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# The reactivity of new (1,5-cyclooctadiene)rhodium acylpyrazolonates towards N- and P-donor ligands: X-ray structures of [Rh(1,5-COD)$Q^s$], [Rh(1,5-COD)(phen)]$Q^s \cdot 0.5H_2O$ ($HQ^s$ = 1-phenyl-3-methyl-4-(2-thenoyl)-pyrazol-5-one) and $[Rh(1,5\text{-}COD)Br]_2$

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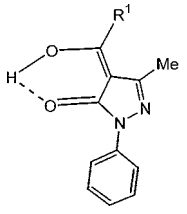
**Abstract**

Complexes [Rh(1,5-COD)(Q)] have been prepared by the reaction between $[Rh(1,5\text{-}COD)Cl]_2$ (1,5-COD = 1,5-cyclooctadiene) and HQ (where HQ = 1-phenyl-3-methyl-4-R-pyrazol-5-one: R = 2-thenoyl (**$HQ^s$**), 2-furanoyl (**$HQ^o$**) or *tert*-butylacetyl (**$HQ^T$**). [Rh(1,5-COD)(Q)] react with $N_2$-donor ligands such as 1,10-phenanthroline (phen) or 2,2-bipyridyl (bipy) yielding ionic compounds [Rh(1,5-COD)($N_2$-donor)]Q. The substitutional lability of 1,5-COD in [Rh(1,5-COD)(Q)] versus mono- and di-organophosphine ligands was also investigated. In all cases 1,5-COD has been displaced. Reaction with two equivalents of $PPh_3$ gave, upon oxidation of the Rh(I) centre, $[Rh(PPh_3)_2(O_2)(Q)]$ species containing a $\eta^2$-peroxo-group. Reaction of [Rh(1,5-COD)(Q)] with the chelating $P_2$-donor 1,2-bis(diphenylphosphino)ethane (dppe) or 4,4′-bis(diphenylphosphino)ferrocene (dppf) yields the peroxo Rh(III) compounds $[Rh(dppe)_2O_2]Q^T$ and $[Rh(dppf)O_2(Q^s)]$ or Rh(I) species [Rh(dppf-$O_2$)($Q^T$)] containing the diphosphine in the oxidised form. Finally the reaction between [Rh(1,5-COD)(Q)] and allylbromide yields the well-known $[Rh(1,5\text{-}COD)Br]_2$. All complexes have been characterised by analytical and spectral data (IR, $^1H$ and $^{31}P\{^1H\}$-NMR spectra). The crystal structures of [Rh(1,5-COD)($Q^s$)], [Rh(1,5-COD)(phen)]$Q^s$ and $[Rh(1,5\text{-}COD)Br]_2$, all containing a Rh(I) atom in a square coordinate environment, are also reported. 

*Keywords:* Rhodium; 4-Acylpyrazolones; β-Diketones; Phosphines; Structures; $^{31}P$-NMR; Oxidation

## 1. Introduction

The important role of rhodium and iridium complexes containing β-diketones, olefins and phosphines in homogeneous catalysis is well established [1–3] since they were discovered and characterised in the middle of 1960. The main efforts in this field were made on the investigation of the structure and properties of rhodium acetylacetonate, trifluoroacteylacetonate and hexafluoroacetylacetonate derivatives containing a wide series of phosphines [4–9]. On the other hand only few




**$HQ^s$**: $R^1$ = 2-thicnyl
**$HQ^o$**: $R^1$ = 2-furyl
**$HQ^T$**: $R^1$ = neopentyl

Fig. 1. Proligands HQ used in this work.

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data have been reported in the literature on rhodium complexes containing 1-phenyl-3-methyl-4-R(C=O)-pyrazol-5-ones HQ (R = Me or Ph) (Fig. 1) — a family of heterocyclic proligands analogues of β-diketones [10,11]. In order to understand the influence of the 4-R(C=O) fragment on the geometry and stability of rhodium complexes containing pyrazolonate ligands we describe here the synthesis and characterisation of rhodium derivatives with different 4-acylpyrazolones containing substituents with additional donor atoms (such as 2-thienyl, 2-furanyl groups) or sterically hindered ones (neo-pentyl group), namely 1-phenyl-3-methyl-4-(2-furoyl)-pyrazole-5-one (**HQ$^{o}$**), 1-phenyl-3-methyl-4-(2-thenoyl)-pyrazole-5-one (**HQ$^{s}$**), and 1-phenyl-3-methyl-(4-*tert*-butylacetyl)-pyrazole-5-one (**HQ$^{T}$**) (Fig. 1). The reactivity of [Rh(1,5-COD)Q] derivatives toward N-donor such as 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) or P-donors such as triphenylphosphine ($PPh_3$), 1,2-bis(diphenylphosphino)ethane (dppe) and 4,4-bis(diphenylphosphino)ferrocene (dppf) has also been investigated. The results of the reaction of [Rh(1,5-COD)Q] with allyl bromide are also reported. The crystal structures of $[Rh(1,5\text{-}COD)(\mu\text{-}Br)]_2$, [Rh(1,5-COD)Q$^{s}$] and [Rh(1,5-COD)(Phen)]Q$^{s}\cdot 0.5H_2O$ were determined. The latter one is the first example of anionic acylpyrazolonate in rhodium complexes.

## 2. Experimental

Solvents were used as supplied or distilled using standard methods. The samples for microanalyses were dried in vacuum to constant weight (293 K, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in-house with Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 $cm^{-1}$ using a Perkin–Elmer System 2000 FT-IT instrument. $^1H$ spectra were recorded in a VXR-300 Varian spectrometer operating at 300 MHz or in a V-200 Varian operating at 200 MHz. $^{31}P$-NMR spectra were recorded in a VXR-300 Varian spectrometer operating at 121.4 MHz. Proton chemical shifts are reported in ppm versus $Me_4Si$ while phosphorus chemical shifts are in ppm versus 85% $H_3PO_4$. Melting points (m.p.) were taken in a SMP3 Stuart scientific instrument and in a capillary apparatus.

Triphenylphosphine ($PPh_3$), 1,2-bis(diphenylphosphino)ethane (dppe), 1,1′-bis(diphenyl-phosphino)ferrocene (dppf), 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy) and allylbromide were purchased from Aldrich (Milwaukee) and used as received. $[Rh(COD)Cl]_2$ was synthesised from $RhCl_3\cdot 3H_2O$ (Aldrich) and purified using a standard procedure [12].

### 2.1. Synthesis of the ligands

#### 2.1.1. *HQ$^{s}$*

To a hot dioxane solution of 3-methyl-1-phenylpyrazole-5-one (15 g, 0.088 mol) $Ca(OH)_2$ (12 g, 0.162 mol) was added and the resulting mixture refluxed for 30 min. Then 2-thiophenecarbonyl chloride (12.61 g, 0.086 mol) was added dropwise to the suspension and the reaction mixture refluxed for 24 h. The yellow precipitate formed was treated with 350 ml of 2 N HCl and then filtered off and re-crystallised from MeOH (78% yield), m.p. 152–155 °C. Anal. Calc. for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 63.39; H, 4.35; N, 9.86; S, 11.21%. IR (Nujol, $cm^{-1}$): 2700br $\nu$(O···H), 1634s, 1596s, 1558m $\nu$(C=O, C=C); 429s, 383 s; 369s; 315m, 295s, 277 s. $^1H$-NMR ($CDCl_3$, 300 MHz): $\delta$ 2.43 (s, 3H, 3-C$H^{s}_{3Q}$), 7.17 (d, 1H, $C_4H_3S$), 7.29 (t, 1H, $C_4H_3S$), 7.47 (t, 2H, $C_6H_5$), 7.72 (t, 1H, $C_6H_5$), 7.74 (d, 1H, $C_4H_3S$), 7.84 (d, 2H, $C_6H_5$), 12.1 (br, 1H, O*H*).

#### 2.1.2. *HQ$^{o}$*

The compound **HQ$^{o}$** (yellow) has been obtained as described for **HQ$^{S}$** using 2-furoyl chloride. M.p. 103–105 °C. Anal. Calc. for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.19; H, 4.57; N, 10.40%. IR (Nujol, $cm^{-1}$): 2700br $\nu$(O···H), 1625m, 1585 s; 1531 s $\nu$(C=O, C=C), 690s; 604s; 585s, 509s; 391m; 355s; 282s. $^1H$-NMR ($CDCl_3$, 300 MHz): $\delta$ 2.59 (s, 3H, 3-C$H^{o}_{3Q}$), 6.62 (t, 1H, $C_4H_3O$), 7.25 (t, 1H, $C_4H_3O$), 7.42 (m, 3H, $C_6H_5$), 7.69 (d, 1H, $C_4H_3O$), 7.85 (d, 2H, $C_6H_5$).

#### 2.1.3. *HQ$^{T}$*

The ligand **HQ$^{T}$** has been prepared according to the method outlined in the literature [13].

### 2.2. Synthesis of complexes

#### 2.2.1. *[Rh(COD)(Q$^{s}$)] (1)*

To an EtOH solution of **HQ$^{s}$** (0.49 g, 1.0 mmol), $[Rh(COD)(\mu\text{-}Cl)]_2$ (0.54 g, 2.0 mmol) and $NEt_3$ (0.28 ml, 2 mmol) were added. The reaction mixture was stirred for 1 h under reflux, and then cooled to room temperature (r.t.); a yellow precipitate formed was filtered off, washed with $Et_2O$ and dried in vacuo to constant weight to give 1.20 g of **1** (62.5% yield). M.p. 146 °C. Anal. Calc. for $C_{23}H_{23}N_2O_2RhS$: C, 55.88; H, 5.67; N, 5.67; S, 6.48. Found: C, 55.67; H, 5.75; N, 5.70; S, 6.54%. IR (Nujol, $cm^{-1}$): 1602s, 1588s, 1557s, 1537s, 1530s $\nu$(C=O, C=C), 1470sh $\nu$(C=C, COD), 775s, 685s ($\rho$(C–H), $\nu$(COD)), 572m, 510m, 478m $\nu$(Rh–C–H), 410m, 390m $\nu$(Rh–O), 384m, 365m $\nu$(Rh–C). $^1H$-NMR ($CDCl_3$, 200 MHz): $\delta$ 1.74–1.86 (m, 4H, C$H_{2COD}$), 2.07 (s, 3H, 3-C$H^{s}_{3Q}$), 2.48–2.53 (m, 4H, C$H_{2COD}$), 4.18 (s, 2H, C$H_{COD}$), 4.28 (s, 2H, C$H_{COD}$), 7.08 (m, 1H, $C_4H_3S$), 7.18 (t, 1H, $C_6H_5$),

7.32–7.40 (m, 3H, $C_6H_5 + C_4H_3S$), 7.56 (d, 1H, $C_4H_3S$), 7.87 (d, 2H, $C_6H_5$).

*2.2.2. [Rh(COD)($Q^o$)] (**2**)*

Compound **2** (yellow) has been prepared as described for **1** (80% yield). M.p. 171 °C. Anal. Calc. for $C_{23}H_{23}N_2O_3Rh$: C, 57.75; H, 4.85; N, 5.86. Found: C, 57.65; H, 5.00; N, 5.62%. IR (Nujol, $cm^{-1}$): 1596s, 1563s, 1520s $\nu$(C=O, C=C), 1470sh $\nu$(C=C, COD), 778s, 688s ($\rho$(C–H), $\nu$(COD)), 572w, 515m, 490m, 475m $\nu$(Rh–C–H), 415w, 398sh $\nu$(Rh–O), 386m, 379m $\nu$(Rh–C). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ 1.74–1.87 (m, $CH_{2COD}$), 2.21 (s, 3H, 3-$CH^o_{3Q}$), 2.50–2.60 (m, 4H, $CH_{2COD}$), 4.18 (s, 2H, $CH_{COD}$), 4.29 (s, 2H, $CH_{COD}$), 6.55 (m, 1H, $C_4H_3O$), 6.98 (d, 1H, $C_4H_3O$), 7.18 (t, 1H, $C_6H_5$), 7.36 (t, 2H, $C_6H_5$), 7.59 (d, H, $C_4H_3O$), 7.87 (d, 2H, $C_6H_5$).

*2.2.3. [Rh(COD)($Q^T$)] (**3**)*

Compound **3** (pale-yellow) has been prepared as described for **1** (91% yield). M.p. 175 °C. Anal. Calc. for $C_{24}H_{31}N_2O_2Rh$: C, 59.75; H, 6.48; N, 5.81. Found: C, 60.00; H, 6.61; N, 5.75%. IR (Nujol, $cm^{-1}$): 1614sh, 1599s, 1570br, 1537s, 1500s $\nu$(C=O, C=C), 1475sh $\nu$(C=C, COD), 775w, 690s ($\rho$(C–H), $\nu$(COD)), 612m, 510m, 485s $\nu$(Rh–C–H), 410w, 395m $\nu$(Rh–O), 385m, 356m $\nu$(Rh–C). $^1$H-NMR ($CDCl_3$, 300 MHz): 1.03 (s, 9H, $CH^T_{3Q}$), 1.82–1.89 (m, 4H, $CH_{2COD}$), 2.25 (s, 3H, 3-$CH^T_{3Q}$), 2.46–2.52 (m, 4H, $CH_{2COD}$), 2.62 (s, 2H, $CH^T_{2Q}$), 4.18 (s, 2H, $CH_{COD}$), 4.23 (s, 2H, $CH_{COD}$), 7.19 (t, 1H, $C_6H_5$), 7.31 (t, 2H, $C_6H_5$), 7.83 (d, 2H, $C_6H_5$).

*2.2.4. [Rh(COD)(phen)]$Q^s$·0.5$H_2O$ (**4**)*

To a MeOH (20 ml) suspension of **1** (0.32 g, 0.64 mmol) phen (0.115 g, 0.64 mmol) was added. The orange solution formed was stirred overnight. After the addition of $Et_2O$ (20 ml) a red precipitate formed which was re-crystallised from MeOH–$Et_2O$ 1/1. About 0.380 g of pure **4** was obtained (88% yield). M.p. 170–172 °C. Anal. Calc. for $C_{35}H_{32}N_4O_{2.5}RhS$: C, 61.49; H, 4.72; N, 8.20; S, 4.69. Found: C, 61.43; H, 4.67; N, 8.27; S, 4.71%. IR (Nujol, $cm^{-1}$): 1614s, 1588s, 1552s $\nu$(C=O, C=C), 1475sh $\nu$(C=C, COD), 770s, 698m ($\rho$(C–H), $\nu$(COD)), 599m, 516m, 492m $\nu$(Rh–C–H), 361m, 344m $\nu$(Rh–C), 301w $\nu$(Rh–N). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ 1.95–2.11 (m, 4H, $CH_{2COD}$), 2.30 (s, 3H, 3-$CH^s_{3Q}$), 2.55–2.70 (m, 4H, $CH_{2COD}$), 4.56 (s, 4H, $CH_{COD}$), 6.87–7.00 (m, 2H, $C_4H_3S$), 7.05 (t, 1H, $C_4H_3S$), 7.18 (t, 1H, $C_6H_5$), 7.36 (d, 1H, $C_4H_3S$), 7.57 (d, 2H, $CH_{phen}$), 7.60 (m, 1H, $C_6H_5$), 7.86 (t, 2H, $CH_{phen}$), 7.95 (d, 2H, $CH_{phen}$), 8.32 (d, 2H, $C_6H_5$), 8.79 (d, 2H $CH_{phen}$).

*2.2.5. [Rh(COD)(phen)]$Q^o$ (**5**)*

Compound **5** (yellow) has been prepared as described for **4** (90% yield). M.p. 282 °C. Anal. Calc. for $C_{35}H_{31}N_4O_3Rh$: C, 63.83; H, 4.74; N, 8.51. Found: C, 63.73; H, 4.68; N, 8.47%. IR (Nujol, $cm^{-1}$): 1613s, 1588s, 1543sh $\nu$(C=O, C=C), 1460sh $\nu$(C=C, COD), 775s, 718s ($\rho$(C–H), $\nu$(COD)), 600m, 510m, 491sh, 480sh $\nu$(Rh–C–H), 364m $\nu$(Rh–C), 306w $\nu$(Rh–N). $^1$H-NMR ($CD_3OD$, 300 MHz): $\delta$ 2.20–2.23 (m, 4H, $CH_{2COD}$), 2.33 (s, 3H, 3-$CH^o_{3Q}$), 2.63–2.67 (m, 4H, $CH_{2COD}$), 4.83 (s, 4H, $CH_{COD}$), 6.51 (m, 1H, $C_4H_3O$), 7.07 (t, 1H, $C_4H_3O$), 7.19 (t, 2H, $C_6H_5$), 7.62 (t, 1H, $C_6H_5$), 7.71 (d, 2H, $CH_{phen}$), 7.86 (d, 1H, $C_4H_3S$), 7.93 (t, 2H, $CH_{phen}$), 8.12 (d, 2H, $CH_{phen}$), 8.36 (d, 2H, $C_6H_5$), 8.75 (d, 2H $CH_{phen}$).

*2.2.6. [Rh(COD)(bipy)]$Q^s$·2$H_2O$ (**6**)*

Compound **6** (red–orange) has been prepared as described for **4** by using bipy instead of phen (80% yield). M.p. (dec.) 80 °C. Anal. Calc. for $C_{33}H_{35}N_4O_4RhS$: C, 57.73; H, 5.14; N, 8.16; S, 4.67. Found: C, 57.62; H, 4.87; N, 8.02; S, 4.58%. IR (Nujol, $cm^{-1}$): 3400br $\nu$(O–H), 1614s, 1602s, 1588s, 1539s, 1504s $\nu$(C=O, C=C), 1454s $\nu$(C=C, COD), 768s, 725m ($\rho$(C–H), $\nu$(COD)), 600m, 513m, 484m $\nu$(Rh–C–H), 418sbr, 398s br, 380sh, 360m $\nu$(Rh–C), 302w $\nu$(Rh–N). $^1$H-NMR ($CDCl_3$, 200 MHz, 295 K): $\delta$ 1.90–2.05 (m, 4H, $CH_{2COD}$), 2.38 (s, 3H, 3-$CH^s_{3Q}$), 2.50–2.60 (m, 4H, $CH_{2COD}$), 4.35 (br, 4H, $CH_{COD}$), 7.00 (m, 2H, $C_4H_3S$), 7.20–7.30 (m, 2H, $C_6H_5 + C_4H_3S$), 7.50–7.60 (m, 2H, $C_6H_5 + C_4H_3S$), 7.60 (d, 2H, $CH_{bipy}$), 7.90–8.10 (m, 4H, $CH_{bipy}$), 8.40 (m, 2H, $C_6H_5$), 8.70–8.80 (m, 2H, $CH_{bipy}$). $^1$H-NMR ($CDCl_3$, 200 MHz, 223 K): $\delta$ 2.10 (m, 4H, $CH_{2COD}$), 2.44 (s, 3H, 3-$CH^s_{3Q}$), 2.54 (m, 4H, $CH_{2COD}$), 4.40 (br, 4H, $CH_{COD}$), 7.01 (m, 2H, $C_4H_3S$), 7.30 (m, 2H, $C_6H_5 + C_4H_3S$), 7.50 (d, 2H, $CH_{bipy}$), 7.53 (m, 4H, $C_6H_5 + C_4H_3S$), 8.07 (m, 4H, $CH_{bipy}$), 8.96 (m, 2H, $CH_{bipy}$).

*2.2.7. [Rh(COD)(bipy)]$Q^o$·2$H_2O$ (**7**)*

Compound **7** (red–orange) has been prepared as described for **4** by using bipy (85% yield). M.p. (dec.) 170 °C. Anal. Calc. for $C_{33}H_{35}N_4O_5Rh$: C, 59.11; H, 5.26; N, 8.36. Found: C, 59.12; H, 5.07; N, 8.22%. IR (Nujol, $cm^{-1}$): 3400br $\nu$(O–H), 1610sh, 1602s, 1567s, 1524S $\nu$(C=O, C=C), 1470sh $\nu$(C=C, COD), 768m, 726m ($\rho$(C–H), $\nu$(COD)), 600m, 511m, 484w $\nu$(Rh–CH), 448w, 418w, 398v w, 360w $\nu$(Rh–C), 304w $\nu$(Rh–N). $^1$H-NMR ($CDCl_3$, 200 MHz, 293 K): $\delta$ 2.05 (m, 4H, $CH_{2COD}$), 2.48 (s, 3H, 3-$CH^s_{3Q}$), 2.20–2.40 (m, 4H, $CH_{2COD}$), 4.40 (br, 4H, $CH_{COD}$), 6.50 (br, 1H, $C_4H_3O$), 7.0–8.0 (m br, 7H, $C_6H_5 + C_4H_3O$), 7.83 (d, 2H, $CH_{bipy}$), 8.07 (m, 2H, $CH_{bipy}$), 8.36 (d, 2H, $CH_{bipy}$), 8.72 (m, 2H, $CH_{bipy}$).

*2.2.8. Synthesis of [Rh($PPh_3$)$_2$($O_2$)($Q^s$)] (**8**)*

To a $Et_2O$ suspension (30 ml) of **1** (0.5 g, 1 mmol) $PPh_3$ (053 g, 2 mmol) dissolved in the same solvent (30 ml) was added. A dark-red solution formed was stirred

vigorously for 1 h. A brownish precipitate (0.78 g) formed was filtered off and washed with $Et_2O$ (83% yield). M.p. (dec.) 136 °C. Anal. Calc. for $C_{51}H_{41}N_2O_4P_2RhS$: C, 64.97; H, 4.38; N, 2.97; S, 3.40. Found: C, 64.68; H, 4.59; N, 2.87; S. 3.35%. IR (Nujol, $cm^{-1}$): 1600s, 1588s, 1562s, 1530s $\nu$(C–O, C–C), 1462sh, 1450s $\nu$(P–Ph), 858s br $\nu$(O–O), 540s, 524s, 514s, 493s $\nu$(C–P–C), 457m, 444m, 429m $\nu$(Rh–O), 366m, 322w. $^1$H-NMR ($CDCl_3$, 200 MHz, 295 K): $\delta$ 1.76 (s, 3H, Me), 6.85–7.60 (m, 36H, $C_6H_5 + C_4H_3S$), 7.80 (d, 2H, $C_4H_3S$). $^{31}$P-NMR ($CDCl_3$, 121.4 MHz, 295 K): $\delta$ 15.8d ($J_{Rh-P} = 89.6$ Hz).

*2.2.9. Synthesis of [Rh(PPh$_3$)$_2$(O$_2$)(Q$^o$)] (**9**)*

Compound **9** (brownish) has been prepared as described for **8** in toluene (76% yield) by using compound **2** as the starting reagent. M.p. (dec.) 120 °C. Anal. Calc. for $C_{51}H_{41}N_2O_5P_2Rh$: C, 66.10; H, 4.46; N, 3.02. Found: C, 66.08; H, 4.63; N, 2.97%. IR (Nujol, $cm^{-1}$): 1603m, 1579s, 1551s, 1527sh $\nu$(C–O, C–C), 1461s $\nu$(P–Ph), 883br $\nu$(O–O), 541s, 520s, 511s, 496sh $\nu$(C–P–C), 456m, 440w, 420w $\nu$(Rh–O). $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 1.65 (s, 3H, 3-C$H^o_{3Q}$), 6.50 (d, 1H, $C_4H_3O$), 6.50 (d, 1H, $C_4H_3O$), 7.0–8.0 (m br, 31H, $C_6H_5 + C_4H_3O$). $^{31}$P-NMR ($CDCl_3$, 121.4 MHz): $\delta$ 15.86 (d, $J_{Rh-P} = 88$ Hz). $^1$H-NMR ($C_6D_6$, 300 MHz): $\delta$ 1.93 (s, 3H, 3-C$H^o_{3Q}$), 5.90 (br, 1H, $C_4H_3O$), 6.60 (d, 1H, $C_4H_3O$), 6.80–8.2 (m br, 36H, $C_6H_5 + C_4H_3O$). $^{31}$P-NMR ($C_6D_6$, 121.4 MHz): $\delta$ 17.16 (d, $J_{Rh-P} = 90$ Hz).

*2.2.10. Synthesis of [Rh(PPh$_3$)$_2$(O$_2$)(Q$^T$)] (**10**)*

Compound **10** (brownish) has been prepared as described for **8** (79% yield). M.p. (dec.) 170 °C. Anal. Calc. for $C_{52}H_{49}N_2O_4P_2Rh$: C, 67.10; H, 5.31; N, 3.01. Found: C, 66.90; H. 5.51; N, 2.96%. IR (Nujol, $cm^{-1}$): 1603s, 1590s, 1577s, 1568s, 1532s $\nu$(C–O, C–C), 1442s $\nu$(P–Ph), 889m $\nu$(O–O), 544s, 524s, 511s, 490m $\nu$(C–P–C), 468m, 453m, 435m $\nu$(Rh–O), 418m, 398w, 357m, 325w. $^1$H-NMR ($C_6D_6$, 300 MHz, 295 K): $\delta$ 1.19 (s, 9H, $C_4H^T_{9Q}$), 1.54 (s, 2H, $CH^T_{2Q}$), 2.14 (s, 3H, 3-C$H^T_{3Q}$), 6.70–7.10, 7.6–7.8 (m, 35H, $C_6H_5$). $^{31}$P-NMR ($C_6D_6$, 121.4 MHz): $\delta$ 16.7 (d, $J_{Rh-P} = 109.2$ Hz).

*2.2.11. [Rh(dppf )(O$_2$)(Q$^s$)] (**11**)*

To a $Et_2O$ suspension of compound **1** (0.32 g, 0.64 mmol), dppf (0.35 g, 0.64 mmol) was added. After 2 h a clear orange solution formed was concentrated under vacuum. A yellow-brownish precipitate was filtered off washed with diethyl ether and recrystallised from MeOH (89% yield). M.p. (dec.) 190 °C. Anal. Calc. for $C_{49}H_{39}FeN_2O_4P_2RhS$: C, 60.51; H, 4.04; N, 2.88; S, 3.30. Found: C, 60.54, H, 4.38; N, 2.82; S, 2.93%. IR (Nujol, $cm^{-1}$): 1590s, 1568s, 1531s, 1509s $\nu$(C–O, C–C), 1445sh $\nu$(P–Ph), 550s, 516m, 493s, 462m, 434m $\nu$(C–P–C), 347w, 302w. $^1$H-NMR ($CDCl_3$): $\delta$ 2.54 (s, 3H, 3-C$H^S_{3Q}$), 4.19 (br, 4H, C$H_{dppf}$), 4.33 (br, 4H, C$H_{dppf}$), 6.80–8.0 (m br, 28H, $C_6H_5 + C_4H_3S$). $^{31}$P-NMR ($CDCl_3$, 121 MHz, 295 K): $\delta$ 44.11 (d, $J_{Rh-P} =$ 145.8 Hz), 43.1 (d, $J_{Rh-P} = 129.1$ Hz)

*2.2.12. [Rh(dppe)$_2$(O$_2$)](Q$^T$) (**12**)*

Compound **12** (brownish) has been obtained as described for **11** in THF (40% yield). M.p. (dec.) 195 °C. Anal. Calc. for $C_{68}H_{67}N_2O_4P_4Rh$: C, 67.89; H, 5.61; N, 2.33. Found: C, 67.60; H. 5.80; N, 2.20%. IR (Nujol, $cm^{-1}$): 1618s, 1590s, 1580s, 1574sh, 1568s, 1558s, 1532s, 1520s $\nu$(C–O, C–C), 1450br $\nu$(P–Ph), 879br $\nu$(O–O), 536s, 505s, 482s $\nu$(C–P–C), 469m, 441m, 423m $\nu$(Rh–O), 397w, 386w, 358w,m, 350m, 325w, 301w. $^1$H-NMR ($CDCl_3$, 200 MHz, 295 K): $\delta$ 1.10 (s, 9H, $C_4H^T_{9Q}$), 2.11 (br, 8H, C$H_{2dppe}$), 2.46 (s, 3H, 3-C$H^T_{3Q}$), 2.53 (s, 2H, $CH^T_{2Q}$), 6.8–7.8 (m, 45H, $C_6H_5$). $^{31}$P-NMR ($CDCl_3$, 121.4 MHz): $\delta$ 51.06 (double triplet, $J_{Rh-P} =$ 126 Hz, $J_{P-P} = 17$ Hz), 44.97 (double triplet, $J_{Rh-P} = 91$ Hz, $J_{P-P} = 17$ Hz).

*2.2.13. [Rh(dppf-O$_2$)(Q$^T$)] (**13**)*

Compound **13** (brownish) has been obtained from the reaction of 1 mmol of **3** with 2 mmol of dppf in THF. The reaction mixture was stirred for 24 h. A precipitated formed when $Et_2O$ was added to the solution was re-crystallised from THF–$Et_2O$ 1/1 (30% yield). M.p. (dec.) 225 °C. Anal. Calc. for $C_{50}H_{47}FeN_2O_4P_2Rh$: C, 62.52; H, 4.93; N, 2.92. Found: C, 62.80; H. 4.80; N, 2.80%. IR (Nujol, $cm^{-1}$): 1599s, 1587s, 1574s, 1530m $\nu$(C–O, C–C), 1470sh $\nu$(P–Ph), 1090 $\nu$(P–O), 566s, 523s, 513s, 496s $\nu$(C–P–C), 472m, 462m, 437m $\nu$(Rh–O), 397w, 351m, 325w. $^1$H-NMR ($CDCl_3$, 200 MHz, 295 K) $\delta$ 0.91 (s, 9H, $C_4H^T_{9Q}$), 2.13 (s, 3H, 3-C$H^T_{3Q}$), 2.16 (s, 2H, $CH^T_{2Q}$), 4.16, 4.22, 4.27, 4.28 (4s, 8H, C$H_{dppf}$), 7.0–8.2 (m, 25H, $C_6H_5$). $^{31}$P-NMR ($CDCl_3$, 121.4 MHz): $\delta$ 28.53br.

*2.2.14. [Rh(COD)($\mu$-Br)]$_2$ (**14**)*

Compound **14** has been obtained when 1 mmol of either compound **1** or **3** reacts with 2 mmol of allylbromide in benzene. Yellow-brownish crystals formed when the concentrated benzene solution was stored for 24 h at 277 K. Physical and analytical data correspond to those reported in Ref. [14].

*2.3. Crystallographic study*

The data for complexes **1**, **4** and **14** were collected in an Image-Plate diffractometer (IPDS, Stoe) using graphite monochromated Mo–$K_\alpha$ radiation ($\lambda =$ 0.71073 Å). Numerical absorption correction was applied only for the bromine-containing complex **14**. The structures were solved by direct methods (SHELXS 86 [15a]) and refined anisotropically for all non-hydrogen atoms using SHELXL 93 [15b]. Hydrogen atoms (except

Table 1
Crystal data and structure refinement parameters for Rh(COD) derivatives

| | [Rh(1,5-COD)($Q^s$)] | Rh(1,5-COD)(phen)$Q^s$·0.5$H_2O$ | [Rh(1,5-COD)(μ-Br)]$_2$ |
|---|---|---|---|
| Empirical formula | $C_{23}H_{23}N_2O_2RhS$ | $C_{35}H_{32}N_4O_{2.5}RhS$ | $C_{16}H_{24}Br_2Rh_2$ |
| Formula weight | 494.40 | 683.82 | 581.99 |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic |
| Space group | $P2_1/c$ | *Pbca* | $I2/m$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 7.796(2) | 20.153(3) | 11.830(3) |
| $b$ (Å) | 13.190(3) | 22.240(4) | 11.555(3) |
| $c$ (Å) | 20.125(4) | 26.337(5) | 12.443(3) |
| $\beta$ (°) | 97.75(3) | 90 | 97.78(3) |
| $V$ (Å$^3$) | 2050.8(8) | 11 804(4) | 1692.3(7) |
| $Z$ | 4 | 16 | 4 |
| Absorption coefficient (mm$^{-1}$) | 0.957 | 0.691 | 6.661 |
| Crystal size (mm) | 0.5 × 0.5 × 0.2 | 0.3 × 0.3 × 0.2 | 0.5 × 0.3 × 0.2 |
| Temperature/K | 180 | 180 | 180 |
| $\theta$ Range for data collection (°) | 2.5–27.0 | 2.5–25.8 | 3.5–27.8 |
| Reflections collected | 9880 | 57 805 | 4971 |
| Independent reflections | 4347 [$R_{int} = 0.059$] | 11 204 [$R_{int} = 0.145$] | 2055 [$R_{int} = 0.081$] |
| Data/parameters | 3307/275 | 7656/786 | 1647/94 |
| $wR_2$ (on $F^2$) | 0.0691 | 0.1290 | 0.1045 |
| $R_1$ [$I \geq 2\sigma(I)$] | 0.0385 | 0.0565 | 0.0413 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.698 and −0.764 | 0.965 and −0.668 | 1.364 and −1.440 |

those of the water molecule in the structure of **4**) were included in the calculated positions and refined in the riding mode.

Crystallographic data and some details of data collection and structures refinement are reported in Table 1. The interatomic distances for Rh environment are listed in Table 2.

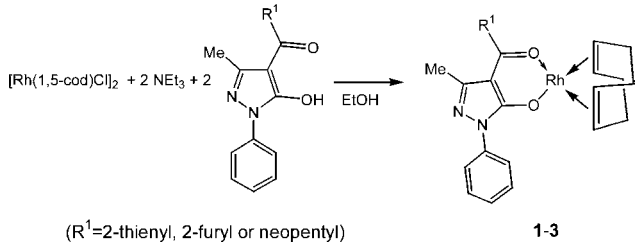
## 3. Results and discussion

The ligands **HQ$^T$**, **HQ$^o$** and **HQ$^s$** were prepared by a standard procedure reported by Pettinari et al. [13] and Jensen [16]. **HQ$^T$** has already been reported by Pettinari et al. [13] in an investigation on barium(II) complexes, while **HQ$^o$** and **HQ$^s$** according to our knowledge were prepared by us with the aim to investigate the influence of 2-thienyl and 2-furanyl substituents on the structure and reactivity of rhodium complexes. While this work has been in progress the ligand **HQ$^s$** has been reported and structurally characterised [17].

The interaction between [Rh(COD)Cl]$_2$ and **HQ$^T$**, **HQ$^o$** or **HQ$^s$** in the presence of $NEt_3$ results in the formation of [Rh(COD)Q] complexes **1**–**3** (Scheme 1) which are yellow solids soluble in methanol, acetone and chlorinated solvents and slightly soluble in non-polar solvents. They are sufficiently stable in air and can be synthesised without using the Schlenk technique. In the IR spectra of **1**–**3** the $\nu$(C···O, C···C) bands at 1500–1600 cm$^{-1}$ clearly indicate the bidentate-chelating mode of the acylpyrazolonate as already found in the analogous β-diketonate derivatives containing dienes and olefins [8,10,11,18]. The presence of $\nu$(Rh–C) and $\nu$(Rh–O) stretching vibrations at ca. 390–360 and 420–390 cm$^{-1}$, typical of Rh–COD and Rh(I)–β-diketonates complexes, respectively, confirms the formation of the products. In the $^1$H-NMR spectra of **1**–**3** there are sets of signals due to the COD and acylpyrazolonate moieties. All the olefin resonances are shifted downfield with respect to the free ligand that confirms the coordination [19].

Table 2
Coordination of the Rh atom (distances in Å) in the crystal structures of **1**, **4**, and **14**

| Distance | **1** (X = O) | **4** (X = N) Rh(1) | Rh(2) | **14** (X = Br) |
|---|---|---|---|---|
| Rh–C(1) | 2.100(3) | 2.139(8) | 2.125(6) | 2.119(6) |
| Rh–C(2) | 2.110(2) | 2.124(8) | 2.146(7) | 2.117(6) |
| Rh–C(5) | 2.103(3) | 2.144(7) | 2.145(7) | 2.110(5) |
| Rh–C(6) | 2.127(2) | 2.129(8) | 2.154(8) | 2.117(6) |
| Rh–X(5) | 2.067(2) | 2.085(5) | 2.090(5) | 2.538(1) |
| Rh–X(6) | 2.077(2) | 2.109(7) | 2.089(6) | 2.535(1) |




Scheme 1.

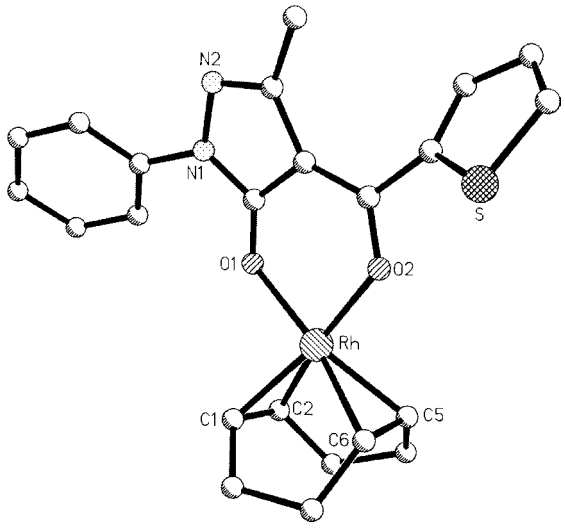
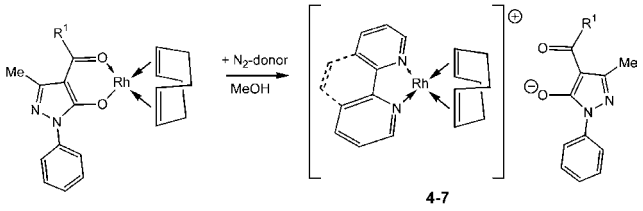



Fig. 2. Molecular structure of derivative **1**.




($R^1$=2-thienyl or 2-furyl; $N_2$-donor=phen or bipy))

Scheme 2.

The structure of **1** was confirmed by X-ray single crystal crystallography (Fig. 2). The Rh(I) atom adopts an usual square-planar coordination with the carbonyl oxygens and the centres of the double bonds on the sides of the square. The average Rh–C distance, 2.110 Å, corresponds well to the values for Rh(COD)(β-diketonate) complexes known from the literature: 2.102 Å in a previous acetylacetonate complex [20] or 2.115 Å in the trifluoroacetylacetonate complex [8]. The average Rh–O distance, 2.072 Å, is also well comparable with the similar distances, 2.060 and 2.062 Å, found in the two complexes mentioned above.

The reactivity of **1–3** toward N- and P-donor ligands has also been investigated. The reaction of **1** or **2** with phen or bipy results in the formation of the ionic complexes **4–7** by the displacement of the acylpyrazolonate ligand from the Rh(I) coordination sphere by the $N_2$-donor ligand as shown in Scheme 2.

In the IR spectra of **4–7** the $\nu$(C···O, C···C) bands are typical of complexes containing anionic not coordinated β-diketonate species [11]. The presence of Rh–N (ca. 300 $cm^{-1}$) and Rh–C (ca. 360 $cm^{-1}$) stretching vibrations is in accordance with the formation of $Rh(COD)(N–N)]^+$ species which were already known as perchlorate, chloride, tetraphenylborate or hexafluorophosphate salts [21], but have never been described in the case of rhodium complexes with β-diketones such as acetylacetone or hexafluoroacetylacetone. Signals multiplicity and patterns of chemical shifts in $^1$H-NMR spectra of **4–7** are also in accordance with these formulations. A similar substitution for [Rh(COD)L] derivatives has been recently reported by N-donor ligands such as aliphatic diamines, imidazoles, pyridines and related compounds [22]. The reaction of $[Rh(1,5\text{-}COD)X]_2$ (X = Cl, Br) with N–N ligand was also shown to give the ionic compounds $[Rh(COD)(N–N)][Rh(COD)X_2]$ [23], but in our case no analogous complexes have been obtained, may be due to the sterical hindrances in a hypothetical $[Rh(COD)(Q)_2]^-$anion. Recently it has been reported that β-diketonate ligands (e.g. acetylacetonate) can be easily substituted by other N-donors, such as tris(pyrazolyl)borates [24], some O-donors (*N*-acetyl-3-butanoyl-1,5-dihydro-4-hydroxy-2H-pyrrol-2-one [25]) and mixed O,P-donors (polyether bridged diphosphines [26]) that confirms the dependence of the substitution on the nucleophility of the entering group.

The phen-containing complexes **4** and **5** are much more stable with respect to bipy derivatives and can be isolated with almost quantitative yield even if the synthesis was performed in air. The bipy derivatives **6** and **7** can be obtained in good yields only when the reactions were carried out in nitrogen atmosphere. Complexes **6** and **7** are air sensitive to oxidation and hydration. Complexes **6** and **7** always crystallise with two molecules of water that can be explained by the more flexible nature of bipy with respect to phen and by the possibility of H-bonding between $H_2O$ and heteroatoms of acylpyrazolonate anion. Such difference has been already mentioned in 1-phenyl-3-methylpyrazole-5-one derivatives [11]. The crystal structure of **4**, $[Rh(COD)(phen)](Q^s)\cdot 0.5\ H_2O$, has been determined that confirms the ionic nature of the compound (Fig. 3). The square coordination of the two independent Rh atoms is characterised by the average Rh–C distance of 2.146 Å and Rh–N distance of 2.103 Å. These values are close to the corresponding distances found for the related structure of $[Rh(COD)(bipy)](PF_6)$: 2.135 and 2.095 Å [27]. The Rh–C distances in both these cationic complexes are somewhat longer than those in the neutral [Rh(COD)(β-diketonate)] derivatives. It should be noticed that both $Q^s$ anions in **4** have a different configuration from that found in **1** where $Q^s$ acts as a chelating ligand. Due to the rotation around the C–C bond the *trans*-orientation of the carbonyl groups is close to that in the free ligand [17]. It can be concluded on the basis of the distances from the $O(5)_w$ to both anionic ligands: O5···O4, 2.837 Å and O5···N6′, 3.098 Å, that the water molecule connects them to the dimer by means of weak H-bonds (Fig. 4).

The reaction of [Rh(COD)Q] complexes **1–3** with triphenylphosphine results in the substitution of the

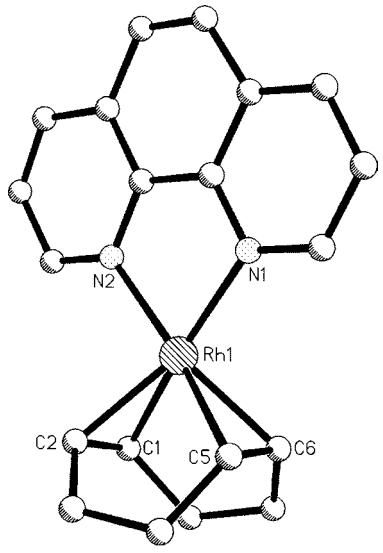



Fig. 3. Molecular structure of cation in derivative **4**.

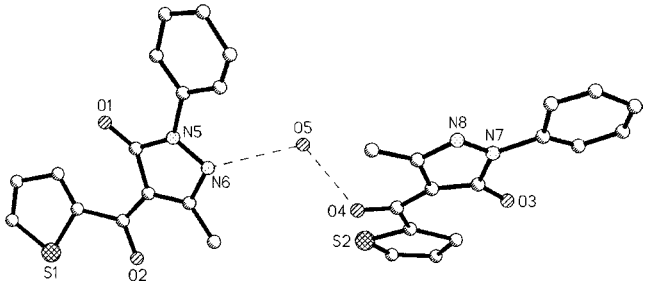
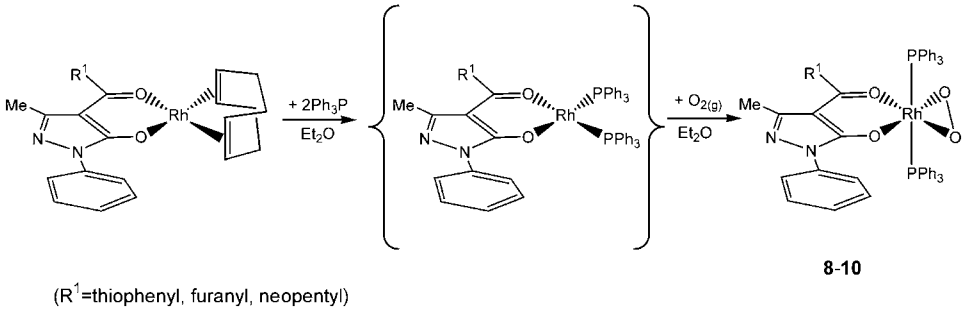


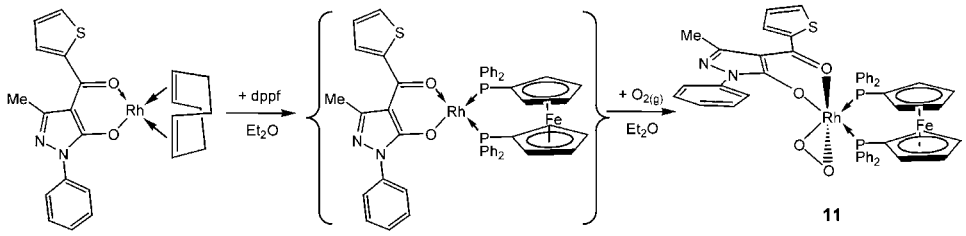

Fig. 4. H-bonding interconnection between two anions in **4**.

labile COD ligand by $PPh_3$ with the formation of $[RhQ(PPh_3)_2]$ intermediates analogous to those reported in Refs. [11,26] which in this case can be detected only by $^{31}P\{^1H\}$-NMR spectroscopy but are very sensitive toward even negligible traces of oxygen. The $[RhQ(PPh_3)_2]$ intermediates immediately reacts with $O_2$ yielding the Rh(III) species $[RhQ(O_2)(PPh_3)_2]$ **8–10** (Scheme 3). In fact, in the IR spectra of **8–10** there are stretching bands at 850–890 $cm^{-1}$ due to the presence of $\eta^2$-peroxo-groups [28]. This reaction was also monitored by NMR: two double doublets at ca. 34 and 37 ppm ($^{31}P-^{103}Rh$ coupling constants of ca. 150.5 and 140.9 Hz, respectively; $^{31}P-^{31}P$ coupling constants of 28.6 and 28.8 Hz, respectively) were immediately detected in the $^{31}P\{^1H\}$-NMR of a benzene solution containing 0.1 mmol of **1** and 0.2 mmol of $PPh_3$. After 5 min these signals disappear and the same signals found in the spectra of **8–10** appear (see below). The $\nu$(C···O) and $\nu$(C···C) vibrations in the IR spectra of **8–10** fall in region typical for the coordinated acylpyrazolone [10,11]. The P–C bands are similar to those reported for other triphenylphosphine derivatives, e.g. $Rh(PPh_3)_3Cl$ [29] and different from those found in triphenylphosphine–oxide complexes [28a,30]. The $^1H$-NMR spectra of **8–10** exhibit all resonances due to the acylpyrazolonate moiety and $PPh_3$. The methyl resonance is upfield shifted with respect to that found in **1–3**. The $^{31}P$-NMR spectra of **8–10** exhibit a doublet at ca. 16.0 ppm with $J_{Rh-P}$ typical of Rh(III) complexes containing $PPh_3$ and β-diketones (23.0 d ($J_{Rh-P} = 90.9$ Hz) in $RhCl_2(PPh_3)_2(acac)$ and 24.7 d ($J_{Rh-P} = 99.6$ Hz) in $RhCl(OOH)(PPh_3)_2(acac)$ [28b]). The large difference in the $J_{Rh-P}$ coupling constant values of complexes **8** and **9** with respect to **10** can be due to both large difference in steric and electronic properties of the pyrazolonato ligand and different isomeric *cis*- or *trans*-$P_2Rh$ configuration. While heating or during storage the peroxide complexes can decompose: in this case the $\nu$(O–O) bands in the IR spectra disappear, while the intensity of P=O stretching at 1120 and 1160 $cm^{-1}$ increases clearly indicating the oxidation of triphenylphosphine [28a,30]. Such process has already been studied and described for the Wilkinson catalyst, $[Rh(CO)I(PPh_3)_2]$ [31] and in the case of interaction between $[Rh(acac)(CO)(PPh_3)]$ with salicilyc acid [28c]. It is well known that π-acceptors such as COD, NBD, COE, CO and ethylene stabilise Rh in the low oxidation state +1, so that the compounds are air stable to oxidation during storage. Even the mixed ligand complexes containing both CO and $PPh_3$ ligands are sufficiently air stable. $PPh_3$ acts as a chemical Janus toward Rh centre. From one side, refluxing $RhCl_3$ in ethanol in the presence of the excess of $PPh_3$ is an important method to prepare the Wilkinson catalyst or $[Rh(PPh_3)_2Cl]_2$, i.e. to stabilise Rh in +1 state, since




($R^1$=thiophenyl, furanyl, neopentyl)

Scheme 3.




Scheme 4.

both $Rh(PPh_3)_3Cl$ and $[Rh(PPh_3)_2Cl]_2$ are sufficiently air stable as solids. On the other hand the full substitution of the labile soft carbon π-acceptor (CO, COD) by $PPh_3$ results in a complete destabilisation of Rh toward oxidation, so that the isolation of $Rh(PPh_3)_2$(dik) complexes in many cases is not possible. Recently such complexes with some tertiary phosphines were shown to be thermodynamically unstable [32]. So, the only possible way to stabilise Rh(I) is to use a large excess of phosphine as it was shown to be a method used in the preparation of the Wilkinson catalyst from $[Rh(COD)Cl]_2$.

In the literature there are indications on the existence of mixed ligand Rh(I) cycloalkadiene (COD, NBD)–$PPh_3$ complexes such as $[Rh(COD)(PPh_3)_2]Cl$ [33] or $[Rh(NBD)(PPh_3)_2]ClO_4$ [34]. Such complexes were really isolated and characterised in the case of less donor tri(*p*-fluorophenyl)phosphine [35] and chelating alkoxy aryl- and alkylarylphosphines as tris(2,4,6-trimethoxyphenyl)phosphine [36] or benzylbis(2-ethoxyethyl)phosphine [37]. It has also been shown [8] that alyphatic phosphines such as $PMe_3$, being more basic withrespect to $PPh_3$, completely substitute cyclooctadiene in Rh(COD)(dik) giving $(PMe_3)_2Rh$(dik) or even ionic $[Rh(PMe)_4]$dik.

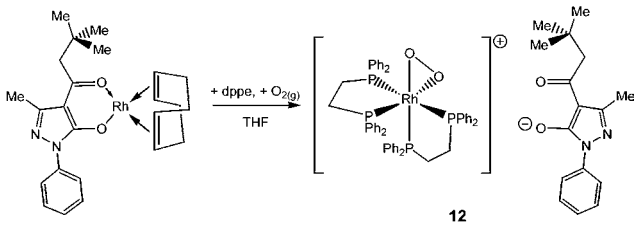
The reactivity of Rh–COD complexes toward bidentate chelating phosphine has also been investigated. The interaction of **1** with dppf resulted in the formation of the oxidation product **11** (Scheme 4). In fact the sharp band at 874 $cm^{-1}$ in the IR spectrum of **11** is typical of $\eta^2$-peroxo-complexes, while the C–O, C–C adsorptions are similar to those found in the spectrum of **1**, indicating the chelating nature of acylpyrazolone. The $^{31}$P-NMR spectrum of **11** exhibit a signal similar to that found in Rh(III) species containing not-oxidised dppf ligands [38].

When **3** reacts with an excess of dppe the complex $[Rh(dppe)_2O_2]Q^T$ (**12**) was formed (Scheme 5). Analogous complexes $[Rh(dppe)_2O_2]X$ have been reported ($X = Cl^-$ and $BF_4^-$). The spectral data of our complex are in accordance with those reported in Ref. [39].

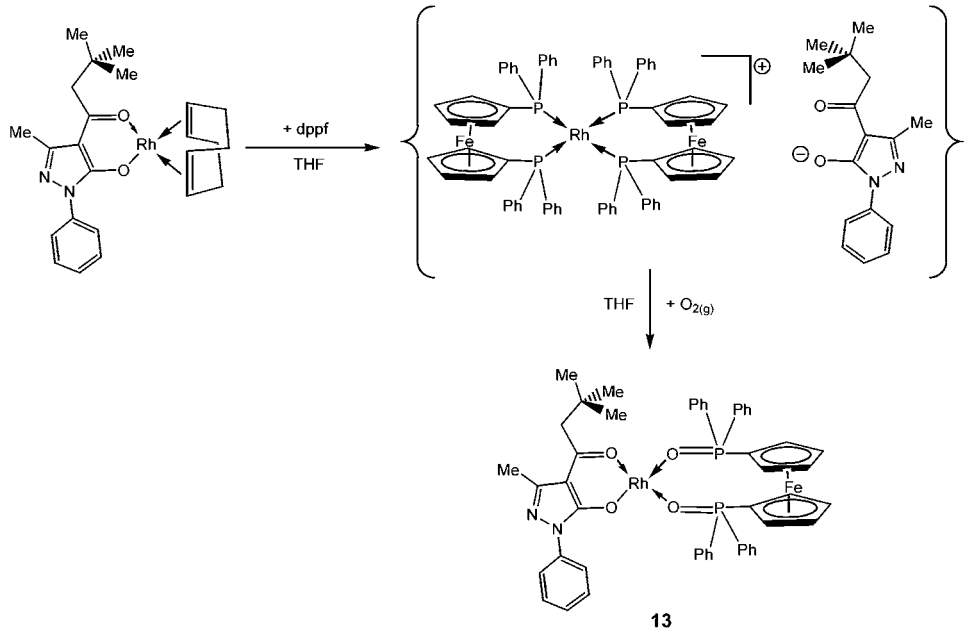
Finally when compound **3** reacts with an excess of dppf and the reaction is carried out for more than 24 h, then compound **13** (Scheme 6) containing the oxidised dppf-$O_2$ ligand is formed. This reaction was also monitored by $^{31}$P-NMR spectra. After 15 min the $^{31}$P-NMR spectrum exhibited signals typical of $[Rh(dppf)_2]^+$ species [40]. After 2 h signals analogous to those found in the spectrum of **11** appeared which disappeared completely after 24 h. At this point only a broad signal typical of oxidised dppf-$O_2$ was present. Unfortunately this compound is soluble only in chlorinate solvents, in which it decomposes to not clearly identifiable species.

The oxidative addition of allyl bromide to complex **1** has been studied. It was shown that in the absence of $PPh_3$ no oxidation occurs, but the reaction proceeds via the substitution pathway quantitatively giving $[Rh(COD)(\mu\text{-}Br)]_2$ (**14**). In the presence of $PPh_3$ the yellowish colour of the solution of **1** in THF turns to brownish immediately and a mixture of oxidation products forms. Further investigation of this reaction will be reported elsewhere.

The structure of $[Rh(COD)Br]_2$ (**14**) resembles that of the corresponding chloride [41]. However, both structures are not isomorphous crystallographically. The two independent Rh atoms in **14** are lying in the mirror plane of the molecule (Fig. 5). Both Rh atoms have a slightly distorted square-planar environment with two bromine atoms and two centres of the double bonds. The average Rh–C distance, 2.116 Å, is close to the corresponding values, 2.12 Å, calculated from the data in Ref. [41]. As expected, the Rh–Br distances, 2.54 Å, are considerably longer than those of Rh–Cl, 2.38 Å [41]. Two square-planar Rh fragments are folded around the Br···Br line by 31°. This feature has not been noticed in the original publication [41] where the whole dimeric fragment was considered as nearly planar.




Scheme 5.




Scheme 6.

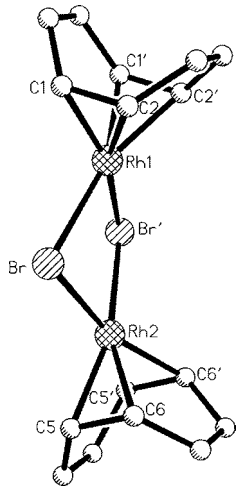



Fig. 5. Molecular structure of derivative **14**.

## 4. Conclusions

It was shown that the additional donor atoms in 4-R group of acylpyrazolones do not change the structure, geometry and reactivity of Rh(I) complexes. Chelating N-donor ligands such as bipy and phen replace acylpyrazolonate anion in [Rh(COD)Q] derivatives giving ionic complexes. In the presence of the phosphines ($PPh_3$, dppe, dppf), rhodium centre becomes more sensitive toward oxidation. Rh(I) derivatives were isolated only in the case of dppf due to the sterical hindrances in dppf that make a complex more stable to oxidation.

## 5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 173303–173305. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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