Hydrogen bonds and protonation of carbonyl-containing polynuclear rhodium complexes

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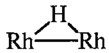
According to IR spectroscopy data, the interaction of bi-, tri-, and tetranuclear cyclopentadienylcarbonyl rhodium complexes with rather weak protic acids (phenols, fluoroalcohols) in low-polarity media results in the formation of hydrogen bonds of the OH...O=C type with bridged carbonyl groups. According to ^{1}H NMR data, protonation of these complexes with strong acids (CF_3COOH and HBF_4) occurs at the the Rh—Rh bond to give the symmetrical  $\overset{\mathrm{H}}{\mathrm{Rh{-}Rh}}$ bridge.

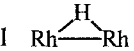
Key words: hydrogen bond, protonation, polynuclear cyclopentadienylcarbonyl rhodium complexes.

Protonation of the binuclear complex $[RhCp(CO)]_2(\mu\text{-}CO)$ (**1**) with a strong acid (HBF_4) in nitromethane has been studied previously.[1] The purpose of the present work is to investigate the peculiarities of the hydrogen bonds and the protonation on going from binuclear complex **1** to a trinuclear compound, $[RhCp(\mu\text{-}CO)]_3$ (**2**), and a tetranuclear compound, $[RhCp]_4(\mu_3\text{-}CO)_2$ (**3**). The study was carried out using IR and ^{1}H NMR spectroscopy and protic acids of various strengths (phenol, hexafluoroisopropanol (HFIP), perfluorobutanol (PFB), trifluoroacetic acid (TFA), and HBF_4)) in low-polarity media (CCl_4, CH_2Cl_2).

Results and Discussion

The formation of hydrogen bonds between compounds **1**—**3** and protic acids was detected on the basis of the ν(OH) region in phenol, HFIP, and PFB. The spectra of solutions of the latter compounds (at concentrations that rule out self-association) containing compounds **1**—**3** exhibit broad bands of bound OH groups in the 3400—3130 cm^{-1} region (Table 1). The bridging carbonyl groups act as the sites of proton coordination, which has been proved by low-frequency shifts of the ν(CO) bands typical of hydrogen bonds of the type XH...OC.[2] The character of the hydrogen bonds in this case is similar to that observed previously in binuclear complexes of iron and ruthenium ($[CpM(CO)_2]_2$)[3] and differs from the type OH...M H-bonds formed by mononuclear compounds of Rh and Ir ($Cp^*M(CO)_2$) containing terminal CO groups.[4,5] An additional competing formation of hydrogen bonds with Rh atoms, manifested as the appearance of weak high-frequency bands of the bridging CO groups ($\Delta\nu$ = +40 cm^{-1}), was observed in the case of binuclear complex **1**.

As can be seen from Table 1, the shift of the $\nu(OH)_{bound}$ maximum and the increase in the basicity factor, E_j,[6] that result from the H-bonding increase in the sequence **1** < **2** < **3**, which coincides with the order in which the ν(CO) frequencies decrease. Thus, the electron-donating properties of the metal atom with respect to the CO groups and the ability to form H-bonds (parallel to the basicity) increase on going from bi- to tri- and tetranuclear rhodium compounds.

The protonation of the complexes with TFA and the stronger acid HBF_4 in a CH_2Cl_2 solution results in the appearance of high-frequency ν(CO) bands in the IR spectra (see Table 1) and the signal of a hydride proton in the ^{1}H NMR spectra. The spectra of the protonated forms of **1** and **2** (at T < 0°C) exhibit symmetrical triplets ($\delta = -10.67$, $^1J_{Rh-H}$ = 18.3 Hz for **1**,[1] $\delta = -17.98$, $^1J_{Rh-H}$ = 24.8 Hz for **2**). In the case of tetranuclear cluster **3**, the signal of the hydride proton is a triplet of triplets ($\delta = -12.94$, $^1J_{Rh-H}$ = 29.4 Hz, and $^2J_{Rh-H}$ = 14.7 Hz), because of the additional splitting on the rhodium nuclei. These data attest to protonation of the Rh—Rh bond enriched in electrons in clusters **2** and **3** to form the symmetrical  $\overset{\mathrm{H}}{\mathrm{Rh{-}Rh}}$ fragment (as has been reported for binuclear compound **1** (see Ref. 1)). The ratio between the intensities of the high-field signal of the proton and the signal of the Cp-ring protons indicates that the clusters are monoprotonated.

Thus, we have shown that the protonation of polynuclear rhodium complexes may be preceded by the formation of OH...O=C type hydrogen bonds with the

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Table 1. The ν(OH) bands of phenol involved in the H-bonds with **1—3**, the basicity factors, and the ν(CO) bands of **1—3** in the H-complexes and protonated forms after the addition of PFB and HBF_4

Compound	ν(OH)/cm^{-1} PhOH	Δν	E_j	ν(CO)/cm^{-1}		
				CH_2Cl_2	PFB	HBF_4
1	3388	198	0.86	1978 vs	2013 w,	2085 m, 2063 s*
				1806 s	1846 sh, 1760 m	1867 s
2	3360	226	0.94	1837 vs**	1810 s	1890 s
				1781 s	1760 s	1840 s
3	3331	255	1.02	1706 sh	1650 sh	1744 sh
				1670 s	1610 s	1720 s

* In CH_3NO_2 2082, 2058, 1977, and 1869 cm^{-1}. ** All of the measurements for compounds **2** and **3** were carried out at T = 200 K.

bridging carbonyl groups. The protonation occurs along an edge to give the symmetrical $\overset{\mathrm{H}}{\mathrm{Rh}\frown\mathrm{Rh}}$ bridge.

Experimental

Compounds **1—3** were prepared by the previously described procedures.[7] The IR spectra were recorded on Specord M-82 and Specord M-80 spectrophotometers. The ^{1}H NMR spectra were measured on Bruker AMX-400 and Bruker WP-200-SY instruments. The concentrations of the protic acids varied in the 5×10^{-2}—1×10^{-4} mol L^{-1} range, those of the organometallic complexes were in the 1×10^{-2}—1×10^{-4} mol L^{-1} range. The studies were carried out at 200—300 K in CH_2Cl_2.

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Electrosynthesis of tetraethylsilane from elemental silicon

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Electrolysis of alkylation reagents at silicon-containing electrodes results in alkylsilanes in both cathodic and anodic processes. A mechanism for the reaction is proposed.

Key words: electrosynthesis; silicon-containing electrodes; alkylsilanes.

At present, direct synthesis of chlorosilanes and/or silicon hydrides[1] followed by their treatment with organomagnesium (or lithium) reagents[2] or with unsaturated compounds is the main method for the preparation of organosilicon compounds from inorganic silicon derivatives. Previously[3] an alternative method for the synthesis of organosilicon compounds from silicon dioxide *via* pentacoordinated intermediates was reported. Whereas

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