An Electrophilic Displacement Reaction on Rhodium(I)

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Abstract: The compound $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ reacts rapidly with sulfur dioxide giving $\pi\text{-}C_5H_5Rh(C_2H_4)SO_2$, apparently through electrophilic attack. Restricted rotation of coordinated ethylene in the product was demonstrated below $-10°$.

There is a striking difference in the ease of exchange of free ethylene with coordinated ethylene in the compounds acetylacetonatodiethylenerhodium (1) and π-cyclopentadienyldiethylenerhodium (2); the exchange

$$(C_2H_4)_2Rh(C_5H_7O_2) \qquad (C_2H_4)_2Rh(\pi\text{-}C_5H_5)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

rate of 1 is $>10^4$ sec^{-1} at 25°, but no exchange with 2 is detectable after 5 hr at 100°.[1] This difference in the rate of ethylene exchange extends to other displacement reactions. Thus, triphenylphosphine, carbon monoxide, or cyanide ion, all of which quickly displace ethylene from 1, have no effect upon 2. Displacements of ligands in coordination compounds can generally be described as nucleophilic reactions,[2] and on this basis together with some structural assumptions we can account for the difference in reactivity between 1 and 2. Adopting a valence bond description, the three ligands of acetylacetonatodiethylenerhodium can be said to donate eight electrons to Rh(I) giving it the electronic structure $[Kr]5s^24d^{10}5p^4$, which is two electrons short of rare gas configuration. With a relatively small increase in energy, this ion can accommodate two electrons of an entering ligand (thus attaining rare gas configuration) to form a five-coordinate intermediate for an S_N2 displacement. However, if it is assumed that the cyclopentadienyl group donates six electrons, the electronic structure of Rh in π-cyclopentadienyldiethylenerhodium will be $[Kr]5s^24d^{10}5p^6$, and the electrons of an incoming group in an S_N2 reaction would have to enter a relatively high-energy 6s orbital. Accordingly, substitution would be a much slower reaction.

Although rhodium in the cyclopentadienyl complex 2 has attained rare gas configuration, it is only five-coordinate and so may be considered to have a pair of unshared electrons in an orbital appropriate for coordination of a sixth ligand. Accordingly, it might be expected to be subject to electrophilic attack. This is, indeed, found to be the case. Such a weak Lewis acid as sulfur dioxide readily displaces ethylene from 2 at $-80°$. A suggested mechanism for reaction with sulfur dioxide is summarized in Figure 1.

Other substances which readily displace ethylene from the cyclopentadienyl complex 2, and which may be described as acids in the sense that they are electrophilic,[3] are iodine,[4] Ag(I), and tetracyanoethylene. Protonic

acids also attack 2 but the hydride, which is presumed to be formed, quickly combines with coordinated ethylene to yield an ethylrhodium compound.[5] Previously reported coordination compounds of transition metals in which the ligand is the acceptor rather than donor of electrons have been complexes of boron compounds (BF_3[6a] or BH_3[6b]).

The product of the reaction of sulfur dioxide with π-cyclopentadienyldiethylenerhodium, $\pi\text{-}C_5H_5Rh(SO_2)(C_2H_4)$ (3), may have ethylene protons in nonidentical environments, and we were curious to learn if the phenomenon of hindered rotation of coordinated ethylene first observed in π-cyclpentadienyldiethylenerhodium[1] was also to be found in 3. The nmr spectrum was measured in SO_2 solution over a range of temperatures from -50 to $+8°$ using tetramethylsilane as internal reference. At $-2°$ the nmr spectrum has a single absorption for ethylene protons at -3.32 ppm. As the solution is cooled, this absorption is split into two broad, poorly defined peaks and finally at $-50°$ into two pairs of doublets which are shown in Figure 2.

Nmr absorption for coordinated ethylene in 2 converges into a single peak only above 57°, indicating a greater restriction of ethylene rotation in 2 than in 3. This is not surprising if restricted rotation is explained by back-bonding, because a sulfur dioxide ligand is expected to reduce electron density at rhodium and, thereby, weaken the π bond between metal and olefin. In view of the information that it may provide concerning the strength of the π bond, the energy barrier to rotation of coordinated ethylene in 2 has been remeasured and will be reported later. This became more urgent as the method initially used[1] appears to be imprecise.[7] The activation energy for rotation of ethylene in 3 and in other olefin complexes of rhodium(I) will also be reported.

Experimental Section

π-Cyclopentadienyldiethylenerhodium(I) was prepared by the method described by King,[8] vacuum sublimed, and recrystallized from ethanol. Other reagents were commercial reagent grade.

(1) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).
(2) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 91, 96–103.
(3) M. Usanovich, *J. Gen. Chem. USSR*, **9**, 182 (1939).
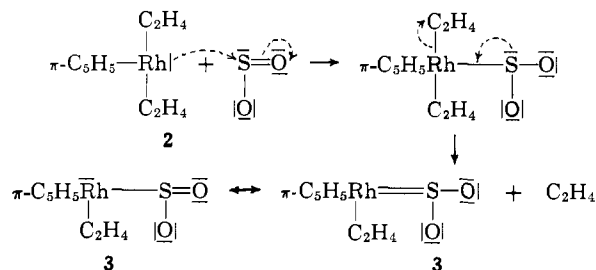(4) Displacement of CO from $\pi\text{-}C_5H_5Co(CO)_2$ by halogens [R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964); R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965)] also may involve an electrophilic attack on cobalt. F. Basolo, A. T. Brault, and A. J. Poë [*J. Chem. Soc.*, 676 (1964)] found that CO exchange of some "inert" iron carbonyls is catalyzed by trifluoroacetic acid. They propose that CO becomes labile following addition of proton to the iron carbonyl, an analog of the scheme shown in Figure 1.
(5) R. Cramer, *J. Am. Chem. Soc.*, **88**, 2272 (1966).
(6) (a) D. F. Shriver, *ibid.*, **85**, 3809 (1963); (b) G. W. Parshall, *ibid.*, **86**, 361 (1964).
(7) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *ibid.*, **88**, 3185 (1966).
(8) R. B. King, *Inorg. Chem.*, **2**, 528 (1963).

Figure 1. Displacement of ethylene by sulfur dioxide.

Figure 2. Proton nmr spectrum of coordinated ethylene in π-$C_5H_5Rh(SO_2)(C_2H_4)$ at $-50°$ dissolved in SO_2 with TMS internal standard and 60-Mc spectrometer.

Synthesis of π-$C_5H_5Rh(SO_2)(C_2H_4)$. A 500-ml flask was charged with 0.88 g of π-$C_5H_5Rh(C_2H_4)_2$ (3.4 mmoles), chilled to $-80°$, and evacuated. When 500 ml of gaseous SO_2 was admitted, the yellow complex immediately turned red and dissolved. In a few moments the red solution effervesced through release of ethylene which was identified by its infrared absorption pattern. Excess SO_2 was distilled and the residual solid sublimed at 60° (0.02 mm). The sublimate does not melt but darkens and decomposes when heated above 120°.

Anal. Calcd for $C_7H_9RhSO_2$: C, 32.32; H, 3.49; S, 12.33. Found: C, 32.66; H, 3.97; S, 12.08, 11.92.

The infrared spectra in KBr wafer and Nujol mull have the following common absorption bands: 3095 (m), 1639 (m), 1504 (w), 1429 (w), 1408 (m), 1258 (s), 1170 (s, broad), 1105–1093 (s), 1044 (m), 1010 (w), 830 (w), and 816 (s, broad) cm^{-1}. The absorption at 3095 cm^{-1} is attributed to C–H of coordinated ethylene and at 1504 cm^{-1} to C=C; those at 1105–1093 and 1258 cm^{-1} are attributed to SO_2 coordinated to rhodium.[9]

The nmr spectrum of π-$C_5H_5Rh(C_2H_4)SO_2$ in liquid sulfur dioxide has a peak due to cyclopentadienyl protons at -5.60 ppm (tetramethylsilane, internal standard), split into a doublet (1 cps) by rhodium, and (at 8°) a broad absorption ascribed to coordinated ethylene centered at -3.32 ppm.

Electrophilic Displacement of Ethylene by Other Lewis Acids. These reactions were demonstrated in a gas cell with removable NaCl windows sealed to the cell with O rings. A dilation of the cell wall held the reaction mixture. To demonstrate the activity of iodine, 2 ml of toluene and 0.02 g of π-$C_5H_5Rh(C_2H_4)_2$ were placed in the dilation of the cell. This solution was frozen by liquid nitrogen, and 0.2 g of I_2 was added. The cell windows were positioned, the cell was evacuated, and the solution in the dilation was warmed. As toluene thawed, a vigorous evolution occurred of a gas which was identified as ethylene by its infrared spectrum. To show the effectiveness of Ag^+, a similar procedure was employed with ethylene glycol as solvent and $AgNO_3$ as the source of Ag^+

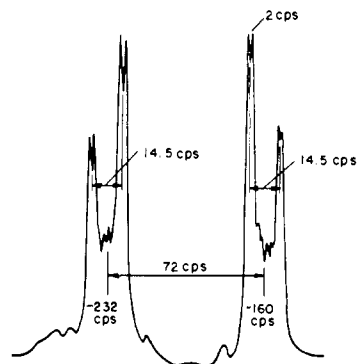(9) L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).

ion. A rapid evolution of ethylene ensued. Ag^+ does not displace ethylene from acetylacetonatodiethylenerhodium under similar conditions.

Reaction with tetracyanoethylene was conducted on a larger scale. A stirred solution of 0.45 g of π-$C_5H_5Rh(C_2H_4)_2$ (1.7 mmoles) in 20 ml of anhydrous tetrahydrofuran was blanketed with nitrogen at $-30°$, and 0.26 g of $C_2(CN)_4$ (2 mmoles) in 20 ml of anhydrous tetrahydrofuran was added during 0.5 hr. The homogeneous solution was concentrated after 3 hr under vacuum while the temperature was maintained below $-20°$. A black, gleaming crystalline solid (0.54 g) was recovered which appears to be the product of displacement of one molecule of coordinated ethylene by one of tetracyanoethylene. Attempts to purify the crude product were unsuccessful.

Anal. Calcd for $C_{13}H_9RhN_4$: C, 48.16; H, 2.80; N, 17.29. Found: C, 44.78; H, 2.76; N, 15.65.

The infrared spectrum (KBr wafer) contains absorptions at 3095 (C–H in coordinated ethylene), 2925 and 2855 (weak, saturated C–H), and 2222 and 2155 cm^{-1} (C≡N corresponding to a shift from CN in tetracyanoethylene toward ionic CN).

Ethylene Rotation in π-$C_5H_5Rh(SO_2)(C_2H_4)$. An nmr tube charged with 0.05 ml of tetramethylsilane and 0.12 g of π-C_5H_5Rh-$(C_2H_4)_2$ (0.5 mmole) was chilled in liquid nitrogen and evacuated. Then 250 ml of gaseous SO_2 (10 mmoles) was condensed into the tube which was sealed, and spectra were recorded with a Varian HR-60 instrument between 8 and $-70°$. The spectra all contain three areas of absorption: (1) a temperature-invariant absorption at -5.60 ppm due to cyclopentadienyl protons, (2) a temperature-invariant absorption at -5.46 due to the free ethylene displaced from π-$C_5H_5Rh(C_2H_4)_2$ by SO_2, and (3) a temperature-variable absorption centered at -3.32 ppm above about $-2°$ and splitting into a doublet at lower temperatures.