*Journal of Organometallic Chemistry*, 312 (1986) 249–262
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# OLEFIN LIGANDS. SYNTHESES AND STRUCTURES OF 2,6-DIALLYLPYRIDINE (DAP) COMPLEXES OF RHODIUM(I); CRYSTAL STRUCTURES OF [Rh(COD)(DAP)][$RhCl_2$(COD)] AND [Rh(COD)(DAP)][$CuCl_2$]

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(Received April 4th, 1986)

## Summary

The olefinic ligand 2,6-diallylpyridine (DAP) has been shown to react with various rhodium(I) compounds to give complexes of the type $[RhCl(DAP)]_n$, RhCl(L)(DAP) (L = CO, $PPh_3$), [Rh(diene)(DAP)]Y (diene = cycloocta-1,5-diene (COD), bicyclo[2.2.1]hepta-2,5-diene (NBD); Y = [$RhCl_2$(diene)], [$CuCl_2$], $ClO_4$). These complexes have been characterised by chemical and spectroscopic means. In addition, the crystal structures of [Rh(COD)(DAP)][$RhCl_2$(COD)] (**1**) and [Rh(COD)(DAP)][$CuCl_2$] (**2**) have been determined by X-ray methods. Crystals of **1** are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a$ 10.481(4), $b$ 13.041(4), $c$ 10.456(4) Å, $\alpha$ 106.77(2), $\beta$ 112.10(2), $\gamma$ 79.57(1)°. Crystals of **2** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimension $a$ 14.303(8), $b$ 10.453(5), $c$ 13.412(6) Å, $\beta$ 110.95(4)°. Both structures were solved from diffractometer data by direct and Fourier methods and refined by blocked full-matrix least-squares to $R = 0.0316$ (2204 observed reflections) for **1** and by full matrix least-squares to $R = 0.0545$ (1897 observed reflections) for **2**. The crystals consist of cationic $[Rh(COD)(DAP)]^+$ and anionic $[Rh(COD)Cl_2]^-$ (**1**) and $[CuCl_2]^-$ (**2**) complexes. The cations are similar in the two compounds, and the coordination around the $Rh^I$ atoms can be described as trigonal bipyramidal, with a "short" Rh–N axial bond and four $\eta^2$-C=C olefinic interactions. The DAP acts as a tridentate ligand.

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0022-328X/86/$03.50 

## Introduction

Much research has been directed toward the synthesis, characterization, reactions, and catalytic properties of transition metal complexes since catalysis of hydrogenation of olefins by the Wilkinson catalyst $RhCl(PPh_3)_3$ was first reported [1]. In recent years, several transition metal complexes with multidentate ligands possessing different types of donor atoms have been synthesized, and their catalytic abilities in homogeneous hydrogenation, isomerization and hydroformylation reactions investigated [2].

We describe here the synthesis and characterization of some rhodium(I) complexes containing the tridentate ligand 2,6-diallylpyridine (DAP), of formula $[RhCl(DAP)]_n$, RhCl(L)(DAP) (L = CO, $PPh_3$), [Rh(dien)(DAP)]Y (dien = cycloocta-1,5-diene (COD), bicyclo[2.2.1]hepta-2,5-diene (NBD); Y = $ClO_4$, [$RhCl_2$(COD)], [$CuCl_2$]), together with the X-ray structure determination of [Rh(COD)(DAP)]Y (Y = [$RhCl_2$(COD)], [$CuCl_2$]).

## Results and discussion

The potentially tridentate ligand 2,6-diallylpyridine, DAP, reacts with $[RhCl(COD)]_2$ in benzene solution to give yellow crystals whose infrared spectra show absorption bands in the 1500–1650 $cm^{-1}$ region, assignable to the olefinic ligands (Table 2). The elemental analysis of the product (Table 1) is consistent with the empirical formula $Rh_2Cl_2(COD)_2(DAP)$, and the conductivity measurements in MeCN ($\Lambda_M$ 126 $ohm^{-1}$ $mol^{-1}$ $cm^2$) suggest for the compound the ionic formulation [Rh(COD)(DAP)][$RhCl_2$(COD)] (complex **1**), and an X-ray analysis (see below) confirmed this interpretation. Treatment of this compound with a benzene solution of $CuCl(SMe_2)$ gave the ionic [Rh(COD)(DAP)][$CuCl_2$] (complex **2**).

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

| Compound | Colour | M.p. (°C) | Analysis (Found (calcd.) (%) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | N | Cl |
| $[RhCl(DAP)]_n$ | orange | 210–215 | 43.98 (44.40) | 4.49 (4.40) | 4.63 (4.71) | 11.66 (11.91) |
| [Rh(COD)(DAP)][$RhCl_2$(COD)] | yellow | 134–135 | 49.32 (49.71) | 5.91 (5.77) | 2.09 (2.15) | 9.91 (10.87) |
| [RhCl(NBD)(DAP)][$RhCl_2$(NBD)] | yellow | 148–150 | 46.38 (48.41) | 4.75 (4.71) | 2.14 (2.26) | 10.32 (11.4) |
| [RhCl(COD)(DAP)]$ClO_4$ | yellow | 180–185 | 47.90 (48.58) | 5.50 (5.36) | 3.10 (2.98) | 7.65 (7.55) |
| [RhCl(NBD)(DAP)]$ClO_4$ | yellow | 156 (dec.) | 47.30 (47.65) | 4.82 (4.67) | 3.19 (3.09) | 7.75 (7.81) |
| [Rh(COD)(DAP)][$CuCl_2$] | yellow | 132–135 | 42.24 (45.21) | 4.94 (4.99) | 2.73 (2.77) | 14.18 (14.05) |
| RhCl(CO)(DAP) | yellow | 100–102 | 43.76 (44.27) | 4.08 (4.02) | 4.23 (4.30) | 10.20 (10.89) |
| RhCl($PPh_3$)(DAP) [a] | yellow | 178–180 | 61.99 (62.21) | 5.05 (5.04) | 2.23 (2.50) | 6.28 (6.33) |

[a] P: found: 5.45, calcd. 5.53%.

TABLE 2

INFRARED ABSORPTIONS IN NUJOL MULLS ($cm^{-1}$)

| | $\nu$(Rh–Cl) | Other bands |
|---|---|---|
| $[RhCl(DAP)]_n$ | 315m, 250s | 3660m, 3020m, 1600m, 1555m, 1420m, 1235s, 1180sh 1170s, 1100w, 1070m, 870m, 798s, 728m |
| $[Rh(COD)(DAP)][RhCl_2(COD)]$ | 265sh, 250s | 3080m, 1609s, 1575w, 1430m, 1415w, 1385m, 1345m 1245m, 1225m, 1179s, 995m, 965s, 955m, 935m, 865w, |
| $[Rh(NBD)(DAP)][RhCl_2(NBD)]$ | 265ls | 3660w, 1600m, 1340m, 1305s, 1285m, 1270s, 1030w, 980m 970m, 880m, 815s, 780s |
| $[Rh(COD)(DAP)]ClO_4$ | | 1602s, 1570w, 1360s, 1340w, 1228s, 1178m, 1100vs, 930w, 845m, 805m, 628s |
| $[Rh(NBD)(DAP)]ClO_4$ | | 3080m, 1600m, 1310m, 1190w, 1160w, 1100vs, 1040w, 905m, 871w, 818s, 735m, 628s |
| $[Rh(COD)(DAP)][CuCl_2]$ | | 1600m, 1170m, 1095s, 1035w, 922w, 840w, 800m, 775w, 700s, 680w |
| $RhCl(PPh_3)(DAP)$ | 238s | 3080s, 1600s, 1575s, 1440s, 1420s, 1245s, 1200s, 1160s, 1095vs, 955s, 790m, 770m, 760s, 750sh, 700vs, 545s, 530s, 505s |
| RhCl(CO)(DAP) [a] | 250s | 3070m, 3040m, 3020m, 1605s, 1575w, 1430m, 1425m, 1385m, 1246w, 1180m, 1172m, 1100w, 1075w, 1045w, 1025w, 965m, 950m, 931m, 900m, 820s, 750w, 570s |

[a] $\nu$(CO) 2010 $cm^{-1}$.

In order to establish inequivocally the molecular geometry of the cation $[Rh(COD)(DAP)]^+$, X-ray crystal structure determinations were carried out on complexes **1** and **2**.

The molecular structures of the cationic complexes **1** and **2** and the anionic complex **1** with atom numbering schemes are illustrated in Figs. 1 and 2, respectively. Bond lengths and angles are listed in Table 4.

In the cation the rhodium atom is five-coordinate, with a trigonal bipyramidal arrangement. The DAP ligand acts as tridentate, with the pyridinic N in one apical position and the midpoints of the two olefin bonds occupying two equatorial positions. The COD molecule completes the coordination around $Rh^I$, with the two carbon–carbon double bonds occupying axial and equatorial positions, respectively. To our knowledge this is the first example of trigonal bipyramidal coordinated $Rh^I$ complex with four $\eta^2$-C=C bonds. The only other example of complex with four $\eta^2$-C=C bonds, namely $[RhCl(C_4H_6)]_2$, has a square pyramidal coordination around the Rh atom [3].

The Rh atoms are displaced toward the axial olefin group from the equatorial plane M(1)M(2)M(3) (defined by the C=C midpoints), by 0.190(2) and 0.184(1) Å, for **1** and **2**, respectively. The equatorial olefinic bonds are slightly tilted with respect to the above equatorial plane, C(7)=C(8) by 17.2(7), 15.9(1.0), C(10)=C(11) by 15.9(7), 15.3(1.1) and C(12)=C(13) by 8.4(5), 1.9(1.1)° (the second value refers to **2**). The cation **2** has a pseudo $C_s$ symmetry, with the pseudo-mirror plane passing through C(3)NRhM(3)M(4). In **1** the $C_s$ symmetry is maintained for the DAP molecule but not for COD, and this is reflected in the significantly different angle values of M(1)–Rh(1)–M(3) and M(2)–Rh(1)–M(3) (118.3(4) and 125.6(4)°). This different conformation of COD is best indicated by the torsion angles reported in Table 5. The Rh–C distances (2.195(12)–2.293(8) Å) are within the expected range

TABLE 3

$^1$H NMR DATA FOR THE LIGANDS AND FOR THE $Rh^I$-COMPLEXES ($\delta$ in ppm)

| Compound | Solvent | Py | DAP | | | COD | | NBD | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | =CH | $=CH_2$ | $CH_2$ | =CH | $CH_2$ | =CH | ≡CH | $CH_2$ |
| [RhCl(COD)(DAP)][$RhCl_2$(COD)] | $C_6D_6$ | 7.08(t,1)<br>6.71(d,2) | 6.12(m,2) | 5.05(m,4) | 3.55(d,4) | 4.35(s,8) | 2.10(m,8)<br>1.32(m,8) | | | |
| [Rh(COD)(DAP)][$CuCl_2$] | $CDCl_3$ | 7.52(t,1)<br>7.10(d,2) | 6.08(m,2) | 4.04(m,4) | 3.36(d,4) | 4.57(2d,2)<br>3.85(d,2) | 2.98(m,2)<br>2.48(m,4)<br>2.03(m,2) | | | |
| [Rh(COD)(DAP)]$ClO_4$ | $CDCl_3$ | 7.52(t,1)<br>7.10(d,2) | 6.08(m,2) | 4.03(m,4) | 3.35(d,4) | 4.54(2d,2)<br>3.82(d,2) | 2.96 (m,2)<br>2.46(m,4)<br>2.00(m,2) | | | |
| RhCl(CO)(DAP) | $CD_2Cl_2$ | 7.45(t,1)<br>7.00(d,2) | 4.90(m,2) | 4.01(m,4) | 3.72(d,2)<br>3.06(2d,2) | | | | | |
| RhCl($PPh_3$)(DAP) | $CD_2Cl_2$ | 7.27(t,1)<br>6.92(d,2) | 3.46(m,2) | 4.02(m,4) | 3.24(m,2)<br>2.78(d,2) | | | | | |
| [Rh(NBD)(DAP)][$RhCl_2$(NBD)] | $CDCl_3$ | 7.50(t,1)<br>7.09(d,2) | 6.72(m,2) | 5.06(m,2)<br>4.20(m,2) | 3.39(m,2)<br>3.18(d,2) | | | 3.94(d,6)<br>3.87(t,6) | | 1.39(m,2)<br>1.09(m,2) |
| [Rh(NBD)(DAP)]$ClO_4$ | $CDCl_3$ | 7.48(t,1)<br>7.06(d,2) | 6.68(m,2) | 5.01(m,2)<br>4.12(m,2) | 3.31(m,2)<br>3.18(d,2) | | | 3.90(m,6) | | 1.40(t,1)<br>1.08(t,1) |
| [RhCl(COD)]$_2$ | $CD_2Cl_2$ | | | | | 4.20(s,8) | 2.45(m,8)<br>1.71(m,8) | | | |
| [RhCl(NBD)]$_2$ | $CD_2Cl_2$ | | | | | | | 6.82(t,8) | 3.6(m,4) | 2.06(t,4) |
| DAP | $CD_2Cl_2$ | 7.51(t,1)<br>6.98(d,2) | 6.03(m,2) | 5.11(m,4) | 3.55(d,4) | | | | | |
| COD | $CD_2Cl_2$ | | | | | 5.58(s,4) | 2.37(s,8) | | | |
| NBD | $CD_2Cl_2$ | | | | | | | 6.70(m,4) | 3.52(m,2) | 2.0(t,2) |

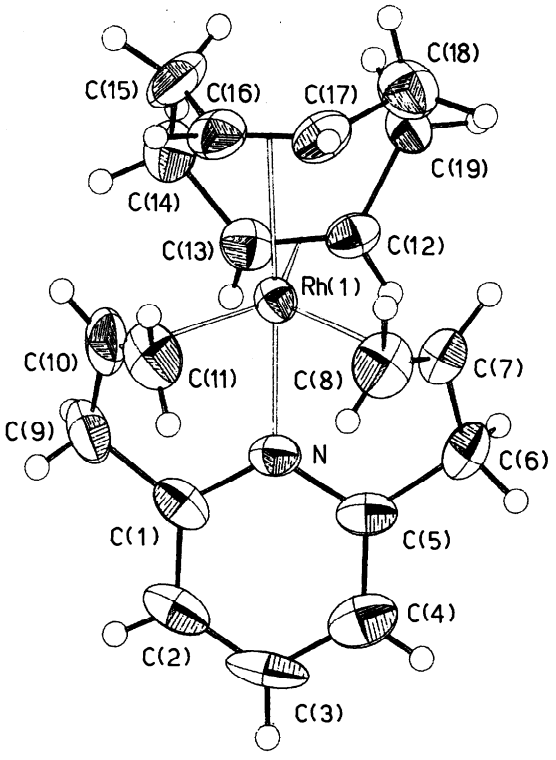



Fig. 1. Perspective view of the cationic complex **1**. Thermal parameters are drawn at the 50% probability level.

and no lengthening of the Rh–C axial distances is observed [4]. The Rh–N distances (2.027(8), 2.016(11) Å) fall within the narrow range noted in the literature [4c] for Rh complexes with at least two-bonded $\eta^2$-carbons even when complexes with $Rh^I$ square-planar coordination are included [5].

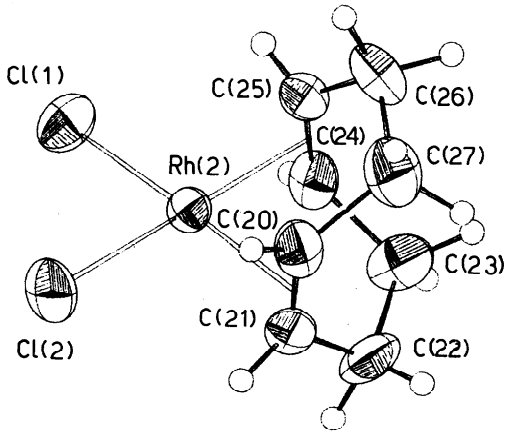



Fig. 2. Perspective view of the anionic complex **1**. Thermal parameters are drawn at the 50% probability level.

TABLE 4

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) FOR COMPOUNDS **1** AND **2** (with e.s.d.'s in parentheses) [a]

| Cation | 1 | 2 | | 1 | 2 |
|---|---|---|---|---|---|
| Rh(1)–N | 2.027(8) | 2.016(11) | C(3)–C(4) | 1.38(2) | 1.42(3) |
| Rh(1)–C(7) | 2.293(8) | 2.252(19) | C(4)–C(5) | 1.37(2) | 1.39(2) |
| Rh(1)–C(8) | 2.289(9) | 2.274(13) | C(5)–N | 1.37(1) | 1.34(2) |
| Rh(1)–C(10) | 2.203(11) | 2.219(17) | C(5)–C(6) | 1.51(1) | 1.51(3) |
| Rh(1)–C(11) | 2.201(10) | 2.237(13) | C(6)–C(7) | 1.50(2) | 1.51(2) |
| Rh(1)–C(12) | 2.230(8) | 2.195(12) | C(7)–C(8) | 1.35(1) | 1.33(2) |
| Rh(1)–C(13) | 2.205(8) | 2.215(12) | C(1)–C(9) | 1.48(1) | 1.46(2) |
| Rh(1)–C(16) | 2.217(12) | 2.237(14) | C(9)–C(10) | 1.50(2) | 1.51(2) |
| Rh(1)–C(17) | 2.229(13) | 2.223(15) | C(10)–C(11) | 1.36(2) | 1.35(2) |
| Rh(1)–M(1) | 2.190(9) | 2.162(16) | C(12)–C(13) | 1.36(1) | 1.39(2) |
| Rh(1)–M(2) | 2.095(11) | 2.123(15) | C(13)–C(14) | 1.51(1) | 1.46(3) |
| Rh(1)–M(3) | 2.111(8) | 2.094(12) | C(14)–C(15) | 1.50(2) | 1.48(2) |
| Rh(1)–M(4) | 2.116(13) | 2.116(14) | C(15)–C(16) | 1.52(1) | 1.52(2) |
| N–C(1) | 1.35(1) | 1.37(2) | C(16)–C(17) | 1.36(1) | 1.41(3) |
| C(1)–C(2) | 1.36(2) | 1.37(2) | C(17)–C(18) | 1.50(1) | 1.47(3) |
| C(2)–C(3) | 1.37(2) | 1.36(3) | C(18)–C(19) | 1.52(2) | 1.52(2) |
| M(3)–M(4) | 2.825(17) | | C(19)–C(12) | 1.52(2) | 1.47(3) |
| N–Rh(1)–M(1) | 80.0(3) | 80.9(6) | C(4)–C(5)–N | 120(1) | 121(1) |
| N–Rh(1)–M(2) | 80.5(4) | 80.7(5) | N–C(5)–C(6) | 115(1) | 116(1) |
| N–Rh(1)–M(3) | 93.6(3) | 92.8(5) | C(4)–C(5)–C(6) | 126(1) | 123(1) |
| N–Rh(1)–M(4) | 176.3(4) | 177.2(6) | C(5)–C(6)–C(7) | 111(1) | 111(1) |
| M(1)–Rh(1)–M(2) | 113.7(5) | 113.1(6) | C(6)–C(7)–C(8) | 123(1) | 123(1) |
| M(1)–Rh(1)–M(3) | 118.3(4) | 121.7(6) | N–C(1)–C(9) | 114(1) | 114(1) |
| M(2)–Rh(1)–M(3) | 125.6(4) | 122.9(6) | C(2)–C(1)–C(9) | 125(1) | 126(1) |
| M(4)–Rh(1)–M(1) | 103.7(5) | 100.9(6) | C(1)–C(9)–C(10) | 112(1) | 112(1) |
| M(4)–Rh(1)–M(2) | 98.8(5) | 100.3(6) | C(9)–C(10)–C(11) | 123(1) | 123(1) |
| M(4)–Rh(1)–M(3) | 83.9(4) | 84.4(6) | C(19)–C(12)–C(13) | 124(1) | 126(2) |
| Rh(1)–N–C(1) | 119(1) | 119(1) | C(12)–C(13)–C(14) | 125(1) | 124(1) |
| Rh(1)–N–C(5) | 121(1) | 120(1) | C(13)–C(14)–C(15) | 112(1) | 118(2) |
| C(1)–N–C(5) | 120(1) | 121(1) | C(14)–C(15)–C(16) | 116(1) | 117(1) |
| N–C(1)–C(2) | 121(1) | 119(1) | C(15)–C(16)–C(17) | 123(1) | 122(2) |
| C(1)–C(2)–C(3) | 120(1) | 122(1) | C(16)–C(17)–C(18) | 124(1) | 123(2) |
| C(2)–C(3)–C(4) | 119(1) | 119(1) | C(17)–C(18)–C(19) | 115(1) | 115(1) |
| C(3)–C(4)–C(5) | 120(1) | 118(1) | C(18)–C(19)–C(12) | 115(1) | 116(1) |

Anion **1**

| | | | | | |
|---|---|---|---|---|---|
| Rh(2)–Cl(1) | 2.395(3) | Rh(2)–Cl(2) | 2.380(2) | Rh(2)–C(20) | 2.093(8) |
| Rh(2)–C(21) | 2.070(10) | Rh(2)–C(24) | 2.105(9) | Rh(2)–C(25) | 2.069(7) |
| Rh(2)–M(5) | 1.963(9) | Rh(2)–M(6) | 1.969(8) | C(20)–C(21) | 1.39(1) |
| C(21)–C(22) | 1.52(2) | C(22)–C(23) | 1.52(1) | C(23)–C(24) | 1.50(2) |
| C(24)–C(25) | 1.38(1) | C(25)–C(26) | 1.50(1) | C(26)–C(27) | 1.51(1) |
| C(27)–C(20) | 1.52(1) | M(5)–M(6) | 2.726(11) | | |

| | | | |
|---|---|---|---|
| Cl(1)–Rh(2)–Cl(2) | 92.7(1) | Cl(1)–Rh(2)–M(5) | 173.8(3) |
| Cl(1)–Rh(2)–M(6) | 90.4(3) | Cl(2)–Rh(2)–M(5) | 89.5(3) |
| Cl(2)–Rh(2)–M(6) | 175.2(3) | M(5)–Rh(2)–M(6) | 87.8(4) |
| C(20)–C(21)–C(22) | 126.8(9) | C(21)–C(22)–C(23) | 111.3(9) |
| C(22)–C(23)–C(24) | 112.4(9) | C(23)–C(24)–C(25) | 124.1(9) |
| C(24)–C(25)–C(26) | 125.9(8) | C(25)–C(26)–C(27) | 111.8(8) |
| C(26)–C(27)–C(20) | 112.6(8) | C(27)–C(20)–C(21) | 123.6(9) |

TABLE 4 (continued)

| Anion **2** | | | |
|---|---|---|---|
| Cu(1)–Cl(1) | 2.079(3) | Cu(2)–Cl(2) | 2.106(3) |

[a] M(1), M(2), M(3), M(4), M(5), M(6) are the midpoints of C(7)=C(8), C(10)=C(11), C(12)=C(13), C(16)=C(17), C(20)=C(21), C(24)=C(25), respectively.

The $[Rh(COD)Cl_2]^-$ anion is a 16-valence electron whereas the rhodium cation is a 18-valence electron complex. The coordination geometry about Rh(2) in **1** is distorted square-planar. A least-squares plane passing through Rh(2), Cl(1), Cl(2), M(5), and M(6) (M(5) is the midpoint of C(20)–C(21) and M(6) the midpoint of C(24)–C(25)) was calculated, and showed deviations in the range 0.002(1)–0.186(9) Å, with the greatest deviation for M(5). The calculated least-square planes Rh(2)Cl(1)Cl(2) and Rh(2)M(5)M(6) form a dihedral angle of 7.0(3)°, thus showing a slight distortion from Rh(2) coordination towards the tetrahedral. The olefin bonds of COD are oriented approximately normal to the coordination plane, with each bond twisted slightly by 6.8(6) and 5.3(4)° for C(20)–C(21) and C(24)–C(25), respectively. The distances involving Rh(2) and the olefinic carbons (2.069(7)–2.105(9) Å) are significantly smaller than these in the five-coordinate Rh cationic complex. **1** is one of the rare examples of complexes containing both cationic and anionic rhodium, coordinated to COD. In **2** the $[CuCl_2]^-$ anion is perfectly linear, as shown by the crystallographic symmetry, and the Cu–Cl distances are quite normal.

The ionic perchlorate complex $[Rh(COD)(DAP)][ClO_4]$ is readily obtained by treating $[RhCl(COD)]_2$ in acetone with stoichiometric amounts of DAP and $AgClO_4$. Its infrared spectrum shows the characteristic strong absorption band of the uncoordinated perchlorate ion at 1100 $cm^{-1}$.

$[RhCl(NBD)]_2$ reacts with DAP in bezene in the same way as its COD analogue to give $[Rh(NBD)(DAP)][RhCl_2(NBD)]$ and, in the presence of silver perchlorate, to give $[Rh(NBD)(DAP)]ClO_4$.

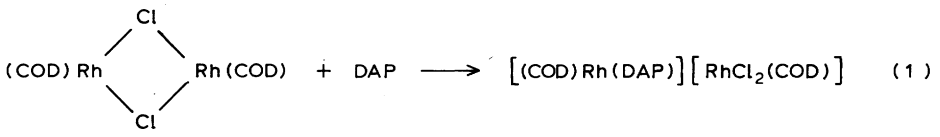
Treatment of $[RhCl(COE)_2]_2$ (COE = cyclooctene) with DAP in benzene gives a yellow-orange microcrystalline precipitate, whose elemental analysis is consistent with the formula RhCl(DAP). The very low solubility of the complex in all solvents examined prevented complete characterization, but the presence of two IR absorption bands at 315 and 250 $cm^{-1}$, in the Rh–Cl characteristic region for compounds containing bridging Cl atoms [6], suggests that in this compound the Rh atom again reaches pentacoordination through Cl bridges. Moreover, its very low solubility suggests that the compound is probably polymeric rather than dimeric.

TABLE 5

SELECTED TORSION ANGLES (°) IN CATIONS **1** AND **2**

| | **1** | **2** | | **1** | **2** |
|---|---|---|---|---|---|
| C(4)–C(5)–C(6)–C(7) | −152(1) | −156(1) | C(2)–C(1)–C(9)–C(10) | 152(1) | 154(1) |
| C(5)–C(6)–C(7)–C(8) | 46(1) | 48(2) | C(1)–C(9)–C(10)–C(11) | −43(2) | −44(2) |
| C(19)–C(12)–C(13)–C(14) | 1(2) | −2(3) | C(15)–C(16)–C(17)–C(18) | −2(2) | 4(3) |
| C(12)–C(19)–C(18)–C(17) | −22(1) | 4(2) | C(13)–C(14)–C(15)–C(16) | −26(1) | −3(2) |

The tridentate ligand DAP completely displaces the monoolefinic ligands from their $Rh^I$ complexes, but does not displace the chelating diolefin ligands. Reaction 1 does not proceed further even in the presence of a large excess of the DAP ligand.




A suspension of $[RhCl(DAP)]_n$ in benzene readily reacts with both carbon monoxide at atmospheric pressure and with triphenylphosphine at room temperature to give respectively the soluble compounds RhCl(CO)(DAP) and $RhCl(PPh_3)$-(DAP), which are non-electrolytes in polar solvents. The same compounds were obtained by treating $[RhCl(CO)_2]_2$ and $RhCl(PPh_3)_3$ with DAP in benzene.

The $^1H$ NMR resonances of the DAP complexes in deuterated solvents are shown in Table 3. The spectrum of the [Rh(COD)(DAP)][$RhCl_2$(COD)] shows the expected shift of the olefinic resonances of the COD ligand upon coordination; however, although the two COD ligands have different environments and the Rh–olefin bond strength of the COD coordinated in the anion differs from that of the same ligand coordinated in the cation (as is shown by the different Rh–olefin bond and double bond–double bond distances in the crystalline compound (Table 4)) the $^1H$ NMR spectrum shows one signal only, at $\delta$ 4.35 ppm (s, 8H) assignable to the CH= protons and only two at $\delta$ 2.10 and 1.32 ppm (mult., 8H each), assignable to the $CH_2$ protons. Moreover, the resonances at $\delta$ 6.12 (mult., 2H), 5.05 (mult., 4H) and 3.55 (d, 4H) ppm., assignable respectively to the CH=, $=CH_2$ and $CH_2$ protons of the coordinated DAP ligand, are very similar to those shown by the free DAP ligand ($\delta$ 6.03, 5.11, 3.55 ppm). Probably, as is found for a number of olefinic complexes of transition metals [7], this compound exhibits fluxional behaviour in solution, most likely involving an equilibrium between bonded and uncoordinated allylic double bonds.

The spectrum of [Rh(COD)(DAP)][$CuCl_2$] is quite similar to that of [Rh(COD)-(DAP)][$ClO_4$]; in both compounds the four =CH protons of the COD ligand show two sets of signals in the ratio 1/1, at 3.85 and 4.57 ppm and at 3.82 and 4.54 ppm, while the eight $CH_2$ protons show three resonances, in the ratio 1/2/1, at about 2.0, 2.5 and 3.0 ppm. The resonances of the terminal olefinic protons of the DAP ligand are shifted upfield by about 1 ppm compared to that of the free ligand. These results are consistent with the structure of the $[Rh(COD)(DAP)]^+$ cation found in the crystals, and show that the rigidity of the $[Rh(COD)(DAP)]^+$ framework in solution depends strongly on the nature of the counter ion.

Also the spectra of the compounds of formula RhCl(L)(DAP) (L = CO, $PPh_3$) are in agreement with a trigonal bipyramidal geometry for the rhodium similar to that found for the $[Rh(COD)(DAP)]^+$ cation, with the chloro and the ligand L in place of the COD double bonds. The equivalence of the four protons of the allylic $=CH_2$ groups ($\delta$ 4.0 ppm) and the splitting of the resonance of the four methylenic protons into two resonances (ratio 1/1) at 3.06 and 3.72 ppm (L = CO) and at 2.78 and 3.24 ppm (L = $PPh_3$) suggest that the ligand L occupies the equatorial position.

The spectrum of [Rh(NBD)(DAP)][$ClO_4$] shows two resonances in the ratio 1/1 at 1.08 and 1.40 ppm, consisting of two irregular triplets assignable to the $CH_2$ protons of the NBD and an unresolved complex resonance centered at 3.90 ppm,

assignable to the olefinic and the bridgehead protons of the NBD ligand (integrated signal = 6 protons). The allylic protons of the DAP ligand show resonances at 6.68 ppm (2H), assignable to the =CH protons, at 5.01 (2H) and 4.12 (2H) ppm, assignable to the $=CH_2$ protons, and at 3.18 (2H) and 3.31 (2H) ppm, assignable to the $CH_2$ protons.

The spectrum of [Rh(NBD)(DAP)][$RhCl_2$(NBD)] is very similar but, in contrast to that of the COD analogue, shows two sets of resonances, at $\delta$ 3.87 and 3.94 ppm, assignable to the olefinic and bridgehead protons of the two dienes, located in different environments.

All the Rh-DAP complexes are active catalysts for homogeneous hydrogenation of olefins and ketones (the results of these experiments will be described elsewhere); in methanol solution, and in absence of reducible substrates, they take up hydrogen to saturate the olefinic bonds and decompose to rhodium metal.

## Experimental

Infrared spectra were recorded on a Perkin–Elmer model 337 grating spectrometer as Nujol mulls between CsI plates. $^1$H NMR spectra were recorded on a Varian XL 200 spectrometer with $Me_4Si$ as an internal reference.

Standard techniques for the manipulation of air-sensitive compounds were used for all reactions, and high-purity nitrogen was used to provide an inert atmosphere. Non-protic solvents were dried over sodium and distilled over clean sodium; the other solvents were deoxygenated by purging with nitrogen. All the chemicals were reagent grade quality and were used without further purification.

The ligand 2,6-diallylpyridine and the starting rhodium complexes were prepared by published methods [8].

*Syntheses of the $Rh^I$-DAP complexes*

*[Rh(COD)(DAP)][$RhCl_2$(COD)].* DAP (70 mg, 0.44 mmol) was added to a solution of [RhCl(COD)]$_2$ (200 mg, 0.406 mmol) in benzene (15 ml). The solution was briefly refluxed then cooled, and the yellow crystals which separated were filtered off, washed with benzene and hexane, and dried in vacuo. Typical yields 85–90%. A crystal suitable for the X-ray analysis was obtained by slow diffusion of hexane into a saturated benzene solution of the complex.

The same compound was obtained by treating [RhCl(COD)]$_2$ with DAP in a 1/3 molar ratio.

*[Rh(COD)(DAP)]$ClO_4$.* (a) Silver perchlorate (249 mg, 1.2 mmol) was added to a suspension of [RhCl(COD)]$_2$ (300 mg, 0.68 mmol) in acetone (10 ml). The mixture was stirred for 30 min, the precipitated silver chloride was filtered off, and DAP (200 mg, 1.26 mmol) was added. The resulting yellow solution was stirred at room temperature for 30 min then concentrated in vacuo to give yellow crystals. Typical yields 70–75%.

(b) Silver perchlorate (70 mg, 0.33 mmol) was added to a suspension of [Rh(DAP)(COD)][$RhCl_2$(COD)] (200 mg, 0.31 mmol) in acetone (10 ml). After 30 min stirring the mixture was filtered and the solution was concentrated in vacuo to give yellow crystals.

*[Rh(COD)(DAP)][$CuCl_2$].* CuCl($Me_2S$) (50 mg, 0.31 mmol) was added to a suspension of [Rh(COD)(DAP)][$RhCL_2$(COD)] (200 mg, 0.31 mmol) in benzene (10

ml). The mixture was stirred for 4 h at room temperature then the precipitate was filtered off and recrystallized from $CH_2Cl_2$/hexane to give yellow crystals. Yellow crystals suitable for the X-ray study were obtained by slow diffusion of hexane into a saturated $CH_2Cl_2$ solution of the complex.

*[Rh(NBD)(DAP)]Y (Y = [RhCl$_2$(NBD)], ClO$_4$).* These compounds were obtained in similar ways as the COD analogues but starting from $[RhCl(NBD)]_2$.

*[RhCl(DAP)]$_n$.* A solution of DAP (100 mg, 0.62 mmol) in benzene (6 ml) was added to a solution of $[RhCl(COE)_2]_2$ (COE = cyclooctene) (200 mg, 0.28 mmol) in benzene (10 ml). After 15 min reflux the mixture was cooled at room temperature, and the orange crystals were filtered off, washed with benzene, and dried under vacuum. Typical yields 65%.

*RhCl(CO)(DAP).* (a) Carbon monoxide was bubbled for 10 min at room temperature through a suspension of $[RhCl(DAP)]_n$ (200 mg, 0.67 mmol) in benzene (10 ml). The yellow solution obtained was concentrated in vacuo, diethyl ether was added, and the yellow crystalline precipitate formed was filtered off and washed with diethyl ether.

(b) DAP (165 mg, 1.04 mmol) was added to a solution of $[RhCl(CO)_2]_2$ (200 mg, 0.66 mmol) and the mixture was stirred at room temperature for 24 h. The yellow precipitate was filtered off, washed with diethyl ether, and dried in vacuo.

*RhCl(PPh$_3$)(DAP).* (a) DAP (60 mg, 0.37 mmol) was added to a solution of $RhCl(PPh_3)_3$ (300 mg, 0.32 mmol) and the mixture was stirred for 4 h then cooled. The yellow crystals were filtered off, washed with diethyl ether, and dried in vacuo. Typical yields 65–70%.

(b) $PPh_3$ (220 mg, 0.84 mmol) was added to a suspension of $[RhCl(DAP)]_n$ (250 mg, 0.84 mmol) in benzene and the mixture was stirred for 12 h at room temperature. The yellow precipitate was filtered off, washed with diethyl ether, and dried in vacuo.

*Crystallographic study of [Rh(COD)(DAP)][RhCl$_2$(COD)] (1) and [Rh(COD)-(DAP)][CuCl$_2$] (2)*

Crystal data and details of the data collection for both compounds are given in Table 6. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. A correction for absorption effects was applied for **1** [9] (maximum and minimum transmission factor values: 1.1474 and 0.8942). Both structures were solved by direct and Fourier methods and refined first by isotropic full-matrix least-squares on $F$ using the SHELX system of computer programs [10] and then by anisotropic blocked full-matrix least-squares and full-matrix least-squares for **1** and **2** respectively. For compound **1** all the hydrogen atoms were located from a difference Fourier synthesis; two final blocked full-matrix least-squares cycles were computed including the H atoms with isotropic thermal parameters. For compound **2** all the hydrogen atoms were located from a $\Delta F$ synthesis except for five (four methylenic and one pyridinic), which in the final full-matrix least-squares cycle were placed at their geometrically calculated positions and were refined by allowing them to ride on their bonded carbon atoms with free isotropic thermal parameters. The atomic scattering factors used, corrected for the anomalous dispersion, were taken from International Tables for X-ray Crystallography [11]. The function minimized in the least-squares procedure was $\Sigma w |\Delta F|^2$; unit weights were used in the first stages of the refinement, and subsequently weights were

TABLE 6

CRYSTAL DATA AND DETAILS OF DATA COLLECTION

| | 1 | 2 |
|---|---|---|
| Formula | $C_{19}H_{25}NRh^+ C_8H_{12}Cl_2Rh^-$ | $C_{19}H_{25}NRh^+ CuCl_2^-$ |
| M.W. | 652.313 | 504.771 |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 10.481(4) | 14.303(8) |
| $b$ (Å) | 13.041(4) | 10.453(5) |
| $c$ (Å) | 10.456(4) | 13.412(6) |
| $\alpha$ (°) | 106.77(2) | 90. |
| $\beta$ (°) | 112.10(2) | 110.95(4) |
| $\gamma$ (°) | 79.57(1) | 90. |
| $V$ (Å$^3$) | 1263.6(8) | 1873(2) |
| $Z$ | 2 | 4 |
| $D_c$ (Mg m$^{-3}$) | 1.714 | 1.790 |
| Reflection for lattice parameters: number | 30 | 30 |
| Reflection for lattice parameters: $\theta$-range (°) | 20–40 | 10–15 |
| Radiation | Cu-$K_\alpha$ (Ni-filtered) | Mo-$K_\alpha$ (Nb-filtered) |
| Wavelength (Å) ($\bar{\lambda}$) | 1.541838 | 0.71073 |
| $F$(000) | 660 | 1016 |
| Temperature (K) | 295 | 295 |
| Crystal size (mm$^3$) | 0.01×0.05×0.36 | 0.14×0.23×0.23 |
| Diffractometer | Siemens AED | Siemens AED |
| $\mu$ (mm$^{-1}$) | 12.925 | 2.297 |
| $\theta$-range (°) | 2.5–60.0 | 3.0–27.0 |
| $h$-range | 0/10 | $\bar{1}8$/17 |
| $k$-range | $\bar{1}4$/13 | 0/13 |
| $l$-range | $\bar{1}1$/10 | 0/16 |
| Standard reflection checked after every 50 s | 1 $\bar{5}$ 2 | $\bar{6}$ 6 2 |
| Intensity variation | none | none |
| Scan speed (° s$^{-1}$) | 0.20–0.10–0.05 | 0.20–0.10 |
| Scan width (°) | 1.20+0.142 tg $\theta$ | 1.10+0.346 tg $\theta$ |
| No. of measured reflections | 3578 | 4212 |
| Condition for observed reflections | $I \geq 2\sigma(I)$ | $I \geq 2\sigma(I)$ |
| No. of reflections used in the refinement | 2204 | 1897 |
| $R = \Sigma\|\Delta F\|/\Sigma\|F_0\|$ (%) | 3.16 | 5.45 |
| $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_0^2]^{1/2}$ (%) | 3.83 | 6.94 |

applied according to the scheme $w = k[\sigma^2(F_0) + gF_0^2]^{-1}$ with $k = 0.1857$ and $g = 0.003878$ in **1** and $k = 0.8992$ and $g = 0.003337$ in **2**.

Final atomic coordinates with equivalent isotropic thermal parameters [12] for the non-hydrogen atoms are given in Table 7. Lists of atomic coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors for both structures can be obtained from the authors on request.

All calculations were performed on the CRAY X-MP/12 computer of the "Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitaro dell' Italia Nord-Orientale (Cineca, Casalecchio, Bologna)" with the financial support

TABLE 7

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2$) FOR THE NON-HYDROGEN ATOMS; (e.s.d.'s are given in parentheses)

| Compound **1** | | | | |
|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
| Rh(1) | 1458(1) | 3431(1) | 2369(1) | 2.57(2) |
| N | 2754(6) | 4281(5) | 2124(7) | 2.93(24) |
| C(1) | 3689(8) | 3750(8) | 1508(9) | 3.90(33) |
| C(2) | 4637(9) | 4282(10) | 1406(11) | 4.67(41) |
| C(3) | 4658(10) | 5369(11) | 1935(11) | 5.24(45) |
| C(4) | 3725(10) | 5909(9) | 2594(11) | 4.72(40) |
| C(5) | 2766(8) | 5368(7) | 2671(8) | 3.26(30) |
| C(6) | 1657(10) | 5868(7) | 3316(10) | 3.65(33) |
| C(7) | 1254(10) | 5077(7) | 3869(9) | 3.50(30) |
| C(8) | 2183(13) | 4444(9) | 4663(10) | 4.47(41) |
| C(9) | 3566(11) | 2580(8) | 979(12) | 4.31(39) |
| C(10) | 2980(11) | 2152(9) | 1805(13) | 4.68(43) |
| C(11) | 3371(11) | 2456(9) | 3245(12) | 4.55(43) |
| C(12) | −458(9) | 4033(7) | 826(8) | 3.10(30) |
| C(13) | 175(10) | 3196(8) | 99(9) | 3.38(32) |
| C(14) | −319(12) | 2083(8) | −554(11) | 4.76(40) |
| C(15) | −540(13) | 1619(9) | 501(13) | 5.26(46) |
| C(16) | 309(11) | 2056(8) | 2053(11) | 3.94(37) |
| C(17) | −153(10) | 2920(7) | 2914(10) | 3.90(35) |
| C(18) | −1510(11) | 3552(10) | 2417(12) | 4.57(41) |
| C(19) | −1758(9) | 3949(7) | 1103(10) | 3.53(32) |
| Rh(2) | 3381(1) | 1302(1) | 7182(1) | 2.62(2) |
| Cl(1) | 2198(2) | 3060(2) | 7267(2) | 4.34(8) |
| Cl(2) | 5571(2) | 1997(2) | 8541(2) | 4.42(8) |
| C(20) | 4367(9) | −216(6) | 6616(9) | 3.77(31) |
| C(21) | 4132(8) | −97(7) | 7873(9) | 3.57(30) |
| C(22) | 3025(10) | −587(9) | 8057(13) | 5.17(41) |
| C(23) | 1612(9) | −383(9) | 6976(12) | 4.59(38) |
| C(24) | 1489(8) | 628(7) | 6517(9) | 3.48(30) |
| C(25) | 1790(8) | 673(7) | 5362(8) | 3.39(29) |
| C(26) | 2280(10) | −265(8) | 4379(10) | 4.54(35) |
| C(27) | 3529(11) | −897(8) | 5187(11) | 5.13(39) |
| Compound **2** | | | | |
| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
| Rh(1) | 2309(1) | 42(1) | 2287(1) | 2.33(2) |
| N | 2268(8) | −1885(10) | 2232(9) | 2.92(31) |
| C(1) | 2747(9) | −2514(13) | 1658(10) | 3.13(41) |
| C(2) | 2680(11) | −3819(13) | 1581(13) | 4.20(51) |
| C(3) | 2161(12) | −4512(15) | 2069(15) | 4.87(54) |
| C(4) | 1671(11) | −3855(12) | 2671(12) | 4.26(47) |
| C(5) | 1730(10) | −2524(12) | 2712(11) | 3.29(43) |
| C(6) | 1213(13) | −1712(15) | 3288(14) | 4.67(56) |
| C(7) | 1026(11) | −376(13) | 2837(14) | 3.86(49) |
| C(8) | 619(9) | −130(18) | 1794(13) | 4.14(47) |
| C(9) | 3317(11) | −1683(13) | 1205(12) | 3.56(46) |
| C(10) | 2886(12) | −349(13) | 986(10) | 3.44(44) |
| C(11) | 1893(11) | −120(18) | 518(10) | 3.67(42) |
| C(12) | 3263(11) | 83(16) | 3983(10) | 4.16(42) |

TABLE 7 (continued)

| Compound **2** | | | | |
|---|---|---|---|---|
| C(13) | 3887(10) | 49(17) | 3396(10) | 3.97(39) |
| C(14) | 4438(12) | 1162(19) | 3236(14) | 5.39(60) |
| C(15) | 3860(11) | 2239(16) | 2594(17) | 6.47(79) |
| C(16) | 2732(11) | 2063(13) | 2097(13) | 3.73(51) |
| C(17) | 2110(13) | 2054(13) | 2710(15) | 3.95(58) |
| C(18) | 2487(17) | 2289(15) | 3871(15) | 7.88(94) |
| C(19) | 3078(15) | 1190(18) | 4557(13) | 5.63(66) |
| Cu(1) | 5000 | 5000 | 5000 | 4.39(8) |
| Cu(2) | 0 | 5000 | 0 | 4.31(8) |
| Cl(1) | 5418(3) | 3326(3) | 5886(3) | 4.36(11) |
| Cl(2) | 339(2) | 3041(3) | −12(3) | 3.57(10) |

from the University of Parma, and on the GOULD-Sel 32/77 computer of the "Centro di Studio per la strutturistica Diffrattrometrica del C.N.R., Parma". The programs PARST [13] and ORTEP [14] were also used.

## Acknowledgement

The authors thank the C.N.R. (Rome) for a financial support and Mr. S. Creti for experimental NMR assistance.

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