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(1-Phenyl-3-methyl-4-acetylpyrazolon-5-ato)rhodium(I) complexes, synthesis, structural and spectroscopical characterization: Reactivity of diolefin- and dicarbonyl-rhodium complexes toward N-, P- and O-donors

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Abstract

Novel complexes of rhodium(I) [Rh(diolefin)(Q″)] (where HQ″ = 1-phenyl-3-methyl-4-acetylpyrazol-5-one and diolefin = cycloocta-1,5-diene (COD), bicyclo[2.2.1]hepta-2,5-diene (NBD) or 1,5-hexadiene (HEX)) were synthesized and characterized by analytical and spectral data. [Rh(COD)(Q″)] interacts with 4,5-dimethyl-1,10-phenanthroline (Me_2Phen) and 2,2′-bipyridil (Bipy) yielding the cationic derivatives [Rh(COD)(Me_2Phen)](Q″)(H_2O), [Rh(COD)(Bipy)](Q″)(H_2O) upon displacement of the $(Q'')^-$ donor from the coordination sphere of the metal center. Whereas [Rh(COD)(Q″)] interacts with 2-benzoylpyridine (Bzpy) yielding the 1:1 adduct [Rh(COD)(Bzpy)(Q″)] in which Bzpy acts as N-monodentate donor. On the other hand the monodentate P-donors triphenylphosphine, triphenylphosphite, tricyclohexylphosphine and the bidentate bis(diphenylphosphino)ethane (DPPE) displace the COD ligand from [Rh(COD)(Q″)] giving the neutral derivatives $[Rh(PR_3)_2(Q'')]$ ($PR_3 = PPh_3$, or $P(OPh)_3$) and [Rh(DPPE)(Q″)](H_2O). HQ″ reacts with the dinuclear $[Rh(CO)_2Cl]_2$. The tetradentate cycloocto-tetraene (COT) reacts with $[Rh(CO)_2(Q'')]$ yielding the derivative $[Rh(CO)_2(HQ'')Cl]$ in which HQ″ acts as neutral monodentate O-donor ligand. Whereas in presence of NEt_3 HQ″ reacts with $[Rh(CO)_2Cl]_2$ yielding $[Rh(CO)_2(Q'')]$. In this complex, one molecule of CO can be replaced by one mole of Phen and Bipy or by two moles of PPh_3 and $AsPh_3$ yielding the derivatives $[Rh(CO)(L)_n(Q'')]\cdot x(H_2O)$ ($L = Me_2Phen$ or Bipy, $n = 1$; $L = PPh_3$ or $AsPh_3$, $n = 2$) whereas one mole of DPPE displaces both the molecules of CO, yielding [Rh(DPPE)(Q″)] yielding the derivative [Rh(COT)(Q″)]. The X-ray crystal structure determination of [Rh(COD)(Q″)] establishes that the rhodium atom is in a square planar configuration with two adjacent sites occupied by the $(Q'')^-$ ligand in the O_2-bidentate form (Rh–O distances = 2.054(2) and 2.061(2) Å). The COD ring has a twisted boat conformation with Rh–C distances in the range 2.101(3)–2.110(3) Å. Comparison was made with structural data reported for several related tetracoordinated (COD)Rh(I) adducts. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Diolefin; Phenanthroline; Bipyridyl

1. Introduction

Rhodium(I) chelates of β-diketones were prepared more than 30 years ago [1]. However, the theoretical and practical importance of this class of complexes containing the chelating unit of the enolizable β-diketones in a rigid environment has only recently been recognized [2]. In particular the interest in metal-β-diketonato olefin compounds stems largely from attempts to elucidate the nature of the metal–olefin interaction, their use as model compounds in homogeneous catalysis and as catalysts in a variety of olefin isomerizations and polymerizations. For example sev-

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eral diolefin-β-diketonato rhodium(I) have temperature-dependent proton nuclear magnetic resonance spectra, indicating exchange of olefinic protons between non-equivalent sites [3]. Depending on the choice of the diolefin and β-diketone, these complexes showed a variety of intermolecular reactions, not all of which caused proton site exchange [4,5].

The fragment [Rh(P-donor)$_2$] also plays an important role in several catalytic reactions. The phosphorous donor influences the activity and selectivity of transformations such as rhodium catalyzed hydrogenation of CO_2 [6–9]. Surprisingly, only a few attempts have been made so far to elucidate the intrinsic influence of structural changes in the phosphine and β-diketone ligands in [RhP$_2$(β-diketone)-type compounds [10].

Therefore, following on our interest in the field of organometallic derivatives of N-, S- and O-donor heterocyclic ligands, we decided to investigate the reactivity of different Rh(I) acceptors towards 4-acyl-5-pyrazolones (QH), which are a class of potentially bidentate ligands originally investigated by Jensen as reagents for radiochemical separations [11]. These molecules are comparable to β-diketones because in both the classes keto-enol tautomerism is possible and they are able to coordinate in the neutral and the anionic form.

Here we report the results obtained with the donor 1-phenyl-3-methyl-4-acetyl-5-pyrazolone (**HQ″**). Some new diolefin-, phosphino- and carbonyl-rhodium(I) complexes were synthesized, characterized and compared with related derivatives. The reactivity of diolefin- and dicarbonyl-rhodium(I) compounds was also examined toward other N- and P-donors, mono or bidentate. The X-ray crystal structure of [(1-phenyl-3-methyl-4-acetylpyrazolon-5-ato)rhodium(I)(cycloocta-1, 5-diene)], the first rhodium(I)pyrazolonate structurally characterized, was also determined. Comparison was made with some related rhodium(I) compounds.

2. Experimental section

[Rh(COD)Cl]$_2$, [Rh(CO)$_2$Cl]$_2$, [Rh(NBD)Cl]$_2$, [Rh(HEX)Cl]$_2$ and [Rh(PPh$_3$)$_3$Cl] were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The donor HQ″ was prepared according to literature [12]. The samples for microanalyses were dried in vacuo to constant weight (20°C, ca. 0.1 torr). Elemental analyses (C, H, N, S) were carried out with a Fison Instrument 1108 CHNS-O Elemental Analyzer. Molecular weight determinations were carried out with a Knauer membrane osmometer. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin Elmer System 2000 FT-IR instrument. ^{1}H, ^{13}C and ^{31}P-NMR spectra were recorded on a VXR-300 Varian Spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C and 121.5 MHz for ^{31}P). Melting points were taken on an IA 8100 Electrothermal Instrument. The electronic conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

2.1. Synthesis of the complexes

2.1.1. Synthesis of [Rh(COD)(Q″)] (1)

[Rh(COD)Cl$_2$ (493 mg, 1.0 mmol) was added with stirring to a solution of the ligand HQ″ (430 mg, 2.0 mmol) and NEt$_3$ (280 μl, 2.0 mmol) in methanol (30 cm^3). The precipitate formed was stirred for 2 h and then filtered off and washed with methanol. Yield 68%. M.p. 165–170°C. Anal. Calc. for $C_{20}H_{23}N_2O_2Rh$: C, 56.3; H, 5.4; N, 6.6%. Found: C, 56.1; H, 5.6; N, 6.3%. ^{1}H-NMR (CDCl$_3$): δ(COD), 1.82q, 2.50qr (8 H, CH$_2$), 4.09br, 4.29br (4 H, –CH=CH–); δ(Q″), 2.38s, (3 H, C^6–CH$_3$), 2.42s (3 H, C^3–CH$_3$), 7.15t, 7.35t, 7.83d (5 H, N^1–C$_6$H$_5$); ^{1}H-NMR (toluene-d$_8$): δ(COD), 1.60br, 2.30br (8 H, CH$_2$), 4.22br, 4.26br, (4 H, –CH=CH–); δ(Q″), 1.86s, (3 H, C^6–CH$_3$), 2.06s (3 H, C^3–CH$_3$),

Table 1
Crystal data: data collection and refinement of the structure for Rh(COD)(Q″) **1**

Formula	$RhO_2N_2C_{20}H_{23}$
Formula weight	426.319
Space group	$P\bar{1}$
a (Å)	10.027(2)
b (Å)	10.251(3)
c (Å)	9.627(2)
α (°)	105.48(2)
β (°)	96.10(2)
γ (°)	70.73(2)
V_c (Å^3)	900.1(4)
Z	2
$D_{calc.}$ (g cm^{-3})	1.5731
μ(Mo–K$_\alpha$) (cm^{-1})	9.474
F(000)	436.0
Radiation (monochromated)	Mo–K$_\alpha$ (λ = 0.71069 Å)
T of data collection (K)	296
Scan mode	$\omega/2\theta$
Scan width	0.6° below K$_{\alpha1}$, 0.6° above K$_{\alpha2}$
Scan speed (° min^{-1})	min = 1.502, max = 14.648
Background/scan ratio	0.5
Data collection range (°)	$4.0 \leq 2\theta \leq 55.0$
$h\ k\ l$ range	−13/12; −13/12; 0/12
Standards (measured every 97 reflections)	21–1; 11–3; 31–2
Number of unique reflections measured	4538
Number of data with $\lvert F_o\rvert \geq 6\sigma(\lvert F_o\rvert)$	3492
Refinement	Full matrix least squares on F
Number of parameters refined	226
R[a]	3.11
Rw[b]	3.93
S[c] (goodness of fit)	1.32

[a] $R = (\Sigma\|\lvert F\rvert - k\lvert F_c\rvert\|)/\Sigma\lvert F_o\rvert$.
[b] $R_w = (\Sigma w(\lvert F_o\rvert - k\lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$.
[c] $S = = [\Sigma w(\lvert F_o\rvert - k\lvert F_c\rvert)^2/(N_{obs} - N_{par})]^{1/2}$.

Table 2
Interatomic distances (Å) with e.s.d.'s in parentheses, for Rh(COD)(Q″) **1**

Rh(1)–O(14)	2.061(2)
Rh(1)–O(15)	2.054(2)
Rh(1)–C(17)	2.103(3)
Rh(1)–C(20)	2.106(3)
Rh(1)–C(21)	2.101(3)
Rh(1)–C(24)	2.110(3)
Rh(1)–X(1)[a]	1.988(3)
Rh(1)–X(2)[b]	1.979(3)
O(15)–C(5)	1.274(3)
O(14)–C(13)	1.269(4)
N(1)–N(2)	1.397(4)
N(1)–C(5)	1.366(4)
N(1)–C(6)	1.416(4)
N(2)–C(3)	1.294(5)
C(3)–C(4)	1.446(4)
C(3)–C(12)	1.509(5)
C(4)–C(5)	1.421(4)
C(4)–C(13)	1.402(5)
C(6)–C(7)	1.382(5)
C(6)–C(11)	1.391(5)
C(7)–C(8)	1.391(5)
C(8)–C(9)	1.368(7)
C(9)–C(10)	1.351(7)
C(10)–C(11)	1.392(6)
C(13)–C(16)	1.511(4)
C(17)–C(24)	1.397(5)
C(17)–C(18)	1.503(6)
C(18)–C(19)	1.492(7)
C(19)–C(20)	1.508(6)
C(20)–C(21)	1.397(6)
C(21)–C(22)	1.504(6)
C(22)–C(23)	1.500(5)
C(23)–C(24)	1.507(5)
X(1)…X(2)	2.771(4)
O(15)…C(7)	2.855(5)
O(15)…H(7)	2.180(5)
N(2)…C(11)	2.760(5)
N(2)…H(11)	2.401(5)

[a] X(1) is the center of the double bond between C(17) and C(24).
[b] X(2) is the center of the double bond between C(20) and C(21).

Table 3
Bond angles (°) with e.s.d.'s in parentheses, for Rh(COD)(Q″) **1**

O(14)–Rh(1)–O(15)	90.82(9)	C(5)–C(4)–C(3)	103.6(3)
X(1)[a]–Rh(1)–X(2)[b]	88.6(1)	O(15)–C(5)–N(1)	122.2(3)
O(14)–Rh(1)–X(1)	179.0(1)	O(15)–C(5)–C(4)	131.2(3)
O(14)–Rh(1)–X(2)	90.4(1)	N(1)–C(5)–C(4)	106.6(2)
O(15)–Rh(1)–X(1)	90.2(1)	O(14)–C(13)–C(4)	123.5(3)
O(15)–Rh(1)–X(2)	178.4(1)	O(14)–C(13)–C(16)	114.3(3)
O(14)–Rh(1)–C(17)	160.6(1)	C(4)–C(13)–C(16)	122.2(3)
O(14)–Rh(1)–C(20)	91.5(1)	C(7)–C(6)–C(11)	119.3(3)
O(14)–Rh(1)–C(21)	88.9(1)	N(1)–C(6)–C(7)	122.0(3)
O(14)–Rh(1)–C(24)	160.6(1)	N(1)–C(6)–C(11)	118.7(3)
O(15)–Rh(1)–C(17)	88.4(1)	C(6)–C(7)–C(8)	119.6(4)
O(15)–Rh(1)–C(20)	159.4(1)	C(7)–C(8)–C(9)	120.7(5)
O(15)–Rh(1)–C(21)	161.8(1)	C(8)–C(9)–C(10)	120.1(4)
O(15)–Rh(1)–C(24)	91.9(1)	C(9)–C(10)–C(11)	120.7(4)
C(17)–Rh(1)–C(20)	82.7(2)	C(6)–C(11)–C(10)	119.7(4)
C(17)–Rh(1)–C(21)	97.8(1)		
C(17)–Rh(1)–C(24)	38.7(1)	Rh(1)–C(17)–C(18)	111.1(3)
C(20)–Rh(1)–C(21)	38.8(2)	Rh(1)–C(17)–C(24)	70.9(2)
C(20)–Rh(1)–C(24)	92.7(1)	C(18)–C(17)–C(24)	124.9(4)
C(21)–Rh(1)–C(24)	82.6(1)	C(17)–C(18)–C(19)	114.6(4)
		C(18)–C(19)–C(20)	114.7(3)
Rh(1)–O(14)–C(13)	127.8(1)	Rh(1)–C(20)–C(19)	112.3(3)
Rh(1)–O(15)–C(5)	120.6(2)	Rh(1)–C(20)–C(21)	70.4(2)
N(2)–N(1)–C(5)	111.1(3)	C(19)–C(20)–C(21)	124.5(4)
N(2)–N(1)–C(6)	118.9(3)	Rh(1)–C(21)–C(20)	70.8(2)
C(5)–N(1)–C(6)	130.1(3)	Rh(1)–C(21)–C(22)	110.7(2)
C(3)–N(2)–N(1)	106.4(3)	C(20)–C(21)–C(22)	125.1(3)
N(2)–C(3)–C(4)	112.2(3)	C(21)–C(22)–C(23)	115.1(3)
N(2)–C(3)–C(12)	118.4(3)	C(22)–C(23)–C(24)	113.4(3)
C(4)–C(3)–C(12)	129.3(4)	Rh(1)–C(24)–C(17)	70.4(2)
C(3)–C(4)–C(13)	131.6(3)	Rh(1)–C(24)–C(23)	113.0(2)
C(5)–C(4)–C(13)	124.7(3)	C(17)–C(24)–C(23)	123.7(3)
C(7)–H(7)…Q(15)	123.3(4)		
C(11)–H(11)…N(2)	100.2(4)		

[a] X(1) is the center of the double bond between C(17) and C(24).
[b] X(2) is the center of the double bond between C(20) and C(21).

7.00t, 7.22t, 8.24d (5 H, N^1–C_6H_5). ^{13}C-NMR ($CDCl_3$): δ(COD), 30.4, 30.7, 30.9, 31.0 (CH_2), 76.9d, $J_{(Rh-C)} = 14.2$ Hz, 77.8d, $J_{(Rh-C)} = 14.4$ Hz (–CH=CH–); δ(Q″), 27.3, (C^6–CH_3), 18.0 (C^3–CH_3), 106.7 (C^4), 139.3 (C^3), 190.3 (C^5), 163.2 (C^6), 120.5, 126.8, 129.0, 148.8 (N^1–C_6H_5). IR (nujol) cm^{-1}; 1592s, ν(C=O); 508m, 479s, ν(Rh–C), 403m, 391s, ν(Rh–O).

2.1.2. Synthesis of [Rh(HEX)(Q″)] (2)

[Rh(HEX)Cl]$_2$ (441 mg, 1.0 mmol) was added with stirring to a solution of the ligand HQ″ (430 mg, 2.0 mmol) and NEt_3 (280 μl, 2.0 mmol) in methanol (30 cm^3). The precipitate formed was stirred for 2 h and then filtered off and washed with methanol. Yield 58%. M.p. 142–146°C Anal. Calc. for $C_{18}H_{21}N_2O_2Rh$: C, 54.0; H, 5.3; N, 7.0%. Found: C, 53.7; H, 5.5; N, 7.0%. ^{1}H-NMR ($CDCl_3$): δ(HEX), 2.20–2.50m (4 H, CH_2), 3.20d, $J_{(Rh-H)} = 1.38$ Hz, 3.24d, $J_{(Rh-H)} = 1.28$ Hz, 3.30d, $J_{(Rh-H)} = 1.39$ Hz, 3.34d, $J_{(Rh-H)} = 1.29$ Hz, 4.42br, 4.60br (6 H, –CH=CH–); δ(Q″), 2.38s, (3 H, C^6–CH_3), 2.41s (3 H, C^3–CH_3), 7.15t, 7.35t, 7.83d (5 H, N^1–C_6H_5). IR (nujol) cm^{-1}: 1591s, ν(C=O); 507m, 476s, ν(Rh–C), 434m, 417s, 406m, 387m ν(Rh–O).

2.1.3. Synthesis of [Rh(NBD)(Q″)] (3)

TlQ″ (419 mg, 1.0 mmol) was added with stirring to a solution of [Rh(NBD)Cl]$_2$ (461 mg, 0.5 mmol) in dichloromethane (25 cm^3). The TlCl formed was filtered off and the complex was precipitated by the addition of methanol. Yield 39%. M.p. 178°C dec. Anal. Calc. for $C_{19}H_{19}N_2O_2Rh$: C, 55.6; H, 4.7, N, 6.8%. Found: C, 55.8; H, 4.9; N, 6.9%. ^{1}H-NMR ($CDCl_3$): δ(NBD), 1.25s (2 H, CH_2), 3.85br (2 H, CH), 3.95br (4 H, –CH=CH–); δ(Q″), 2.35s (3 H, C^6–CH_3), 2.40s (3 H, C^3–CH_3), 7.15t, 7.34t, 7.80d (5 H, N^1–C_6H_5); ^{1}H-NMR (toluene-d$_8$): δ(NBD), 0.91pt (2 H, CH_2), 3.40m (2 H, CH), 3.77q (4 H, –CH=CH–); δ(Q″), 1.86s (C^6–CH_3), 2.06 (C^3–CH_3), 6.92t, 7.20, 8.14d (N^1–

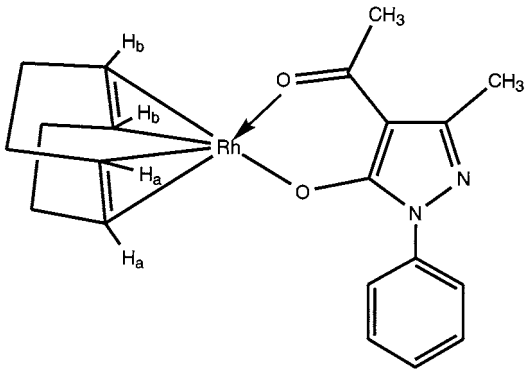

Fig. 1. The olefinic protons H_a and H_b in **1**.

C_6H_5). IR (nujol (cm^{-1}: 1592s, ν(C=O); 510m, 500m, 472vs, ν(Rh–C), 420m, 414s, 404m, 380s ν(Rh–O).

*2.1.4. Synthesis of [Rh(COD)(Me$_2$Phen)](Q″)(H$_2$O) (**4**)*

To a solution of [Rh(COD)(Q″)] **1** (213 mg, 0.5 mmol) in diethyl ether (50 cm^3) under nitrogen, the stoichiometric amount of 4,7-dimethyl-1,10-phenanthroline (104 mg, 0.5 mmol) was added. A red precipitate formed immediately, which was filtered off and washed with diethyl ether. Yield 30%. M.p. 168–173°C. Anal. Calc. for $C_{32}H_{38}N_4O_3Rh$: C, 62.6; H, 5.7; N, 8.6%. Found: C, 62.5; H, 5.6; N, 8.5%. Λ_m (CH_2Cl_2): 21.9 Ω^{-1} cm^2 mol^{-1}, $0.9\cdot10^{-3}$ M. Λ_m (acetone): 89.6 Ω^{-1} cm^2 mol^{-1}, $0.6\cdot10^{-3}$ M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.85br (2 H); δ(COD), 2.15qbr, 2.65mbr (8 H, CH_2), 4.64d, $J_{(Rh-H)}$= 1.4 Hz (4 H, –CH=CH–); δ(Me$_2$Phen), 2.81s, 2.84s (6 H, CH_3), 7.46d, 7.66d, 8.01d, 8.05d, 9.05d (6 H); δ(Q″), 2.44s (3 H, C^6–CH_3), 2.48s (3 H, C^3–CH_3), 7.40t, 7.55t, 8.00d (5 H, N^1–C_6H_5). IR (nujol) cm^{-1}: ν(H_2O), 3200 br, ν(C=O), 1623s, ν(Rh–C), 511s, 483m, ν(Rh–N), 296vs, 248m.

*2.1.5. Synthesis of [Rh(COD)(Bipy)](Q″)(H$_2$O) (**5**)*

To a solution of [Rh(COD)(Q″)] **1** (213 mg, 0.5 mmol) in diethyl ether (50 cm^3) under nitrogen, the stoichiometric amount of 2,2′-bipyridil (78 mg, 0.5 mmol) was added. A red precipitate formed immediately, which was filtered off and washed with diethyl ether. Yield 70%. M.p. 155–156°C. Anal. Calc. for

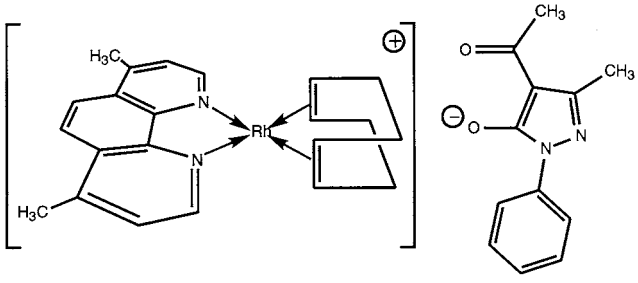

Fig. 2. Structure proposed for derivative **4**.

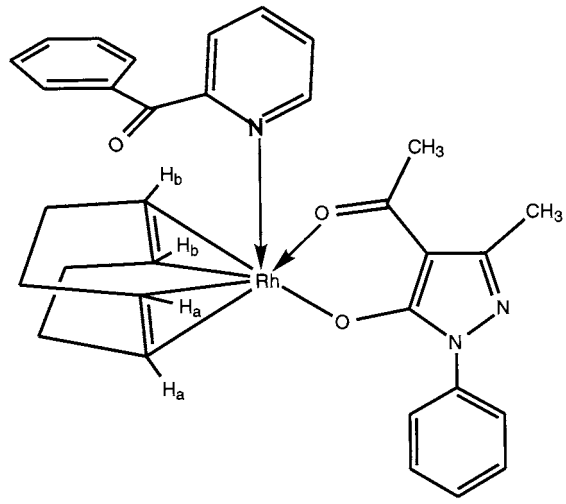

Fig. 3. Structure proposed for derivative **6**.

$C_{30}H_{35}N_4O_3Rh$: C, 59.8; H, 5.9; N, 9.3%. Found: C, 60.2; H, 5.6; N, 9.5%. Λ_m (CH_2Cl_2): 3.4 Ω^{-1} cm^2 mol^{-1}, $0.8\cdot10^{-3}$ M. Λ_m (Acetone): 25.5 Ω^{-1} cm^2 mol^{-1}, $0.9\cdot10^{-3}$ M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.81d br (2 H); δ(COD), 1.81d br, 2.46mbr (8 H, CH_2), 4.18mbr (4 H, –CH=CH–); δ(Bipy), 7.30br, 7.83s, 8.42d, 8.68d (8 H); δ(Q″), 2.38s (3 H, C^6–CH_3), 2.41s (3 H, C^3–CH_3), 7.15t, 7.30br, 7.85d (5 H, N^1–C_6H_5). IR (nujol) cm^{-1}: ν(H_2O), 3430br, ν(C=O), 1623s, ν(Rh–C), 509s, 481m, ν(Rh–N), 298vs, 254m.

*2.1.6. Synthesis of [Rh(COD)(Bzpy)(Q″)] (**6**)*

To a solution of [Rh(COD)(Q″)] **1** (213 mg, 0.5 mmol) in diethyl ether (50 cm^3) under nitrogen, the stoichiometric amount of 2-benzoylpyridine (92 mg, 0.5 mmol) was added. A reddish-yellow precipitate formed immediately, which was filtered off and washed with diethyl ether. Yield 95%. M.p. 90°C dec. Anal. Calc. for $C_{36}H_{32}N_3O_3Rh$: C, 63.1; H, 5.3; N, 6.9%. Found: C, 63.4; H, 5.4; N, 6.9%. ^{1}H-NMR ($CDCl_3$): δ(COD), 1.82qbr, 2.50mbr (8 H, CH_2), 4.20dbr (4 H, –CH=CH–); δ(Bzpy), 7.50–7.66m, 7.90t, 8.05–8.12m, 8.74d (9 H); δ(Q″), 2.37s (3 H, C^6–CH_3), 2.41s (3 H, C^3–CH_3), 7.14t, 7.35t, 7.82d (5 H, N^1–C_6H_5). IR (nujol) cm^{-1}: ν(H_2O), 3200 br, ν_{Bzpy}(C=O), 1668vs, $\nu_{Q''}$(C=O), 1592s, ν(Rh–C), 509m, 478s, ν(Rh–O), 400s, 389m, ν(Rh–N), 229m.

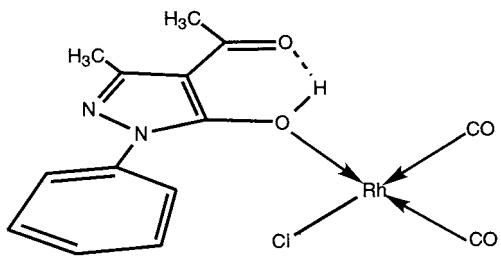

Fig. 4. Structure proposed for derivative **10**.

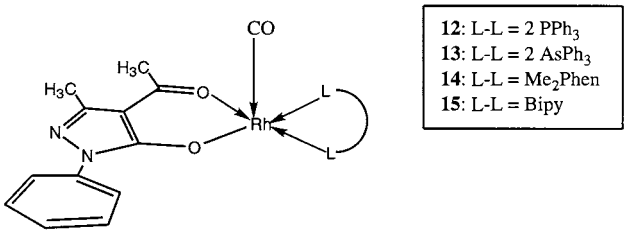

Fig. 5. Structure proposed for derivatives **12–15**.

2.1.7. Synthesis of [Rh(PPh$_3$)$_2$(Q″)] (7)

PPh_3 (261 mg, 1.0 mmol) was added to a solution of [Rh(COD)(Q″)] **1** (213 mg, 0.5 mmol) in diethyl ether (30 cm^3). A yellow precipitate was formed slowly, which was filtered off and washed with diethyl ether. Yield 94%. M.p. 77°C dec. Anal. Calc. for $C_{48}H_{41}N_2O_2P_2Rh$: C, 68.4; H, 4.9; N, 3.3%. Found: C, 68.6; H, 4.9; N, 3.4%. ^{1}H-NMR ($CDCl_3$): δ(PPh_3), 6.90–7.75mbr (30 H); δ(Q″), 1.86s, 2.00s, 2.08s, 2.12s (6 H, C^6–CH$_3$ and C^3–CH$_3$), 6.90–7.75mbr (5 H, N^1–C$_6$H$_5$). ^{31}P-NMR ($CDCl_3$): 34.51dd, $J_{(Rh-P)} = 131.7$ Hz, $J_{(P-P)} = 28.6$ Hz; 33.32dd, $J_{(Rh-P)} = 121.7$ Hz, $J_{(P-P)} = 28.6$ Hz. IR (nujol) cm^{-1}: ν(C=O), 1605s, ν(PPh_3), 541vs, 523vs, 515s, ν(Rh–O), 455m, 439s, 433m.

2.1.8. Synthesis of [Rh(P(OPh)$_3$)$_2$(Q″)] (8)

P(OPh)$_3$ (310 mg, 1.0 mmol) was added to a solution of [Rh(COD)(Q″)] **1** (213 mg, 0.5 mmol) in dichloromethane (30 cm^3). The solution was stirred for 2 h. By the addition of hexane, a yellow precipitate was afforded, which was filtered off and washed with hexane. Yield 77%. M.p. 111–113°C dec. Anal. Calc. for $C_{48}H_{41}N_2O_8P_2Rh$: C, 61.2; H, 4.5; N, 2.9%. Found: C, 61.4; H, 4.4; N, 3.0%. ^{1}H-NMR ($CDCl_3$): δ(P(OPh)$_3$), 7.08–7.32 mbr (30 H): δ(Q″), 1.99s (3 H, C^6–CH$_3$), 2.27s, (3 H, C^3–CH$_3$), 7.08–7.32mbr, 7.52t, 7.85d (5 H, N^1–C$_6$H$_5$). ^{31}P-NMR ($CDCl_3$): −40.9dd, $J_{(Rh-P)} = 194.2$ Hz, $J_{(P-P)} = 103.8$ Hz; 43.4dd, $J_{(Rh-P)} = 183.4$ Hz, $J_{(P-P)} = 104.4$ Hz. IR (nujol) cm^{-1}: ν(C=O), 1609s, ν(P(OPh)$_3$), 507vs, 500vs, 492vs, 482vs, ν(Rh–O), 454m, 417m.

2.1.9. Synthesis of [Rh(DPPE)(Q″)] (H$_2$O) (9)

1,2-Bis(diphenylphosphino)ethane (199 mg, 0.5 mmol) was added to a solution of [Rh(COD)(Q″)] **1** (213 mg, 0.5 mmol) in dichloromethane (30 cm^3). The solution was stirred for 2 h. By addition of diethyl ether a yellow precipitate was afforded, which was filtered off and washed with diethyl ether. Yield 47%. M.p. 178–183°C. Anal. Calc. for $C_{38}H_{37}N_2O_3P_2Rh$: C, 62.1; H,

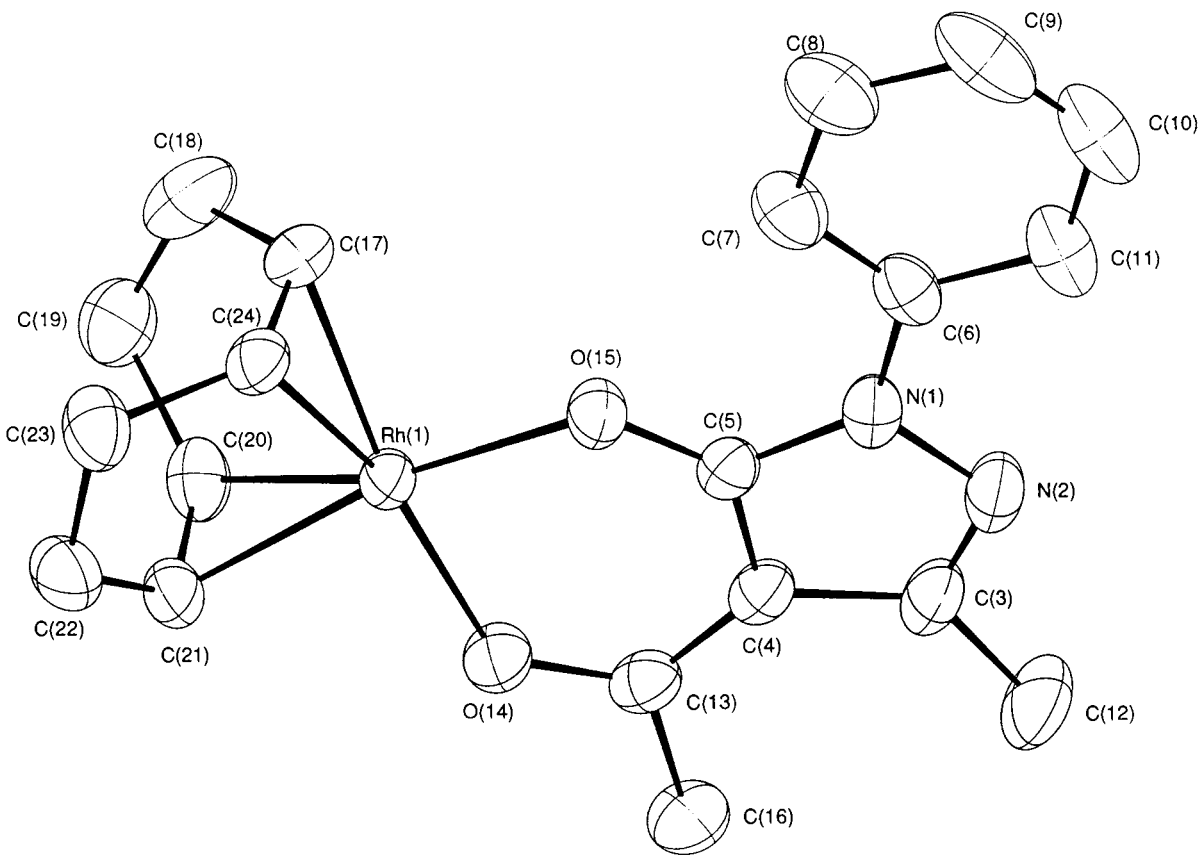

Fig. 6. An ORTEP view of complex [Rh(COD)(Q″)] (**1**).

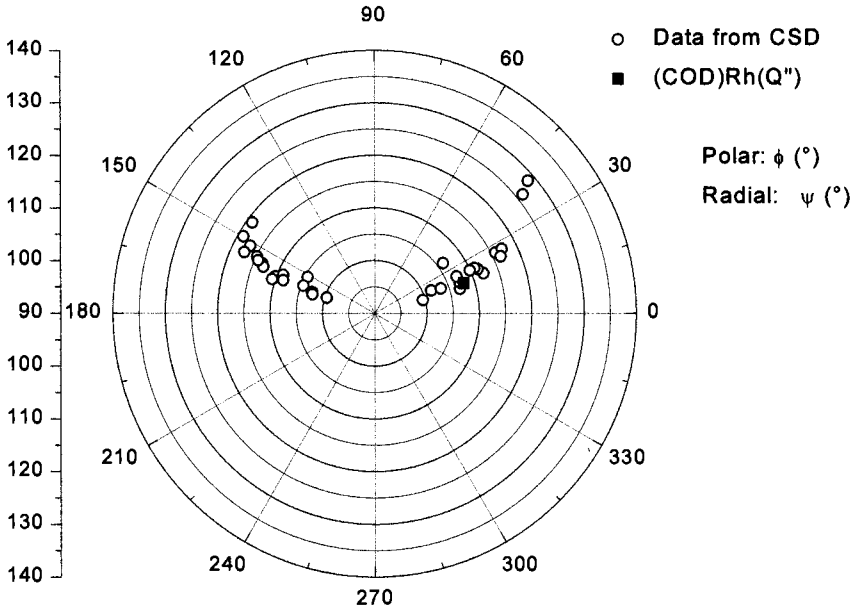

Fig. 7. Plot of ϕ vs ψ for (COD)RhO_2-like adducts.

5.1; N, 3.8%. Found: C, 62.4; H, 5.2; N, 3.6%. ^{1}H-NMR ($CDCl_3$): δ(DPPE), 2.02–2.22mbr (4 H, P–CH_2CH_2–P), 7.10–7.50mbr, 7.62–7.74mbr (20 H, P–C_6H_5); δ(Q″), 2.46s, 2.33s (3 H, C^6–CH_3), 2.52s, 2.30s (3 H, C^3–CH_3), 7.10–7.50mbr, 7.95dbr (5 H, N^1–C_6H_5). ^{31}P-NMR ($CDCl_3$, 20°C): 58.0d, $J_{(Rh-P)}$ = 133.1 Hz. IR (nujol) cm^{-1}: ν(C=O), 1589s, ν(DPPE), 535vs, 507s, 483s, ν(Rh–O), 432s, 385m.

2.1.10. Synthesis of [Rh(CO)$_2$(HQ″)Cl] (10)

The ligand HQ″ (212 mg, 1.0 mmol) was added to a solution of [Rh(CO)$_2$Cl]$_2$ (194 mg, 0.5 mmol) in methanol (30 cm^3). The solution was stirred at 80°C for 2 h, then evaporated to dryness in vacuo. Crystallization was induced by addition of hexane. Yield 40%. M.p. 97–100°C. Anal. Calc. for $C_{14}H_{12}ClN_2O_4Rh$: C, 40.9; H, 2.9; N, 6.9%. Found: C, 40.6; H, 3.0; N, 6.6%. ^{1}H-NMR ($CDCl_3$): δ(HQ″), 2.82sbr, (3 H, C^6–CH_3), 2.52sbr (3 H, C^3–CH_3), 7.52–7.74mbr (5 H, N^1–C_6H_5). IR (nujol) cm^{-1}: (OH···O) 2700br, $\nu_{Q''}$(C=O), 1643sbr, ν(CO), 2076vs, 2025m, 2007s, 1992m, ν(Rh–C), 489vs, 307vs ν(Rh–Cl).

2.1.11. Synthesis of [Rh(CO)$_2$(Q″)] (11)

(i) A mixture of $RhCl_3 \cdot xH_2O$ (209 mg, 1.0 mmol) and an excess of the ligand HQ″ (318 mg, 1.5 mmol) in dimethylformamide (10 cm^3) was refluxed for 1 h. The complex was precipitated by the addition of water and recrystallized from dichloromethane–hexane.

(ii) The ligand HQ″ (212 mg, 1.0 mmol) was added to a solution of [Rh(CO)$_2$Cl]$_2$ (194 mg, 0.5 mmol) and NEt_3 (140 μl, 1.0 mmol) in methanol (30 cm^3) at 70°C. A reddish-brown precipitate was formed which was stirred for 24 h and then filtered off, washed with methanol and recrystallized from hot light petroleum (40–60°C). Yield 92 mg (25%). M.p. 148–152°C. Anal. Calc. for $C_{14}H_{11}N_2O_4Rh$: C, 44.9; H, 3.0; N, 7.5%. Found: C, 44.9; H, 3.0; N, 7.3%. ^{1}H-NMR ($CDCl_3$): δ(Q″), 2.45s, (3 H, C^6–CH_3), n.o. (C^4), 138.6 (C^3), 191.1 (C^5), 162.9 (C^6), 121.1, 126.3, 129.3, 148.8 (N^1–C_6H_5). IR (nujol) cm^{-1}: $\nu_{Q''}$(C=O), 1623cbr, ν(CO), 2101s, 2084sh, 2064s, 2001vs, ν(Rh–C), 468vs, ν(Rh–O), 406m, 386m.

2.1.12. Synthesis of [Rh(CO)(Me$_2$Phen)(Q″)](H$_2$O)$_2$ (12)

A suspension of [Rh(CO)$_2$(Q″)] (187 mg, 0.5 mmol) in diethyl ether was treated with a stoichiometric amount of 4,7-dimethyl-1,10-phenanthroline (Me_2Phen) (104 mg, 0.5 mmol). After stirring for 24 h, the precipitate formed was filtered off and washed with diethyl ether. Yield 54%. M.p. 250°C dec. Anal. Calc. for $C_{25}H_{27}H_4O_5Rh$: C, 54.4; H, 4.4; N, 9.1%. Found: C, 54.0; H, 4.4; N, 9.3%. ^{1}H-NMR ($CDCl_3$): δ(Me_2Phen), 2.85–3.18mbr (6 H, CH_3), 7.10–7.85mbr, 7.95–8.62mbr, 8.78dd (6 H); δ(Q″), 2.20–2.65mbr, (6 H, C^6–CH_3 and C^3–CH_3), 7.10–7.85mbr (5 H, N^1–C_6H_5); δ(H_2O), 1.90br (4 H). IR (nujol) cm^{-1}: ν(H_2O), 3250br, $\nu_{Q''}$(C=O), 1602sbr, ν(CO), 1975sbr, ν(Rh–CO), 481m, ν(Rh–O), 406m, 390m, ν(Rh–N), 293s.

2.1.13. Synthesis of [Rh(CO)(Bipy)(Q″)](H$_2$O)$_2$ (13)

A suspension of [Rh(CO)$_2$(Q″)] (187 mg, 0.5 mmol) in diethyl ether was treated with a stoichiometric amount of 2,2′-bipyridil (Bipy) (78 mg, 0.5 mmol). After stirring for 24 h, the precipitate formed was filtered off and washed with diethyl ether. Yield 58%. M.p. 250°C dec. Anal. Calc. for $C_{23}H_{23}N_4O_5Rh$: C,

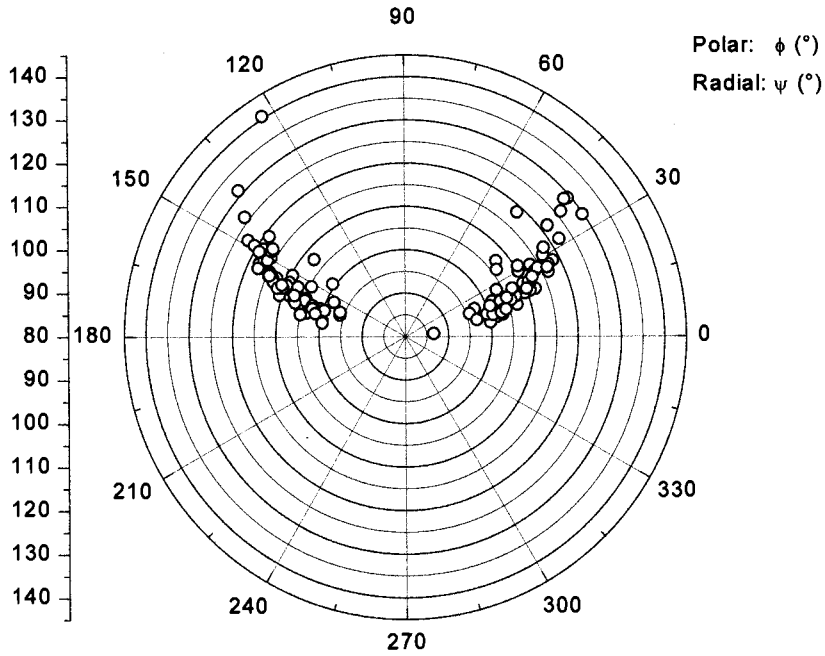

Fig. 8. Plot of ϕ vs ψ for (COD)RhL$_2$-like adducts.

51.3; H, 4.3; N, 10.4%. Found: C, 51.0; H, 4.2; N, 10.3%. ^{1}H-NMR ($CDCl_3$): δ(Bipy), 7.15–7.82mbr, 7.90–8.70mbr (8 H), δ(Q″), 2.20–2.75mbr, (6 H, C^6–CH$_3$ and C^3–CH$_3$), 7.15–7.82mbr (5 H, N^1–C$_6$H$_5$); δ(H$_2$O), 1.85br (4 H). IR (nujol) cm^{-1}: ν(H$_2$O), 3300br, $\nu_{Q''}$(C=O), 1600sbr, ν(CO), 1975sbr, ν(Rh–CO), 489m, ν(Rh–O), 387m, ν(Rh–N), 278m, 295m.

2.1.14. Synthesis of [Rh(PPh$_3$)$_2$(CO)(Q″)](H$_2$O) (14)

PPh$_3$ (262 mg, 1.0 mmol) was added to a solution of [Rh(CO)$_2$(Q″)] (187 mg, 0.5 mmol) in dichloromethane (30 cm^3). Complex **14** was separated by addition of light petroleum. Yield 32%. M.p. 193–197°C. Anal. Calc. for $C_{49}H_{43}N_2O_4P_2Rh$: C, 66.2; H, 4.9; N, 3.1%. Found: C, 66.5; H, 4.8; N, 3.2%. ^{1}H-NMR ($CDCl_3$): δ(PPh$_3$), 7.30–7.48mbr (30 H), δ(Q″), 1.92s (3 H, C^6–CH$_3$), 2.42s (3 H, C^3–CH$_3$), 7.0 6t, 7.18t, 7.55d (5 H, N^1–C$_6$H$_5$), δ(H$_2$O), 1.82br (2 H). ^{31}P-NMR ($CDCl_3$): 28.0d, $J_{(Rh-P)} = 130.6$ Hz, $T = 20$°C; 28.3d $J_{(Rh-P)} = 129.9$ Hz, $T = -55$°C. IR (nujol) cm^{-1}: ν(H$_2$O), 3240br, $\nu_{Q''}$(C=O), 1636sbr, ν(PPh$_3$), 527s, 518s, 506s, ν(Rh–CO), 475m, ν(Rh–O), 381m.

2.1.15. Synthesis of [Rh(AsPh$_3$)$_2$(CO)(Q″)](H$_2$O) (15)

AsPh$_3$ (306 mg, 1.0 mmol) was added to a solution of [Rh(CO)$_2$(Q″)] (187 mg, 0.5 mmol) in dichloromethane (30 cm^3). Complex **15** was separated by addition of light petroleum. Yield 25%. M.p. 166–167°C. Anal. Calc. for $C_{49}H_{43}N_2O_4As_2Rh$: C, 60.3; H, 4.4; N, 2.9%. Found: C, 60.4; H, 4.4; N, 2.8%. ^{1}H-NMR ($CDCl_3$): δ(AsPh$_3$), 7.20–7.50mbr, 7.55–7.68mbr (30 H), δ(Q″), 1.98s (3 H, C^6–CH$_3$), 2.38s, (3 H, C^3–CH$_3$), 7.20–7.50mbr, 7.71d (5 H, N^1–C$_6$H$_5$), δ(H$_2$O), 1.75br (2 H). IR (nujol) cm^{-1}: ν(H$_2$O), 3180br, $\nu_{Q''}$(C=O), 1636sbr, ν(AsPh$_3$), 465vs, 332vs, 320s, ν(Rh–CO), 484s.

2.1.16. Synthesis of [Rh(COT)(Q″)] (16)

Cyclooctatetraene (COT) (52 mg, 0.5 mmol) was added to a solution of [Rh(CO)$_2$(Q″)] (374 mg, 1.0 mmol) in dichloromethane (30 cm^3). Compound **16** was separated by the addition of hexane. Yield 34%. M.p. 135–138°C. Anal. Calc. for $C_{20}H_{19}N_2O_2Rh$: C, 56.9; H, 4.5; N, 6.6%. Found: C, 56.4; H, 4.6; N, 6.6%. ^{1}H-NMR ($CDCl_3$): δ(COT), 4.23d, $J_{(Rh-H)} = 1.38$ Hz, 4.34d, $J_{(Rh-H)} = 0.82$ Hz, 5.89s (8 H, –CH=CH–); δ(Q″), 2.40s, (3 H, C^6–CH$_3$), 2.42s (3 H, C^3–CH$_3$), 7.16t, 7.35t, 7.83d (5 H, N^1–C$_6$H$_5$). ^{13}C-NMR ($CDCl_3$): δ(COT): 136.6, 136.1, 132.5, 129.1, 85.5d, $J_{(Rh-C)} = 19.5$ Hz, 84.8d, $J_{(Rh-C)} = 20.0$ Hz, 83.5d, $J_{(Rh-C)} = 19.8$ Hz, 82.7d, $J_{(Rh-C)} = 20.0$ Hz (–CH=CH–); δ(Q″), 27.0 (C^6–CH$_3$), 18.0 (C^3–CH$_3$), n.o. (C^4), 139.0 (C^3), 190.2 (C^5), 163.4 (C^6), 120.9, 125.7, 129.0, 148.9 (N^1–C$_6$H$_5$). IR (nujol) cm^{-1}: ν(C=O), 1601s; ν(Rh–C), 512m, 481s; ν(Rh–O), 407m, 388m.

2.2. Crystallographic study

Crystal and experimental data are summarized in Table 1. Bond distances and angles are listed in Tables 2 and 3, respectively. Yellow crystals of the compound were obtained by slow evaporation from a dichloromethane/diethyl ether solution of **1**. A crystal with approximate dimensions of $0.3 \times 0.4 \times 0.4$ mm was mounted on Syntex P21 four circle diffractometer and accurate lattice parameters were obtained by least-

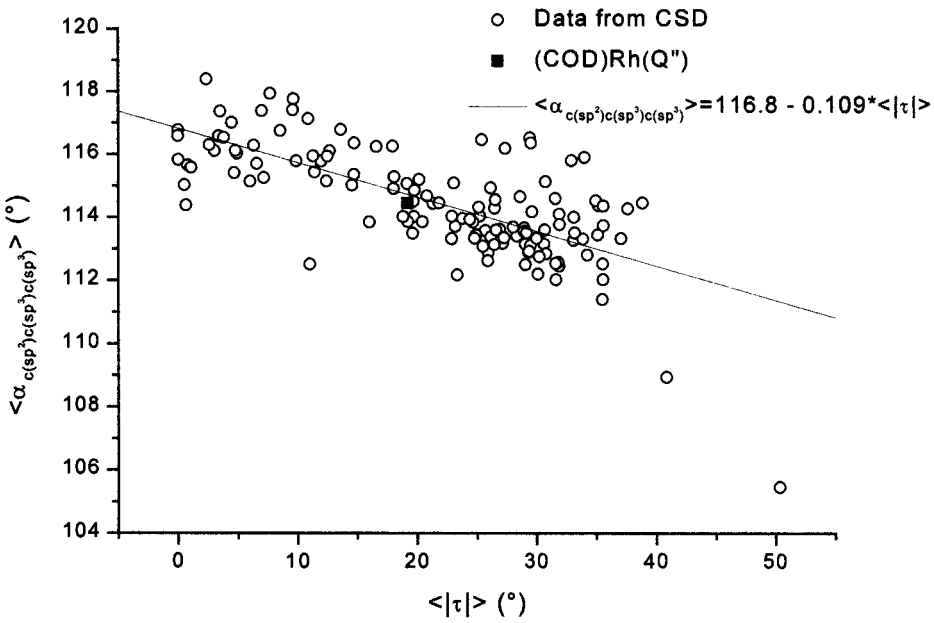

Fig. 9. $\langle C(sp^2)C(sp^3)C(sp^3)\rangle$ angle vs $|\langle\tau\rangle|$ and regression line.

squares refinement of 40 reflections collected in the range $10° \leq 2\theta \leq 25°$. A total of 4538 unique reflections were collected in the range $4° \leq 2\theta \leq 55°$ by a $\omega/2\theta$ scan data collection, of which 3492, with I greater than $3\sigma(I)$, have been used in the successive refinement. A continuous decay ($\approx 3.3\%$) of the standard reflections intensity was observed and a correction was apported; the data were also corrected for Lorentz and polarization effect. The ψ-scan of two reflections (3 0 0, 4 1 − 1) gave a minimum and a maximum transmission factor equal to 0.86 and 1.07; the data were then corrected for the adsorption using a semi-empirical method [13].

The structure was solved finding all the non-hydrogen atoms using the Sir92 program [14]. An isotropic refinement, carried out with the CRYSTALS package [15], gave an R factor equal to 0.091, and the successive anisotropic refinement gave an R equal to 0.040.

The hydrogens were imposed by model with $d = 1.0$ Å and U_{iso} fixed as 30% greater than the bonded atoms. The structure was then anisotropically refined with the hydrogens refined as riding. A final refinement was carried out after an optimization of the weighting scheme [16–18] using an optimized truncated Cheybishev polynomial with coefficients $a_1 = 0.54$, $a_2 = 0.50$, $a_3 = 0.30$.

The R factor was equal to 0.031 at the end of the last refinement cycle, with a maximum r.m.s. shift equal to 0.01.

All the refinements were carried out taking into account the anomalous scattering contributions; the scattering factors and the anomalous contribution were taken from the International Tables [19]. All the calculations were carried out on a personal computer; the programs PARST [20] and PLATON97 [21] have been used for some geometrical calculations.

3. Results and discussion

The proligand 1-phenyl-3-methyl-4-acetylpyrazol-5-one, HQ″, reacts with dinuclear $[Rh(diolefin)Cl]_2$ complexes in the presence of triethyl amine, yielding mononuclear derivatives of formula [Rh(diolefin)(Q″)] (diolefin = 1,5-cyclooctadiene (COD), bicyclo[2.2.1]hepta-2,5-diene (NBD) or 1,5-hexadiene (HEX)) in accordance with Eq. (1):

$$[Rh(diolefin)Cl]_2 + 2HQ'' + 2NEt_3 \xrightarrow{MeOH} \underset{\substack{1:\ diolefin = COD \\ 2:\ diolefin = HEX \\ 3:\ diolefin = NBD}}{2[Rh(diolefin)(Q'')]} + 2Et_3NH^+Cl^- \quad (1)$$

Complex **1** reacts with 1 mol of 4,7-dimethyl-1,10-phenanthroline or 2,2′-bipyridil yielding the ionic complexes **4** and **5** upon displacement of the donor $(Q'')^-$ from the coordination sphere of Rh(I) (Eq. (2)).

$$[Rh(COD)(Q'')] + L \xrightarrow{Et_2O,\ N_2} \underset{\substack{4:\ L = Me_2Phen \\ 5:\ L = Bipy}}{[Rh(COD)(L)](Q'')} \quad (2)$$

This indicates that the existence of the anionic 4-acylpyrazolonate is possible even though compounds of alkali or alkanine earth metals such as $Ba(Q'')_2 \cdot 2H_2O$ or $Na(Q'') \cdot H_2O$ were reported to have negligible electrical conductance value and presumably to be non-ionic [22].

On the other hand the less basic 2-benzoylpyridine reacts with **1** in the same conditions yielding a neutral non-ionic derivative (Eq. (3)):

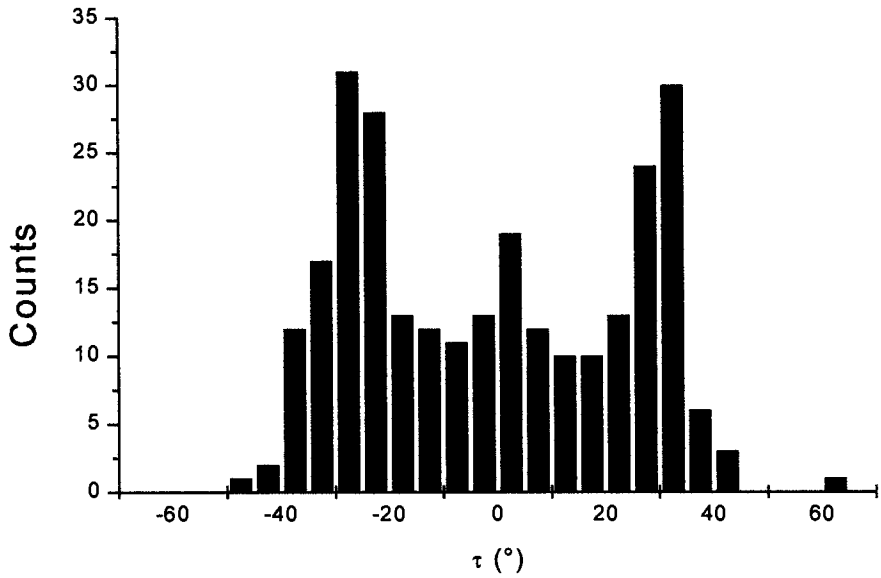

Fig. 10. τ Histogram.

$$[Rh(COD)(Q'')] + Bzpy \xrightarrow{Et_2O,\ N_2} \underset{6}{[Rh(COD)(Bzpy)](Q'')} \quad (3)$$

As with the corresponding β-diketonates [1,2,10,23], triphenylphosphine (PPh_3), triphenylphosphite ($P(OPh)_3$) and 1,2-bis(diphenylphosphino)ethane (DPPE) react with complex **1** in diethyl ether with displacement of the cycloocta-1,5-diene ligand and formation of $[Rh(PPh_3)_2(Q'')]$ (**7**), $[Rh(P(OPh)_3)_2(Q'')]$ (**8**) and $[Rh(DPPE)(Q'')]\cdot H_2O$ (**9**), respectively (Eqs. (4) and (5)).

$$[Rh(COD)(Q'')] + PR_3 \xrightarrow{CH_2Cl_2} \underset{\substack{7:\ R = Ph \\ 8:\ R = OPh}}{[Rh(PR_3)_2(Q'')]} + COD \quad (4)$$

$$[Rh(COD)(Q'')] + DPPE \xrightarrow{CH_2Cl_2/H_2O} \underset{9}{[Rh(DPPE)(Q'')]\cdot H_2O} + COD \quad (5)$$

As can be seen from the reactions carried out with $[Rh(COD)(Q'')]$ π-acceptor ligands displace π-coordinate olefins while mainly σ-donor ligands displace β-diketonate: the entering ligand is able to displace only a chelate of the same nature. The explanation may be that an entering π-acceptor group weakens the metal–olefin bond; on the other hand, mainly σ-donor ligands, by increasing the charge density on the rhodium atom, strengthen the π-olefinic and weaken the metal–oxygen bond, favoring the displacement of β-diketonate.

The addition of HQ″ to light petroleum (40–60°) solution of the dinuclear $[Rh(CO)_2Cl]_2$ produces the derivative $[Rh(CO)_2(HQ'')Cl]$ (**10**) (Eq. (6)).

$$[Rh(CO)_2Cl]_2 + 2HQ'' \xrightarrow{MeOH} \underset{10}{2[Rh(CO)_2(HQ'')Cl]} \quad (6)$$

Instead the addition of HQ″ to the solution obtained by refluxing $RhCl_3\cdot xH_2O$ in dimethylformamide results in the formation of $[Rh(CO)_2(Q'')]$ (Eq. (7)). The latter complex can also be obtained by the reaction of HQ″ with $[Rh(CO)_2Cl]_2$ in presence of triethylamine (Eq. (8)).

$$RhCl_3.xH_2O + 3HQ'' \xrightarrow{HCONMe_2} \underset{11}{[Rh(CO)_2(Q'')]} \quad (7)$$

$$[Rh(CO)_2Cl]_2 + 2HQ'' + 2NEt_3 \xrightarrow{MeOH} \underset{11}{2[Rh(CO)_2(Q'')]} + 2Et_3NH^+Cl^- \quad (8)$$

Complex **11** interacts with one mole of Me_2Phen or Bipy with displacement of only one CO ligand and formation of $[Rh(CO)(Me_2Phen)(Q'')](H_2O)_2$ (**12**) and $[Rh(CO)(Bipy)(Q'')](H_2O)_2$ (**13**), respectively (Eq. (9)).

$$[Rh(CO)_2(Q'')] + N_2 - donor \xrightarrow{Et_2O,\ H_2O} \underset{\substack{12:\ N_2 - donor = Me_2Phen \\ 13:\ N_2 - donor = Bipy}}{[Rh(CO)(N_2 - donor)(Q'')](H_2O)_2} + CO \quad (9)$$

Triphenylphosphine and triphenylarsine are also able to displace one CO group from the coordination sphere of rhodium, giving the complexes $[Rh(PPh_3)_2(CO)(Q'')](H_2O)$ (**14**) and $[Rh(AsPh_3)_2(CO)(Q'')](H_2O)$ (**15**), respectively (Eq. (10)).

$$[Rh(CO)_2(Q'')] + EPh_3 \xrightarrow{CH_2Cl_2,\ H_2O} \underset{\substack{14:\ E = P \\ 15:\ E = As}}{[Rh(EPh_3)_2CO(Q'')](H_2O)} + CO \quad (10)$$

This behavior is different from that described in literature. In fact, it is well known [1,23] that the carbonyl groups in complexes of the type $[Rh(CO)_2(\beta$-diketo-

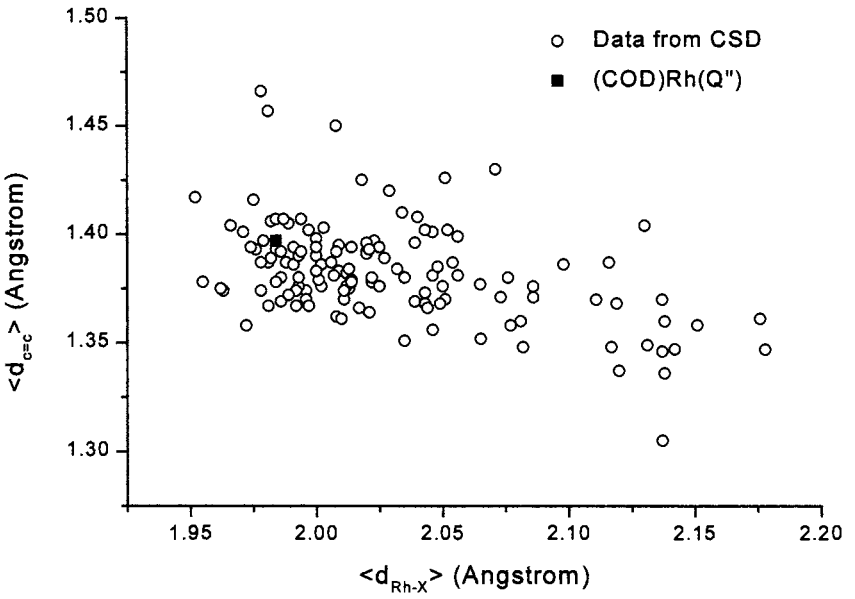

Fig. 11. $\langle d_{Rh-X} \rangle$ vs $\langle d_{C=C} \rangle$.

nate)] can be only partly replaced by ligands such as triphenylphosphine or triphenylarsine, which, however, coordinate rhodium in 1:1 ligand to metal ratio, according to reaction 11:

$$[Rh(CO)_2(\beta - \text{diketonate})] + EPh_3 \rightarrow [Rh(EPh_3)(CO)(\beta - \text{diketonate})] + CO \quad (11)$$

Also in the case of the analogous ligand Q′ (HQ′ = 1-phenyl-3-methyl-4-benzoylpyrazol-5-one) [24] only one EPh_3 group (E = As or P) coordinates the rhodium(I)carbonyl acceptor, yielding complexes of formula $[Rh(EPh_3)(CO)(Q')]$. In our case, an increase of electron density on rhodium resulting from the coordination of 1-phenyl-3-methyl-4-acetyl-pyrazol-5-onate ligand (Q″) which is more basic than (Q′) is likely responsible for the coordination of two π-acceptor EPh_3 groups.

The potentially tetradentate cyclooctatetraene (COT) displaces all the CO ligands from $[Rh(CO)_2(Q'')]$ yielding the derivative [Rh(COT)(Q″)] (**16**) (Eq. (12)).

$$[Rh(CO)_2(Q'')] + COT \xrightarrow{Et_2O,\ H_2O} [Rh(\underset{16}{COT})(Q'')] + 2CO \quad (12)$$

This is a difference with respect to the behavior shown by other β-diketonates [2,24], which always gave dinuclear derivatives of the formula $[Rh_2(COT)(\beta\text{-diketonate})_2]$ when a similar reaction was carried out in excess of $[Rh(CO)_2(\beta\text{-diketonate})]$.

All the complexes **1–16** were identified by elemental analyses, IR spectroscopy, ^{1}H-NMR and, in some cases, by ^{13}C and ^{31}P{^{1}H}-NMR spectroscopy. They are soluble in most common organic solvents. With the exception of compounds **4** and **5**, which show conductance values in acetone and dichloromethane typical of partly ionized complexes likely due to the possibility of ion-pairing effects, all the remaining 4-acetylpyrazolonato complexes **1–3** and **6–16** are non-electrolytes in acetone and dichloromethane. The vaporimetric molecular weight measurements carried out in chloroform only for sufficiently soluble derivatives indicate that complexes **1–3** and **10–16** are mononuclear in solution.

Selected relevant IR and NMR data are reported for all the complexes **1–16** in Section 2.

In the far-IR spectrum of compounds **1–3** it is possible to assign several medium absorptions at ca. 440 cm^{-1} to ν(Rh–O) stretching vibrations, and also a doublet in the 520–490 cm^{-1} region to ν(Rh–C) stretching vibrations [25]. This multiplicity is likely due to asymmetry of the acylpyrazolonato donor and is in accordance with a square pyramidal slightly distorted structure such as found for **1** in the solid state.

According to the bond model of Dewar, Chatt and Duncanson [26,27], the double bond character of the olefin decreases upon coordination. In fact in the IR spectra of **1–3**, we observed a lowering in frequency of ν(C=C) (1460–1480 cm^{-1}) which is coupled to the mode $\delta(CH_2)_{scis}$ and/or $\delta(CH_2)_{bend}$ depending on the olefin [28].

In the ^{1}H-NMR of the cycloocta-1,5-diene- (**1**) and 1,5-hexadiene-(pyrazolonato)rhodium (**2**) complexes the feature of interest is the non-equivalence of the H_a and H_b protons (Fig. 1) due to different CO donor groups of the β-diketonate. On the other hand in the ^{1}H-NMR spectrum ($CDCl_3$ or toluene-d_8) of bicyclo[2.2.1]hepta-2,5-diene derivative **3** the H_a and H_b became equivalent due to a fluxional behavior analogous to that shown by most of the bicyclo[2.2.1]hepta-2,5-diene rhodium(I) derivatives synthesized to date [2,29].

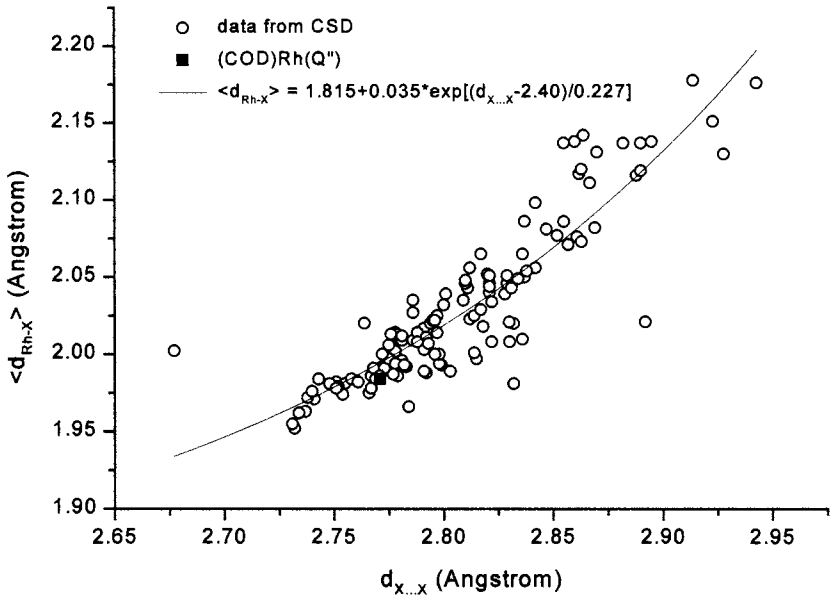

Fig. 12. $d_{X...X}$ vs $\langle d_{Rh-X} \rangle$ with exponential curve fitting.

The temperature dependence of the NMR spectra of complexes **1** and **2** was studied to detect any thermally induced exchange processes. Their solution were heated to 100°C and showed no broadening of the H_a and H_b resonances.

In the ^{1}H and ^{13}C-NMR spectra all the olefin resonances are shifted upfield upon coordination. The $^2J(^{103}Rh-^1H)$ (1–2 Hz) and the $^1J(^{103}Rh-^{13}C)$ (14–15 Hz) coupling constants are of the same order of magnitude as those reported for other β-diketonato rhodium complexes [1,2,24,29].

The similarity between the $^2J(^{103}Rh-^1H_a)$ and $^2J(^{103}Rh-^1H_b)$ and between $^1J(^{103}Rh-^{13}C_a)$ and $^1J(^{103}Rh-^{13}C_b)$ indicates a very similar *trans* influence of each oxygen donor of (Q″).

The shift of the protons and carbons of the pyrazolonate ligand does not show appreciable variation on changing the diolefin. The proton signals are generally shifted downfield upon coordination: the trend and the Δ (Δ is difference in chemical shift between the free donor and the corresponding complex) are analogous to those found in Cu{bis(triorganophosphine)}-(pyrazolonato) [30] and diorganotin(IV)bis(pirazolonato) derivatives [31].

In the case of derivatives **4** and **5**, we hypothesize an ionic structure with the 4-acylpyrazolonate donor out of the coordination sphere of rhodium (Fig. 2). In fact, the ν(Rh–O) stretching vibrations are absent whereas ν(Rh–C) and ν(Rh–N) are clear distinguishable. Analogous complexes have been previously obtained with 2,4-pentanedionato and 1-phenyl-3-methyl-4-benzolypyrazolon-5-ato) ligand [10,24]: the ^{1}H-NMR of these species show the same multiplicity of signals and the same chemical shift found in derivatives **4** and **5**. In addition, in **4** and **5** the ν(C=O) of (Q″) falls at ca. 1615–1630 cm^{-1}; this absorption is analogous to that reported for ionic 1-phenyl-3-methyl-4-acylpyrazolon-5-ato complexes [24].

Our hypothesis is also supported by the fact that in the spectra of **4** and **5** the signals due to H_a and H_b protons of the diolefin are equivalent. According to the structure hypothesized, the four CH and CH_2 groups experience the same metal orbital shielding.

Derivative **6** is likely covalent both in the solid and solution state, where it shows a completely non-electrolyte behavior. The 2-benzoylpyridine ligand acts in the N-monodentate form; in fact, the ν(C=O) is unchanged upon complexation. It has been previously described that $(Q)^-$ ligands can act both in the O-monodentate and O_2-bidentate form, so that at least two different structures (with a four- or a five-coordinate rhodium) are possible; however, in compound **6** the ν(C=O) due to 4-acetylpyrazolonato donor is shifted to lower frequencies in accordance with an involvement of both oxygens of $(Q'')^-$ in the bonding (Fig. 3). The ν(Rh–C) and ν(Rh–O) seem almost unchanged with respect to the spectrum of the starting derivative **1**.

In addition, in the ^{1}H-NMR spectrum of **6** the multiplicity of signals and the pattern of chemical shifts due to olefin and the pyrazolonate moiety are analogous to that found in the spectrum of compound **1**.

Derivatives **7**, **8**, and **9** likely possess a square planar structure in the solid state. In fact, the IR spectra of these compounds are similar to those reported for analogous derivatives, containing acetylacetonate and triorganophosphine donors, for which an almost regu-

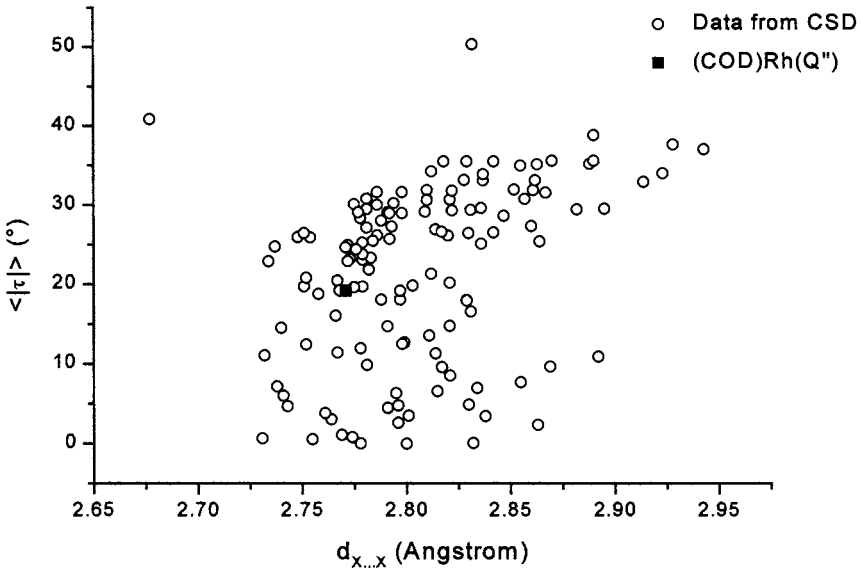

Fig. 13. $d_{X...X}$ vs $|\langle\tau\rangle|$.

lar square planar environment has been found [2,10]. In the 600–200 cm^{-1} region it has been possible to assign with certainty the medium absorption at ca. 400 cm^{-1} to ν(Rh–O) stretching vibrations, whereas a strong broad triplet near 500 cm^{-1} and a group of medium or weak intensity at 270–250 cm^{-1} are likely due to Whiffen's y- and u,x-vibrations, respectively [32].

Compounds **7** and **8** show a very peculiar behavior in solution: in fact, as expected, the ^{1}H-NMR spectra of both complexes exhibit only one set of resonances for each methyl group of Q″. On the other hand, in both ^{31}P-NMR spectra we found two very near double doublets due to very similar phosphorous environments. An analogous pattern has been previously observed in other bis(triorganophosphino)rhodium(I) compounds containing β-diketonates with two different donor arms [2]. The values of the $^1J(^{103}\text{Rh}-^{31}\text{P})$ and $^2J(^{31}\text{P}-^{31}\text{P})$ coupling constants are of the same order of magnitude as those found in square-planar P_2–Rh type derivatives [33,34]. According to literature, the signals are shifted downfield upon coordination; the difference in the ^{31}P(δ) between the complex and the corresponding free donor [35–37] is larger in the complex **8** which contains the triphenylphosphite ligand, a weaker σ-electron donor and a better π-electron acceptor than PPh_3.

The ^{31}P-NMR spectrum of compound **9** is also typical of a tetracoordinate rhodium(I) derivative: the ^{31}P δ is shifted ca. 70 ppm downfield upon coordination, while the value of the Rh–P coupling constant is very close to that of derivative **7** and also to those reported in literature for similar complexes [10,35–38].

Derivative **10** shows an IR spectrum typical of a neutral HQ″ in the keto-enol form. We found a very broad band centered at ca. 2700 cm^{-1} due to the intramolecular H-bond absorption of Q″. Moreover, there are four bands due to ν(CO) stretching vibrations typical of a *cis*-bonded $Rh(CO)_2$ moiety [39] and a strong ν(Rh–Cl) at 307 cm^{-1} [40]. All these data concur to indicate the arrangement in Fig. 4.

In the ^{1}H-NMR spectrum of **10**, the most interesting feature is the strong deshielding of the methyl resonances. Analogous downfield shift was observed in the proton spectra of tin(IV) derivatives containing the donor in the same neutral keto-enol form [41].

The IR spectrum of derivative **11** exhibits four absorptions due to ν(CO) likely attributable to different Rh–OC moieties: in **11** the Q″ ligand is less strongly bonded to rhodium than in **1–3** or in **7–9**: in fact, the ν(C=O) due to acylpyrazolonato falls at 1623 cm^{-1}, indicating a lower donation due to *trans* effect of both the CO groups. In the far-IR region, we observed some absorptions at ca. 510 and 470 cm^{-1} assignable to ν(Rh–C) and others to ν(Rh–O) at ca. 407 and 386 cm^{-1}, similar to those found in the analogous $Rh(CO)_2$(acac) [39].

In the ^{13}C-NMR spectrum of **11**, broad resonances due to coordinate CO groups are found at 182.2 and 184.3 ppm, in accordance with the non-equivalence of the two carbonyls found in the IR spectrum.

Derivatives **12–15** are hydrated and likely possess a square-pyramidal geometry with the β-diketonato acting in the bidentate fashion (Fig. 5): the CO stretching vibrations were found at very low frequencies (ca. 1975 cm^{-1}) typical of pentacoordinate rhodium derivatives containing a CO donor in the apical position [42–45]. In the ^{1}H-NMR spectra of **12** and **13** the methyl resonances due to pyrazolonate show the same chemical shift (ca. 2.40 and 1.90 ppm) of parent compounds **7** and **8** containing two triorganophosphino groups. The ^{31}P-NMR spectrum of **12** is typical of both penta-

and tetracoordinate species: in fact the $^1J(^{103}Rh-^{31}P)$ coupling constant is ca. 130 Hz [10,35–38]. We do not exclude a partial dissociation of the P and/or O-donor in solution.

In the ^{1}H-NMR spectra of **14** and **15**, we found several broad multiplets of signals for each equivalent proton group, likely due to the existence of different isomers in solution.

Complex **16** is likely mononuclear with the cyclooctatetraene ligand coordinated to rhodium in the bidentate form: two different sets of signals were found for the carbons linked to rhodium and also for the corresponding protons. The signals are shifted highfield upon coordination. The not-bonded CH groups exhibit a singlet in the ^{1}H and four singlet in the ^{13}C-NMR spectrum. These signals are shifted slightly upfield with respect to the same signals in the spectrum of the non-coordinated olefins [46,47].

*3.1. Description of crystal structure of [Rh(COD)(Q″)] (**1**)*

3.1.1. Rhodium coordination sphere

The adduct (Fig. 6) presents a slightly distorted square planar coordination which is best evident from the rhodium coordination bond angles (see Table 3) and from the slightly non-planar arrangement of the Rh, the oxygens atom of Q″ and the double bond centroids of 1,5-cyclooctadiene. This distortion with respect to the ideal geometry seems to be a common feature of almost all of the (COD)Rh adducts with 1,3-diketo ligands [2,10,48–56]. The mean value of X–Rh–X (X's are the centroids of the double bonds in COD) and O–Rh–O for 15 similar independent fragments are in fact 88.611 and 89.853°, not far from the values found in our structure. The distances for Rh–C and Rh–O agree with those reported for similar structures. A small but significant difference is observed between the two Rh–O distances, probably due to the unequal sharing of the negative charge onto the different oxygens and possibly related, through a sort of *trans* effect, to the small differences observed for the two Rh–X and four Rh–C distances.

The adduct does not show any Rh···Rh interaction below 4.0 Å, as observed for other similar square planar adducts [57–59], but it is interesting anyway to note the presence of a relatively weak intermolecular contact at 3.665(5) Å, 0.3 Å less than the sum of the Van der Waals radii [60] between Rh and C(11).

This Rh–C(sp^2) weak interaction seems to be not exclusive to this structure: a closer inspection of several other (COD)Rh square planar adducts with O-donor ligands, indicates the presence of non-bonding contacts. We found that for 17 different structures [2,49–52,55–57,59,61–68] a similar kind of interaction was present, and the spatial distribution of the weakly interacting atoms led us to define a preferred way of interaction. This is evident by considering the angle ϕ between the interacting atom, the Rh and the normal of the coordination plane, and the angle ψ between the interacting atom, the Rh and the centroid of the four C(sp^2) atoms in COD. Fig. 7 shows that for the structures investigated (34 different Rh···Y interactions) these angular values are all clustered around well defined values for both ψ and ϕ: $99.5° \leq \psi \leq 128.4°$ and $15.3° \leq \phi \leq 40.6°$ (atoms approaching Rh from 'above') or $143.6° \leq \phi \leq 162.1°$ (atoms approaching Rh from 'below'). We find for (COD)Rh(Q″) $\phi = 18.5°$ and $\psi = 107.9°$. The distribution of ψ and ϕ is independent from the chemical nature of the atoms, and from the inter or intramolecular nature of the interaction (we considered only intramolecular interactions due to atoms far at least four bonds from Rh). As a general trend (as expected anyway) C(sp^3) have the longest non-bonding distance (the mean difference Δ with respect to the Van der Waals radii is 0.08 Å for the intermolecular contacts) with respect e.g. C(sp^3), which have a Δ equal to 0.19 Å for the same conditions, or alogens (only one structure reported with $\Delta = 0.23$ Å). Intramolecular contacts tend to be shorter with respect to the intermolecular ones, probably due to the intrinsic geometrical constraints imposed. We are not able, due to the generality of the phenomena, to give a precise explanation for these interactions.

Most probably the plot of Fig. 7 just maps, in terms of the chosen angles, which region around the COD–Rh–O_2 presents the less repulsive potential, in agreement with the qualitative observation of the bulkiness of COD, and maybe defines a preferential way of approach to Rh itself. This statement is reinforced from the fact that a more general analysis, irrespective of the nature of the ligand, gave us the same general trend (Fig. 8).

A possible path to pentacoordination, as suggested for different tetracoordinated adducts [69], cannot be excluded, but we do not observe any correlation between the out-of-plane shift of the Rh atom and the non-bonding distances. This is probably due to the geometrical constraints imposed by the bidentate COD in this kind of adduct and even due to weakness of the interaction.

3.1.2. COD geometry

As already indicated in several different adducts of this type, COD ligand shows a twisted boat conformation in the Rh(COD)(Q″) adduct structure. The skewness of COD can be assessed considering several different descriptors: the puckering parameters [70–72], the C(sp^2)C(sp^3)C(sp^3)C(sp^2) torsion angles (τ hereafter), or the ring-crossed C··· (non-bonding contacts) [49]. All of these parameters can be used in order to describe the COD conformation, the puckering parameters giving probably the most complete description, and

the torsion angles giving the most pictorial. An interesting feature emerging from the conformational analysis of COD, in square planar rhodium complexes, is the conformational rearrangement which COD undertakes upon complexation. It is well established that the free COD, still in a twisted-boat conformation, presents a greater skewness with respect to the COD as a ligand in adducts. Hagen et al. [73] reported a value for τ of 63.8° for the free COD in gas-phase (C_2 symmetry), and two independent crystallographic structures of differently substituted dibromoCOD [74,75] give the values of 65 and 63.8°.

The situation is rather different when we consider the COD as a ligand as showed by a simple statistical analysis through the Cambridge Crystallographic Database (CSD hereafter, version 5.14, October 1997) [76] on the (COD)Rh square planar adducts. The analysis of 134 independent fragments (104 different Ref. codes) with a reliable geometry, which have *R* factors less than 10%, no structural disorder of polymeric structures (but no restraints were imposed on standard deviations), showed that $C(sp^2)C(sp^3)C(sp^3)C(sp^2)$ torsion angles are distributed between -49 and 60°, with three maxima for τ at $\sim \pm 28$ and $\sim 0°$, and most of the data are in the range -40 to 40° (we found -20.7 and $-17.7°$ for Rh(COD)(Q″)). This behavior of the torsion angle distribution is easily interpreted as a result of the two major forces acting on the COD conformations: the intramolecular steric repulsion in COD, and the geometrical requirements for a π-bond between COD and Rh, according to the Chatt–Dewar–Duncanson model [17,18]. The intramolecular steric repulsion obviously tends to distort the molecule from the more symmetric boat conformation, an extreme case in this sense is that of 1,2,5,6-tetrakis(trimethylsilylethynyl)COD [77] which assumes a twist-chair conformation in order to minimize the interatomic repulsions between the four bulky trimethylsilylethynyl groups. On the other side, an ideal π-bond would require the olefinic fragments symmetrically arranged around the metal atom, due to the symmetry of its d-orbitals. Such a restraint would impose a more symmetrical C_{2v} conformation on COD, which is in practice seldom observed because of the steric relief of the structure, mainly on the bond angles (see Fig. 9) and less on the bond distances. The distribution reported in Fig. 10 is therefore indicative of the energy balance between the two opposite forces acting on the COD conformation: a gain in bonding energy is possible only with an increase of the strain, and then in energy, in COD structure. Many of the structures found in the CSD have $|\langle\tau\rangle|$ between 20 and 35°, with a maximum at around 28°, whereas several others have a torsional angle nearer to 0°, indicating a dominance of the bonding effects over interatomic repulsion and angle strains.

The plot of $\langle d_{X-Rh}\rangle$ versus $\langle d_{C=C}\rangle$ shows a not unexpected trend (see Fig. 11), with X–Rh distance decreasing as the $\langle C{=}C\rangle$ increase (the same trend is observed, even if less clear, for $d_{X\ldots X}$ vs $\langle d_{C=C}\rangle$). This result is in agreement with the expected effects of the donation/backdonation interplay between the olefin and the metal atom, and of the lengthening of the double bonds for stronger Rh–olefin interactions. The $d_{X\ldots X}$ distance versus $\langle d_{X-Rh}\rangle$ shows a good correlation (Fig. 12) of these two parameters. The data have been best fitted by using an exponential function, relating force of the olefin–Rh interaction, as represented by the $\langle d_{X-Rh}\rangle$, with the bite angle requirements ($d_{X\ldots X}$) for such a kind of adduct.

Finally a check for possible relationship between $\langle|\tau|\rangle$ and the $d_{X\ldots X}$ distance was done (Fig. 13), but a clear correlation was not found. The only observation we can make is the almost random distribution of $d_{X\ldots X}$ for $0° < |\langle\tau\rangle| < 20°$, and a broad linear correlation for values of the mean absolute torsion angle greater than 20°. A possible explanation for this behavior relies on the plot of Fig. 10, which shows that for values of $\langle|\tau|\rangle$ less than 20° the internal bond angles in COD are substantially strained. The COD structural rearrangement, when the torsion angle falls below 20° is therefore not purely torsional, but even due to a greater strain of the structure. For torsion angles greater than 20° the COD rearrangement seems to be due mostly to a torsion around the $C(sp^3)$–$C(sp^3)$ bonds, explaining the broad correlation between $|\langle\tau\rangle|$ and $d_{X\ldots X}$ observed for such values of the absolute torsion angles.

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