ELSEVIER

Inorganica Chimica Acta 254 (1997) 93-98

Inorganica Chimica Acta

Dinuclear Rh(I,I) and Rh(II,II) complexes containing bridging asymmetrically 2,7-disubstituted naphthyridines

Markus Mintert, William S. Sheldrick

Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Postfach 102148, D-44780 Bochum, Germany

Received 28 November 1995; revised 2 February 1996

Abstract

The dirhodium(I) complex *cis*-[$Rh_2(mphonp)_2(CO)_4$] (1) was prepared by reaction of 5-methyl-7-phenyl-1,8-naphthyridin-2-one (Hmphonp) with [{$RhCl(CO)_2$}$_2$] in methanol in the presence of base (NaOMe). The mphonp$^-$ ligands adopt a head–tail orientation relative to one another and bridge the Rh(I) atoms in the O2,N1 coordination mode. Treatment of $RhCl_3 \cdot 3H_2O$ with mphonp$^-$ in methanol affords the dirhodium(II) complex [$Rh_2(mphonp)_4$] (2) in which cyclometalation leads to a novel chelating N8,C72 mode by two of the naphthyridine ligands. The Rh(II) atoms are bridged by the remaining mphonp$^-$ ligands with the O2,N1 coordination pattern being supplemented by N^8 as an axial donor atom. This mode requires a pronounced tilting of the bridging ligands towards the Rh–Rh axis leading to very long Rh–O2 distances (av. 2.30(2) Å) and wide Rh–N1–C2 angles (av. 133(2)°). The Rh–Rh distances are 2.883(4) and 2.566(3) Å in complexes 1 and 2, respectively (X-ray analyses).

Keywords: Crystal structures; Dirhodium complexes; Substituted naphthyridine complexes

1. Introduction

A number of rhodium complexes containing dinucleating 2- or 2,7-substituted 1,8-naphthyridines have been reported in the past ten years. The presence of a donor atom X (e.g. O, N, P) in the 2-position provides such ligands with an ambidentate character, as exemplified by the dirhodium(I) complexes [$Rh_2(\mu$-onp$)_2(CO)_4$] (Honp = 1,8-naphthyridin-2-one) and [$Rh_2Cl_2(CO)_2(\mu$-dpnapy$)_2$] (dpnapy = 2-diphenylphosphino-5,7-dimethyl-1,8-naphthyridine), which exhibit respectively $1\kappa N^1{:}2\kappa N^8$ and $1\kappa X^2{:}2\kappa N^8$ (X = P) bridging modes [1,2]. A trinucleating function $1\kappa X^2{:}2\kappa N^1{:}3\kappa N^8$ (X = O) has also been observed for onp$^-$ in [$Rh_3(\mu$-onp$)_2(CO)_2(cod)_2]ClO_4$ [3]. However, an example for the potential dinucleating $1\kappa X^2{:}2\kappa N^1$ coordination mode has not previously been reported for Rh(I,I) complexes.

The Rh–Rh bond in [$Rh_2(np)_4]Cl_4$ is bridged by four 1,8-naphthyridines (np) [4]. Further examples of dirhodium(II) complexes with analogous dinucleating ligands are restricted to the P-axial and -equatorial isomers of [$Rh_2\{CH(NC_6H_4Me$-p$)_2\}_2(O_2CCF_3)_2$(dpnapy)] [5] and to compounds of the type [$Rh_2(OAc)_3L]PF_6$, which contain crescent-shaped naphthyridine derivatives such as dpnp (2,7-bis(2-pyridyl)-1,8-naphthyridine) [4,6]. This neutral ligand was also employed in the preparation of the diruthenium(II) complexes [$Ru_2Cl_2(bpy)_2(\mu$-dpnp$)](PF_6)_2$ and [$Ru_2(OAc)_3(\mu$-dpnp$)]PF_6$, both of which contain a $1\kappa N^1{:}2\kappa N^8$ bridged Ru_2^{4+} core and axially coordinating dpnp pyridine rings [7]. We have recently reported the quadruply bridged dinuclear complexes [$Mo_2(monp)_4$] and [$Ru_2(monp)_4$], in which the asymmetrically 2,7-disubstituted ligands monp$^-$ (Hmonp = 7-methyl-1,8-naphthyridin-2-one) exhibit respectively O2,N1 and N1,N8 bridging modes [8]. An extension of this approach led us to study the reaction of [$Ru_2(OAc)_4Cl$] with Hmphonp (5-methyl-7-phenyl-1,8-naphthyridin-2-one, Fig. 1) in methanol at reflux, which leads to successive formation of [$Ru_2Cl(mphonp)_2(OAc)_2$], [$Ru_2(mphonp)_2(OAc)_2$] and [$Ru_2(mphonp)_4$] [9]. The reduction of the Ru_2^{5+} core in the diruthenium(II,III) complex is accompanied by a change in the bridging mode from O2,N1 to N1,N8

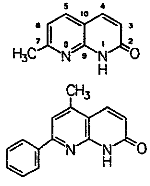

Fig. 1. The ligands Hmonp and Hmphonp with the numbering scheme.

PII S0020-1693(96)05147-X

in $[Ru_2(mphonp)_2(OAc)_2]$. Steric interactions between adjacent phenyl substituents force the adoption of the electronically less favourable O2,N1 coordination pattern [9] by three of the $mphonp^-$ ligands in the fully substituted polar complex $[Ru_2(mphonp)_4]$. We have also demonstrated that $monp^-$ and $mphonp^-$ are capable of adopting a trinucleating function in the linear three-atom clusters *cis*-$[Ru_3(monp)_2(CO)_6]$ and *cis*-$[Ru_3(mphonp)_2(CO)_6]$ [10].

These findings prompted us to extend our investigations to dirhodium complexes and we now report the preparation and structural characterisation of *cis*-$[Rh_2(mphonp)_2(CO)_4]$ (**1**), $[Rh_2(mphonp)_4]$ (**2**) and $[Rh_2(monp)_4]$ (**3**). X-ray structures are provided for **1** and **2**.

2. Experimental

IR spectra were recorded as KBr discs on a Perkin-Elmer 1760 spectrometer and electronic spectra on a Perkin-Elmer Lambda 15. ^{1}H NMR spectra were registered on a Bruker AM 400 with values reported as ppm relative to the signal of the relevant deuterated solvent. FAB mass spectra were measured on a VG Autospec employing 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed on a Carlo Erba 1106 analyser. All reactions were carried out under argon by use of standard Schlenk techniques. Solvents were dried and distilled under argon before use. The 2,7-disubstituted naphthyridine derivatives Hmonp [11] and Hmphonp [9] were synthesised according to literature procedures. $[\{RhCl(CO)_2\}_2]$ and $[Rh_2(OAc)_4(CH_3OH)_2]$ were prepared [12,13] from $RhCl_3 \cdot 3H_2O$, which was a gift from Degussa AG.

2.1. Preparation of the complexes 1–3

2.1.1. Cis-$[Rh_2(mphonp)_2(CO)_4]$ (1)

Hmphonp (0.024 g, 0.1 mmol) in 20 ml methanol was stirred with $[\{RhCl(CO)_2\}_2]$ (0.019 g, 0.05 mmol) for 4 h in the presence of 0.1 ml 1M NaOMe/HOMe. The resulting red precipitate was filtered off and dried in vacuum to afford 0.028 g of **1** (yield 71%). Crystals for the X-ray analysis were grown by slow gas diffusion of pentane into a chlorobenzene solution of the product.

Anal. Found: C, 51.4; H, 3.0; N, 7.1. Calc. for $C_{34}H_{22}N_4O_6Rh_2$ ($M=788.4$): C, 51.8; H, 2.8; N, 7.1%. FAB-MS: m/z (%) 788 (100) $[M^+]$. IR: ν(CO) 2079s, 2011s; ν(C2–O2) 1626s cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.65 (s, 6H, CH_3), 6.91 (d, 2H, H3), 7.28 (s, 2H, H6), 7.50 (m, 6H, C_6H_5), 7.81 (d, 2H, H4), 8.01 (m, 4H, C_6H_5) ppm. UV–Vis (CH_2Cl_2): λ_{max} (ϵ (l mol^{-1} cm^{-1})) 498 (6.15×10^3).

2.1.2. $[Rh_2(mphonp)_4]$ (2)

Hmphonp (0.236 g, 1 mmol) in 25 ml methanol was stirred with 1 ml 1M NaOMe/ HOMe to yield a deep brown solution. Addition of $RhCl_3 \cdot 3H_2O$ (0.066 g, 0.5 mmol) followed by stirring at reflux for 5 h led to precipitation of a brown solid. This was filtered off, washed with diethyl ether and dried under vacuum to afford 0.249 g of **2** (yield 87%). Crystals for the X-ray analysis were grown by gas diffusion of diethyl ether into an anisole solution of the product.

Anal. Found: C, 61.7; H, 4.5; N, 8.5. Calc. for $C_{60}H_{44}N_8O_4Rh_2$ ($M=1146.9$): C, 62.8; H, 3.9; N, 9.8%. FAB-MS: m/z (%) 1147 (100) $[M^+]$, 910 (13) $[M-mphonp]^+$, 675 (53) $[M-2mphonp]^+$, 574 (9) $[M-2mphonp-Rh]^+$. IR: ν(NH) 3054m, ν(C2–O2) 1667s, 1618s cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.55 (s, 6H, CH_3), 2.65 (s, 6H, CH3), 6.47 (d, 2H, H3), 6.88 (d, 2H, H3), 6.95 (m, 12H, C_6H_5), 7.20 (s, 2H, H6), 7.49 (s, 2H, H6), 7.59 (d, 2H, H4), 8.00 (d, 2H, H4′), 8.00 (m, 4H, C_6H_5), 8.20 (m, 2H, C_6H_5) ppm. UV–Vis ($CHCl_3$): λ_{max} (ϵ (l mol^{-1} cm^{-1})) 343 (22.33×10^3).

2.1.3. $[Rh_2(monp)_4]$ (3)

Hmonp (0.161 g, 1 mmol) was refluxed for 4 h with $[Rh_2(OAc)_4(CH_3OH)_2]$ (0.127 g, 0.25 mmol) in 20 ml H_2O in the presence of NaOH (0.040 g, 1 mmol). The resulting green precipitate was filtered off and dried in vacuum to afford 0.182 g of **3** (yield 86%).

Anal. Found: C, 52.4; H, 3.7; N, 13.5. Calc. for $C_{36}H_{28}N_8O_4Rh_2$ ($M=842.5$): C, 51.3; H, 3.4; N, 13.3%. FAB-MS: m/z (%) 843 (40) $[M^+]$, 743 (100) $[M-Rh]^+$, 684 (2) $[M-monp]^+$, 522 (18) $[M-2monp]^+$. IR: ν(C2–O2) 1613s (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.62 (s, 6H, CH_3), 2.85 (s, 6H, CH_3), 6.35 (d, 2H, H3), 6.46 (d, 2H, H3), 6.57 (d, 2H, H6), 6.77 (d, 2H, H6), 7.08 (d, 2H, H4), 7.39 (d, 2H, H4), 7.57 (d, 2H, H5), 7.75 (d, 2H, H5) ppm. UV–Vis ($CHCl_3$): λ_{max} (ϵ (l mol^{-1} cm^{-1})) 742 (0.12×10^3), 619 (0.24×10^3), 370 (1.54×10^3), 297 (2.28×10^3).

2.2. X-ray structural analyses

Unit cell constants were obtained for crystals of **1** and **2** from least-squares fits to settings of 25 reflections centred on a Siemens P4 diffractometer. The crystals were of relatively poor quality with wide mosaic spreads. Intensity data were collected on the four-circle diffractometer at varied scan rates in the ω mode for Mo Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections (ψ scans) were applied to the registered intensities. The structures were solved by standard heavy atom methods and refined by full-matrix least-squares. $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$ with weights given by the expression $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Calculations were performed with the SHELXTL program system (Siemens Analytical Instruments).

cis-$[Rh_2(mphonp)_2(CO)_4] \cdot 1/2CH_3OH$ ($\mathbf{1} \cdot 1/2CH_3OH$), orthorhombic, space group *Pccn*, $a=24.750(5)$, $b=27.442(5)$, $c=9.709(2)$ Å, $V=6595(2)$ Å^3, $Z=8$, $F(000)=3208$, $M=804.4$, $D_c=1.620$ g cm^{-3}. 4255 independent reflections were collected in the range $2\theta \leq 45°$ for a crystal of size $0.64 \times 0.07 \times 0.06$ mm ($\mu = 10.5$ cm^{-1}, max./

min. transmission 0.425/0.337). Terminal reliability indices were $R=0.075$ and $R_w=0.075$ ($g=0.0013$) for 1555 reflections with $F_o^2>2\sigma(F_o^2)$. With the exception of the disordered methanol atoms all non-hydrogen atoms were assigned anisotropic temperature factors. The 7-substituents were refined as rigid phenyl groups. Hydrogen atoms were included at geometrically calculated sites. Residual peaks in the final ΔF synthesis were 0.75 (max.) and −0.79 e Å^{-3} (min.).

[Rh_2(mphonp)$_4$]·$C_6H_5OCH_3$·1/2$(C_2H_5)_2O$(2·$C_6H_5OCH_3$·1/2$(C_2H_5)_2O$), monoclinic, space group $P2_1/c$, $a=19.485(4)$, $b=11.964(2)$, $c=25.859(5)$ Å, $\beta=100.19(3)°$, $V=5933(2)$ Å^3, $Z=4$, $F(000)=2644$, $M=1292.0$, $D_c=1.446$ g cm^{-3}. 6765 independent reflections were collected in the range $2\theta\leq45°$ for a crystal of size 0.53×0.42×0.35 mm ($\mu=6.16$ cm^{-1}, max./min. transmission 0.300/0.266). Terminal reliability indices were $R=0.089$, $R_w=0.090$ ($g=0.0019$) for 2924 reflections with $F_o^2>2\sigma(F_o^2)$. With the exception of the disordered diethyl ether atoms all non-hydrogen atoms were assigned anisotropic temperature factors. The 7-substituents were refined as rigid phenyl groups. Hydrogen atoms were included for the mphonp$^-$ ligands at geometrically calculated sites. Residual peaks in the final ΔF synthesis were 0.96 (max.) and −1.17 e Å^{-3} (min.). As a result of the poor quality of the crystals, the discussion of bond lengths and angles will be restricted to the Rh coordination spheres in **1** and **2**. Atom coordinates with equivalent isotropic temperature factors for compounds **1** and **2** are listed in Table 1. See also Section 4.

3. Discussion

Treatment of [{RhCl(CO)$_2$}$_2$] with mphonp$^-$ in methanol at room temperature yields the dinuclear complex **1** (Fig. 2), in which the *cis* sited ligands adopt a head–tail orientation relative to one another and bridge the rhodium(I) atoms in the O2,N1 coordination mode. C_2 symmetry is observed for the complex in CD_2Cl_2 solution. In contrast to **1**, the bridging onp$^-$ ligands in the analogous complex *cis*-[Rh_2(onp)$_2$(CO)$_4$] exhibit the alternative N1,N8 bridging mode [1]. It may reasonably be assumed that the adoption of a similar coordination mode in **1** is prevented by the presence of bulky phenyl groups as 7-substituents in the naphthyridine derivative. Interestingly the Rh···Rh distance in **1** (2.883(4) Å) and *cis*-[Rh_2(onp)$_2$(CO)$_4$] (2.880(2) Å) is unaffected by the change in the bridging mode of the naphthyridine derivatives. A similar distance of 2.899(2) Å has been observed in the polar complex [Rh_2(hp)$_2$(CO)$_4$] [14], in which the hpy$^-$ ligands (Hhp = pyridin-2-one) also adopt the O2,N1 coordination pattern. However, the pyridine derivatives exhibit a head–head orientation in this dirhodium(I) complex and individual moieties are orientated to enable the formation of a linear rhodium(I) chain with alternating shorter (2.899(2) Å) and longer (3.410(2) Å)

Table 1
Atom coordinates (×10^4) with equivalent isotropic temperature factors (Å^2×10^3)

Atom	*x*	*y*	*z*	U_{eq}
Compound 1				
Rh(1)	342(1)	3894(1)	5264(3)	42(1)
C(10)	−403(11)	3979(9)	5649(33)	53(13)
O(10)	−828(7)	3999(7)	6021(30)	92(11)
C(11)	339(13)	4476(11)	4157(31)	50(13)
O(11)	375(9)	4819(7)	3568(25)	74(10)
Rh(2)	889(1)	4366(1)	7521(3)	46(1)
C(20)	257(15)	4438(11)	8560(42)	85(18)
O(20)	−131(9)	4492(9)	9208(32)	113(14)
C(21)	907(11)	5032(11)	7071(36)	65(15)
O(21)	894(8)	5440(7)	7052(28)	96(12)
N(11)	384(9)	3265(7)	6512(24)	51(10)
C(12)	734(9)	3226(8)	7528(37)	59(14)
O(12)	977(7)	3621(6)	8051(21)	64(9)
C(13)	881(10)	2768(9)	8155(24)	34(10)
C(14)	675(10)	2362(9)	7620(34)	65(15)
C(15)	41(13)	1953(11)	5970(38)	71(17)
C(151)	119(12)	1456(9)	6532(43)	93(17)
C(16)	−338(13)	2032(8)	4969(37)	71(16)
C(17)	−485(9)	2506(9)	4438(25)	37(11)
C(172)	−1083(8)	3066(6)	3188(20)	60(14)
C(173)	−1493	3144	2229	80(16)
C(174)	−1722	2751	1531	85(17)
C(175)	−1540	2278	1792	109(21)
C(176)	−1130	2200	2751	77(16)
C(171)	−901	2593	3449	40(11)
N(18)	−222(8)	2904(7)	5003(26)	49(10)
C(19)	137(11)	2837(9)	6032(32)	51(14)
C(110)	276(10)	2385(9)	6569(28)	41(12)
N(21)	1580(9)	4262(7)	6316(25)	45(10)
C(22)	1598(10)	3935(10)	5323(33)	55(13)
O(22)	1152(7)	3741(5)	4766(22)	50(8)
C(23)	2097(10)	3776(9)	4700(33)	66(14)
C(24)	2574(10)	3942(10)	5129(33)	51(13)
C(25)	3065(12)	4503(11)	6740(35)	64(15)
C(251)	3618(9)	4343(12)	6168(38)	89(16)
C(26)	2962(12)	4863(12)	7678(38)	69(16)
C(27)	2454(11)	5043(9)	8204(31)	70(16)
C(272)	1877(8)	5545(7)	9668(23)	101(19)
C(273)	1810	5930	10593	87(17)
C(274)	2256	6205	11005	105(20)
C(275)	2768	6096	10492	118(22)
C(276)	2835	5711	9567	109(20)
C(271)	2390	5436	9156	56(14)
N(28)	2009(8)	4792(8)	7711(26)	43(10)
C(29)	2083(10)	4444(9)	6748(29)	38(12)
C(210)	2574(10)	4296(10)	6199(28)	35(11)
O(1′)	2500	2500	1993(103)	322(38)
C(2′)	2500	2500	536(103)	308(59)
Compound 2				
Rh(1)	3341(1)	665(2)	1020(1)	49(1)
Rh(2)	2036(1)	510(2)	1052(1)	52(1)
N(11)	3010(11)	1335(16)	317(7)	50(9)
C(12)	2374(13)	1693(21)	54(11)	51(11)
O(12)	1853(8)	1550(12)	296(6)	46(6)
C(13)	2339(14)	2111(20)	−443(11)	58(12)
C(14)	2871(14)	2256(27)	−678(10)	83(14)
C(15)	4223(18)	2064(25)	−542(11)	79(14)
C(151)	4226(16)	2508(32)	−1107(12)	131(20)

(*continued*)

Table 1 (*continued*)

Atom	x	y	z	U_{eq}
C(16)	4804(14)	1799(27)	−208(12)	80(15)
C(17)	4751(15)	1337(20)	282(11)	61(12)
C(172)	5339(8)	679(19)	1158(7)	111(17)
C(173)	5917	424	1541	136(20)
C(174)	6588	549	1429	114(17)
C(175)	6680	928	936	177(27)
C(176)	6102	1182	554	117(18)
C(171)	5431	1058	665	50(11)
N(18)	4149(11)	1205(17)	432(7)	56(9)
C(19)	3575(14)	1501(22)	94(11)	55(8)
C(110)	3558(16)	1996(22)	−398(10)	69(13)
N(21)	2079(10)	−775(17)	577(8)	51(9)
C(22)	2601(15)	−1313(25)	438(10)	60(13)
O(22)	3232(8)	−997(13)	559(6)	58(7)
C(23)	2410(18)	−2380(23)	156(11)	73(14)
C(24)	1753(18)	−2779(26)	33(11)	82(15)
C(25)	483(15)	−2383(26)	90(10)	65(13)
C(251)	216(15)	−3470(23)	−222(12)	101(16)
C(26)	43(15)	−1670(27)	288(11)	75(14)
C(27)	319(15)	−698(23)	598(9)	57(12)
C(272)	121(7)	781(17)	1220(7)	86(13)
C(273)	−297	1450	1478	106(16)
C(274)	−1021	1355	1358	78(14)
C(275)	−1327	590	979	94(15)
C(276)	−909	−79	720	71(12)
C(271)	−184	17	841	48(10)
N(28)	981(10)	−466(18)	668(8)	53(8)
C(29)	1399(14)	−1149(24)	460(9)	49(12)
C(210)	1200(14)	−2148(24)	176(11)	56(12)
N(31)	1656(9)	3173(22)	1001(10)	62(10)
C(32)	1532(17)	4302(34)	808(17)	91(17)
O(32)	1529(10)	4509(21)	351(9)	96(10)
C(33)	1459(19)	4977(37)	1189(16)	118(21)
C(34)	1451(15)	4768(28)	1692(21)	124(23)
C(35)	1677(14)	3163(30)	2389(17)	83(16)
C(351)	1579(17)	3877(29)	2882(13)	120(18)
C(36)	1843(14)	2073(32)	2502(13)	81(15)
C(37)	1960(13)	1328(27)	2091(14)	78(15)
C(373)	2314(8)	−1595(15)	1726(7)	68(12)
C(374)	2417	−2117	2216	85(15)
C(375)	2383	−1496	2667	98(18)
C(376)	2245	−352	2628	93(16)
C(371)	2141	171	2138	70(13)
C(372)	2176	−451	1687	60(7)
N(38)	1877(10)	1717(19)	1583(8)	21(5)
C(39)	1756(14)	2759(25)	1504(12)	68(13)
C(310)	1603(15)	3576(32)	1874(14)	82(16)
N(41)	3936(9)	−1751(20)	1491(9)	57(10)
C(42)	4074(16)	−2938(31)	1553(13)	82(16)
O(42)	3997(12)	−3521(18)	1153(10)	117(12)
C(43)	4316(15)	−3185(30)	2058(14)	89(10)
C(44)	4421(13)	−2512(31)	2466(13)	98(15)
C(45)	4279(13)	−526(30)	2804(11)	67(12)
C(451)	4553(16)	−844(31)	3385(11)	120(18)
C(46)	4096(14)	529(28)	2656(11)	77(13)
C(47)	3832(12)	801(22)	2128(12)	59(11)
C(473)	3310(7)	3120(16)	1215(5)	64(11)
C(474)	3355	4052	1544	76(12)
C(475)	3549	3921	2086	78(9)
C(476)	3697	2859	2300	70(12)
C(471)	3651	1928	1971	56(11)
C(472)	3458	2058	1429	34(6)

(*continued*)

Table 1 (*continued*)

Atom	x	y	z	U_{eq}
N(48)	3752(10)	31(19)	1759(8)	45(8)
C(49)	3979(13)	−1039(29)	1903(12)	59(13)
C(410)	4241(14)	−1322(24)	2420(14)	68(14)
C(1′)	9826(14)	6266(26)	1865(14)	140(25)
C(2′)	9570	6515	1340	141(23)
C(3′)	9118	5773	1032	183(32)
C(4′)	8923	4781	1251	231(41)
C(5′)	9179	4532	1776	333(60)
C(6′)	9631	5275	2084	224(33)
O(11′)	10325(15)	7104(30)	2109(12)	182(19)
C(11′)	10448(24)	8036(34)	1830(18)	172(25)
C(12′)	3024(28)	5356(103)	−721(32)	268(53)
C(13′)	3405(24)	5112(107)	−163(29)	280(58)
C(14′)	4516(27)	4793(59)	248(19)	133(27)
C(15′)	5252(23)	4823(58)	129(21)	105(23)
O(16′)	4114(21)	5106(63)	−243(20)	246(33)

Equivalent isotropic temperature factors U_{eq} are defined as one third of the trace of the orthogonalized U_{ij} tensor.

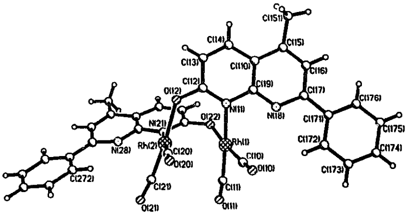

Fig. 2. Molecular structure of *cis*-[$Rh_2(mphonp)_2(CO)_4$] (1). Selected bond lengths (Å) and angles (°): Rh(1)···Rh(2) 2.883(1), Rh(1)–O(22) 2.10(2), Rh(2)–O(12) 2.12(2), Rh(1)–N(11) 2.11(2), Rh(2)–N(21) 2.09(2), Rh(1)–C(10) 1.90(3), Rh(1)–C(11) 1.93(3), Rh(2)–C(20) 1.87(4), Rh(2)–C(21) 1.88(3); Rh(2)–Rh(1)–N(11) 84.7(6), Rh(1)–Rh(2)–N(21) 84.1(6), Rh(1)–N(11)–C(12) 122(2), Rh(2)–N(21)–C(22) 122(2), Rh(1)–O(22)–C(22) 128(2), Rh(2)–O(12)–C(12) 130(2).

Rh···Rh distances. A direct comparison with **1** or *cis*-[$Rh_2(onp)_2(CO)_4$] is, therefore, of limited value.

The Rh–N distances in **1** (2.11(2), 2.09(2) Å) are similar to those in *cis*-[$Rh_2(onp)_2(CO)_4$] and [$Rh_2(hpy)_2(CO)_4$], the Rh–O distances (2.10(2), 2.12(2) Å) close to those in the latter polar complex (2.08(1) Å). A bonding axial interaction between naphthyridine N8 atoms and the square planar coordinated rhodium(I) atoms may be ruled out on the basis of the Rh(1)···N(18) and Rh(2)···N(28) distances of 3.07(2) and 3.01(2) Å. Likewise, the Rh(1)···H(172) and Rh(2)···H(272) spacings of 3.82 and 3.67 Å are far too long for an agostic interaction. The wide Rh(1)–O(22)–C(22) and Rh(2)–O(12)–C(12) angles of 128(2) and 130(2)° indicate that the metal centres in **1** strive to obtain an interatomic distance in the typical region for dinuclear rhodium(I) complexes [15,16]. This aspiration is also underlined by the observed angle of 25.5(4)° between the square planar coordination spheres of Rh(1) and Rh(2).

Bridged dirhodium(II,II) complexes may generally be prepared by either the reaction of the ligand anion with $RhCl_3 \cdot 3H_2O$ in methanol or with $[Rh_2(OAc)_4(CH_3OH)_2]$ in methanol or water [16]. The former method affords a higher yield of $[Rh_2(mphonp)_4]$ (**2**). In contrast, the reaction of $[Rh_2(OAc)_4(CH_3OH)_2]$ with monp$^-$ in water is the preferred synthetic route to $[Rh_2(monp)_4]$ (**3**). The treatment of monp$^-$ with $RhCl_3 \cdot 3H_2O$ or $[Rh_2(OAC)_4(CH_3OH)_2]$ in methanol leads to a mixture of isomeric products, which could not be separated by column chromatography for reasons of solubility and complexity. On the basis of steric considerations we had expected the formation of an O2,N1 bridged dimer for **2** with either *cis*-Rh(O2)$_2$(N1)$_2$ or *trans*-Rh(O2)$_2$(N1)$_2$ geometries for the individual rhodium(II) atoms. Both isomers have recently been isolated and structurally characterised for the analogous dimolybdenum(II) complex $[Mo_2(mphonp)_4]$ [17]. Idealised molecular structures for the *cis* and *trans* isomers of $[Rh_2(mphonp)_4]$ (**2**) should adopt respectively C_{2h} or D_{2d} symmetry, leading to an expectation of magnetic equivalence for the resonances of the ligand protons registered in the ^1H NMR spectra of such complexes in solution. To our surprise, a CD_2Cl_2 solution of **2** exhibits two sets of markedly differing ligand proton resonances in a 1:1 ratio, with the exception of the *ortho*-substituted phenyl hydrogens (2:1 ratio). This observation indicates that a cyclometalation must have taken place for two of the mphonp$^-$ ligands, a finding which is confirmed by the X-ray structure of **2** depicted in Fig. 3. The individual rhodium(I) atoms are both chelated in the novel N8,C72 mode by one naphthyridine ligand and bridged in the expected basically O2,N1 coordination mode by two further ligands. This unusual complex exhibits C_2 symmetry in solution and represents, to our knowledge, the first example of a dinuclear complex $[M_2L_4]$ with M–M bonding, in which identical ligands L$^-$ exhibit both chelating and dinucleating properties. Previously characterised dirhodium(II) compounds with both coordination modes were of the mixed types $[Rh_2L_2X_2Y]$ or $[Rh_2L_2X_2Y_2]$ (L = bridging, X = chelating, Y = axial), with examples being provided by $[Rh_2(OAc)_2\{CF_3C(O)CHC(O)CH_3\}_2(py)]$ [18], $[Rh_2(O_2CH)_2(phen)_2Cl_2]$ [19] and $[Rh_2(OAc)_2(phen)_2(NMim)_2](ClO_4)_2$ (NMim = *N*-methyl-imidazole) [20]. The Rh–Rh single bond length of 2.566(3) Å in **2** is similar to that in the above mentioned dinuclear complexes (2.534(1)–2.576(1) Å) and markedly longer than in compounds with only four bridging ligands such as $[Rh_2(OAc)_3(dpnp)]PF_6$ [4] (2.405(2) Å) or $[Rh_2(mhp)_4]$ [21] (2.370(1) Å) (Hmhp = 6-methylpyridin-2-one).

Inspection of the intermolecular contacts to the rhodium(II) atoms Rh(1) and Rh(2) in **2** indicates the involvement of N(18) and N(28) as axial donor atoms in the respective coordination spheres of these atoms. Thus the N(18)–Rh(1) and N(28)–Rh(2) distances of 2.46(2) and 2.42(2) Å are much shorter than in **1** (3.07(2) and 3.01(2) Å), this state of affairs being achieved by means of a pronounced tilting of the bridging ligands towards the Rh–Rh axis. This inclination leads to Rh(1)–O(22) and Rh(2)–O(12) bond lengths of 2.31(2) and 2.29(2) Å, which are much longer than the Rh–N distances to the second bridging donor atoms N(11) and N(21) (1.99(2) Å, 1.98(2) Å). The Rh–N1–C2 angles of 134(2) and 132(2)° are much larger than the idealised 120° trigonal planar angle and the Rh–N1–C9 angles of 107(2) and 104(2)° are much smaller. Chelate ring formation also produces a marked narrowing of the exocyclic ligand angle N1–C9–N8 from 117.3(4)° in $[H_2mphonp]Cl$ [9] to an average value of only 110(2)° in **2**. As a result, the average N1···N8 distance of 2.19(3) Å in **2** is 0.13 Å shorter than the analogous distance in the dirhodium(I) complex **1**. Despite the severe distortion of the bridging O2,N1 coordination mode necessary in **2** to enable a weak axial N8–Rh interaction, the Rh–Rh–N8 angles of 141.7(4) and 142.8(5)° still deviate in a pronounced fashion from the ideal axial angle of 180°. The inclination of the bridging mphonp$^-$ ligands and the relative shortening of the Rh–Rh distance from 2.883(4) to 2.566(3) Å also cause a dramatic narrowing of the Rh–O2–C2 angles from 130(2) and 128(2)° in **1** to 118(1) and 112(2)° in **2**. The above considerations lead to a description of the coordination mode in **2** as μ-1κO^2:2$\kappa^2 N^1$,N^8, a bridging pattern previously observed

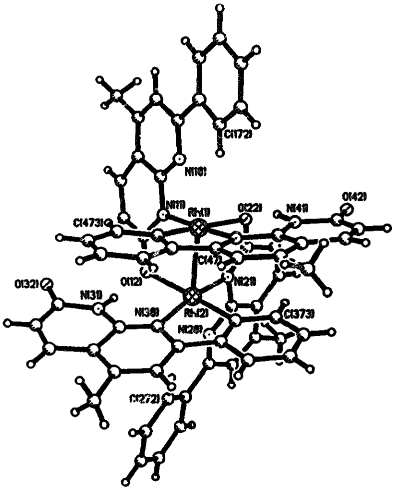

Fig. 3. Molecular structure of $[Rh_2(mphonp)_4]$ (**2**). Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.566(3), Rh(1)–N(11) 1.99(2), Rh(2)–N(21) 1.98(2), Rh(1)–O(22) 2.31(2), Rh(2)–O(12) 2.29(2), Rh(1)–N(48) 2.08(2), Rh(2)–N(38) 2.05(2), Rh(1)–C(472) 1.97(2), Rh(2)–C(372) 1.98(2); Rh(2)–Rh(1)–N(11) 84.0(6), Rh(1)–Rh(2)–N(21) 83.4(6), Rh(2)–Rh(1)–N(18) 141.7(4), Rh(1)–Rh(2)–N(21) 83.4(6), Rh(2)–Rh(1)–N(18) 141.7(4), Rh(1)–Rh(2)–N(28) 142.8(5), Rh(2)–Rh(1)–O(22) 85.3(6), Rh(1)–Rh(2)–O(12) 86.5(4), N(11)–Rh(1)–N(18) 57.9(8), N(21)–Rh(2)–N(28) 59.8(8).

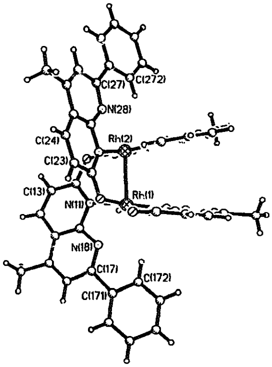

Fig. 4. Projection of the structure of **2** parallel to the planes of the chelating mphonp$^-$ ligands.

in *cis*-$[Ru_2(mbznnp)_2(CO)_4]$ (Hmbznnp = 2-benzylamino-7-methyl-1,8-naphthyridine) [10]. It is apparent from Fig. 3 that severe steric crowding of the 7-phenyl substituents would prevent not only the formation of an exclusively N1,N8 bridged isomer $[Rh_2(mphonp)_4]$ but also of both *cis* and *trans* isomers with four O2,N1 bridging mphonp$^-$ anions.

The twist angles O(12)–Rh(1)–Rh(2)–N(11) and O(22)–Rh(1)–Rh(2)–N(21) (−8.3, −7.0°) for the bridging ligands in **2** are somewhat narrower than for the analogous angles between the chelating mphonp$^-$ anions (−9.9, −12.7°). As a result of the bonding Rh(1)–Rh(2) distance of 2.566(3) Å, a number of short intermolecular interactions cannot be avoided between atoms of the chelating ligands, as evidenced by the N(38)···C(472) and N(48)···C(372) distances of 3.20 and 3.10 Å. However the relative tilting of the square planar coordination spheres of the metal atoms at an interplanar angle of 17.6(4)° means that the effectively planar chelating aromatic systems are inclined away from one another (15.4(4)°) as depicted in Fig. 4. Dihedral angles of 4.3(3) and 6.3(4)° are observed between the 7-phenyl rings and the bicyclic naphthyridine skeletons for the chelating mphonp$^-$ anions. The respective angles are 5.2(3) and 14.0(3)° for the bridging ligands.

Treatment of $[Rh_2(OAc)_4(CH_3OH)_2]$ with monp$^-$ in aqueous solution affords the fully substituted dinuclear complex $[Rh_2(monp)_4]$ (**3**). This compound also exhibits two sets of proton resonances in a 1:1 ratio, as was observed for **3**. However, the presence of the less bulky methyl groups as 7-substituents in the monp$^-$ anions means that a bridging N1,N8 mode must be taken into consideration for two of the ligands in **3**. Indeed, this coordination pattern which was previously established for $[Ru_2(monp)_4]$ [8], should be electronically favoured for M_2^{4+} cores with occupied antibonding orbitals (e.g. Ru_2^{4+}, Rh_2^{4+}), as it will enhance the interaction between the δ^* orbital of the dimetal core and the π^* molecular orbitals of the bridging aromatic anions [9]. The μ-1κO^2:2$\kappa^2 N^1$,N^8 mode as observed in **2** and N1,N8 chelating mode as in $[Ru(napy)_4]Cl_2$ [22] must also be considered for complex **3**. An unequivocal assignment of the coordination modes of the two differing ligand pairs is not possible on the basis of the spectroscopic data.

4. Supplementary material

Full details of the crystal structure analyses may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen by citing the deposition numbers CSD-404799 and CSD-404800, the authors and the journal reference.

Acknowledgements

The authors thank the Fonds der Chemischen Industrie for support and Degussa AG, Hanau for a gift of $RhCl_3 \cdot 3H_2O$.

References

[1] A.M. Manotti Lanfredi, A. Tiripicchio, R. Usón, L.A. Oro, M.A. Ciriano and B.E. Villaroya, *Inorg. Chim. Acta, 88* (1984) L9.
[2] M. Grassi, G. DeMunno, F. Nicolo and S. Lo Schiavo, *J. Chem. Soc., Dalton Trans.*, (1992) 2367.
[3] A. Tiripicchio, F.J. Lahoz, L.A. Oro, M.A. Ciriano and B.E. Villaroya, *Inorg. Chim. Acta, 111* (1986) L1.
[4] W.R. Tikkanen, E. Binamira-Soriaga, W.C. Kaska and P.C. Ford, *Inorg. Chem., 23* (1984) 141.
[5] S. Lo Schiavo, M.S. Sinicropi, G. Tresoldi, C.G. Arena and P. Piraino, *J. Chem. Soc., Dalton Trans.*, (1994) 1517.
[6] W.R. Tikkanen, E. Binamira-Soriaga, W.C. Kaska and P.C. Ford, *Inorg. Chem., 22* (1983) 1147.
[7] (a) E. Binamira-Soriaga, N.L. Keder and W.C. Kaska, *Inorg. Chem., 29* (1990) 3167; (b) J.-P. Collin, A. Jouati, J.-P. Sauvage, W.C. Kaska, M.A. McLoughlin, N.L. Keder, W.T.A. Harrison and G.D. Stucky, *Inorg. Chem., 29* (1990) 2238.
[8] W.S. Sheldrick and M. Mintert, *Inorg. Chim. Acta, 219* (1994) 23.
[9] M. Mintert and W.S. Sheldrick, *Inorg. Chim. Acta, 236* (1995) 13.
[10] M. Mintert and W.S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1995) 2663.
[11] (a) E.V. Brown, *J. Org. Chem., 30* (1965) 1607; (b) M. Wozniak and M. Skiba, *Pol. J. Chem., 55* (1981) 2429.
[12] J.A. McCleverty and G. Wilkinson, *Inorg. Synth., 8* (1966) 211.
[13] G.A. Rempel, P. Legzdins, H. Smith and G. Wilkinson, *Inorg. Synth., 13* (1972) 90.
[14] M.A. Ciriano, B.E. Villaroya, L.A. Oro, M.C. Apreda, C. Foces-Foces and F.H. Cano, *J. Organomet. Chem., 366* (1989) 377.
[15] A. Tiripicchio, M. Tiripicchio-Camellini, R. Usón, M.A. Ciriano and F. Viguri, *J. Chem. Soc., Dalton Trans.*, (1984) 125.
[16] F.A. Cotton and R.A. Walton, in *Multiple Bonds between Metal Atoms*, Clarendon, Oxford, 2nd edn., 1993, pp. 400–415.
[17] M. Mintert, *Ph.D. Thesis*, Ruhr-Universität Bochum, 1995.
[18] H.J. McCarthy and D.A. Tocher, *Polyhedron, 8* (1989) 1117.
[19] T. Glowiak, H. Pasternik and F. Pruchnik, *Acta Crystallogr., Sect. C, 43* (1987) 1036.
[20] M. Calligaris, L. Campana, G. Mestroni, M. Tornatore and E. Alessio, *Inorg. Chim. Acta, 127* (1987) 103.
[21] F.A. Cotton and T.R. Felthouse, *Inorg. Chem., 20* (1981) 584.
[22] M. Mintert and W.S. Sheldrick, unpublished results.