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New Rhodium(I) Complexes with the Bridging 1,8-Naphthyridine-2-one Ligand

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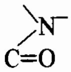
The preparation of dinuclear rhodium(I) complexes with bridging ligands, that can hold together two metal atoms in close proximity, is currently receiving a great deal of attention [1, 2]. We report here the preparation of di- or trinuclear rhodium complexes with the anionic form of the 1,8-naphthyridine-2(1H)-one ligand (tautomer with 2-hydroxy-1,8-naphthyridine) [3]. This uncommon ligand was selected due to the ability of the parent 1,8-naphthyridine ligand (napy) to bridge two rhodium atoms at 2.916(3) Å in the cationic complex $[Rh_2(\mu\text{-napy})_2(NBD)_2]^{2+}$ [4], and to the presence of the potential amido donor



group, having no β-hydrogens in order to avoid decomposition via β-elimination [5, 6].

Our primary purpose using this type of ligand is to supply new electronic and steric environments that can provide some degree of rhodium–rhodium interaction.

The compounds $[RhCl(diolefin)]_2$ [diolefin = norbornadiene (NBD) and tetrafluorobenzobarrelene (TFB)] react with 1,8-naphthyridine-2(1H)-one and potassium hydroxide in methanol giving red-purple solutions. From them, air-stable dark-red or orange solids of formula $Rh_2(\mu\text{-Onapy})_2(diolefin)_2$ were isolated after working up. These compounds crystallize with molecules of solvent and have been identified by elemental analysis, molecular weight measurements, IR and NMR spectroscopy.

Bubbling of carbon monoxide through a dichloromethane solution of $Rh_2(\mu\text{-Onapy})_2(NBD)_2$ leads to the formation of $Rh_2(\mu\text{-Onapy})_2(CO)_4$, which is isolated as a violet solid and identified by standard analytical and spectroscopic techniques. The IR spectrum of the carbonyl complex in dichloromethane shows three absorptions at 2085(s), 2056(m) and 2017(s) cm^{-1}, indicative of a *cis*-disposition of the carbonyl groups at each rhodium center. On the other hand, the electronic spectra of the above mentioned diolefin or carbonyl dinuclear complexes exhibit a strong band in the visible region in the range 545–510 nm, suggesting a close proximity of the rhodium atoms [7, 8]. In particular, the carbonyl complex $Rh_2(\mu\text{-Onapy})_2(CO)_4 \cdot \frac{1}{2}H_2O$ was further characterized by a single-crystal X-ray diffraction study. Crystal data. $C_{20}H_{10}N_4O_6Rh_2 \cdot \frac{1}{2}H_2O$, M 1234.28, monoclinic, space group *C2/c*, *a* 33.910(9), *b* 8.859(2), *c* 16.279(4) Å, β 113.65(2)°, *V* 4480(2) Å^3, *Z* = 8, D_c 1.830 g cm^{-3}, *F*(000) 2408, $\mu(Cu\text{-}K_\alpha)$ 126.08 cm^{-1}. Final *R* value: 0.076 for 3281 observed reflections $(I \geqslant 2\sigma(I))$ of 4171 independent measured $(3 \leqslant \theta \leqslant 70°)$ on a Siemens AED diffractometer using the Ni-filtered Cu-K_α radiation. The structure was solved by Patterson and Fourier methods and refined by

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.'s in Parentheses for the Non-hydrogen Atoms.

	x/a	y/b	z/c
Rh(1)	1055(1)	−251(1)	1251(1)
Rh(2)	959(1)	2639(1)	381(1)
O(1)	215(4)	−290(15)	1387(11)
O(2)	738(4)	−2255(14)	−372(8)
O(3)	27(3)	3276(16)	−220(9)
O(4)	785(4)	1276(16)	−1395(7)
O(5)	1602(4)	4857(12)	559(8)
O(6)	1578(3)	−1005(11)	3076(7)
N(1)	1638(3)	2310(12)	846(7)
N(2)	1674(3)	−229(11)	1217(6)
N(3)	1304(3)	1200(11)	2360(6)
N(4)	1075(3)	3491(11)	1665(7)
C(1)	526(4)	−269(15)	1331(10)
C(2)	853(5)	−1543(16)	236(10)
C(3)	383(7)	3022(18)	1(10)
C(4)	860(4)	1842(19)	−754(8)
C(5)	1866(4)	1030(15)	1104(7)
C(6)	1831(5)	3684(17)	782(9)
C(7)	2293(5)	3647(20)	988(10)
C(8)	2506(5)	2403(21)	1169(10)
C(9)	2307(4)	1007(18)	1264(9)
C(10)	2536(6)	−377(22)	1533(13)
C(11)	2316(6)	−1651(20)	1602(13)
C(12)	1886(5)	−1535(16)	1418(9)
C(13)	1258(3)	2682(12)	2427(7)
C(14)	1528(4)	353(14)	3148(8)
C(15)	1673(5)	1157(17)	4023(9)
C(16)	1603(4)	2594(14)	4099(9)
C(17)	1389(4)	3440(14)	3280(8)
C(18)	1304(5)	5014(14)	3294(10)
C(19)	1129(5)	5793(14)	2467(10)
C(20)	1016(5)	5026(14)	1718(10)
O	0	−3936(18)	2500

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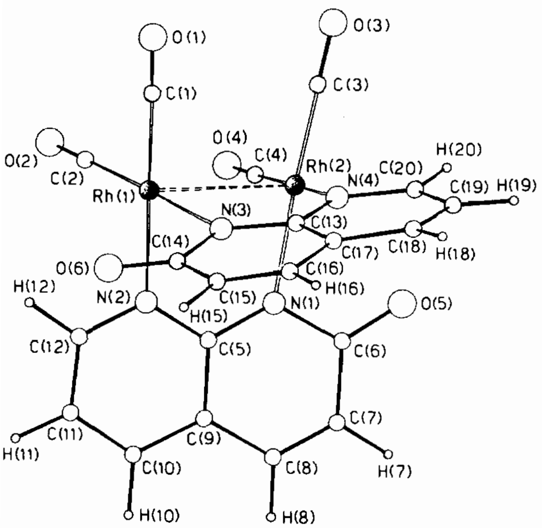

Fig. 1. View of the complex $[Rh_2(\mu\text{-Onapy})_2(CO)_4]$ with the atomic numbering scheme. Important bond distances (Å): Rh(1)–C(1) 1.850(16), Rh(1)–C(2) 1.898(15), Rh(1)–N(2) 2.122(12), Rh(1)–N(3) 2.098(9), N(1)–C(6) 1.41(2), C(6)–C(7) 1.46(2), C(7)–C(8) 1.29(2), C(8)–C(9) 1.45(2), N(1)–C(5) 1.34(2), C(5)–C(9) 1.41(2), N(2)–C(5) 1.34(2), N(2)–C(12) 1.33(2), C(11)–C(12) 1.37(3), C(10)–C(11) 1.38(3), C(9)–C(10) 1.42(2), C(6)–O(5) 1.26(2); Rh(2)–C(3) 1.829(18), Rh(2)–C(4) 1.878(14), Rh(2)–N(1) 2.136(10), Rh(2)–N(4) 2.106(11), N(3)–C(14) 1.42(1), C(14)–C(15) 1.49(2), C(15)–C(16) 1.31(2), C(16)–C(17) 1.45(2), N(3)–C(13) 1.33(1), C(13)–C(17) 1.44(2), N(4)–C(20) 1.38(2), N(4)–C(13) 1.35(1), C(19)–C(20) 1.31(2), C(18)–C(19) 1.41(2), C(17)–C(18) 1.43(2), C(14)–O(6) 1.23(2).

full matrix least squares, first with isotropic and then anisotropic thermal parameters for all non-hydrogen atoms, which were introduced at the calculated positions in the last structure factor calculation. The final atomic coordinates for the non-hydrogen atoms are given in Table I. Thermal parameters and a list of structure factors are available from the authors on request.

The structure of complex $[Rh_2(\mu\text{-Onapy})_2(CO)_4]$ is shown in Fig. 1 together with the most important bond parameters. The complex is binuclear with two Onapy ligands bridging the two metals through the nitrogen atoms, the square planar coordination around each Rh atom being completed by two carbon atoms from terminal carbonyl groups. The Onapy ligands are roughly planar and nearly perpendicular to one another (the dihedral angle between the mean planes passing through them is 81.5(3)°). The distance between the bridged Rh atoms is rather short, 2.880(2) Å, and is comparable with the one found [2.916(3) Å [4]] in the cationic binuclear complex $[Rh_2(\mu\text{-napy})_2(NBD)_2]^{2+}$ with the similar but neutral 1,8-naphthyridine bridging ligand. This separation is generally considered indicative of the presence of a metal–metal interaction even if, as in the present case, the deviation of the metal from the square coordination plane towards the other metal is not significant. The packing of the complexes and of the water molecules is determined by normal van der Waals contacts, no hydrogen bond being involved.

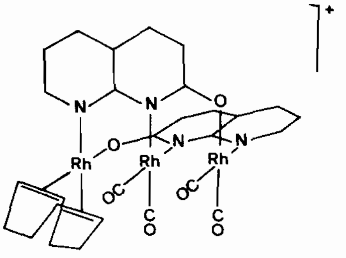

Fig. 2. Possible structure of $[Rh_3(\mu\text{-Onapy})_2(CO)_4(COD)]^+$.

The above-mentioned dinuclear complex still has two non-coordinated oxygen atoms, one from each bridging ligand. Thus, the complex $Rh_2(\mu\text{-Onapy})_2(CO)_4$ reacts with $[Rh(COD)(Me_2CO)_x]\text{-}ClO_4$ (COD: 1,5-cyclooctadiene) affording a new cationic dark-blue complex analyzing as $[Rh_3(\mu\text{-Onapy})_2(CO)_4(COD)]ClO_4$. This behaves as a 1:1 electrolyte in nitromethane solutions and presents ν(CO) absorptions at 2097(s), 2080(vs), 2035(s) and 2025(vs) cm^{-1} (in CH_2Cl_2), as well as characteristic bands of uncoordinated perchlorate anion (nujol). A possible structure consistent with all these data is shown in Fig. 2. Recently trinuclear rhodium complexes with the bis[(diphenylphosphino)methyl]-phenylphosphine ligand have been reported [9].

Further work in this area is in progress.

References

1 R. P. Hughes, in G. Wilkinson, F. G. A. Stone and E. W. Abel (Eds.), 'Comprehensive Organometallic Chemistry', Pergamon Press, Oxford, 1982, vol. 5, p. 277, and refs. therein.

2 R. J. Puddephatt, *Chem. Soc. Rev., 12,* 99 (1983) and refs. therein.

3 W. Roszkiewicz and M. Wozniak, *Synthesis,* 691 (1976).

4 A. Tiripicchio, M. Tiripicchio Camellini, R. Usón, L. A. Oro, M. A. Ciriano and F. Viguri, *J. Chem. Soc., Dalton Trans.,* 125 (1984).

5 B. Cetinkaya, M. F. Lappert and S. Torroni, *J. Chem. Soc., Chem. Commun.,* 843 (1979).

6 M. D. Fryzuk and P. A. MacNeil, *Organometallics, 2,* 355 (1983).

7 A. L. Balch and B. Tulyathan, *Inorg. Chem., 16,* 2840 (1977).

8 A. L. Balch and R. D. Cooper, *J. Organometal. Chem., 169,* 97 (1979).

9 M. M. Olmstead, R. R. Guimerans and A. L. Balch, *Inorg. Chem., 22,* 2474 (1983) and ref. therein.