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Reactivity of rhodium-β-diketonato cyclooctadiene derivatives with mono- and di-phosphines. Synthesis, structural and spectroscopic characterization of Rh(I) and Rh(III) species containing unsymmetrical β-diketonate and P-donor ligands

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Abstract

From the reaction of [Rh(Q)(1,5-cod)] (HQ = 1-phenyl-3-methyl-4-R-pyrazol-5-one: R = 2-thenoyl (HQ^S) or 2-furanoyl (HQ^O)) with PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp) in anhydrous solvents under N_2 the complexes [Rh(Q)(PPh_3)$_2$], [Rh(dppe)$_2$](Q) (Q = Q^S or Q^O), and [Rh(dppp)(Q^O)] were obtained. The reactions of [Rh(Q^S)(1,5-cod)] with CH_3I, I_2, HCl and C_3H_5Br in the presence of PPh_3 were also investigated. All compounds obtained were characterized by elemental analyses, FT-IR, ESI-MS spectroscopy, ^{1}H-, ^{31}P- and in selected cases by ^{13}C-NMR spectroscopy. [Rh(Q^S)(PPh_3)$_2$], [Rh(dppe)$_2$](Q^S), [Rh(Q^O)(dppp)] and [Rh(Q^S)Cl_2(PPh_3)$_2$], were also characterized in the solid state by single crystal X-ray diffraction. In the air oxidation of [Rh(Q)(PR_3)$_2$] and [Rh(Q^O)(dppp)] occurred, species containing a η^2-peroxo group being always identified.

Keywords: Rhodium; Oxidative addition; P-donor ligands; Beta-diketonate ligands; ^{31}P-NMR spectroscopy

1. Introduction

Complexes of the form [Rh(β-diketonate)L_2] (where L = alkene, CO, triorgano-phosphine or -phosphite) are receiving considerable attention as catalyst precursors for a variety of reactions including for example alkene hydroboration [1], and diboration [2], CO_2 hydrogenation [3], hydroformylation [4] and the addition of arylboronic acids to aldehydes [5] as well as in stoichiometric and structural studies [6]. [Rh(acac)$(CO)_2$] (acac = acetylacetonate) in the presence of tertiary phosphines or phosphites is a well established catalytic system for hydroformylation, hydrogenation, and isomerization reactions of olefins [7]. Four coordinate cationic complexes of Rh(I) containing olefin (and especially 1,5-cod) and tertiary-phosphine are commonly used precursor in homogeneous catalytic hydrogenation [8]. Rh(I) olefin β-diketonates are suitable precursor for the formation of highly dispersed rhodium particles either in colloidal solution or supported on metal oxides relevant for their catalytic hydrogenation activity. These compounds are particularly useful due to the possibility to substitute the olefin ligands with stronger donor ligands such as amines or phoshines and to remove the β-diketonate ligands completely at low temperatures. The chemistry of [Rh(β-diketonate)(1,5-cod)] [9] has been extensively studied, but few data are available on their interaction with monodentate or bidentate phosphines. The fragment [Rh(β-diketonate)(P_2)] system (P_2 = chelating bidentate phosphine of general formula $R_2P–(X)–PR_2$) also plays a crucial role

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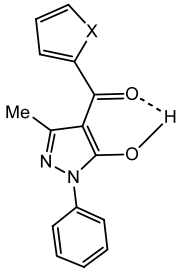
in a plethora of catalytic reactions [3,10], and the controlling influence of the chelating phosphine ligand on the activity and selectivity of such transformations is well documented [11]. A monoolefin complex [Rh(acac)(cyclooctene)(PCy_3)] has been reported to be a useful starting material for the preparation of new organometallic rhodium compounds including π-alkyne, hydrido-alkynyl and cationic five-coordinate metal alkenyl derivatives [12].

Until to date the reactivity of [Rh(β-diketonate)(P_2)] towards small molecules such as O_2, HX, RX is scarcely investigated, mainly due to intrinsic instability of species containing β-diketones such as acac [13].

4-Acyl-pyrazol-5-ones (namely HQ) are a class of potentially tridentate ligands (Fig. 1) which were firstly investigated by Jensen as reagent for radiochemical separation [14]. These molecules are comparable to β-diketones because in both the classes keto–enol tautomerism is possible, the enolic hydrogen may be replaced by a metal ion, and a variety of substituents can be easily introduced in the ligands. They are able to coordinate soft metals such as silver [15] and lead [16] also through the nitrogen of pyrazole ring. We have previously started an investigation of the coordination chemistry of these molecules toward Rh(I). The synthesis and structure of a number of π-diene-rhodium compounds containing the {Rh(Q)} fragment has been reported and their reactivity toward phosphorous- and nitrogen-donors explored [17]. Attempts to obtain [Rh(Q)(P-donor)$_2$] species were previously unsuccessful, being them very sensitive to oxygen from air and immediately forming O_2-adducts that rapidly evolve to Rh(III) compounds [17c].

Since the knowledge of the mechanism of catalytic activity requires an understanding of the species existent in solution and till now little attention has been given to the spectroscopic and structural features of [Rh(β-diketonate)(PR_3)$_2$] compounds [18] we have decided to undertake a systematic investigation on the interaction of rhodium compounds with 4-acylpyrazol-5-ones in the presence of auxiliary ligands. Here we report on the interaction of [Rh(Q)(1,5-cod)] with different P- and P_2-donors and the reactivity of [Rh(Q)(P-donor)$_2$] towards O_2, I_2, CH_3I, HCl, C_3H_7Br.



HQ^S: X = S
HQ^O: X = O

Fig. 1. Structure of the ligands employed in this work.

2. Experimental

All reagents were obtained from commercial sources and were used without further purification. Solvents were distilled using the standard methods. The sample for microanalysis was dried in vacuum to constant weight (293 K, ca. 0.1 Torr). Elemental analysis (C, H, N, S) were performed with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} using a Perkin–Elmer System 2000 FT-IR instrument. UV–vis spectra were recorded on a Hewlett–Packard HP-8453 spectrometer. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (r.t.) (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121.4 MHz for ^{31}P). Proton and carbon chemical shifts are reported in parts per million versus Me_4Si, while phosphorous chemical shifts are reported in parts per million versus $CFCl_3$ and H_3PO_4 (85%), respectively. Melting points (m.p.) were undertaken with a SMP3 Stuart scientific instrument and in a capillary apparatus and were uncorrected. The electrical conductances of solutions of the complexes were measured with a Crison CDTM 522 conductimeter at r.t. The positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg ml^{-1}) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro isotipic abundance simulator (version 2.1) [19].

2.1. Syntheses

The ligands HQ^S and HQ^O were prepared according to the method outlined in the literature [14,17]. [Rh(1,5-cod)Cl]$_2$ was synthesised from $RhCl_3 \cdot 3H_2O$ (Aldrich) and purified using a standard procedure [20].

2.1.1. [Rh(Q^S)(1,5-cod)]

Na(Q^S) (0.600 g, 2 mmol) was added to a toluene solution (20 ml) of [Rh(1,5-cod)Cl]$_2$ (0.490 g, 1 mmol). A colorless precipitate formed (NaCl) which was filtered off. The solution was then evaporated under vacuum and the residue washed with *n*-hexane and shown to be [Rh(Q^S)(1,5-cod)]. The spectroscopic and analytical data are consistent with those reported in literature [17c].

2.1.2. [Rh(Q^O)(1,5-cod)]

[Rh(Q^O)(1,5-cod)] was prepared similarly to [Rh(Q^S)(1,5-cod)]. The analytical and spectroscopic data are consistent with those reported in literature [17c]. $^{13}C\{^1H\}$-NMR (C_6D_6, 293 K, δ): 17.5 (s, 3-CH_3), 30.9 (s, CH_{2cod}), 76.5 (d, $^1J_{Rh-C}$: 68 Hz, CH_{cod}), 112.2, 116.6, 120.8, 125.5, 129.2, 144.9, 148.4, 152.3 (s, $C_{aromatics}$), 106.5 (s, $C4_Q$), 140.2 (s, $C3_Q$), 165.4 (s, $C5_Q$), 174.3 (s, CO_Q).

*2.1.3. [Rh(Q^S)(PPh_3)$_2$] (**1**)*

Triphenylphosphine (PPh_3, 0.524 g, 2 mmol) was added to a toluene solution of [Rh(Q^S)(1,5-cod)] (0.494 g, 1 mmol) prepared according to literature [17c]. The reaction mixture was stirred at r.t. under nitrogen for 6 h, and then the solvent evaporated under vacuum. The residue was then washed with *n*-hexane. A yellow–orange powder was obtained which was filtered off, washed with *n*-hexane and shown to be compound **1**. Yellow–orange crystals of **1** were obtained upon slow evaporation of benzene. Yield 78%. M.p.: 143 °C. Λ_M (acetone, 10^{-3} M): 3.2 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{51}H_{41}O_2N_2P_2RhS$: C, 67.25; H, 4.54; N, 3.08; S, 3.52. Found: C, 67.43; H, 4.76; N, 2.88; S, 3.23%. IR (Nujol, cm^{-1}): 3140br, 3100br [ν(C–H)], 1601s, 1590s, 1575sh, 1567s, 1550br, 1531s [ν(C⋯O), ν(C⋯C), ν(C⋯N),], 525s, 518s, 491s, 458m, 442m, 417m, 367m [ν(P–Ph); ν(Rh–O_Q)], 302w, 291w, 281w. ^{1}H-NMR (C_6D_6, 293 K, δ): 2.21 (s, 3H, 3-CH_3), 6.4 (dd, 1H, C_4H_3S), 6.8 (dd, 1H, C_4H_3S), 6.9 (dd, 1H, C_4H_3S), 7.0–7.2, 7.4, 7.8 (m br, 35H, C_6H_5). ^{1}H-NMR (C_6D_6, 293 K, recorded after 15 min, δ): 1.79, 1.98, 2.11 (3s, 3H, 3-CH_3), 6.5 (m, 1H, C_4H_3S), 6.8–7.3 (m, 24H, $C_6H_5+C_4H_3S$), 7.5 (m br, 2H, $C_6H_5+C_4H_3S$), 7.8–8.0 (m, 10H, $C_6H_5+C_4H_3S$), 8.45 (d, 1H, C_6H_5). $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 60.2 (dd, $^1J_{Rh-P}$: 201 Hz, $^2J_{P-P}=59$ Hz), 52.7 (dd, $^1J_{Rh-P}$: 200 Hz, $^2J_{P-P}=59$ Hz). ESI-MS (CH_3CN, conc. $=10^{-3}$ M): (+) 579(60) [(Ph_3P=O)$_2$Na]$^+$, 927 (42) [Rh(Q^S)(Ph_3P=O)(PPh_3)+H]$^+$, 943 (100) [Rh(Q^S)(Ph_3P=O)$_2$+H]$^+$. ESI-MS (CH_3CN–H_2O 1:1) conc. $=10^{-3}$M): (+) 557 (20) [(Ph_3P=O)$_2$H]$^+$, 579(100) [(Ph_3P=O)$_2$Na]$^+$, 927 (15) [Rh(Q^S)(Ph_3P=O)(PPh_3)+H]$^+$, 943 (35) [Rh(Q^S)(Ph_3P=O)$_2$+H]$^+$.

*2.1.4. [Rh(Q^O)(PPh_3)$_2$] (**2**)*

Compound **2** was prepared in toluene as for **1** by using PPh_3, (0.524 g, 2 mmol) and [Rh(Q^O)(1,5-cod)] [16c] (0.478 g, 1 mmol). Recrystallised from toluene. Yield 72%. M.p.: 101–103 °C. Λ_M (acetone, 10^{-3} M): 4.3 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{51}H_{41}O_3N_2P_2Rh$: C, 68.46; H, 4.62; N, 3.13. Found: C, 68.23; H, 4.86; N, 2.81%. IR (Nujol, cm^{-1}): 3060sh [ν(C–H)], 1602s, 1589s, 1580sh, 1552s, 1525s [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 520vs, 503s, 491s, 463m, 447m, 416m, 390m [ν(P–Ph), ν(Rh–O_Q)]. ^{1}H-NMR (C_6D_6, 293 K, δ): 2.10 (s, 3H, 3-CH_3), 6.8 (dd, 1H, C_4H_3O), 7.0–7.2, 7.4, 7.6, 7.8 (m br, 37H, $C_6H_5+C_4H_3O$). ^{1}H-NMR (C_6D_6, 293 K, after 15 min, δ): 1.82, 2.00, 2.03 (s, 3H, 3–CH_3), 5.80, 5.85, 6.10 (dd, 1H, C_4H_3O), 6.60, 6.70, 6.78 (dd, 1H, C_4H_3O), 6.80–7.20 (m, 24H, $C_6H_5+C_4H_3O$), 7.60–7.80 (m, 10H, C_6H_5), 7.90 (d, 1H, C_6H_5), 8.40 (d, 1H, C_6H_5). $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 61.4 (dd, $^1J_{Rh-P}$: 201 Hz, $^2J_{P-P}=58$ Hz), 52.3 (dd, $^1J_{Rh-P}$: 198 Hz, $^2J_{P-P}=59$ Hz). ESI-MS (CH_3CN, conc. $=10^{-3}$ M): (+) 911 (75) [Rh(Q^O)(Ph_3P=O)(PPh_3)+H]$^+$, 927 (100) [Rh(Q^O)(Ph_3P=O)$_2$+H]$^+$. ESI-MS (CH_3CN–H_2O 1:1) conc. $=10^{-3}$ M): (+) 579 (60) [(Ph_3P=O)$_2$Na]$^+$, 911 (55) [Rh(Q^O)(Ph_3P=O)(PPh_3)+H]$^+$, 927 (100) [Rh(Q^O)(Ph_3P=O)$_2$+H]$^+$.

*2.1.5. [Rh(dppe)$_2$](Q^S) (**3**)*

1,2-bis(Diphenylphosphino)ethane (dppe, 0.796 g, 2 mmol) was added to a benzene solution of [Rh(Q^S)(1,5-cod)] (0.494 g, 1 mmol). The reaction mixture was stirred at r.t. under nitrogen for 6 h. A yellow precipitate formed which was filtered off, washed with *n*-hexane and shown to be compound **3**. Yellow crystals of 3 were obtained upon slow evaporation of benzene solution. Yield 84%. M.p.: 159–160 °C. Λ_M (acetone, 10^{-3} M): 13.2 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 10^{-3} M): 19.8 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{67}H_{59}O_2N_2P_4RhS$: C, 68.02; H, 5.03; N, 2.37; S, 2.71. Found: C, 67.73; H, 5.20; N, 2.32; S, 2.52%. IR (Nujol, cm^{-1}): 3080sh [ν(C–H)], 1615s, 1586s, 1566m, 1524s [ν(C⋯O), ν(C⋯C), (C⋯N),], 530s, 505m, 481s, 430s, 380w, 351m, 325w, 300w, 285w, 277w, 253w, 246w, 225w, 209w [ν(P–Ph); ν(Rh–O), ν(Rh–P)]. ^{1}H-NMR (C_6D_6, 293 K, δ): 2.06 (s, 3H, 3-CH_3), 2.33 (m, 8H, CH_{2dppe}), 6.82 (dd, 1H, C_4H_3S), 7.0 (dd, 1H, C_4H_3S), 7.2–7.5 (m br, 43H, C_6H_5), 8.40 (dd, 1H, C_4H_3S), 8.45 (d, 2H, C_6H_5). $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 58.2d ($^1J_{Rh-P}$: 132 Hz). UV–vis (nm, CH_3CN, 0.99×10^{-5} M): 200, 248, 266, 400. ESI-MS (CH_3CN, conc. $=10^{-3}$M M): (+) 899 (100) [Rh(dppe)$_2$]$^+$, 932 (5) [Rh(dppe)$_2$+O_2]$^+$.

*2.1.6. [Rh(dppe)$_2$](Q^O) (**4**)*

1,2-bis(Diphenylphosphino)ethane (dppe, 2 mmol, 0.796 g) was added to a benzene solution of [Rh(Q^O)(1,5-cod)] (0.478 g, 1 mmol). The reaction mixture was stirred at r.t. under nitrogen for 6 h. A yellow precipitate formed which was filtered off, washed with *n*-hexane and shown to be compound **4**. Yield 83%. M.p.: 164–165 °C. Λ_M (acetone, 10^{-3} M): 13.5 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 10^{-3} M): 19.7 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{67}H_{59}O_3N_2P_4Rh$: C, 68.90; H, 5.18; N, 2.40. Found: C, 69.12; H, 5.54; N, 2.23%. IR (Nujol, cm^{-1}): 3080sh [ν(C–H)], 1633s, 1620s, 1584m, 1574s, 1551m, 1524 [ν(C⋯O), ν(C⋯C), (C⋯N),], 535s, 507s, 481s, 450w, 431m, 418m, 387 [ν(P–Ph); ν(Rh–O), ν(Rh–P)]. ^{1}H-NMR (C_6D_6, 293 K, δ): 1.95 (s, 3H, 3-CH_3), 2.08 (m, 8H, CH_{2dppe}), 6.39 (dd, 1H, C_4H_3O), 6.90 (dd, 1H, C_4H_3O), 7.1–7.45 (m br, 44H, C_6H_5+

C_4H_3S), 8.10 (d, 2H, C_6H_5). $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 58.2 (d, $^1J_{Rh-P}$: 132 Hz). UV–vis (nm, CH_3CN, 0.66×10^{-5} M): 196, 284, 344, 410. ESI-MS (CH_3CN, conc. $= 10^{-3}$ M): (+) 899(100) $[Rh(dppe)_2]^+$, 932 (5) $[Rh(dppe)_2+O_2]^+$.

2.1.7. $[Rh(Q^O)(dppp)]$ (5)

1,3-bis(Diphenylphosphino)propane (dppp, 1 mmol, 0.412 g) was added to a benzene solution of $[Rh(Q^O)(1,5\text{-cod})]$ (0.478 g, 1 mmol). The reaction mixture was stirred at r.t. under nitrogen for 6 h. A yellow precipitate formed which was filtered off, washed with *n*-hexane and shown to be compound 5. Yield 64%. M.p.: 140–141 °C. Λ_M (acetone, 10^{-3} M): 5.0 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 10^{-3} M): 0.8 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{42}H_{37}O_3N_2P_2Rh$: C, 64.46; H, 4.77; N, 3.58. Found: C, 64.12; H, 4.84; N, 3.53%. IR (Nujol, cm^{-1}): 3060sh [ν(C–H)], 1601s, 1583s, 1564s, 1524m [ν(C⋯O), ν(C⋯C), (C⋯N)], 520m, 509m, 485w, 443w, 398w, 377br w, 352w, 325w, 301w [ν(P–Ph), ν(Rh–O), ν(Rh–P)], 279m, 247m, 225m. ^{1}H-NMR (C_6D_6, 293 K, δ): 2.1 (s, 3H, 3-CH_3), 2.2 (m, 2H, CH_{2dppp}), 2.5 (m, 4H, CH_{2dppp}), 6.3 (dd, 1H, C_4H_3O), 6.6 (dd, 1H, C_4H_3O), 6.8 (dd, 1H, C_4H_3O), 7.2–7.4, 7.7–7.9 (m br, 43H, C_6H_5), 7.9 (d, 2H, C_6H_5). $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 41.3 (dd, $^1J_{Rh-P}$: 185 Hz, $^2J_{P-P}$: 76 Hz), 36.3 (dd, $^1J_{Rh-P}$: 186 Hz, $^2J_{P-P}$: 76 Hz). UV–vis (nm, CH_3CN, 0.28×10^{-4} M): 203, 221, 270. ESI-MS (CH_3CN, conc. $= 10^{-3}$M): (+) 445 (100) $[(dppp+O_2+H]^+$, 467 $[(dppp+O_2+Na]^+$, 815 (40) $[Rh(Q^O)(dppp)+O_2+H]^+$, 857 (60) $[(dppp)_2+O_2+H]^+$; 911 (75) $[(dppp+O_2)_2+Na]^+$; 1296 (20) $[Rh_2(dppp)_2(Q^O)]^+$.

2.1.8. $[Rh(Q^S)I_2(PPh_3)_2]$ (6)

Triphenylphosphine (PPh_3, 0.524 g, 2 mmol) was added under argon to a tetrahydrofuran solution of $[Rh(Q^S)(1,5\text{-cod})]$ (0.494 g, 1 mmol) prepared according to literature [17c]. The reaction mixture was stirred at r.t., then sublimated I_2 was added. After 2 h the solution was evaporated under vacuum and the residue washed twice with heptane (15 ml). A red-brownish powder was obtained which was filtered off and shown to be compound **6**. Yield 43%. M.p.: 143 °C. Λ_M (acetone, 10^{-3} M): 6.2 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{51}H_{41}I_2O_2N_2P_2RhS$: C, 52.60; H, 3.55; N, 2.41; S, 2.75. Found: C, 52.33; H, 3.44; N, 2.88; S, 2.96%. IR (Nujol, cm^{-1}): 3140br, 3100br [ν(C–H)], 1601s, 1590s, 1575sh, 1567s, 1550br, 1531s [ν(C⋯O), ν(C⋯C), ν(C⋯N),], 525s, 518s, 491s, 458m, 442m, 417m, 367m [ν(P–Ph); ν(Rh–O_Q)], 302w, 291w. ^{1}H-NMR (acetone-d_6, 293 K, δ): 2.08 (s, 3H, 3-CH_3), 7.0–8.4 (m, 38H, $C_4H_3S+C_6H_5$) $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 17.5 (d, $^1J_{Rh-P}$: 90 Hz).

2.1.9. $[Rh(Q^S)Br(C_3H_5)(PPh_3)]$ (7)

Triphenylphosphine (PPh_3, 0.524 g, 2 mmol) was added under argon to a tetrahydrofuran solution of $[Rh(Q^S)(1,5\text{-cod})]$ (0.494 g, 1 mmol) prepared according to literature [17c]. The reaction mixture was stirred at r.t., then allylbromide (C_3H_5Br) was added. After 1 h the solution was evaporated under vacuum and the residue washed twice with heptane (15 ml). A brownish powder was obtained which was filtered off and shown to be compound **7**. Yield 54%. M.p.: 202 °C dec. Λ_M (acetone, 10^{-3} M): 5.2 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{36}H_{31}BrO_2N_2PRhS$: C, 56.19; H, 4.06; N, 3.64; S, 4.17. Found: C, 55.96; H, 4.02; N, 3.88; S, 3.96%. IR (Nujol, cm^{-1}): 3140br, 3100br [ν(C–H)], 1601s, 1590s, 1575sh, 1567s, 1550br, 1531s [ν(C⋯O), ν(C⋯C), ν(C⋯N),], 525s, 518s, 491s, 458m, 442m, 417m, 367m [ν(P–Ph); ν(Rh–O_Q)]. ^{1}H-NMR (acetone-d_6, 293 K, δ): 2.24 (s, 3H, 3-CH_3), 3.02 (d, 1H, CH_{al}), 3.14 (d, 1H, CH_{al}), 3.80 (dd, 1H, CH_{al}), 4.82 (dd, 1H, CH_{al}), 5.60 (m, 1H, CH_{al}), 7.0–8.2 (m, 23H, $C_4H_3S+C_6H_5$). $^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 38.9 (d, $^1J_{Rh-P}$: 115 Hz).

2.1.10. $[Rh(Q^S)Cl_2(PPh_3)_2]\cdot 1/2thf$ (8)

Triphenylphosphine (PPh_3, 0.524 g, 2 mmol) was added under argon to a tetrahydrofuran solution of $[Rh(Q^S)(1,5\text{-cod})]$ (0.494 g, 1 mmol) prepared according to literature [17c]. The reaction mixture was stirred at r.t., then HCl (0.2 g, 35%) was added. After 1 h the solution was evaporated under vacuum and the residue washed twice with tetrahydrofuran (20 ml). A orange precipitate was obtained which was filtered off and shown to be compound **8**. Yield 85%. M.p.: 215–217 °C dec. Λ_M (acetone, 10^{-3} M): 4.2 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{51}H_{41}Cl_2O_2N_2P_2RhS$: C, 62.40; H, 4.21; N, 2.85; S, 3.27. Found: C, 62.34; H, 4.12; N, 2.88; S, 3.46%. IR (Nujol, cm^{-1}): 3110sh, 3080br [ν(C–H)], 1588s, 1573m, 1557s, 1519m [ν(C⋯O), ν(C⋯C), ν(C⋯N),], 512s, 498s, 454m, 426w, 419w, 383m, 337m, 279w [ν(P–Ph); ν(Rh–O_Q), ν(Rh–Cl)]. ^{1}H-NMR ($CDCl_3$, 293 K, δ): 1.62 (s, 3H, 3-CH_3), 1.83 (m, 1H, CH_{thf}), 3.76 (m, 1H, CH_{thf}), 6.60 (d, 1H, C_4H_3S), 6.80 (m, 1H, C_4H_3S), 7.0–8.2 (m, 36H, $C_4H_3S+C_6H_5$). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 293 K, δ): 15.8 (d, $^1J_{Rh-P}$: 89 Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 223 K, δ): 16.2 (d, $^1J_{Rh-P}$: 89 Hz). ^{13}C-NMR ($CDCl_3$, 293 K, δ): 16.8 (s, CH_3), 25.8 (s, CH_{2thf}), 68.2. (s, CH_{2thf}), 106.9 (s, $C4_Q$), 125.4, 131.4, 132.3 (d, C_{PPh3}) 127.8, 128.5, 129.0, 129.5, 129.9, 130.2, 135.2, 138.4, 139.7 (s, $C_{aromatics}$) 147.3 (s, $C3_Q$), 161.6 (s, $C5_Q$), 180.1 (s, CO_Q).

2.2. $^{31}P\{^1H\}$-NMR data of benzene solution containing Rh(Q)(1,5-cod) and P-donors

2.2.1. $Rh(Q^S)(1,5\text{-cod})+PPh_3$ 1:2

$^{31}P\{^1H\}$-NMR (C_6D_6, 293 K, δ): 60.2 (dd $^1J_{Rh-P}$: 201 Hz, $^2J_{P-P} = 59$ Hz), 52.7 (dd, $^1J_{Rh-P}$: 200 Hz, $^2J_{P-P} =$

58 Hz). $^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, after O_2 addition, δ): 37.9 (dd, $^{1}J_{Rh-P}$: 153 Hz, $^{2}J_{P-P} = 27$ Hz), 37.3 (dd, $^{1}J_{Rh-P}$: 147 Hz, $^{2}J_{P-P} = 27$ Hz), 36.3 (dd, $^{1}J_{Rh-P}$: 143 Hz, $^{2}J_{P-P} = 26$ Hz), 34.3 (dd, $^{1}J_{Rh-P}$: 151 Hz, $^{2}J_{P-P} =$ 26 Hz), 11.8 (d, $^{1}J_{Rh-P}$: 108 Hz).

2.2.2. Rh(Q^S)(1,5-cod) +PPh_3 1:2

$^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, δ): 61.4 (dd, $^{1}J_{Rh-P}$: 201 Hz, $^{2}J_{P-P} = 58$ Hz), 52.3 (dd, $^{1}J_{Rh-P}$: 198 Hz, $^{2}J_{P-P} = 59$ Hz). $^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, after O_2 addition, δ): 37.5 (dd, $^{1}J_{Rh-P}$: 148 Hz, $^{2}J_{P-P} = 26$ Hz), 36.6 (dd, $^{1}J_{Rh-P}$: 145 Hz, $^{2}J_{P-P} = 26$ Hz), 35.9 (dd, $^{1}J_{Rh-P}$: 141 Hz, $^{2}J_{P-P} = 27$ Hz), 34.9 (dd, $^{1}J_{Rh-P}$: 147 Hz, $^{2}J_{P-P} = 26$ Hz). 11.8 (d, $^{1}J_{Rh-P}$: 108 Hz).

2.2.3. Rh(Q^O)(1,5-cod) +dppe 1:1.

$^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, δ): 75.2 (dd, $^{1}J_{Rh-P}$: 200 Hz, $J_{P-P} = 48$ Hz), 73.5 (dd, $^{1}J_{Rh-P}$: 200 Hz, $J_{P-P} =$ 48 Hz), 58.1 (d, $^{1}J_{Rh-P}$: 132 Hz). $^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, after O_2 addition, δ): 29.7 (dd, $^{1}J_{Rh-P}$: 184 Hz, $J_{P-P} = 46$ Hz).

2.2.4. Rh(Q^O)(1,5-cod) +dppp 1:1

$^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, δ): 41.3 (dd, $^{1}J_{Rh-P}$: 185 Hz, $J_{P-P} = 76$ Hz), 36.4 (dd, $^{1}J_{Rh-P}$: 19 Hz, $J_{P-P} =$ 76 Hz), 10.4 (d, $^{1}J_{Rh-P}$: 137 Hz), 8.6 (d, $^{1}J_{Rh-P}$: 131 Hz). $^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, after O_2 addition, δ): 26.1 (dd, $^{1}J_{Rh-P}$: 138 Hz).

2.2.5. Rh(Q^S)(1,5-cod) +2PPh_3 +CH_3I

$^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, δ): 14.4 (d, $^{1}J_{Rh-P}$: 99 Hz), 15.5 (d, $^{1}J_{Rh-P}$: 101 Hz), 18.9 (d, $^{1}J_{Rh-P}$: 106 Hz), 20.0 (d, $^{1}J_{Rh-P}$: 105 Hz), 22.1 (d, $^{1}J_{Rh-P}$: 179 Hz). ^{1}H-NMR (C_6D_6, 293 K, δ): 1.26, 1.40, 1.73 (m, 3H, Rh–CH_3) 1.90, 2.00, 2.17, 2.36 (m br, 3H, 3-CH_{3Q}), 6.00, 6.30, 6.40, 6.70 (m br, 2H, C_4H_3S), 6.90–8.00 (m br, 36H, $C_6H_5 + C_4H_3S$).

2.2.6. Rh(Q^S)(1,5-cod) +2PPh_3 +2HCl

$^{31}P\{^{1}H\}$-NMR (C_6D_6, 293 K, δ): 45.7 (d br, $^{1}J_{Rh-P}$: 140 Hz), 37.0–38.0 (br), 33.0 (s), 25.9 (d, $^{1}J_{Rh-P}$: 95 Hz). $^{31}P\{^{1}H\}$-NMR (thf-d_8, 293 K, δ): 44.6 (d, $^{1}J_{Rh-P}$: 146 Hz). ^{1}H-NMR (C_6D_6, 293 K, δ): 1.98 (s, 3H, 3–CH_{3Q}), 2.20 (m, 8H, C_8H_{12}), 5.69 (s br, 4H, C_8H_{12}) 6.20 (dd, 1H, C_4H_3S), 6.70 (dd, 1H, C_4H_3S), 7.00–7.80 (m br, 36H, $C_4H_3S + C_6H_5$). ^{1}H-NMR (thf-d_8, 293 K, δ): 1.65 (s, 3H, 3-CH_{3Q}), 2.20 (s, 8H, C_8H_{12}), 5.40 (m, 4H, C_8H_{12}), 6.90–8.10 (m br, 38H, $C_4H_3S + C_6H_5$).

2.3. X-ray crystallography

The data for complexes [Rh(Q^S)(PPh_3)$_2$] (**1**), [Rh(dppe)$_2$](Q^S) (**3**) [Rh(dppp)(Q^O)]·C_6H_6 (**5**) [Rh(Q^S)Cl_2(PPh_3)$_2$]·0.5thf (**8**), were collected on an Image-Plate diffractometer (IPDS, Stoe) using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97 [21]) and refined anisotropically for all non-hydrogen atoms using SHELXL-97 [22]. Hydrogen atoms were included in the calculated positions and refined in a riding mode. In the crystal structure of **3**, the Q^S anion is obviously slightly disordered around the anion centre which resulted in an overlap of the components from thienyl and phenyl rings. However, due to a small disorder degree, it was not included in the final refinement.

Crystallographic data and some details of data collection and structures refinement for compounds **1**, **3**, **5** and **8** are found in Table 1. The interatomic distances and angles for Rh environment are listed in Table 2.

3. Results and discussion

The compounds [Rh(Q)(1,5-cod)] (Q = Q^S or Q^O) were prepared by the standard procedure reported previously [17c] or more conveniently from the reaction of NaQ with [(1,5-cod)RhCl]$_2$ in toluene. When [Rh(Q)(1,5-cod)] (Q = Q^S or Q^O) reacts with an excess of PPh_3 in anhydrous toluene under N_2, the 1,5-cod ligand is completely displaced by two molecules of the P-donor yielding the complexes **1**–**2** (Scheme 1).

Complexes **1**–**2** are stable if stored in anhydrous conditions, whereas by exposure on air they rapidly react with oxygen affording Rh(I) adducts of general formula [Rh(Q)(PR_3)$_2$(O_2)], which slowly transform into Rh(III)-peroxo complexes of formula [RhO_2(Q)(PR_3)$_2$] reported previously [17c].

The structure of [Rh(Q^S)(PPh_3)$_2$] (**1**) was confirmed by X-ray single crystal crystallography (Fig. 2). The Rh(I) atom lies in slightly distorted square planar coordination with the acylpyrazolonate oxygen atoms and the phosphorous atoms of PPh_3. The average Rh–O distance, 2.106 Å is slightly longer than that of related complexes [Rh(acac)(PCy_3)$_2$] (acac = acetylacetonate) (2.086 Å) [12], and [Rh(tfa)(PMe_3)$_2$] (tfa = trifluoroacetylacetonate) (2.084 Å) [10a]. Such difference in the value of Rh–O distances could be explained by larger electronegativity of the PPh_3 with regard to PCy_3 and PMe_3. The average Rh–P distance 2.211 Å corresponds well to the value of Rh–P distance 2.206 Å found in complex [Rh(tfa)(PMe_3)$_2$] [10a], but it is shorter than that of [Rh(acac)(PCy_3)$_2$] [12] (2.256 Å). The P(1)–Rh–P(2) angle of [Rh(Q^S)(PPh_3)$_2$] 95.25° is statistically identical with the P(1)–Rh–P(2) angle of [Rh(tfa)(PMe_3)$_2$] (95.1°), but significantly smaller than that of [Rh(acac)(PCy_3)$_2$] (105.63°), which experiences a large steric hindrance.

The reaction of **1**–**2** with dioxygen has been investigated in C_6D_6 solution by ^{1}H- and ^{31}P-NMR investigations: $^{31}P\{^{1}H\}$-NMR spectra of **1**–**2** in deoxygenated

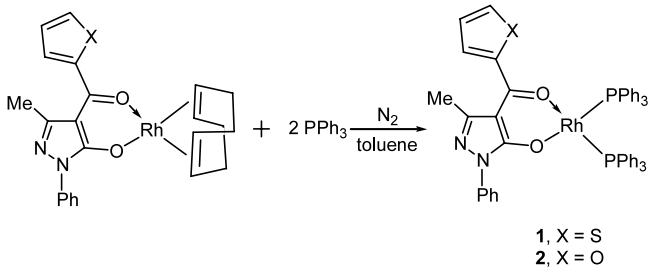
Table 1
Crystal data and refinement

	$[RhQ^S(PPh_3)_2]$ (**1**)	$[Rh(dppe)_2]Q^S$ (**3**)	$[RhQ^O(dppp)]\cdot C_6H_6$ (**5**)	$[RhQ^S(PPh_3)_2Cl_2]\cdot 0.5thf$ (**8**)
Empirical formula	$C_{51}H_{41}N_2O_2P_2SRh$	$C_{67}H_{59}N_2O_2P_4RhS$	$C_{48}H_{43}N_2O_3P_2Rh$	$C_{53}H_{45}N_2O_{2.5}P_2SCl_2Rh$
Formula weight	910.77	1183.01	860.69	1017.72
Crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	*Pbca*	$P\bar{1}$
Unit cell dimensions				
a (Å)	13.301(4)	12.388(2)	12.447(2)	11.060(2)
b (Å)	13.698(3)	16.489(3)	23.505(4)	17.843(5)
c (Å)	14.089(3)	28.485(6)	28.320(3)	25.212(5)
α (°)	102.36(3)	90	90	108.18(3)
β (°)	94.86(3)	101.03(2)	90	96.07(2)
γ (°)	118.68(3)	90	90	96.99(3)
V (Å^3)	2146.6(9)	5711(2)	8285(2)	4637(1)
Z	2	4	8	4
Absorption coefficient (mm^{-1})	0.564	0.495	0.534	0.643
Crystal size (mm^3)	$0.28 \times 0.28 \times 0.05$	$0.40 \times 0.40 \times 0.08$	$0.50 \times 0.20 \times 0.03$	$0.32 \times 0.12 \times 0.03$
Temperature (K)	180	180	170	180
θ Range for data collection (°)	2.6–28.1	2.5–25.3	2.8–25.7	2.6–26.0
Reflections collected	18455	37921	39729	26382
Independent reflections (R_{int})	9541 (0.038)	10425 (0.1317)	7855 (0.1301)	16770 (0.090)
Data/parametres	8501/533	10425/696	7855/507	16770/1147
wR_2 (on F^2)	0.0616	0.0951	0.0614	0.0760
R_1 [$I \geq 2\sigma(I)$]	0.0304	0.0477	0.0358	0.0412

C_6D_6 under dry N_2 reveal two double doblets in the range 50–60 ppm, with $^1J_{Rh-P}$ of ca. 200 Hz and $^2J_{P-P}$ of ca. 58 Hz, as expected due to inequivalence of the PPh_3 ligands in $Rh(Q)(PPh_3)_2$. By addition of O_2 these resonances immediately disappear and a complex pattern emerges, constituted by four overlapped double

Table 2
Coordination environment of Rh atoms (Å, °) in the crystal structures **1**, **4**, **6** and **10**

Distance/angle	**1**	**4**	**6**	**10**	**10**
				Rh(1)	Rh(2)
Bond lengths					
Rh–O(1)	2.098(2)		2.112(3)	2.057(4)	2.060(4)
Rh–O(2)	2.114(3)		2.117(2)	2.049(4)	2.044(4)
Rh–P(1)	2.204(1)	2.326(2)	2.194(1)	2.410(2)	2.410(2)
Rh–P(2)	2.218(1)	2.323(2)	2.201(1)	2.394(2)	2.393(2)
Rh–P(3)		2.319(2)			
Rh–P(4)		2.333(2)			
Rh–Cl(1)			2.352(2)	2.352(2)	
Rh–Cl(2)			2.337(2)	2.339(2)	
Bond angles					
O(1)–Rh–O(2)	88.24(8)		88.5(1)	92.8(1)	91.5(2)
O(1)–Rh–P(1)	178.67(7)		175.53(7)	91.1(1)	94.8(1)
O(1)–Rh–P(2)	83.70(8)		89.89(7)	87.7(1)	87.5(1)
O(2)–Rh–P(1)	92.71(7)		89.90(7)	91.4(1)	89.1(1)
O(2)–Rh–P(2)	170.30(7)		176.97(7)	89.7(1)	89.8(1)
P(1)–Rh–P(2)	95.25(5)	82.90(6)	91.53(4)	178.46(6)	177.56(6)
P(1)–Rh–P(3)		176.28(7)			
P(1)–Rh–P(4)		99.21(6)			
P(2)–Rh–P(3)		95.69(6)			
P(2)–Rh–P(4)		171.74(7)			
P(3)–Rh–P(4)		82.68(7)			
O(1)–Rh–Cl(1)				177.1(1)	178.2(1)
O(2)–Rh–Cl(2)				178.6(1)	176.7(1)
Cl(1)–Rh–Cl(2)				94.85(6)	95.01(6)



Scheme 1.

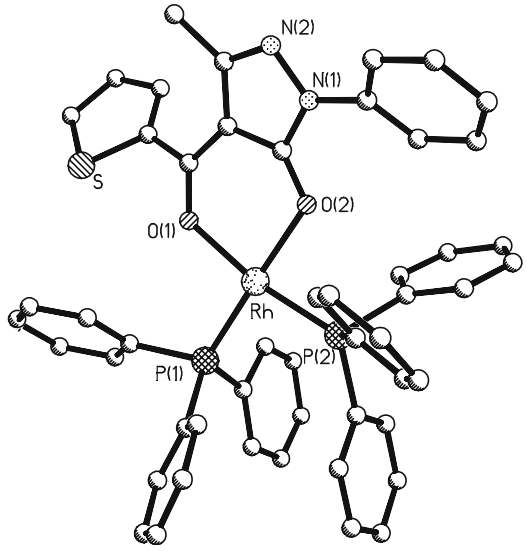


Fig. 2. Molecular structure of derivative **1**, $[Rh(Q^S)(PPh_3)_2]$.

doublets in the range 35–40 ppm, with $^1J_{Rh-P}$ of ca. 140–155 Hz and $^2J_{P-P}$ of ca. 25–30 Hz. This pattern can be assigned to a Rh(I)–O_2 adduct in a five-coordinated trigonal bipiramid geometry [18], likely containing the O_2 coordinated only through one O atom with a dative bonding O:→Rh [23] or, alternatively through both O atoms coordinated with a π bond pair from O_2. The number and typology of signals well agree with the existence of solution of the four different isomers shown in Fig. 3. The ESI-MS spectra confirm the oxidation reaction. In CH_3CN a signal due to $[Rh(Q^O)(Ph_3P{=}O)(PPh_3)+H]^+$ was found, the intensity of which decreases when water was added to the solution. In a CH_3CN:H_2O 1:1 solution the most abundant species is $Ph_3P{=}O$ or its derivatives such as $[(Ph_3P{=}O)_2+H]^+$ and $[Rh(Q^S)(Ph_3P{=}O)_2+H]^+$.

The Rh(I)–O_2 adducts are enough stable in the solid state to be investigated also by IR spectroscopy, which shows strong bands at ca. 890 and 550 cm^{-1} due to ν(O–O) and ν(Rh–O–O), respectively [24].

Finally, the ^{31}P-NMR spectra of warmed C_6D_6 solution of **1**–**2** exhibit a doublet at ca. 12 ppm, likely due to Rh(III)-peroxo species. The presence of this unique doublet, with $^1J_{Rh-P}$ of ca. 110 Hz, is in fact typical for a *trans*-(β-diketonate)$Rh(PPh_3)_2$(O–O) compound containing a Rh(III) centre [17c]. After 24 h in solution all species decompose delivering triarylphosphino-oxide in quantitative yield.

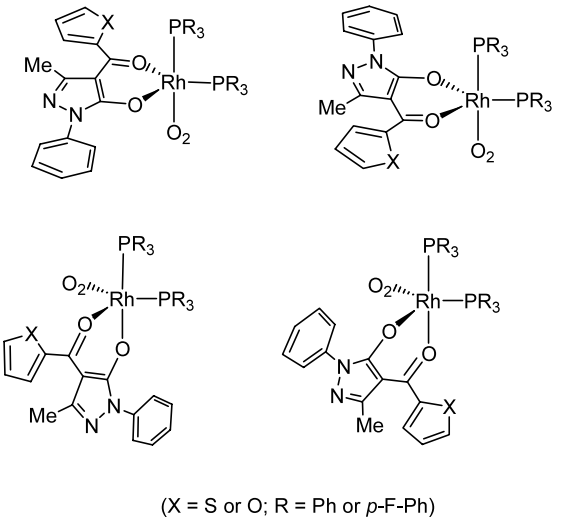
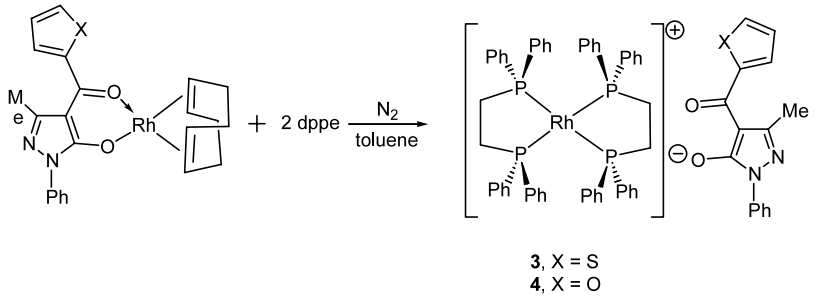


Fig. 3. Isomers possible for the O_2 adducts of derivatives **1**–**3**.

By reaction of one equivalent Rh(Q)(1,5-cod) with two equivalents 1,2-bis(diphenylphosphino)ethane (dppe), the complexes $[Rh(dppe)_2](Q^S)$ (**3**) and $[Rh(dppe)_2](Q^O)$ (**4**) afforded (Scheme 2). They are 1:1 electrolytes in dichloromethane but only partially ionic in acetone, where dissociation of one dppe ligand and re-association of Q ligand to rhodium is likely. The ^{31}P-NMR spectra show a doublet at 58 ppm with $^1J_{Rh-P}$ of 132 Hz, typical of $Rh(dppe)_2X$ compounds [3a]. A crystallographic study of $[Rh(dppe)_2](Q^S)$ has been performed which indicates a distorted square planar coordination geometry around the rhodium center, with both dppe acting as chelating ligands (Fig. 4). As previously described for the analogous [Rh{1,2-bis(dicyclohexyl)ethane}$_2$]hfacac [25] (hfacacH = hexafluoroacetylacetonate) the amount of tetrahedral distortion in the $[Rh(dppe)_2]^+$ cation is due to a compromise between the classical square planar arrangement of a d^8 transition metal center and the steric repulsion of the four PPh_2 groups [26]. The Rh–P distances and the P–Rh–P angles well compare with those found for [Rh{1,2–bis(dicyclohexylphosphino)ethane}$_2$]hfacac [25].

The reaction of $Rh(Q^O)$(1,5-cod) with dppe in a 1:1 molar ratio in deoxygenated C_6D_6 has been followed by ^{1}H- and ^{31}P-NMR spectroscopy: in the ^{31}P-NMR spectrum a double doublet at 74.4 ppm, with $^1J_{Rh-P}$ of 200 Hz and J_{P-P} of 48 Hz, immediately appears, likely due to formation of the neutral complex $[Rh(Q^O)(dppe)]$, together with a minor double resonance at 58 ppm ($^1J_{Rh-P}$ = 132 Hz), assignable to the ionic $[Rh(dppe)_2](Q^O)$. Then, addition of O_2 causes disappearing of previous resonances and formation of a double doublet at 29.7 ppm ($^1J_{Rh-P}$ = 184 Hz, J_{P-P} =



3, X = S
4, X = O

Scheme 2.

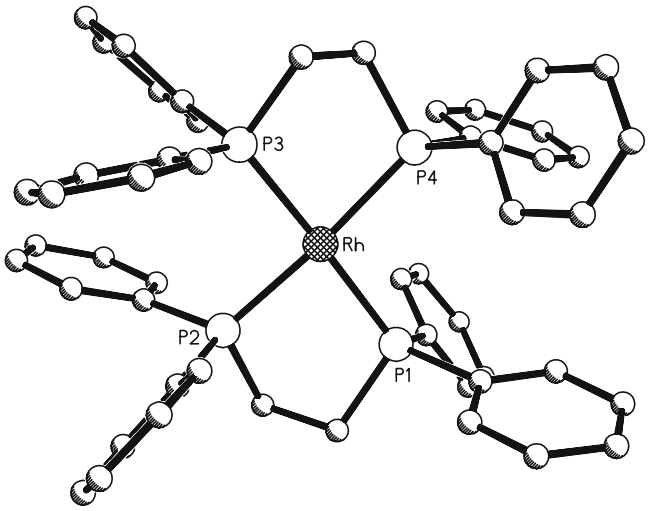


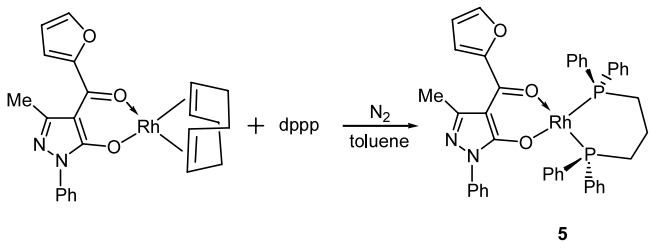
Fig. 4. Molecular structure of the cation of derivative **4**, $[Rh(dppe)_2](Q^S)$.

46 Hz), in accordance with formation of a Rh(III) species as $[Rh(O_2)(dppe)_2](Q^O)$ [3,24].

The existence of $[Rh(dppe)_2]^+(Q)^-$ and $[Rh(dppe)_2+O_2]^+(Q)^-$ species in solution has been confirmed from the ESI-MS spectra of **3** and **4** in CD_3CN, signals due to both the species being the more relevant.

Interaction of $[Rh(Q^O)(1,5\text{-cod})]$ with equimolar amount of dppp gave compound $[Rh(Q^O)(dppp)]$ (**5**) (Scheme 3). This compound is stable on air whereas in not rigourously anhydrous benzene solution is slowly oxidized. ^{31}P-NMR shows two double doublets with $^1J_{Rh-P}$ of ca. 185 Hz, typical for [Rh(β-diketonate)(P_2-donor)] species [3,27]. **5** has been recrystallised by anhydrous benzene and the solvate $[Rh(Q^O)(dppp)]\cdot C_6H_6$ has been investigated by X-ray crystallography. The structure of $5\cdot C_6H_6$ (Fig. 5) shows the Rh(I) atom in slightly distorted square planar coordination due to the oxygen of the acylpyrazolonate and to the phosphorous atoms of dppp. The average Rh–O 2.106 Å distance corresponds well to the value of Rh–O distance found in related complex [Rh(hfacac)(dppp)] (2.097 Å) [3a]. The P(1)–Rh–P(2) angle of $[Rh(Q^O)(dppp)]\cdot C_6H_6$ 91.53° is effectively identical with the P(1)–Rh–P(2) angle of [Rh(hfacac)(dppp)] (90.77°). So, we can conclude that the nature of the β-diketonate fragment has only little effect on the P(1)–Rh–P(2) angle.

A comparison with the structure of **1** shows that the nature of the acylpyrazolonate ligand (Q^S or Q^O) has virtually no influence on the average length of the Rh–O distances. Apparently, a larger asymmetry of the chelate ring in **1** is caused by a more sterically demanding thionyl fragment as compared with the furanyl one. The replacement of two PPh_3 phosphine ligands by one diphosphine results in a slightly smaller P–Rh–P angle due to the rigid ligand geometry of dppp.



5

Scheme 3.

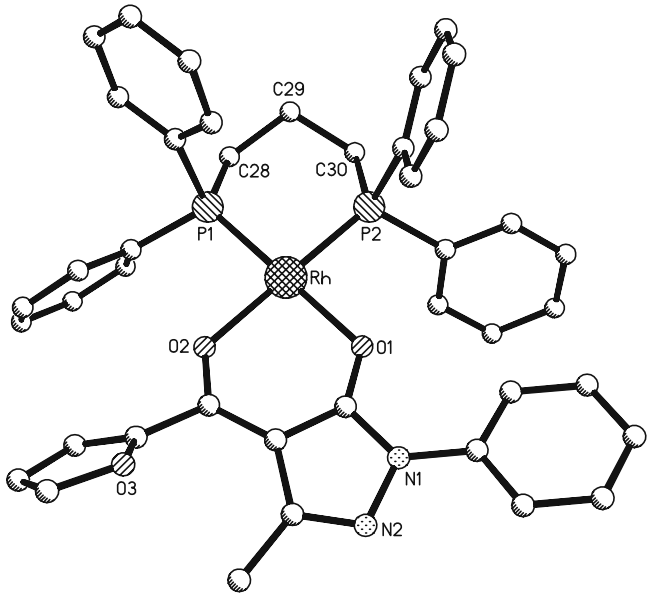


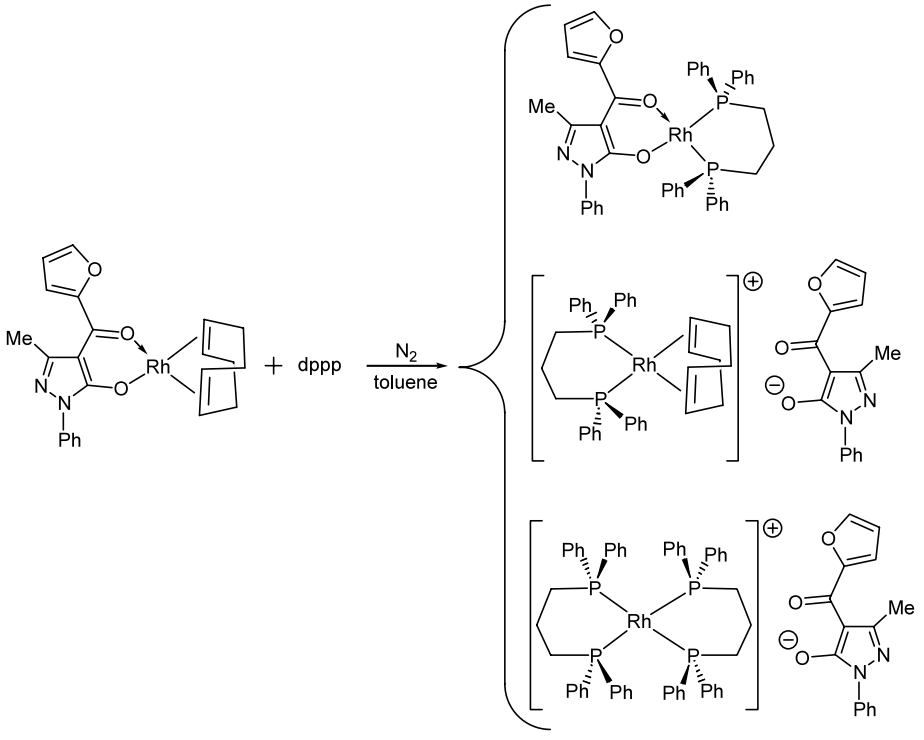
Fig. 5. Molecular structure of derivative **5**, $[Rh(Q^O)(dppp)]$.

As previously for derivatives **1**–**4**, also the formation of **5** in C_6D_6 has been followed by ^{31}P-NMR: together with resonances due to **5**, two minor resonances appear as doublets at 10.4 ppm ($^1J_{Rh-P} = 137$ Hz) and at 8.6 ppm ($^1J_{Rh-P} = 131$ Hz), likely due to [Rh(dppp)$_2$](Q^O) and [Rh(dppp)(1,5-cod)](Q^O) species, respectively (Scheme 4). After addition of O_2 all disappear and a doublet at 26.1 ($^1J_{Rh-P} = 138$ Hz) emerges, likely due to a Rh(III) species as [Rh(dppp)$_2$(O$_2$)](Q^O) [3,24,27]. This species has been also detected in CD_3CN by ESI-MS spectroscopy.

The oxidative addition of molecular iodine and allylbromide to complex Rh(Q)(1,5-cod) in the presence of excess PPh_3 under argon using throughly deoxygenated solvents has been investigated. In both cases oxidation occurs and two brownish precipitates have been obtained, the first having the formula [Rh(Q^S)I$_2$(PPh$_3$)$_2$] (**6**) and the latter [Rh(Q^S)Br(C$_3$H$_5$)(PPh$_3$)] (**7**). Derivatives **6** and **7** have been characterized by IR, ^{1}H- and ^{31}P-NMR spectroscopy. The ^{31}P-NMR of **6** exhibits a doublet at 17.5 ppm which corresponds to the resonance of two magnetically equivalent ^{31}P nuclei split by the coupling with ^{103}Rh. The equivalence of the two phosphine ligands indicates that PPh_3 ligands occupy the *trans* position to each other. In fact, in *cis*-(PPh$_3$)$_2$Rh(β-diketonate)I$_2$ (where the β-diketonate is not symmetrical) the two PPh_3 should be not equivalent [13].

Two different coordination modes (η^1 or η^3) could be found for the allyl moiety in derivative **7**. It has been previously observed that for not symmetrical M(η^3-allyl) (M = Rh or Pd) the five hydrogens are not equivalent, the *anti* hydrogens, closer to the metal showing a lower ppm value than the *syn* hydrogens and the signal of H_{meso} appearing above 5.0 ppm, whereas M(η^1-allyl) [28–30] exhibit generally a fine structure for the olefinic CH_2 unit. On the basis of these reports [28–30] a η^1-ally moiety is likely in our complex. The ^{31}P-NMR spectrum also shows a doublet at 38.9 with a $^1J_{Rh-P}$ of 115 Hz consistent with a Rh(III) species containing only one P-donor [31].

The oxidative addition of HCl 35% to Rh(Q)(1,5-cod) in thf in the presence of excess PPh_3 yielded derivative [Rh(Q^S)(PPh$_3$)$_2$Cl$_2$] (**8**). The ^{31}P-NMR spectrum of **8** exhibits a doublet at 16.2 ppm which corresponds to the resonance of two magnetically equivalent ^{31}P nuclei split by the coupling with ^{103}Rh. The equivalence of the two phosphine ligands indicates that PPh_3 ligands occupy the *trans* position to each other as confirmed also by the X-ray study (see below). This compound is stable in $CDCl_3$ solution for a long time as suggested by the invariance of the ^{1}H- and ^{13}C-NMR spectra after a week. The reaction was repeated several times but in any cases no hydride species formed nor hydrogenation of 1,5-cod was observed. The reaction was also followed by ^{1}H- and ^{31}P-NMR spectroscopy which seems to suggest a first fast step of formation of Rh-peroxo species and a second very slow step of formation of the dichloride species **8**. The structure of the [Rh(Q^S)(PPh$_3$)$_2$Cl$_2$] complex **8** is characterized by a distorted octahedral



Scheme 4.

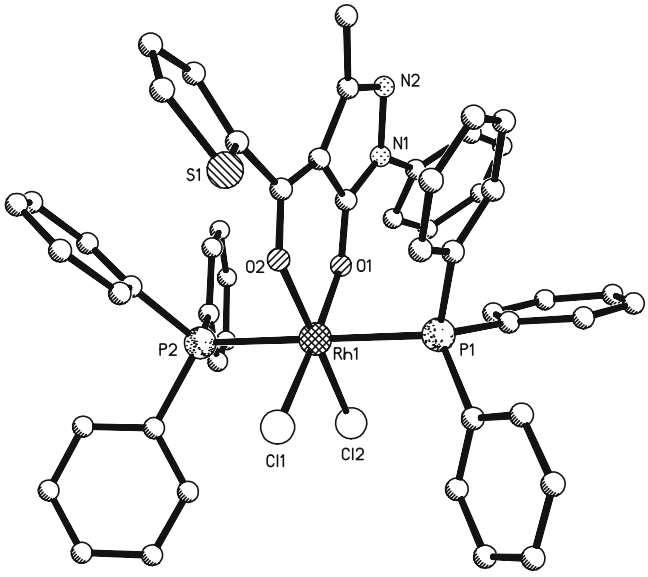


Fig. 6. Molecular structure of derivative **8**, $[Rh(Q^S)(Cl)_2(PPh_3)_2]$.

coordination of the Rh(III) atom (Fig. 6). The geometry of two crystallographically independent Rh complexes is nearly identical (Table 2). This structure shows a close analogy to the Rh(III)–dichloride complex earlier reported by us [17b]. A comparison of the square planar Rh(I) (**1** and **5**) and octahedral Rh(III) (**8**) complexes reveals remarkable changes of the Rh–O and Rh–P bond lengths. The smaller radius of the Rh(III) atom is partially compensated by a larger coordination number. Due to a more polar bonding, the Rh(III)–O bonds to the Q^S ligand are remarkably shorter (avg. 2.052 Å) than the Rh(I)–O bonds (avg. 2.113 Å). The polar Rh–Cl bonds (avg. 2.345 Å) in **1a** are in *trans*-positions to the Rh–O bonds. Finally, two less polar and, therefore, longer Rh–P bonds (avg. 2.402 Å compared with avg. 2.214 Å in **1** and **6**) are in *trans* position to each other.

Finally we have investigated the oxidative addition of iodomethane to $[Rh(Q^O)(1,5\text{-cod})]$ in the presence of excess PPh_3 under argon. The spectra were recorded immediately after mixing the reactants (5–15 min upon mixing). The reactions were performed at an equimolar reactant ratio or with a twofold excess of iodomethane at room temperature. The ^{1}H- and ^{31}P-NMR spectra do not show the signals corresponding to the starting complex suggesting higher reactivity of our species with respect to analogous previous reported [32,33]. In the ^{31}P-NMR spectrum four doublets of different intensities can be detected. On the basis of the $^1J_{Rh-P}$ coupling constant values we hypothesize that these signals could be due to the different isomers possible for the derivative $[Rh(Q)(CH_3)I(PPh_3)_2]$.

4. Conclusions

Several triorganophosphino- and bis(diorgano)phosphino-rhodium acyl-pyrazolonate (Q) complexes have been obtained by 1,5-cod displacement in [Rh(Q)(1,5-cod) as dry species and fully characterized for the first time, also by X-ray crystallography. They are very sensitive to oxygen of atmosphere. Their interaction with oxidative agents, as O_2, I_2, HCl, and allylbromide has been investigated by ^{1}H- and ^{31}P-NMR techniques: the presence of triphenylphosphine activates rhodium(I) as suitable centre for the oxidative addition of little molecules. In the case of O_2 addition, intermediate Rh(I) species, enough stable to be characterized, can be isolated. They further transform in solution to a Rh(III) species by prolonged warming. Diphosphine ligands react with [Rh(Q)(1,5-cod)] affording neutral [Rh(Q)(P–P)] or ionic $[Rh(P–P)_2](Q)$ derivatives, depending on the amount and nature of the diphosphine employed. In our condition only 1:2 adducts $[Rh(P–P)_2](Q)$ have been obtained with dppe and a 1.1 adduct Rh(Q)(P–P)] with dppp, likely due to steric (bite angle) differences in the two P–P ligands. However on the basis of solution NMR experiments we cannot exclude the possibility to obtain 1:1 adducts with dppe and 1:2 adducts with dppp. In fact the $[Rh(P–P)_2](Q)$ and Rh(Q)(P–P) obtained can give rise to several species in equilibrium in solution, where the solvent polarity seems to be an important factor in forcing the equilibrium in one direction or another.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 218867; 218868; 218869; 218870. 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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