groups with idealized geometry (d(C–H) = 1.08 Å, tetrahedral angle). Final R values are $R(F)$ 0.028 and $R_w(F)$ = 0.034 for 1795 independent reflections. A final F synthesis clearly showed the bridging hydrides as the strongest residual maxima, both with 0.64 e/Å³. Refinements were carried out with the SHELX76 program system. Final atom parameters are collected in Table III.

Supplementary Material Available: Tables of positional and thermal parameters, bond distances and angles, and least-squares planes (10 pages); listings of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

Bis(phenol) Adduct of Cp*Ru(η5-oxocyclohexadienyl), a Doubly Symmetrical Hydrogen-Bridged Ruthenium Complex

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Reaction of [Cp*Ru(OMe)]₂, Cp* = η5-C₅Me₅, (1) with phenol leads to the title complex Cp*Ru-(C₆H₅=O)···(H-OC₆H₅)₂ (2) as an integral molecule in solution and in the solid state. The structure of 2 was elucidated by single-crystal X-ray analysis (orthorhombic space group *Pbca*, a = 14.306 (5), b = 21.240 (4), c = 16.326 (4), Z = 8) and consists of two phenols hydrogen bonded to an oxocyclohexadienyl unit complexed to Cp*Ru. The C–C– and C–O distances in the oxocyclohexadienyl part are close to the values typical for an aromatic η6-ligand. Similar π-complexes are formed with 2-hydroxyacetophenone, salicylaldehyde, and 5-hydroxy-1,4-naphthoquinone.

The coordinatively unsaturated Ru complex [Cp*Ru(OMe)]₂ (Cp* = η5-C₅Me₅)[1-3] (1) in solution readily exchanges bridging methoxo groups as shown by rapid exchange of complexed CH₃O (δ 4.9 ppm) for CD₃O in benzene-d_6.[1,2] With higher alcohols an equilibrium is established, where the alkoxide of the more acidic (lower) alcohol predominates.[3]

In the light of these findings rapid exchange of the bridging alkoxide can be expected with the more acidic phenol. In contrast to aliphatic alcohols, phenol can act either as an alcohol, forming the binuclear bridged σ-complex analogous to 1, structure type I, or as an acid and an arene, giving rise to mononuclear π-complexes, structure type II (Scheme I).

The structural dichotomy similarly holds for aromatic α-hydroxy carbonyl compounds like salicylaldehyde or 2-hydroxyacetophenone, which likewise offer the possibility of forming either mononuclear σ-complexes with Ru coordinated to two oxygen atoms (type IV in Scheme III), cationic π-complexes of type II, or neutral oxocyclohexadienyl complexes III. Structure type IV is represented by the complex Cp*Ru(acac)[4] and derivatives,[5] which are readily obtained from 1 and the respective β-dicarbonyl compounds. Type II is formed by treating 1 with protic acids[6] in the presence of an arene.[7-9] Type III can be obtained by deprotonation of II similar to CpFe(phenol), which gave the neutral η2-6 oxocyclohexadienyl complex with base.[10] The same structure type was found in the complex Cp*Ru(2,6-di-*t*-BuC₆H₃=O), formed in the reaction of [Cp*RuCl]₄ with (2,6-di-*t*-Bu)phenolate.[3]

We report on the reaction of the methoxo complex 1 with phenol and carbonyl derivatives thereof. In any case

Scheme I
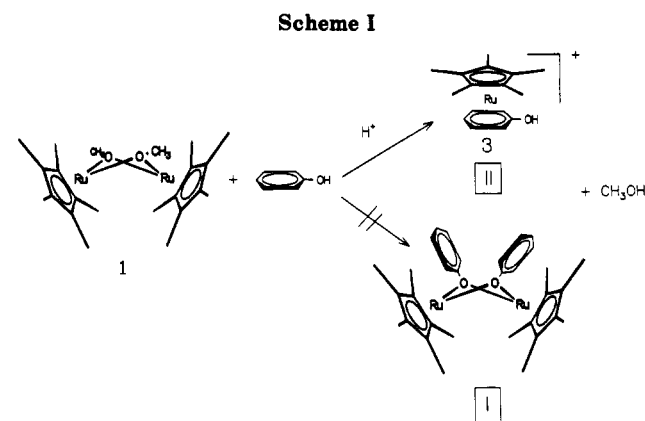
sandwich complexes of structure types II and III were formed.

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(1) Koelle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* 1988, 549.

(2) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* 1989, *362*, 383.

(3) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Don Tilley, T.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* 1989, *111*, 4712.

(4) Koelle, U.; Kossakowski, J.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* 1990, *29*, 773.

(5) Koelle, U.; Rietmann, C. To be published.

(6) There is spectroscopic evidence for cationic solvent complexes [Cp*(Ru(S)]⁺ formed from 1 and protonic acid in e.g. acetone solution. These species can be shown by NMR to react rapidly with arenes to the cationic π-complexes. However, we have not been able to isolate a solvent complex salt. The experiment described in ref 9 to produce the solvent complex ion [Cp*Ru(MeOH)₃]⁺, i.e. protonation of 1 in THF/methanol, in our hands exclusively and quantitatively gave the cluster cation [(Cp*Ru)₃(MeO)₂]⁺ ⁷), easily identified through its characteristic OMe absorption at δ 5.06 (acetone-d_6). Note that this cation also reacts with arenes to form the respective arene π-complexes.[7]

(7) (a) Koelle, U.; Kossakowski, J.; Boese, R. *J. Organomet. Chem.* 1989, *378*, 449. (b) Koelle, U. Conf. Organomet. Chem., Turino, 1988, Abstract XXVI.

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†Institute for Inorganic Chemistry.
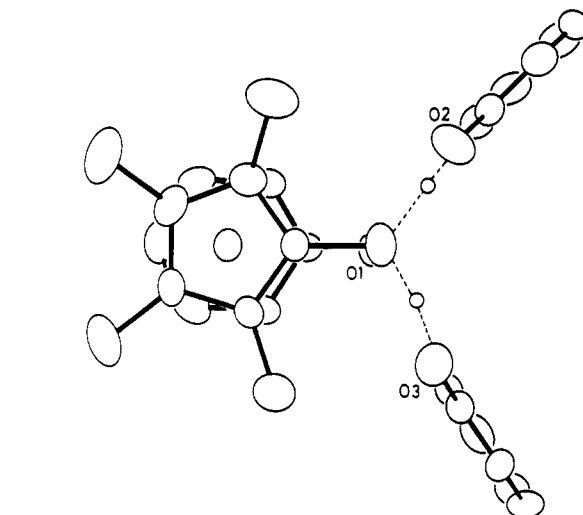‡Institute for Organic Chemistry.

Scheme II
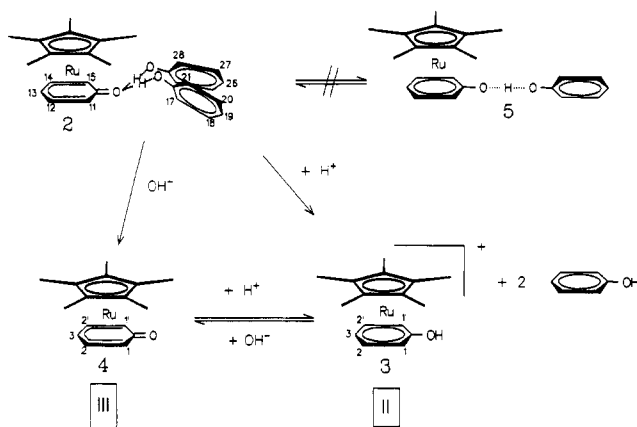
Results

Reaction with Phenol. Reaction of 1 with phenol[9] in pentane proceeds slowly at ambient temperature and requires 3 mol of phenol per mole of Ru to go to completion. Less phenol yields the same product but leaves unreacted 1. From the ensuing weakly colored solution an off-white solid was obtained after crystallization or column chromatography. The ^{1}H NMR spectrum shows a singlet for the Cp* protons and two sets of multiplets for phenolic protons in a ratio Cp* (δ = 1.9, CD$_2$Cl$_2$) to complexed phenol ($\delta \approx$ 5, m) to uncomplexed phenol ($\delta \approx$ 7, m) as 1:1:2, indicating the composition Cp*Ru(C$_6$H$_5$O)·2PhOH (2) as has been observed by Chaudret.[9] In this solvent the protons due to complexed phenol (or oxocyclohexadienyl respectively, see below) appear as a multiplet of two plus three protons (Table I). Addition of excess phenol to the NMR solution increases the intensity of the signals for uncomplexed phenol, indicating rapid exchange between phenol involved in hydrogen bonding and phenol free in solution. However, the ratio 1:2 of complexed to uncomplexed phenol in 2 did not change after repeated recrystallization from dichloromethane/ether or acetone/ether, nor did phenol sublime from the sample under vacuum. The solid compound completely lacks the smell of phenol. The adduct 2 thus behaves as an integral compound in solution and in the solid state. Similar strong hydrogen bonding of phenols or acidic alcohols to the oxygen atom of Rh[11] or Pd[12] alkoxo complexes has been observed.

The phenolic protons appear as a single, somewhat broadened, absorption in the ^{1}H NMR spectrum (CD$_2$Cl$_2$) at δ = 9.8. Medium strong hydrogen bonding is inferred from a broadened band at 3590 cm^{-1} in the infrared (CH$_2$Cl$_2$ solution), which did not change on dilution. Along with bands at 1245, 1275, and 1300 cm^{-1} in the region of phenolic ν_{CO} a characteristic band, not present in phenol, is observed at 1515 cm^{-1} and has to be compared to the ν_{CO} band at 1542 cm^{-1} in 4.

Protic Equilibria. Acidification of the adduct 2 with mineral acid liberates excess phenol and generates the known cation complex 3,[13] which can be precipitated as the hexafluorophosphate salt (Scheme II). As expected, aromatic ring protons in 3 exhibit less chemical shift

(8) Koelle, U.; Wang, M. H. *Organometallics* 1990, *9*, 195.

(9) Chaudret, B.; Xiaodong, H.; Huang, Y. *J. Chem. Soc., Chem. Commun.* 1989, 1844.

(10) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* 1979, *168*, 87.

(11) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1987, *109*, 6563.

(12) Braga, D.; Sabatino, P.; Di Bugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* 1987, *334*, C46.

(13) Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1986, *2*, 492 (Engl. Transl. UDC 542.91).

Figure 1. ORTEP drawing of phenol adduct 2. Bond lengths (Å): Ru-C(1) 2.166 (4), Ru-C(2) 2.166 (5), Ru-C(3) 2.186 (5), Ru-C(4) 2.185 (6), Ru-C(5) 2.164 (5), Ru-C(16) 2.34, Ru-C(11) 2.202 (6), Ru-C(12) 2.188 (5), Ru-C(13) 2.194 (6), C(11)-C(16) 1.432, C-(11)-C(12) 1.400 (8), C(12)-C(13) 1.39 (1), C(16)-O(1) 1.284 (7), O(1)-O(2) 2.626 (6), O(1)-O(3) 2.663 (7).
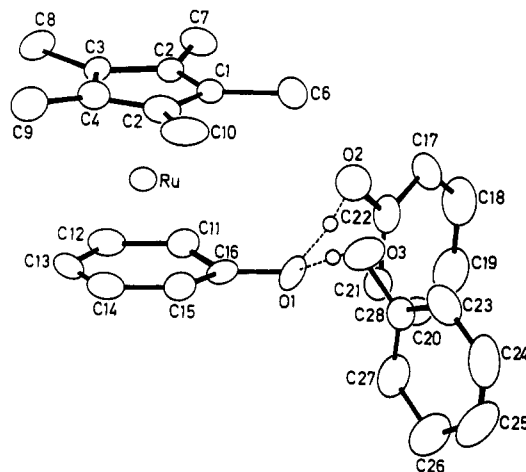
Figure 2. Top view of phenol adduct 2 showing relative orientation of phenol rings to sandwich, and Ru atom to oxocyclohexadienyl ring.

difference than in 2 and appear as a narrow multiplet of five protons centered at 5.9 ppm. Addition of NaOH to the aqueous acetone solution restores a spectrum closely resembling that of 2, which is assigned to the oxocyclohexadienyl complex 4. Compound 4 can be extracted into methylene chloride from alkaline aqueous solution, albeit in poor yield. Obviously there is strong hydrogen bonding to the solvent, which renders the neutral complex better soluble in water than in organic solvents.

Acidimetric and alkalimetric titration in aqueous solution from acidic to alkaline and vice versa affords one single step respectively, characteristic for a medium strong acid with pK_a of 6.2 for the interconversion 3 ↔ 4, derived from the pH at half neutralization. The complexed phenol is thus a considerably stronger acid as compared to free phenol (p$K \approx$ 12).

Molecular Structure of 2. The structure of the hydrogen-bonded adduct 2 was elucidated by a single-crystal X-ray structure analysis with crystals grown from acetone/ether at 0 °C. The compound crystallizes in orthorhombic space group *Pbca* (no. 61) with a = 14.306 (5), b = 21.240 (4), and c = 16.326 (4) Å. With Z = 8 the number of electrons in the unit cell amounts to F(000) = 2144. The

Table I. ¹H NMR Shifts (δ, ppm) and Coupling Constants (Hz) of Complexes 2-11 in CD_3COCD_3

compd	Cp*	1,1'	2,2'	3	other protons
2	1.84	4.81 (dd)	5.33 (t)	5.11 (t)	6.83 (m, $H^{17,19,21...}$) 7.12 (tt, $H^{18,20...}$)
		$J_{1,1} = 5.66$, $J_{2,3} = 4.8$, $J_{1,3} = 1.3$			
3·CF₃COOH	1.99	5.86-5.96 (m)			9.0 (OH)
4	1.89	4.47 (d)	5.08 (m)		
		$J_{1,2} = 7.0$, $J_{2,3} = 4.75$, $J_{1,3} = 1.0$			
CD₃CN[a]	1.87	4.68 (d)	5.05-5.26 (m)		
		$J_{1,2} = 6.05$, $J_{2,3} = 4.84$			
THF-d_8[a]	1.88	4.48 (d)	4.92-5.05 (m)		
		$J_{1,2} = 5.9$, $J_{2,3} = 4.4$			
CDCl₃[a]	1.87	4.75 (d)	4.83 (t)	5.01 (t)	
		$J_{1,2} = 5.86$, $J_{2,3} = 4.38$, $J_{1,3} = 1.09$			

compd	Cp	1	2	3	4	other protons
8	1.89	5.66 (m)	5.90 (dt)	5.66 (m)	6.13 (dd)	2.65 (s, CH₃)
		$J_{1,2} = 6.61$, $J_{1-3} = 1.20$, $J_{2,3} = 5.41$, $J_{2,4} = 0.60$, $J_{3,4} = 6.0$				
9	1.80	4.67 (dd)	5.4 (dt)	5.22 (dt)	5.79 (dd)	2.48 (s, CH₃)
		$J_{1,2} = 6.37$, $J_{1,3} = 0.99$, $J_{2,3} = 5.36$, $J_{2,4} = 1.71$, $J_{3,4} = 5.66$				
10	1.83	4.38 (d)	5.5 (m)	5.36 (m)	5.61 (dd)	10.1 (H^5)
		6.97 ($H^{1'}$)	7.58 (H^2)	7.03 (H^3)	7.75 (H^4)	10.27 ($H^{5'}$)
		$J_{1,2} = 6.48$, $J_{2,3} = 5.86$, $J_{3,4} = 5.0$, $J_{1',2'} = 7.26$, $J_{2',3'} = 7.86$, $J_{3',4'} = 7.65$				
11	1.93	5.88-6.17 (m)				10.4 (H^5) 6 (br, OH)
12	1.85	5.29 (d)	5.4-5.7 (m)		5.83 (dd)	10.0 (H^5)
13[b]	1.47	3.9 (d)	5.83 (d)	6.7 (d)	6.43 (t)	6.17 (d) (H^5)
		$J_{1,2} = 6.78$, $J_{3,4} = 6.90$, $J_{4,5} = 6.90$				

[a] NMR shifts in different solvents (see text). [b] CD₃Cl.

molecular weight 517.6 and the volume of the unit cell of 4960.8 Å³ result in a density of 1.386 g/cm³. ORTEP drawings of the molecule are shown in Figures 1 and 2. Table II lists atomic coordinates.

The molecular arrangement consists of a Cp*Ru fragment bound to an oxocyclohexadienyl unit, which is almost symmetrically connected via two hydrogen bonds to a pair of phenol molecules. Being oriented toward the metal their planes enclose an angle of 101° and are almost perpendicular to the cyclohexadienyl plane so as to minimize steric interaction with the Cp* methyl groups. Apart from the Cp* ligand this arrangement is basically the same as one proposed for the phenol adduct Ru(H)(PPh₃)₂(π-C₆H₅=O)·2PhOH (5) by Wilkinson et al. in analogy to a methanol adduct Ru(H)(PPh₃)₂(π-C₆H₅=O)·MeOH (6), for which elements of an X-ray crystal structure analysis were reported.[14] The C16-O1 bond in 2 (1.284 (7) Å) is clearly shorter than a typical phenolic C-O bond (1.353-1.373 Å[15]). Being very similar to the corresponding bond in 6 (1.277 Å) it is considerably longer than in a closely related oxocyclohexadienyl complex Cp*Ru(π-(2,6-di-t-Bu)(C₆H₃=O) (1.256 (4)), 7,[3] or a recently published similar oxocyclohexadienyl complex of Cp*Rh.[16] However, different from the situation in these oxocyclohexadienyl complexes, where the dienone moiety has a boat conformation and the C=O group is bent outward from the cyclohexadienyl plane by 15-20°, this segment is much closer to planarity in 2. Atoms C11-C15 virtually lie in a plane and the distance of the defining atoms from their best plane does not exceed 0.011 Å. The plane defined by C11, C15, C16, and O1 is bent from this plane not more than 4°. Thus the distance of C16 from the cyclohexadienyl plane is 0.1 and for O1 it is 0.15 Å. As a result the distances of Ru to C11-C15 are quite similar (about

2.2 Å) and only the one to C16 (2.34 Å) is significantly longer. Accordingly, the projection of Ru on the plane C11-C16 is not more than 0.07 Å displaced from the center of gravity (away from the oxygen atom). In accord with the near planarity of the oxocyclohexadienyl segment C=C bond lengths within this segment (C16-C15(11) (1.42) > C15(12)-C14(11) (1.41) > C13-C14(12) (1.39)) are shorter and closer to each other than the corresponding distances in 7 (1.467 > 1.418 > 1.401). The oxocyclohexadienyl oxo to phenol oxygen distances of 2.626 (6) and 2.663 (7) Å are in agreement with medium to strong hydrogen bonds.[17] Electron density assigned to the bridging hydrogen atoms could be located close to the O-O vectors and has been included with fixed positions in the final refinements (see Figure 2).

Reaction with Carbonylic Phenols. o-Hydroxyacetophenone readily reacts with 1 in ether. From the upfield shift of the aromatic protons by 2.5-3.5 ppm formation of a π-complex is inferred. A characteristic feature of the ¹H NMR spectrum in the aromatic region is a doublet at δ 4.67 ppm assigned to H¹ (Scheme III, R = CH₃), the terminal proton of a dienyl system, which is taken as indicative for a oxocyclohexadienyl structure 8. Addition of acid followed by PF₆⁻ metathesis precipitates the phenolic cation 9.

The reaction with salicylaldehyde was found to be more complicated. An excess of the phenolic component added to 1 in ether precipitated a product which contained, according to its ¹H NMR spectrum, complexed as well as uncomplexed salicylaldehyde in a 1:1 ratio. However, on attempted recrystallization decomposition occurred, which means the adduct 10 in this case is far less stable than for simple phenol. Again, addition of excess salicylaldehyde to an NMR solution let the signals due to the uncomplexed phenolic aldehyde grow, signalizing rapid exchange on the NMR time scale. The assignment for the aldehydic proton at δ 10.27 was made in that way. A pure phenol derivative 11 could be obtained as a PF₆⁻ salt after acidification. This

(14) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995.

(15) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

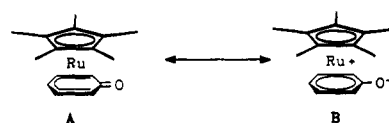(16) El-Amouri, H.; Gruselle, M.; Jackson, P. A.; Gérard, J.; Vaisserman, J. *Organometallics* **1990**, *9*, 2871.

(17) Vinogradov, S. N.; Linell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: New York, 1971; p 177 ff.

Table II. Atom Coordinates and Isotropic Thermal Parameters

	x/a	y/b	z/c	U
Ru	1.11960 (2)	0.15962 (2)	0.23470 (3)	0.0425 (2)
O(1)	0.7670 (3)	0.7903 (2)	0.5994 (2)	0.067 (3)
O(2)	0.6579 (3)	1.1780 (2)	0.5869 (3)	0.090 (3)
O(3)	1.1484 (4)	1.1453 (3)	0.5192 (3)	0.108 (4)
C(1)	1.0096 (3)	0.8212 (3)	0.7008 (3)	0.053 (3)
C(2)	1.0055 (3)	0.7832 (3)	0.7716 (3)	0.047 (3)
C(3)	1.0038 (4)	0.8234 (3)	0.8411 (4)	0.059 (4)
C(4)	1.0053 (4)	0.8872 (3)	0.8123 (4)	0.059 (4)
C(5)	1.0084 (3)	0.8848 (3)	0.7246 (4)	0.057 (4)
C(6)	1.0163 (4)	0.7964 (3)	0.6148 (4)	0.070 (4)
C(7)	1.0093 (4)	0.7133 (3)	0.7755 (4)	0.077 (5)
C(8)	1.0031 (5)	0.8017 (4)	0.9284 (4)	0.092 (5)
C(9)	1.0093 (5)	0.9441 (3)	0.8637 (5)	0.095 (6)
C(10)	1.0143 (4)	0.9404 (3)	0.6696 (5)	0.088 (5)
C(11)	0.7650 (4)	0.7738 (3)	0.7439 (3)	0.055 (4)
C(12)	0.7571 (4)	0.7984 (3)	0.8232 (4)	0.066 (4)
C(13)	0.7529 (4)	0.8629 (4)	0.8354 (4)	0.068 (4)
C(14)	0.7590 (4)	0.9028 (3)	0.7686 (5)	0.064 (4)
C(15)	0.7661 (4)	0.8782 (3)	0.6886 (4)	0.057 (4)
C(16)	0.7631 (4)	0.8128 (3)	0.6724 (4)	0.052 (3)
C(17)	0.6809 (5)	1.0732 (3)	0.5520 (4)	0.074 (5)
C(18)	0.7394 (7)	1.0244 (3)	0.5326 (4)	0.091 (6)
C(19)	0.8340 (7)	1.0330 (4)	0.5298 (4)	0.092 (6)
C(20)	0.8695 (4)	1.0918 (4)	0.5455 (4)	0.082 (5)
C(21)	0.8126 (5)	1.1410 (3)	0.5654 (3)	0.065 (4)
C(22)	0.7176 (4)	1.1314 (3)	0.5681 (3)	0.059 (4)
C(23)	1.1674 (6)	1.0996 (3)	0.6475 (5)	0.093 (6)
C(24)	1.2221 (9)	1.0801 (4)	0.7105 (5)	0.114 (8)
C(25)	1.316 (1)	1.0864 (4)	0.7066 (6)	0.124 (8)
C(26)	1.3538 (6)	1.1124 (4)	0.6389 (7)	0.112 (7)
C(27)	1.3008 (6)	1.1332 (3)	0.5741 (4)	0.079 (5)
C(28)	1.2048 (5)	1.1264 (3)	0.5789 (4)	0.072 (5)
H(11)	0.7723	0.7271	0.7363	0.0380
H(12)	0.7543	0.7691	0.8709	0.0380
H(13)	0.7456	0.8808	0.8913	0.0380
H(14)	0.7579	0.9494	0.7757	0.0380
H(15)	0.7735	0.9079	0.6413	0.0380
H(17)	0.6120	1.0660	0.5545	0.0380
H(18)	0.7134	0.9818	0.5207	0.0380
H(19)	0.8775	0.9974	0.5169	0.0380
H(20)	0.9384	1.0991	0.5432	0.0380
H(21)	0.8398	1.1836	0.5779	0.0380
H(23)	1.0981	1.0946	0.6515	0.0380
H(24)	1.1926	1.0613	0.7602	0.0380
H(25)	1.3559	1.0720	0.7529	0.0380
H(26)	1.4238	1.1171	0.6351	0.0380
H(27)	1.3309	1.1524	0.5245	0.0380
H(61)	0.9613	0.8150	0.5853	0.0380
H(62)	1.0752	0.8143	0.5923	0.0380
H(63)	1.0167	0.7509	0.5978	0.0380
H(71)	0.9556	0.6988	0.7414	0.0380
H(72)	1.0693	0.7017	0.7487	0.0380
H(73)	1.0064	0.6865	0.8261	0.0380
H(81)	0.9467	0.7748	0.9340	0.0380
H(82)	1.0608	0.7756	0.9350	0.0380
H(83)	1.0023	0.8305	0.9773	0.0380
H(91)	0.9533	0.9414	0.9003	0.0380
H(92)	1.0674	0.9394	0.8974	0.0380
H(93)	1.0103	0.9886	0.8437	0.0380
H(101)	0.9583	0.9668	0.6836	0.0380
H(102)	1.0723	0.9631	0.6866	0.0380
H(103)	1.0160	0.9386	0.6087	0.0380
H(33)	0.8240	0.8300	0.5294	0.0380
H(22)	0.8110	0.7339	0.5857	0.0380

Scheme III

Scheme IV

Scheme V

in turn was converted to the cyclohexanone form 12 on treatment with hydroxide or *n*-BuLi.

Finally, reaction of 1 with 5-hydroxynaphthoquinone was investigated. In toluene or ether as solvent a green precipitate is formed rapidly. A ^{1}H NMR spectrum (Table I) has two characteristic features. First an AB quartet with δ_A 3.9 and δ_B 5.8 ppm and second multiplets of three protons in the shift region for complexed arenes. The AB pattern is assigned to the quinone protons, since no other coupling is observed in this part. The large separation in
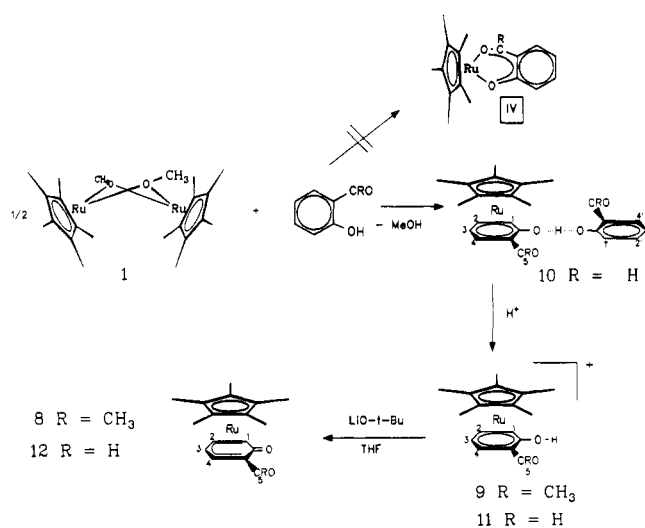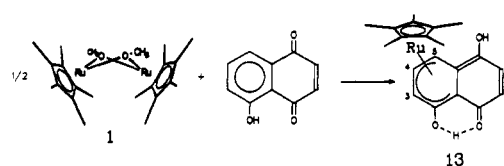
chemical shift of these protons is in marked contrast to the spectrum of the free quinone, where these protons are nearly equivalent and lends strong support to the asymmetric structure depicted in Scheme IV. Since one of the two doublets for the terminal protons of the remaining ABC system is at lowest field (6.7 vs. 6.43/6.17, Table I), characteristic for the inner proton of a dienyl system, a bonding position of the Cp*Ru as indicated appears best compatible with spectroscopic data. Hydrogen bonded protons are not observed in the spectrum. Product 13 frequently decomposed on attempted purification and could not be obtained analytically pure.

Conclusion

In all cases investigated the reaction between methoxo complex 1 and an aromatic hydroxo compound leads to π-bonding rather than to a bridged oxy complex as exemplified by the starting material 1, or a chelating coordination IV analogous to Cp*Ru(acac), even if the aromatic system is highly disturbed as in the naphthoquinone. The formation of an oxocyclohexadienyl complex through elimination of methanol as the driving force of the reaction is circumvented in the case of phenol and salicylaldehyde by formation of strong to medium hydrogen bonding to excess phenol.

Structural characteristics within the oxocyclohexadienyl ring of a bis(phenol) adduct 2 and its bonding geometry to the Ru atom closely resemble a fully symmetrical arene (phenol). Double hydrogen bonding to the formally oxo oxygen releases electron density of this oxygen in the zwitterionic form B (Scheme V) to an extent as to largely

preserve the aromaticity of this ring. ¹H NMR data, showing only small shift anisotropy of protons H¹¹ to H¹⁵ in 2, corroborate this interpretation. Interestingly this structure is favored over a hydrogen-bridged phenol phenolate (structure 5, Scheme II) as a conceivable alternative. The near-planar geometry of the oxocyclohexadienyl ligand further explains the rapid proton transfer between 3 and 4 previously noted by Chaudret et al.,[9] where only a very slight deformation of the oxocyclohexadienyl ligand may have to occur.

The relative importance of resonance forms A and B was probed by recording ¹H NMR spectra of 4 in different solvents (Table I). The spectra are similar in acetone, acetonitrile, and THF with a doublet assigned to protons in positions 1 and 1' at higher field and a multiplet at lower field for protons 2, 2', and 3 with the chemical shift sequence ortho (δ 4.45) > meta and para (δ 5.1) appropriate for a cyclohexadienylic structure. In CDCl₃ the chemical shift difference is less and the sequence is ortho (4.75) > para (4.85) > meta (5.05), conforming to an aromatic phenoxide structure. The latter obviously is stabilized through hydrogen bonding to the solvent. The NMR pattern found for 2 as well as for 4 generated from 3 in water by addition of NaOH is again indicative of the cyclohexadienylic structure.

In the carbonylic phenols, salicylaldehyde and acetophenone steric hinderance may be responsible for obviously weaker hydrogen bonding. Note that the NMR pattern of hydrogen-bonded salicylaldehyde in 10 is slightly different from the free ligand in the same solvent. Steric hinderance may prevent adduct formation in the case of acetophenone altogether and allows the oxocyclohexadienyl complex to be formed in the reaction with 1 directly.

Experimental Section

All reactions were performed under an inert atmosphere. Ligands were purified by recrystallization or distillation.

(Oxocyclohexadienyl)(pentamethylcyclopentadienyl)ruthenium–Bis(phenol) (2) and (Pentamethylcyclopentadienyl)(phenol)ruthenium Hexafluorophosphate (3). Excess phenol (260 mg, 2.76 mmol) was added to 200 mg (0.72 mmol Ru) [Cp*Ru(OMe)]₂ (1) in 50 mL of pentane. The mixture was warmed to 30 °C for 2 h after which the color changed from dark red to pale yellow. The residue was collected by filtration and washed with pentane to remove excess phenol. After recrystallization from acetone 219 mg (58%) of off-white crystals were recovered. Anal. Calcd (found): C 64.88 (64.84), H 6.19 (6.16). Complex 2 (210 mg, 0.41 mmol) was dissolved in ether and was treated with HBF₄·Et₂O. The precipitate collected was washed with ether dissolved in 50% aqueous acetone and treated with excess NH₄PF₆. After recrystallization from acetone/ether 170 mg (0.45 mmol) was obtained.

(2-Acetyloxocyclohexadienyl)(pentamethylcyclopentadienyl)ruthenium (8). An excess (305 mg, 2.24 mmol) 2-hydroxyacetophenone was added to a pentane solution of 225 mg (0.84 mmol) of 1. Within 30 min the color change from red to orange was noted. After 2 h at ambient temperature the precipitate was collected and washed with pentane. It was recrystallized from ether/pentane to give 278 mg (0.75 mmol, 90%). Anal. Calcd (found): C 58.21 (58.09), H 5.97 (5.87).

(Pentamethylcyclopentadienyl)(2-formylphenol)ruthenium Hexafluorophosphate (11). As above 250 mg (0.93 mmol) of 1 was treated in pentane with 300 mg (2.46 mmol) of salicylaldehyde. After 2 h the precipitate of 10 was collected, washed with pentane, and dried under vacuum. Addition of CF₃SO₃H to an ether solution of 10 precipitated 11·CF₃SO₃, which crystallized from acetone/ether as the acetone solvate 11·CF₃SO₃· acetone (¹H NMR). Anal. Calcd (found): C 44.56 (44.36), H 4.77 (4.29).

Structure Determination. A total of 6457 reflections (+h, +k, +l) has been collected on an ENRAF-NONIUS four cycle diffractometer at ambient temperature employing graphite monochromated Mo Kα radiation (λ = 0.710 69 Å) and $\omega/2\theta$ technique. Data have been corrected for Lorentz and polarization effects while no absorption correction has been applied (μ(Mo Kα) = 6.48 cm⁻¹).

The structure was solved by means of the heavy atom method employing the XTAL2.6 program package.[18] Hydrogen positions could partly be located in a difference Fourier map, and idealized calculated loci have been used for the remaining H atoms. A total of 3264 observed reflections ($I > 2\sigma(I)$, and sin θ/λ_{max} = 0.6) have been included in a least-squares full-matrix refinement of 289 parameters, resulting in a final R value (weighted R value) of 0.052 (R_w = 0.061). The final shift/error ratio was less than 0.08, and the final residual electron density was 0.7 e/Å³. Lists of structure factors, anisotropic thermal parameters, H atoms coordinates, and tables of bond distances and angles may be obtained through the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, FRG, by referring to the CDS No. (CSD-55064), the authors, and the bibliographical data.

Supplementary Material Available: Tables of anisotropic thermal parameters, H atom coordinates, bond distances, and bond angles (13 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

(18) *XTAL 2.6 Users Manual*; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1989.