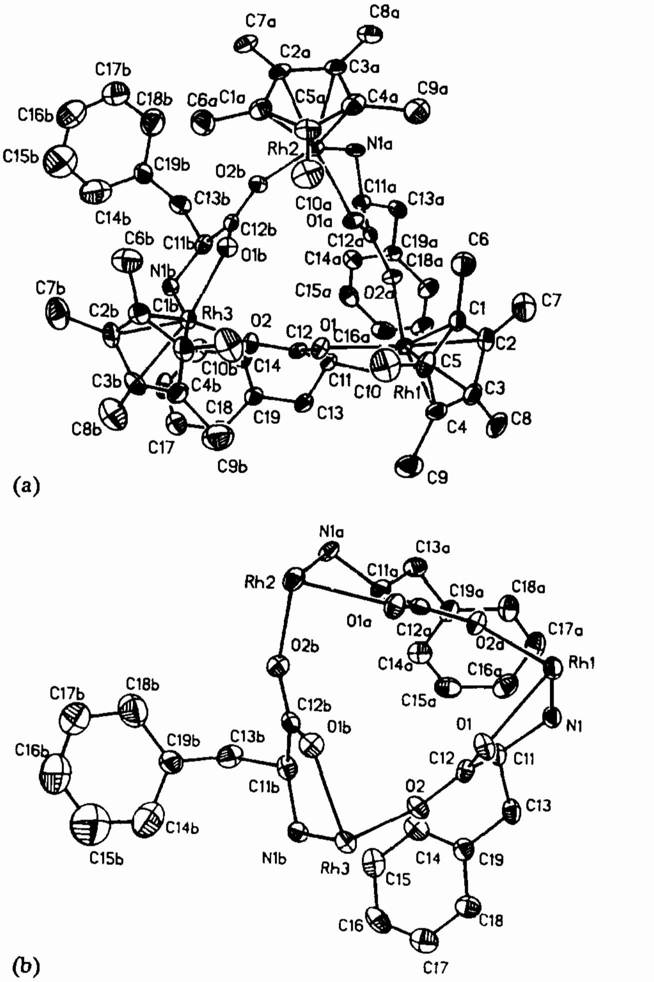

Fig. 1. Molecular structure of **2**. (a) H atoms have been omitted; 20% probability ellipsoids. (b) C_5Me_5-ligands have been omitted.

ether. The optical configuration of the chiral centers is $R_{Rh}S_{Rh}R_NS_N$. Selected bond lengths and angles are listed in Table 5.

The bridging amide N atoms N2 and N2a have a distorted tetrahedral environment. The bridge is almost symmetrical, the difference between the bond lengths Rh–N2 (212.0 pm) and Rh–N2a (216.4 pm) being small. Very similar bond lengths of the M–N–M unit are found in $(PPh_3)(OC)Ru(\mu\text{-}NHCOC_6H_4)(\mu\text{-}NHCOPh)(\mu\text{-}H)Ru(CO)(PPh_3)_2$ [7].

The coordinated urethane N atom N1 is trigonal planar (sum of bond angles Rh–N1–C12, Rh–N1–C13, C12–N1–C13: 359.9°). Atom N2 has no free electron pair for amide resonance with the carbonyl group C11–O3. Therefore the amide bond C11–N2 (138.6(7)

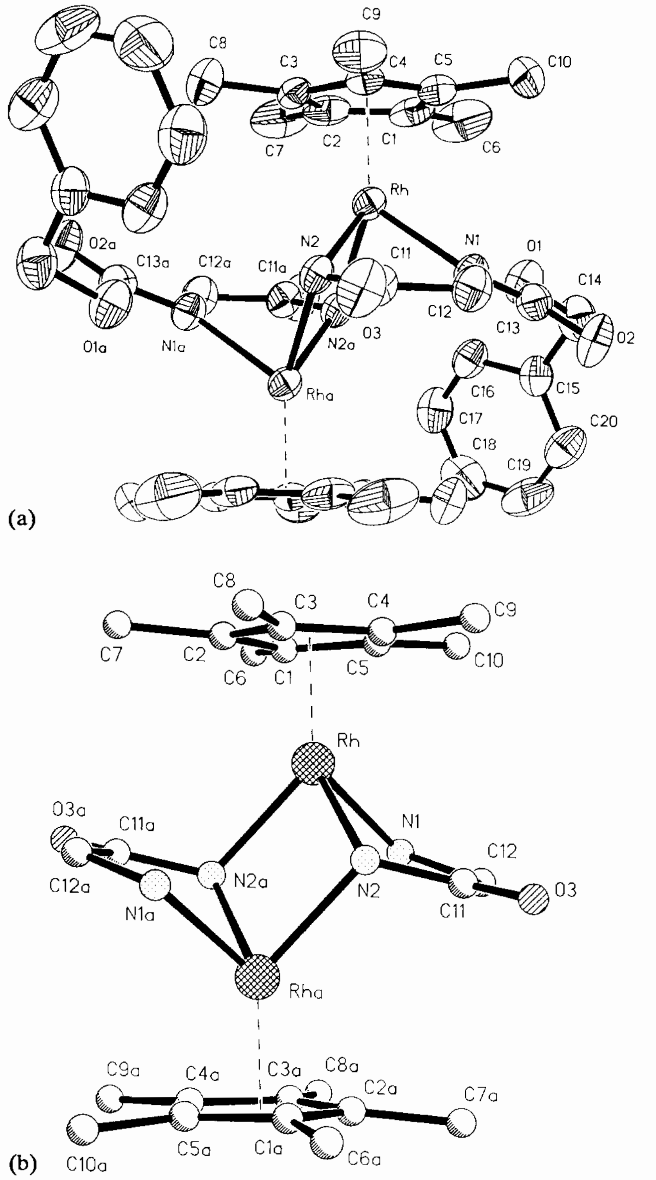

Fig. 2. Molecular structure of **3**. (a) H atoms have been omitted; 50% probability ellipsoids. (b) A view of the centrosymmetric dimer **3** with arbitrary atomic radii. Hydrogen atoms and the $-COOCH_2C_6H_5$ substituents have been omitted for sake of clarity.

pm) is longer than in glycine amide complexes (e.g. $[(H_3N)_4RuNHCOCH_2NH_2]_2$, 133.4(6) pm [9]) with a non-bridging amide N atom. On the other hand the C11–O3 distance (121.6(7) pm) is shorter than the C–O bond length in glycine amide complexes [9].

Supplementary material

Listings of thermal parameters, hydrogen atom positions, bond distances and angles, and observed and calculated structure factors have been deposited with Fachinformationszentrum, Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, W-7514 Eggenstein-Leopoldshafen 2, FRG, under CSD 5592.

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