Journal of Organometallic Chemistry, 81 (1974) 217—225

# CRYSTAL STRUCTURES OF RHODACYCLOPENTANE DERIVATIVES

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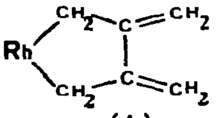
(Received May 6th, 1974)

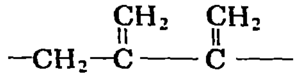
## Summary

Two complexes containing a rhodacyclopentane ring, viz. (acac)Rh($C_6H_8$)(py)$_2$ and (acac)$_2$Rh$_2$($C_6H_8$)(PPh$_3$) have been studied by X-ray diffraction. The ring forms through oxidative coupling of two allene molecules giving the structure A with trivalent, octahedrally-coordinated rhodium. In the second complex the unsaturated hydrocarbon part is also π-bonded to another Rh atom, and one acac group acts as a five-electron donor.



(A)

## Introduction

In a previous communication [1] we reported the formation and the essential structural data of the two rhodacylopentane derivatives: (acac)Rh($C_6H_8$)(py)$_2$ (I), and (acac)$_2$Rh$_2$($C_6H_8$)(PPh$_3$)$_2$ (II), acac = $C_5H_7O$ = acetylacetonato, py = $C_5H_5N$ = pyridine, PPh$_3$ = P($C_6H_5$)$_3$ = triphenylphosphine, $C_6H_8$ being the bidentate group  $-CH_2-\overset{\overset{\displaystyle CH_2}{\|}}{C}-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_2-$. In this paper the complete results of the single-crystal X-ray diffraction investigations and further discussion on the resulting structures are given.

## Experimental

X-ray diffraction experiments were performed with Philips single crystal diffractiometer PW-1100, using a graphite monochromator and Mo-$K_\alpha$ radiation for intensity measurements and Cu-$K_\alpha$ radiation (λ 1.5418 Å) for lattice constants determination.

*Crystal data*

I: (acac)Rh($C_6H_5$)(py)$_2$ $M$ = 440.3, $a$ = 13.167(1), $b$ = 9.108(1), $c$ = 9.185 Å, $\alpha$ = 107.93(1), $\beta$ = 81.12(1), $\gamma$ = 93.17(1)°, $D_m$ = 1.4 g cm$^{-3}$, $D_c$ = 1.41 g cm $Z$ = 2, $F$(000) = 452, space group $P\bar{1}$, $\mu$ = 8.14 cm$^{-1}$; II: (acac)$_2$Rh$_2$($C_6H_5$)(PPh$_3$ $M$ = 1008.8, $a$ = 17.866(4), $b$ = 14.993(4), $c$ = 10.297(3) Å, $\alpha$ = 99.22(2), $\beta$ = 91.19(2), $\gamma$ = 108.26(2)°, $D_m$ = 1.3 g cm$^{-3}$, $D_c$ = 1.29 g cm$^{-3}$, $Z$ = 2, $F$(000) = 1032, space group $P\bar{1}$, $\mu$ = 7.19 cm$^{-1}$.

Crystals of regular shape, ~ 0.3 mm in size, were sealed in low absorption glass capillaries. For accurate lattice parameter determination the diffraction angles $\theta$ for 46 and 85 reflections for the two compounds respectively were measured following the standard procedure of the PW-1100 system [2]; the par eters were obtained by minimizing the function $\Sigma(\sin\theta_{obs}\text{-}\sin\theta_{calc})^2$.

Integrated intensities were measured by the $\omega$-scan method for complex I and by the $\omega$-2$\theta$-scan method for complex II. For I 3640 reflections having $\theta < 23°$ and $l \geqslant 0$ were measured and 3373 of these with I > 3$\sigma$ were used in structure determination and refinement. For compound II 5530 reflections having $\theta < 21°$ and $l \geqslant 0$ were measured and 4473 used. The absorption correction was disregarded ($\mu R < 0.2$ in both cases).

*Structure determination and refinement*

The structures were resolved by the heavy atom method and the parameter of the non-hydrogen atoms were refined by the least squares method, minimizin $\Sigma w(F_{obs}\text{-}F_{calc})^2$ with unitary weight factors, anisotropic thermal parameters and the 9 × 9 block-diagonal approximation. Crystallographic programs given in ref. 3 and the atomic scattering factors given in ref. 4 were used with a constant correction of −1.1 electrons for Rh and +0.1 for P to account for anomalous scattering. In the last two refinement cycles the hydrogen atoms belonging to the pyridine and phosphine groups were introduced in calculated positions. The hydrogen atoms belonging to the $C_6H_5$ groups and that attached to the central C atom in acac groups were localized by means of difference Fourier syntheses, but no acceptable hydrogen positions were obtained for the acac methyl groups.

The final disagreement factor was 0.033 for I and 0.041 for II. Final coordinates are listed in Table 1. Bond lengths and valence and torsion angles are given in Tables 2 and 3 respectively. A list of observed and calculated structure factors may be obtained from the author on request.

(continued on p. 222)

TABLE 1

FRACTIONAL COORDINATES AND STANDARD DEVIATIONS

| atom | $x/a$ ($\sigma$) | $y/b$ ($\sigma$) | $z/c$ ($\sigma$) |
|---|---|---|---|
| *Complex I* | | | |
| RH | 0.26141(2) | 0.38289(3) | 0.11337(3) |
| C-1 · 1 | 0.40711(37) | 0.30428(62) | −0.35783(48) |
| C-1 · 2 | 0.33319(31) | 0.28334(48) | −0.22151(43) |
| C-1 · 3 | 0.26146(33) | 0.16465(48) | −0.24693(43) |
| C-1 · 4 | 0.19286(33) | 0.11549(45) | −0.13886(46) |
| C-1 · 5 | 0.11800(42) | −0.01054(59) | −0.19965(61) |
| O-1 · 1 | 0.34625(21) | 0.38234(30) | −0.09234(28) |
| O-1 · 2 | 0.18792(22) | 0.16776(31) | 0.00641(30) |

*(continued)*

TABLE 1 (continued)

| Atom | $x/a$ ($\sigma$) | $y/b$ ($\sigma$) | $z/c$ ($\sigma$) |
|---|---|---|---|
| N-1 | 0.38775(25) | 0.25855(37) | 0.15429(35) |
| C-7 | 0.48406(32) | 0.30913(50) | 0.13733(49) |
| C-8 | 0.56610(37) | 0.23521(64) | 0.15879(62) |
| C-9 | 0.54667(43) | 0.09952(66) | 0.19750(62) |
| C-10 | 0.44763(42) | 0.04602(57) | 0.21472(57) |
| C-11 | 0.37097(35) | 0.12856(50) | 0.19210(49) |
| N-2 | 0.18056(24) | 0.38312(36) | 0.32201(34) |
| C-12 | 0.09393(36) | 0.30502(59) | 0.32910(49) |
| C-13 | 0.03969(38) | 0 29052(66) | 0.46643(58) |
| C-14 | 0 07837(37) | 0.36209(60) | 0.60258(50) |
| C-15 | 0.16520(39) | 0 44346(62) | 0.59595(49) |
| C-16 | 0.21599(34) | 0.45416(56) | 0.45627(47) |
| C-1 | 0.13144(66) | 0.76634(85) | 0.06263(99) |
| C-2 | 0.16649(40) | 0 66810(60) | 0.12030(64) |
| C-3 | 0.23630(39) | 0.71291(55) | 0.23700(57) |
| C-4 | 0.22189(50) | 0.83367(69) | 0.36367(74) |
| C-5 | 0.14655(38) | 0.49865(60) | 0.07040(54) |
| C-6 | 0.32076(37) | 0.59904(55) | 0.20104(52) |
| H-1 | 0.1525 | 0.8716 | 0.0670 |
| H-1′ | 0.0883 | 0.7231 | −0.0203 |
| H-4 | 0.1666 | 0.8856 | 0 3783 |
| H-4′ | 0.2760 | 0 8509 | 0.4334 |
| H-5 | 0.1226 | 0.4553 | −0 0330 |
| H-5′ | 0.0781 | 0 4676 | 0.1313 |
| H-6 | 0.3662 | 0.6167 | 0.1231 |
| H-6′ | 0 3598 | 0.6182 | 0.2859 |
| H-1 · 3 | 0.2580 | 0.1013 | −0.3666 |
| *Complex II* | | | |
| RH‴ | 0.77800(5) | 0.79544(6) | 0.61711(8) |
| P-1 | 0 76251(17) | 0.93596(20) | 0.60547(28) |
| A-1 · 1 | 0.68960(62) | 0 97296(77) | 0.70743(120) |
| A-1 · 2 | 0.67682(73) | 1.05867(87) | 0.70268(130) |
| A-1 · 3 | 0 62674(78) | 1.08943(97) | 0.77782(134) |
| A-1 · 4 | 0.58201(81) | 1.03088(99) | 0.85885(127) |
| A-1 · 5 | 0.59150(81) | 0.94519(99) | 0.86210(99) |
| A-1 · 6 | 0.64660(66) | 0 91636(85) | 0 78888(99) |
| A-1 · 7 | 0.73464(69) | 0 96307(80) | 0.44661(99) |
| A-1 · 8 | 0.77226(78) | 1.05291(86) | 0.41117(123) |
| A-1 · 9 | 0.74567(86) | 1.07231(95) | 0.29591(123) |
| A-1 · 10 | 0.68375(82) | 1.00531(94) | 0.21301(124) |
| A-1 · 11 | 0.64823(82) | 0.91862(92) | 0.24879(125) |
| A-1 · 12 | 0.67351(68) | 0.89615(82) | 0.36321(99) |
| A-1 · 13 | 0.85498(65) | 1.03001(74) | 0.66263(99) |
| A-1 · 14 | 0.91781(74) | 1 04583(83) | 0.57902(121) |
| A-1 · 15 | 0.99051(69) | 1.11434(84) | 0.61736(132) |
| A-1 · 16 | 1.00358(73) | 1.16843(91) | 0.74253(139) |
| A-1 · 17 | 0.94626(84) | 1.15286(99) | 0.82971(144) |
| A-1 · 18 | 0.86970(74) | 1.08399(90) | 0.79029(99) |
| C-1 · 1 | 0.80056(86) | 0.84642(99) | 1.05919(120) |
| C-1 · 2 | 0.82509(72) | 0 84419(82) | 0.91767(99) |
| C-1 · 3 | 0.90422(71) | 0.87232(88) | 0.89829(99) |
| C-1 · 4 | 0.94080(70) | 0 87908(78) | 0.77874(99) |
| C-1 · 5 | 1.03007(68) | 0.91719(99) | 0.78055(132) |
| O-1 · 1 | 0.76662(46) | 0.81442(54) | 0.82887(70) |
| O-1 · 2 | 0.90421(42) | 0.85615(51) | 0.66243(71) |
| RH′ | 0.69412(5) | 0.54391(6) | 0.39180(9) |

*(continued)*

TABLE 1 (continued)

| atom | *x/a* (σ) | *y/b* (σ) | *z/c* (σ) |
|---|---|---|---|
| P-2 | 0.65556(17) | 0.38609(20) | 0.28688(28) |
| A-2 · 1 | 0.58217(64) | 0.36267(73) | 0.14917(99) |
| A-2 · 2 | 0.60388(77) | 0.39650(88) | 0.03370(99) |
| A-2 · 3 | 0.55043(90) | 0.38342(98) | -0.07068(132) |
| A-2 · 4 | 0.46885(83) | 0.33428(95) | -0.05934(142) |
| A-2 · 5 | 0.44725(77) | 0.30161(97) | 0.05552(135) |
| A-2 · 6 | 0.50177(73) | 0.31559(85) | 0.15828(120) |
| A-2 · 7 | 0.60686(62) | 0.29441(76) | 0.38219(99) |
| A-2 · 8 | 0.56926(70) | 0.32057(85) | 0.49330(99) |
| A-2 · 9 | 0.52749(78) | 0.25146(94) | 0.56162(129) |
| A-2 · 10 | 0.52548(79) | 0.15714(96) | 0.52544(135) |
| A-2 · 11 | 0.56336(96) | 0.13296(95) | 0.41911(154) |
| A-2 · 12 | 0.60479(82) | 0.20046(87) | 0.34672(136) |
| A-2 · 13 | 0.73198(69) | 0.34005(79) | 0.21162(99) |
| A-2 · 14 | 0.80481(76) | 0.37045(97) | 0.27946(151) |
| A-2 · 15 | 0.86471(92) | 0.33374(99) | 0.23222(183) |
| A-2 · 16 | 0.84787(99) | 0.26791(99) | 0.11817(168) |
| A-2 · 17 | 0.77730(94) | 0.23864(99) | 0.04878(145) |
| A-2 · 18 | 0.71864(85) | 0.27301(94) | 0.09577(127) |
| C-2 · 1 | 0.71103(88) | 0.59196(97) | 0.82511(123) |
| C-2 · 2 | 0.73086(70) | 0.58859(79) | 0.68070(99) |
| C-2 · 3 | 0.80575(69) | 0.65412(79) | 0.65502(99) |
| C-2 · 4 | 0.84958(67) | 0.62677(78) | 0.54546(122) |
| C-2 · 5 | 0.93878(75) | 0.66243(99) | 0.56321(150) |
| O-2 · 1 | 0.68195(46) | 0.52757(51) | 0.59460(74) |
| O-2 · 2 | 0.81845(45) | 0.57276(52) | 0.43774(77) |
| C-1 | 0.71657(83) | 0.61677(78) | 0.23312(110) |
| C-2 | 0.71714(61) | 0.68584(69) | 0.35132(99) |
| C-3 | 0.64977(61) | 0.66342(72) | 0.42775(99) |
| C-4 | 0.58693(61) | 0.57268(74) | 0.37925(121) |
| C-5 | 0.78902(69) | 0.76678(76) | 0.41424(99) |
| C-6 | 0.65857(60) | 0.72406(77) | 0.56400(99) |
| H-1 | 0.7634 | 0.6332 | 0.1720 |
| H-1' | 0.6703 | 0.5890 | 0.1618 |
| H-4 | 0.5483 | 0.5428 | 0.4519 |
| H-4' | 0.5627 | 0.5513 | 0.2796 |
| H-5 | 0.8431 | 0.7520 | 0.3805 |
| H-5' | 0.8138 | 0.8379 | 0.3734 |
| H-6 | 0.6314 | 0.6808 | 0.6301 |
| H-6' | 0.6216 | 0.7716 | 0.5607 |
| H-1 · 3 | 0.9408 | 0.8912 | 0.9787 |
| H-2 · 3 | 0.8476 | 0.6998 | 0.7430 |

TABLE 2

PRINCIPAL BOND LENGTHS$^{c}$ (Å)

| | | | | | |
|---|---|---|---|---|---|
| *Complex I* | | | | | |
| *$C_6H_8$ moiety* | | | | | |
| C-1—C-2 | 1.307 | Rh—C-5 | 2.042 | C-4—H-4' | 1.00 |
| C-2—C-3 | 1.467 | Rh—C-6 | 2.045 | C-5—H-5 | 1.00 |
| C-3—C-4 | 1.329 | C-1—H-1 | 0.97 | C-5—H-5' | 1.06 |
| C-2—C-5 | 1.489 | C-1—H-1' | 0.99 | C-6—H-6 | 0.91 |
| C-3—C-6 | 1.492 | C-4—H-4 | 0.86 | C-6—H-6' | 0.97 |

*(continued)*

TABLE 2 (continued)

| | | | | | |
|---|---|---|---|---|---|
| *Acac group* | | | | | |
| C-1.1—C-1.2 | 1.517 | C-1.4—O-1 5 | 1.500 | C-1.3—H-1.3 | 1.08 |
| C-1.2—C-1.3 | 1.384 | C-1.2—O-1.1 | 1.280 | Rh—O-1.1 | 2.040 |
| C-1.3—C-1.4 | 1.398 | C-1 4—O-1.2 | 1.264 | Rn—O-1.2 | 2 154 |
| *Other bond lengths involving Rh atoms* | | | | | |
| Rh—N-1 | 2.203 | Rh—N-2 | 2.043 | | |
| *Complex II* | | | | | |
| $C_6H_8$ *moiety* | | | | | |
| C-1—C-2 | 1.453 | Rh'''—C-6 | 2.078 | C-1—H-1' | 1.02 |
| C-2—C-3 | 1.435 | Rh'—C-1 | 2 096 | C-4—H-4 | 1.09 |
| C-3—C-4 | 1.465 | Rh'—C-2 | 2.153 | C-4—H-4' | 1.06 |
| C-2—C-5 | 1.503 | Rh'—C-3 | 2.156 | C-5—H-5 | 1.11 |
| C-3—C-6 | 1.610 | Rh'—C-4 | 2.097 | C-5—H-5' | 1.17 |
| Rh'''—C-5 | 2.085 | C-1—H-1 | 1.05 | C-6—H-6 | 1.04 |
| | | | | C-6—H-6' | 1.12 |
| *Acac groups* | | | | | |
| 1) *acac*$_1$ | | | | | |
| C-1:1—C-1.2 | 1.528 | C-1.4—C-1.5 | 1.515 | C-1.3—H-1.3 | 0 99 |
| C-1.2—C-1.3 | 1.372 | C-1.2—O-1.1 | 1.286 | Rh'''—O-1.1 | 2.172 |
| C-1.3—C-1.4 | 1.410 | C-1 4—O-1.2 | 1.290 | Rh'''—O-1.2 | 2 157 |
| | | | | Rh'''—C-2.3 | 2.413 |
| 2) *acac*$_2$ | | | | | |
| C-2.1—C-2 2 | 1.532 | C-2.4—C-2.5 | 1.510 | C-2 3—H-2 3 | 1.13 |
| C-2.2—C-2.3 | 1.451 | C-2 2—O-2.1 | 1.255 | Rh'—O-2 1 | 2.152 |
| C-2.3—C-2.4 | 1.460 | C-2.4—O-2.2 | 1.256 | Rh'—O-2.2 | 2.151 |
| *Phosphine groups* | | | | | |
| Rh'''—P-1 | 2.232 | P-1—A-1 13 | 1.811 | P-2—A-2.7 | 1 833 |
| P-1—A-1 1 | 1.848 | Rh'—P-2 | 2.304 | P-2—A-1.13 | 1.842 |
| P-1—A-1.7 | 1.847 | P-2—A-2.1 | 1.821 | | |

[a] Average standard deviations for bond lengths: Rh—P 0.005, Rh—X 0.010, P—X 0.012, X—X 0.020, X—H 0.010 Å (X = C, N or O).

TABLE 3

VALENCE[a] AND TORSION ANGLES (°)

| | | | |
|---|---|---|---|
| *Complex I* | | | |
| $C_6H_8$ *moiety* | | | |
| C-5—Rh—C-6 | 83.98 | C-6—C-3—C-2 | 111.25 |
| Rh—C-6—C-3 | 108.33 | C-1—C-2—C-3 | 122 92 |
| Rh—C-5—C-2 | 110.78 | C-4—C-3—C-2 | 124.13 |
| C-5—C-2—C-3 | 112.05 | | |
| C-5—C-2—C-3—C-6 | 39.85 | C-1—C-2—C-3—C-4 | 47.57 |
| *Acac group* | | | |
| C-1.2—C-1.3—C-1.4 | 122.88 | C-1.2—C-1.3—H-1.3 | 115.5 |
| Rh—O-1.1—C-1.2 | 123.19 | C-1.4—C-1.3—H-1.3 | 115.5 |
| Rh—O-1.2—C-1.4 | 121 03 | O-1.1—Rh—O-1.2 | 91.60 |

*(continued)*

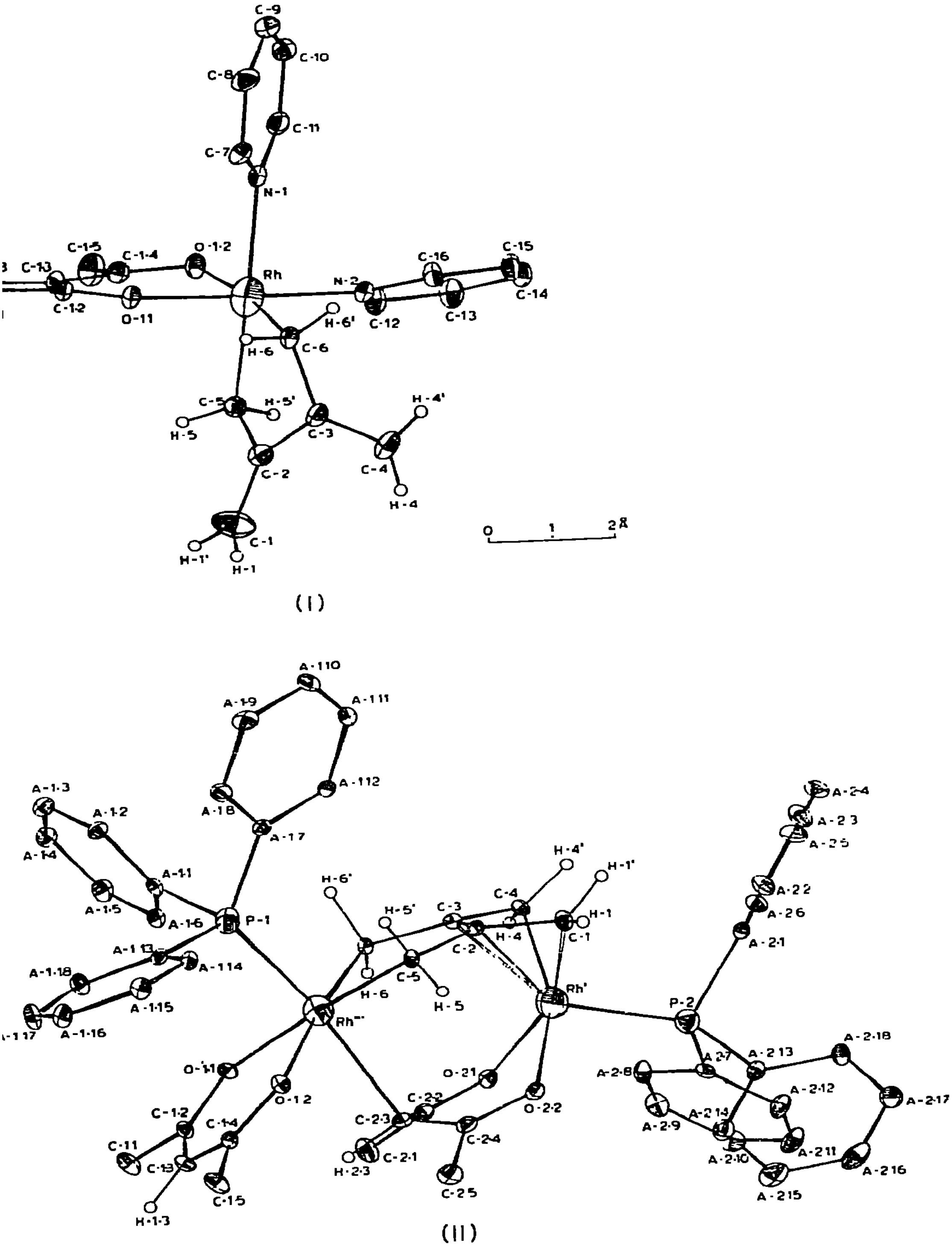
TABLE 3 (continued)

| | | | |
|---|---|---|---|
| *Other valence angles involving Rh atoms* | | | |
| N-1—Rh—N-2 | 90.28 | N-2—Rh—C-6 | 93.18 |
| N-1—Rh—C-5 | 178.53 | N-2—Rh—O-1.1 | 178.23 |
| N-1—Rh—C-6 | 95.79 | N-2—Rh—O-1.2 | 89.22 |
| N-1—Rh—O-1.1 | 88.14 | C-5—Rh—O-1.1 | 90.40 |
| N-1—Rh—O-1.2 | 90.77 | C-5—Rh—O-1.2 | 89.40 |
| N-2—Rh—C-5 | 91.18 | C-6—Rh—O-1 1 | 86.18 |
| | | C-6—Rh—O-1.2 | 173.00 |
| *Complex II* | | | |
| *$C_6H_8$ moiety* | | | |
| C-5—Rh‴—C-6 | 84.11 | C-6—C-3—C-2 | 116.28 |
| Rh‴—C-6—C-3 | 108 71 | C-1—C-2—C-3 | 117.09 |
| Rh‴—C-5—C-2 | 108.34 | C-4—C-3—C-2 | 116.74 |
| C-5—C-2—C-3 | 117.11 | | |
| C-5—C-2—C-3—C-6 | 0.03 | C-1—C-2—C-3—C-4 | 0.20 |
| *Acac groups* | | | |
| 1) *acac*$_1$ | | | |
| C-1.2—C-1.3—C-1.4 | 122.82 | C-1.2—C-1.3—H-1.3 | 116 0 |
| Rh‴—O-1.1—C-1.2 | 124.64 | C-1.4—C-1.3—H-1.3 | 115.1 |
| Rh‴—O-1.2—C-1.4 | 126.06 | O-1.1—Rh‴—O-1.2 | 87.43 |
| 2) *acac*$_2$ | | | |
| C-2.2—C-2.3—C-2.4 | 120 70 | C-2 2—C-2 3—H-2.3 | 118.0 |
| Rh′—O-2.1—C-2.2 | 117.37 | C-2.4—C-2.3—H-2.3 | 110.9 |
| Rh′—O-2.2—C-2.4 | 117.94 | O-2.1—Rh′—O-2.2 | 85.43 |
| *Other valence angles involving Rh atoms* | | | |
| P-1—Rh‴—C-5 | 91.70 | C-6—Rh‴—O-1.2 | 174.04 |
| P-1—Rh‴—C-6 | 91.42 | C-6—Rh‴—C-2.3 | 94.11 |
| P-1—Rh‴—O-1.1 | 92.61 | O-1.1—Rh‴—C-2.3 | 82.05 |
| P-1—Rh‴—O-1.2 | 93.74 | O-1.2—Rh‴—C-2.3 | 81.01 |
| P-1—Rh‴—C-2.3 | 172.64 | P-2—Rh′—O-2.1 | 100.58 |
| C-5—Rh‴—O-1.1 | 175.66 | P-2—Rh′—O-2.2 | 101.58 |
| C-5—Rh‴—O-1.2 | 92.76 | P-2—Rh′—C-1 | 102.44 |
| C-5—Rh‴—C-2.3 | 93.69 | | |
| C-6—Rh‴—O-1.1 | 95.31 | P-2—Rh′—C-4 | 100.81 |
| *Phosphine groups* | | | |
| Rh‴—P-1—A-1.1 | 118.13 | A-1.1—P-1—A-1.7 | 99.13 |
| Rh‴—P-1—A-1 7 | 121 37 | A-1.1—P-1—A-1.13 | 103.70 |
| Rh‴—P-1—A-1.13 | 108 73 | A-1 7—P-1—A-1.13 | 103.57 |
| Rh′—P-2—A-2.1 | 111.32 | A-2.1—P-2—A-2.7 | 102.17 |
| Rh′—P-2—A-2.7 | 118.09 | A-2 1—P-2—A-2.13 | 103.43 |
| Rh′—P-2—A-2.13 | 117.64 | A-2.7—P-2—A-2.13 | 102.11 |

[a] Average standard deviations for valence angles: X-Rh-X 0.20, P-Rh-X 0.15, Rh-P-X 0.35, X-P-X 0.30, Rh-X-X 0.55, P-X-X 0.65, X-X-X 0.65, C-C-H ~ 6.0° (X = C, N or O).

## Results and comments

A view of the two structures is shown in Fig. 1. Complex I displays octahedral geometry with acac and $C_6H_8$ bonded as chelate ligands and the two pyridine ligands in mutually *cis* relation. The hydrocarbon ligand exerts con-



(I)

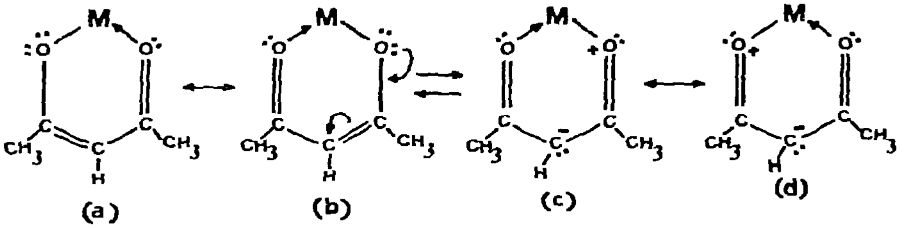
(II)

Fig. 1. Projection of the structures of the complexes I and II. Only the hydrogen atoms belonging to the $C_6H_8$ groups and those bonded to the central carbon atom in acac groups are indicated.

siderable *trans* influence: the Rh—N bond lengths *cis* and *trans to* the Rh—C-5 bond differ by 0.16 Å and the Rh—O bond lengths *cis* and *trans* to the Rh—C-bond differ by 0.12 Å. Also the C—C and C—O bond lengths in the acac group are asymmetrical as though a minor electron delocalization had been induced in the coordinated acac molecule (the trend is toward structure a see scheme below).

The geometry of the rhodacyclopentane ring is noteworthy: neither the 5-atom ring, nor the conjugated diene group is planar. The bonds C-2—C-5 and C-3—C-6 are staggered by 39.9° and the bonds C-2—C-1 and C-3—C-4 by 48.2°. The bond lengths for the conjugated diene fragment do not differ appreciably from the values for the gaseous butadiene [5] (C—C = 1.464. C=C = 1.337 Å). The observed conformation for the diene fragment substantiates the results of ab initio LCAO SCF MO calculations, according to which the conformational energy in the neighbourhood of the *cis* conformation does not change significanly for a rotation of the order of 40° [6].

Complex II displays a two-centre coordination geometry with two differen rhodium atoms in different environments. The rhodium atom Rh′ is bonded to one acac group, (labelled $acac_2$), one $PPh_3$ molecule, and is also $\pi$-bonded to the *cis*-diene group of the $C_6H_8$ moiety; the coordination geometry is a tetragonal pyramid. The second rhodium atom Rh‴ is bonded to the other acac group (labelled $acac_1$), the other $PPh_3$ molecule and to the $C_6H_8$ group through two $\sigma$ bonds, and to the $acac_2$ molecule via its central carbon atom; the coordination geometry is octahedral. One interpretation of the bonding of II, coherent with the observed geometry and with the 18 electron rule [7], is to consider the Rh′ atom to be in oxidation state 1 and Rh‴ in oxidation state 3 with two electrons donated from the central $C_3$ atom of $acac_2$, which therefore acts as a 5-electron donor. For a chelated acac group the following valence-bond structures may be considered:



In our case, the zwitterionic structures (c) and (d) (isoelectronic with *N*-acethylacetamide) should be considered for $acac_2$ making the central $C_3$ atom anionic with a lone pair available for donation. This interpretation is coherent: (i) with the tetrahedral coordination displayed by the central $C_3$ atom; (ii) with the observed $C_2$—$C_3$ and $C_3$—$C_4$ bond lengths (1.45, 1.46 Å), both longer than in $acac_1$ (1.37, 1.41 Å); (iii) the C=O distances (1.25, 1.26 Å) both shorter than in $acac_1$ (1.29, 1.29 Å) (the C=O distances in the related KI-bis(*N*-acethylacetamide) complex [8] are 1.22 and 1.27 Å); (iv) the Rh‴—$C_3$ bond length (2.43 Å) which is much longer than a covalent Rh—C bond (2.09 Å). Similar bonding of the acetylacetonato group with silver [9] and platinum [10] has been proposed.

The *cis*-diene fragment coordinated to Rh′ is planar and the angular deviations of the substituents are similar to those observed, for example, in $\pi$-diene

Fe(CO)$_3$ complexes [11]. The conformation of the rhodacyclopentane ring is of the "envelope" type with the C-2—C-1 and the C-3—C-4 bonds eclipsed and the Rh$'''$ displaced by 0.57 Å from the C-5—C-2—C-3—C-6 plane. With respect to the above-cited Fe-diene complexes, a significant difference is seen in the C—C bond lengths of the coordinated diene group: 1.47, 1.44, 1.47 for II and 1.41, 1.40, 1.41 Å for $\pi$-butadiene—Fe(CO)$_3$ [12]. According to Churchill and Mason [13], these variations can be correlated with the $\pi$-acceptor ability of the ligand *trans* to the diene. In the $\pi$-diene—Fe(CO)$_3$ compounds, the strong $\pi$-acceptor C=O ligands reduce the metal-to-diene back-donation, whereas in our case the *trans* acac and PPh$_3$ ligands have much lower $\pi$-acceptor ability and thus greater back-bonding to the diene should occur.

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