Amides of Rhodium and Iridium Derived from 2-Aminothiophenol and Diaminonaphthalene: X-ray Crystal Structure of $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$

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Abstract

The synthesis of the dinuclear $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2$ ($2\text{-}(NH_2)(SH)C_6H_4$ = 2-aminothiophenol; cod = 1,5-cyclooctadiene) complexes is described. The carbonyl compounds $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(CO)_2(PPh_3)_2$, $Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$, $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$, $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$, ($(NH_2)_2C_{10}H_6$ = diaminonaphthalene) are obtained by carbonylation of the 1,5-cyclooctadiene derivatives. $Rh_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_4$ has been characterized by X-ray diffraction: monoclinic, space group $I2/a$, $a = 13.5748(11)$, $b = 8.8092(5)$, $c = 12.7360(9)$ Å, $\beta = 98.640(6)°$; $Z = 4$; $D = 2.09$ g cm^{-3}. The structure was solved by Patterson and difference direct methods and refined to conventional agreement factors equal to 0.054. The complex presents a square planar coordination around the rhodium atom, with a N–Rh–N angle of 75.7(3)° and a Rh–Rh distance of 2.810(1) Å.

Introduction

There has been recent interest in complexes containing amido groups [1]. Several amide rhodium and iridium complexes have been made by reaction of the lithium amide salt with a metal chloride compound [2–5], by oxidative addition of an N–H bond to the metal [6–8] or by indirect procedures [9–13]. The stability of the M–N bond in most of these compounds is conferred by the presence of withdrawing electron groups attached to the nitrogen [14]. Recently we reported [15, 16] the preparation of stable dinuclear amide rhodium and iridium complexes containing deprotonated diaminonaphthalene $[(NH)_2C_{10}H_6]^{2-}$, in which the two amide centers are bound to the metals in both a bridging and chelating manner. This paper describes the preparation of a number of new rhodium and iridium amide complexes derived from diaminonaphthalene and 2-aminothiophenol. We also report the characterization of $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$ by single-crystal X-ray diffraction.

Experimental

All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques. $[Rh(\mu\text{-}OMe)(cod)]_2$ [17], $Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(cod)_2$ [16] and $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(cod)_2$ [16] were prepared as previously reported. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer.

$Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2$

$[Rh(\mu\text{-}OMe)(cod)]_2$ (200 mg, 0.41 mmol) was added to a solution of $2\text{-}(NH_2)(SH)C_6H_4$ (52 mg, 44 μl, 0.41 mmol) in diethylether. The mixture was allowed to react for 30 min at room temperature, during which time a yellow precipitate was formed. The precipitate was filtered, washed with diethylether and dried under vacuum: yield 180 mg (79%). *Anal.* Found: C, 48.0; H, 5.2; N, 2.6. Calc. for $C_{22}H_{29}NRh_2S$: C, 48.4; H, 5.3; N, 2.6%. IR: ν(N–H)(Nujol), 3340 cm^{-1}.

$Rh_2(\mu\text{-}2(NH)(S)C_6H_4)(CO)_2(PPh_3)_2$

Carbon monoxide was bubbled through a solution of $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2$ (75 mg, 0.14 mmol) in tetrahydrofuran for 20 min, and then PPh_3 (72 mg, 0.28 mmol) was added. The mixture was allowed to react for 10 min. After concentration of the solution, addition of hexane gave an orange precipitate which was filtered, washed with hexane and dried under vacuum: yield 75 mg (60%). *Anal.* Found: C, 58.5; H, 3.9; N, 1.4. Calc. for $C_{44}H_{35}NO_2P_2Rh_2S$: C, 58.1; H, 3.9; N, 1.5%. IR: ν(N–H)(Nujol), 3350 cm^{-1}; ν(C≡O) (tetrahydrofuran), 1980 and 1965 cm^{-1}.

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$Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$

Carbon monoxide was bubbled through a suspension of $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(cod)_2$ (100 mg, 0.13 mmol) in diethylether for 20 min. The solution was concentrated and then addition of hexane gave a yellow precipitate which was filtered, washed with hexane and dried under vacuum: yield 60 mg (70%). *Anal.* Found: C, 26.2; H, 1.3; N, 4.3. Calc. for $C_{14}H_8Ir_2N_2O_4$: C, 25.8; H, 1.2; N, 4.3%. IR: ν(N–H)(Nujol), 3380 and 3310 cm^{-1}; ν(C≡O)(dichloromethane), 2065, 2040 and 1990 cm^{-1}.

$Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$

Carbon monoxide was bubbled through a suspension of $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(cod)_2$ (500 mg, 0.66 mmol) in diethylether for 20 min, and then PPh_3 (347 mg, 1.32 mmol) was added. The resulting orange suspension was stirred for 15 min, after which the orange precipitate was filtered, washed with diethylether and dried under vacuum: yield 676 mg (91%). *Anal.* Found: C, 51.9; H, 3.4; N, 2.5. Calc. for $C_{48}H_{38}Ir_2N_2O_2P_2$: C, 51.4; H, 3.4; N, 2.5%. IR: ν(N–H)(Nujol), 3340 cm^{-1}; ν(C≡O)(dichloromethane), 1940 cm^{-1}.

$Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$

The complex was prepared by using the procedure described for $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$, with $Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(cod)_2$ (400 mg, 0.69 mmol) and PPh_3 (363 mg, 1.38 mmol). The yellow $Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$ complex was obtained in a 425 mg (65%) yield. *Anal.* Found: C, 61.0; H, 4.4; N, 2.8. Calc. for $C_{48}H_{38}N_2O_2P_2Rh_2$: C, 61.1; H, 4.1; N, 2.9%. IR: ν(N–H)(Nujol), 3360 cm^{-1}; ν(C≡O)(dichloromethane), 1955 cm^{-1}.

Determination and Refinement of the Structure

The orange single-crystals were obtained from a dichloromethane–pentane solution. Crystal data are listed in Table 1. The stability of the crystal was checked every 90 min and no decay was observed in the two monitored standard reflections. An empirical absorption correction was applied [18]. In the final cycles of the refinement weighting schemes were applied as to give no trends in $\langle w\Delta^2F\rangle$ *versus* $\langle F_o\rangle$ and $\langle \text{sen}\,\theta/\lambda\rangle$. Computer and programs: VAX 11/75'0, XRAY 76 System [19] and DIRDIF [20]. Scattering factors: International Tables for X-Ray Crystallography [21]. The atomic coordinates, selected bond distances and angles are displayed in Tables 2 and 3. See also 'Supplementary Material'.

TABLE 1. Crystal Data for $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$

Crystal data	
Formula	$C_{10}H_8N_2(CO)_4Rh_2$
Crystal habit	prism of regular triangular base
Crystal size (mm)	0.25 × 0.17
Symmetry	monoclinic *I2/a*
Unit cell determination	least-squares fit from 70 reflections ($\theta < 45°$)
Unit cell dimensions	a = 13.5748(11) b = 8.8092(5) c = 12.7360(9) Å β = 98.640(6)°
Packing: V (Å^3), Z	1505.73(18), 4
D_c (g cm^{-3}), M, F(000)	2.091, 474.0, 912
μ (cm^{-1})	183.37
Experimental data	
Technique	four circle diffractometer bisecting geometry graphite oriented monochromator: Cu Kα $\omega/2\theta$ scans, scan width 1.5° detector apertures 1.0 × 1.0°
Total measurements	up 65° in θ
Speed	1 min/reflection
No. reflections	
measured	1283
independent	1283
observed	1201 [$3\sigma(I)$ criterion]
Standard reflections	2 reflections every 90 min variation: no
Max–min transmission factors	1.534–0.394
R values before and after absorption correction	0.171–0.073
Solution and refinement	
Solution	Patterson function and DIRDIF
Refinement	L.S. on Fobs with 1 block
Parameters	
no. variables	117
degrees freedom	1084
ratio freedom	10.3
H atoms	difference synthesis
Final shift/error	0.13
Final ΔF peaks	1.01 e A^{-3}
Final R and R_w	0.054–0.068
Computer and programs	VAX 11/750 XRAY76 System [19], DIRDIF [20],
Scattering factors	International Tables for X-Ray Crystallography [21]

Results and Discussion

Reaction of $[Rh(\mu\text{-}OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) with 2-aminothiophenol ($2\text{-}(NH_2)(SH)C_6H_4$) leads to the formation of the dinuclear $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2$ compound, according to the following equation

$$[Rh(\mu\text{-}OMe)(cod)]_2 + 2\text{-}(NH_2)(SH)C_6H_4 \longrightarrow Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2 + 2MeOH$$

Elemental analysis (see 'Experimental') is in agreement with the proposed formulation. The infrared spectrum of $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2$ shows only one ν(N–H) signal at 3340 cm^{-1}, no bands assignable to ν(S–H) are observed. These data support a dinuclear structure in which the ligand is bridging the two Rh(cod) units by the amido and thiolate groups, similar to that previously reported for the complexes containing the diaminonaphthalene ligand [16]. The low stability of the compound has prevented molecular weight measurements; the dinuclear nature of the complex is confirmed by the infrared spectrum of the carbonyl derivative.

Treatment of $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(cod)_2$ with carbon monoxide in tetrahydrofuran gives an air-sensitive red solution, which presents in the infrared spectra four carbonyl bands at 2070, 2050, 1996 and 1988 cm^{-1} indicative of the formation of the dinuclear $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(CO)_4$ species (C_s symmetry). By addition of PPh_3 to this solution, the $Rh_2(\mu\text{-}2\text{-}(NH)(S)C_6H_4)(CO)_2(PPh_3)_2$ compound is formed. This complex has been isolated, after concentration of the solution and addition of hexane, as an orange powder. Formulation of the complex is deduced by elemental analyses and infrared spectra (two carbonyl bands at 1980 and 1965 cm^{-1}, tetrahydrofuran solution).

We have extended the preparation of dinuclear carbonyl complexes containing the diamidonaphthalene ligand [16]. $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$ has been synthesized by displacement of the diolefin in $Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(cod)_2$ with carbon monoxide. Carbonylation of $Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(cod)_2$ in dichloromethane leads to a solution containing $Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(CO)_4$ as is deduced by the presence of three ν(C≡O) bands (C_{2v} symmetry) at 2074, 2050 and 1980 cm^{-1} in the infrared spectrum; the low stability of the complex has prevented further characterization. Treatment of the solutions containing the tetracarbonyl species with PPh_3 gives *trans*-$Ir_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$ and *trans*-$Rh_2(\mu\text{-}2,3\text{-}(NH)_2C_{10}H_6)(CO)_2(PPh_3)_2$ respectively. Elemental analyses and infrared data are consistent with the proposed formulation.

TABLE 2. Fractional Atomic Coordinates for $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$

Atom	x/a	y/b	z/c
Rh(1)	0.21763(4)	0.12607(7)	0.09973(5)
N(1)	0.3414(5)	0.2265(9)	0.0462(6)
C(11)	0.3364(7)	0.3868(10)	0.0449(7)
C(12)	0.4203(8)	0.4673(14)	0.0922(9)
C(13)	0.4182(11)	0.6270(14)	0.0931(10)
C(14)	0.3368(11)	0.7063(13)	0.0464(10)
C(15)	0.2500	0.6271(16)	0.0000
C(16)	0.2500	0.4652(15)	0.0000
C(1)	0.0994(8)	0.0374(12)	0.1267(8)
O(1)	0.0274(6)	−0.0181(11)	0.1404(7)
C(2)	0.2904(8)	0.0357(13)	0.2192(8)
O(2)	0.3358(7)	−0.0253(13)	0.2871(6)

X-ray Crystal Structure of $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$

To further characterize the carbonyl $M(\mu\text{-}(NH)_2C_{10}H_6)(CO)_4$ complexes we have determined the

TABLE 3. Selected Bond Distances (Å) and Angles (°) for $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$ [a]

Rh(1)–Rh(1i)	2.8100(9)	Rh(1)–N(1)	2.101(8)
Rh(1)–C(1)	1.862(11)	Rh(1)–C(2)	1.864(10)
N(11)–C(11)	1.414(12)	Rh(1)–N(1i)	2.106(7)
N(1)–N(1i)	2.582(10)		
C(1)–Rh(1)–C(2)	92.1(5)	C(1)–Rh(1)–N(1i)	96.6(4)
N(1i)–Rh(1)–N(1)	75.7(3)	N(1)–Rh(1)–C(2)	95.3(4)
Rh(1)–N(1)–Rh(1i)	83.8(3)	Rh(1)–N(1)–C(11)	112.6(6)
Rh(1i)–N(1)–C(11)	113.5(5)		

Selected least-square planes or lines. Deviations (Å) in brackets.

(i) N(1), N(1i), C(1), C(2) [Rh(1): −0.068(1) C(11): −1.181(9)]
(ii) N(1), N(1i), C(1i), C(2i)
(iii) Rh(1), C(1).C(2)
(iv) Rh(1), N(1), N(1i)
(v) C(11)....C(16)

Planes or lines	Angles (°)
i–ii	69.1(2)
i–v	55.9(6)
ii–v	55.1(3)
iii–iv	5.4(3)

[a] i: $\frac{1}{2} - x, y, -z$.

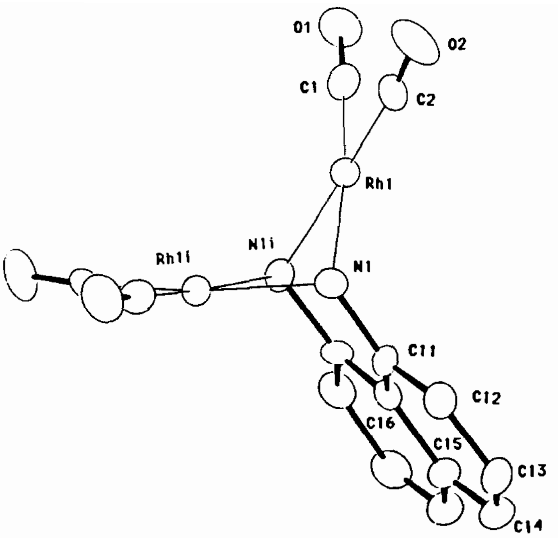

Fig. 1. Crystal structure of $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$.

crystal structure of the previously reported $Rh_2(\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6)(CO)_4$ [16]. The complex presents a square-planar coordination around the rhodium atom (see Fig. 1) [22], the deviation of the rhodium from the coordination plane (N, N, C, C) is 0.068(1) Å towards the $(NH)_2C_{10}H_6$ group. Half of the molecule is related to the other part by a crystallographic binary axis along the C(15)–C(16) bond. The small N–Rh–N angle (75.7(3)°) is most likely imposed by the chelating nature of the ligand. The Rh–N bond lengths (2.101(8) and 2.106(7) Å) are similar to those found in other amido complexes [3, 10, 15]. The intermetallic Rh–Rh distance is 2.810(1) Å and lies in the upper part of the range of distances (2.62–2.84 Å) observed for other rhodium dimers where a single bond is thought to exist [23–25].

Supplementary Material

Tables of hydrogen parameters, thermal factors and structure factors are available from the authors.

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References

1 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, West Sussex, U.K., 1980.
2 M. D. Fryzuk and P. A. MacNeil, *Organometallics, 2* (1983) 355.
3 M. D. Fryzuk, P. A. MacNeil and S. J. Rettig, *Organometallics, 5* (1986) 2469.
4 P. R. Sharp and Y-W. Ge, *J. Am. Chem. Soc., 109* (1987) 3796.
5 F. J. Lahoz, F. Viguri, M. A. Ciriano, L. A. Oro, C. Foces-Foces and F. H. Cano, *Inorg. Chim. Acta, 128* (1987) 119.
6 S. Park, D. Hedden and D. M. Roundhill, *Organometallics, 5* (1986) 2151.
7 D. Hedden and D. M. Roundhill, *Inorg. Chem., 25* (1986) 9.
8 A. L. Casalnuovo, J. C. Calabrese and D. Milstein, *Inorg. Chem., 26* (1987) 973.
9 A. Nutton and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.,* (1981) 2339.
10 G. J. Organ, M. K. Cooper, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.,* (1984) 2377.
11 R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, *J. Chem. Soc., Chem. Commun.,* (1986) 1622.
12 S. T. McKenna, R. A. Andersen and E. L. Muetterties, *Organometallics, 5* (1986) 2233.
13 S. T. McKenna and E. L. Muetterties, *Inorg. Chem., 26* (1987) 1296.
14 S. W. Buckner and B. J. Freiser, *J. Am. Chem. Soc., 109* (1987) 4715.
15 L. A. Oro, M. J. Fernández, J. Modrego, C. Foces-Foces and F. H. Cano, *Angew. Chem., Int. Ed. Engl., 23* (1984) 913.
16 L. A. Oro, M. J. Fernández, J. Modrego and J. M. López, *J. Organomet. Chem., 287* (1985) 409.
17 R. Usón, L. A. Oro and J. A. Cabeza, *Inorg. Synth., 23* (1985) 126.
18 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
19 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, *The X-ray System, Technical Report TR-446,* Computer Science Center, University of Maryland, College Park, MD, 1976.
20 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, E. M. van der Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, V. Parthasarathi, H. J. Bruins Slot and R. C. Haltiwanser, *Dirdif System,* Crystallography Laboratory, Toocrnooivel, Nijmegen, The Netherlands, 1983.
21 *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
22 C. K. Johnson, *ORTEP, Report ORNL-3794,* Oak Ridge National Laboratory, TN, 1965.
23 M. Cowie and S. K. Dwight, *Inorg. Chem., 19* (1980) 209.
24 S-K. Kang, T. A. Albright, T. C. Wright and R. A. Jones, *Organometallics, 4* (1985) 666.
25 T. S. Targos, G. L. Geoffroy and A. L. Rheingold, *Organometallics, 5* (1986) 12.