Model for the CO Poisoning of Hydrodesulfurization Catalysts. Synthesis and Structure of \{Ru(CO)[PPh2SC12H7)]2Cl2\}.2CH2Br2

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MODEL FOR THE CO POISONING OF HYDRODESULFURIZATION CATALYSTS. SYNTHESIS AND STRUCTURE OF [Ru(CO)[(PPh₂SC₁₂H₇)]₂Cl₂] • 2CH₂Br₂.

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ABSTRACT

The treatment of [Ru(P₉SC₁₂H₇)]Cl₂ with CO at ambient conditions results in, after work-up, in the isolation of the monocoordinated species [Ru(CO)(P₉SC₁₂H₇)]Cl₂. I. Crystals of I (C₉H₉Br₂Cl₂OPRuSC₂F₃W = 1284.6) are triclinic; P = a = 11.387(3), b = 13.010(4), c = 17.309(4) Å, α = 93.32(2)°, β = 106.51(2)°, γ = 91.29(2)°, Z = 2; V = 2495(1) Å³; d(calcd.) = 1.709 g cm⁻³ λ(Mo Kα) = 0.71073 Å, μ = 37.7 cm⁻¹; R = 0.0748; R₁ = 0.0714 for 4141 unique reflections. The geometry about the Ru(II) center is pseudoctahedral, with the phosphine ligands in the trans configuration. The Ru-S bond distance is 2.425(3) Å.

INTRODUCTION

The hydrosulfurization (HDS) of fossil fuels is the industrial process for the removal of sulfur from fossil fuel feedstocks (eq. 1).

R-S-R + 2H₂ ↔ 2R-H + H₂S

The resulting hydrocarbons are then suitable for the refined cracking and reforming catalysts downstream. Hydrocarbons fuels are also desirable because they generate fewer acid rain precursors upon combustion.

The molecular basis of the HDS process involves the activation of the crude feedstock in hydrodealkylation by metal catalysts. Molybdenum-based catalysts are widely used, although recent work has shown that ruthenium-based systems are even more active (Pecoraro and Chianelli, 1981; Chianelli et al., 1984; Harris and Chianelli, 1984). The organosulfur compounds targeted by HDS consists of thiols, thioethers and thiophenes, especially benzo- and dibenzothiophenes (DBT). In order to elucidate the nature of the substrate-catalyst interactions we sought to prepare ruthenium complexes of DBT-dervatives. In 1984 we reported the first such complex in the form of [Ru(P₉SC₁₂H₇)O₂Cl] where P₉SC₁₂H₇ is 4-diphenyl-phosphinoDBT, a P-S chelating ligand (Blocknor et al., 1984). As this was the first S-bound DBT complex, we are interested in probing its reactivity in order to evaluate the lability of the Ru-S bonds. We selected CO as the competing ligand since it was known that CO poisons HDS catalysts (Lombardo et al., 1980).

MATERIALS AND METHODS

The compound [Ru(CO)](P₉SC₁₂H₇)Cl₂, I, was prepared by purging a dichloromethane solution of [Ru(CO)](P₉SC₁₂H₇)Cl₂ with CO gas. The resulting solution was concentrated and chromatographed on silica gel, eluting with dichloromethane. The yellow band was evaporated to give yellow microcrystals. Anal. calc. for C₉H₉Br₂Cl₂OPRuSC₂: C, 62.82; H, 6.71; N, 0.713; Cl, 7.59. Found: C, 63.34; H, 3.79; Cl, 7.66. IR (CHCl₃ soln): υₖ = 1988 cm⁻¹. 31P NMR (CDCl₃): 50.63, 41.56, 20.64, 11.62 ppm; δP = 45.38, δS = 16.84, J = 366 Hz. The elemental analysis was performed at the School of Chemical Sciences, University of Illinois. 31P[¹H] NMR spectra were obtained on an NMR-250 spectrometer.

Single crystals were grown by the slow diffusion of diethyl ether into a solution of I in dibromomethane. A yellow crystal, 0.30 x 0.35 x 0.36 mm, was mounted on a glass fiber. Intensities were measured on a Nicolet R3m µ diffractometer using the ω-scan technique, scan speed varied 5-20 deg. min⁻¹. The unit cell was determined from the least-squares analysis of angle data for 25 reflections with 19 < 2θ < 26°. Data were collected to (sin θ)/λ = 0.56 Å⁻¹, ± h, ± k, ± l. Three standard reflections collected every 197 reflections decreased < 2% over data collection. Corrections to the intensity data for Lp effects, absorption (empirical) and for decay were applied. A total of 7785 reflections were measured with 7374 unique (R(int) = 1.86 %) and 4141 observed reflections with F(int) < 4σ(F₂). The structure was solved by direct methods which provided the location of one heavy atom (Ru) and four initially confusing peaks of apparent Z greater than P, S, or Cl that proved to be the Br atoms of the two positionally disordered molecules of Cl₂Br₂. The remaining nonhydrogen atoms were obtained from subsequent difference Fourier syntheses. The final refinement model incorporated a rigid, planar hexagonal constraint to the P-bound phenyl rings, and the C-Br distances were collectively refined to a common value of 1.86(1) Å. All nonhydrogen atoms were refined with anisotropic temperature factors, and the hydrogen atoms were included as idealized, isotopic contributions, but were not refined. For a total of 567 parameters, R = 0.0748, R₁ = 0.0714, S = 1.407. Final (Δ/σ)max < 0.09 e Å⁻³ on the final difference map. All computations were carried out using SHELXTL (5.1) software (Nicolet Corp., Madison, WI).

RESULTS

Crystal data are given in Table 1. The structure of [Ru(CO)][(P₉SC₁₂H₇)]Cl₂ • 2CH₂Br₂, I, is seen in Fig. 1. Atomic and equivalent thermal parameters are given in Table 2. Selected bond distances and angles can be seen in Table 3.

Table 1. Crystal Data for [Ru(CO)][(P₉SC₁₂H₇)]Cl₂ • 2CH₂Br₂

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₉H₉Br₂Cl₂OPRuSC₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWT</td>
<td>1284.6</td>
</tr>
<tr>
<td>Space group</td>
<td>triclinic P₁</td>
</tr>
<tr>
<td>a</td>
<td>11.387(3) Å</td>
</tr>
<tr>
<td>b</td>
<td>13.010(4) Å</td>
</tr>
<tr>
<td>c</td>
<td>17.309(4) Å</td>
</tr>
<tr>
<td>α</td>
<td>93.32(2)°</td>
</tr>
<tr>
<td>β</td>
<td>106.51(2)°</td>
</tr>
<tr>
<td>γ</td>
<td>91.29(2)°</td>
</tr>
<tr>
<td>υₖ</td>
<td>1988 cm⁻¹</td>
</tr>
<tr>
<td>δP</td>
<td>45.38 ppm</td>
</tr>
<tr>
<td>δS</td>
<td>16.84 ppm</td>
</tr>
<tr>
<td>J</td>
<td>366 Hz</td>
</tr>
<tr>
<td>S</td>
<td>2</td>
</tr>
<tr>
<td>d(ave)</td>
<td>1.709 g cm⁻³</td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>37.7 cm⁻¹</td>
</tr>
<tr>
<td>NoH</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0748/0.0714</td>
</tr>
</tbody>
</table>

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The addition of CO results in the breakage of one of the Ru-S bonds in \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_2 \text{Cl}_2] \) and causes a rearrangement of the phosphine ligands from the all cis configuration to a trans geometry, as seen in the structure of I (Fig. 1). One of the phosphine ligands remains chelated through the thiophenic sulfur. The Ru-S bond distance of 2.425(3) Å is slightly longer than the two comparable distances in \([\text{Ru}(\text{p-tolyl})_2(\text{SC}_2 \text{H}_4)_2 \text{Cl}_2] \): Ru-S(1), 2.343(5); Ru-S(2), 2.402(5) Å (Bucknor et al., 1984). The pyramidal nature of the coordinated sulfur is evident by the angle defined by Ru-S(2)-C(C midpoint). This angle of 131.8° in I compares favorably with the two independent angles (132.0° and 130.1°) in \([\text{Ru}(\text{p-tolyl})_2(\text{SC}_2 \text{H}_4)_2]_2 \text{Cl}_2] \) (Bucknor et al., 1984). In the \([\text{Ru}(\text{thiol})_2(\text{PPh}_3)_2 \text{Br}] \) complex, the Ru-S(C-C midpoint) angle is 126° and the Ru-S bond distance is 2.408(1) Å (Draganjac et al., 1985). The pyramidal nature of the thiophenic sulfur upon coordination has also been observed in the \(\text{CpFe(CO)}_3 \text{DBT}^+ \) (Goodrich et al., 1987) and \(\text{Cp}^+ \text{IrCl}_2 \text{DBT} \) (Rao et al., 1991) complexes. Angelici (1990) and Rauchfuss (1991) have reviewed structural aspects of thiophene coordination.

Reflecting acetanilide solutions of I in the presence of trimethylamine oxide for 24 hrs did not result in decarboxylation. This fact and the ease of thiophene displacement by CO may be relevant to the CO poisoning of the HDS catalysts (Lombardo et al., 1980).

**SUPPLEMENTAL MATERIAL**

Anisotropic Thermal Parameters, Positional Parameters for the Hydrogen Atoms, Bond Lengths and Angles, and Structure Factor Tables (25 pages) are available from the authors upon request.
LITERATURE CITED


