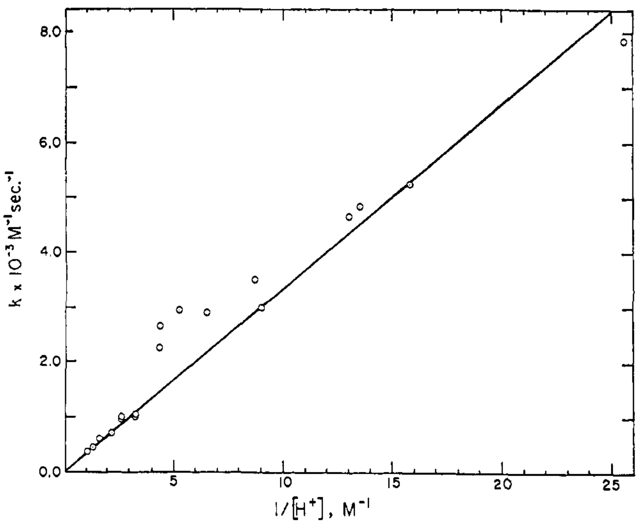

Figure 1. Low pH acid dependence of the Cr^{2+}/*trans*-Co(*trans*-[14]diene)$(OH_2)_2{}^{3+}$ reaction.

Several (but not all) mechanisms compatible with the observed rate law have been discussed at length by Haim.[15] A representative mechanism which satisfies features noted above includes the following steps (for

$$CoL_5OH_2 + Cr(OH_2)_6{}^{2+} \rightleftharpoons L_5Co^{III}\text{-}OH\text{-}Cr^{II}(OH_2)_5 + H^+ \quad (k_1, k_{-1})$$

$$L_5Co^{III}\text{-}OH\text{-}Cr^{II}(OH_2)_5 \rightleftharpoons L_5Co^{III}\text{-}O\text{-}Cr^{II}(OH_2)_5 + H^+ \quad (\text{rapid}, K_2)$$

$$L_5Co^{III}\text{-}X\text{-}Cr^{II}(OH_2)_5 \longrightarrow \text{products} \quad (k_{OH}, k_O)$$

$X = OH^-$ or O^{2-}). From data presented in Figures 1 and 2, values for the parameters in (1) may be estimated. If we assume a steady state is achieved in the dinuclear species, then the kinetic parameters can be related to the suggested mechanism: $a = K_1k_{OH} \simeq 3 \times 10^2$ sec^{-1}, $b/c = k_1K_2(k_O/k_{OH}) \simeq 1.2 \times 10^2$ sec^{-1}, and $a/c = k_1 \simeq 9 \times 10^3$ M^{-1} sec^{-1}. These and some related systems are still being investigated, and a full mechanistic discussion will be presented elsewhere. However, it is important to note that neither our observations nor the suggested mechanism require long lifetimes (*e.g.*, greater than 10^{-6} sec) for the precursor complexes.

A final point to note is that precursor complexes can not be formed in outer-sphere reactions. Thus the $Ru(NH_3)_6{}^{2+}$ reduction of *trans*-Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ is independent of $[H^+]$ in the range $1 \leq pH \leq 4$ ($k = (8.2 \pm 0.8) \times 10^2$ M^{-1} sec^{-1}). A few preliminary experiments at higher pH indicate the expected lower reactivity of *trans*-Co(*trans*[14]diene)$(OH_2)OH^{2+}$, but are complicated by the dimerization of the hydroxyaquo complex ($K_D \sim 90$ M^{-1} and $t_{1/2}$ for the formation of dimer is about 12 hr in 10^{-3} M *trans*-Co(*trans*[14]diene)$(OH_2)OH^{2+}$).

Complexes were prepared and characterized as described elsewhere.[17,18] Rates were obtained from absorbance changes using syringe, stopped-flow, and deaeration techniques described elsewhere.[11,12,19]

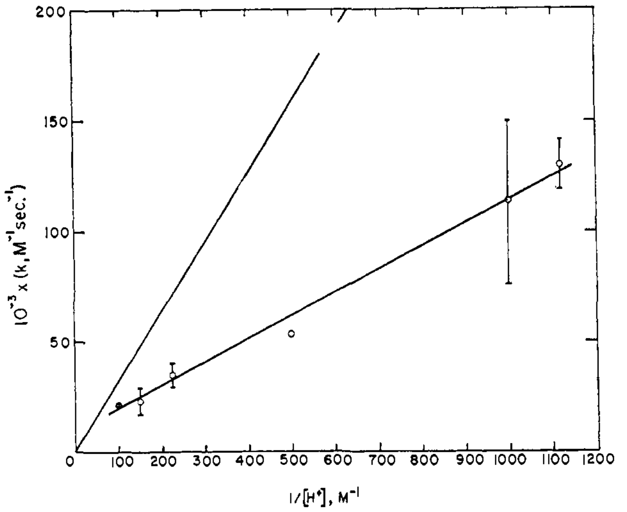

Figure 2. Acid dependence of the Cr^{2+}/*trans*-Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ reaction. The extrapolated line from the low pH region (Figure 1) is included for comparison. Entries with error flags represent mean values (and mean deviations) of three to five determinations at the same $[H^+]$. In the cases of these duplicate determinations the total [Co(III)] was varied by a factor of about 2 and the excess [Co(III)] by a factor of up to 7.

Reduction potentials were calculated from potential changes during redox titrations with Cr^{2+} using the titration of Fe^{3+} as a reference. Acid dissociation constants were determined from pH measurements (Instrumentation Laboratories Model 145 pH meter) during titration with standard acid or standard base at 25° and constant ionic strength.

All kinetic determinations were made at unit ionic strength ($NaClO_4$ or $LiClO_4$) and 25°. Acid concentrations were determined by dilution and by pH measurement.

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[20] NASA Trainee, 1966–1969.

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Received April 14, 1969

Structure of a Complex Containing a Metallocyclopentadiene Ring, $RhCl((C_6H_5)_3Sb)_2C_4(CF_3)_4 \cdot CH_2Cl_2$[1]

Sir:

The reactions of iron and cobalt carbonyls with acetylenic compounds produce a wide variety of complexes, some of which have been shown to contain heterocycles in which the transition metal is the heteroatom.[2] More recently, interest in the oxidative addition to d^8 complexes of the heavy transition metals has led to the preparation of a number of apparently similar species by the reactions of substituted acetylenes with, *e.g.*, RhL_3Cl ($L = As(C_6H_5)_3$, $Sb(C_6H_5)_3$),[3] $RhH(P(C_6H_5)_2C_6H_4)(P(C_6H_5)_3)_2$,[4] and $IrCl(N_2)(P(C_6H_5)_3)_2$,[5] but no definitive

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[1] Work supported by National Science Foundation Grant GP-8066.

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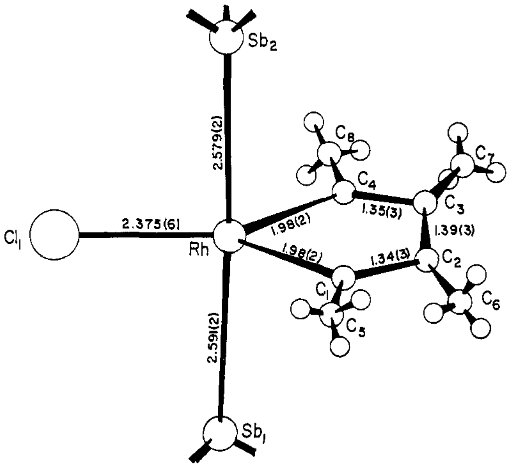

Figure 1. The $RhCl((C_6H_5)_3Sb)_2C_4(CF_3)_4$ molecule with the phenyl rings omitted for clarity.

structural evidence has been presented. In view of the great interest in this area, we wish to communicate the preliminary results of a structural study on the complex prepared from $RhCl(Sb(C_6H_5)_3)_3$ and hexafluorobutyne-2 which show that a rhodiacylopentadiene moiety is indeed present as originally postulated.[3]

Chlorobis(triphenylstibine)tetrakis(trifluoromethyl)-rhodiacyclopentadiene crystallizes as yellow-orange prisms from methylene chloride–diethyl ether. When prepared in this manner the complex is obtained as a dichloromethane solvate. The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ observed on Weissenberg and precession photographs (Cu Kα radiation) uniquely determine the space group as $P2_1/c$ (C_{2h}^5, No. 14).[6] The monoclinic unit cell has a = 13.257, b = 25.592, c = 16.801 Å; β = 125.58°; V = 4636 Å.[3] The observed density of 1.75 g/cc agrees well with the calculated value of 1.797 g/cc for $Z = 4$. A total of 3418 unique reflections within the sphere having $\sin \theta/\lambda \leq 0.5$ were collected on a Picker, automated, four-circle diffractometer (Cu Kα radiation, Ni filtered) using the θ–2θ scan procedure. Of these, 158 were considered to be unobserved, and all data were corrected for absorption (μ = 137.2 cm^{-1}). The structure was solved by Patterson and difference-Fourier techniques and refined by block-diagonal least-squares methods to a current conventional residual of 0.101 with all nonhydrogen atoms except for the phenyl group carbons allowed to vibrate anisotropically. Refinement is continuing with attempts being made to better treat the large thermal motions of the trifluoromethyl groups (particularly those containing C_6 and C_7).

Figure 1 gives a perspective view of the molecule. The data clearly show that the fluorocarbon moiety is σ-bonded to the rhodium giving a rhodiacyclopentadiene ring which is planar within experimental error (σ_{ring} = 0.02 Å). Relevant angles are Sb_2–Rh–Cl_1, 88; Sb_1–Rh–Cl_1, 90; Sb_1–Rh–Sb_2, 178; Cl_1–Rh–C_1, 139; Cl_1–Rh–C_4, 142; C_1–Rh–C_4, 78; Rh–C_1–C_2, 118; C_1–C_2–C_3, 113; C_2–C_3–C_4, 115; C_3–C_4–Rh, 117°. The coordination about rhodium is thus that of a slightly distorted trigonal bipyramid. The data further indicate that the solvent molecule has no strong tendency to occupy a sixth coordination position about rhodium since the angles Cl_1–Rh–C_1 and Cl_1–Rh–C_4 are very nearly equal.

It can be seen from Figure 1 that although the distances C_1–C_2 and C_3–C_4 are not significantly different from the corresponding values for 1,3-butadiene (1.337 (5) Å), the C_2–C_3 distance is noticeably shorter ($\Delta/\sigma \sim 3$) than in the latter compound (C_2–C_3 = 1.483 (10) Å in C_4H_6).[7] Also, the Rh–C_1 and Rh–C_4 distances appear shorter than that found in π-$C_5H_5Rh(CO)IC_2F_5$ (2.08 (3) Å),[8] but when account is taken of the difference in radius between sp^2 and sp^3 carbon atoms (~0.03 Å) this difference is not significant at the level of accuracy of our determination. If the metal is considered to be formally Rh(III), it lacks two electrons of possessing the rare gas configuration when π interaction with the rest of the ring is neglected. It would appear that although some degree of delocalization in the ring is likely, it is not possible at this point to draw any definite conclusions concerning it, and in particular no assessment can yet be made to what extent there is Rh–C multiple bonding. The fact that the complex reacts readily with donors such as carbon monoxide suggests that the tendency of the metal to attain the rare gas configuration through π overlap with the remainder of the ring is probably not very large. Hopefully more definite conclusions concerning this point can be reached when the structure is further refined.

Acknowledgment. We thank Dr. Charles Fritchie, Jr., for the use of the diffractometer.

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(6) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1959.

(7) Special Publication No. 18, The Chemical Society, London, 1965, M109s.

(8) M. R. Churchill, *Inorg. Chem.*, 4, 1734 (1965).

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Received April 7, 1969

The Thermal Dependence of Photoannelation[1]

Sir:

The effects of temperature on photochemical reactions in the condensed phase have been but sporadically studied. The references to a thermal effect in photoannelation are even more sparse although in a few specific cases the products and quantum efficiency have been shown to be temperature dependent.[2] We wish to report here the results of our study of temperature variation on the photoaddition of 2-cyclopentenone to olefins. The observations are striking and suggest immediate practical consequences. They may be interpreted, also, as supporting our present hypothesis of reversible intermediate formation in photoannelation.

In Table I are given the quantum yields of adduct formation from 2-cyclopentenone and four olefins at several different temperatures.[3] It can be seen that the quantum efficiencies do depend on temperature, and to different extents with different olefins. With *trans*-3-

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(1) Photochemical Synthesis, Part XXVII. Part XXVI: P. de Mayo, A. A. Nicholson, and M. F. Tchir, *Can. J. Chem.*, 47, 711 (1969).

(2) See, for instance, A. Cox, P. de Mayo, and R. W. Yip, *J. Amer. Chem. Soc.*, 88, 1043 (1966); D. Bryce-Smith and A. Gilbert, *Chem. Commun.*, 19 (1968).

(3) Details of the apparatus and procedures used will be published at a later date. All irradiations, including Stern-Volmer plots, were performed on an optical bench.