for providing the quantitative vibrational analysis of $Cp_2V_2(CO)_5$ isotopomers using his least-squares program.

Registry No. $Cp_2V_2(CO)_5$, 41699-43-8; $CpV(CO)_4$, 12108-04-2; $Cp_2V_2(CO)_4PPh_3$, 68875-54-7; $CpV(CO)_3PPh_3$, 12213-09-1; $Cp_2V_2(CO)_4(dpm)$, 73557-86-5; $CpV(CO)_3(dpm)$, 73574-37-5; $CpV(CO)_2(dpm)$, 61818-84-6; $CpV(CO)_3(dppe)$, 73557-87-6; $CpV(CO)_2(dppe)$, 12304-19-7; $CpV(CO)_3(PEt_2Ph)$, 12184-66-6; *cis*-$CpV(CO)_2(PEt_2Ph)_2$, 73610-20-5; $Cp_2V_2(CO)_4(PEt_2Ph)$, 73557-88-7; $Cp_2V_2(CO)_4(THF)$, 73557-89-8; $CpV(CO)_3(THF)$, 73557-90-1.

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Comparative Studies of Hydridorhodoxime and Its Conjugate Base, Bis(dimethylglyoximato)rhodate(1–) Ion

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Various reactions of the title compounds have been studied, with determinations of products, stoichiometry, and kinetics in aqueous methanol. Hydridorhodoxime, $HRh(dmgH)_2P(C_6H_5)_3$, has $pK_a \approx 9.5$. A study of the forward and reverse rates of neutralization reveals three pathways corresponding to reactions of the rhodium(I) anion with H_3O^+, H_2O, and Tham buffer. Hydridorhodoxime is further protonated at the oxime oxygens in acidic solution and decomposes under these conditions to hydrogen and the dimeric Rh(II) derivative $[Rh(dmgH)_2P(C_6H_5)_3]_2$. Both title compounds react with organic halides, the base in an S_N2 reaction to form alkyl and aralkyl organorhodoximes and the acid by hydrogen transfer forming the hydrocarbon. The rate constants (k, M^{-1} s^{-1}) in the former reactions are 1.66×10^4 (benzyl bromide), 1.04×10^3 (benzyl chloride), 9.6×10 (1-phenylethyl chloride), and 5.2×10^{-1} (*n*-butyl bromide); the respective values for hydridorhodoxime are 9.6×10^2, 5.4×10, and 1.8×10 M^{-1} s^{-1} (with *n*-butyl bromide not determined, owing to interference from decomposition). Various competition kinetic experiments were also performed to confirm the processes being studied. Reaction mechanisms are presented to account for the results obtained.

Introduction

The study of the catalytic properties of transition-metal–hydride complexes is a field of growing interest[1-5] in which there is a continuing need for quantitative data on the mode of M–H bond breaking and on the mechanism of hydrogen-transfer reactions. We set out to explore a number of quantitative issues relating to bis(dimethylglyoximato) complexes. Considering the cobalt complexes (so-called "cobaloximes"),[6] one recognizes that $HCo(dmgH)_2B$ and $Co(dmgH)_2B^-$ are related as conjugate acid and base.[7] Hydridocobaloxime[8] is, however, unstable toward hydrogen evolution:

$$2HCo(dmgH)_2B = H_2 + 2Co(dmgH)_2B \qquad (1)$$

This reaction is of interest in its own right[9] but interferes with a quantitative study of some of the chemistry underlying these compounds, such as the acid–base neutralization reactions and the role of the hydrido complex as a hydrogen-transfer reagent.

On the other hand there are several reports of the relatively higher kinetic stability of the rhodium–hydrogen bond as compared to the cobalt–hydrogen bond.[10,11] It has also been experimentally demonstrated that hydridorhodoximes such as $HRh(dmgH)_2P(C_6H_5)_3$ have catalytic properties in hydrogenation and hydrosilylation reactions.[12,13] Thus we have now investigated the formation and decomposition reactions of $HRh(dmgH)_2P(C_6H_5)_3$. In addition the reactions of alkyl halides with hydridorhodoxime and comparisons with the already reported[14] alkylation reactions of the conjugate base, $Rh(dmgH)_2P(C_6H_5)_3^-$, are of considerable interest. We have hence studied the reactions of benzyl chloride and bromide, α-phenylethyl chloride, and *n*-butyl bromide with $Rh(dmgH)_2P(C_6H_5)_3^-$ and $HRh(dmgH)_2P(C_6H_5)_3$ in aqueous methanolic (1:1) medium. Comparisons of the relative reactivities and the nature of products formed in these reactions have been made.

Experimental Section

Materials. Doubly distilled benzyl chloride, *n*-butyl bromide, 4-bromobenzyl bromide and 4-bromotoluene were used. Chloro(triphenylphosphino)bis(dimethylglyoximato)rhodium(III), $ClRh(dmgH)_2P(C_6H_5)_3$, was prepared by standard methods;[15] its purity was established by satisfactory elemental analyses and by the ^1H NMR spectrum. Anal. Calcd: C, 49.50; H, 4.63; N, 8.88. Found: C, 49.55; H, 4.62; N, 8.78.

(Triphenylphosphino)bis(dimethylglyoximato)rhodium(III) hydride, $HRh(dmgH)_2P(C_6H_5)_3$, was prepared by an adaptation of a published procedure.[16] Since it was found that rigorously oxygen-free conditions

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are essential for this preparation, all work was done under argon in a suitable experimental set up with a three-necked flask and a filter-funnel assembly. A dispersion of finely powdered $ClRh(dmgH)_2P(C_6H_5)_3$ (315 mg) in water–methanol (1:9) mixture (15 mL) was taken in a 50-mL three-necked round-bottomed flask. The slurry was stirred magnetically and cooled by an ice–salt mixture while extensively purged with argon. Sodium borohydride (25 mg) was added in five equal portions over a 60-min period while the temperature was maintained below 5 °C. Within about 30 min after the addition of $NaBH_4$ was complete, a bluish gray precipitate was obtained, which was filtered in an argon atmosphere and washed with ice-cold deaerated water. This product, which was contaminated with a reddish yellow impurity, was further washed with air-free methanol twice (10 mL each) and vacuum dried, yielding a bluish gray solid. Anal. Calcd for $HRh(dmgH)_2P(C_6H_5)_3$: C, 52.36; H, 5.07; N, 9.39. Found: C, 51.75; H, 5.16; N, 8.98. The IR spectrum, taken on a Nujol mull made in an argon-filled glovebag, indicated the presence of the Rh–H stretching vibration at 1980 cm^{-1}.

Chloro(triphenylphosphino)bis(difluoro(dimethylglyoximato)boron)rhodium(III), $ClRh(dmgBF_2)_2P(C_6H_5)_3$, was prepared by addition of boron trifluoride etherate (1 mL) to a suspension of $ClRh(dmgH)_2P(C_6H_5)_3$ (250 mg) in diethylene glycol monomethyl ether (10 mL). The mixture was stirred on a magnetic stirrer for 4 h at ca. 35 °C, during which the mixture became homogeneous. The addition of 8 volumes of ethyl ether to the filtered reaction mixture yielded a brownish green precipitate. This product was then dissolved in chloroform–acetone (8:1) mixture (27 mL), and ethyl ether (3 mL) was added. A minor amount of a precipitate was filtered. The cooled filtrate yielded crystals of a product which gave rise to a single spot on TLC (R_f = 0.22) whereas the parent complex $ClRh(dmgH)_2P(C_6H_5)_3$ has R_f = 0.3 with a chloroform–ethyl ether (4:1) mixture as the developing medium.

Dimeric (triphenylphosphino)bis(dimethylglyoximato)rhodium(II), $[Rh(dmgH)_2P(C_6H_5)_3]_2$, was prepared from decomposition of hydridorhodoxime in hydrochloric acid. A solution of $Rh(dmgH)_2P(C_6H_5)_3^-$ (10 mL, 5×10^{-2} M), obtained by the sodium borohydride reduction of $ClRh(dmgH)_2P(C_6H_5)_3$ in 0.2 M sodium hydroxide in methanol under argon, was treated with a deaerated solution of hydrochloric acid (1.1 mL, 2 M) and maintained at room temperature for 6 h. Addition of deaerated water (23 mL) gave rise to a red precipitate of the desired product, which was filtered and recrystallized twice from benzene under argon. The crystals obtained were then dried in vacuo and identified by NMR spectrum[17] and elemental analysis. Anal. Calcd for $[Rh(dmgH)_2P(C_6H_5)_3]_2$: C, 52.45; H, 4.91; N, 9.41. Found: C, 52.35; H, 4.52; N, 9.34.

Methanolic solutions of $Rh(dmgH)_2P(C_6H_5)_3^-$ were prepared in three ways: (a) reaction of the hydrido complex with 0.1 M sodium hydroxide, (b) controlled-potential reduction at a mercury electrode of alkaline solutions of $ClRh(dmgH)_2P(C_6H_5)_3$ at various voltages and alkali concentrations, (c) reduction of Rh(III) or Rh(II) complexes with sodium borohydride. The first method yielded impure solutions with varying amounts of a species, believed to be $[Rh(dmgH)_2P(C_6H_5)_3]_2$, with an intense visible absorption spectrum. Electrochemical reduction also gave largely the Rh(II) dimer, and at more negative potentials only an insoluble black product was obtained, consistent with published reports.[18] The starting complex for borohydride reduction was either $ClRh(dmgH)_2P(C_6H_5)_3$ or $[Rh(dmgH)_2P(C_6H_5)_3]_2$, but the former gave a purer product. The reduction was successful only if a stoichiometric quantity of sodium borohydride was used; unlike the cobalt analogue, reduction with excess sodium borohydride was quite difficult. Solutions of $Rh(dmgH)_2P(C_6H_5)_3^-$ were obtained by the reduction of $ClRh(dmgH)_2P(C_6H_5)_3$ (36–60 mg) dissolved in 0.2 M NaOH in methanol (3–5 mL) by sodium borohydride (3–5 mg) in an argon atmosphere. These solutions were purified on an air-free and ice-cooled Sephadex LH 20 gel-filtration column (0.8 × 25 cm), which had been preequilibrated with 0.2 M NaOH. Rhodium complexes were eluted from the gel with 0.20 M NaOH in methanol usually in three chromatographic bands. The yellow (unreduced Rh(III)) and red (believed to be Rh(II) dimer) bands moved faster than the major purplish brown band (the desired Rh(I) product). The rhodium(I) solutions thus obtained were remarkably sensitive to oxygen and were of the concentration (~3–50) × 10^{-3} M, corresponding to yields of about 50–60%. In a few preparations an unidentified and much slower moving green product (less than 5% on the basis of total Rh) was also observed. Since chromatographic separation of Rh(I) from this green product was quite distinct, no efforts to characterize the green product were made. The separation procedure generally took 12–16 h, and the solutions of $Rh(dmgH)_2P(C_6H_5)_3^-$ were stable for a period of ca. 18 h when kept cooled at ca. 0 °C in an argon atmosphere. The UV–visible spectrum of this rhodium(I) complex, shown in Figure 1, has absorption maxima λ 463 nm (ε 1935 ± 40 M^{-1} cm^{-1}) and 550 (450 ± 15), compared to that of $Rh(dmg_2H_3)\cdot 3H_2O$, 458 (7060) and 575 (670). The latter compound[19] is not completely pure; considering the high absorption at 458 nm and the intense absorption of the rhodium(II) dimer at this wavelength, traces of the latter may contaminate this compound.

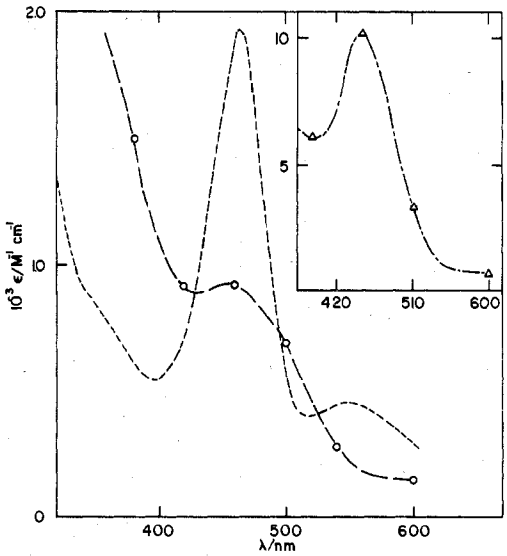

Figure 1. UV–visible spectra of $Rh^I(dmgH)_2P(C_6H_5)_3^-$ in 0.1 M NaOH in methanol (---), $HRh(dmgH)_2P(C_6H_5)_3$ in 0.03 M glycine buffer, pH 3.3 (-o-), and (inset) $[Rh(dmgH)_2P(C_6H_5)_3]_2$ in methanol. The spectrum of hydridorhodoxime has to be considered approximate owing to the ready decomposition into strongly absorbing products.

Solutions of $HRh(dmgH)_2P(C_6H_5)_3$ for use in kinetic studies were prepared by neutralization of Rh(I) solutions (obtained by a chromatographic separation) with either HCl or glycine buffer–HCl mixtures (0.01–0.025 M, to give a final pH of 2.0–3.3) or tris(hydroxymethyl)aminomethane (Tham) buffer–HCl mixtures (to give a final pH of 7.0–8.5). In view of the poor stability of these solutions at room temperature, the solutions of the hydrido complex for kinetic studies were freshly made and maintained at 5 °C. Solutions aged for more than 30 min were not used for kinetic measurements. Ionic strength adjustments were made with sodium chloride, as perchlorate ions showed some tendency to be reduced by the rhodium(I) solutions.

Analyses. The concentration of rhodium in Rh(I) solutions was estimated by standard methods,[20] which essentially consist of conversion to a rhodium(III) diphenylcarbazone complex, with a molar absorptivity of 6.1 × 10^4 M^{-1} cm^{-1} at 565 nm. Routine analysis of Rh(I) concentrations was spectrophotometric at 463 nm (ε 1.9 × 10^3 M^{-1} cm^{-1}). A gc separation was used for 4-bromotoluene, a product of the reaction of hydridorhodoxime and 4-bromobenzyl bromide. Solutions 10^{-4}–10^{-3} M in 1:1 H_2O–CH_3OH could be successfully separated and detected by using an operating temperature of 210 °C on a Tenax column with an electron-capture detector.

Results

Reactions and Products. We first present information on the various reactions occurring and in later sections give a detailed study of the kinetics of selected reactions. The spectrum of $Rh(dmgH)_2P(C_6H_5)_3^-$ in H_2O–CH_3OH (1:1) was

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analyzed as a function of pH in the range 7–12. It was observed that the spectrum is independent of pH in the range 10–12; in the pH region 7.0–9.5 (in Tham buffer), it is converted to a product having much smaller optical density at 460 nm. The latter product decomposed slowly with time to give a product having an intense absorption maximum at 457 nm. Further examination of the spectrum of Rh(I) solutions after being mixed with glycine buffer (in the pH range 2.2–3.5) also pointed out that there were two distinctly separated kinetic processes, one with $t_{1/2}$ ca. 0.5–5 s and another $t_{1/2}$ ca. 7–10 min. The slower step was also associated with gas evolution and a substantial increase in optical density at 460 nm. Formation of a hydridorhodoxime with a pK_a of 9.5 is consistent with the present experimental evidence and with the assignment of Schrauzer et al.;[14] its spectrum is also shown in Figure 1. The first kinetic step corresponds to the formation of hydridorhodoxime (eq 2) and the second step to its decomposition with the evolution of hydrogen (eq 3).

$$Rh(dmgH)_2P(C_6H_5)_3^- + H_3O^+ = HRh(dmgH)_2P(C_6H_5)_3 + H_2O \quad (2)$$

$$2HRh(dmgH)_2P(C_6H_5)_3 = H_2 + [Rh(dmgH)_2P(C_6H_5)_3]_2 \quad (3)$$

The final spectrum at the end of the second step depended on the pH of the reaction mixture. The addition of water to such a reaction mixture resulted in a precipitate of the Rh(II) dimer, but ion-exchange chromatography of the same reaction mixture on a Dowex 50W-X8 also indicated the presence of an air-stable cationic rhodium byproduct, possibly Rh(III).

Since eq 2 and 3 imply that a relatively unstable hydridorhodoxime is formed, the reactions of an aralkyl halide (benzyl chloride) and alkyl halide (*n*-butyl bromide) with unacidified and preacidified solutions of the complex $Rh(dmgH)_2P(C_6H_5)_3^-$ were investigated in 1:1 H_2O–CH_3OH. At 0.1 N NaOH, where the predominant form is the rhodium(I) anion, a single stage reaction with a large decrease in absorbance at 460 nm was observed with both benzyl chloride and *n*-butyl bromide, the former giving a product with an absorption spectrum (λ_{max} 390 nm) typical of organorhodoximes. Therefore the reaction at 0.1 N NaOH with benzyl chloride and *n*-butyl bromide (RX) can be written as in eq 4.

$$Rh(dmgH)_2P(C_6H_5)_3^- + RX = RRh(dmgH)_2P(C_6H_5)_3 + X^- \quad (4)$$

Hydridorhodoxime, on the other hand, reacts with benzyl chloride and *n*-butyl bromide to produce a mixture of the rhodium(II) dimer and a rhodium(III) complex. Toluene is detected in the former reaction, but practical difficulties prevented a quantitative assay. With 4-bromobenzyl bromide, however, 4-bromotoluene was found in 90% yield. Thus the sequence of reactions of hydridorhodoxime with aralkyl halides (and presumably alkyl halides) is

$$HRh(dmgH)_2P(C_6H_5)_3 + RX + H_2O \rightarrow RH + (H_2O)Rh(dmgH)_2P(C_6H_5)_3^+ \quad (5a)$$

$$(H_2O)Rh(dmgH)_2P(C_6H_5)_3^+ + HRh(dmgH)_2P(C_6H_5)_3 \rightarrow H_3O^+ + [Rh(dmgH)_2P(C_6H_5)_3]_2 \quad (5b)$$

The overall stoichiometry of reaction between hydridorhodoxime and RX to produce RH will thus vary between 2:1 and 1:1 depending on the relative rates of eq 5a,b and the identity of RX. With a fast reacting RX such as benzyl bromide or 4-bromobenzyl bromide, eq 5a seems to be the dominant reaction to produce nearly 0.9 mol of RH/mol of hydridorhodoxime used. With benzyl chloride as RX, typically 15% of the rhodium was converted to the rhodium(II) dimer.

The addition of alkali to a solution of hydridorhodoxime in H_2O–CH_3OH (1:1) in glycine buffer at pH 3.3–3.5 immediately produced a change in absorption spectrum to that of the rhodium(I) anion, further identified by its ready reaction with benzyl chloride. The chief reaction occurring is thus

$$HRh(dmgH)_2P(C_6H_5)_3 + OH^- = Rh(dmgH)_2P(C_6H_5)_3^- + H_2O \quad (6)$$

with side reactions which did not, however, interfere with a kinetic study of the reaction. The side reactions may be eq 3 and perhaps a reaction of a Rh(III) complex, derived from decomposition of hydridorhodoxime, with Rh(I), to form $[Rh^{II}]_2$.

Kinetic Studies, Eq 2. Formation of hydridorhodoxime was monitored at 460 nm by using a Durrum stopped-flow spectrophotometer under conditions of varying H_2O:CH_3OH ratios, $[Rh]_T = (0.5–2) \times 10^{-4}$ M, 25.0 °C, and ionic strength 0.30 M (NaCl). Effective $[H^+]$ control was obtained by neutralization of NaOH contained in Rh(I) solutions with calculated amounts of acid (HCl) contained in suitable buffers. Tham buffer was used for $[H^+] = 1 \times 10^{-7}$ to 3.2×10^{-10} M and $[Tham]_T = 0.01–0.03$ M, glycine buffer for $[H^+] = 1 \times 10^{-2}$ to 4×10^{-4} M and $[glycine]_T = 0.01–0.025$ M, and HCl for $[H^+] = 1 \times 10^{-2}$ to 1×10^{-1} M. The pH measured after such neutralization of NaOH was reproducible within 0.15 unit with Tham buffer and 0.05 unit with glycine buffer (except in the range of 3.5). At 460 nm and $[H^+] = 2 \leq 10^{-2}$ M, a decrease in absorbance for reaction 2 was observed. At $[H^+] = 2 \times 10^{-2}$ M, it was observed that the accompanying side reaction of eq 3, which has associated with it a large increase in absorbance at this wavelength, gave rise to inaccurate final absorbance readings. At 510 nm such complications did not arise and pseudo-first-order plots were linear to at least 3.5 half-lives, with an increase in absorbance for reaction 2 at this wavelength. The kinetic data are used to evaluate a pseudo-first-order rate constant for this process designated k_2. An interesting reversal in the direction of absorbance change is seen at 460 nm (a phenomenon unrelated to the decomposition reaction of eq 3, which occurs much more slowly; see the next section). Thus at $[H^+] \leq 0.02$ M, the absorbance decreases at 460 nm with occurrence of reaction 2, whereas it increases at 510 nm. In all cases, however, the rate constants agreed at both wavelengths irrespective of $[H^+]$ and the direction of absorbance change. We attribute the reversal in direction at 460 nm to an equilibrium rapidly established after reaction 2, resulting in a mixture of hydridorhodoxime and a protonated derivative, the order of molar absorptivities at 460 nm being $HRh(dmg_2H_3)P(C_6H_5)_3^+ > Rh(dmgH)_2P(C_6H_5)_3^- > HRh(dmgH)_2P(C_6H_5)_3$. The equilibrium referred to, for which independent evidence is given in the next section, is

$$HRh(dmgH)_2P(C_6H_5)_3 + H^+ \overset{K_7}{\rightleftharpoons} HRh(dmg_2H_3)P(C_6H_5)_3^+ \quad (7)$$

The value of k_2 varied with the concentration of Tham (but not glycine) buffer as shown in Table I and also with solvent composition (H_2O:CH_3OH ratio), which may be due either to the dependence of rate on the concentration of water or to changes in activity coefficients with solvent composition. At a fixed H_2O:CH_3OH ratio, the variation of k_2 is expressed by eq 8. A least-squares fit of data to eq 8 gave values $k_a = (2.3 \pm 1.1) \times 10^{-2}$ s^{-1}, $k_b = 6.0 \pm 0.68$ M^{-1} s^{-1}, $k_c = 36 \pm 1.2$ M^{-1} s^{-1} at 25.0 °C and ionic strength 0.3 M (NaCl) in 1:1 H_2O/CH_3OH.

$$k_2 = k_a + k_b[Tham]_T + k_c[H^+] \quad (8)$$

Kinetic Studies, Eq 3. The kinetics of decomposition of hydridorhodoxime were monitored at either 410 or 460 nm $[H^+] = (0.1–20) \times 10^{-3}$ M, $[glycine]_T = 0.03$ M, and $[Rh]_T = (0.3–2) \times 10^{-4}$ M in 1:1 H_2O–CH_3OH. The first-order rate

Table I. Kinetic Data[a] for Reaction of $Rh(dmgH)_2P(C_6H_5)_3^-$ with Acids According to Eq 2

10^2[buffer]/M	$[H^+]$/M	k_2/s^{-1} obsd	k_2/s^{-1} calcd[b]
1.00 (T)	3.0×10^{-9}	0.080 ± 0.003	0.083
1.00 (T)[c]	7.1×10^{-8}	0.082 ± 0.002	0.083
1.60 (T)[c]	3.1×10^{-8}	0.13 ± 0.01	0.119
2.25 (T)	1.0×18^{-8}	0.157 ± 0.003	0.158
2.25 (T)	2.0×10^{-8}	0.14 ± 0.01	0.158
2.25 (T)	3.1×10^{-8}	0.150 ± 0.003	0.158
2.25 (T)	8.3×10^{-8}	0.166 ± 0.004	0.158
3.00 (T)	3.1×10^{-8}	0.200 ± 0.004	0.203
2.50 (G)	4.5×10^{-3}	(0.149 ± 0.004)[e]	0.184
2.50 (G)	6.3×10^{-3}	0.295 ± 0.01	0.250
2.0 (G)	1.0×10^{-2}	0.34 ± 0.02	0.383
...	1.0×10^{-2}	0.34 ± 0.01	0.383
...	3.0×10^{-2}	1.15 ± 0.14	1.10
...	5.0×10^{-2}	1.64 ± 0.07	1.82
...	5.0×10^{-2}	1.96 ± 0.02	1.82
...	7.5×10^{-2}	2.96 ± 0.05	2.72
...	1.0×10^{-1}	3.75 ± 0.15	3.62
...	5.0×10^{-2}	1.71 ± 0.06[e,f]	1.82
...	2.0×10^{-2}	0.86 ± 0.01[e,f]	0.74
2.25 (T)[c]	1.0×10^{-8}	0.102 ± 0.005	
2.25 (T)[c]	1.0×10^{-7}	0.114 ± 0.004	
2.25 (T)[d]	1.0×10^{-8}	0.208 ± 0.002	
2.25 (T)[d]	3.1×10^{-8}	0.220 ± 0.003	
2.25 (T)[d]	1.0×10^{-7}	0.198 ± 0.004	
1.0 (T)[d]	3.1×10^{-8}	0.134	

[a] Conditions: 25.00 ± 0.03 °C, ionic strength 0.30 M (sodium chloride) in H_2O-CH_3OH (1:1 by volume, except as noted) with $[Rh]_T = (0.8–4.0) \times 10^{-4}$ M, studied at 460 and 510 nm with Tham (T), glycine (G) or no buffer present. [b] Calculated k_2 according to eq 8 with parameters as given in the text. [c] 1:1.57 H_2O-CH_3OH. [d] 1.57:1 H_2O-CH_3OH. [e] Not used in data analysis. [f] Added $P(C_6H_5)_3$, 2.0×10^{-3} M.

Table II. Kinetics[a] of Decomposition of Hydridorhodoxime According to Eq 3

$10^4[H^+]$/M	$10^4 k_3/s^{-1}$ obsd	$10^4 k_3/s^{-1}$ calcd[b]
0.90	0.60	0.609
5.00	1.95	1.56
10.0	2.50	2.67
16.0	3.75	3.95
63.0	12.5	12.1
89.0	15.6	15.5

[a] Conditions: 25.00 ± 0.03 °C, ionic strength 0.30 M (sodium chloride) in H_2O-CH_3OH (1:1 by volume). [b] Calculated k_3 according to eq 9 with parameters as given in the text.

plots were linear to 4–5 half-lives. The rate constants, k_3, are given in Table III. The dependence of k_3 on $[H^+]$ is described by the rate law in eq 9. A nonlinear least-squares fit of k_3

$$k_3 = \frac{k_d + k_e K_7 [H^+]}{1 + K_7 [H^+]} \quad (9)$$

to eq 9 gave values of $k_d = (3.95 \pm 0.6) \times 10^{-5}$ s^{-1}, $K_7 = 45 \pm 25$ M^{-1}, and $k_e K_7 = 0.24 \pm 0.03$ M^{-1} s^{-1} at 25.0 °C, and the ionic strength was 0.1 M (NaCl). This rate law can be easily rationalized as in the case of analogous cobalt(III) systems by eq 10–12. Since the buffer dependence of k_3 was

$$HRh(dmgH)_2P(C_6H_5)_3 + H_2O \xrightarrow{k_d} H_2 + HORh(dmgH)_2P(C_6H_5)_3 \quad (10)$$

$$HRh(dmg_2H_3)P(C_6H_5)_3^+ + H_2O \xrightarrow{k_e} H_2 + H_2ORh(dmgH)_2P(C_6H_5)_3^+ \quad (11)$$

$$HRh(dmgH)_2P(C_6H_5)_3 + H_2ORh(dmgH)_2P(C_6H_5)_3^+ \xrightarrow{\text{fast}} [Rh(dmgH)_2P(C_6H_5)_3]_2 + H_3O^+ \quad (12)$$

Table III. Kinetic Data[a] for Reaction of Hydridorhodoxime with Organic Halides According to Eq 5

10^2[RX]/M	k_5/s^{-1}	$k_5[RX]^{-1}/M^{-1}$ s^{-1}
	(a) $C_6H_5CH_2Cl$	
0.60	0.30 ± 0.001	50.0
1.10	0.61 ± 0.001	55.5
1.50	0.87 ± 0.01	58.0
2.20	1.08 ± 0.04	49.1
2.20	1.18 ± 0.08	53.6
3.00	1.78 ± 0.05	59.3
	av	53.7 ± 2.2
	(b) $C_6H_5CH_2Br$	
0.250	2.45 ± 0.25	980
0.510	4.3 ± 0.1	843
0.760	7.5 ± 0.1	987
	av	960 ± 30
	(c) $C_6H_5CH(CH_3)Cl$	
0.125	0.021	16.8
0.250	0.046	18.4
0.625	0.123	19.7
	av	18.3 ± 1.5

[a] Conditions: 25.00 ± 0.03 °C; $[H^+] = 5 \times 10^{-4}$ M with 0.013 M total glycine buffer at ionic strength 0.30 M (sodium chloride) in H_2O-CH_3OH (1:1 by volume).

not analyzed, it is difficult to distinguish the reactant in eq 10 as to whether it is H_2O, as shown, or protonated glycine. However the k_d term corresponds to the intercept in a plot of k_3 against $[H^+]$ and at $[H^+] \leq 3 \times 10^{-4}$ M, and the proportion of protonated glycine (with an apparent dissociation constant of 2.34×10^{-3} M in 1:1 H_2O–CH_3OH) was quite small under these acid conditions, suggesting water to be the more probable reactant in eq 10.

Kinetic Studies, Eq 4. The alkylation reactions of the rhodoxime(I) anion and organic halides are well-characterized reactions.[14] The rates are described by the second-order expression

$$-d[Rh(dmgH)_2P(C_6H_5)_3^-]/dt = k_f[Rh(dmgH)_2P(C_6H_5)_3^-][RX] \quad (13)$$

and the reaction is believed to occur by an S_N2 mechanism. The rate constants under the conditions of interest here (1:1 H_2O–CH_3OH, 0.1 M OH^- at 25.0 °C) are $k_f = 0.52 \pm 0.01$ M^{-1} s^{-1} (*n*-butyl bromide), $(1.04 \pm 0.03) \times 10^3$ (benzyl chloride), $(1.66 \pm 0.08) \times 10^4$ (benzyl bromide), and 96 ± 2 (α-phenylethyl chloride).

Kinetic Studies, Eq 5. The reaction of hydridorhodoxime with benzyl chloride was monitored at 460 nm by using a large excess of the latter reagent, $(0.6–3.0) \times 10^{-2}$ M. Other conditions were $[Rh]_T = (0.7–1.5) \times 10^{-4}$ M, $[glycine]_T = 0.013$ M, $[H^+] = 3 \times 10^{-4}$ M, and ionic strength 0.1 M (NaCl) at 25 °C in 1:1 H_2O–CH_3OH. Solutions of $HRh(dmgH)_2P(C_6H_5)_3$ were made up by the acidification of Rh(I) with glycine buffer–HCl mixtures of appropriate concentrations. The decomposition of hydridorhodoxime was minimized by cooling of the stock solutions to ~5 °C; the decomposition products, Rh(II) dimer and Rh(III) complexes, did not react with benzyl chloride on the time base of interest. The rate plots were linear to 3–4 half-lives and the rate constants, k_5, exhibited a first-order dependence on benzyl chloride concentrations:

$$k_5 = k_g[C_6H_5CH_2Cl] \quad (14)$$

A least-squares fit of the data in Table III to eq 14 gave $k_g = 53.7 \pm 2.2$ M^{-1} s^{-1}.

Similar studies were carried out by using benzyl bromide ($k = (9.6 \pm 0.3) \times 10^2$ M^{-1} s^{-1}) and α-phenylethyl chloride ($k = 18.3 \pm 1.5$ M^{-1} s^{-1}). Reaction with *n*-butyl bromide occurs too slowly for accurate measurement, and the bulk of

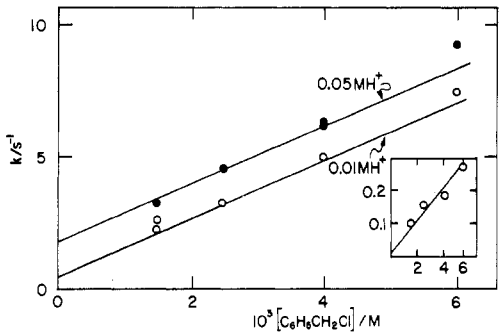


Figure 2. Plots of the observed pseudo-first-order rate constants for experiments involving competitive reactions of $Rh(dmgH)_2P(C_6H_5)_3^-$ with HCl and $C_6H_5CH_2Cl$. The lines drawn are those calculated according to eq 15. Inset: The slower stage seen in the competition kinetics corresponds to the reaction of hydridorhodoxime and benzyl chloride; the line is the theoretical one according to eq 5 and 14.

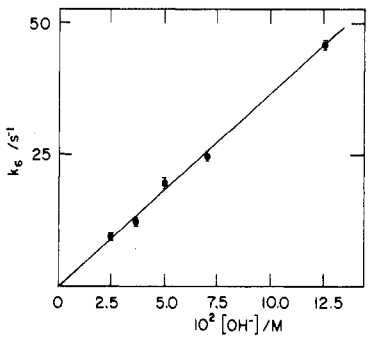


Figure 3. A plot of k_6 for the reaction of hydridorhodoxime with alkali vs. $[OH^-]$ showing the linear dependence as in eq 17.

the reaction observed corresponds to decomposition of hydridorhodoxime according to eq 3.

Competitive Kinetics, Reactions 2 and 4. When basic solutions of the rhodium(I) rhodoxime anion are mixed with HCl solutions of benzyl chloride, reaction with the former to produce hydridorhodoxime or with the latter to produce benzylrhodoxime may occur. Such experiments will yield no new information, but the occurrence of competitive reactions will serve to confirm the nature of the individual processes. Indeed, reactions conducted in this manner do give the expected behavior. There is a rapid first stage which is expected to be reactions 2 and 4 together, followed by a slower step which is consistent with the reaction of hydridorhodoxime formed in eq 2 reacting with benzyl chloride according to eq 5. The pseudo-first-order rate constants for the faster stage are plotted as a function of $[PhCH_2Cl]$ in Figure 2 which shows data at 0.010 M H^+ and 0.050 M H^+. The lines shown in the figure are those drawn to correspond to the theoretical value according to relation 15 with use of values of k_a, k_c, and k_g from

$$k = k_a + k_c[H^+] + k_g[C_6H_5CH_2Cl] \qquad (15)$$

the separate determinations. As shown from the data depicted in this figure, the observed rate constants do correspond within experimental error to the calculated values.

When such competitive reactions were monitored at 510 nm, the first stage always corresponded to an increase in absorbance, consistent with the molar absorptivities in eq 2 and 4. At 460 nm, however, the faster stage was represented by an absorbance decrease at 0.01 M H^+ but an increase at 0.05 M H^+. This too is consistent with the opposite direction of absorbance change associated with these reactions at this wavelength, dependent upon the ratio of $[H^+]$ to $[PhCH_2Cl]$. As stated in the preceding paragraph and shown in Figure 2, the observed rate constants are internally consistent and wavelength independent.

A detailed analysis of the second stage was not made, but the rates are expected to be those corresponding to the sum for the competing decomposition (eq 3) and hydride-transfer (eq 5) reactions:

$$k' = k_3 + k_g[PhCH_2Cl] \qquad (16)$$

Figure 2 also shows the values of k' (at 0.01 M H^+) plotted against $[PhCH_2Cl]$, the line being the theoretical one according to eq 8 with use of the independently determined rate constants.

Kinetic Studies, Eq 6. The kinetics of reaction of hydroxide ions with hydridorhodoxime were monitored at 460 nm where the rhodium(I) product has the higher molar absorptivity. The complex $HRh(dmgH)_2P(C_6H_5)_3$ was generated from the Rh(I) anion by addition of glycine buffer to pH 3.3–3.5. Subsequent addition of alkali gave rise to a kinetic step measurable by using the stopped-flow technique. Kinetic studies were carried out at 25.0 °C in H_2O–CH_3OH (1:1 by volume), at ionic strength 0.30 M (sodium chloride) over a range of sodium hydroxide concentrations, 0.025–0.125 M. The pseudo-first-order rate constant, k_6, showed a direct dependence upon $[OH^-]$ (eq 17) as illustrated in Figure 3. Although the decomposition reactions of hydridorhodoxime did not seem to influence the measured rates of reaction 6, the magnitude of the observed absorbance changes did decrease with the age of the solutions. A least-squares analysis gives $k_h = 374 \pm 6\ M^{-1}\ s^{-1}$.

$$k_6 = k_h[OH^-] \qquad (17)$$

Competitive Kinetics, Reactions 5 and 6. Only a few experiments were carried out on the reaction of hydridorhodoxime with a mixture of sodium hydroxide and benzyl chloride, this being done under conditions where the rhodoxime(I) anion produced in eq 6 would then react very rapidly with benzyl chloride in the alkylation process shown in eq 4. The experiments were designed to test that reaction of hydridorhodoxime with alkali does, indeed, produce the Rh^I compound and is not some other neutralization process such as an equilibrium involving oxime oxygens. Thus the experiments were performed at 460 nm, a wavelength at which the expected sequence of reactions (eq 6, followed rapidly by eq 4) will lead to a decrease in absorbance whereas reaction 4 or 5 would itself give increases. Indeed an absorbance decrease was observed, because the decrease associated with the sequence chosen by concentration adjustment to be dominant (eq 6, then eq 4) was only partially offset by the opposing change accompanying the direct reaction of hydridorhodoxime with benzyl chloride (eq 5). The rate constants observed under the usual conditions at 0.010 M OH^- were $4.34 \pm 0.06\ s^{-1}$ (1.25×10^{-2} M $C_6H_5CH_2Cl$) and $5.17 \pm 0.07\ s^{-1}$ (1.57×10^{-2} M). These compare satisfactorily with predicted values calculated according to eq 18, which are 4.41 ± 0.09 and $4.58 \pm 0.10\ s^{-1}$, respectively.

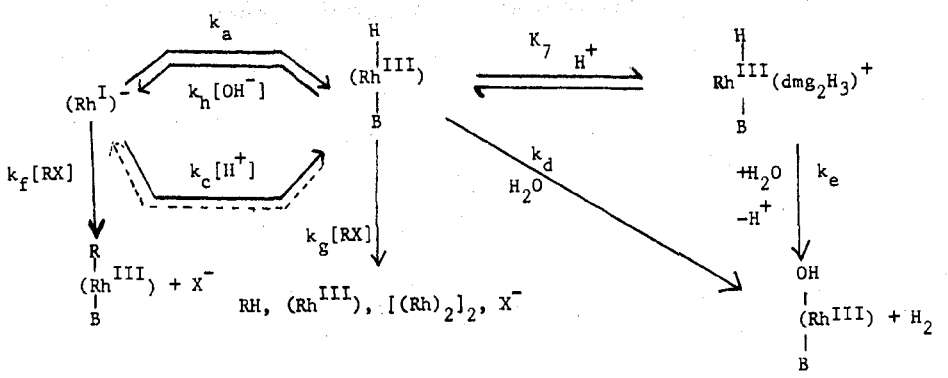
$$k = k_g[C_6H_5CH_2Cl] + k_h[OH^-] \qquad (18)$$

Discussion

Under the different conditions examined, a number of independent reactions were examined. A summary of the various reactions is given in Scheme I, in which the rate constants are symbolized in the same manner as in the preceding presentation of the results. In the paragraphs that follow, selected aspects of this chemistry will be discussed further.

Several lines of evidence developed in this work show the interconvertibility of hydridorhodoxime and its conjugate base, the anionic rhodium(I) rhodoxime, by neutralization reaction involving H^+, H_2O, and OH^-. The kinetic studies of forward

Scheme I



and reverse reactions were carried out under very different pH conditions, however, and it is necessary to show how the different sets of results can be accounted for consistently. The kinetic data suggest that there are two parallel neutralization pathways:

$$HRh(dmgH)_2P(C_6H_5)_3 + OH^- \rightleftarrows Rh(dmgH)_2P(C_6H_5)_3^- + H_2O \quad (19)$$

$$HRh(dmgH)_2P(C_6H_5)_3 + H_2O \rightleftarrows Rh(dmgH)_2P(C_6H_5)_3^- + H_3O^+ \quad (20)$$

The rate constants are identified as $k_{19} = k_h$, $k_{-19} = k_a$, and $k_{-20} = k_c$. The former pair led to a value of the equilibrium constant $K_{19} = k_{19}/k_{-19} = 1.6 \times 10^4$ M^{-1}; this value agrees adequately with a value $K_{20} \approx 3 \times 10^4$ M^{-1} estimated from the pK_a for hydridorhodoxime ($pK_a = pK_{20}$) and K_w. On the basis of $K_{20} = 10^{-9.5}$ and the value $k_{-20} = 36$ M^{-1} s^{-1}, the value of k_{20} should be 1.1×10^{-8} s^{-1}. The forward step of eq 20 should thus be an unimportant component of the reactions of hydridorhodoxime at the high $[OH^-]$ concentrations used in these studies; the nearly zero intercept in Figure 3 is consistent with this formulation. It should be noted, of course, that the acid–base equilibrium at rhodium is established very slowly compared to diffusion-controlled rates usually encountered at oxygen or nitrogen. The slowness of rate is consistent with findings on deuteriocobaloxime.[9,21]

Hydridorhodoxime appears to be an acid of strength comparable to that of the cobalt analogue[8,9] but much greater than that of related compounds such as $HRh(en)_2OH^+$ (pK_a = 12),[22] $HRh(NH_3)_5^{2+}$,[10] or $HCo(CN)_5^{3-}$ ($pK_a \approx 20$).[23] In keeping with this, its rate of reaction ($k_{19} = 3.7 \times 10^2$ M^{-1} s^{-1}) is much higher than the corresponding process for $HCo(CN)_5^{3-}$ ($k = 9.7 \times 10^{-2}$ M^{-1} s^{-1}).[23]

Whereas $HRh(NH_3)_5$ is known to be very stable against hydrogen evolution even in high acid concentrations,[10] the relative ease with which $HRh(dmgH)_2P(C_6H_5)_3$ decomposes to give hydrogen is striking. At the low rhodium concentrations employed, limited by the production of insoluble materials at higher concentrations, heterolytic pathways having a first-order dependence on the concentration of hydridorhodoxime seemed to dominate in hydrogen evolution. Possibly the strong-field phosphine and $dmgH^-$ ligands contribute to the relative ease of hydrogen loss. The strongly acid-catalyzed pathway for H_2 evolution suggests either a much higher rate of hydrogen from the protonated derivative as compared to the unprotonated (i.e., k_e for eq 11 >> k_d for eq 10) or that the elementary reaction in place of eq 11 is really a hydride-transfer reaction such as

$$HRh(dmgH)_2P(C_6H_5)_3 + H_3O^+ \rightarrow [H_2ORh(dmgH)_2P(C_6H_5)_3]^+ + H_2 \quad (21)$$

with $k_{21} = k_eK_7 = 0.24$ M^{-1} s^{-1}. The latter appears to be a reasonable but not unique formulation. The value of k_{21} is quite comparable to that found[9] for the cobaloxime analogue, 0.42 M^{-1} s^{-1}. A further analogy can be drawn in the two systems: protonation of oxime oxygens of hydridorhodoxime is characterized by the equilibrium constant $K_7 = 45 \pm 25$ M^{-1} in comparison to the value[9] for hydridocobaloxime, 130 ± 10 M^{-1}.

Either formulation requires a fast reaction follow to complete the net overall process. This is the reaction of hydridorhodoxime and rhodium(III) as shown in eq 12. There is ample evidence for a fast reaction[18] between Rh(I) and Rh(III) complexes, much like that between the cobalt analogues,[24] and the reaction shown is also a very reasonable first reaction.

The reactions of the rhodium(I) anion with alkyl and aralkyl halides occur by nucleophilic substitution. In contrast the nature of the reactions employing hydridorhodoxime is quite different; the products are those from hydride transfer, including toluene (from benzyl chloride) and 4-bromotoluene (from 4-bromobenzyl bromide), as shown in eq 5. Similar reactions of trialkyl metal hydrides such as tri-*n*-butyltin hydride, $(n\text{-}Bu)_3SnH$, have been reported.[25] These probably occur by radical mechanisms, however, and the validity of any comparisons is questionable. It is useful to compare the rate constants determined here for the two rhodium systems.

	k/M^{-1} s^{-1}	
RX	H(Rh)	$(Rh)^-$
$C_6H_5CH_2Br$	960	16600
$C_6H_5CH_2Cl$	54	1040
$C_6H_5CH(CH_3)Cl$	18	96

It is clear that the rhodium(I) reagent shows greater differences in reactivity as the nature of the halide is varied and also greater steric requirements. This is not surprising considering this nucleophile attacks directly at the α-carbon atom of RX. Hydridorhodoxime, on the other hand, is believed to function as a hydride donor, and while the reactivity order might be similar, a less severe change in rate is to be expected. It should also be noted that such a process or rate limiting step

$$HRh(dmgH)_2P(C_6H_5)_3 + RX \rightarrow Rh^{III}(dmgH)_2P(C_6H_5)_3^+ + RH + X^- \quad (22)$$

must then be followed by the fast reaction of eq 12 to complete the overall process.

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Another mechanism consistent with the experimental data for the reaction of hydridorhodoxime and organic halides involves radical intermediates. Such a possibility is shown by reactions 23–26.

$$HRh(dmgH)_2P(C_6H_5)_3 + RX \rightarrow RH + Rh^{II}(dmgH)_2P(C_6H_5)_3 + X\cdot \quad (23)$$

$$2Rh^{II}(dmgH)_2P(C_6H_5)_3 \rightarrow [Rh^{II}(dmgH)_2P(C_6H_5)_3]_2 \quad (24)$$

$$Rh^{II}(dmgH)_2P(C_6H_5)_3 + X\cdot \rightarrow XRh(dmgH)_2P(C_6H_5)_3 \quad (25)$$

$$HRh(dmgH)_2P(C_6H_5)_3 + X\cdot \rightarrow H^+ + Rh^{II}(dmgH)_2P(C_6H_5)_3 + X^- \quad (26)$$

According to this proposal eq 23 is rate-limiting; the monomeric rhodium(II) complex would have a lifetime similar to at least the $Rh(NH_3)_4^{2+}$ complex.[26] The contrasting features of hydridorhodoxime compared to hydridocobaloxime are that both cobalt complexes, $(Co^I)^-$ and H(Co), are reported[8] to form alkylcobaloximes at comparable rates in protic media (but not in organic solvents; further comments have been given[27]). Hydridorhodoxime, therefore, exhibits more similarities in this regard with $HCo(CN)_5$ which reduces alkyl halides to alkanes[28] and epoxides to alcohols.[29] The reactivity order exhibited by reagents such as $Co(CN)_5^-$ and $(n\text{-}Bu)_3SnH$ which react by free-radical mechanisms with RX is tertiary > secondary > primary. The limited data on hydridorhodoximes, however, are more in keeping with a nucleophilic type mechanism where sterical factors have a larger role than in a free-radical process.

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Registry No. $HRh(dmgH)_2P(C_6H_5)_3$, 21220-16-6; $Rh(dmgH)_2P(C_6H_5)_3^-$, 73597-10-1; *n*-butyl bromide, 109-65-9; $C_6H_5CH_2Cl$, 100-44-7; $C_6H_5CH_2Br$, 100-39-0; $C_6H_5CH(CH_3)Cl$, 672-65-1; $[Rh(dmgH)_2P(C_6H_5)_3]_2$, 21057-94-3; $ClRh(dmgH)_2P(C_6H_5)_3$, 31249-66-8; $ClRh(dmgBF_2)_2P(C_6H_5)_3$, 73597-11-2.

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Electron Paramagnetic Resonance and Structural Studies of Small-Ring Metallacycles. Bonding in a Metallacyclopropene Formed by the Oxidative Addition of an Acetylene to Vanadocene

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A combination of electron paramagnetic resonance and X-ray diffraction methods has been employed to obtain quantitative information about the structural and bonding characteristics associated with acetylene derivatives of vanadocene, $(\eta^5\text{-}C_5H_5)_2V(C_2R_2)$. The outcome of an X-ray diffraction analysis of the dimethyldicarboxyacetylene adduct has revealed that the symmetrical attachment of the acetylene is accompanied by (1) an appreciable canting of the two cyclopentadienyl rings, (2) an ca. 0.08 Å increase in the multiple carbon–carbon distance, and (3) a displacement of the methylcarboxylate substituents such that the C–C–R bond angles have been reduced from 180° (free acetylene) to 143.5° (average). The metallacyclopropene structure (C_{2v}-*mm*2) of the central VC_2 moiety can be described as an isosceles triangle with two equivalent V–C bonds of 2.09 Å (average) and a multiple carbon–carbon bond distance of 1.276 (3) Å. These structural changes associated with the coordinated acetylene reflect its transformation toward the geometry of a cis olefin. Solution and frozen-glass EPR measurements have provided an opportunity to determine the metal-orbital character of the unpaired electron. From computer simulation of the frozen-glass spectrum of $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2CH_3)_2)$, the values of the principal components of the **g** and T tensors are $g_x = 2.0130$, $g_y = 1.9815$, $g_z = 2.0020$, $T_x = (-)58.5$ G, $T_y = (-)77.0$ G, and $T_z = (-)2.0$ G. On the basis of the same ligand field model applied to d^1 $(\eta^5\text{-}C_5H_5)_2VL_2$ complexes (with the smallest hyperfine component, T_z, directed normal to the plane which bisects the L–V–L bond angle), the anisotropy in the ^{51}V hyperfine interaction similarly arises from an admixture of $3d_{z^2}$ and $3d_{x^2-y^2}$ character in the HOMO of a_1 symmetry for the acetylene complexes. The larger ratio of mixing coefficients, $a(d_{z^2})^2/b(d_{x^2-y^2})^2$, of $-0.995^2/0.100^2 = 99/1$ compared to that for $(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$ of 20/1 is consistent with the appreciably smaller C–V–C bond angle (35.58 (8)°) and reflects a smaller contribution from the $d_{x^2-y^2}$ AO. A qualitative molecular orbital description, which is consistent with the structural and EPR data, is discussed for $(\eta^5\text{-}C_5H_5)_2V(C_2R_2)$ complexes.

Introduction

The interaction of unsaturated molecules such as olefins and acetylenes with transition metals plays a crucial role in a wide variety of chemical processes including polymerization, isomerization, hydrogenation, hydroformylation, and cyclization.[1,2] Olefin and acetylene derivatives are known for bis(cyclopentadienyl) transition-metal complexes of Ti,[3,4] V,[5,6] and Mo[7] and have been suggested as models for reactive intermediates in several of these reactions. In particular, Tsumara and Hagihara[8] have reported that vanadocene catalytically polymerizes acetylene at 80 °C and 250–300 psi. Under milder conditions, however, acetylene derivatives of vanadocene,

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