Rhodium-Stabilized *o*-Quinone Methides: Synthesis, Structure, and Comparative Study with Their Iridium Congeners

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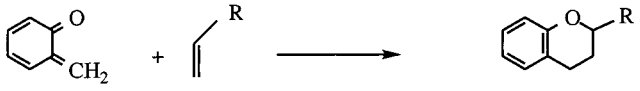
The parent *o*-quinone methide (*o*-QM) cannot be observed in condensed phases above −100 °C, but in this work, *o*-QM and its dimethyl derivative are stabilized by complexation to Cp*Rh. Precursor oxo-dienyl rhodium complexes [(η^5-Cp*)Rh(η^5-2-alkyl-oxodienyl)][BF_4] (**5a**,**b**) were isolated as yellow microcrystalline solids in 85−90% yields and fully characterized. In addition the X-ray molecular structure of **5b** is reported. Selective alkyl deprotonation by *t*-BuOK in CH_2Cl_2 provided the first series of rhodium−*o*-QM complexes [(η^5-Cp*)Rh(η^4-$(R)_2C_7H_4O$)] (R = H, **6a**; R = Me, **6b**). The *o*-QM is stabilized through η^4-coordination to the metal center, as shown by the X-ray structure of **6b**. Structural and reactivity studies on **6a**,**b** show that the rhodium−*o*-QM complexes are less stable than their iridium congeners.

Introduction

o-Quinone methides[1] (*o*-QM, **1**) are versatile reactive intermediates in organic synthesis[2] and biochemistry.[3] *o*-QMs act as heterodienes in inter- and intramolecular Diels−Alder [2+4] cycloadditions with alkenes to give various substituted chromans (Scheme 1), a key ring system in some natural products. In biochemistry, some antitumor and antibiotic drugs such as mitomycin C are suggested to produce transient electrophilic *o*-QM intermediates, which can act as alkylating agents of DNA.[3] The high reactivity of simple *o*-QMs (those without substituents on the exocyclic double bond) is illustrated by the fact that in condensed phases the parent compound has been characterized spectroscopically only at temperatures below −100 °C.[4] In contrast,

Scheme 1



1 **Chroman**

we recently reported[5,6] a general and unprecedented synthetic procedure to Cp*Ir−η^4-*o*-quinone methide complexes **2** including that of the unsubstituted *o*-quinone methide (**2a**). Unlike the parent molecule **1**, complex **2a** is thermally stable, yet shows interesting reactivity. The importance of metal complexation to stabilize related *p*-quinone methides was beautifully illustrated by Milstein and co-workers.[7] However these *p*-quinone methide complexes show important differ-

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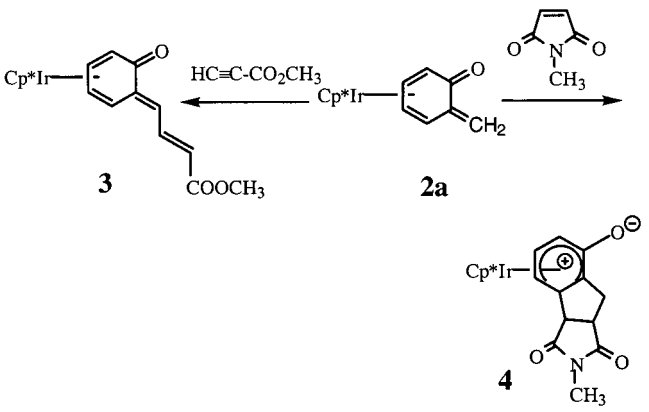
Scheme 2



ences in bonding and reactivity compared with the *o*-QM complexes presented here.

Recently we showed that complexation of the metal in **2a** reverses the polarity of the *o*-QM ligand, leading to nucleophilic character of the exocyclic methylene carbon toward electron-poor alkenes and alkynes.[6] For instance, **2a** reacted with methyl propynoate to yield the new *o*-quinone methide complex **3** as a result of a regioselective coupling reaction between the electrophilic alkyne and the exocyclic carbon (=CH_2) of complex **2a**. Alternatively, treatment of **2a** with *N*-methylmaleimide gave the tricyclic iridium complex **4** as a result of an unprecedented [2+3] cycloaddition with part of the *o*-QM ligand (Scheme 2).

It is well known that relatively small changes in the identity of a metal fragment can lead to surprisingly large changes in reactivity. Therefore, in this paper we describe studies of *o*-QM complexes involving the Cp*Rh moiety. First, we report the synthesis of the phenoxo precursors [Cp*Rh(η^5-2-R-C_6H_4O)][BF_4] (R = $-CH_3$, **5a**; R = $-CH(CH_3)_2$, **5b**) including the X-ray molecular structure of **5b**. Subsequent alkyl deprotonation by *t*-BuOK affords the related Cp*Rh$-\eta^4$-*o*-quinone methide complexes **6a**,**b.** The X-ray molecular structure of [Cp*Rh(η^4-$(Me)_2C_7H_4O$)] (**6b**) is reported and represents the second reported structure for this class of complexes. Finally, a comparison of Cp*Rh and Cp*Ir congeners' structure and reactivity is presented.

Results and Discussion

Formation and Characterization of Phenoxo Complexes. Treatment of [Cp*Rh(acetone)$_3$][BF_4]$_2$ prepared in situ with the 2-alkylphenols {2-R-C_6H_4OH; R = Me; R = *i*-Pr} in acetone followed by O-deprotonation with NEt_3 afforded the related 2-alkyl phenoxo complexes [Cp*Rh(η^5-2-alkyloxodienyl)][BF_4] (**5a**,**b**) in 85−90% yield isolated as microcrystalline yellow solids (Scheme 3). Complexes **5** were completely characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopic methods and microanalytical data. For instance, the ^{1}H NMR of **5a** recorded in acetone-d_6 showed the presence of four multiplets in the range 5.50−6.80 ppm attributed to protons of the η^5-phenoxo ring and two singlets at 2.13 ppm (15 H) and 1.88 (3 H) assigned to the methyl protons of the η^5-Cp* ligand and the phenoxo methyl substituent, respectively. Similarly the ^{1}H NMR spectrum of **5b** recorded in CD_3CN showed the presence of four multiplets in the region 5.40−6.50 ppm, as expected for the four protons of the η-phenoxo ligand. In addition, the *i*-Pr group gave rise to two signals, a septet centered at 2.76 ppm (methine proton) and a pair of doublets at 1.09 and 1.20 ppm attributed to the protons of the two diastereotopic methyl groups. Finally, the singlet at 1.99 ppm was assigned to the methyl groups of the η^5-Cp* ligand.

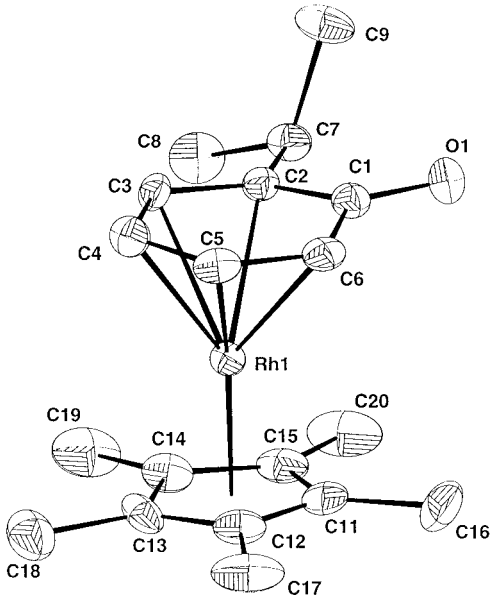


Figure 1. X-ray molecular structure of [Cp*Rh(η^5-(*i*-Pr)-C_6H_4O)]$^+$ (**5b**) with atom-numbering system. ORTEP view shows thermal ellipsoids at 30% probability, without hydrogens for clarity.

An X-ray structural determination carried out on **5b** confirmed the solution studies. Crystals of **5b** were obtained by slow crystallization from CH_2Cl_2/Et_2O solution. Crystallographic data for **5b** are shown in Table 1. Selected bond distances and angles for **5b** are shown in Table 2. Compound **5b** crystallizes in the orthorhombic space group *Pbca*. Figure 1 shows a view of the cation [Cp*Rh(η^5-(*i*-Pr)C_6H_4O)]$^+$ with its atom-numbering system. The structure shows that the "Cp*Rh" unit is coordinated to only five carbons of the phenyl ring: the distances from the metal to the centers of the π-bonded carbons are 1.73 Å for the phenoxo ligand and 1.81 Å for the η^5-C_5Me_5 ligand, whereas the bond distance Rh−C(1) is 2.475 Å, out of effective bonding range. Loss of aromaticity in the bonded phenoxo unit is manifested by the irregularity of the arene C−C bond lengths. Another important feature of this structure is that the bond distance C1−O1 = 1.236 (8) Å is shorter than that reported for the analogous iron and ruthenium derivatives [Cp*Fe(η^5-PhO)] and [Cp*Ru(η^5-PhO)·2PhOH] with C−O distances of 1.25 and 1.28 Å, respectively.[8,9] The dihedral angle θ between the plane C2−C1−C6 and the rest of the ring in **5b** is 14°,

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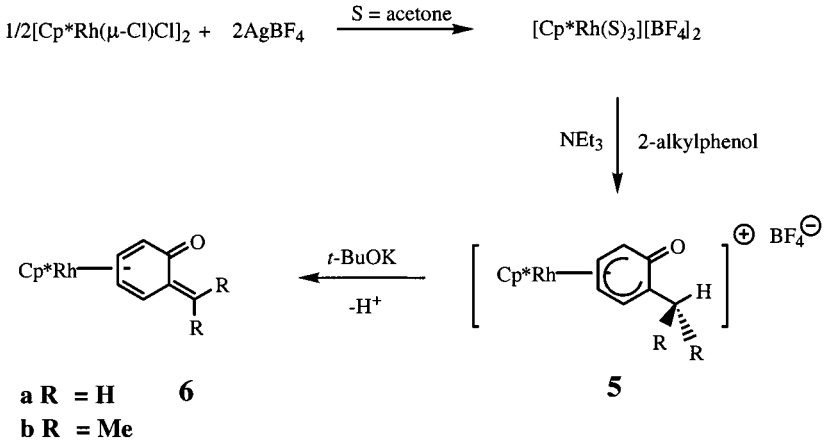
Scheme 3: Synthetic Route for 5a,b and 6a,b Complexes



significantly greater than that reported for the iron (2°) and ruthenium (4°) complexes just mentioned.

Treatment of the oxo-dienyl complex **5a** with 1 equiv of *t*-BuOK in CH_2Cl_2 resulted in the rapid formation of a red solution that darkened after several minutes; reaction workup and ^{1}H NMR analysis of the resulting material did not give any identifiable complex. This behavior contrasts completely with that of the related iridium derivative.[5,6] Thus the reaction was repeated but at low temperature (−60 °C). Subsequent solution workup allowed the isolation of a red microcrystalline substance, for which a ^{1}H NMR spectrum was rapidly recorded. The data confirmed the formation of [Cp*Rh-(η^4-C_7H_6O)] (**6a**), particularly when compared with those of the Cp*Ir analogue **2a**. For **6a** in toluene-d_8, six multiplets are visible in the region 3.5−5.4 ppm. The two resonances at 5.36 and 4.35 ppm showing a small mutual coupling J_{H-H} = 1.6 Hz are attributed to the geminal protons of the exocyclic double bond. Further the signals at 4.86 and 4.45 ppm were attributed to the two internal protons of the diene unit, whereas the two other multiplets at 3.71 and 3.58 ppm were assigned to the protons at the diene termini. Unfortunately **6a** decomposed rapidly in solution; hence its ^{13}C NMR spectrum could not be recorded.

Although the IR and ^{1}H NMR spectra confirmed formation of **6a**, it was thought that the Me-substituted rhodium *o*-QM complex [Cp*Rh(η^4-$(Me)_2C_7H_4O$)] (**6b**) might be more stable. In fact, treatment of the requisite phenoxo complex complex **5b** with 1 equiv of *t*-BuOK in CH_2Cl_2 at −20 °C resulted in the formation of a red solution. Reaction workup followed by hexane extraction and subsequent solvent evaporation provided red crystals of **6b**, which was stable enough to be completely characterized by spectroscopic methods and elemental analysis. The ^{1}H NMR of **6b** recorded in toluene-d_8 showed the presence of two pair of triplets centered at δ 4.89 and 4.57 ppm, (J_{H-H} = 5.6 Hz) attributed to the two internal protons of the diene unit, whereas the two other doublets at 3.63 and 3.56 ppm (J_{H-H} = 5.6 Hz) were assigned to the protons at the diene termini. Two additional singlets assigned to the two methyl groups are visible at δ 2.49 and 1.71 ppm, respectively, and finally the methyl protons of the bonded (η^5-Cp*) displayed a singlet centered at 1.67 ppm. The ^{13}C NMR spectrum was in complete accord with the proposed formula. Most remarkably the C═O function of the η^4-diene unit exhibited a singlet centered at δ 182.18 ppm, diagnostic of exocyclic carbonyl function of such rare *o*-QM complexes.[5,6]

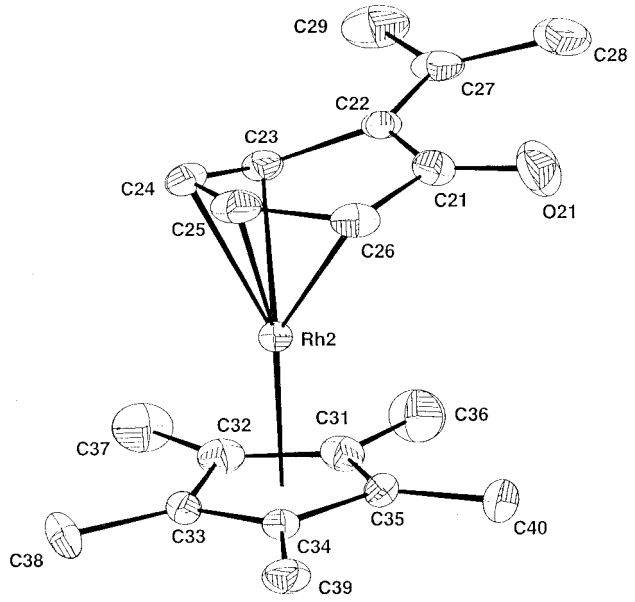


Figure 2. X-ray molecular sructure of [Cp*Rh (η^4-$(Me)_2C_7H_4O$)] (**6b**) with atom-numbering system. ORTEP view shows thermal ellipsoids at 30% probability. Depicted is one of the two independent molecules, without hydrogens for clarity.

The X-ray molecular structure of **6b** confirmed the spectroscopic studies and provided comparative data on the effects of the Cp*Rh and Cp*Ir fragments on the *o*-QM π-system. Convenient crystals of **6b** were obtained from a concentrated hexane solution at −20 °C. The compound crystallizes in the triclinic unit cell space group $P\bar{1}$. There are two independent molecules in the unit cell. Crystallographic data for **6b** are shown in Table 1. Selected bond distances and angles for **6b** are shown in Table 3. The structure of **6b** (Figure 2) clearly shows the loss of aromaticity in the six-membered ring and coordination of Cp*Rh to four ring carbons. Loss of aromaticity is manifested by the irregularity of the C−C bond distances; the length of the uncoordinated bond C(21)−C(22) is 1.48(1) Å, whereas the C(21)−O(21) bond

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Table 1. Crystal Data for 5b and 6b

fw	460.12	372.3
a (Å)	9.125(2)	8.775(4)
b (Å)	13.966(3)	13.159(3)
c (Å)	31.289(6)	15.042(2)
α (deg)	90	91.32(1)
β (deg)	90	98.77(2)
γ (deg)	90	93.87(3)
V (Å^3)	3987(1)	1711.7(9)
Z	8	4
cryst syst	orthorhombic	triclinic
space group	*Pbca*	$P\bar{1}$
linear abs coeff μ (cm^{-1})	8.8	9.78
density ρ (g.cm^{-3})	1.53	1.44
diffractometer	CAD4 Enraf-Nonius	
radiation	Mo Kα (λ = 0.71069 Å)	
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ
θ limits (deg)	1−25	1−25
temp of measurement	295 K	295 K
octants collected	0,10; 0,16; 0,37	0,10; −15,15; −17,17
no. of data collected	3982	6451
no. of unique data collected	3501	6019 (R_{int} = 0.02)
no. of unique data used for refinement	2212 $(F_o)^2 > 3\sigma(F_o)^2$	3536 $(F_o)^2 > 3\sigma(F_o)^2$
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0488	0.0486
R_w[a] $= [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.0582	0.0559
S	1.06	1.09
extinction param	70	11
no. of variables	223	381
Δ_{min} (e Å^{-3})	−0.98	−1.37
Δ_{max} (e Å^{-3})	0.65	0.82

[a] $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w' = 1/\sum rA_rT_r(X)$ with 3 coefficients 7.20, 0.988, and 5.28 for a Chebyshev series, for which X is F_c/F_c(max).

distance is 1.24(1) Å, which is characteristic of a C═O double bond and in the range expected for substituted quinones. Further the C(22)−C(27) bond distance is 1.35(1) Å, slightly longer than that reported for the same double bond in the iridium congener [1.34(1) Å].[5,6] The distances from the metal to the centers of the π-bonded carbons is 1.71 Å for the quinonoid ligand and 1.83 Å for the η-C_5Me_5 ligand. The uncoordinated part of the quinonoid ligand is bent away from the metal, as the dihedral angle of the "hinge" across C(23)−C(26) is 25°. This value is less than that observed for the related iridium complex, 33°.[5,6] In summary it is evident that the structural data suggest that the *o*-QM ligand is more stabilized by the iridium moiety than by the rhodium one. This difference is also noted in the reactivities of *o*-QM complexes of the two metals.

To our knowledge this is the first X-ray structure of a rhodium−*o*-QM complex and the second known complex displaying an *o*-QM unit as a ligand after the iridium congener.[4]

Preliminary experiments involving carbonylation of **6b** in C_6D_6 solution at 1 atm and room temperature for 60 min gave a dark red solution, the ^{1}H NMR spectrum of which showed the formation of 2-isopropylphenol and presumably the carbonyl rhodium complex Cp*Rh(CO)$_2$. The carbonylation reaction was slower in $CDCl_3$, providing 2-propanol and a singlet at 2.13 ppm which corresponds to the methyl groups of Cp*Rh(CO)$_2$.[10] The related iridium complex, under the same experimental conditions, remained inert even after 2 days. Furthermore, unlike the iridium *o*-QM complex, the Rh−*o*-QM complex **6b** did not give identifiable products with electron-poor alkenes and alkynes. For instance, treatment of **6b** with *N*-maleimide or methyl propynoate resulted in decomposition of the starting material.

Conclusions

In this paper, the first *o*-QM complexes of rhodium are reported, including an X-ray structure of one derivative and preliminary evaluation of their reactivity. These studies show that the Cp*Rh moiety allows observation of *o*-QM complexes, although the products are less stable than the iridium congeners. Such a stability trend has been recently reported by Sheldrick and coworkers in the case of arene π-complexes of amino acids to Cp*M moieties (M = Rh, Ir).[11] These authors have shown that the iridium complexes are more stable, a behavior confirmed by their theoretical calculations. Our future efforts will be directed toward the study of the catalytic behavior of these *o*-QM complexes, thus taking advantage of their enhanced reactivity.

Experimental Section

General Procedures. All manipulations were carried out under argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. Acetone was distilled over K_2CO_3, hexane over Na, and CH_2Cl_2 over CaH_2. All reagents obtained from commercial sources were used without further purification. ^{1}H NMR were recorded on Bruker AM 250 and 400 MHz instruments. ^{1}H NMR chemical shifts are reported in parts per million referenced to residual solvent proton resonance.

Synthesis of [Cp*Rh(η^5-(Me)C_5H_4O)][BF_4] (5a). A solution of $AgBF_4$ (195 mg, 1.0 mmol) in acetone (10 mL) was added to [(η^5-C_5Me_5)Ir(μ-Cl)Cl]$_2$ (199 mg, 0.25 mmol) in acetone (20 mL), to give rapidly a white precipitate of AgCl. The reaction mixture was stirred for 15 min, then the resulting orange solution of [(η^5-C_5Me_5)Ir(acetone)$_3$][BF_4]$_2$ was filtered into a dry Schlenk tube kept under argon. To this orange solution was then added *o*-cresol (110 mg, 1.0 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 2 h, during which the solution became lighter and a white precipitate was obtained. The reaction mixture was treated with NEt_3 (100 μL) for 1 h before the light yellow solution was concentrated under vacuum. Subsequent addition of Et_2O (40 mL) afforded more white precipitate. This compound was separated and washed several times with Et_2O and dried under vacuum, leaving **5a**. Yield: 85% (183 mg). Spectroscopic data for **5a**: IR (KBr disk)/cm^{-1} ν(C═O) 1615, ν(BF_4^-) 1080; ^{1}H NMR (CD_3CN, 250 MHz) δ 1.71 (s, 3H, −CH_3), 2.10 (s, 15H, η^5-C_5Me_5), 5.53 (d, 1H dienyl C−H), 5.53 (m, 3H dienyl C−H); ^{13}C{^{1}H} NMR (62.87 MHz, (CD_3)$_2$-CO) δ 161.89 (C═O), 107.47 (d, J_{Rh-C} = 3 Hz, C−*Me*, dienyl,), 105.81 [d, J_{Rh-C} = 5 Hz, $C_5(CH_3)_5$, −C═C−], 104.72, 103.98, 92.05, 88.92 (d, J_{Rh-C} = 6 Hz, −C═C−, dienyl), 9.51 [$C_5(CH_3)_5$], 9.10 (−CH_3). Anal. Calcd for $C_{17}H_{22}BF_4RhO$: C, 47.22; H, 5.09. Found: C, 47.12; H, 5.17.

Synthesis of [Cp*Rh(η^5-(*i*-Pr(C_5H_4O)][BF_4] (5b). This compound was prepared in a fashion similar to that used for **5a** and isolated as a yellow microcrystalline solid in 87% yield (200 mg): IR (KBr disk)/cm^{-1} ν(C═O) 1615, ν(BF_4^-) 1080; ^{1}H NMR (CD_3CN, 250 MHz) δ 1.71 (s, 3H, −CH_3), 2.10 (s, 15H, η^5-C_5Me_5), 5.53 (d, 1H dienyl C−H), 5.53 (m, 3H dienyl C−H); ^{13}C{^{1}H} NMR (62.87 MHz, (CD_3)$_2$CO) δ 160.54 (C═O), 118.87 (d, J_{Rh-C} = 2 Hz, C-*i*-Pr, dienyl), 106.97 [d, J_{Rh-C} = 6 Hz, $C_5(CH_3)_5$, −C═C−], 104.22, 100.95, 92.38, 88.67 (d, J_{Rh-C} = 6 Hz, −C═C−, dienyl), 27.24 (−CH, *i*-Pr), 22.02 (−CH_3, *i*-Pr),

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Table 2. Seleted Bond Distances (Å) and Angles (deg) for 5b

Rh(1)−C(1)	2.475(7)	Rh(1)−C(2)	2.292(6)	Rh(1)−C(3)	2.239(6)
Rh(1) − C(4)	2.206(6)	Rh(1)−C(5)	2.206(6)	Rh(1)−C(6)	2.241(6)
Rh(1)−C(11)	2.137(7)	Rh(1)−C(12)	2.146(7)	Rh(1)−C(13)	2.184(6)
Rh(1)−C(14)	2.166(7)	Rh(1) − C(15)	2.166(6)	O(1)−C(1)	1.236(8)
C(1)−C(2)	1.47(1)	C(1)−C(6)	1.42(1)	C(2)−C(3)	1.394(9)
C(2)−C(7)	1.51(1)	C(3)−C(4)	1.418(9)	C(4)−C(5)	1.43(1)
C(5)−C(6)	1.40(1)	C(7)−C(8)	1.54(1)	C(7)−C(9)	1.54(1)
C(11)−C(12)	1.43(1)	C(11)−C(15)	1.42(1)	C(11)−C(16)	1.49(1)
C(12)−C(13)	1.41(1)	C(12)−C(17)	1.49(1)	C(13)−C(14)	1.40(1)
C(13)−C(18)	1.51(1)	C(14)−C(15)	1.43(1)	C(14)−C(19)	1.51(1)
C(15)−C(20)	1.48(1)				

C(2)−C(1)−C(6)	114.1(6)	C(2)−C(1)−O(1)	122.8(7)
O(1)−C(1)−C(6)	122.6(7)	C(2)−C(7)−C(8)	113.8(6)
C(2)−C(7)−C(9)	110.9(6)	C(8)−C(7)−C(9)	110.1(7)
C(1)−C(6)−C(5)	124.2(6)	C(1)−C(2)−C(3)	120.2(6)

Table 3. Seleted Bond Distances (Å) and Angles (deg) for 6b

Molecule (a)

Rh(1)−C(3)	2.163(7)	Rh(1)−C(4)	2.141(7)	Rh(1)−C(5)	2.143(7)
Rh(1)−C(6)	2.186(7)	Rh(1)−C(11)	2.168(7)	Rh(1)−C(12)	2.182(7)
Rh(1)−C(13)	2.248(7)	Rh(1)−C(14)	2.289(7)	Rh(1)−C(15)	2.180(7)
O(1)−C(1)	1.23(1)	C(1)−C(2)	1.48(1)	C(1)−C(6)	1.45(1)
C(2)−C(3)	1.48(1)	C(2)−C(7)	1.36(1)	C(3)−C(4)	1.43(1)
C(4)−C(5)	1.39(1)	C(5)−C(6)	1.43(1)	C(7)−C(8)	1.48(2)
C(7)−C(9)	1.50(2)	C(11)−C(12)	1.42(1)	C(11)−C(15)	1.43(1)
C(12)−C(13)	1.43(1)	C(13)−C(14)	1.44(1)	C(14)−C(15)	1.43(1)

C(1)−C(2)−C(3)	112.2(6)	C(2)−C(1)−C(6)	115.5(6)	O(1)−C(1)−C(2)	126.2(8)
C(7)−C(2)−C(1)	123.9 (8)	C(8)−C(7)−C(9)	114.8(9)		

Molecule (b)

Rh(2)−C(23)	2.189(7)	Rh(2)−C(24)	2.112(8)	Rh(2)−C(25)	2.115(8)
Rh(2)−C(26)	2.178(8)	Rh(2)−C(31)	2.163(8)	Rh(2)−C(32)	2.143(7)
Rh(2)−C(33)	2.262(7)	Rh(2)−C(34)	2.244(7)	Rh(2)−C(35)	2.183(7)
O(21)−C(21)	1.24(1)	C(21)−C(22)	1.48(1)	C(21)−C(26)	1.45(1)
C(22)−C(23)	1.48(1)	C(22)−C(27)	1.35(1)	C(23)−C(24)	1.42(1)
C(24)−C(25)	1.41(1)	C(25)−C(26)	1.40(1)	C(27)−C(28)	1.48(2)
C(27)−C(29)	1.51(2)	C(31)−C(32)	1.42(1)	C(31)−C(35)	1.40(1)
C(32)−C(33)	1.45(1)	C(33)−C(34)	1.41(1)	C(34)−C(35)	1.47(1)

C(21)−C(22)−C(23)	112.1(7)	C(22)−C(21)−C(26)	115.4(8)
O(21)−C(21)−C(22)	124.0(8)	C(27)−C(22)−C(21)	125.4 (8)
C(28)−C(27)−C(29)	114.9(9)		

19.46 (−CH_3, *i*-Pr), 9.06[$C_5(CH_3)_5$]. Anal. Calcd for $C_{19}H_{26}BF_4RhO$: C, 49.60; H, 5.70. Found: C, 49.47; H, 5.77.

Synthesis of [Cp*Rh (η^4-C_7H_6O)] (6a). To a solution of [Cp*Rh(η^5-(Me)(C_5H_4O)][BF_4] (**5a**) (250 mg, 0.57 mmol) in CH_2Cl_2 (20 mL) was added *t*-BuOK (67 mg, 0.6 mmol), and the temperature of the reaction was kept at −60 °C. The resulting red solution was stirred for 20 min before the reaction mixture was concentrated under vacuum. Extraction of the residue by hexane (50 mL), concentration of the hexane solution, and storage of the residue under vacuum afforded **6a** as a red microcrystalline material, which decomposes in solution (unstable complex): yield 69%; IR (KBr) ν(CO) 1630; ^{1}H NMR (toluene-d_8) δ 1.75 (s, 15H, η^5-Cp*), 3.71 (d, J = 5.4 Hz, 1H, diene), 3.58 (d, J = 5.4 Hz, 1H, diene), 4.35 (d, J = 1.6 Hz, 1H, =CH_2 exo), 4.45 (d, J = 5.2 Hz, 1H, diene), 4.86 (d, J = 5.2 Hz, 1H, diene). Anal. Calcd for $C_{17}H_{21}RhO$: C, 59.31; H, 6.15. Found: C, 58.29; H, 6.60.

Synthesis of [Cp*Rh (η^4-(Me2)-C_7H_4O)] (6b). In a manner similar to that used for **6a**, **5b** (250 mg, 0.54 mmol) was used to make **6b**, which was isolated as a red microcrystalline solid (170 mg, 85%). Spectroscopic data for **6b**: IR(KBr) ν(CO) 1632 (shp), ν(C=C) = 1600 (s); ^{1}H NMR (toluene-d_8) δ 1.65 (s, 15H, −Cp*), 1.70 (s, 3H, −CH_3), 2.50 (s, 3H, −CH_3) 3.55 (d, J = 5.2 Hz, 1H, diene-H) 3.63 (d, J = 5.2 Hz, 1H, diene-H), 4.60 (t, J = 5.2 Hz, 1H, diene-H), 4.95 (t, J = 5.2 Hz, 1H, diene-H); ^{13}C NMR (toluene-d_8) δ 10.04 (s, −CH_3, Cp*), 21.46 (s, −CH_3), 21.60 (s, −CH_3), 59.77 (d, J_{Rh-C} = 12 Hz, C-diene), 69.26 (d, JRh−C = 12 Hz, C-diene), 75.85 (d, JRh−C = 12 Hz, C-diene), 79.22 (d, J_{Rh-C} = 8 Hz, C-diene), 95.47 (d, J_{Rh-C} = 6 Hz, C=C, −Cp*), 137.8 (C=), the signal for =CMe_2 was not observed probably because it was obscured by solvent resonances, 182.17 (s, C=O). Anal. Calcd for $C_{19}H_{25}RhO$: C, 61.62; H, 6.21. Found: C, 61.23; H, 6.85.

X-ray Crystal Structure Determination for 5b and 6b. Suitable crystals **5b** were obtained using slow diffusion techniques from CH_2Cl_2/ether solution, while those of **6b** were obtained from cooling a concentrated hexane solution. The selected crystal of complex **5b** or **6b** was mounted on top of a glass rod. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collection. The ψ-scan curve of **5b** or **6b** was flat; hence no absorption correction was applied. Complete crystallographic data and collection parameters for **5b** and **6b** are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[12] Scattering factors and corrections for anomalous dispersion were taken from ref 13. The structures of these compounds were refined by full-matrix least-squares with anisotropic thermal parameters for all non hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. Fractional

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(13) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

parameters, anisotropic thermal parameters, and all bond lengths and angles are given in the Supporting Information for complexes **5b** and **6b**.

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Supporting Information Available: X-ray crystallographic data for the structure determinations of **5b** and **6b**. The material is available free of charge via the Internet at http://pubs.acs.org.

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