also show similar dynamic behavior, suggests that the crystal building process (at least for small organic and organometallic molecules in the absence of strong directional intermolecular interactions) is essentially a process of molecular self-assembling based on the *shape* of the molecules or component fragments.

Acknowledgment. Financial support by Ministero della Università e della Ricerca Scientifica e Tecnologica is acknowledged.

Registry No. C_6H_6, 71-43-2; C_6Me_6, 87-85-4; $(C_6H_6)_2Cr$, 1271-54-1; $(C_6H_6)Cr(CO)_3$, 12082-08-5; $(C_6Me_6)Cr(CO)_3$, 12088-11-8; (1,3,5-$C_6H_3Me_3$)$Mo(CO)_3$, 12089-15-5.

Reactions of [Cp*RuOMe]$_2$. 7.[†] Intramolecular Transformation of a RuOCH$_3$ Unit into a Ru(CO)H Unit: Crystal and Molecular Structure of Cp*Ru(μ-H)$_2$(μ-CO)RuCp*

Byung-Sun Kang,[‡] Ulrich Koelle,*[,‡] and Ulf Thewalt[§]

Institute for Inorganic Chemistry, Technical University of Aachen, W-5100 Aachen, FRG, and Center of X-ray Crystallography, University of Ulm, W-7900 Ulm/Donau, FRG

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Electrophilic ((Me$_3$Si)$_2$NH) as well as nucleophilic (H$^-$) degradation of [Cp*RuOMe]$_2$ (1) (Cp* = η^5-C$_5$Me$_5$) affords high yields of the dimeric carbonyl hydride Cp*Ru(μ-H)$_2$(μ-CO)RuCp* (2). The course of the reaction is elucidated by labeling 1 with ^{13}CD$_3$O or ^{12}COD$_3$, and it is shown that both CO and the bridging hydrides in 2 originate from the OMe group in 1. The molecular structure of 2, determined by single-crystal X-ray diffraction (space group, *Pa*, *a* = 12.621 (3) Å, *b* = 8.574 (2) Å, *c* = 10.089 (2) Å, β = 108.56 (3)°, *Z* = 2), shows close similarity to that of the related tetrahydride Cp*Ru(μ-H)$_4$RuCp* (3) with nearly identical cell parameters and Ru$\equiv$Ru distances (2.444 Å in 2, 2.463 (1) Å in 3).

Alkoxo derivatives of the late transition metals offer an interesting pattern of reactivities.[1] Alkoxide transfer, electrophilic as well as nucleophilic substitution, insertion into the M–OR bond, and β-hydrogen abstraction with formation of hydrides are among the reactions studied. Aldehyde elimination in some cases occurs directly in the course of nucleophilic exchange of e.g. halide for alkoxide so as to give the hydride as the sole product.[2] A free coordination site has been presumed as a prerequisite for those hydrogen-transfer reactions.[1]

The dimeric alkoxo complex [Cp*RuOMe]$_2$[3,4] (1), despite its coordinative unsaturation (16 VE), is thermally stable under an inert atmosphere to about 90 °C. Aldehyde elimination with formation of a hydride was observed at 60 °C in the presence of strongly coordinating 1,5-cyclooctadiene.[5] When 1 is treated with electrophilic or nucleophilic reagents that cleave one methoxo group from the dimer, C–H bond activation of the residual methoxo group, leading to the dimeric carbonyl hydride 2, is observed and is described as follows.

Results

Reaction with (Me$_3$Si)$_2$NH. Refluxing [Cp*RuOMe]$_2$ with a molar quantity of hexamethyldisilazane in hexane (eq 1) affords, after cooling, the known complex 2[6] in up to 90% yield by direct crystallization from the reaction mixture.

$$\underset{1}{[\mathrm{Cp^*RuOMe}]_2} + (\mathrm{Me_3Si})_2\mathrm{NH} \xrightarrow[\text{reflux, 12 h}]{n\text{-hexane}} \underset{2}{\mathrm{Cp^*Ru}(\mu\text{-H})_2(\mu\text{-CO})\mathrm{RuCp^*}} + \mathrm{Me_3SiOMe} + \mathrm{Me_3SiNH_2} \qquad (1)$$

Rhombic plates of 2 crystallize from the concentrated solution. The compound is readily identified by a high-field hydridic absorption at δ −12.98 in the ^{1}H NMR spectrum and by a characteristic band at 1793 cm^{-1} in the infrared spectrum, in agreement with the data of ref 6.

Hydrido carbonyl complex 2 has been obtained as the photolysis product of the corresponding dicarbonyl [Cp*Ru(CO)(μ-H)]$_2$ (4).[6] Apart from reaction 1, we did observe the compound as one of the reaction products of 1 with diolefins, e.g. 1,3-cyclohexadiene, and with various olefinic alcohols. Finally, it is isolated as one of the products from the thermal decomposition of 1 (see below).

The diversity of reactions that lead to 2 suggests this molecule to form a deep pitch in the Cp*Ru–H–CO reaction surface. Reaction 1 in particular provides an easy, high-yield access to 2 from readily prepared 1,[3d] which may

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[†] Part 6: See ref 3d.

[‡] Technical University of Aachen.

[§] University of Ulm.

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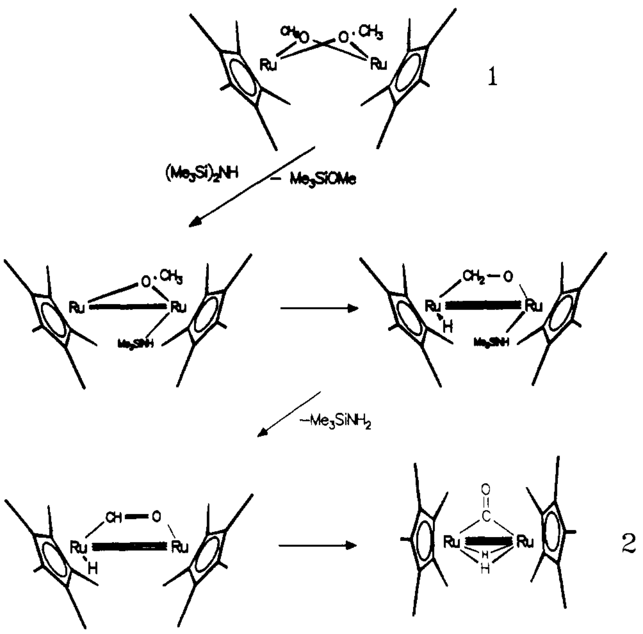
Table I. Mass Distribution (%) in Main Fragment Ions of 2 and Labeled 2

	$[Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}CO)RuCp^*]$		$[Cp^*Ru(\mu\text{-}D)_2(\mu\text{-}^{13}CO)RuCp^*]$	
m/z	calcd	obsd	calcd[a]	obsd
501	78	94	20	72
502	79	99	39	69
503	99	96	51	93
504	100	100	75	99
505	55	84	75	100
506	73	72	97	100
507	16	19	100	96
508	20	18	60	70
509	4.5		78	69
510			27	29
511			25	25
512			13	8

[a] For an isotopic composition of 12% $[Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}CO)RuCp^*]$ and 88% $[Cp^*Ru(\mu\text{-}D)_2(\mu\text{-}^{13}CO)RuCp^*]$

Scheme I



allow closer investigation of the chemistry of this interesting unsaturated hydride.

In order to unambiguously establish the origin of the CO group and the bridging hydrogens in 2, the starting complex 1 was labeled by exchanging OMe groups with $^{13}CD_3OD$.[3b] The product of reaction 1 performed with labeled 1 was mainly $Cp^*Ru(\mu\text{-}D)_2(\mu\text{-}^{13}CO)RuCp^*$. The ^{13}CO stretch in the IR spectrum was found at 1740 cm^{-1}, shifted by 50 cm^{-1}. A strong CO absorption, at δ 228 ppm, exceeding the intensity of the Cp* methyl groups, is seen in the ^{13}C NMR spectrum. Residual bridging protons, due to some unlabeled 1 in the starting material, amount to about 12% and appear equally distributed among the isotopomers $Ru(\mu\text{-}H)_2Ru$ and $Ru(\mu\text{-}H)(\mu\text{-}D)Ru$, as shown by a sharp signal overlaying a broad one at δ −13 in the ^1H NMR spectrum. From the width of the broad signal attributed to the $Ru(\mu\text{-}H)(\mu\text{-}D)Ru$ isotopomer is estimated an H–D coupling constant of about 2 Hz, corresponding to an H–H coupling of about 15 Hz. The pattern of isotopic distribution in the mass spectrum (Table I), which for the molecular ion of unlabeled 2 closely agrees with the one calculated on the basis of natural isotopic abundances, is displaced by three mass units to higher masses for the molecular ion with high-intensity peaks from *m/z* 501 to *m/z* 504 in the unlabeled and from *m/z* 504 to *m/z* 507 in the labeled compound, in full agreement with the spectral data. The most intense fragment has *m/z* 466 to *m/z* 472 corresponding to $(Cp^*Ru)_2 - 2H$ to $(Cp^*Ru)_2 - 6H$.[7] Interestingly, this fragment appears displaced by two mass units to higher masses in the labeled compound. This means that loss of up to six hydrogen atoms together with CO must have occurred exclusively from the methyl groups, leaving the bridged hydride/deuteride in the fragment.

On the basis of these findings, the framework of a possible reaction mechanism is outlined in Scheme I. Electrophilic attack of the silylating agent (or protonation by the acidic amine with subsequent methanolysis of the amide ion) leads to substitution of one OMe group in the dimer with stabilization of the $NHSiMe_3$ residue on one Ru atom, followed by a sequence of intramolecular C–H activation steps, which lead via formaldehyde and formyl intermediates to the observed product.

We propose conservation of the dimeric unit throughout the reaction, which serves to attenuate the degree of unsaturation at the metal centers through intermediate formation of the required number of Ru–Ru bonds and helps in stabilizing CH_nO fragments. In contrast, upon dissociation into monomeric intermediates such as $Cp^*Ru(CO)H$ and Cp^*RuH_n, 3 and 4 are expected as byproducts from dimerization of these fragments. Both these complexes are easily detected by characteristic high-field ^1H NMR signals or by IR absorptions (see below) and would not have escaped observation.

It was made sure by control experiments that 4 does not convert into 2 in a thermal reaction under these conditions.

Reaction with $LiBHEt_3$. Reaction of 1 with $LiBHEt_3$ in THF/hexane gave a mixture of dinuclear hydrides, analyzed by ^1H NMR spectroscopy (see Experimental Section) with 2 and 3 as major products and 4 as a byproduct (eq 2). The relative proportions of 2 and 3 depend

$$1 + LiBHEt_3 \rightarrow 2 + \underset{3}{Cp^*Ru(\mu\text{-}H)_4RuCp^*} + \underset{4}{(Cp^*Ru)_2(\mu\text{-}H)_2(CO)_2} \quad (2)$$

on the stoichiometry; increasing amounts of hydride produce more 3 at the expense of 4. Note that the reaction and workup are conducted under completely aprotic conditions, where reaction products are crystallized from pentane without any chromatographic separation. This excludes the uptake of hydrogen from a protic solvent by a metalated intermediate as is often the case in the syntheses of transition-metal polyhydrides.[8]

It was further checked that the product did not contain deuterium when the reaction was run in THF-d_8. On the other hand, when completely labeled 1, $[Cp^*RuOCD_3]_2$, was used as the substrate, no hydrogen was found in the bridging position of the product 2 by NMR spectroscopy. Thus, also in this case, bridging hydrogen in 2 stems exclusively from C–H activation of the methoxo group, supporting the mechanism given in Scheme II.

As outlined in Scheme II, in this case nucleophilic attack with substitution of OMe for hydride is proposed as the activating step, which produces a coordinatively unsaturated hydride similar to the one suggested in Scheme I. Note that the amount of hydridic hydrogen in the final

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(7) Fragments of mass *m/z* 472–476 frequently appear in the mass spectra of dimeric Cp*Ru complexes $[Cp^*RuX_n]_2$[3] and originate from loss of HX from the molecular ion.

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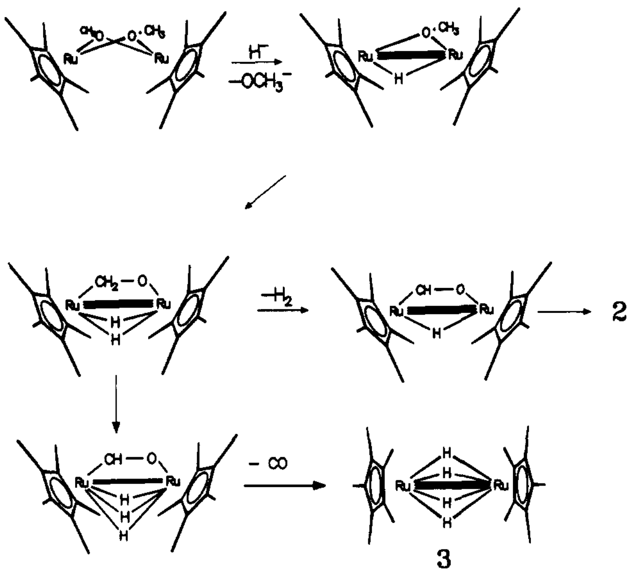
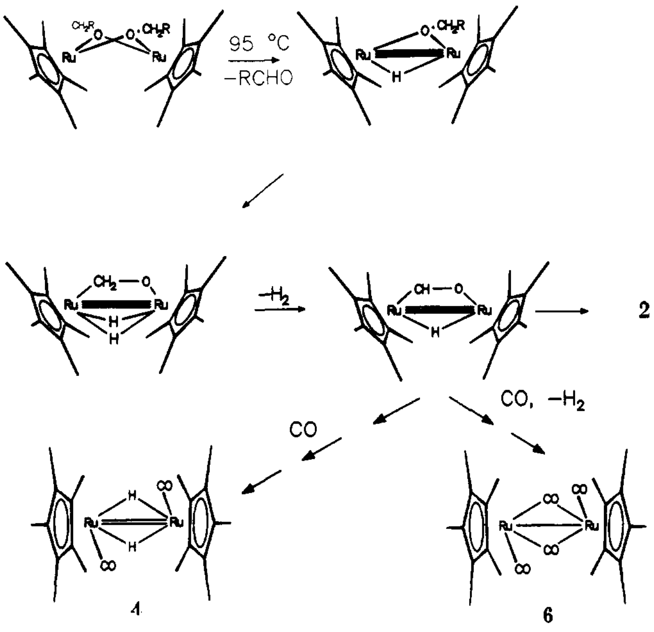
Scheme II



Scheme III



products always exceeds hydrogen that could be delivered from $LiBHEt_3$, thus C-H activation must occur similar to the reaction discussed above. The main difference between the degradation initiated with $(Me_3Si)_2NH$ and with $LiBHEt_3$ may be seen in the lower reaction temperature in the latter case. This may prevent evolution of H_2 from the intermediate after the first C-H activation step and lead to liberation of CO instead, which produces **3** instead of **2**.

Thermolysis of Dimeric Alkoxo Complexes [Cp*RuOR]₂ (R = Me (1), *n*-Bu (5)). The methoxo complex **1** exhibits remarkable thermal stability. Decomposition can be effected by heating it to >90 °C in toluene. The resulting product mixture after chromatography was found to consist of about 40% **2**, 10% **4**, and 30% of the dimeric dicarbonyl $[Cp^*Ru(CO)_2]_2$ (**6**). A similar result was obtained by thermolyzing the bridged butoxo complex **5**,[3b] best obtained from $[Cp^*RuCl]_4$ and *n*-BuOLi. Decomposition required about the same temperature as the methoxide and led to a similar product distribution. Note that no alkylidene-bridged complexes were isolated but rather bridged hydrides **2** and **4**.

Table II. Bond Lengths (Å) and Bond Angles (deg) for 2[a]

Bond Lengths

Ru(1)···Ru(2)	2.444 (1)	C(1)-O(1)	1.183 (8)
Ru(1)-H(1)	1.88	C(1)···H(1)	2.23
Ru(1)-H(2)	1.78	H(1)···H(2)	2.23
Ru(2)-H(1)	1.74	Ru(2)-C(31)	2.168 (5)
Ru(2)-H(2)	1.89	Ru(2)-C(32)	2.180 (6)
Ru(1)-C(1)	2.004 (6)	Ru(2)-C(33)	2.179 (6)
Ru(2)-C(1)	2.052 (6)	Ru(2)-C(34)	2.223 (5)
Ru(1)-C(11)	2.178 (5)	Ru(2)-C(35)	2.233 (5)
Ru(1)-C(12)	2.187 (6)	Ru(1)-Z(11)	1.82
Ru(1)-C(13)	2.203 (6)	Ru(2)-Z(31)	1.83
Ru(1)-C(14)	2.183 (6)	C-C(endo)	1.44 ± 0.04
Ru(1)-C(15)	2.236 (6)	C-C(exo)	1.51 ± 0.04

Bond Angles

Ru(1)-C(1)-Ru(2)	74.1 (2)	C(1)-Ru(1)-H(1)	84.9
Ru(1)-H(1)-Ru(2)	84.7	C(1)-Ru(1)-H(2)	88.5
Ru(1)-C(1)-O(1)	147.1 (5)	H(1)-Ru(1)-H(2)	75.1
Ru(2)-C(1)-O(1)	138.7 (5)	C(1)-Ru(2)-H(1)	87.2
Ru(1)-H(2)-Ru(2)	83.5	C(1)-Ru(2)-H(2)	84.2
Z(11)-Ru(1)-Ru(2)	177.5	H(1)-Ru(2)-H(2)	75.7
Z(31)-Ru(2)-Ru(1)	178.0		

[a] Abbreviations: endo = endocyclic; exo = exocyclic; Z = center of Cp* ring.

Table III. Selected Crystallographic and Bonding Parameters for Compounds 2 and 3

	2	3[a]
Cell Parameters (Å and deg)		
a	12.621 (3)	12.291 (2)
b	8.574 (2)	8.521 (1)
c	10.089 (2)	10.053 (2)
β	108.56 (3)	108.519 (12)
Bond Lengths[a] (Å)		
Ru-Ru	2.444 (1)	2.465 (1)
Ru-Z[b]	1.825	1.806
Ru-H	1.78/1.89	1.59/1.68
	1.88/1.74	1.55/1.63
H···H	2.23	1.42/1.51
Bond Angles (deg)		
Ru-H-Ru	84.7/83.5	94.5/101.6

[a] Bonding parameters for **3** were calculated from the coordinates given for the structure refined in a different space group, *P*2/*a*.[10] [b] Ru-center of Cp* ring distance.

A plausible mechanism accounting for the formation of these products, which starts with aldehyde elimination, is depicted in Scheme III. Uptake of CO, which is liberated through the accompanying decomposition reactions (see Experimental Section) can lead to enhanced amounts of **4** and **6**.

In summary the above reactions testify to a hitherto unobserved transformation of an alkoxo group: different from the well-documented formation of a hydride through elimination of an aldehyde following the development of one vacant coordination site.[1] In the present case the higher degree of coordinative unsaturation, produced in the dimeric unit by alkoxide abstraction, keeps the aldehyde coordinated to the dimer, finally causing its fragmentation into hydrogen and CO.

Structure of 2. Carbonyl hydride **2** and tetrahydride **3**,[9] crystallizing in the space group *Pa* and *P*2/*a*, respectively,[10] are structurally related to such an extent that crystallographic data at first glance seemed to argue for the common identity of the two compounds. Bond lengths and distances for **2** are collected in Table II, and a comparison of crystallographic and bonding parameters for the

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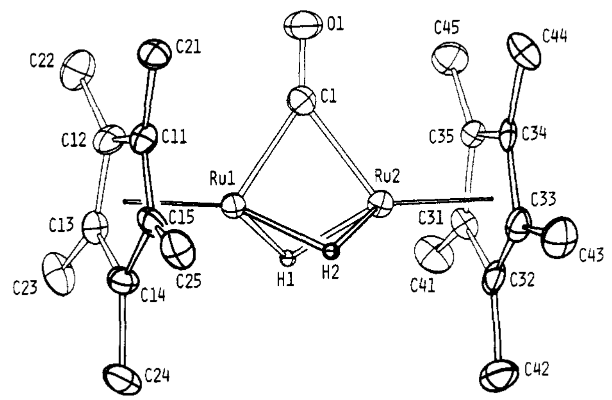

Figure 1. ORTEP view of 2 with ellipsoids drawn at 20% probability.

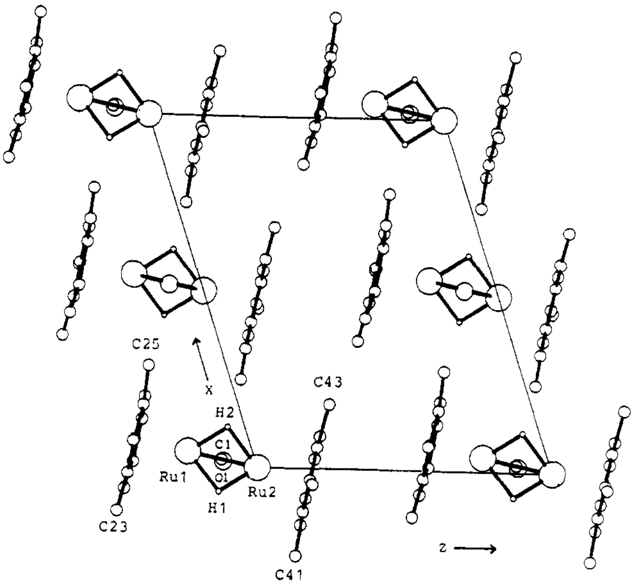

Figure 2. Projection of the unit cell of 2 down *b*.

two compounds is given in Table III. A view of the molecule 2 is shown in Figure 1, and a projection of the cell down *b* is shown in Figure 2.

The largest difference in the otherwise very similar cell constants is found along *a*, a fact not reflected in the molecular geometry, since the principal deviation there occurs along *b*. Interestingly, the molecular symmetry 2*mm* is not reflected by the crystal symmetry. Ru–Ru distances in the two molecules are identical within 0.8% in agreement with a bond order of 3 in both cases. Ru–Cp* distances are nearly identical in the two molecules. The same metal–metal distance is found in dinuclear Re complexes [$C_6H_6Re(\mu\text{-}H)_2(\mu\text{-}CHR)ReC_6H_6$][11] (7) (2.439 Å) and [$CpRe(\mu\text{-}CO)_3ReCp$][12] (2.411 Å) and appears characteristic for bond order 3[13] in these complexes.

In contrast to 3, which has Cp* rings exactly parallel, these are tilted by 3.4° in 2 due to the asymmetry introduced by the CO bridge. Tilting is even more pronounced (18°) in 7 with a bridging alkylidene group.

Metal–hydrogen distances are, in the mean, longer in 2, with hydrogen atoms located closer to the Ru≡Ru bond in 3. As a consequence, the Ru–H–Ru angle in 2 is more acute. H–H distances for bridging hydrogen atoms in both compounds are compatible with a hydride rather than a dihydrogen structure.

The most obvious conclusion drawn from the above comparison is the quasi-isosteric substitution of two bridging H for CO, which not only preserves principal bond distances within the molecule but also preserves the molecular arrangement within the crystal. This is certainly due to the shape of the linear Cp*—Ru≡Ru—Cp* arrangement as two big wheels fixed on a thin axis where small nuts or fringes in between have no influence on the crystallographic packing.

Experimental Section

All experiments were conducted under nitrogen with absolute, nitrogen-saturated solvents by using conventional Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on Bruker SY 80 and WH 270 instruments, and IR spectra, on a Perkin-Elmer 842 instrument. Mass spectra were obtained at 70-eV nominal electron energy with a Varian CH-5 DF spectrometer. Elemental analyses were done by Analytische Laboratorien Engelskirchen.

Cp*Ru(μ-H)$_2$(μ-CO)RuCp* (2). To a solution of 0.22 g of [Cp^*RuOMe]$_2$ (1) (0.82 mmol Ru) in 20 mL of *n*-hexane was added 0.13 mL (0.63 mmol) of ($(Me_3Si)_2NH$), and the solution heated under reflux for 12 h. After cooling, the solvent was removed in vacuo. The residue was extracted with 30 mL of ether and the solvent reduced to 5 mL. Dark yellow crystals of 2 (0.20 g, 90% of theoretical value) separated within 1 week on cooling the solution to −10 °C. Spectroscopic data: see text, Table I, and ref 6. Anal. Calcd for $C_{21}H_{32}ORu_2$ (M_r 502.6): C, 50.18; H, 6.42. Found: C, 50.05; H 6.61.

Cp*Ru(μ-D)$_2$(μ-^{13}CO)RuCp*. A solution of 0.3 g of 1 (1.14 mmol Ru) in 10 mL of benzene was stirred with 1 mL of $^{13}CD_3OD$ (99% ^{13}C, 99.5% D) for 5 h at room temperature and the solvent removed in vacuo. The reaction with $(Me_3Si)_2NH$ was carried out as above. ^{13}C NMR (C_6D_6): δ 228.9 (CO), 90.17 (C_5Me_5), 10.9 ($C_5\mathit{Me}_5$). IR (KBr): 1740 cm^{-1} (^{13}CO).

Reaction of 1 with LiBHEt$_3$. To a solution of 0.15 g of 1 (0.56 mmol of Ru) in 30 mL of *n*-pentane was added 0.56 mL (0.56 mmol) of 1 M $LiBHEt_3$ in THF. After 2 h at room temperature the solvent was removed in vacuo and the residue was extracted with 20 mL of ether. The ether extract was reduced to 5 mL. After cooling of the solution to −10 °C for 1 week, 0.13 g (about 90%) of a product mixture had separated. Analysis by ^1H NMR spectroscopy (C_6D_6) gave ($Cp^*Ru)_2(\mu\text{-}H)_2(\mu\text{-}CO)$ (2) (Cp*, δ 1.78; H_{hydr}, δ −12.9) (25%), [$Cp^*Ru(\mu\text{-}H)_2$]$_2$ (3) (Cp*, δ 1.86; H_{hydr}, δ −14.0) (56%), and [$Cp^*Ru(\mu\text{-}H)(CO)$]$_2$ (4) (Cp*, δ 1.67; H_{hydr}, δ −15.9) (19%). An identical experiment, carried out with 0.26 g of 1 (0.97 mmol of Ru) in 30 mL of pentane and 0.48 mmol of $LiBHEt_3$ in THF, yielded 2 (62%) and 3 (32%).

Thermolysis of 1 and 5. A sample of 0.2 g (0.72 mmol of Ru) of 1 was heated in 30 mL of toluene at 95 °C for 4 h. After cooling it was concentrated to 5 mL and the mixture chromatographed over Al_2O_3 (5% H_2O) by using 5:1 pentane/toluene as eluent. The first violet band contained 30 mg (10%) of [$Cp^*RuCO(\mu\text{-}H)$]$_2$ (4), the second band consisted of 80 mg (40%) of 2, and a third band, eluted with toluene, contained 60 mg (30%) of [$Cp^*RuCO(\mu\text{-}CO)$]$_2$ (6). The same experiment conducted with 0.25 g (0.8 mmol of Ru) 5 gave 50 mg (20%) of 4 and 50 mg (20%) of 2, the rest being decomposition products, which could not be identified.

Crystal Structure Determination. X-ray diffraction was performed with graphite-monochromatized Mo Kα radiation (λ 0.71069 Å) on a Philips PW-1100 diffractometer with a crystal (0.1 × 0.4 × 0.9 mm) mounted without protection on a glass fiber. Crystal data: see Table III. The density calculated for $Z = 2$ is 1.613 g/cm^3. In the $\theta/2\theta$ mode, $\theta < 25°$, 3846 reflections were scanned at room temperature with $\pm h, \pm k, l$. The structure was solved by the patterson method. After localization of all non-hydrogen atoms an empirical absorption correction (μ = 12.2 cm^{-1}) was applied[14] and the F_0 values of equivalent reflections were averaged. An *F* synthesis of the refinement with anisotropic temperature factors located all hydrogen atoms. Optimization in the final refinement cycles was carried out by placing rigid CH_3

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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/Å^3. Refinements were carried out with the SHELX76 program system. Final atom parameters are collected in Table III.

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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(η^5-oxocyclohexadienyl), a Doubly Symmetrical Hydrogen-Bridged Ruthenium Complex

Ulrich Koelle,[*,†] Maja Hong Wang,[†] and Gerhard Raabe[‡]

Institute for Inorganic Chemistry and Institute for Organic Chemistry, Technical University of Aachen, W-5100 Aachen, FRG

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Reaction of [Cp*Ru(OMe)]$_2$, Cp* = η^5-C$_5$Me$_5$, (1) with phenol leads to the title complex Cp*Ru(C$_6$H$_5$=O)···(H-OC$_6$H$_5$)$_2$ (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 η^6-ligand. Similar π-complexes are formed with 2-hydroxyacetophenone, salicylaldehyde, and 5-hydroxy-1,4-naphthoquinone.

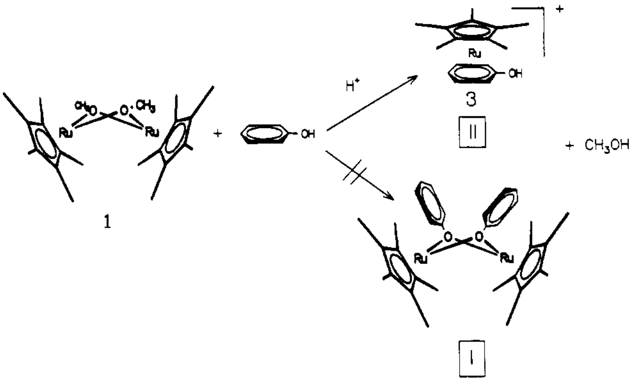
The coordinatively unsaturated Ru complex [Cp*Ru(OMe)]$_2$ (Cp* = η^5-C$_5$Me$_5$)[1-3] (1) in solution readily exchanges bridging methoxo groups as shown by rapid exchange of complexed CH$_3$O (δ 4.9 ppm) for CD$_3$O in benzene-d_6.[1,2] With higher alcohols an equilibrium is established, where the 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 η^{2-6} oxocyclohexadienyl complex with base.[10] The same structure type was found in the complex Cp*Ru(2,6-di-*t*-BuC$_6$H$_3$=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 sandwich complexes of structure types II and III were formed.

Scheme I



[†] Institute for Inorganic Chemistry.

[‡] Institute for Organic Chemistry.

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(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]

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