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2,2′-Bipyridine Derivatives of Hexarhodium Carbonyl Cluster

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Synopsis. The properties of [Rh$_6$(CO)$_{12}$(bpy)$_2$](bpy: 2,2′-bipyridine), prepared recently from substitution of carbonyl ligands in [Rh$_6$(CO)$_{16}$] by 2,2′-bipyridine have been investigated.

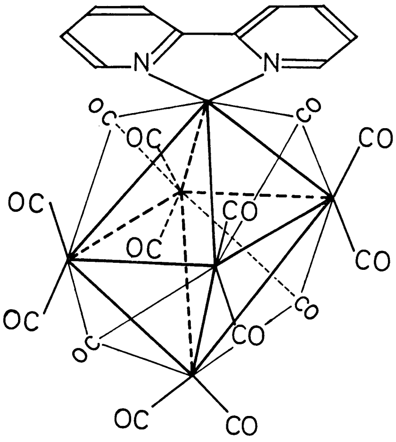
Though hexadecacarbonylhexarhodium is generally considered to be a stable, rather unreactive compound, its derivatives substituted by dienes, halogens, phosphines and phosphites have been reported.1–5) Recently we have found that the treatment of [Rh$_6$(CO)$_{16}$] with 2,2′-bipyridine in dichloromethane at room temperature under nitrogen atmosphere gives rise to a successive replacement of two carbonyl groups by 2,2′-bipyridine and results in the formation of [Rh$_6$(CO)$_{12}$(bpy)$_2$]. Further replacement of carbonyl groups did not occur. Darkbrick-colored crystals were isolated from the deep brown solution. This compound is more soluble in dichloromethane and chloroform than [Rh$_6$(CO)$_{16}$], and stable to air oxidation on the solid state. In the synthetic reaction unis(bipyridine)-substituted cluster was not obtained.

The IR spectrum of [Rh$_6$(CO)$_{12}$(bpy)$_2$] in the carbonyl stretching region shows ν(CO) at 2050, 2015 cm^{-1} (terminal) and 1785 cm^{-1} (face-bridging) in dichloromethane. In comparison with [Rh$_6$(CO)$_{16}$] which has sharp bands at 2075 and 2025 cm^{-1} due to terminal carbonyls and at 1801 cm^{-1} due to face-bridging carbonyl group in chloroform, all bands were shifted to the lower frequency. The symmetry (A_1+B_1) of terminal carbonyls implies that two bipyridine ligands coordinate, in place of four carbonyl groups, to the terminal sites in the trans-position of the hexarhodium unit. The coordination mode of the bipyridine ligand is similar to that of the dienes such as norbornadiene, 1,4-cyclohexadiene and 1,5-cyclooctadiene in [Rh$_6$(CO)$_{14}$(diene)].1)

Under carbon monoxide atmosphere, the bipyridine ligand of [Rh$_6$(CO)$_{12}$(bpy)$_2$] can be readily replaced with carbon monoxide at room temperature. By monitoring IR spectra it was found that the cluster had been returned to parent carbonyl [Rh$_6$(CO)$_{16}$] *via* [Rh$_6$(CO)$_{14}$(bpy)] as an intermediate, the existence of which was confirmed by ^{13}C-NMR data described later. The resulting [Rh$_6$(CO)$_{16}$] is almost excluded from the solution because of its low solubility.

$$\begin{tikzcd}
[\mathrm{Rh_6(CO)_{16}}] \arrow[r, "\mathrm{bpy}", "-\mathrm{CO}"'] & [\mathrm{Rh_6(CO)_{12}(bpy)_2}] \arrow[d, "\mathrm{CO}"', "-\mathrm{bpy}"] \\
 & [\mathrm{Rh_6(CO)_{14}(bpy)}] \arrow[lu, "\mathrm{CO}", "-\mathrm{bpy}"']
\end{tikzcd}$$

Under carbon monoxide atmosphere the direct carbonyl exchange also proceeds on the cluster during the coordinated bipyridine-CO exchange. For 100 h reaction of [Rh$_6$(CO$_{12}$)(bpy)$_2$] (27 mg) in dichloromethane (4 ml) with excess ^{13}C-enriched carbon monoxide (*ca.* 91 atom%) at room temperature, the labelled unis(bipyridine)substituted cluster was predominantly existent in the solution. The proton-decoupled ^{13}C-NMR spectrum of the cluster showed the presence of two nonequivalent carbonyl resonances at a lower field (δ 231.8, 243.2 ppm: quartet J(Rh–C) *ca.* 26 Hz) and three nonequivalent carbonyl resonances at a higher field (δ 180.2, 181.6, 184.0 ppm: doublet J(Rh–C) 71.6±0.3 Hz). As observed for [Rh$_6$(CO)$_{16}$] (terminal carbonyl; δ 180.1 ppm, doublet J(Rh–C) 70.2 ±0.6 Hz, face-bridging carbonyl; δ 231.5 ppm, quartet J(Rh–C) 24.4±0.6 Hz),6) the lower field signals are due to the face-bridging carbonyl groups and the higher field signals due to the terminal carbonyl groups. The intensity ratio of the terminal carbonyls exhibits 4: 4: 2. Since these intensities should reflect the relative abundances in this region, the spectrum is compatible with Structure (1).



Structure (1).

The result that two resonances of the terminal carbonyls attached to the square plane in the Rh$_6$ unit are nonequivalent is similar to the result that two resonances of terminal carbonyls attached to the basal plane are nonequivalent relative to the apical rhodium in [Rh$_4$(CO)$_{12}$].7)

The reaction product between [Rh$_4$(CO)$_{12}$] and dienes is reported to give the same product, [Rh$_6$(CO)$_{14}$(diene)] obtained by the reaction of [Rh$_6$(CO)$_{16}$] with dienes.1) However, the reaction of [Rh$_4$(CO)$_{12}$] with bipyridine under the aforementioned synthetic conditions produces exclusively an unidentified black solid, which is insoluble in almost organic solvents.

Experimental

^{13}C-NMR spectra were recorded in the Fourier transform mode on a Varian Associates XL-100-15 spectrometer in dichloromethane-d_2 solution, using 0.05M Cr(acac)$_3$ as a relaxation reagent and using tetramethylsilane as an internal standard. IR spectra were recorded on a Model EPI-G3 of Hitachi Grating Infrared Spectrophotometer.

2,2′-Bipyridine was recrystallized from a mixture of ethanol and water. Hexadecacarbonylhexarhodium, [Rh$_6$(CO)$_{16}$], was purchased from the commercial source (Strem Chemical Incorporated). The ^{13}CO (91 atom%) enclosed in a glass tube with a breakable seal, purchased from B.O.C. Ltd. (Prochem), was connected with vacuum line and used without further purification. Solvents, CH$_2$Cl$_2$ and CD$_2$Cl$_2$, were dried over P$_2$O$_5$, and were vacuum-distilled before use.

Preparation of [Rh$_6$(CO)$_{12}$(bpy)$_2$]. The 2,2′-bipyridine (bpy: 176 mg, 1.13 mmol) was added to [Rh$_6$(CO)$_{16}$] (200 mg, 0.19 mmol) suspended in dichloromethane (10 ml) on stirring at room temperature. During the stirring the evolved carbon monoxide was evacuated from time to time and replaced with dry nitrogen. After the 100 h reaction at about 30 °C, the reaction mixture was filtered out under dry nitrogen. (The residue was dark-green and air-stable.) Excess hexane was added to the deep brown filtrate, the solution of which was kept overnight at −78 °C. The solid obtained was washed several times with hexane, recrystallized from a mixture of dichloromethane and hexane, and then dried *in vacuo.* The yield was about 30%. It was stored under nitrogen in an ice box. Found: C, 30.19; H, 1.99; N, 4.75%. Clacd for $C_{32}H_{16}O_{12}N_4Rh_6$: C, 30.33; H, 1.26; N, 4.42%.

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