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Syntheses, Structures, and Reactivity of New Pentamethylcyclopentadienyl-Rhodium(III) and -iridium(III) 4-Acyl-5-Pyrazolonate Complexes

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New [Cp*M(Q)Cl] complexes (M = Rh or Ir, Cp* = pentamethylcyclopentadienyl, HQ = 1-phenyl-3-methyl-4R(C=O)-pyrazol-5-one in general, in detail HQ^{Me}, R = CH_3; HQ^{Et}, R = CH_2CH_3; HQ^{Piv}, R = CH_2–$C(CH_3)_3$; HQ^{Bn}, R = CH_2–(C_6H_5); HQ^{S}, R = CH–(C_6H_5)$_2$) have been synthesized from the reaction of [Cp*MCl_2]$_2$ with the sodium salt, NaQ, of the appropriate HQ proligand. Crystal structure determinations for a representative selection of these [Cp*M(Q)Cl] compounds show a pseudo-octahedral metal environment with the Q ligand bonded in the *O*,*O*′-chelating form. In each case, two enantiomers (S_M) and (R_M) arise, differing only in the metal chirality. The reaction of [Cp*Rh(Q^{Bn})Cl] with $MgCH_3Br$ produces only halide exchange with the formation of [Cp*Rh(Q^{Bn})Br]. The [Cp*Rh(Q)Cl] complexes react with PPh_3 in dichloromethane yielding the adducts Cp*Rh(Q)Cl/PPh_3 (1:1) which exist in solution in two different isomeric forms. The interaction of [Cp*Rh(Q^{Me})Cl] with $AgNO_3$ in MeCN allows generation of [Cp*Rh(Q^{Me})(MeCN)]NO_3·$3H_2O$, whereas the reaction of [Cp*Rh(Q^{Me})Cl] with $AgClO_4$ in the same solvent yields both [Cp*Rh(Q^{Me})(H_2O)]ClO_4 and [Cp*Rh(Cl)(H_2O)$_2$]ClO_4; the H_2O molecules derive from the not-rigorously anhydrous solvents or silver salts.

Introduction

The chemistry of Rh(I) β-diketonates has been extensively investigated and a number of complexes of the form [Rh(β-diketonate)(L)$_2$] (where L = alkene, CO, P(aryl)$_3$, and P(alkyl)$_3$) have found applications in a variety of reactions including, for example, alkene hydroboration,[1] CO hydrogenation,[2] and hydroformylation.[3] [Rh(acac)(CO)$_2$] is a known catalytic system in the presence of tertiary phosphines for hydroformylation, hydrogenation, and isomerization reactions of olefins.[4] By contrast, only a limited number of Rh(III) β-diketonate complexes, containing the pentamethylcyclopentadienyl ligand (Cp*), have been synthesized, and of these, only the dinuclear cationic compound [Rh_2(η^5-Cp*)$_2$(acac)$_2$][BF_4]$_2$ has been structurally characterized.[5] Optically active half-sandwich metallocene complexes of rhodium(III) and iridium(III) have recently attracted considerable attention because of their ability to act as active stereospecific catalysts.[6] Other Cp*M compounds, such as the cationic iridium complex, [Cp*IrMe(PMe_3)($ClCH_2Cl$)]$^+$[BAr_4]$^-$ (Ar = aryl), exhibit highly interesting reactivity in the C−H activation reactions of various functionalized substrates at ambient temperature.[7] A number of complexes containing N^N[8] and N^O[9] bidentate ligands have been described and employed for enantioselective hydrogen transfer reactions.[10] Most of the organometallic chiral-at-metal compounds are half-sandwich complexes containing a Cp*, a halide ligand, and an unsymmetrical

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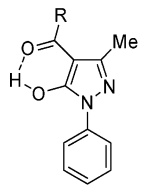

R	HQ
CH_3	HQ^{Me}
CH_2CH_3	HQ^{Et}
$CH_2C(CH_3)_3$	HQ^{Piv}
$CH_2C_6H_5$	HQ^{Bn}
$CH(C_6H_5)_2$	HQ^{CHPh2}

Figure 1. 4-Acyl-5-pyrazolone (HQ) pro-ligands employed in this work.

anionic chelate ligand with a chiral carbon atom. This type of system has been thoroughly investigated and has been reported to yield two diastereomers differing in the metal configuration. As the configuration at the metal is often labile, epimerization processes have been observed in solution.[11] Analogous chemistry with related O,O-donors has received less attention, one reason being that Rh−O and Ir−O linkages are considered to be characteristically weak because of a mismatch of the hard basic ligands with the soft late-transition-metal centers.

4-Acyl-5-pyrazolones (HQ) (Figure 1) have often been described as analogues of β-diketone ligands and employed in their anionic chelating σ-donor forms in complexes of different metal acceptors.[12] They can be easily functionalized in the acyl fragment, and their complexes are generally more stable than the corresponding β-diketonates.

We have previously reported that the acylpyrazolonates are suitable ligands for the synthesis of stable Rh(I) metal complexes, which have been widely investigated by X-ray crystallography and NMR spectroscopy.[13] As an extension of the previous investigations on compounds that contain the $\{(\eta^5\text{-Cp*})M\}$ fragments (M = Rh, Ir),[14] we report, here, a systematic study of the reactions of $[\{(\eta^5\text{-Cp*})MCl\}_2(\mu\text{-}Cl)_2]$ (M = Rh, Ir) compounds with HQ ligands (Figure 1). The reactivities of some of these derivatives toward Grignard reagents, PPh_3 and AgX (X = NO_3 or ClO_4) are also included.

Experimental Section

Materials and Methods. All chemicals and reagents were of reagent grade quality and were used as received without further purification. All solvents were distilled prior to use. Toluene and light petroleum (40−60 °C) were dried by refluxing over freshly cut sodium. Methanol was dried over CaO. Dichloromethane was freshly distilled from CaH_2. Other solvents were dried and purified by standard procedures. The samples were dried in vacuo to constant weight (20 °C, ~ 0.1 Torr). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNSO-elemental analyzer. IR spectra in the range of 4000−150 cm^{-1} were recorded with a Perkin-Elmer System 2000 FT-IR instrument. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a VXR-300 Varian Spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C, and 121.4 MHz for ^{31}P). Melting points are uncorrected and were measured on an SMP3 Stuart scientific instrument and on a capillary apparatus. 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) for electrospray-ionization mass spectrometry (ESI-MS) were prepared using reagent-grade acetone or acetonitrile. For the ESI-MS data, masses and intensities were compared to those calculated using the IsoPro Isotopic Abundance Simulator Version 2.1.[15]

Syntheses of Complexes. [Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-acetylpyrazolon-5-ato)rhodium(III)], [Cp*Rh(Q^{Me})Cl] (1). A toluene solution (10 mL) containing $[Cp^*RhCl_2]_2$ (0.200 g, 0.32 mmol) and NaQ^{Me} (0.157 g, 0.64 mmol) was stirred overnight under N_2 at room temperature to give a red-orange precipitate, which was filtered off and washed with 5 mL of toluene. The orange-brown residue was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C) and shown to be compound **1** (0.190 g, 0.38 mmol, 60% yield). mp: 255−258 °C. Anal. Calcd for $C_{22}H_{26}ClN_2O_2Rh$: C, 54.06; H, 5.36; N, 5.73. Found: C, 53.73; H, 5.45; N, 5.45. IR (Nujol, cm^{-1}): 1606s, 1590s, 1575s, 1539s, ν(C···C, C···N), 514m, 456s, 445sh, 398m, 301w, 259s ν(Rh−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.67 (s, 15H, CH_{3Cp^*}), 2.35 (s, 3H, 3-CH_3), 2.44 (s, 3H, COCH_3), 7.15−7.40m, 7.97d (5H, N−C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.96 (s, CH_{3Cp^*}), 17.65 (s, 3-CH_3), 28.22 (COCH_3), 92.30, 92.49 (d, C_{Cp^*}, $J(^{103}Rh-^{13}C)$ = 9.5 Hz), 105.80 (s, *C4*), 120.88, 124.94, 128.59, 139.18 (s, N−C_6H_5 of Q), 148.90 (s, *C3*), 162.57 (s, *C5*), 190.26 (s, *C*O).

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-acetylpyrazolon-5-ato)iridium(III)], [Cp*Ir(Q^{Me})Cl] (2). A toluene solution (10 mL) containing $[Cp^*IrCl_2]_2$ (0.201 g, 0.25 mmol) and NaQ^{Me} (0.132 g, 0.55 mmol) was stirred overnight under N_2 at room temperature to give an orange precipitate, which was filtered off and washed with 5 mL of toluene. The residue was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C) and shown to be compound **2** (0.161 g, 0.28 mmol, 55% yield). mp: 278−280 °C. Anal. Calcd for $C_{22}H_{26}ClIrN_2O_2$: C, 45.71; H, 4.53; N, 4.85. Found: C, 45.24; H, 4.85; N, 4.83. IR (Nujol, cm^{-1}): 1602s, 1590s, 1575s, 1539s, ν(C···C, C···N), 513w, 466m, 455w, 270s ν(Ir−Cl). ^1H NMR ($CDCl_3$, 293 K): δ 1.64 (s, 15H, CH_{3Cp^*}), 2.37 (s, 3H, 3-CH_3), 2.41 (s, 3H, COCH_3), 7.17−7.43m, 7.85d, 7.95d (5H, N−C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.13 (s, CH_{3Cp^*}), 17.47 (s, 3-CH_3), 27.68 (COCH_3), 83.57 (s, C_{Cp^*}), 106.61 (s, *C4*), 120.90, 125.19, 128.67, 138.98 (s, N−C_6H_5), 148.94 (s, *C3*), 161. 16 (s, *C5*), 189.22 (s, *C*O).

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-propionylpyrazolon-5-ato)rhodium(III)], [Cp*Rh(Q^{Et})Cl] (3). Orange compound **3** (0.090 g, 0.17 mmol, 64% yield) was prepared following a procedure similar to that reported for **1** using

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$[Cp^*RhCl_2]_2$ and NaQ^{Et} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp 217−219 °C. Anal. Calcd for $C_{23}H_{28}ClN_2O_2Rh$: C, 54.94; H, 5.61; N, 5.57. Found: C, 54.90; H, 5.84; N, 5.20. IR (Nujol, cm^{-1}): 1605s, 1589s, 1576s, 1534s, ν(C···C, C···N), 461m, 270s ν(Rh−Cl).^{1}H NMR ($CDCl_3$, 293K): δ 1.24 (t, 3H, CH_2CH_3), 1.67 (s, 15H, CH_{3Cp^*}), 2.35 (s, 3H, 3-CH_3), 2.59 (dd, ^2J(A−X) = 7.32 Hz, $\Delta\delta\nu/J$ = 2.04), 2.66 (dd, ^2J(A−X) = 7.32 Hz, $\Delta\delta\nu/J$ = 1.93), 2.80 (dd, ^2J(A−X) = 7.32 Hz, $\Delta\delta\nu/J$ = 2.00), 2.88 (dd, ^2J(A−X) = 7.32 Hz, $\Delta\delta\nu/J$ = 2.00), 7.12−7.20m, 7.32−7.40m, 7.95d (5H, N−C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.92 (s, CH_{3Cp^*}), 9.84 (s, CH_2CH_3), 17.76 (s, 3-CH_3), 32.14 (s, CH_2CH_3), 92.19, 92.38 (d, C_{Cp^*}, J(^{103}Rh−^{13}C) = 9.4 Hz), 105.80 (s, *C4*), 120.88, 124.86, 128.56, 139.26 (s, N−C_6H_5), 148.44 (s, *C3*), 162.80 (s, *C5*), 193.80 (s, *C*O).

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(3,3-dimethylbutanoyl)pyrazolon-5-ato)rhodium(III)], [Cp*Rh(Q^{Piv})Cl] (4). Dark yellow compound **4** (0.092 g, 0.17 mmol, 63% yield) was prepared following a procedure similar to that reported for **1** using $[Cp^*RhCl_2]_2$ and NaQ^{Piv} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp: 235−238 °C. Anal. Calcd for $C_{26}H_{34}ClN_2O_2Rh$: C, 57.31; H, 6.29; N, 5.14. Found: C, 56.93; H, 6.31; N, 5.03. IR (Nujol, cm^{-1}): 1606s, 1591s, 1578s, 1537s ν(C···C, C···N), 510m, 472s, 266s ν(Rh−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.12 (s, 9H, $CH_2C(CH_3)_3$), 1.71 (s, 15H, CH_{3Cp^*}), 2.39 (s, 3H, 3-CH_3), 2.49, 2.55, 2.68, 2.74 (q, $2H_{gem}$, $CH_2C(CH_3)_3$, ^2J(A−X) = 13.18 Hz, $\Delta\delta\nu/J$ = 2.88), 7.16−7.41m, 7.95d (5H, N−C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.90 (s, CH_{3Cp^*}), 18.25 (s, 3-CH_3), 30.43 (s, $CH_2C(CH_3)_3$), 32.55 (s, $CH_2C(CH_3)_3$), 50.09 (s, $CH_2C(CH_3)_3$), 91.99, 92.13 (d, C_{Cp^*}, J(^{103}Rh−^{13}C) = 9.2 Hz), 120.73, 124.66, 128.28, 138.99 (s, N−C_6H_5), 148.19 (s, *C3*), 192.84 (s, *C*O), *C4* and *C5* not observed.

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(3,3-dimethylbutanoyl)pyrazolon-5-ato)iridium(III)], [Cp*Ir(Q^{Piv})Cl] (5). Yellow compound **5** (0.105 g, 0.16 mmol, 58% yield) was prepared following a procedure similar to that reported for **3** using $[IrCp^*Cl_2]_2$ and NaQ^{Piv} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp: 160−162 °C. Anal. Calcd for $C_{26}H_{34}ClIrN_2O_2$: C, 49.24; H, 5.40; N, 4.42. Found: C, 49.07; H, 5.35; N, 4.20. IR (Nujol, cm^{-1}): 1603s, 1591s, 1578s, 1537m ν(C···C, C···N), 510w, 476w, 279s ν(Ir−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.11 (s, 9H, $CH_2C(CH_3)_3$), 1.66 (s, 15H, CH_{3Cp^*}), 2.41 (s, 3H, 3-CH_3), 2.46, 2.53, 2.67, 2.74 (q, $2H_{gem}$, $CH_2C(CH_3)_3$, ^2J(A−X) = 13.19 Hz, $\Delta\delta\nu/J$ = 3.20), 7.15−7.41m, 7.91d (5H, N−C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 9.32 (s, CH_{3Cp^*}), 18.33 (s, 3-CH_3), 30.63 (s, $CH_2C(CH_3)_3$), 32.65 (s, $CH_2C(CH_3)_3$), 49.96 (s, $CH_2C(CH_3)_3$), 83.48 (s, C_{Cp^*}), 108.13 (s, *C4*), 120.94, 125.14, 128.62, 138.04 (s, N−C_6H_5). 148.52 (s, *C3*), 161. 86 (s, *C5*), 192.24 (s, *C*O).

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(2-phenylacetyl)pyrazolon-5-ato)rhodium(III)], [Cp*Rh(Q^{Bn})Cl] (6). Brown-red compound **6** (0.110 g, 0.19 mmol, 59% yield) was prepared following a procedure similar to that reported for **1** using $[Cp^*RhCl_2]_2$ and NaQ^{Bn} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp: 230−233 °C. Anal. Calcd for $C_{28}H_{30}ClN_2O_2Rh$: C, 59.53; H, 5.35; N, 4.96. Found: C, 59.53; H, 5.61; N, 4.95. IR (Nujol, cm^{-1}): 1607s, 1590s, 1577s, 1531s ν(C···C, C···N), 512w, 456s, 264s ν(Rh−Cl). ^{1}H NMR ($CDCl_3$, 293K): δ 1.48 (s, 15H, CH_{3Cp^*}), 2.43 (s, 3H, 3-CH_3), 3.79, 3.87, 4.23, 4.31 (q, $2H_{gem}$, $COCH_2C_6H_5$, ^2J(A−X) = 15.40 Hz, $\Delta\delta\nu/J$ = 5.81), 7.12−7.40, 7.94−7.99 (m, 10H, Ph). ^{1}H NMR ($CDCl_3$, 318 K): δ 1.48 (s, 15H, CH_{3Cp^*}), 2.41 (s, 3H, 3-CH_3), 3.81, 3.86, 4.22, 4.26 (q, $2H_{gem}$, $CH_2C_6H_5$, ^2J(A−X) = 14.90 Hz, $\Delta\delta\nu/J$ = 8.18), 7.12−7.40m, 7.96d (10H, N−C_6H_5 and $COCH_2C_6H_5$). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.65 (s, CH_{3Cp^*}), 17.74 (s, 3-CH_3), 44.86 (s, $CH_2C_6H_5$), 92.25, 92.44 (d, C_{Cp^*}, J(^{103}Rh−^{13}C) = 9.5 Hz), 120.86, 124.98, 126.80, 128.54, 128.58, 129.83, 136.38, 139.14 (s, N−C_6H_5 and $COCH_2C_6H_5$), 148.34 (s, *C3*), 189.98 (s, *C*O), C_4 and C_5 not observed.

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(2-phenylacetyl)pyrazolon-5-ato)iridium(III)], [Cp*Ir(Q^{Bn})Cl] (7). Dark-yellow compound **7** (0.075 g, 0.15 mmol, 55% yield) was prepared following a procedure similar to that reported for **3** using $[Cp^*IrCl_2]_2$ and NaQ^{Bn} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp: 180−185 °C. Anal. Calcd for $C_{28}H_{30}ClIrN_2O_2$: C, 51.41; H, 4.62; N, 4.28. Found: C, 51.20; H, 4.70; N, 4.10. IR (Nujol, cm^{-1}): 1605s, 1590m, 1577s, 1532m ν(C···C, C···N), 512m, 462w, 273s ν(Ir−Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.47 (s, 15H, CH_{3Cp^*}), 2.44 (s, 3H, 3-CH_3), 3.77, 3.84, 4.22, 4.30 (q, $2H_{gem}$, $COCH_2C_6H_5$, ^2J(A−X) = 15.20 Hz, $\Delta\delta\nu/J$ = 6.02), 7.18−7.41m, 7.93d (10H, N−C_6H_5 and $COCH_2C_6H_5$). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.88 (s, CH_{3Cp^*}), 17.58 (s, 3-CH_3), 44.57 (s, CH_2(Ph)), 83.56 (s, C_{Cp^*}), 106.66 (s, *C4*), 120.86, 125.23, 126.89, 128.60, 128.67, 129.67, 135.85, 138.91 (s, N−C_6H_5 and $COCH_2C_6H_5$), 148.41 (s, *C3*), 161.61 (s, *C5*), 188.83 (s, *C*O).

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(2,2-diphenylacetyl)pyrazolon-5-ato)rhodium(III)], [Cp*Rh(Q^{S})Cl] (8). Orange compound **8** (0.101 g, 0.16 mmol, 57% yield) was prepared following a procedure similar to that reported for **1** using $[Cp^*RhCl_2]_2$ and NaQ^{S} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp: 226−228 °C. Anal. Calcd for $C_{34}H_{34}ClN_2O_2Rh$: C, 63.71; H, 5.35; N, 4.37. Found: C, 63.90; H, 5.45; N, 4.20. IR (Nujol, cm^{-1}): 1607s, 1591s, 1579s, 1531m, ν(C···C, C···N), 459m, 278s ν(Rh−Cl).^{1}H NMR ($CDCl_3$, 293 K): δ 1.43 (s, 15H, CH_{3Cp^*}), 2.29 (s, 3H, 3-CH_3), 5.72 (s, 1H, $CH(C_6H_5)_2$), 7.10−7.41m, 7.93d (15H, N−C_6H_5 and $CH_2(C_6H_5)_2$). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.62 (s, CH_{3Cp^*}), 17.57 (s, 3-CH_3), 58.26 (s, $CH(C_6H_5)_2$), 92.30 (d, C_{Cp^*}, J(^{103}Rh−^{13}C) = 9.4 Hz), 120.93, 124.98, 126.8, 127.17, 128.22, 128.56, 129.40, 129.60, 130.12, 138.87 (s, N−C_6H_5 and $CH_2(C_6H_5)_2$), 148.39 (s, *C3*), 161.80 (s, *C5*), 189.85 (s, *C*O), *C4* not observed.

[Chloro(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(2,2-diphenylacetyl)pyrazolon-5-ato)iridium(III)], [Cp*Ir(Q^{S})Cl] (9). Orange compound **9** (0.120 g, 0.16 mmol, 55% yield) was prepared following a procedure similar to that reported for **3** using $[IrCp^*Cl_2]_2$ and NaQ^{CH-Ph2} and was recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C). mp: 151−154 °C. Anal. Calcd for $C_{34}H_{34}ClIrN_2O_2$: C, 55.92; H, 4.69; N, 3.84. Found: C, 55.88; H, 4.84; N, 3.83. IR (Nujol, cm^{-1}): 1605s, 1591s, 1578s, 1532m, ν(C···C, C···N), 509w, 465w, 280s ν(Ir−Cl).^{1}H NMR ($CDCl_3$, 293 K): δ 1.39 (s, 15H, CH_{3Cp^*}), 2.31 (s, 3H, 3-CH_3), 5.73 (s, 1H, $CH(C_6H_5)_2$), 7.10−7.55m, 7.95d (15H, N−C_6H_5 and $CH_2(C_6H_5)_2$). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.81 (s, CH_{3Cp^*}), 17.42 (s, 3-CH_3), 57.92 (s, $CH(Ph)_2$), 83.60 (s, C_{Cp^*}), 120.92, 125.21, 126.94, 127.26, 127.68, 128.26, 128.64, 129.07, 129.64, 130.12, 138.46, 141.23 (s, N−C_6H_5 and $CH_2(C_6H_5)_2$), 148.08 (s, *C3*), 189.32 (s, *C*O), *C4* not observed.

[(Pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-acetylpyrazolon-5-ato)(acetonitrile)rhodium(III)]nitrate Trihydrate, [Cp*Rh(Q^{Me})(MeCN)]NO_3·$3H_2O$ (10). A CH_3CN solution (10 mL) containing [Cp*Rh(Q^{Me})Cl] (0.120 g, 0.24 mmol) and $AgNO_3$ (0.048 g, 0.28 mmol) under N_2 at room temperature was stirred overnight. After 48 h, a colorless precipitate formed, which was filtered of and shown to be AgCl. The clear yellow solution obtained was evaporated under vacuum; the yellow residue was washed with light petroleum (40−60 °C) and was identified as **10**. mp: 200−201 °C. Anal. Calcd for $C_{24}H_{35}N_4O_8Rh$: C, 47.22; H,

5.78; N, 9.18. Found: C, 46.90; H, 5.81; N, 9.22. IR (Nujol, cm^{-1}): 1604s, 1589s, 1574s, 1519s, ν(C⋯C, C⋯N), 1450sh, 1277sbr ν-(NO_3), 514m, 456m.^{1}H NMR ($CDCl_3$, 293 K): δ 1.6 (s br, 21H, CH_{3Cp^*} + H_2O), 2.0 (s br, 3H, MeCN), 2.32 (s, 3H, 3-CH_3), 2.41 (s, 3H, COCH_3), 7.10−7.40, 7.92−7.96 (m, 5H, N-*Ph*). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.83 (s, CH_{3Cp^*}), 17.48 (s, 3-CH_3), 27.83 (CO*C*H_3), 92.47, 92.61 (d, C_{Cp^*}, J(^{103}Rh−^{13}C) = 10.5 Hz), 120.77 (s, *C2* and C6$_{Ph-Q}$), 125.19 (s, *C4*$_{Ph-Q}$), 128.69 (s, *C3* and *C5*$_{Ph-Q}$), 138.92 (s, *C1*$_{Ph-Q}$), 148.84 (s, *C5*$_{Py}$).

[(Pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-acetylpyrazolon-5-ato)(aqua)rhodium(III)]perchlorate, [Cp*Rh(Q^{Me})(H$_2$O)]ClO$_4$ (11). Compound **11** was prepared following a procedure similar to that reported for **10** using [Cp*Rh(Q^{Me})Cl] and $AgClO_4$. After 48 h, a pale-yellow precipitate formed, which was removed by filtration and shown to be AgCl and AgQ. The clear red-yellow solution obtained was evaporated under vacuum; the red-yellow residue was washed with light petroleum (40−60 °C) and was identified as a mixture of **11** and **[Cp*Rh(Cl)(H$_2$O)$_2$]ClO$_4$**. Recrystallization from CH_3CN/Et_2O yields microcrystalline **11** (0.200 g, 0.35 mmol, 70% yield). mp: 230−233 °C. Anal. Calcd for $C_{22}H_{28}ClN_2O_7Rh$: C, 46.29; H, 4.94; N, 4.91. Found: C, 45.87; H, 5.10; N, 4.85. IR (Nujol, cm^{-1}): 3400 br, 1606s, 1589sh, 1577s, 1530m, ν(C⋯C, C⋯N), 1080sbr ν(ClO_4), 509w, 463m.^{1}H NMR ($(CD_3)_2CO$), 293K): δ 1.73(s, 15H, CH_{3Cp^*}), 2.18 (s, 2H, H_2O), 2.37 (s, 3H, 3-CH_3), 2.56 (s, 3H, COCH_3), 7.20−7.37m, 7.42−7.58m, 7.98d (5H, N-*Ph*). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.39 (s, CH_{3Cp^*}), 16.92 (s, 3-CH_3), 27.67 (CO*C*H_3), 94.43, 94.57(d, C_{Cp^*}, J(^{103}Rh−^{13}C) = 10.5 Hz), 105.47 (s, *C4*), 120.98, 125.93, 129.08, 138.79 (s, N−C_6H_5 of Q), 149.59 (s, *C5*$_{Py}$), 162.35 (s, *C5*), 192.34 (s, *C*O).

[Bromo(pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(2-phenylacetyl)pyrazolon-5-ato)rhodium(III)], [RhCp*(Q^{Bn})Br] (12). [Cp*$RhCl_2$]$_2$ (0.140 g, 0.22 mmol) was dissolved in 10 mL of THF, and 0.45 mL of Grignard reagent ($MgCH_3Br$ solution, 1.0 M in hexane) was added. The red solution was stirred for 48 h under N_2 at room temperature, evaporated under vacuum, and treated with CH_2Cl_2. A colorless precipitate formed, which was filtered off and shown to be $MgCl_2$. The filtrate was dried under vacuum; then 10 mL of toluene was added to give a red solution, and finally NaQ^{Bn} was added. The mixture was stirred overnight under N_2 at room temperature to give a red-orange precipitate, which was filtered off, washed with 5 mL of toluene, and then recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C); it has been identified as **12**. Anal. Calcd for $C_{28}H_{30}BrN_2O_2Rh$: C, 55.19; H, 4.96; N, 4.60. Found: C, 54.98; H, 5.10; N, 4.30. IR (Nujol, cm^{-1}): 1609s, 1591s, 1581s, 1528m ν(C⋯C, C⋯N), 512w, 450w. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.52 (s, 15H, CH_{3Cp^*}), 2.42 (s, 3H, 3-CH_3), 3.79, 3.87, 4.21, 4.29 (q, 2H$_{gem}$, COCH_2C$_6$H$_5$, ^2J(A−X) = 15.40 Hz, $\Delta\delta\nu/J$ = 5.57), 7.12−7.40m, 7.94d (10H, N−C_6H_5 and COCH$_2$C$_6$*H*$_5$).

[(Pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-acetylpyrazolon-5-ato)(triphenylphosphine)rhodium(III)]chloride, [Cp*Rh(Q^{Me})(PPh$_3$)]Cl (13). A dichloromethane solution (10 mL) containing RhCp*(Q^{Me})Cl (0.085 g, 0.17 mmol) and PPh_3 (0.044 g, 0.17 mmol) was stirred for 72 h under N_2 at room temperature. The orange solution was dried in a vacuum and recrystallized from 1:1 CH_2Cl_2/light petroleum (40−60 °C), and the crystals were shown to be compound **13** (0.102 g, 0.136 mmol, 80% yield). mp: 100 °C (dec). Anal. Calcd for $C_{40}H_{41}ClN_2O_2PRh$, C, 63.96; H, 5.50; N, 3.73. Found: C, 64.12; H, 5.68; N, 3.57. IR (Nujol, cm^{-1}): 3180w ν(Ph), 1610sh, 1592m, 1570s, ν(C⋯C, C⋯N), 1096s, 1021s, 521s, 511s, 499msh, 396vs. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.15 (d, 15H, CH_{3Cp^*}, ^4J(^{31}P−^{1}H) = 3.36 Hz), 1.34 (d, 15H, CH_{3Cp^*}, ^4J(^{31}P−^{1}H) = 3.66 Hz), 2.08 (d, 3H, 3-CH_3), 2.38 (d, 3H, COCH_3), 7.15−7.82m, 8.08m (5H, N−C_6H_5, 15H, P(C_6H_5)$_3$). ^{13}C NMR ($CDCl_3$, 293 K): δ 8.96 (d, ^2J(^{103}Rh−^{13}C) = 4.55 Hz, CH_{3Cp^*}), 9.01 (d, ^2J(^{103}Rh−^{13}C) = 4.46 Hz, CH_{3Cp^*}), 16.90, 17.22 (s, 3-CH_3), 27.72, 28.24 (CO*C*H_3), 99.34 (d, ^1J(^{103}Rh−^{13}C) = 6.7 Hz, C_{Cp^*}), 99.38 (d, ^1J(^{103}Rh−^{13}C) = 6.8 Hz, C_{Cp^*}), 106.12, 104.30 (s, *C4*), 118.93, 120.45, 126.10, 127.14, 129.55, 129.71, 138.17, 138.82 (s, N−C_6H_5 of Q), 128.86 (d, ^3J(^{31}P−^{13}C) = 11.06 Hz, *m*-C), 129.42 (d, ^3J(^{31}P−^{13}C) = 10.90 Hz, *m*-C), 129.75 (d, ^4J(^{31}P−^{13}C) = 3.82 Hz, *p*-C), 131.32 (sbr, *p*-C), 132.71 (d, ^1J(^{31}P−^{13}C) = 15.64 Hz, *i*-C), 132.77 (d, ^1J(^{31}P−^{13}C) = 16.78 Hz, *i*-C), 134.74, (d, ^2J(^{31}P−^{13}C) = 10.30 Hz, *o*-C), 135.68 (d, ^2J(^{31}P−^{13}C) = 9.54 Hz, *o*-C), 148.69, 149.82 (s, *C3*), 161.95, 163.84 (s, *C5*), 191.71, 193.02 (s, *C*O).^{31}P NMR ($CDCl_3$, 293 K): 30.71, (d, ^1J(^{31}P−Rh) = 147.7 Hz), 30.44 (d, ^1J(^{31}P−Rh) = 143.9 Hz).

[(Pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(3,3-dimethylbutanoyl)pyrazolon-5-ato)(triphenylphosphine)rhodium(III)]chloride, [Cp*Rh(Q^{Piv})(PPh$_3$)]Cl (14). Red compound **14** (0.167 g, 0.20 mmol, 76% yield) was prepared following a procedure similar to that reported for **13** using [Cp*Rh(Q^{Piv})Cl] and PPh_3. mp: 100 °C (dec). Anal. Calcd for $C_{44}H_{49}ClN_2O_2PRh$: C, 65.47; H, 6.12; N, 3.47. Found: C, 65.51; H, 6.28; N, 3.42. IR (Nujol, cm^{-1}): 1621m, 1589m, 1566s, 1522w ν(C⋯C, C⋯N), 523s, 510m, 497m, 394sbr. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.90 (s, 9H, $CH_2C(CH_3)_3$), 1.06 (s, 9H, $CH_2C(CH_3)_3$), 1.10 (d, 15H, CH_{3Cp^*}, ^4J(^{31}P−^{1}H) = 2.60 Hz), 1.36 (d, 15H, CH_{3Cp^*}, ^4J(^{31}P−^{1}H) = 2.66 Hz), 2.23 (s, 3H, 3-CH_3), 2.36 (m, 3H, 3-CH_3), 7.30−7.50, 7.70−7.85, 8.05 (m, 5H, N-*Ph*). 2.08 (d, 3H, 3-CH_3), 2.38 (d, 3H, COCH_3), 7.15−7.82m, 8.08m (5H, N−C_6H_5, 15H, P(C_6H_5)$_3$).^{13}C NMR ($CDCl_3$, 293 K): δ 9.02 (d, ^2J(^{103}Rh−^{13}C) = 2.87 Hz, CH_{3Cp^*}), 9.12 (d, ^2J(^{103}Rh−^{13}C) = 2.65 Hz, CH_{3Cp^*}), 17.92, 18.40 (s, 3-CH_3), 29.85, 30.41 (s, $CH_2C(CH_3)_3$), 49.87, 50.12 (s, $CH_2C(CH_3)_3$), 99.70 (d, ^1J(^{103}Rh−^{13}C) = 6.1 Hz, C_{Cp^*}), 99.95 (d, ^1J(^{103}Rh−^{13}C) = 5.7 Hz, C_{Cp^*}), 120.45, 121.10, 126.02, 126.74, 127.92, 128.62, 137.50, 138.17 (s, N−C_6H_5), 127.82 (d, ^3J(^{31}P−^{13}C) = 14.55 Hz, *m*-C), 128.91 (d, ^3J(^{31}P−^{13}C) = 18.22 Hz, *m*-C), 128.30 (d, ^4J(^{31}P−^{13}C) = 4.27 Hz, *p*-C), 130.76 (sbr, *p*-C), 133.10 (d, ^1J(^{31}P−^{13}C) = 19.42 Hz, *i*-C), 133.27 (d, ^1J(^{31}P−^{13}C) = 23.10 Hz, *i*-C), 134.47, (d, ^2J(^{31}P−^{13}C) = 10.35 Hz, *o*-C), 134.93 (d, ^2J(^{31}P−^{13}C) = 9.67 Hz, *o*-C), 147.14, 148.42 (s, *C3*), 160.67, 162.18 (s, *C5*), 190.80, 192.62 (s, *C*O). ^{31}P NMR ($CDCl_3$, 293 K): δ 30.04 (d, ^1J(^{31}P−Rh) = 149.8 Hz), 30.43 (d, ^1J(^{31}P−Rh) = 144.1 Hz).

[(Pentamethylcyclopentadienyl)(1-phenyl-3-methyl-4-(2,2-diphenylacetyl)pyrazolon-5-ato)(triphenylphosphine)rhodium(III)]chloride, [RhCp*(Q^{S})(PPh$_3$)]Cl (15). Orange compound **15** (0.150 g, 0.16 mmol, 75% yield) was prepared following a procedure similar to that reported for **13** using RhCp*(Q^{S})Cl and PPh_3. Anal. Calcd for $C_{52}H_{49}ClN_2O_2PRh$: C, 69.14; H, 5.47; N, 3.10. Found: C, 68.80; H, 5.28; N, 3.02. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.84 (d, 15H, CH_{3Cp^*}, ^4J(^{31}P−^{1}H) = 3.20 Hz), 1.37 (d, 15H, CH_{3Cp^*}, ^4J(^{31}P−^{1}H) = 3.78 Hz), 2.01 (s, 3H, 3-CH_3), 2.34 (s, 3H, 3-CH_3), 5.22 (s, 1H, C*H*(C_6H_5)$_2$), 5.35 (s, 1H, C*H*(C_6H_5)$_2$), 7.00−8.01 (m, 5H, N−C_6H_5, 15H, P(C_6H_5)$_3$). ^{31}P NMR ($CDCl_3$, 293 K): δ 28.97 (d, ^1J(^{31}P−Rh) = 149.6 Hz), 30.44 (d, ^1J(^{31}P−Rh) = 144.1 Hz). Compound **15** has been also obtained when the reaction was carried out at −80 °C for 5 min.

X-ray Diffraction Studies. Full spheres of CCD area-detector diffractometer data were measured at ca. 153 K (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation, λ = 0.71073 Å) yielding $N_{t(otal)}$ reflections; those merging to N unique (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered "observed", were used in the full-matrix least-squares refinement, refining anisotropic

Table 1. Crystal and Refinement Data

	1[a]	**2**	**4**[b]	**6**
formula	$C_{22}H_{26}ClN_2O_2Rh$	$C_{22}H_{26}ClIrN_2O_2$	$C_{26}H_{34}N_2O_2Rh$	$C_{28}H_{30}ClN_2O_2Rh$
M_r	488.8	578.1	544.9	564.9
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	8.540(1)	8.6997(6)	16.059(5)	7.582(2)
b (Å)	17.163(3)	17.049(1)	19.606(7)	21.345(6)
c (Å)	13.769(2)	13.9360(9)	8.081(3)	15.458(5)
α (deg)				
β (deg)	97.287(4)	96.470(2)	92.177(7)	102.037(7)
γ (deg)				
V (Å^3)	2002	2054	2542	2447
D_c (g cm^{-3})	1.622	1.869	1.424	1.533
Z	4	4	4	4
μ (mm^{-1})	1.01	6.7	0.80	0.84
specimen (mm)	0.44× 0.22 × 0.15	0.12× 0.08 × 0.06	0.19× 0.14 × 0.02	0.19× 0.14 × 0.08
$'T'_{min/max}$	0.84	0.73	0.58	0.90
$2\theta_{max}$ (deg)	75	75	50	55
N_t	42157	42837	20656	25402
N (R_{int})	10628 (0.039)	10806 (0.045)	4564 (0.16)	5542 (0.062)
N_o	8115	7799	1685	4294
R	0.044	0.035	0.079	0.043
R_w	0.050	0.040	0.103	0.067

	7	**8**	**12**
formula	$C_{28}H_{30}ClIrN_2O_2$	$C_{34}H_{34}ClN_2O_2Rh$	$C_{28}H_{30}BrN_2O_2Rh$
M_r	654.2	641.0	609.4
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$ (#14)	$P\bar{1}$(#2)	$P2_1/c$ (#14)
a (Å)	7.5905(7)	8.2875(6)	7.618(1)
b (Å)	21.337(2)	13.778(1)	21.329(4)
c (Å)	15.560(2)	14.610(1)	15.605(3)
α (deg)		109.429(2)	
β (deg)	101.893(2)	95.937(2)	101.784(3)
γ (deg)		106.875(2)	
V (Å^3)	2466	1468	2482
D_c (g cm^{-3})	1.762	1.450	1.630
Z	4	2	4
μ (mm^{-1})	5.6	0.71	2.3
specimen (mm)	0.18× 0.10 × 0.08	0.15× 0.09 × 0.06	0.15× 0.09 × 0.07
$'T'_{min/max}$	0.65	0.92	0.84
$2\theta_{max}$ (deg)	75	75	50
N_t	51205	27373	17150
N (R_{int})	12742 (0.048)	15079 (0.025)	4512 (0.054)
N_o	9804	11973	3482
R	0.037	0.043	0.038
R_w	0.049	0.044	0.043

[a] $(x,y,z,U_{iso})_H$ refined. [b] Weak and limited data would support meaningful anisotropic displacement parameter refinement for Rh, Cl only.

displacement parameter forms for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ constrained at estimated values. Conventional residuals R and R_w on $|F|$ at convergence (weights = $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted. Neutral atom complex form factors were employed within the Xtal 3.7 program system.[16] Pertinent results are given below and in Tables 1 and 3 and the figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms; the hydrogen atoms have an arbitrary radii of 0.1 Å.

Results and Discussion

The $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (M=Rh, Ir)[17] compounds were reacted at room temperature with stoichiometric amounts of the sodium salt of acylpyrazolone NaQ in toluene to produce [Cp*M(Q)Cl] derivatives **1**−**9** (eq 1)

$$[MCp^*Cl\}_2(\mu\text{-}Cl)_2] + 2QNa \rightarrow \underset{\mathbf{1-9}}{[Cp^*M(Q)Cl]} + 2NaCl \quad (1)$$

1: M = Rh, Q = Q^{Me} **2**: M = Ir, Q = Q^{Me}

3: M = Rh, Q = Q^{Et} **4**: M = Rh, Q = Q^{Piv}

5: M = Ir, Q = Q^{Piv} **6**: M = Rh, Q = Q^{Bn}

7: M = Ir, Q = Q^{Bn} **8**: M = Rh, Q = Q^{S}

9: M = Ir, Q = Q^{S}

Slow diffusion of petroleum ether into toluene or dichloromethane solutions of [Cp*M(Q)Cl] compounds produced, in a number of cases, single crystals suitable for X-ray structure analyses. Complexes **1**−**9** are air-stable and soluble in chlorinated and other common solvents such as toluene,

(16) Hall, S. R., du Boulay, D. J., Olthof-Hazekamp, R., Eds. *The Xtal 3.7 System*; University of Western Australia: Crawley, Australia, 2001.
(17) White, C.; Yates, A.; Maitlis, P. M.; Heinekey, D. M. *Inorg Synth.* **1992**, *29*, 228−234.

Table 2. Selected Geometries, [Cp*MQX][a]

M/X/Q	**1** Rh/Cl/Q^{Me}	**2** Ir/Cl/Q^{Me}	**4** Rh/Cl/Q^{Piv}	**6** Rh/Cl/Q^{Bn}	**7** Ir/Cl/Q^{Bn}	**8** Rh/Cl/Q^{S}	**12** Rh/Br/Q^{Bn}
			distances (Å)				
M−X	2.3996(6)	2.4065(9)	2.378(5)	2.414(1)	2.4058(9)	2.4208(5)	2.5457(6)
M−O(41)	2.100(2)	2.111(3)	2.13(1)	2.111(3)	2.113(3)	2.126(1)	2.103(3)
M−O(5)	2.093(2)	2.108(2)	2.11(1)	2.095(3)	2.107(3)	2.122(2)	2.104(3)
M−C(Cp*)	2.106(2)	2.127(3)	2.01(2)	2.113(4)	2.124(3)	2.125(2)	2.120(4)
	−2.128(2)	−2.144(3)	−2.17(2)	−2.144(4)	−2.140(4)	−2.139(2)	−2.148(4)
<M−C(Cp*)>	2.119(9)	2.136(6)	2.10(6)	2.131(12)	2.134(6)	2.132(6)	2.125(13)
M−C(0)	1.740	1.752	1.74	1.752	1.750	1.750	1.752
			angles (deg)				
C(0)−M−X	127.8	129.4	127.5	127.4	128.6	126.6	126.4
C(0)−M−O(41)	124.3	125.3	126.8	126.6	127.6	126.7	126.5
C(0)−M−O(5)	128.0	129.2	128.5	126.4	127.8	127.1	126.7
X−M−O(41)	88.73(4)	86.09(7)	87.8(4)	86.29(7)	84.31(7)	86.94(4)	86.91(8)
X−M−O(5)	86.54(4)	84.24(7)	86.0(3)	89.34(7)	86.76(7)	89.38(4)	89.95(8)
O(41)−M−O(5)	88.62(6)	88.2(1)	86.2(5)	87.8(1)	87.05(11)	87.09(5)	87.6(1)
M−O(41)−C(41)	129.0(1)	129.4(2)	130(1)	128.7(3)	130.0(3)	126.0(1)	129.1(3)
M−O(5)−C(5)	122.1(1)	122.5(2)	122(1)	121.9(3)	123.0(2)	117.2(1)	121.9(3)
			interplanar dihedral angles (deg)				
N_2C_3/C_6	4.64(8)	6.0(1)	4.4(7)	5.7(1)	5.5(1)	24.04(8)	5.3(2)
N_2C_3/C_5	49.60(9)	51.7(1)	55.4(9)	68.9(2)	68.7(1)	89.47(8)	70.1(2)
			out-of-plane deviations (Å)				
$\delta M/C_3N_2$	0.143(4)	0.163(7)	0.22(4)	0.322(8)	0.260(7)	0.882(4)	0.330(9)
$\delta M/C_5$	1.737(1)	1.747(1)	1.737(2)	1.750(1)	1.747(1)	1.746(1)	1.750(1)

[a] C(0) is the centroid of Cp*.

Table 3. Selected Ligand Geometries[a]

	1	**2**	**6**	**7**	**8**	**12**
			distances (Å)			
N(1)−N(2)	1.390(3)	1.401(4)	1.403(4)	1.400(4)	1.396(2)	1.402(5)
N(1)−C(5)	1.362(3)	1.362(4)	1.379(5)	1.364(5)	1.368(3)	1.371(6)
N(1)−C(11)	1.405(3)	1.431(4)	1.422(5)	1.425(5)	1.416(3)	1.423(6)
N(2)−C(3)	1.305(3)	1.315(5)	1.310(5)	1.311(5)	1.317(3)	1.308(6)
C(3)−C(4)	1.426(3)	1.430(5)	1.431(5)	1.440(5)	1.430(2)	1.441(6)
C(4)−C(41)	1.403(3)	1.404(5)	1.417(5)	1.411(5)	1.415(3)	1.408(5)
C(4)−C(5)	1.418(3)	1.429(5)	1.428(5)	1.424(5)	1.429(2)	1.430(6)
C(41)−O(41)	1.253(3)	1.267(4)	1.254(5)	1.262(4)	1.265(2)	1.263(5)
C(5)−O(5)	1.261(3)	1.267(4)	1.265(5)	1.275(4)	1.272(2)	1.267(5)
O(41)···O(5)	2.929(2)	2.934(6)	2.916(4)	2.906(4)	2.927(2)	2.912(5)
			angles (degrees)			
	1	**2**	**6**	**7**	**8**	**12**
N(2)−N(1)−C(5)	111.9(2)	112.5(3)	111.5(3)	111.0(3)	111.9(2)	111.9(4)
N(2)−N(1)−C(11)	118.5(2)	117.8(3)	119.0(3)	118.6(3)	118.0(2)	118.1(3)
C(5)−N(1)−C(11)	129.6(2)	129.7(3)	129.4(3)	130.4(3)	129.6(1)	129.8(3)
N(1)−N(2)−C(3)	105.9(2)	105.2(3)	106.3(3)	106.4(3)	105.8(2)	105.9(3)
N(2)−C(3)−C(4)	111.7(2)	112.0(3)	111.4(3)	111.2(3)	111.6(1)	112.0(4)
N(2)−C(3)−C(31)	118.4(2)	118.3(3)	117.5(3)	118.0(3)	118.3(2)	117.9(4)
C(4)−C(3)−C(31)	129.9(2)	129.6(3)	131.0(4)	130.3(4)	129.5(2)	130.1(4)
C(3)−C(4)−C(5)	105.0(2)	104.9(3)	105.6(3)	104.1(3)	105.0(2)	104.6(3)
C(3)−C(4)−C(41)	130.5(2)	130.8(3)	132.2(3)	132.2(2)	131.5(1)	132.2(4)
C(5)−C(4)−C(41)	124.6(2)	124.3(3)	121.9(3)	123.4(3)	123.1(1)	122.8(4)
C(4)−C(41)−O(41)	123.6(2)	123.7(3)	124.9(3)	123.7(1)	123.0(2)	124.2(4)
C(4)−C(41)−C(42)	121.3(2)	121.8(3)	121.4(3)	122.6(3)	120.1(1)	122.2(4)
O(41)−C(41)−C(42)	115.1(2)	114.5(3)	113.6(3)	113.7(3)	116.8(2)	113.6(4)
N(1)−C(5)−C(4)	105.5(2)	105.3(3)	105.0(3)	106.8(3)	105.4(1)	105.6(4)
N(1)−C(5)−O(5)	122.9(2)	123.1(3)	122.7(3)	122.4(3)	123.5(2)	123.0(4)

[a] **4** is less precise and is, therefore, omitted.

acetonitrile, or acetone. The moderate yields (55−63%) are often the result of the large solubility of **1**−**9** in the solvents employed during the workup. No evidence of a cyclometalation reaction has been found in the case of the Ir(Cp*) derivatives. The IR spectra of **1**−**9** show the absence of broad absorptions in the range of 2300−2800 cm^{-1}, ascribed to intramolecular ν(O−H···O) in the neutral free HQ proligands. In addition, the shift to lower frequencies of the ν(C═O) band (at ca. 1600 cm^{-1}) is in accordance with the deprotonation of HQ and the subsequent coordination of the heterocycle to the metal in the anionic form. In the far-IR region, several absorptions have been detected in the 480−

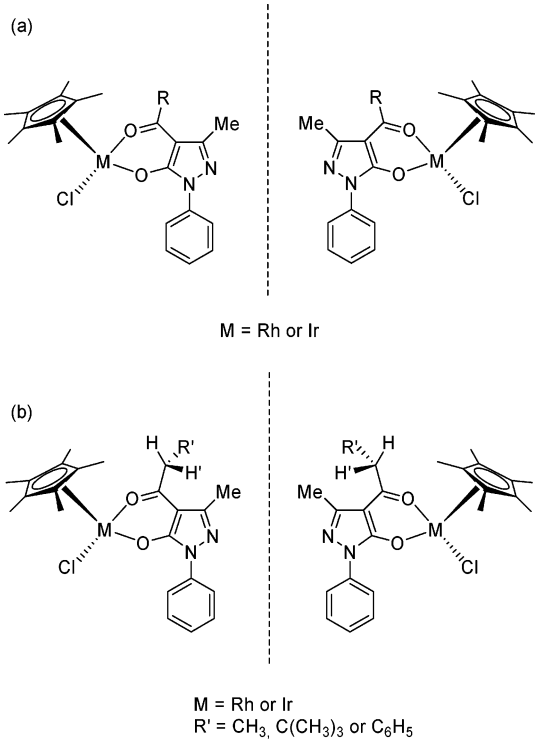
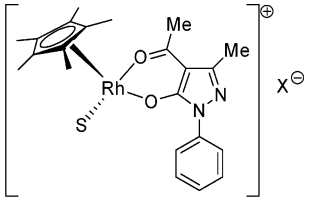


Figure 2. Two enantiomers of complexes **1**−**9**.

440 and 290−260 cm^{-1} ranges. These may be assigned to ν(M−O) and ν(M−Cl), respectively.[18] The ^{1}H NMR spectra of compounds **1**−**9**, recorded in $CDCl_3$, agree well with the formulas proposed. Thus, the presence of an η^5-Cp* group is inferred from the observation of a unique signal from the methyl protons that invariably appears in the proximity of 1.65 ppm. Moreover, the Cp* ring-carbon nuclei resonate at 92 ppm in the ^{13}C{^{1}H} NMR spectrum, exhibiting a coupling of ca. 9 Hz with the ^{103}Rh nucleus. Resonances from the Q ligand are analogous to those found for other rhodium acylpyrazolonates previously reported, consistent with *O*,*O*′-chelation to the metal (see the X-ray single-crystal studies below).[13] These organometallic compounds are chiral-at-metal, and they can exist as a couple of two enantiomers (Figure 2a). In addition, the geminal methylene protons of the Q-acyl substituent in complexes **3**−**7** are diastereotopic and produce the expected AB quartets (see Experimental section). For this reason, we have explored the use of the diasterotopic CH_2 protons of bonded Q^{Et}, Q^{Piv}, and Q^{Bn} as a probe in coalescence experiments carried out to understand the stability of metal configuration in solution (Figure 2b).

We performed some VT NMR experiments by warming the solution of derivatives **3**, **4**, and **6**, and no change was observed in the $CDCl_3$ spectra up to 55 °C; the AB quartets were always present. On the other hand, complexes **3**, **4**, and **6** immediately dissociate in the strongly coordinating deuterated solvents DMSO and CD_3CN which can displace the Q ligand from the metal coordination sphere, totally, or at least partially, upon rupture of one diketonate arm. In fact, in these solvents, quartets are not present both at low and



10: S = MeCN, X = NO_3; **11**: S = H_2O, X = ClO_4

Figure 3. Proposed ionic structure for compounds **10** and **11**.

room temperature. Coalescence studies (also in different solvents) were not possible in the case of the Ir complexes **5** and **7** because decomposition commences at temperatures above 40 °C. Decomposition is also observed in nitromethane or benzene solutions.

The reactions of [Cp*Rh(Q^{Me})Cl] **1** with AgX in not-anhydrous MeCN yielded derivatives **10** and **11**.

$$[Cp^*Rh(Q^{Me})Cl] + AgX \xrightarrow{Solv} [Cp^*Rh(Q^{Me})(Solv)]X + AgCl \quad (2)$$

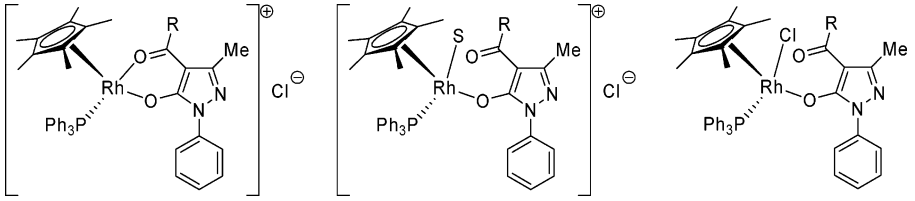
10: X = NO_3; Solv = MeCN

11: X = ClO_4; Solv = H_2O

They are salt-like, both in solution and in the solid state. The latter assumption is confirmed from their IR spectra, which exhibit bands from noncoordinated nitrate (**10**) and perchlorate groups (**11**). In both cases, the halide exchange is accompanied by coordination of a solvent molecule, consistent with the low tendency of Rh to coordinate NO_3 and ClO_4 groups. A byproduct in the synthesis of compound **11** is [Cp*Rh(Cl)(H_2O)$_2$]ClO_4, which we have always found in the mother liquor or in the precipitate, independent of the amount of silver salt employed. The ^{1}H and ^{13}C NMR spectra of **10** and **11** exhibit the same pattern found in the spectrum of **1**, suggesting O_2-chelating bidentate coordination for Q and η^5-coordination for Cp*, in accordance with the structure proposed in Figure 3.

Attempts to alkylate compounds **1**−**9** led only to halide exchange, as revealed for example by the reaction of **6** with CH_3MgBr. This produces the complex [Cp*Rh(Q^{Bn})Br], **12**, where a chloride ligand has been displaced by bromide in the rhodium coordination sphere. It is worth noting that halogen-exchange reactions often require a 10-fold excess of NaX (X = Br or I) and that, after a short time, the reaction mixture reaches equilibrium. In the present case, the reaction is fast, and the chloride displacement by bromide is complete within about 2 min. The spectroscopic features of **12** are similar to those found for the parent compound **6**, the only difference being the expected displacement of the band, because of Rh−X, from 260 cm^{-1} in **6** to 240 cm^{-1} in **12**. Chloride dissociation is also observed in the interactions of derivatives **2**, **4**, and **6** with PPh_3 yielding complexes [Cp*Rh(Q)(PPh_3)]Cl, **13**−**15**. The displacement of the Cl from the Rh-coordination sphere and the formation of an ionic compound has been confirmed by the disappearance of the IR band for ν(Rh−Cl). In no case was the coordination of two PPh_3 groups observed, nor when the reaction was carried out in a large excess of the P donor. In contrast to

(18) Nakamura, Y.; Isobe, K.; Morita, H.; Yamazaki, S.; Kawaguchi, S. *Inorg. Chem.* **1972**, *11*, 1573−1578.



I II III

Figure 4. Three possible isomers for compounds **13**−**15**.

Table 4. Selected ESI-MS Data (CH_3CN)

compound or mixture	$[Cp^*M(Q)]^+$	$\{[Cp^*M(Q)]_2Cl\}^+$	$\{[Cp^*M(Br)]_2Cl\}^+$	$(Cp^*)_2M_2Br_3^+$	$[Cp^*M(PPh_3)(Q)]^+$	$[Cp^*MCl(MeCN)]^+$	$(Cp^*)_2M_2Cl_3^+$
1[a]	453 (100)	941 (10)					
1 + RBr	453 (55)		670 (25)	715 (100)			
2[b]	543 (100)	1121 (10)				404 (70)	
2 + RBr	543 (10)		849 (23)	893 (100)			
8[c]	605 (100)	1245 (8)					
9[d]	695 (100)	1425 (5)				404 (70)	
11[e]						314 (100)	580 (20)
11 + RBr			670 (75)	715 (10)			580 (40)
13[f]	453 (5)				715 (100)		
13 + RBr	453 (5)				715 (100)		
14[g]					771 (100)		

[a] [Cp*Rh(QMe)Cl]. [b] [Cp*Ir (Q^{Me})Cl]. [c] [Cp*Rh(Q^S)Cl]. [d] [Cp*Ir(Q^S)Cl]. [e] [Cp*Rh(Q^{Me})H_2O]ClO_4. The most abundant peak in the positive spectrum of **11** is *m*/*z* 627 (100) $\{[Cp^*Rh(Cl)]_2Br\}^+$. In the negative spectrum of **11**, the most abundant peaks are *m*/*z* 99 (100) $[ClO_4]^-$ and *m*/*z* 534 (20) $[Rh(Cp)(ClO_4)_3]^-$. [f] [Cp*Rh(Q^{Me})(PPh_3)]Cl. [g] [Cp*Rh(Q^{Piv})(PPh_3)]Cl.

the situation described above for complexes **1**−**9**, the ^1H and ^{31}P NMR spectra of compounds **13**−**15** exhibit signals from the two possible isomers (for instance, doublets δ 30.71 and 30.44, with a ^1J(P−Rh) value of ca. 145 Hz can be detected in the $^{31}P\{^1H\}$ NMR of **13**). In $CDCl_3$ solution at room temperature, the equilibrium concentration of isomers is approximately 4:1 for all compounds **13**−**15**. We hypothesize that in solution the breaking of one of the $Rh-O_{diketonate}$ bonds (likely to be dependent on the steric hindrance of the P donor) and the coordination of solvent molecules or of the same chloride ions, occurs with the formation of two different species, for example, two of those reported in Figure 4. This seems to be supported by the IR spectra of **13**−**15** in which the C═O stretching frequencies have different values from those reported for the corresponding [Cp*Rh(Q)(Cl] containing a bidentate Q ligand. However, we cannot exclude the possibility of a complete dissociation of **13**−**15** in solution and formation, for example, of [Cp*Rh(PPh_3)(Solv)(Cl] species.

Table 4 summarizes the ESI MS data for selected derivatives **1**, **2**, **8**, **9,** **11**, **13**, and **14** and also for mixtures containing derivative **1** or **8** and $AgClO_4$, PR_3, benzylbromide, or Grignard reagents. The *m*/*z* values of prominent peaks corresponding to rhodium or iridium cations are given together with formula assignments. It is to point out that, in the case of the halide derivatives **1**, **2**, **8**, and **9**, the most abundant signal is that from the $[Cp^*M(Q)]^+$ cation. In the ESI spectra of **1**, **2**, **8**, and **9**, a signal ascribed to a dinuclear species generated by the loss of one halide group wherein two cyclopentadienyl-metal moieties are likely bridged by an halide or a pyrazolonate ligand is also present. When an equimolar quantity or an excess of benzyl bromide or Grignard reagent, RMgX (R = Et, Bu^n; X = Br), was added to a MeCN solution of **1** or **8**, signals corresponding to the $[(Cp^*)_2Rh_2Br_3]^+$ and $[(Cp^*)_2Rh_2Br_2Cl]^+$ species were immediately identified. In the case of PR_3 derivatives **13**−**14**, the signals from the ionic species $[Cp^*Rh(PR_3)(Q)]^+$ were always the most abundant. No change was observed in the ESI spectra when benzyl bromide was added to a solution containing derivative **13**, suggesting a high stability for these species in solution.

A different behavior has been found in the positive spectrum of derivative **11**, the most abundant species detected in solution being $[Cp^*Rh(Cl)]^+$, $[(Cp^*)_2Rh_2(Cl)_3]^+$, and $[(Cp^*)_2Rh_2(Cl)_2(ClO_4)]^+$. The anionic ligand Q^- is present, unassociated, in the negative spectrum together with signals from the ClO_4^- and $[Cp^*Rh(ClO_4)_3]^-$ anions. This suggests a high instability of compound **11** in MeCN solution where it immediately dissociates yielding a plethora of species, which also contain coordinated perchlorate groups, and confirming the possibility of displacing anionic ligands, such as the pyrazolonate donors, from the metal coordination sphere with solvent molecules, such as MeCN or H_2O.

Finally, when benzyl bromide was added to a solution of **11** in MeCN, the ESI-MS spectrum exhibits, in the positive mode, a number of peaks from dinuclear species containing bridging-halide groups: $[(Cp^*)_2Rh_2(Cl)_3]^+$, $[(Cp^*)_2Rh_2(Cl)Br_3]^+$, $[(Cp^*)_2Rh_2(Cl)_2Br]^+$, and $[(Cp^*)_2Rh_2(Br)_3]^+$. In the positive spectra, no signals containing the β-diketonate donor, the most abundant species found in the negative ESI spectra, have been detected.

The result of the "low-temperature" single-crystal X-ray structure determinations are consistent with the above formulations in terms of stoichiometry and connectivity; in all cases, the species take the form [Cp*M(Q)X] with one mononuclear neutral molecule, devoid of crystallographic symmetry and no intrinsic molecular symmetry, comprising the asymmetric unit of each structure (Figure 5); all

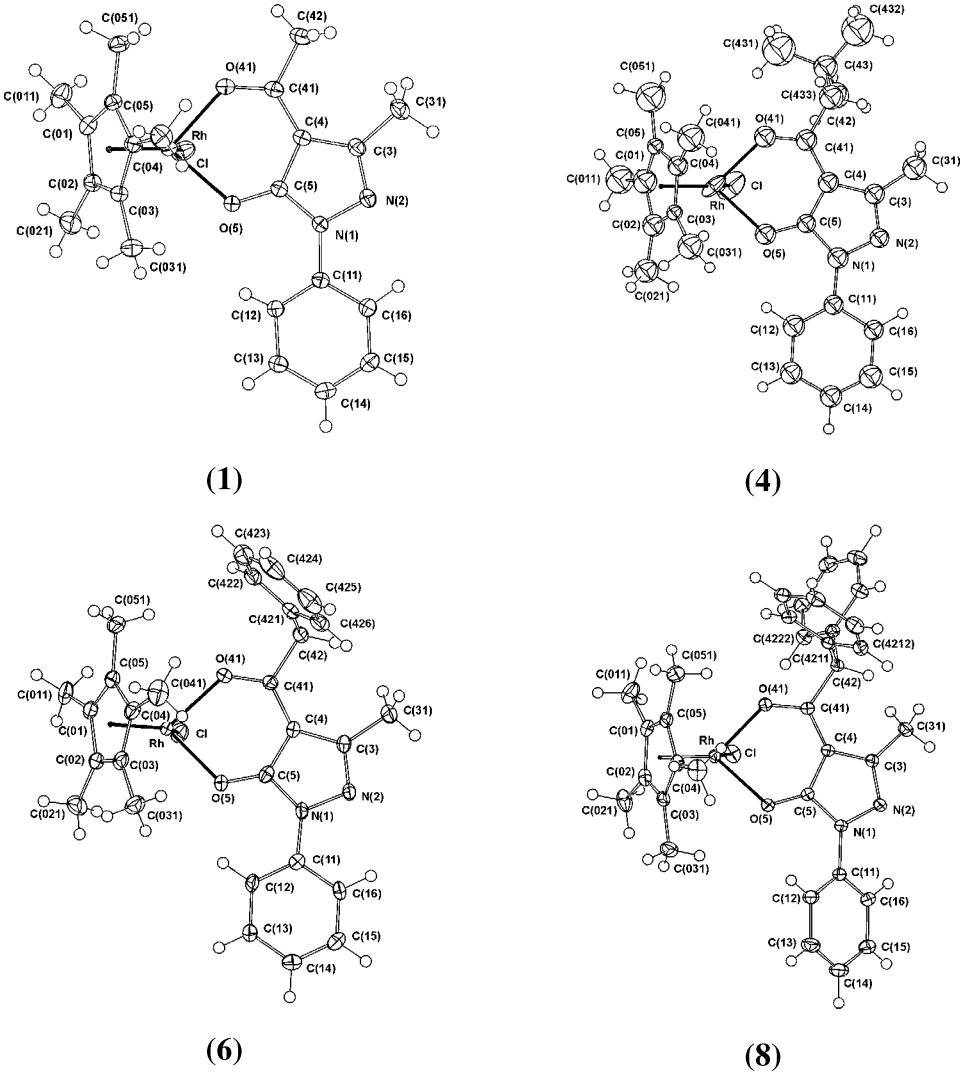


Figure 5. Projections of individual molecules of **1**, **4**, **6**, and **8** (as representative) normal to their ligand planes.

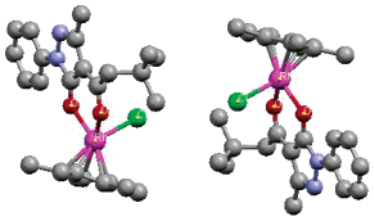


Figure 6. Racemic mixture found in the crystals of **1**, **2**, **6**, **7**, **8**, and **12**.

compounds crystallize in centrosymmetric space groups (i.e., the specimens were racemic) (Figure 6).[19] Isomorphous arrays are found for M = Rh, Ir; X = Cl (**1**, **2, 6**, and **7**) and M = Rh, X = Br (**12**) permitting the comparison of different metal atoms in similar other-atom environments and of different halides in otherwise similar systems. In all such systems, except **12**, where X = Br, and **4**, where the precision is limited, the metal−donor atom distances are remarkably invariant (Table 2); the angles are slightly more diverse, but not so much as to suggest the presence of any unusual or unexpected trends, and although the oxygen donors are of two rather different types, their M−O distances are similar, although the M−O−C angles differ between O(41 and 51). Some differences are evident for **8**, most notably in the N_2C_3/C_5 interplanar dihedral angle, perhaps dependent on some steric effect derivative of the bulk of the ligand substituent, but also in respect of the angle, at O(5), where the effect may be electronic, contingent on both the substituent and the change in torsion of the nearly phenyl group. An inspection of the distances and angles within the conjugated section of the aromatic ligand across the series shows remarkable insensitivity in this dimension (Table 3). Not surprisingly, crystal packings appear to be primarily determined by inversion-related parallel dispositions of the planar components.

Conclusions

Rh(III) diketonate complexes of formula [Cp*M(Q)Cl] (M = Rh or Ir, Cp* = pentamethylcyclopentadienyl, HQ = 1-phenyl-3-methyl-4R(C═O)-pyrazol-5-one) can be easily synthesized by reaction of $[Cp^*MCl_2]_2$ with the adequate sodium salt NaQ. [Cp*M(Q)Cl] complexes exist as enantiomers, both in the solid state and in solution, the metal being a center of chirality. It is noteworthy that [Cp*M(Q)Cl] complexes are stable in the solid state and in the atmosphere

(19) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761−778.

for a long time, and they are also stable in weak polar solvents (such as $CHCl_3$) and up to 55 °C. No signal from the coalescence of the geminal methylene-proton quartets in derivatives **3**−**7** has been found. This is a probe of the lack of interconversion and of the stability of both conformations in solution. These compounds are resistant to carbanionic attack by RMgX or RX species. Br^- is however able to displace the Cl^- from the Rh center. The Cl^- can be also displaced by solvent molecules, as in the exchange reaction of [Cp*M(Q)Cl] with AgX (X = NO_3, ClO_4), in which ionic species [Cp*M(Q)(MeCN)]X or [Cp*M(Q)(H_2O)]X are obtained. Finally P donors, such as PPh_3, are able to coordinate [Cp*Rh(Q)Cl], easily displacing Cl^- from the metal coordination sphere and yielding ionic chiral-at-metal complexes [Cp*Rh(Q)(PPh_3)]Cl. Also, the acylpyrazolonate ligand, Q, can be expelled from the metal coordination sphere, as demonstrated by ESI-MS studies and by the formation of byproducts such as [Cp*Rh(Cl)(H_2O)$_2$]ClO_4 in the reaction of [Cp*Rh(Q)Cl] with an excess $AgClO_4$.

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Supporting Information Available: Full crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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